

### Reports coupling of Fe and P dynamics in lakes

#### Lead author

Professor dr. S. Peiffer UBT

Universitätstrasse 30 95444, Bayreuth Germany

Telephone: +49 (0)921 - 55 2251 Email: s.peiffer@uni-bayreuth.de

Delivery month Annex I24Actual delivery month30Lead participant: UBTWoVersion: 1

30 Work package: 2

Nature: Report

Dissemination level: CO



This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 813438.



D2.1: Reports coupling of Fe and P dynamics in lakes

#### Table of contents

1. Executive Summary
2. Introduction
2.1 Background4
2.2 Scope of the deliverable4
3. Content
3.1 Establishing a P balance for the Brombachsee lake system
3.1.1 Stratification, oxygen depletion and total P-stock in the deep lakes of Franconian lake country
3.1.2 Monthly resolved P balance constructed by combing P concentrations and the hydrological balance
3.2 Coupling of element cycles in sediments from two contrasting lakes
3.2.1 Sediment geochemistry in the deep, seasonally-stratified lake Kleiner Brombach- see (KBS)
3.2.2 Lake Terra Nova9
3.3 Effects of organic ligands on Fe(III)-precipitate formation and P uptake12
4. Conclusion and possible impact13
5. Dissemination & Exploitation14
6. References14
7. Deliverable history



D2.1: Reports coupling of Fe and P dynamics in lakes

# **1. Executive Summary**

The successful reduction of internal phosphorus (P) loading by iron (Fe) addition in lakes requires wellfunded knowledge about the lakes as a biogeochemical system. Thus, our research goals were:

- Assessing the importance of internal P loading for the P budget in the lakes
- Understanding the link of the Fe cycling in lake sediments with P and other key elements and the effect of Fe addition on the coupling of elemental cycles.
- Unravelling the role of organic ligands on formation and transformation of Fe precipitates

To assess the impact of internal loading on the P budget in lakes, a P balance was set up over the three lakes Altmühlsee (AMS), Kleiner Brombachsee (KBS), and Großer Brombachsee (GBS) of the Brombachsee lake system in Franconia. These are deep lakes which experience stratification and bottom water oxygen depletion during the summer months. In KBS the sediments were found to be the source of P to the water column triggered by the summer deep water anoxia. Contrastingly, GBS experienced peak P concentrations only after refilling of the reservoir, despite of deep-water anoxia, which suggest an external source of the P load. This shows that the source of excess P in the water column needs to be investigated before deciding for restoration measures.

To investigate the link of Fe and P cycling in sediments we selected two lakes of differing character: 1) the seasonally stratified lake Kleiner Brombachsee (KBS) in Germany and 2) the well-mixed, shallow peat lake Terra Nova (to which Fe had been added in the past) in the Netherlands. Both lakes are in recreational use and are regularly affected by blue algae blooms due to the high concentrations of P.

In both lakes the sediment P pools were studied using the SEDEX sequential extraction procedure. Results from KBS show that Fe bound P is the largest pool of P in the sediment. Thus, this lake behaves "according to textbook", following the classical model of Fe and P coupling in lake sediments. In stratified lakes, this model predicts seasonal release of P during bottom water anoxia in summer due to reductive dissolution of Fe oxides, followed by coprecipitation and adsorption of P with and to Fe oxides upon reoxygenation of the bottom water in the colder months.

Lake Terra Nova was treated with Fe salt (FeCl<sub>3</sub>) in 2010 to increase the P-retention capacity. The beneficial effects however only lasted for 2 years and were not sustainable. The SEDEX revealed that the amount of reactive Fe at the sediment-water-interface (SWI) was increased and no increase in iron disulphide (FeS<sub>2</sub>) was observed. However, this did not result in a higher retention capacity on the long term. Therefore, we propose that associations of Fe, organic matter (OM) and P in the form of ternary complexes or P adsorbed to Fe-OM coprecipitates might have become dominant over phosphate adsorbed to Fe hydroxides. These associations seem to release P more readily. Thus, Terra Nova does not behave as would be expected based on the available research and OM seems to be the key factor to explain the sedimentary Fe and P dynamics.

To study the role of organic ligands for the transformation and precipitation of Fe precipitates, laboratory precipitation experiments of Fe(III) with several organic model compounds and P adsorption experiments to the formed compounds were executed. The experiments showed that OM increases the amount of amorphous Fe(III) precipitates by altering the coordination sphere of the Fe and lowering the crystallinity of the precipitates, which then leads to enhanced P uptake. These results suggest that the alteration of the Fe surface structure by the OM dominates over competition for adsorption sites when it comes to the effect of OM on the adsorption P on Fe minerals.

Based on these results we conclude that the extent of internal P loading is strongly controlled by lake specific features. To control the P dynamics in the sediment, Fe is the key element. However, the cycling of Fe in the sediment and its effect on the P retention or release is highly dependent on the sediment properties. While literature suggests that mainly sulphur can disturb the coupling of Fe and P in sediments, our research shows that also OM can have a major impact. And even though we showed that



D2.1: Reports coupling of Fe and P dynamics in lakes

OM can enhance the ability of Fe minerals to adsorb P, our results also suggest that in a natural environment these P-Fe-OM associations can have a negative effect on the P retention capacity of sediments. In spite of these findings, Fe addition can still be seen as a feasible restoration method even for peaty lakes, but the lake system has to be analysed thoroughly and Fe dosage has to be adjusted carefully.

# 2. Introduction

### 2.1 Background

In the euphotic zone of lakes, P lifts the limitation on growth of algae. During spring and summer, when many deeper lakes become stratified, this can lead to toxic algae and diatom blooms with strong economic and ecological consequences. While biomass from the epilimnion (surface of the lake) sinks to the bottom, it is degraded by consuming dissolved oxygen. Due to the stratification of the water body, consumed oxygen cannot be replenished via air-water exchange in lower water layers. In the hypolimnion (deeper lake) the result is oxygen depletion and unwanted reducing, anaerobic conditions.

As scientist and policy makers became aware of P as main cause for the eutrophic conditions of lakes, requirements on discharged waste waters have become increasingly stringent. Still, for many lakes that saw a decrease in external P-load, problems with P have remained (Steinman & Spears, 2020; Søndergaard, 2007). This is explained by the oxygen-dependent model for sediment P-retention (James, 2016; Mortimer, 1941). In this model Fe plays a crucial role. Under oxic conditions Fe will be present as Fe (oxyhydr)oxides (Fe(III)O(OH), Fe(II,III)<sub>x</sub>O<sub>y</sub>), which in sediments are mainly present as the minerals goethite, lepidocrocite, ferrihydrite, magnetite, and hematite and will further be referred to as Fe oxides. P adsorbs to Fe oxides as a ligand. In contrast, under anoxic conditions Fe(III) from Fe oxides is reduced to [Fe<sup>2+</sup>]-ions with a concomitant release of P as a result. Another major factor for anaerobic P release is sulphate reduction forming metastable Fe sulfide (FeS<sub>x</sub>) minerals, which decreases the amount of Fe available for P-immobilization (Edgeworth, Freemont, & Hogg, 1989).

In summer, when lakes become stratified and anoxia prevails, the above-mentioned mechanisms cause a strong release of P into the hypolimnion. This also holds true for shallow non-stratified lakes that can develop temporal anoxia in summer due to high oxygen demand during times of little wind. Therefore, even if external inputs have been diminished due to policy measures, lakes can still suffer elevated trophic states due to the sediment's internal P-loading. To mitigate this P-release, previous addition of aluminium salts has been performed and successfully immobilized P (Cooke, Welch, Peterson, & Nichols, 2016). Unfortunately, this has also resulted multiple times in a release of toxic aluminium-ions, even after careful planning (Connor & Martin, 1989). An alternative could be Fe salts which are less toxic. For a long time, Fe salts were deemed unsuitable for stable P-immobilization due to the redox-sensitivity of Fe as described above (Cooke et al., 2016; Molen & Boers, 1994). Recently, Fe salt amendments were also shown to result in lowering of P release from the sediment, albeit with certain prerequisites to the prospected lake's properties (Deppe & Benndorf, 2002; Immers et al., 2015; Kleeberg, Herzog, & Hupfer, 2013). Thus, further investigation into the response of the P dynamics in lake sediments upon Fe addition are needed to be able to predict the long-term effects and to design successful lake treatment campaigns.

### 2.2 Scope of the deliverable

In this deliverable we summarize the insights we have gathered from the works of ESR 9, ESR 11 and ESR7 on the relationship between primarily Fe, P and OM and its influence on P-fixation in lake sediments. This deliverable will allow to establish new and more detailed prerequisites related to lake sediment characteristics that allow for the successful application of Fe sludge therein.



D2.1: Reports coupling of Fe and P dynamics in lakes

The deliverables D2.1, D2.2 and the milestone MS14 are complementing each other.

## 3. Content

### 3.1 Establishing a P balance for the Brombachsee lake system

In order to investigate the role of sediments in the observed P dynamics in the Brombachsee lake system consisting of lake Altmühlsee (AMS), Kleiner Brombachsee (KBS), and Großer Brombachsee (GBS), a mass balance for P was established using both hydrological and P data that were collected within the last three years and kindly provided by the local water authorities (Wasserwirtschaftsamt Ansbach). Starting from the hydrological balance (data not shown) a monthly resolved P balance was made by multiplying the transported waters with mean total phosphate concentrations. Aim was to investigate whether the phosphate observed in the lakes mainly originated from the sediment (*internally loaded*) or were mostly imported from AMS (*externally loaded*).

# 3.1.1 Stratification, oxygen depletion and total P-stock in the deep lakes of Franconian lake country

A major parameter involved in P released from the sediment is the onset of anoxic conditions at the sediment surface. This is caused by thermal stratification leading to inability for complete mixing to occur. Both, KBS and GBS are deep lakes and therefore can be thermally stratified. Shallow lakes generally stay well mixed even during summer time.

### a) KBS

For KBS, stratification and subsequent anoxia was observed. From May till October reduced oxygen concentrations were found at depths larger than 5 m (Fig. 1). The cumulative overview of the total P over the monitoring period is given in Fig. 2.

To assess the effect of oxygen depletion we calculated the total P content in the lake water volume based on the P depth profiles. Measurements ranged from spring until fall and were conducted at five specific depths (Fig. 2). Based on these calculations we could observe a strong correlation between







Fig. 2: Cumulative overview of total P found in KBS at different depth for the period 2017-2019.

oxygen depletion and P levels in the summer. The spring starts with a take-up of P by algae, which decreased the lake P content. The algae matter then sinks to the bottom where it is degraded resulting



a low oxygen content at the sediment's surface. Two months after anoxia set in the lake (April/May) a

rise in P can be observed (July/August). The main portion of this P was found at the bottom where anoxic conditions prevail. In the late summer months, the released P decreased again. Then in fall (October/November) the P concentrations increased again as a result of mixing. This pattern is persistent over the years. The severity of the seasonal cycle differs, which could be explained by environmental conditions such as the warm and dry year 2018, during this year the highest P concentrations were reached.

Main observations and conclusions are:

- Peak concentrations for the KBS occurred in summer when there is no water being transported through the reservoir. We conclude this P must come from the sediment and represent the internal load of the lake.
- A clear seasonal cycle could be observed. However, this amplitude of the summer increase seems to be dependent on other factors (possibly severity of stratification and anoxia). This requires further analysis.

### b) GBS

#### For the GBS we observed a rather sim-

Fig. 4: Cumulative overview of total P found in GBS at different depths for the period 2017-2019.

S

ilar oxygen depth profile (Fig. 3, Fig. 4). However, the process of anoxia developed slightly slower than in the KBS. Deep anoxia was only achieved in July/August although the effects of stratification started in April/May already. This could be explained by lower primary productivity and a larger lake volume. The sediment release was also observed to occur one month later than for KBS. Another interesting difference in the TP content of the lake is the increase observed during winter, which coincided with the refilling of the reservoir. This was likely a consequence of the higher P concentration in the inflow (cf. milestone MS3 for a description of the lake management) as compared to the lake.

Main conclusions for the GBS are

- Peak concentrations for the GBS occurred in winter, which correlates with the refilling of the reservoir. We conclude that this lake's total P content was highly determined by external influx.
- Every year a similar seasonal cycle can be observed. However, the amplitude of P loads during summer seem to be dependent on other factors (possibly severity of stratification and anoxia). This requires further analysis.



Fig. 3: Monthly resolved oxygen depth profiles of GBS for the period of 2017-2019





# 3.1.2 Monthly resolved P balance constructed by combing P concentrations and the hydrological balance

A P mass balance was constructed by multiplying the cumulated monthly inflowing water with the mean total P concentration (Fig. 5).

In the winter up to 10 tons of P was transported into the Brombachsee system. This is twice as much as the standing P-stock of the GBS. Of the  $10*10^3$  kg of P inflowing in the 2017 / 2018 winter period only  $2*10^3$  kg could be directly retrieved in the waters.

Hence, 80 % of the P was considered to immediately go into the sediment sink. A similar pattern was observed in the



Fig. 5: P mass balance for the lake system

2018 / 2019 winter. We hypothesise that the majority of the external P load is bound to particles, which sediment in the GBS and, by this, remove the majority of the imported P. The summer releases are rather small in comparison to the inflowing P. However, relative to the standing stocks in the summer they can amount to 75% of the total P in the lakes.

Main observations and conclusions were:

- The majority of inflowing P is never retrieved in the lake water of the Brombachsee reservoirs but rather goes towards the sediment.
- The majority of inflowing P goes towards the GBS. This lake is considered to be externally loaded.
- For the KBS peak P concentrations correlate to anoxic periods in the summer. This lake is considered to be internally loaded.

### 3.2 Coupling of element cycles in sediments from two contrasting lakes

We compared results from sediment characterisation performed in two contrasting lakes, namely the shallow lake Terra Nova (Loosdrecht Lake Complex, The Netherlands), to which Fe was added earlier, and the deeper lake Kleiner Brombachsee.

The latter is part of major water management activity established in the 1980's and received substantial loads of nutrients from water from a channel crossing the Danube / Rhine watershed.

To investigate how P is bound in the sediment we took sediment cores and performed porewater and solid phase analysis including sequential extraction

Table 1: Overview of the steps in the SEDEX protocol for the sequential extraction of  ${\sf P}$ 

Sequential Extraction Step	Chemical + Incubation
1. Exchangeable P	1 M MgCl <sub>2</sub> , 0.5 h
(possible extra step (O'Connell et al., 2020)	1 M NaHCO pH 7.6, 16h
IIa. Humic acid bound P	
IIb. Washing step	1 M MgCl <sub>2</sub> , 0.5 h
2a. Fe-bound P	0.3 M Citrate+1 M NaHCO <sub>3</sub> +0.25
	M Na₂S₂O₄ pH 7.6, 8 h
2b. Washing step	1 M MgCl <sub>2</sub> , 0.5 h
3a. Apatite (Ca-bound)	1 M Acetate buffer pH 4.5, 6 h
3b. Washing step	1 M MgCl <sub>2</sub> , 0.5 h
4. Detrital P	1 M HCl, 24 h
5. Organic P	1 M HCl, 24 h

 Table 2: Sequential extraction of Fe

 Sequential
 Extractor

 Chemical + Incubation

tion Step	
1. Amorphous Fe	0.17 M sodium citrate, 0.6 M NaHCO <sub>3</sub> , 0.057 M Ascorbic acid, 24 h
2. Easily reducible Fe	1 M HCl, 4 h
3. Crystalline Fe	0.35 M HAc, 0.2 M NaCitrate, 50 g/L Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (CBD) pH 4.8, 4 h
4. Recalcitrant Fe	0.2 M NH₄Oxalate, 0.17 M HOxalate pH 3.2, 6 h
5. Pyrite Fe	65 % concentrated HNO <sub>3</sub> , 2 h



D2.1: Reports coupling of Fe and P dynamics in lakes

of P following the SEDEX protocol (Table 1) (O'Connell et al., 2020; Ruttenberg, 1992; Slomp, Epping, Helderl, & Raaphorst, 1996). In a similar vein sequential extraction of Fe (Table 2) was performed to distinguish different types of Fe (Dijkstra, Slomp, Behrends, & Scientists, 2016). All sequential extractions rely on the principle of adding extraction solutions of increasing strength. In this way one can distinguish and guantify more readily available sources of P and Fe which gives an idea on the effect Fe amendments will have.

Additionally, sediment incubation experiments were performed. In these experiments, cores were taken from the lake and incubated at the lake's temperature for a few weeks. During this time the overlying water was monitored for P. Fe and a variety of other ionic species. This yields the release rate of the sediment and hence allows to quantify the severity of internal release from the sediment.



Fig. 6: Overview of sediment core locations, taken in the KBS on 22 May 2020.



Fig. 7: Overview of SEDEX results for the cores taken in the KBS on 22 May 2020

#### 3.2.1 Sediment geochemistry in the deep, seasonally-stratified lake Kleiner Brombachsee (KBS)

The lake Kleiner Brombachsee (KBS) is part of a reservoir chain described in milestone MS3. As the main aim of Fe amendment in lake restoration is the decrease in severity of internal loading events we decided to focus on the KBS. The KBS had larger summer releases as compared to GBS. Here we performed a first assessment of how the P was bound. To this effect we went to the KBS in May 2020 and took four cores across the lake (Fig. 6). Upon return we immediately sliced the cores and performed the sequential extraction as described in Table 1 (Fig. 7).

In summary, the majority of P was associated with Fe minerals. The next largest fraction was the organic P fraction. This suggests that the internal release observed in the KBS likely follows the classic model of Mortimer, which states that the reductive dissolution of Fe oxides leads to the release of phosphate adsorbed onto these Fe oxides (Mortimer, 1941).



D2.1: Reports coupling of Fe and P dynamics in lakes

#### 3.2.2 Lake Terra Nova

Lake Terra Nova of the Loosdrechtse Plassen lake area in the Netherlands (Fig. 8) is an artificial lake that developed due to peat excavation. Terra Nova is shallow (2 m maximum depth), well mixed and eutrophic with peaty sediment. Blue algae are present all year round with blooms in summer which is why it was subjected to several treatments in the early 2000s. The first measure was to remove burying fish (bream) which by resuspending the sediment can cause redistribution of P from the sediment into the water column. Since this measure did not show the desired effects the lake was treated with FeCl<sub>3</sub> (33 g Fe\*m<sup>-2</sup>) in 2010 (Immers et al., 2015). The Fe salt treatment significantly lowered the total P concentrations in the water column for about 2 vears. Afterwards, the P concentrations in the surface water started rising again and are now higher than before the treatment (Voort, 2019, Fig. 9).

These observations suggest, that the Fe treatment had a significant effect on the P load in the water column only for a short while. On the long term the Fe treatment could not fixate the P in the sediment or might even have triggered processes releasing P from the sediment into the water



Fig. 8: Lake Terra Nova (TN) and core sampling locations



**Fig. 9:** Surface water total P concentrations during and after measures of lake restoration. Fe was added from 2010 on for a year (blue), after a short lag time P concentrations started to increase again (purple). (Voort, 2019)

column. The data also suggests that the removal of the bream had a major effect and introduced a certain seasonality into the P concentrations in the surface water. Probably, the bream constantly reworked the sediment, keeping the top sediment layer oxic at all times. After their removal the seasonal P peaks suggest seasonal anoxic events.

To further investigate the reasons for this counter-intuitive effect, sediment cores were taken at multiple locations (Fig. 8). The coupling of P and Fe becomes most evident in the pore water concentrations. The pore water P concentrations follow the pattern of the pore water Fe concentrations suggesting that while Fe(II) gets released by reduction, P is released as well (Fig. 10).



Sequential extraction of the Fe pools further suggests that the main source of dissolved Fe is easily reducible Fe which gets reduced by sulfide originating from sulfate reduction (profile not shown) and transforms into pyrite. However, this process is not able to quantitatively remove Fe from the redox active pool (easily reducible Fe) and the Fe added in 2010 is still present in redox active form in the top 6 cm of the sediment (Fig. 11). Also, more P is released into the porewater than Fe (Fig. 10) suggesting that another mechanism is at play than the reductive dissolution of Fe oxides, which would release more Fe than P into the porewater.



**Fig. 10**: Location A: Pore water concentrations of Fe and P.

**Fig. 11**: Location A: Sequential Fe extraction and detailed depth profile of easily reducible Fe and pyrite.

The collected data from Terra Nova imply a more important role of OM in the sedimentary Fe-P-interaction than anticipated. So far, the main assumption was that the availability of Fe for the binding of P depends mainly on the abundance of sulphur (S) in the sediment, since the formation of Fe sulphides and pyrite disrupt the "Fe-wheel", hence making Fe unavailable for P-binding (Kleeberg, Köhler, & Hupfer, 2012; Rothe, Kleeberg, Grüneberg, Friese, & Pérez-, 2015).



**Fig. 12:** Terra Nova location A: sediment depth profiles of the P sequential extraction without (SEDEX) and with (expanded SEDEX) additional extraction step for organic matter associated P.

However, results from sequential extractions show that a large pool of P is associated with OM, most probably in the form of humic and fluvic acids with Fe as a bridging agent (Gerke, 2010;).

Fig. 12 shows the results of the sequential P extraction of a sediment core from location A with and without the step distinguishing for OM associated P (1 M NaHCO<sub>3</sub>). The comparison of the two extractions shows that a significant part of the sedimentary P is bound to OM, a part that is otherwise extracted with the Fe-bound P. Here the question remains whether the Fe is bound to the OM in colloidal form or as ternary complexes and also what this



would mean for the binding of P under different redox conditions. Thus, for Terra Nova, the data suggests that OM disrupts the "Fe-wheel" by binding Fe which then still exhibits affinity for P, but is more redox sensitive than Fe oxides, thus constituting a highly available pool for OM mineralisation and releasing P more readily.

This hypothesis is also affirmed by the results of the sediment incubation experiments. In the anoxic incubation experiments up to 10 times more P was released from the sediment compared to the incubation experiments in which the overlying water was constantly purged with air.

Furthermore, the flux of P from the sediment was up to 7 times larger than the flux of Fe from the sediment (Fig. 13) under anoxic conditions. The increase in P fluxes can be explained by





the reduction of Fe accompanied by the mobilization of P, which was bound to Fe in the oxidized form. If this is the case, the finding suggest that the reduced Fe is retained in the sediment while the released P can escape from the sediment. Together with the findings from the sequential extractions it can be hypothesised that the OM stabilises the Fe in the sediment in a form that is less reactive towards P. However, it needs to be investigated whether OM also binds a relevant part of the oxidized form of Fe and whether this OM-bound Fe is able to form complexes with P or not.

Regarding the long-term effects of Fe addition, the data collected for Terra Nova confirm that the Fetreatment has ceased to be effective. Even though sequential extractions indicate that the pool of reactive Fe has been increased due to the Fe treatment, the prevailing processes in the sediment do not seem to follow the classical coupling of P and Fe oxides and our results suggest the pivotal role of OM in this peaty lake sediment. Results presented in section 3.3 suggest that coprecipitation of Fe with OM actually increases the amount of P that can be bound by Fe. However, the data collected at Terra Nova suggests that the behaviour of these aggregates in a natural sediment might not be favourable for P retention. Further research will be required to clarify the nature of P-Fe-OM associations and to quantify their properties, especially with regard to redox sensitivity.

Nevertheless, comparison of the 3 sampling locations in Terra Nova show that location D, which received most Fe during the treatment, has the largest reactive Fe pool in the surface sediments (Fig. 14) as well as the lowest P release rates from the sediment. This suggests that also in a lake with high OM content in the sediment Fe-addition is still an option, but the amounts of Fe added must be adjusted. Also, the role of vivianite as a long-term sink for P in the sediment remains to be investigated. Preliminary synchrotron measurements of the zone in the sediment where vivianite formation would be expected did not render any evidence of its presence.





### 3.3 Effects of organic ligands on Fe(III)-precipitate formation and P uptake



**Fig. 15:** Organic compounds selected for Fe(III)-precipitate formation experiments: (A) Oxalic acid (OA) (B) Citric acid (CA). (C) Galacturonic acid (GA). (D) 2,4-dihydroxybenzoic acid (HBA). (E) Leonardite humic acid (LHA). Blue arrows indicate the carboxylic groups in the low molecular weight organic acids.

Laboratory tests were undertaken to test the interference of organic carbon with ferric minerals and PO<sub>4</sub>. Organic ligands can bind Fe(III) and thereby affect Fe(III) polymerization and precipitation and interfere with P uptake of Fe(III) compounds. To date, however, mechanistic studies on the effect of OM on the formation, structure, and properties of Fe(III)precipitates formed by Fe(II) oxidation under environmentally relevant conditions and on implications for P trapping and retention are still scarce. We expanded on earlier work on the effects of P, silicon (Si) and calcium (Ca) on the structure of fresh Fe oxidation products formed in bicarbonate-buffered solutions by studying how different types of organic compounds over a range of concentrations and in combination with various levels of P, Si, and Ca affect the structure, and reactivity of the Fe(III)-precipitates.

The organic compounds considered in these experiments (Fig. 15) include four low molecular weight organic acids with varying structure and number of carboxylic groups: Oxalic acid (OA) and citric acid (CA), which may be relevant compounds in soil pore waters and galacturonic acid (GA) and 2,4-dihydroxybenzoic acid (HBA), which represent structural motives of more complex natural compounds such as polygalacturonic acid or humic acid (degradation products of different plant components). Stock solutions of the organic acids were adjusted to pH 7 using sodium hydroxide (NaOH), and thus contained the ligands with deprotonated carboxyl groups.

In the experiments performed thus far, the effects of the organic compounds on precipitate formation were tested in Na and Ca electrolytes at molar P/Fe ratios of 0.05, 0.25, 0.75 and with molar C/Fe ratios ranging from 0.1 to 9.6. Initial unfiltered and final unfiltered solutions were analysed by ICP-MS (Na, Ca,



P, As, Cd) as well as by TOC-L-analyser for total organic carbon (TOC). Solids were analysed by XAS and Fourier-transform infrared spectroscopy (FTIR) for structural characterization.

Suspensions were sampled from unfiltered, centrifuged (with two different schematics; 800 or 1200 rounds per minute for 10 minutes, supernatant collected after) and filtered solutions after the oxidation for measurement with Dynamic Light Scattering (DLS) to determine the size distribution of the suspended particles.

For experiments with GA, HBA and leonardite humic acid (LHA) in Na and Ca electrolytes at a molar P/Fe ratio of 0.05, residual dissolved P concentrations (ICP-MS) as a function of increasing C/Fe ratios are shown in Fig. 16. In both the Na and Ca electrolyte, and for all three ligands, the residual dissolved P fractions decrease with increasing initial C/Fe ratio. A preliminary analysis of XAS results (not shown) indicates that all three ligands affect the local Fe coordination by either decreasing the crystallinity of the dominant lepidocrocite phase and/or increasing the share of amorphous Fe(III)-precipitate. These changes in precipitate structure in turn may explain the enhanced P uptake (decreasing residual dissolved P) with increasing C/Fe ratios. In line with this interpretation, the decrease in residual dissolved P is smallest in the case of HBA, which also has the least effect on local Fe coordination in the precipitates.

Overall, the results suggest that the effect of the three ligands on Fe(III)-precipitate structure and (enhanced) P uptake dominates over their sorption competition with P, which would



**Fig. 16:** Fractions of dissolved P as % of total initial P in the precipitate suspensions (filtered with 0.2 µm cut-off nylon filters), at initial molar P/Fe ratio of 0.05 (0.025 mM P), in (A) Na or (B) Ca electrolytes with organic ligands (GA, HBA, LHA) at initial molar C/Fe 0.3, 0.6, 1.2, and 2.4.

have resulted in an increase in residual dissolved P with increasing C/Fe.

In conclusion, the results on the effects of organic ligands on precipitate structure, P uptake and particle size indicate that organic ligands can enhance P uptake by reducing the crystallinity of the formed solids. At the same time, the organic ligands may decrease particle aggregation and size, thereby enhancing the colloidal stability of the formed solids. The relevance of these effects also depends on Ca, which affects both the interaction of organic ligands with Fe(III) as well as particle aggregation.

### 4. Conclusion and possible impact

Both the studies in KBS and Terra Nova show that the biogeochemical cycling of Fe strongly influences the P cycling in the sediment and thus internal loading in lakes. This implies that P fluxes from the sediment to the surface water can potentially be controlled by Fe addition with the goal to enhance the P retention capacity of the sediment. Our studies as well as literature show that the form in which the Fe is cycling in the sediment is crucial and depends on the sediment characteristics. Our data shows that the presence of large amounts of OM, while theoretically able to enhance the amount of P that can



D2.1: Reports coupling of Fe and P dynamics in lakes

be bound in the sediment, diminish the P retention efficiency of a sediment and the lifetime of Fe treatment. The reason seems to be the complexation of Fe with OM, which albeit keeping the Fe cycling within the sediment, makes this Fe less prone to bind P in a stable way. However, our research also suggests that higher Fe dosages could potentially solve this problem, emphasizing the need to investigate the sediment properties of a lake to be able to design Fe amendment campaigns. Our research also surprisingly shows, that the sediment and surface water properties might be more important for the success of lake restoration using Fe addition than the type of lake. Surprisingly, in both the cases of a stratified or a polymictic lake the sedimentary processes play a key role rather than the oxygen conditions. In both types of lakes periods of oxygen depletion occur, if on different timescales.

# 5. Dissemination & Exploitation

The results of our studies have been presented at several conferences in the course of 2021 (EGU, Lahti Lakes, Goldschmidt Conference) and several scientific publications based on the collected data are in the writing. Follow up research is planned or ongoing, which will also be presented on conferences and publish in scientific journals.

## 6. References

- Steinman, A.D. and Spears, B.M. (2020). Internal Phosphorus Loading in Lakes: Causes, Case Studies, and Management, J. Ross publishing.
- Connor, J. N., & Martin, M. R. (1989). An assessment of sediment phosphorus inactivation, Kezar lake, New Hampshire. *Journal of the American Water Resources Association*, *25*(4), 845–853. https://doi.org/10.1111/j.1752-1688.1989.tb05400.x
- Cooke, G. D., Welch, E. B., Peterson, S., & Nichols, S. A. (2016). *Restoration and management of lakes and reservoirs*. CRC press.
- Deppe, T., & Benndorf, J. (2002). Phosphorus reduction in a shallow hypereutrophic reservoir by in-lake dosage of ferrous iron. *Water Research*, 36(18), 4525–4534. https://doi.org/10.1016/S0043-1354(02)00193-8
- Dijkstra, N., Slomp, C. P., Behrends, T., & Scientists, E. (2016). Vivianite is a key sink for phosphorus in sediments of the Landsort Deep, an intermittently anoxic deep basin in the Baltic Sea. *Chemical Geology*, 438, 58–72. https://doi.org/10.1016/j.chemgeo.2016.05.025
- Edgeworth, J., Freemont, P., & Hogg, N. (1989). Evidence for sulfphate-controlled phosphorus release from sediments of aquatic systems. *Nature*, *342*(September), 189–192. https://doi.org/10.1038/340301a0
- Gerke, J. (2010). Humic (organic matter)-Al(Fe)-phosphate complexes: An underestimated phosphate form in soils and source of plant-available phosphate. *Soil Science*, *175*(9), 417–425. https://doi.org/10.1097/SS.0b013e3181f1b4dd
- Immers, A. K., Bakker, E. S., Van Donk, E., Ter Heerdt, G. N. J., Geurts, J. J. M., & Declerck, S. A. J. (2015). Fighting internal phosphorus loading: An evaluation of the large-scale application of gradual Fe-addition to a shallow peat lake. *Ecological Engineering*, 83, 78–89. https://doi.org/10.1016/j.ecoleng.2015.05.034
- James, W. (2016). Internal P Loading: A Persistent Management Problem in Lake Recovery. *Lakeline*, (Spring), 6–9.
- Kleeberg, A., Herzog, C., & Hupfer, M. (2013). Redox sensitivity of iron in phosphorus binding does not impede lake restoration. *Water Research*, 47(3), 1491–1502. https://doi.org/10.1016/j.watres.2012.12.014
- Kleeberg, A., Köhler, A., & Hupfer, M. (2012). How effectively does a single or continuous iron supply affect the phosphorus budget of aerated lakes? *Journal of Soils and Sediments*, *12*(10), 1593–



D2.1: Reports coupling of Fe and P dynamics in lakes

1603. https://doi.org/10.1007/s11368-012-0590-1

- Molen, D., & Boers, P. (1994). Influence of internal loading on phosphorus concentration in shallow lakes before and after reduction of the external loading. Hydrobiologia, 275-276, 379-389. https://doi.org/10.1007/BF00026728
- Mortimer, C. H. (1941). The Exchange of Dissolved Substances Between Mud and Water in Lakes. Journal of Ecology, 29(2), 280-329. https://doi.org/10.2307/2256395
- O'Connell, D. W., Ansems, N., Kukkadapu, R. K., Jaisi, D., Orihel, D. M., Cade-Menun, B. J., ... Van Cappellen, P. (2020). Changes in Sedimentary Phosphorus Burial Following Artificial Eutrophication of Lake 227, Experimental Lakes Area, Ontario, Canada. Journal of Geophysical Research: Biogeosciences, 125(8). https://doi.org/10.1029/2020JG005713
- Rothe, M., Kleeberg, A., Grüneberg, B., Friese, K., & Pérez-, M. (2015). Sedimentary Sulphur: Iron Ratio Indicates Vivianite Occurrence: A Study from Two Contrasting Freshwater Systems. 1–18. https://doi.org/10.1371/journal.pone.0143737
- Ruttenberg, C. (1992). Development of a sequential extraction method for different forms of phosphorus in marine sediments, 37(7), 1460-1482.
- Slomp, C. I., Epping, E. H. G., Helderl, W., & Raaphorst, W. Van. (1996). A key role for iron-bound phosphorus in authigenic apatite formation in North Atlantic continental platform sediments. Journal of Marine Research, 54, 1179-1205.
- (2007). Søndergaard, M. Nutrient dynamics in lakes. Retrieved from http://www.dmu.dk/Pub/Doktor MS.pdf

Voort, S. Van Der. (2019). Eindrapport maatregelanalyse Terra Nova, internal report, Waternet.

7. Deliverable history			
Date	Activity	Comments	
December 2020	First planning / responsibilities	Definition of content with respect to complementing deliverable D2.2 and milestone MS14	
March 2021	Postponing deliverables	Deliverables D2.1, D2.2 and MS14 post- poned to project month 30 in agreement with PO	
August 2021	First draft circulated	First draft circulated between lead au- thor, co-authors and management for feedback	
September 2021	Final draft circulated	Final draft submitted to project manage- ment for final check	
September 2021	Deliverable submitted	D2.1 submitted to REA	