



BACHELOR THESIS

TESTING PHOSLOCK[®] AS AN
ARTIFICIAL TRACER:
MOBILITY OF LANTHANUM IN LAKE
SEDIMENT UNDER LABORATORY
CONDITIONS

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CONDITIONS

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DECLARATION OF ACADEMIC INTEGRITY

With this statement I declare that I have independently completed the bachelor thesis entitled with “Testing Phoslock® as an artificial tracer: Mobility of lanthanum in lake sediment under laboratory conditions”. The thoughts taken directly or indirectly from external sources are properly marked as such. This thesis was not previously submitted to another academic institution and has also not yet been published.

Sylvia Schuster, 25th of June 2015, Leeuwarden, Netherlands

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EXECUTIVE SUMMARY

The goal of this thesis has been to test Phoslock® as an artificial tracer that can be used as a time marker in the sediment. The application of Phoslock® is a method to restore a lake by removing phosphate from water. Phoslock® consists of bentonite and lanthanum. It was decided to test Phoslock® because a prior internship showed that lanthanum is easily retraceable in lake sediment by elemental analysis.

The bachelor thesis was closely connected to the internship results but investigates the mobility of lanthanum in sediment under laboratory conditions and the possible application in the field.

Literature research was done about the properties of Phoslock®, the application of Phoslock® and the environmental behaviour of lanthanum.

For the experiment of the mobility, sediment cores were taken from the Rappbode Pre-dam, Harz Mountains. The original sediment was analysed to get an understanding of the sediment composition that is used for this experiment. Small calculated dosages of Phoslock® were added to the sediment cores to get a thin layer as a time marker in the sediment. About 5cm sediment was put on top of the Phoslock® layer. These sediment columns were stored in the lab and analysed after one, seven and ten weeks of storage to see how the lanthanum migrated, thus if higher La-concentrations were found in the top or lower layers or if the Phoslock® layer stayed where it was applied.

Results show clear lanthanum peaks in all cores. The layer of three cores stayed exactly where it was applied while for the other three cores, the layer was significantly deeper than expected. The deeper layer was most likely caused by irregularities in the sediment core preparation. However, this means that the duration of this experiment was too short to explain the lanthanum distribution only by diffusion.

Another experiment was carried out to investigate the solubility of substances containing lanthanum in water. To test this, two different dosages of Phoslock® were brought into beakers filled with 1l of water. The same was done for two different amounts of sediment mixed with different dosages of Phoslock®. Water analyses were taken according to a schedule for a total of 13 weeks and the lanthanum concentration was analysed. The duration of this test was too short, equilibrium was not reached. Among other parameters, the equilibrium concentration is needed to estimate with the help of a model calculation the diffusion of lanthanum in sediment. However, the results show that the amount of released La³⁺ ions in comparison to the amount of added Phoslock® and what therefore could be released was extremely small.

At the end, first thoughts on the possible application of the tracer in the field are presented. The company Phoslock® already uses a technique that could be used. Certain factors that have to be kept in mind for the size and location of the traced area are described as well.

It is recommended to set up another long-time experiment of at least one year while Phoslock® and sediment should be applied with greatest caution. In addition, it is also recommended to investigate the amount of La³⁺ ions which is released in the field to further examine if the lanthanum stays in the sediment or migrates into the pore water. The application methods have to be further examined and if possible, tested in the field as well.

Considering the results of the literature research, the internship and the bachelor thesis, Phoslock® is indeed retraceable in form of high lanthanum concentrations but there are certain possible disturbances that have to be kept in mind to ensure the tracer stays where it was applied.

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1 INTRODUCTION

The stratigraphy of sediments can be altered by physical, chemical and biological processes. Under certain circumstances, individual annual layers, called varves, can be found (Figure 1).



Figure 1 Vertical profile of a sediment core taken from Silbersee in Stuhr, Germany. Light thin layers show the varves (Photo: Sylvia Schuster).

These varves can be used as time markers to date the sediment and to learn more about processes in the sediment (Beer & Sturm, 1995). Anthropogenic contamination like the nuclear catastrophe of Chernobyl can be time markers as well as tephra layers coming from volcanic ash or deposits of natural catastrophes like floods (Zolitschka, 2007).

The goal of the project is to test an artificial tracer that can be used as a time marker in the sediment. Ideally, tracers do not disturb the labelled system though being clearly detectable and easy to quantify. Accordingly, ideal tracers do not occur naturally in the labelled compartment of the environment and are inert and not toxic or harmful for other reasons. Additionally, they should not be too expensive. Only very few substances fulfil these conditions.

After careful consideration, it was decided to investigate if Phoslock^{®1} could be used as an artificial tracer. The application of Phoslock[®] is a method to restore a lake by removing phosphate from water. An important advantage of Phoslock[®] is that it is approved in drinking water reservoirs. Phoslock[®] consists of bentonite and lanthanum. There are more and more water bodies in need of a restoration because of high levels of nutrients in the water. These water bodies are eutrophic which means that there is a high quantity of mineral and organic nutrients such as phosphate present that promote a proliferation of algae and aquatic plants. This can result in a reduction of dissolved oxygen and thus, fish mortality (Schwoerbel, 1984). Phoslock[®] strips dissolved phosphorus from the water column and intercepts phosphorus released from the sediments. This product is used against eutrophication in stagnant water bodies and was invented in the mid-1990s by the Commonwealth Scientific and Industrial Research Institution in Australia (Phoslock, 2015).

¹ Bentophos[®] is the German company name while Phoslock[®] is used internationally. That is why in this report, Phoslock[®] will be used.

To investigate the possible application of Phoslock® as an artificial tracer, an internship was conducted to test the hypothesis that lanthanum in Phoslock® is easily retraceable in lake sediment by elemental analysis which was confirmed. A summary of the conclusions of the internship are presented at the end of this section. The bachelor thesis is closely connected to the internship results but investigates the mobility of lanthanum in sediment under laboratory conditions. Thus, the question of this bachelor thesis is how the lanthanum migrates in the sediment under laboratory conditions. This means that this study is simplified and natural processes of lakes were not given such as bioturbation or external mixing processes. This question is important to find out if an applied tracer stays where it is supposed to be and makes it thus suitable or not.

To examine this question, literature research is done about the properties of Phoslock®, the application of Phoslock® and the environmental behavior of lanthanum. The theoretical section is supposed to help estimate the effect the tracer will have in the lake. Even though the dosages of a Phoslock® tracer are significantly lower than the dosage that would be used in eutrophic water bodies, the tracer will have an impact on the lake.

For the experiment of the mobility, sediment cores prepared with a calculated dosage of Phoslock® and 5cm sediment on top are analysed after storage. To investigate the solubility of substances containing lanthanum in water and their equilibrium, another small beaker experiment was set up. First thoughts of the possibilities of a technical device for application of the tracer in the field are presented as well. The tracers shall be spread within a restricted area on the bottom of a water body (e.g. 50mx50m). The system shall allow for spreading the tracers relatively close to the sediment in order to keep it into the restricted area.

Results are presented along with discussions to give a recommendation about the suitability of Phoslock® as a tracer taking the internship results into account as well.

1.1 PRIOR INTERNSHIP RESULTS

Prior to the bachelor thesis, an internship was conducted at the Helmholtz Centre for Environmental Research - UFZ, Magdeburg in the department Lake Research. The duration of the internship was 20 weeks from 1st of September 2014 until 30th of January 2015.

The explanation why Phoslock[®] was chosen is the hypothesis that the lanthanum in Phoslock[®] might be easily retraceable because lanthanum is a rare earth element and the natural lanthanum concentration in sediments is quite low. This would mean that an application of Phoslock[®] should be detectable through higher levels of lanthanum.

Within the scope of the internship prior conducted to the bachelor thesis, the retraceability of lanthanum was the main focus. One experiment was the mixing of two different sediment types (dry and wet) with Phoslock[®]. The dosage of Phoslock[®] was calculated to get the desired concentration of the mixed sediment of 80µg/g La. Analysis showed indeed higher lanthanum concentrations for both sediment types.

Sediment cores were taken from the lakes Eichbaumsee and Silbersee in Stuhr where Phoslock[®] was already applied as a de-eutrophication measure and analysed. Results show here as well that Phoslock[®] was visible in the sediment cores of both lakes in the form of higher La-concentrations. In addition, the best analysis methods were tested. This includes the microwave pressure digestion system and the multi analysis device of which respectively two are available at the UFZ, Magdeburg, Germany. It is recommended to use the more efficient working microwave pressure digestion system from the American company CEM for future analysis. This device is referred to as CEM throughout the report. CEM is more efficient because 36 samples can be done per day while only 12 can be done using the one from the German company JenaAnalytik. It is also recommended to use the ICP-OES (Inductively coupled plasma optical emission spectrometer) from the American company Perkin Elmer because it is, like the ICP-MS (Inductively coupled plasma mass spectrometer), a multi-element analysis device but it is able to analyse different additional elements that might be of interest for other experiments. Only in cases where the detection limit of certain elements is too low, the ICP-MS 7500c from the American company Agilent Technologies can be used to analyse the samples because the ICP-MS is able to detect very low limits while the ICP-OES cannot.

2 LITERATURE

2.1 PROPERTIES OF PHOSLOCK®

2.1.1 WHAT IS PHOSLOCK®?

Phoslock® is used to remove phosphate from water. It strips dissolved phosphorus from the water column and intercepts phosphorus release from the sediments. One tone of Phoslock® binds 34kg phosphate or 11kg phosphorus. This product is used against eutrophication in stagnant water bodies. 1kg Phoslock® is priced at 9.30€ (Phoslock, 2015).

Phoslock® is comprised of 95% bentonite and 5% lanthanum (Phoslock, 2015). Results of an analysis during the internship showed that the La-concentration is not as homogeneous but ranges from 39030 to 47580µg/g (average: 45000µg/g).

BENTONITE is clay and consists of smectite minerals. There are different types of bentonite, sodium, calcium or magnesium (Phoslock, 2015). These cations are exchangeable as it is in the case of the modified bentonite in Phoslock®. Bentonite is not considered toxic to humans or the environment. It is used in drilling muds, as a binder, for purification and as absorbent, in manufacturing processes of food and drinks, in pharmaceutical products and animal feeds (Asfar & Groves, 2009).

LANTHANUM is the 28th most abundant element and a rare earth element. 34ppm of lanthanum is found in the earth crust (Lanthanum, 2015). Its molar weight is 139 g/mol. It occurs naturally in the silicates Cerite, Orthite and Monazite (Remy, 1961). Lanthanum background concentrations of sediments in the Elbe river basin are around 40µg per 1g sediment (Prange & von Tümpling Jr., 1997). This concentration is confirmed by the Institute Dr. Nowak that analysed the concentrations before Phoslock® applications and found concentrations from 8 to 37 µg/g d.w. (Yasseri & Nowak, 2008). Lanthanum is used in catalysts, as additives in glass, as carbon lighting and in permanent magnets. Lanthanum carbonate is a registered medicine with the name Fosrenol® and is used by patients with hyperphosphataemia to reduce serum phosphate (NICNAS, 2014).

2.1.2 PHYSICAL PROPERTIES

Table 1 was taken over from the Phoslock SNA Report and provides an overview about the physical properties of Phoslock®. Purchased Phoslock® is in granular form (Figure 2).



Figure 2 Purchased Phoslock® in granular form (Photo: Sylvia Schuster)

Table 1 Physical properties of Phoslock® (NICNAS, 2014).

Property	Value
Physical state	Granular solid
Appearance	Brown free-flowing granules
Phoslock TM content	>90%
Dispersing agent	Precipitated silica (2.5-5%)
Water content	2.5-5%
Size of granules	2-4 mm × 1-3 mm
Bulk density	910-960 kg/m ³
pH (1% solution)	6.8-7.5
Dust content	<1% weight of 50 µm particles

A grain size analysis was done during the internship (see 3.6) for ground Phoslock®, Phoslock® in suspension and ground Phoslock® in suspension and is shown in Table 2.

Table 2 Grain size analysis done during the internship. Cilas was used for the analysis of ground Phoslock®, Phoslock® in suspension and ground Phoslock® in suspension.

	Diameter 10% in µm	Diameter 50% in µm	Diameter 90% in µm
Pestled Phoslock®	≤1.86	≤6.98	≤17.66
Phoslock® in suspension	≤1.63	≤5.73	≤23.85
Pestled Phoslock® in suspension	≤1.75	≤5.98	≤17.04

As an example, one measurement is presented for each of the three forms in table 2. The table gives an indication of the grain size of 10%, 50% and 90% of the particles. So 10% of the ground Phoslock® particles have the maximum diameter of 1.86µm etc. ISO 14688 grades silts between 2-63µm. This means that the major part of all three forms is in the category “silt”. Cilas produces additionally graphs that show cumulative curves. An example can be found in 3.6.

2.1.3 CHEMICAL PROPERTIES

Phoslock® is a modified bentonite clay product in which a proportion of exchangeable cations (mainly sodium) are replaced by trivalent lanthanum cations La^{3+} (Figure 3) (NICNAS, 2014).

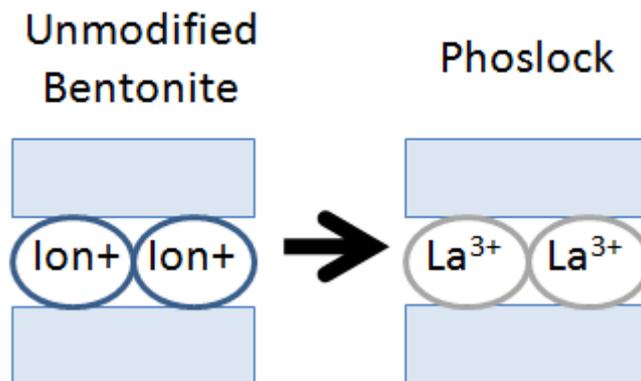


Figure 3 Phoslock® structure showing the modified bentonite in which cations are replaced by lanthanum ions (Phoslock, 2015)

Lanthanum is a strong binder of oxyanions like phosphate or carbonate in hard waters while it prefers carbonate only in significantly higher amounts available than phosphate.

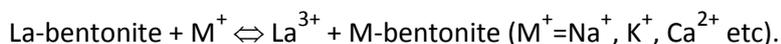
The phosphate is bound by La on the surface of the bentonite and forms the mineral Rhabdophane $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$.



Rhabdophane is integrated in the sediment and retained there under anaerobic conditions in the sediment and over pH 5 to 9 (Robb et al., 2003; Ross et al., 2008; Gibbs et al., 2011) which means that LaPO_4 is stable across wide ranges of pH and redox conditions and highly insoluble. This ensures that no rerelease of lanthanum or phosphate occurs. This implies that the lanthanum is not bioavailable which means that it has not the ability to be integrated into the metabolism of an organism (Davis, 2011).

LaPO_4 has extremely low water solubility of $1.4 \times 10^{-13} \text{ mol/l}$ ($3.274 \times 10^{-7} \mu\text{g/l La}$). The La^{3+} levels in water in equilibrium with solid LaPO_4 are $1.94 \times 10^{-11} \text{ g/l}$ (NICNAS, 2014).

The major part of lanthanum is bound, but one possible mechanism of action in the lake sediment of a limited amount of lanthanum can be:



The solubility of lanthanum will be investigated in 3.10 and 4.6.

The free bentonite acts as a strong binder of heavy metals by cation exchange. Its preference usually is: $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Mn}^{2+}$ (Jasmund & Lagaly, 1993).

2.2 APPLICATION OF PHOSLOCK®

2.2.1 EFFECTIVITY OF PHOSLOCK® AS A RESTORATION PROCESS

An overview of worldwide Phoslock® applications can be found in Appendix 9.1. The overview includes available information such as lake depth, surface area and lake volume, Phosphorus (P) in sediment, in pore water and in the water column before and after the application, P precipitation in the water body, the P bound in sediment, the amount of applied Phoslock® and further information about the lakes in some cases. The overview was supposed to give a general idea of the Phoslock® dosage. On the official website of Phoslock®, 1kg Phoslock® is used per 5m², 1m depth for the prevention of algae bloom which means that 200g Phoslock® are used per 1m². In case of a high eutrophication state, a higher dosage of Phoslock® will be applied (Phoslock, 2015).

Table 3 represents an excerpt of Appendix 9.1 and gives an overview of the studies and their dosages found on the websites of Bentophos® and Phoslock®. The applied amount of Phoslock® (in g) was divided by the surface area (in m²) to get the amount of Phoslock® in g/m².

Table 3 Overview of Phoslock® applications worldwide and the amount used.

Country	Phoslock® in g/m ²
Germany	
Bärensee	183; post-treatment 57
Behlendorfer See	340
Blankensee	294
Eichbaumsee	643.5
Feuersee	947
Silbersee	307; post-treatment 57
Otterstedter	244
Austria	
Reither See	400
The Netherlands	
De Kuil	593
De Rauwbraken	450
Het Groene Eiland	196; post-treatment 55
United Kingdom	
Clatto Reservoir	266
Loch Femington	166
The Serpentine	412.5
South Africa	
Hartbeespoort Dam	240
Australia	
Emu Lake	248

To sum up, different dosages were used between 166g/m² – 947g/m² (16.6mg/cm² – 94.7mg/cm²). The applied Phoslock® dosage as an artificial tracer should have ten times the factor as the natural lanthanum concentration of the sediment to ensure retraceability. If the natural lanthanum concentration is 20µg/g and the end concentration of 200µg/g is desired, 56mg of Phoslock® are added per 1cm layer of sediment in a sediment core tube, diameter 9cm (see 3.2.1). Consequently, 56mg are added per 64cm² meaning that 1.14mg/cm² are added. This means that the tracer concentration will be significantly lower than the dosages used as a de-eutrophication measure.

Different studies were carried out to investigate the effectiveness of Phoslock® by Robb et al. (2003); Ross et al. (2008); Vopel et al. (2008); Haghseresht et al. (2009); Hickey & Gibbs (2009); Egemose et al. (2010); Lürling & Tolman (2010); Van Oosterhout & Lürling (2011); Geurts et al. (2011); Gibbs et al. (2011); Meis et al. (2011); Lürling & Faassen (2012); Lürling & Van Oosterhout (2012); Van Oosterhout & Lürling (2012); Reitzel et al. (2013) and Spears et al. (2013). Most studies found a positive effect of Phoslock® while some determined factors that influence the effectivity negatively.

Ross et al. (2008) and Haghseresht et al. (2009) found out that $\text{pH} \geq 9$ negatively influences Phoslock® while Gibbs et al. (2011) found an increase of the binding capacity from pH 6.1 to 8.9 which means that the effect of Phoslock® depends on the increase or decrease of pH. The decrease of the adsorption capacity at pH higher than 9 is caused by the competition of OH^- with P and consequently the formation of hydroxyl species of the lanthanum ions ($\text{La}^{3+} + \text{OH}^- \rightarrow (\text{LaOH})^{2+} \rightarrow \text{further hydroxo species}$). Reitzel et al. (2013) found out that the negative pH impact is reversible.

The possibility that the bentonite matrix disperses into fine particles at pH 4 to 10 is discussed by Ross et al. (2008) who concludes that larger particles have a lower P adsorption capacity. This confirms that the La of Phoslock® reacts on the interface of the bentonite and water and that the surface size and the short path length for diffusion are crucial. Diffusion takes longer than adsorption.

Results based on a study conducted by Lürling & Faassen (2012) show that interactions between La and humic acids cause an inactivation of Phoslock® because humic substances can be a strong complexing agent for lanthanides. This causes an increase of toxic La^{3+} ions which means an implication in DOC (dissolved organic carbon)-rich inland waters.

Another study of Reitzel et al. (2013) discovered that chironomids increase the Phoslock® binding capacity and thus, P removal. The control of the Reitzel study showed that the Phoslock® layer could be partly supplied with phosphate from the overlying water. Because chironomids increase the water circulations at the sediment surface and the transport mechanisms, it is likely that they contributed to an increase of the sediment binding capacity. Because the mixing occurred not only on the surface but the upper 5cm, Phoslock® encountered more phosphate which also increased the sediment binding capacity. In addition, Phoslock® contains oxidized Fe and the study suggest that chironomids increase the sediment binding capacity by keeping Fe oxidized, especially in deeper sediment layers. Because the chironomids cause bioturbation and bioirrigation that result in a larger oxidized surface area, an increased immobilisation of phosphate onto ferric complexes is suggested.

A modelling of Spears et al. (2013) showed that the concentrations of free La^{3+} ions will be very low in moderately low to high alkalinity lakes while it will be higher in lakes with lower alkalinity. This also means that Phoslock® removes phosphate more efficiently in low alkalinity lakes ($<10 \text{ mg/l CaCO}_3$) than in higher alkalinity lakes ($>50 \text{ mg/l CaCO}_3$). The reason is that carbonate competes with phosphate for binding ($\text{La}^{3+} + \text{CO}_3^{2-} \leftrightarrow \text{La}_2(\text{CO}_3)_3$). Spears also mentions that dissolved cations in the water column may also compete with La for binding with phosphate.

2.2.2 PHOSLOCK® RISK ASSESSMENT

ECO TOXICOLOGICAL RISK

Based on the Phoslock Risk Assessment of April 2011 and the Phoslock SNA report of January 2014, the eco toxicological effects on biota that could be caused after the application of Phoslock®, were investigated with the result of low concern. As stated above, Rhabdophane is not bioavailable and it is unlikely that lanthanum is rereleased. The toxicity was tested on different aquatic species from different trophic levels and sediment-dwelling organisms for mortality, immobilisation, growth, and/or reproduction. If toxic effects were observed, it was not clear if it came from dissolved lanthanum or other factors. Additionally, the EC50 was not exceeded. It is important to state in this context that the amount of Phoslock® that would be used for a tracer will be significantly lower than the amount used as a de-eutrophication measure. However, more in depth studies are undertaken and strongly recommended by most studies.

TOXICITY TO HUMANS

According to the ecotoxicological report of Phoslock Europe GmbH in 2011, lanthanum will pass larger organisms rather than accumulate. To minimise the toxicity risk to humans through the handling of the product and the application procedure, trained staff and protective equipment are recommended (Davis, 2011).

According to the risk assessment of the National Research Centre for Environmental Toxicology in 2007, there is no danger from drinking water or eating fish where Phoslock® was applied because there will be no bioaccumulation. The lanthanum concentrations are much lower than in the medicine Fosrenol® used by patients with hyperphosphataemia. For the worst-case scenario of this risk assessment the proposed dosages of Phoslock® were much higher than the quantity that would be used for a tracer (UniQuest Pty Limited, 2007).

2.2.3 FIELD APPLICATIONS OF PHOSLOCK®

Phoslock® is only applied as suspension. The company Phoslock® developed their own technique of how to apply Phoslock® in a lake as a de-eutrophication measure. To prepare a suspension, a venturi mixing system mixes Phoslock® and lake water. This slurry is then dispersed onto the lake from a spray boom that is mounted on the back of a barge on a swimming platform (Figure 4b). Various configurations can be used for the swimming platform from two to six coupling pontoons (Figure 4a). A telescopic loader, a conveyor belt, or a crane can be used to bring Phoslock® onto the platform. Next to a depth detection system and a flow meter (Figure 4c), a GPS system (Figure 4d) is installed to ensure that Phoslock® is evenly applied in the correct location (Phoslock, 2015).



Figure 4 Swimming platform (a) with spraying system in detail (b) (27East.com). Picture of a flow meter (a) and a GPS system (d) used in the field by Dr. Yasseri (Photos: S.Yasseri, n.d.).

The spraying system can be fixed under the swimming platform with leashes. This way, it is possible to apply Phoslock® either on the surface, into the hypolimnion or in deeper water right above the lake sediment. The size of the spraying system is adjustable up to 6m width (Phoslock, 2015).

2.3 ENVIRONMENTAL BEHAVIOUR OF LANTHANUM

2.3.1 MOBILITY OF LANTHANUM IN LAKE SEDIMENT

In the studies of Meis et al. (2011), a vertical translocation of lanthanum was reported in the Clatto Reservoir, Dundee, United Kingdom. One month after the Phoslock® application, a significant increase in sediment La content was not confined to the sediment surface (0-2cm) but over the upper 8cm of the sediment. Lanthanum was most likely translocated by vertical sedimentation processes such as bioturbation and/or wind induced sediment resuspension. In the study conducted by Reitzel et al., the effect of chironomids on the efficacy of Phoslock® was investigated under laboratory conditions in sediment cores. They found a vertical downward mixing of La and associated it with the bioturbating activity of chironomids (Reitzel et al., 2012).

2.3.2 RELEASE OF LANTHANUM FROM PHOSLOCK® AND OTHER SUBSTANCES CONTAINING LANTHANUM

According to the report of the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) in 2014, the release of lanthanum from Phoslock® preparations is dependent on the chemistry of the water where the tracer is supposed to be applied. First of all, the area and depth of the water body are very important because they influence the period of contact of Phoslock® with water. The degree of turbulence and dispersion are also playing important roles because they influence the mixing. In addition, the phosphorus level, the DOC, hardness (Ca^{2+} and Mg^{2+}), alkalinity, pH and the electrical conductivity are important as well. The electrical conductivity gives an indication of the salinity. In high salinity waters, more dissolved La will be present than in low salinity waters because of exchange processes caused by a higher amount of exchangeable cations such as Ca^{2+} (NICNAS, 2014). As stated in 2.2.1, the pH plays a role in the effectiveness of Phoslock® as well as the DOC and the alkalinity.

NICNAS presents similar studies about the release of lanthanum. To give an example, a study was carried out where the release was measured in 14 different water bodies. Samples were taken from 14 different sampling sites in Australia and an appropriate amount of Phoslock® was added, for example 2g to 2l water. The granules were mechanically agitated for 30 seconds with a glass rod. The result was a decline or remaining of dissolved lanthanum concentrations in half of the samples below 0.1mg/l after 96 hours.

Another study mentioned by NICNAS was conducted by Phoslock Water Solutions. Water samples were taken of the Deep Creek Reservoir in New South Wales, Australia and the release of lanthanum in laboratory scale was tested. Different parameters of the water samples were analysed beforehand. 12, 28 and 100mg of Phoslock® were mixed with 2l of reservoir water in jars. The lowest rate resembles the dosage of Phoslock® used as a de-eutrophication measure. Details about how and how long the jars were mixed are unknown. It is assumed that 10ml samples were taken for water analysis by the ICP-OES. The concentration of dissolved lanthanum was tested right after mixing, 24 and 72 hours later. Results show that the total La release in the water was 17% at the rate 12mg/l and respectively 12.4% and 5.4%. The dissolved La levels after 72 hours were 0.102mg/l, 0.173mg/l and 0.271mg/l respectively. The equilibrium was most likely reached under the test conditions after 72 hours.

A summary of the environmental fate of Phoslock® applications is presented in Table 4. For more details see NICNAS report.

Table 4 Water body characteristics and application details of the various Phoslock™ field applications (NICNAS, 2014).

	Initial FRP (mg/l)	Volume of water body (m ³)	Amount of Phoslock™ applied (tonne)	Calculated amount if 100:1 Phoslock® to FRP ratio is followed (tonne)	Peak total lanthanun levels at 1-3 days post- application (µg/l)	Steady total lanthanum levels (µg/l)
Deep Creek Reservoir	0.02-0.04	4900000	55	19.6	220 (dissolved La)	n.s.
Torrens Lake	0.005	n.s.	50		110 (dissolved La)	<20 after 1 week
	<0.01		12		12 (dissolved La)	<2 after 6 days
Gnowangerup Dam No. 2	0.03	n.s.	0.3		200-250	<20 after 1 week
Bärensee	0.096 & 100 kg in sediment	156000	11.5	11.5	130	<10 at 5 months monitoring
Lake Okareka	130 kg/year in sediment	n.s.	60	39	110	<10 after 1 week
Het Groene Eiland	110 kg	130000	11	11	n.s.	<30 at 5 months monitoring
Zwemplas De Kuil	n.s.	278000	41.5		56	≤20 at 10 months monitoring
De Rauwbraken	0.034-0.091 (total P)	n.s.	20		28 (dissolved La)	n.s.
Loch Flemington	239 kg	122000	25	23.9	n.s.	n.s.
Clatto Reservoir	0.079 and 0.6 in sediment	350000	24	23.8	210	<5 after 13 days

FRP = filterable reactive phosphorus; La = lanthanum; P = phosphorus; n.s. = not specified

Different approaches were used to test the La release and different parameters were suggested that could have influenced the release like the water chemistry. Almost all showed an increase of dissolved La right after the application but a decrease after a certain amount of time after the application. 0-3 days after the application of Phoslock®, the concentrations of dissolved lanthanum were higher than expected (NICNAS, 2014).

3 MATERIALS AND METHODS

3.1 FIELD WORK – SEDIMENT SAMPLING

Ten sediment cores were taken from the sampling location YRH at the Rappbode Pre-dam, Harz Mountains, Germany (Figure 5).

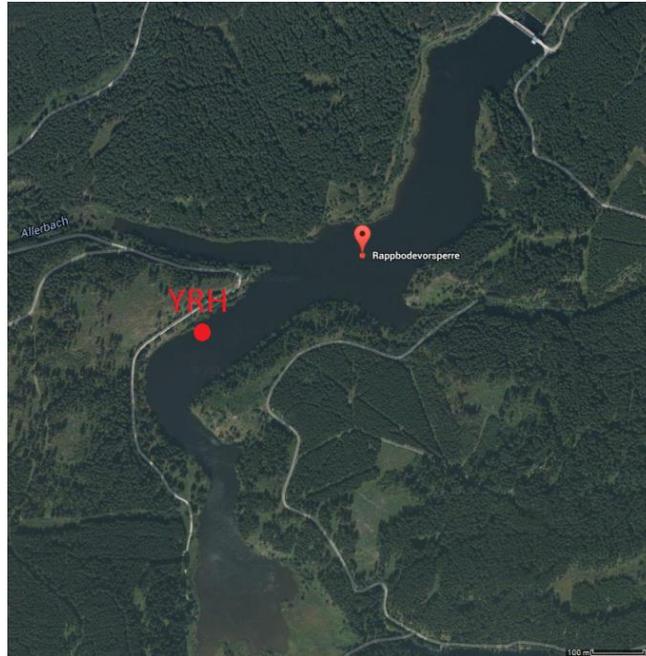


Figure 5 Rappbode Pre-dam, Harz Mountains with sampling location YRH. Map taken from Google Maps (Google, 2015).

Sediment sampling was done with a gravity corer. The gravity corer used is the model MONDSEE CORER from the company Uwitec, Austria.

The corer is lowered from the boat (Figure 6) with a rope to the lakebed.



Figure 6 Preparing the MONDSEE CORER to lower it to the lakebed. The corer is secured with a rope (Photos: Martin Schultze).

Due to its weight, the corers bore the large tube into the sediment. Caps automatically seal off the ends of the corer. It is very important to make sure the caps sealed off before pulling the corer out of the water (Figure 7a) to protect the sample.

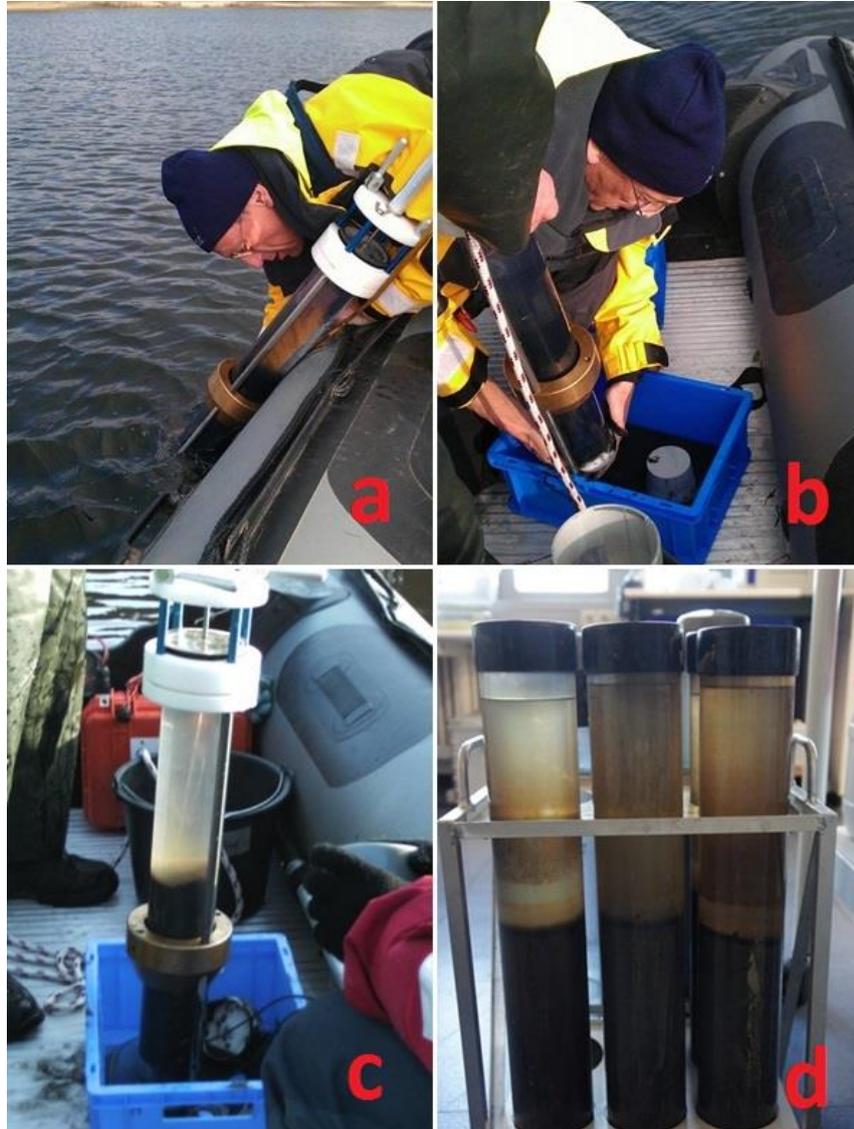


Figure 7 The MONDSEE CORER is pulled out of the water (a) and put on a plug (b) before it is lifted (c). A lid is put on top of the tube (d) (Photos: Sylvia Schuster).

The corer then brings up an intact sediment core within the tube. First, the tube is set on a plug (Figure 7b) and after the MONDSEE CORER is lifted (Figure 7c), a lid is put on top of the tube (Figure 7d).

3.2 SEDIMENT CORE PREPARATION

To test the mobility of lanthanum under laboratory conditions, sediment cores were prepared.

WORKING PROCEDURE

A syringe was used to extract water of the sediment core tubes. This was important to be able to add Phoslock® and the sediment on top to the sediment cores and to shorten the sedimentation time. Seven of the ten cores were prepared with a calculated dosage of ground Phoslock® in suspension (see 3.2.1) to get an end concentration of lanthanum 10 times as high as the natural lanthanum concentration of 1cm layer of sediment. The seventh core was used as a reserve core and was supposed to be stored for a longer time. The two shortest cores were used to analyse the original sediment. Sediment on top for the core preparation was also taken from the two shortest cores and the longest core. All cores were stored in the lab.

An overview over the sediment cores, the sediment and water column in cm, the applied Phoslock® dosage, the sediment on top and additional information can be found in Appendix 9.2. This is important to show where the Phoslock® layer is expected to be in theory.

Demonstration of a prepared sediment core:

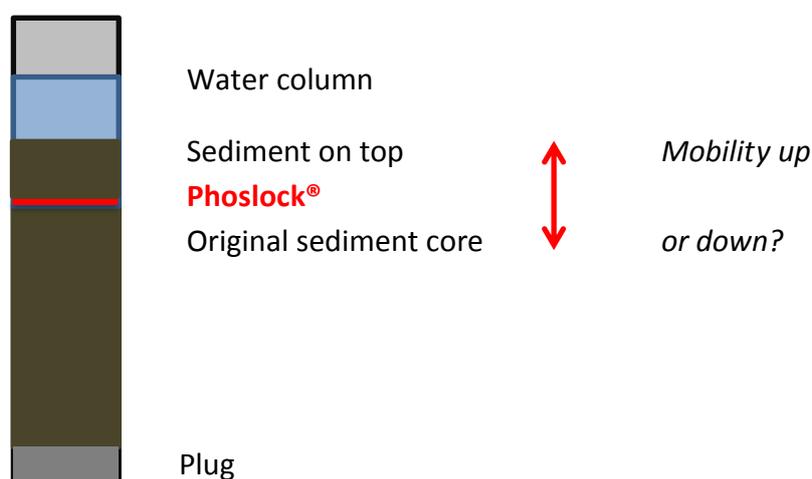


Figure 8 Demonstration of a prepared sediment core

3.2.1 CALCULATION FOR THE QUANTITY OF PHOSLOCK®

Table 5 shows the list of symbols and names with the used units to calculate the dosage of Phoslock® for 1cm layer of sediment.

Table 5 List of symbols and names with the used units that are used to calculate the quantity of Phoslock® needed for this experiment

SYMBOL	NAMES	UNIT
$C_{\text{sedi,mix}}$	Concentration of lanthanum of the mixed sediment (Sediment + Phoslock®)	[$\mu\text{g/g}$]
m_{sedi}	Dry mass sediment original	[g]
C_{sedi}	Concentration of lanthanum of the original sediment	[$\mu\text{g/g}$]
m_{phos}	Dry mass of Phoslock®	[g]
C_{phos}	Concentration of lanthanum in Phoslock®	[$\mu\text{g/g}$]
$V_{\text{sedi,layer}}$	Volume of sediment layer	[cm^3]
$m_{\text{La,sedi}}$	Dry mass of lanthanum in sediment	[$\mu\text{g/g}$]
DBD	Dry Bulk Density	[g/cm^3]

The calculation is based on the assumption of a 1cm sediment layer ($h=1\text{cm}$) with a diameter $d=9\text{cm}$.

Given:

$$DBD = 0.23\text{g/cm}^3 \text{ (Original sediment analysis)}$$

$$C_{sedi} = 20\mu\text{g/g} \text{ (Original sediment analysis)}$$

$$C_{sedi,mix} = 4 \times C_{sedi}$$

$$C_{phos} = 47000\mu\text{g/g} \text{ (Internship outcomes)}$$

$$V_{sedi,layer} = \pi \times r^2 \times h = \pi \times 4.5^2 \times 1 = 63.6\text{cm}^3$$

Wanted:

$$m_{phos} \text{ if } C_{sedi,mix} = 10 \times C_{sedi}$$

$$m_{sedi} = DBD \times V_{sedi,layer} = 14.63\text{g}$$

$$m_{La,sedi} = m_{sedi} \times C_{sedi} = 292.6\mu\text{g}$$

$$m_{phos} \times C_{phos} = 9 \times m_{La,sedi}$$

$$m_{phos} = \frac{(9 \times 292.6\mu\text{g})}{47000\mu\text{g/g}} = 0.05602\text{g}$$

Meaning: 56mg Phoslock® is added to a sediment layer of 1cm. This means that the volume difference and the DBD are negligible.

3.2.2 APPLICATION OF PHOSLOCK®

Different methods were tested in preliminary tests to find the best suitable. To test the methods, an old sediment core tube was prepared with a 2cm sediment layer from the reserve YRH core and a water column on top.

1st TRIAL

To get an evenly distributed Phoslock®-layer, a 1cm layer of Phoslock® was brought into suspension and filled into another old sediment core tube. The tube was put in the freezer. The result was a 2cm ice layer. Warm water was used to loosen the frozen ice core from the tube. The Phoslock® ice core was then put on top of the water column in the prepared sediment core tube. It was expected that the ice layer would smelt slowly and evenly distribute the Phoslock® on the sediment top layer.

Conclusion: Not suitable, because the Phoslock® dosage needed for this experiment is very small, the Phoslock® loss on the edges of the tube would be most likely too high.

2nd TRIAL

An ice core was frozen and put on top of the sediment core tube. The calculated dosage of 56mg Phoslock® was brought into suspension using a small quantity of water. The Phoslock®-suspension was brought on top of the ice core. Because the ice core is not closely “connected” to the margin of the tube, the suspension ran towards the edges of the core. It was also tried to bring the Phoslock® dosage in dry form onto the ice core but it was too difficult to distribute evenly.

Conclusion: Not suitable, because higher concentrations are likely to be found at the edges of the tube and therefore no even distribution is possible.

3rd TRIAL

This Phoslock®-suspension was drawn up into a syringe and dribbled in a spiral form on the sediment core to get an even distribution of Phoslock®.

Conclusion: **Suitable**, because the needed dosage is so small that it worked fine with the syringe, it was easy to handle and easy to dribble and there was no disturbance of the top layer.

3.2.3 APPLICATION OF SEDIMENT

Different methods were tested in preliminary tests to find the best suitable for the application of the 5cm sediment on top as well.

1st TRIAL

Three beaker glasses with a diameter of 9cm were filled with 700ml of water. Sediment was taken from a 1cm sediment layer from the reserve YRH core and mixed with water. The sediment-suspension was dribbled in a spiral form into the beaker glasses with a large container, a small container and a syringe. After 24hours, the sediment settled and showed an even distribution at the bottom of all three beaker glasses.

Conclusion: **Not suitable** for larger quantities. This works fine with small quantities but for the experiment, a 5cm layer of sediment on top is desired.

2nd TRIAL

1cm of the reserve core was taken. A little bit of water was added and filled into an old sediment core tube (Figure 9a). The tube was put in the freezer (Figure 9b). The result was a sediment ice core (Figure 9c). The purpose of the ice core is the hypothesis that it will protect the Phoslock® layer before adding the large quantity of sediment. Warm water was used to loosen the frozen sediment ice core from the tub. The core was then put on top of the water column in the prepared sediment core tube. After the core melted and had time so settle, the remaining 4cm of the reserve core were mixed with water to get a sediment suspension. It was dribbled slowly in the sediment tubes to get roughly 5cm sediment on top. In addition, it is also disputable what happens to the sediment once it is frozen. To have it as much intact as possible, the larger part is just mixed with water rather than frozen.

Conclusion: **Suitable**, because the sediment ice core melted slowly and settled evenly (Figure 9d) on the prior applied tiny Phoslock® layer without disturbing its layer.

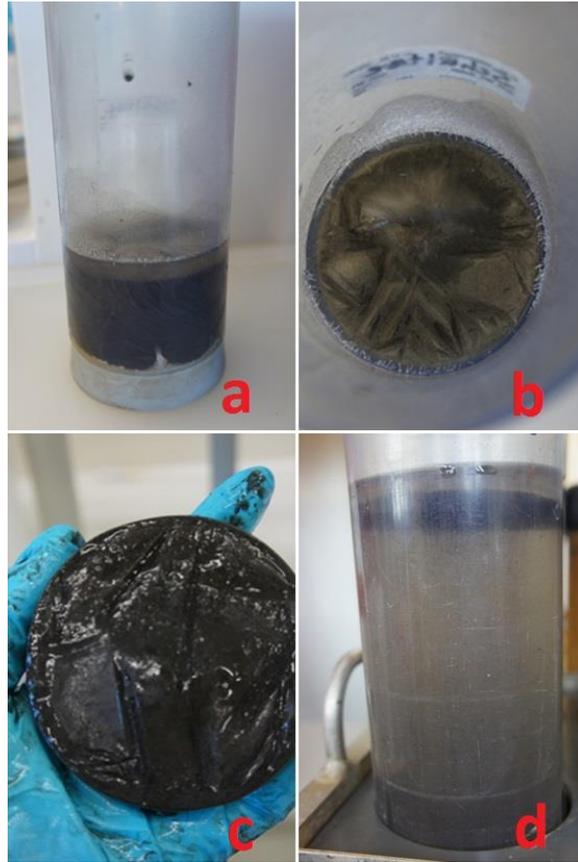


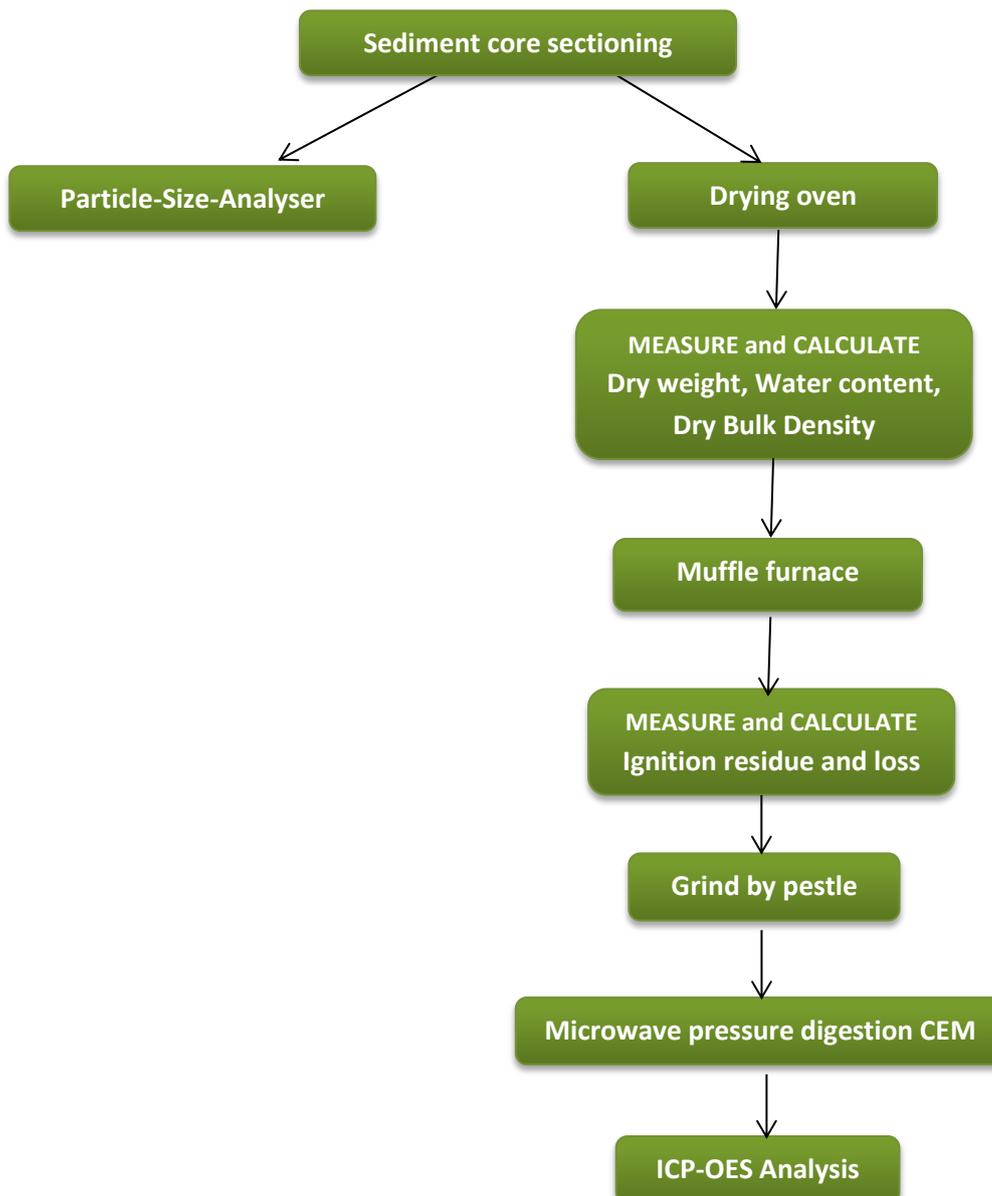
Figure 9 Sediment-suspension is filled into an old sediment tube (a) and put in the freezer (b). The result is a sediment ice sheet (c) which is put on top of the sediment core tube that is supposed to be prepared where it slowly melts (d) (Photos: Sylvia Schuster).

It is important to note that the 5cm sediment on top do not reflect realistic sedimentation. It is supposed to simulate further sediment processes in the lake.

3.3 ORIGINAL SEDIMENT ANALYSIS DIAGRAM

Before starting with the experiment, an analysis was done of the two shortest sediment cores (referred to as PreA1 and PreA2) to get an understanding of the sediment composition. The pre-analysis included a grain size analysis, the analysis of the La, As, Ca, Fe, K, Mg, Mn, Na, P and Zn-concentration, the dry bulk density, the dry weight, the water content and the ignition loss. Because the weight of the subsamples was small, it was carefully considered how to approach the analysis. Certain amounts are necessary for the microwave digestion (at least 250mg) and at least 5ml should be taken for the dry weight for the bulk density calculation and the ignition loss. In Diagram 1, the steps of the pre-analysis are presented.

Diagram 1 Steps of the Pre-Analysis of the sediment

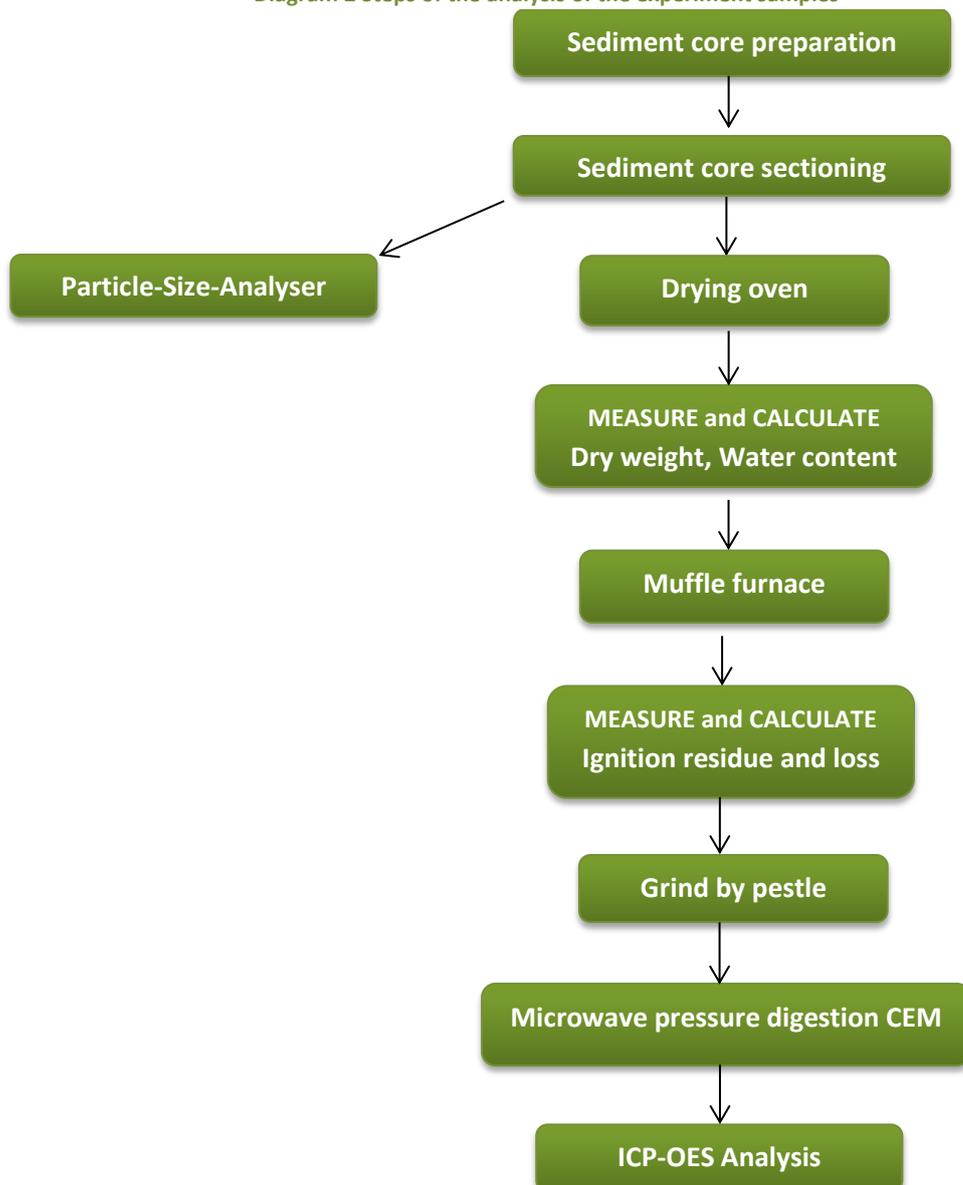


3.4 CORE-EXPERIMENT-ANALYSIS DIAGRAM

The lanthanum concentrations of six cores of the prepared sediment cores were analysed. Two cores were analysed at the same time. After the sediment had time to consolidate, the first analysis was done one week after the start-up to get a picture of the start conditions. The experiment time span was ten weeks. The next two cores were supposed to be analysed half way through the experiment but were in fact analysed after seven weeks storage time because of problems with the analysis devices. The last two cores were analysed at the end of the experiment time after a total storage time of ten weeks.

In Diagram 2, the steps of the experiment samples analysis are presented.

Diagram 2 Steps of the analysis of the experiment samples



The experiment samples analysis included a grain size analysis, the dry weight, the water content, the ignition loss and the lanthanum concentration. No pore water was analysed for the samples because 1cm sections are needed to get enough pore water for the analysis. For this analysis, 0.5cm sections are needed as well as 1cm sections. Because of the small mass of 0.5cm sections, the Dry Bulk Density is not taken into account either.

3.5 SEDIMENT CORE SECTIONING

The tube with the sediment core was firmly put into position using an extruder device (Figure 10a).

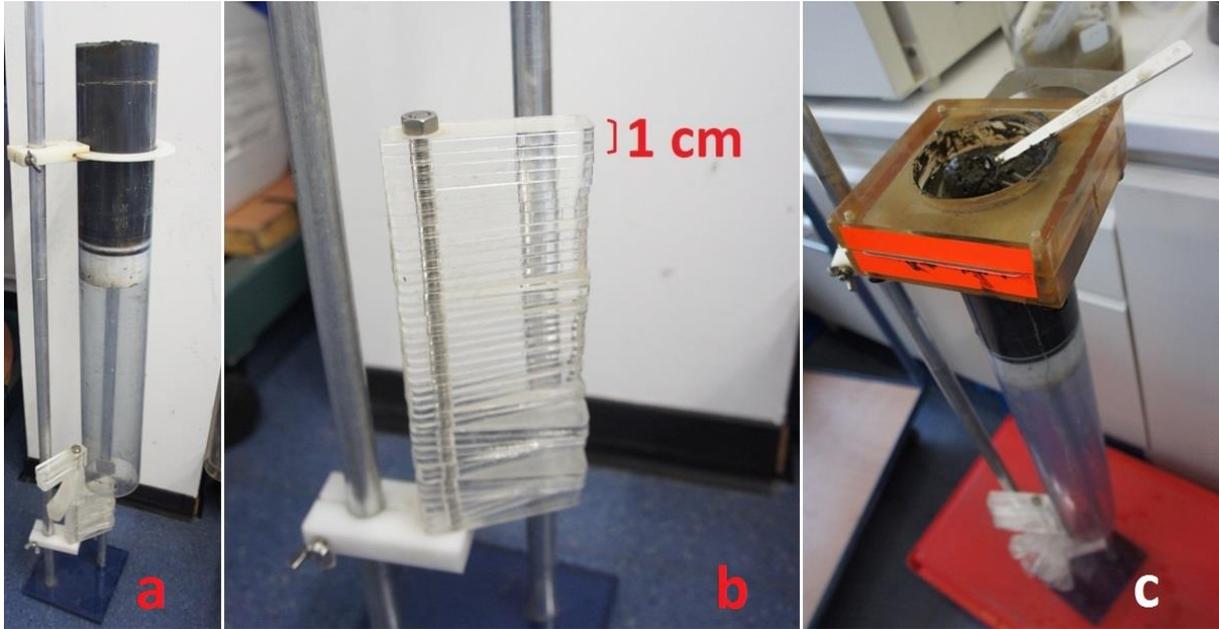


Figure 10 The first picture shows the extruder device (a) followed by the second picture (b) of the device with which the sediment was pushed up. In the last picture (c), the sectioning device is shown (Photos: Sylvia Schuster).

It is important to not disturb the top sediment layer to get intact sediment-water interfaces. When sediment approached the top of the core tube, the last bit of water was carefully removed.

WORKING PROCEDURE

ORIGINAL SEDIMENT ANALYSIS:

The upper 5cm of the two shortest sediment cores were analysed. The sediment was pushed up 0.5cm at a time (Figure 10b). The sediment was sectioned into 0.5cm samples using a sectioning device (Figure 10c).

CORE-EXPERIMENT-ANALYSES:

For the first analysis, the upper 4cm were sectioned into 1cm, the next 3cm were sectioned into 0.5cm and the last 3cm were sectioned into 1cm again. This way, there were 13 samples per core and 10cm of each sediment core analysed.

After the first results, it was decided to change the sectioning for the second and third analysis to 12cm per core because the Phoslock[®] layer was deeper than expected. The upper 4cm were sectioned in 1cm intervals and the next 8cm in 0.5cm intervals which meant 20 samples per core.

3.6 GRAIN SIZE ANALYSIS

The grain size is an important characteristic to understand different processes in the sediment. The grain size was analysed by CILAS 1190 PARTICLE-SIZE-ANALYSER from the company Cilas, France (Figure 11). The measurement principle can be found in the internship report.



Figure 11 Cilas 1190 Particle-Size-Analyser used at UFZ, Magdeburg, Germany (Photo: Sylvia Schuster).

WORKING PROCEDURE

The procedure was the same for the original sediment analysis as for the core-experiment-analyses. 2-3 drops of each sample were enough to analyse each as a triplicate to get a representative mean value. The measurements were conducted in the liquid dispersion mode. The sample was put into the device. A stirrer made of metal prevented an accumulation of the sediment particles. Cilas measurement range is between $0.04\mu\text{m}$ and 2.5mm . A background measurement was performed prior to every measurement to avoid falsification of results due to water impurity. It is important to make sure that the amount of the samples does not cause an obscuration. A high amount of sediment can cause multiple scattering which can lead to a falsification of results (Cilas Particle Size, 2015).

Cilas gives out graphs that show cumulative curves and a belonging table that gives an indication of the cumulative particle size distribution of 10%, 50% and 90% of the particles in volume (μm) (Figure 12). The example shows the results of a measurement of the PreA1 core (0-0.5cm). So 10% of the particles of the PreA1 core (0-0.5cm) have the maximum diameter of $5.48\mu\text{m}$ etc.

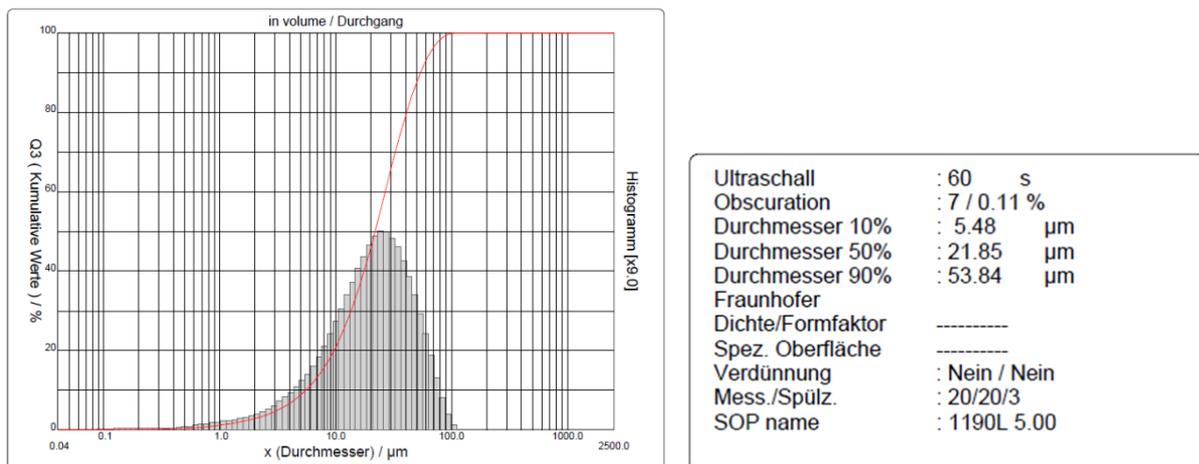


Figure 12 Example graph of the PreA1 core (0-0.5cm) showing a cumulative curve with a table of the values of the maximum diameter 10%, 50% and 90% of the particles.

3.7 DRY WEIGHT, WATER CONTENT, IGNITION LOSS AND DRY BULK DENSITY

The dry weight, the water content, the ignition loss and the Dry Bulk Density (DBD) are important features for the characterisation of the sediment.

WORKING PROCEDURE

ORIGINAL SEDIMENT ANALYSIS:

Before the samples were filled into fireclay crucibles, the crucibles needed to be heated by the muffle furnace to make sure that previous remainder of samples are completely gone. The fireclay crucibles were then weighed and noted (Mass of fireclay crucible (m_f) = m_f). Each sample was made as homogeneous as possible by agitation. To get all the desired values, 5ml (Mass of sample = m_s and Volume of the sample V_s) of each sample was filled into the fireclay crucibles using a small syringe.

The filled fireclay crucibles were then dried for 24 hours in the drying oven at 105°C, weighed and noted again. To make sure that the samples were completely dried, the fireclay crucibles were weighed several times until the constant dry weight was reached (Mass m_f + dry sample = m_{fs}). Table 6 shows a list of symbols and names with used units to calculate the dry weight, the water content and the DBD.

The filled fireclay crucibles were then put in the muffle furnace for 6 hours at 550°C, weighed and noted. At this temperature, the organic and the water of crystallisation component of the sample are removed. The result was the ignition residue which is used for the microwave pressure digestion to avoid strong chemical reaction. It represents an assumption of the amount of inorganic compounds.

Table 6 List of symbols and names with the used units that are used to calculate the dry weight, the water content, the Dry Bulk Density DBD and the loss on ignition

SYMBOL	NAMES	UNIT
m_s	Mass of sample	[g]
m_f	Mass of fireclay crucible (fc)	[g]
m_{fs}	Mass of fc + dry sample	[g]
m_{ds}	Mass dry sample	[g]
m_{sl}	Mass sample loss	[g]
WC	Water content	[%]
V_s	Volume of sample	[cm ³]
DBD	Dry Bulk Density	[g/cm ³]
LOI	Loss on Ignition	[%]
IR	Ignition residue	[g]

To get the *dry sample weight*, the weight of the fireclay crucible is subtracted from the dry weight measured in the end (1).

$$m_{ds} = m_{fs} - m_f \quad (1)$$

With the original weight of the sample m_s , it is possible to calculate the weight loss (m_{sl}) by subtracting the dry weight of the sample from the original weight of the sample (2).

$$m_{sl} = m_s - m_{ds} \quad (2)$$

To get the *water content* (WC), the weight loss m_{sl} is divided by the original weight of the sample m_s and multiplied by the factor 100 to get the percentage of the water content of the sample (3). The water content can also be calculated by calculating the percentage of weight loss first and then subtracting it from 100.

$$WC = \frac{m_{sl}}{m_s} \times 100 \quad (3)$$

The *dry bulk density* (DBD) is calculated by dividing the dry sample weight by the sediment volume (4).

$$DBD = \frac{m_{ds}}{V_s} \quad (4)$$

The *loss on ignition* (LOI) was calculated by subtracting the ignition residue (IR) from the dry weight m_{ds} , dividing it by the dry weight m_{ds} and multiplying it by 100 (5).

$$LOI = \frac{m_{ds} - IR}{m_{ds}} \times 100 \quad (5)$$

CORE-EXPERIMENT-ANALYSES:

The formulas and the procedure were basically the same as for the original sediment analysis with the difference that no Dry Bulk Density was measured because 5ml of sample would have been needed but the mass of the 0.5cm sections were too small. The samples were filled into quartz and fireclay crucibles (Figure 13). The crucibles were weighed without the sample and then with the sample. Everything was noted. The filled crucibles were put in the drying oven at 105°C for 24hours. They were weighed and the constant dry weight was noted. The dry weight was calculated using the calculation (1) and the water content was calculated using the calculations (2) and (3).

The filled crucibles were then put in the muffle furnace for 6 hours at 550°C and weighed again. The result was the ignition residue with which the loss on ignition was calculated (5).



Figure 13 Samples right after sectioning filled in quartz and fireclay crucibles (Photo: Sylvia Schuster).

3.8 GRINDING BY PESTLE AND MICROWAVE PRESSURE DIGESTION

WORKING PROCEDURE GRINDING BY PESTLE

ORIGINAL SEDIMENT ANALYSIS:

To achieve the amount necessary for the microwave digestion, the rest of the samples were put onto petri dishes and in the drying oven for 24 hours. All the variables were already measured, that is why no weighing was necessary as it was for the fireclay crucibles. Because lanthanum is not volatile, it was possible to use the dry sample remaining from the muffle furnace. The dried and ignited part of each sample was ground by pestle together so they would have a homogeneous grain size and a homogeneous distribution of elements (Figure 14). This is very important to get representative samples.

CORE-EXPERIMENT-ANALYSES:

All the samples from the muffle furnace were ground by pestle.



Figure 14 Mortar used for grinding of the samples (samples are in the fire clay crucibles) (Photo: Sylvia Schuster).

WORKING PROCEDURE MICROWAVE PRESSURE DIGESTION

The purpose of microwave digestion systems is to bring the dried, ground and homogenized samples into the form of a solution. This is necessary before they can be inserted in the analysis devices. Lanthanum occurs naturally in the silicates Cerite, Orthite and Monazite (Remy, 1959). All of them are soluble in acid which means that no chemically more aggressive methods were needed and that the Aqua Regia digestion was sufficient (Schorn, 1999-2015). The name Aqua Regia comes from the ability to remove noble metals like gold from substrates (Princeton-University, 2015).

The procedure was the same for the original sediment analysis as for the core-experiment-analyses with the difference that the core-experiment samples were analysed as duplicates. The inverse Aqua Regia (mixture of HCl, 30 % and HNO₃, 65 %) is used for the microwave pressure digestion CEM (Figure 15). 2ml HCl and 6ml HNO₃ were added to 250mg of dried, ignited and ground sample. The sample was inserted in the CEM where it was heated under increasing pressure up to 170°C, oxidized and broken down into a clear solution with the analytes of interest. The overlaying water of the samples was then filled in flasks. After they cooled down, the flasks were filled with purified water until 25ml was reached. The samples from the flasks were then filled into labelled centrifuge tubes for further analysis.



Figure 15 Microwave pressure digestion device by the company CEM (Photo: Sylvia Schuster)

3.9 ELEMENTAL ANALYSIS

To analyse the chemistry of the samples, different methods can be used. At the UFZ, the multi-element analysis devices ICP-MS 7500c, Agilent Technologies and the ICP-OES, Perkin Elmer are most commonly used (Figure 16). While it is possible to only get metals and certain non-metals elements analysed by the ICP-MS, the ICP-OES is able to analyse even more elements. The ICP-OES was therefore used for the different elements in the sediment while the ICP-MS was used to analyse water samples because of a lower detection limit. The measurement principle can be found in the internship report.

WORKING PROCEDURE

The procedure was the same for the original sediment analysis as for the core-experiment-analyses. For the measurement of the sediment samples that were already in a solution because of the microwave pressure digestion, a dilution 1:10 was used. The analysis was done by laboratory staff. The dilution was needed otherwise the concentrations of the samples might be higher than their threshold of measurement.



Figure 16 Inductively coupled plasma mass spectrometry device ICP-MS 7500c by Agilent Technologies and Inductively coupled plasma atomic emission spectroscopy ICP-OES by Perkin Elmer at the UFZ, Magdeburg, Germany (Photos: Sylvia Schuster).

3.10 SOLUBILITY OF SUBSTANCES CONTAINING LANTHANUM

To test the hypothesis that release of lanthanum in water is unlikely, a second small long-time-experiment was carried out. To test the solubility, six beakers were filled with:

Tap water as a blank value:

- ① water as a blank value
- ② water

Different dosages of Phoslock®:

- ③ 20g Phoslock®
- ④ 50g Phoslock®

Different amounts of sediment mixed with different dosages of Phoslock®:

- ⑤ 20g wet sediment + 17mg Phoslock® (from Internship, 21st of Oct 2014)
- ⑥ 60g wet sediment taken from sampling location YRH (\cong 1cm sediment layer from sediment core) + 5g Phoslock®

1l water was added per beaker. They were stored in the dark and with a lid on top. To avoid mechanical overstimulation, the beakers were shaken overhead once per week. Figure 17 shows the two beakers filled with Phoslock®, the two with sediment mixed with Phoslock® and one with water.



Figure 17 Beakes filled with 20g and 50g Phoslock®, 20g wet sediment and 17mg Phoslock® and 60g wet sediment and 5g Phoslock® and water (Photos: Sylvia Schuster).

The first water analysis was done two weeks after the experiment started, the second analysis was done one week later and the third one two weeks later. After that, analysis was done after four weeks and then after four weeks again. The experiment ran for a total of 13 weeks. An end-analysis was done at the end of the experiment to analyse the following parameters: DOC, pH, electrical conductivity, phosphorus (SRP and TP), alkalinity, Ca, La, Mg, Na, K, Cl and SO₄.

The schedule of the lanthanum analyses and the end-analysis is shown in Table 7 (see next page).

Table 7 Schedule for the lanthanum analysis and the end-analysis of the beakers.

WHAT	WHEN	DATE
Lanthanum	Right after experiment start-up	17 th of February 2015
	2 weeks after the 1 st analysis	23 rd of February 2015
	2 weeks after the 2 nd analysis	9 th of March 2015
	4 weeks after the 3 rd analysis	23 rd of March 2015
	4 weeks after the 4 th analysis	20 th of April 2015
Lanthanum End-analysis	4 weeks after the 5 th analysis	18 th of May 2015

WORKING PROCEDURE

For every analysis, 6ml water was taken from each beaker glass to analyse the lanthanum-concentration and another 6ml was taken for duplicates. The samples were filtered using so-called single Minisart High-Flow single use syringe filters with pore width 0.2µm and analysed by the ICP-MS.

For the DOC, 25ml were filtered by glass syringes with filters of 0.45µm. For the element analysis, 15ml were filtered by the 0.2µm filter and analysed by the ICP-MS. For the phosphorus SRP 6ml were filtered with pore width 0.2µm as well. All filters came from the German company Sartorius AG. 50ml were taken unfiltered to analyse the phosphorus TP. For the pH and the electrical conductivity 250ml were taken unfiltered.

4 RESULTS AND DISCUSSION

4.1 ORIGINAL SEDIMENT ANALYSIS

4.1.1 GRAIN SIZE

The grain size for sediment core PreA1 and PreA2 was analysed as triplicate. As an example, the second measurement per layer was selected in Table 8. The table shows the cumulative particle size distribution of 10%, 50% and 90% of the particles. So 10% of the particles of PreA1 (0-0.5cm) have the maximum diameter of 4.81 μ m etc.

Table 8 Grain size results of PreA1 and PreA2.

Sample	Diameter 10% in μ m	Diameter 50% in μ m	Diameter 90% in μ m
PreA1 0-0.5cm	≤4.81	≤19.64	≤50.47
PreA1 0.5-1cm	≤4.74	≤19.92	≤51.41
PreA1 1-1.5cm	≤4.97	≤20.65	≤52.17
PreA1 1.5-2cm	≤5.19	≤21.26	≤51.82
PreA1 2-2.5cm	≤5.44	≤21.82	≤52.29
PreA1 2.5-3cm	≤5.36	≤21.79	≤50.57
PreA1 3-3.5cm	≤5.07	≤20.49	≤48.22
PreA1 3.5-4cm	≤5.47	≤22.17	≤48.87
PreA1 4-4.5cm	≤5.24	≤21.26	≤49.11
PreA1 4.5-5cm	≤5.26	≤21.78	≤50.83
PreA2 0-0.5cm	≤4.64	≤18.15	≤43.16
PreA2 0.5-1cm	≤5.10	≤19.96	≤46.80
PreA2 1-1.5cm	≤4.85	≤19.41	≤47.88
PreA2 1.5-2cm	≤5.51	≤21.00	≤46.21
PreA2 2-2.5cm	≤5.45	≤21.17	≤46.32
PreA2 2.5-3cm	≤4.75	≤19.40	≤47.54
PreA2 3-3.5cm	≤4.76	≤18.88	≤47.18
PreA2 3.5-4cm	≤4.79	≤19.42	≤48.17
PreA2 4-4.5cm	≤4.81	≤19.53	≤47.97
PreA2 4.5-5cm	≤3.90	≤17.57	≤43.21

ISO 14688 grades silts between 2-63 μ m. This means that the pre-analysis of the sediment used for this experiment falls into the category “silt”. This makes it thus suitable for the experiment since ground Phoslock® suspension falls for the most part into the same category as well (see 2.1.2). If the Phoslock® particles would sink into the sediment depends amongst others on the density and the particle size of the Phoslock® and the sediment. If the Phoslock® particles have a greater density (see 2.1.2) than the sediment but the particle size is equal, the Phoslock® particles will not sink. This is important for the purpose as a time marker.

4.1.2 DRY WEIGHT, WATER CONTENT, DRY BULK DENSITY AND IGNITION LOSS

Table 9 shows the results per layer of sediment core PreA1 and PreA2 concerning sample wet and dry weight in g, the water content in %, the Dry Bulk Density in g/cm³ of the sediment volume=5ml and the ignition residue in g and loss in %. The full table including mass of the crucible, sample loss and ignition loss can be found on the CD (this applies for all the following tables).

Table 9 Results of PreA1 and PreA2 of dry weight, water content, Dry Bulk density and ignition residue and loss.

Sample	Sample wet weight	Sample dry weight	Water content	Dry Bulk Density	Ignition residue	Loss on Ignition
	in g	in g	in %	in g/cm ³	in g	in %
PreA1 0-0.5cm	5.422	0.896	83.5	0.1653	0.77	14.1
PreA1 0.5-1cm	5.355	0.971	81.9	0.1813	0.833	14.2
PreA1 1-1.5cm	5.291	1.082	79.6	0.2045	0.933	13.8
PreA1 1.5-2cm	5.417	1.177	78.3	0.2354	1.017	13.6
PreA1 2-2.5cm	5.617	1.226	78.2	0.2183	1.056	13.9
PreA1 2.5-3cm	5.692	1.163	79.6	0.2043	0.991	14.8
PreA1 3-3.5cm	5.389	1.188	78	0.2204	1.017	14.4
PreA1 3.5-4cm	5.797	1.355	76.6	0.2337	1.17	13.7
PreA1 4-4.5cm	5.806	1.417	75.6	0.2441	1.228	13.3
PreA1 4.5-5cm	5.673	1.423	74.9	0.2508	1.229	13.6
PreA2 0-0.5cm	4.92	0.678	86.2	0.1378	0.579	14.6
PreA2 0.5-1cm	5.189	0.922	82.2	0.1777	0.789	14.4
PreA2 1-1.5cm	5.202	0.996	80.9	0.1915	0.857	14.0
PreA2 1.5-2cm	5.226	1.045	80	0.2	0.896	14.3
PreA2 2-2.5cm	5.614	1.198	78.7	0.2134	1.028	14.2
PreA2 2.5-3cm	5.491	1.185	78.4	0.2158	1.018	14.1
PreA2 3-3.5cm	5.979	1.331	77.3	0.2226	1.144	14.0
PreA2 3.5-4cm	5.843	1.314	77.5	0.2249	1.127	14.2
PreA2 4-4.5cm	5.948	1.375	76.9	0.2312	1.183	14.0
PreA2 4.5-5cm	5.729	1.366	76.2	0.2384	1.17	14.3

The water content of the samples decreases per depth. This is logical because the sediment surface is more in contact with the water and thus more watery than the underlying sediment. The Dry Bulk Density increases which is also logical because of the decrease in water content and thus an increase in the sediment weight. The loss on ignition is very similar per depth which means that the organic content stays about the same.

Potential measurement inaccuracy can occur because of measurement difficulties, in this case of the volume=5ml of the sample with which the Dry Bulk Density was calculated.

4.1.3 ELEMENTAL ANALYSIS

Table 10 shows the elemental analysis for sediment core PreA1 and PreA2. Especially lanthanum is important for the experiment.

Table 10 Elemental analysis results of PreA1 and PreA2.

Sample	Element in $\mu\text{g/g}$									
	Al	Ca	Fe	K	La	Mg	Mn	Na	P	Zn
PreA1 0-0.5cm	34195	4319	41398	6497	24	5071	1723	389	1943	495
PreA1 0.5-1cm	28059	4007	38617	4058	21	5054	1378	263	1980	503
PreA1 1-1.5cm	30391	3560	36724	4996	22	4817	1404	270	1883	494
PreA1 1.5-2cm	31739	3486	38217	5197	23	5122	1377	283	1927	510
PreA1 2-2.5cm	23213	3361	36858	2810	20	4720	1305	207	1913	490
PreA1 2.5-3cm	33566	3283	39750	6317	20	4980	1350	351	1965	498
PreA1 3-3.5cm	24161	3253	37955	3036	17	4956	1272	218	1725	486
PreA1 3.5-4cm	29829	3005	37209	4864	19	4530	1188	260	1662	454
PreA1 4-4.5cm	32234	3379	39574	5170	19	5522	1263	292	1972	492
PreA1 4.5-5cm	21749	3113	35650	2399	16	4152	1122	191	1782	489
PreA2 0-0.5cm	23577	4671	41800	2787	16	4924	2511	235	1851	479
PreA2 0.5-1cm	24920	4413	40390	2939	16	5111	1749	229	1910	499
PreA2 1-1.5cm	23142	3765	37088	2880	16	4424	1348	224	1863	467
PreA2 1.5-2cm	30883	3738	37565	4828	17	5370	1248	263	1934	465
PreA2 2-2.5cm	31130	3765	37094	5177	20	4868	1180	275	1817	465
PreA2 2.5-3cm	32867	3548	37332	5645	20	5541	1170	307	1891	478
PreA2 3-3.5cm	33668	3540	40271	5847	20	5066	1215	320	1962	492
PreA2 3.5-4cm	31820	3428	37251	5294	20	5360	1107	285	1864	480
PreA2 4-4.5cm	32862	3469	39286	5547	20	5041	1138	298	1883	497
PreA2 4.5-5cm	38022	4021	43552	6289	21	6166	1259	341	2162	566

The elemental analysis shows that the natural lanthanum concentration of the experiment sediment is around $20\mu\text{g/g}$. The low concentration confirms the typical background concentrations as described in 2.1.1 and means that the natural lanthanum in the lake plays most likely no role for phosphate binding.

The measured elements show high concentrations of aluminum and iron. It looks like the mineral component is quite high.

All measured concentrations show that each core varies slightly even though it was tried to take the cores at the same location. Elements not shown and thus not measured were not of interest.

4.2 CORE-EXPERIMENT-ANALYSIS AFTER ONE WEEK STORAGE

4.2.1 GRAIN SIZE AND DRY WEIGHT, WATER CONTENT AND IGNITION RESIDUE AND LOSS

The grain size for sediment core 1 and 2 and the table showing wet and dry weight, water content, ignition residue and loss can be found in Appendix 9.3.

According to ISO 14688, the particles fall as expected into the category “silt” as well.

The upper 0-2cm of both cores is as expected very watery (WC up to 83%). The water content decreases per layer. The loss on ignition which indicates the organic component is very similar for all the layers (mean LOI: 15.05%).

4.2.2 ELEMENTAL ANALYSIS

The Phoslock® layer was expected to be in the 4-5cm layer for core 1 while it was supposed to be in 5.5-6.5cm layer for core 2. The explanation why the Phoslock® was expected in these layers can be found in Table 14 in Appendix 9.2. It was tried to add 5cm sediment on top. The table shows the original sediment core length as well as the added sediment on top.

As shown in Figure 18, the Phoslock® layer was not where it was expected to be but deeper in the 7-9cm layer. Because duplicates were measured, the mean lanthanum concentration is used.

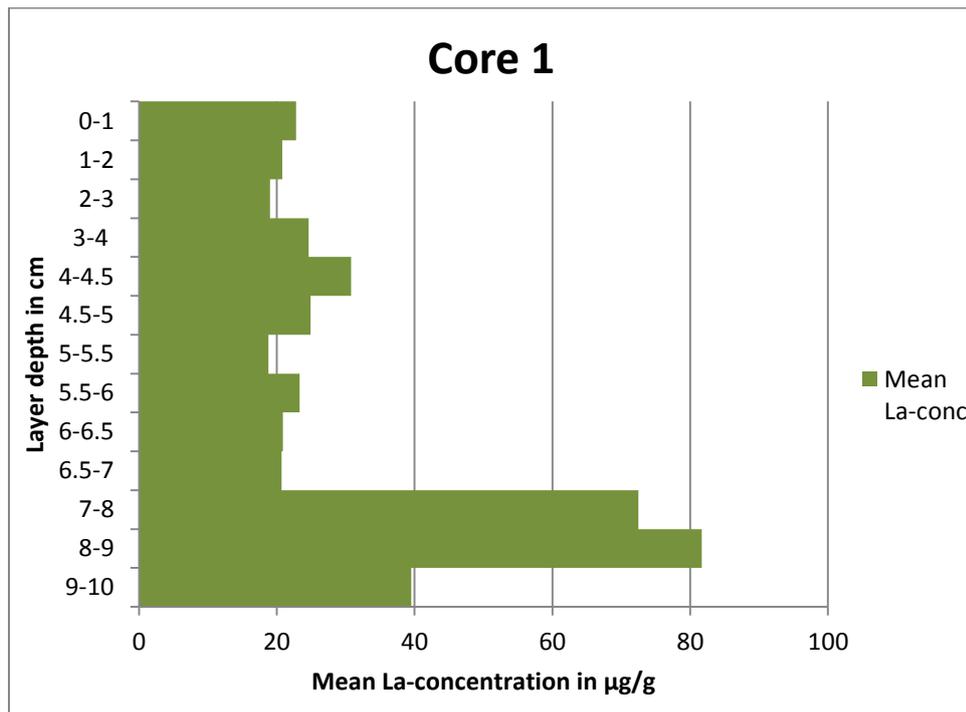


Figure 18 Mean lanthanum concentration in µg/g of the measured sample duplicates per layer depth in cm for core 1.

The same is shown in Figure 19 where the lanthanum peak is clearly visible in layer 7-8cm. During the sediment core preparation, the sediment ice core sunk quite early (see Appendix 9.2). The ice core could have pressed the Phoslock® layer down in core 2 but this still does not explain why it also happened in core 1.

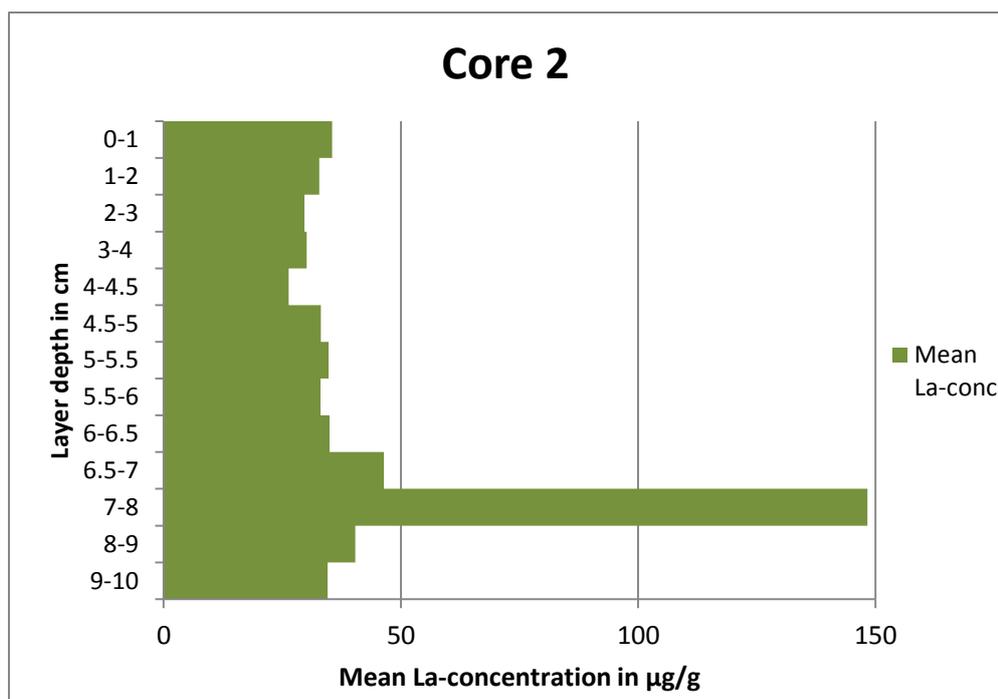


Figure 19 Mean lanthanum concentration in µg/g of the measured sample duplicates per layer depth in cm for core 2.

For core 1, it is most likely that the Phoslock® layer was cut in half by sectioning while the peak in core 2 is clearly visible. It looks like the desired lanthanum concentration of 200µg/g is not reached but is about 150µg/g. This is acceptable because Phoslock® is not as homogeneous and the calculated Phoslock® dosage is based on assumptions of the Dry Bulk Density that changes per layer. According to the results of the original sediment analysis, the smallest calculated Dry Bulk Density was 0.1378 g/cm³ while the largest was 0.2508 g/cm³. The DBD used for the experiment calculation was 0.23g/cm³. As a consequence, the used Phoslock® dosage would be 34mg to 61mg respectively instead of 56mg (see 3.2.1). For this experiment, 56mg were used. This means that a concentration 15 times as high as the natural lanthanum concentration of 1cm layer of sediment was reached for the lowest DBD while it was 8 times as high for the largest DBD. Consequently, the lanthanum end-concentration would be 300µg and 160µm respectively.

Because the Phoslock® layer was deeper than expected, the sectioning was changed from 10cm to 12cm for the second and third analysis.

4.3 CORE-EXPERIMENT-ANALYSIS AFTER SEVEN WEEKS STORAGE

4.3.1 GRAIN SIZE AND DRY WEIGHT, WATER CONTENT AND IGNITION RESIDUE AND LOSS

The grain size for sediment core 3 and 4 and the table showing wet and dry weight, water content, ignition residue and loss can be found in Appendix 9.4.

The particles fall as expected into the category “silt” as well.

The water content of both cores decreases per layer with a slight increase in core 3. This could be caused by measurement errors. The loss on ignition is very similar as it was for the first cores (mean LOI: 14.15%). The mass of the 0-1cm layer of core 3 is almost double which indicates unevenness of the top layer. Inaccurate sectioning most likely caused in the 7-7.5cm layer more mass compared to the other 0.5cm layers.

4.3.2 ELEMENTAL ANALYSIS

The Phoslock® layer was expected to be in the 3-5.5cm layer (see 9.2). An uneven top layer was visible for core 3 before the preparation. The mean lanthanum concentration distribution is shown in Figure 20.

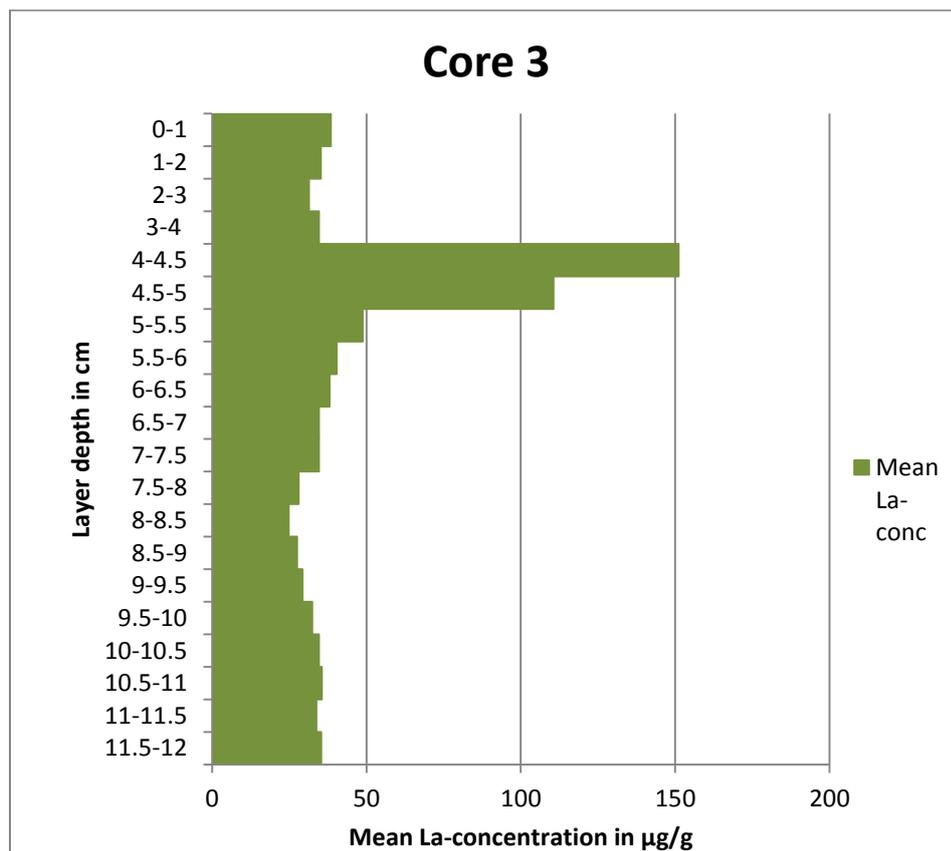


Figure 20 Mean lanthanum concentration in µg/g of the measured sample duplicates per layer depth in cm for core 3.

The Phoslock® layer stayed where it was applied in the 4-5cm layer. The uneven top layer of core 3 shows in the distribution of lanthanum.

The Phoslock® layer was supposed to be in the 4-5cm layer for core 4 (see 9.2). The lanthanum distribution is shown in Figure 21.

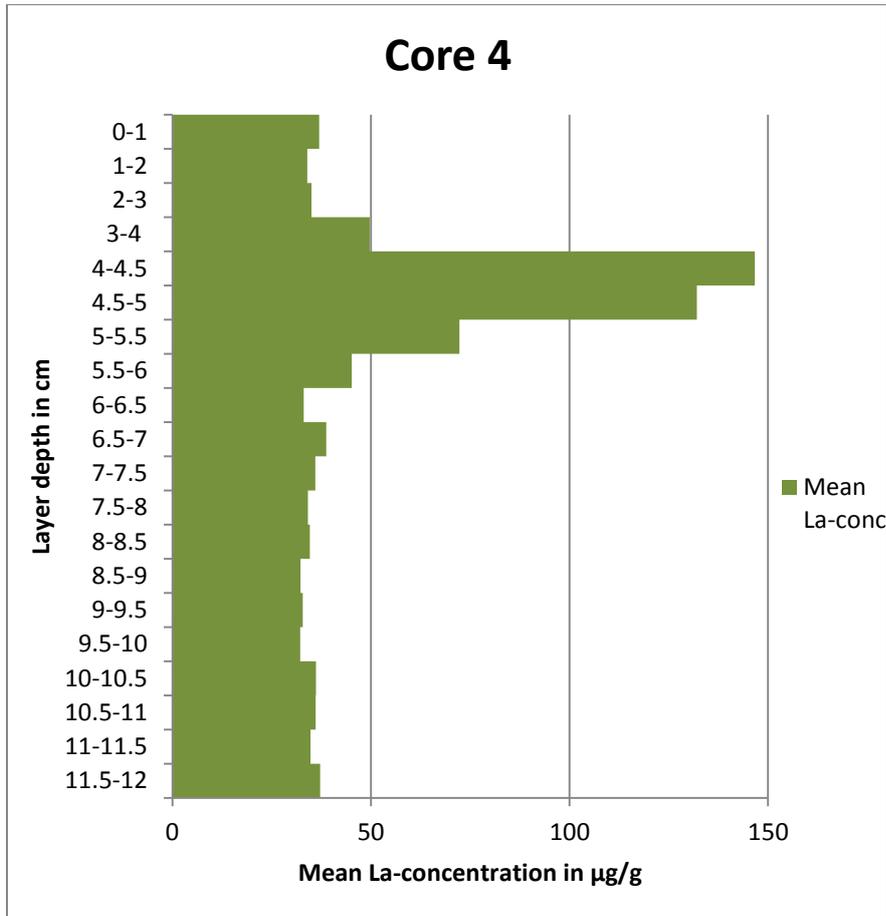


Figure 21 Mean lanthanum concentration in µg/g of the measured sample duplicates per layer depth in cm for core 4.

The results are very similar to core 3. It looks like the tracer layer was cut in half. A possible explanation of the further divided peak could be inaccurate sectioning.

4.4 CORE-EXPERIMENT-ANALYSIS AFTER TEN WEEKS STORAGE

4.4.1 GRAIN SIZE AND DRY WEIGHT, WATER CONTENT AND IGNITION RESIDUE AND LOSS

The grain size for sediment core 5 and 6 and the table showing wet and dry weight, water content, ignition residue and loss can be found in Appendix 9.5.

The particles fall as expected into the category “silt” as well.

The upper 0-2cm of core 6 is very watery (WC up to 87%). The water content of both cores decreases per layer. The loss on ignition is very similar as it was for the other cores (mean LOI: 14.3%).

4.4.2 ELEMENTAL ANALYSIS

The Phoslock® layer was expected to be in the 3-4.5cm layer for core 5 (see 9.2). The mean lanthanum concentration distribution is shown in Figure 22.

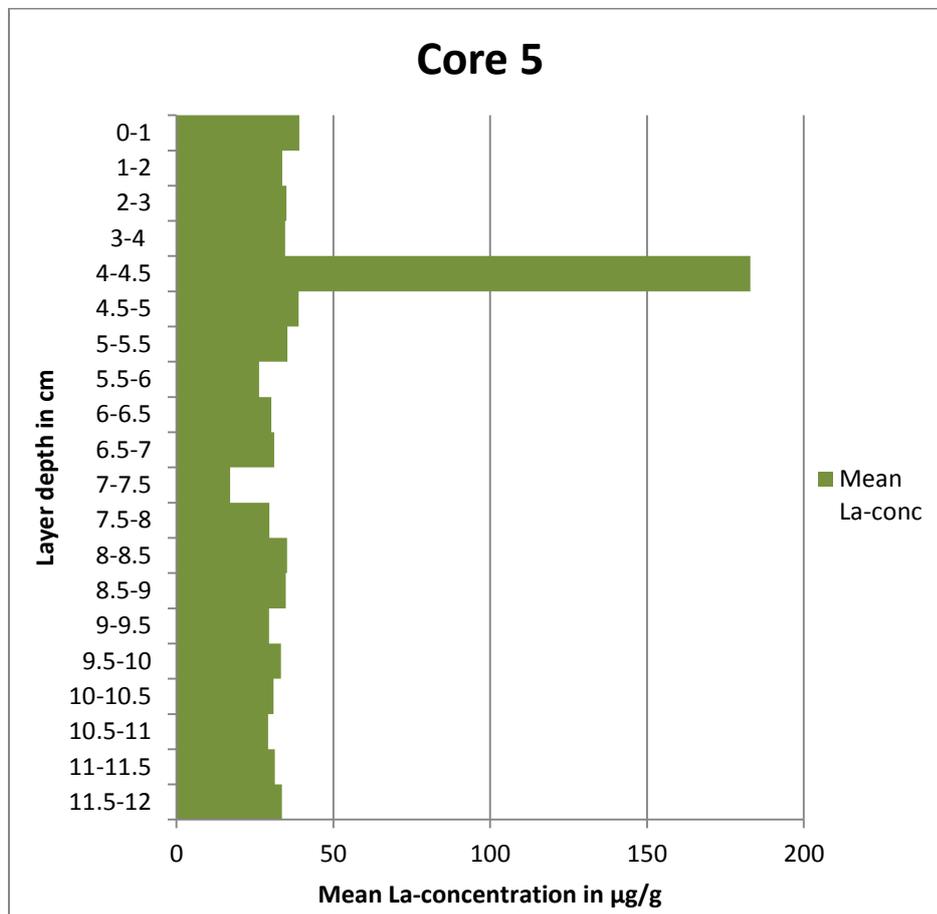


Figure 22 Mean lanthanum concentration in µg/g of the measured sample duplicates per layer depth in cm for core 5.

The lanthanum peak is clearly visible in core 5. The applied Phoslock® stayed exactly where it was supposed to be.

The Phoslock® layer was supposed to be in the 5-6.5cm layer for core 6 (see 9.2). The lanthanum concentration is shown in Figure 23.

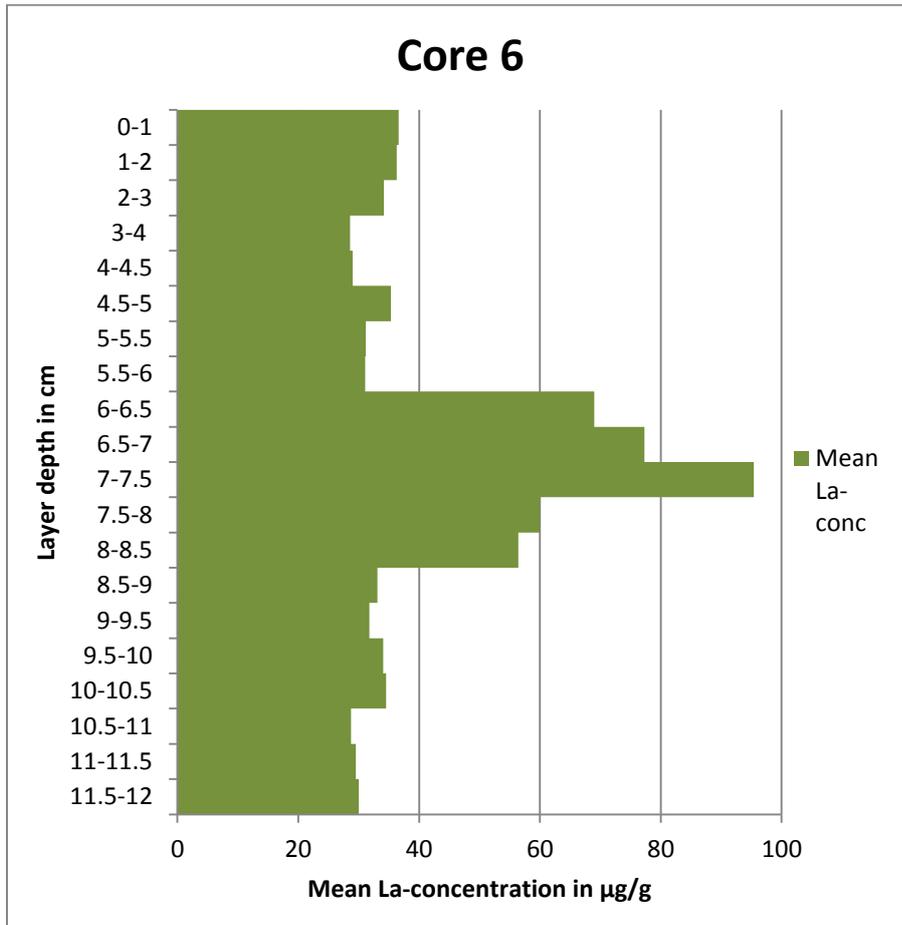


Figure 23 Mean lanthanum concentration in $\mu\text{g/g}$ of the measured sample duplicates per layer depth in cm for core 6.

The duration of this experiment was too short to conclude if diffusion influences the mobility of lanthanum. Even if the lanthanum concentration is distributed over 2.5cm in core 6, the peak in core 5 is clearly visible. The large peak in core 6 is most likely caused by irregularities in the sediment core preparation because the lanthanum peak for core 1 and 2 was found in deeper layers as well. Inaccurate sectioning most likely plays a role as well.

4.5 CORE-EXPERIMENT DISCUSSION

The duration of this experiment was too short to explain the lanthanum distribution only by diffusion. Clear lanthanum peaks were visible in all cores. The divided peaks were most likely caused by inaccurate sectioning because 0.5cm intervals were difficult by hand.

However, the Phoslock® layer of three analysed cores was not where it was expected to be but significantly lower. It is most likely that this was caused by irregularities in the sediment core preparation.

Possible irregularities:

- The weight of the sediment suspension on top pressed the Phoslock® layer downwards
- Sunken sediment ice core pressed down the Phoslock® layer (Core 2)
- Compression caused by sedimentation over time
- Compression during sectioning and pushing the sediment up (Review with Kurt Friese, scientist at UFZ)
- All original cores had different sediment surfaces although taken at the same location
- Irregularities in the sediment core preparation
- Disputable if the used methods for the application of Phoslock® and the sediment were best (Phoslock® layer was most likely more disturbed than assumed)
- "Sediment on top" was different for the first cores than for the last one for which a new intact core was used (more watery)

Additional factors that could have influenced the position of the Phoslock® layer:

- Gas emissions
- Bioturbation (Even though no bioturbation was observed and it is unlikely it cannot be eliminated. Maybe there were organisms present that disturbed the Phoslock® layer)

A table was created with the theoretical and real lengths of the sediment cores after application of Phoslock® and sediment and sectioning to show the possible difference that occurred between the expected Phoslock® layer and where it really was located. The table can be found in Appendix 9.6. The Phoslock® layer stayed where it was applied in core 3, 4 and 5 which is also visible in the differences. However, core 6 suggests that another factor played a role as well. Unfortunately, not all measurements were done completely that is why it is difficult to know where and why the difference occurred for sure.

Within the time frame of the bachelor thesis one possible explanation of the deeper Phoslock® layer was examined. To investigate if the sediment on top pressed the Phoslock® layer downwards, an additional experiment was carried out. Another six sediment cores were taken from the location YRH at the Rappbode Pre-Dam, Harz Mountains. A layer of 0.5-1cm soaked sawdust was applied on four cores (nr. 1, 2, 5 and 6) as suspension and a 0.5-1cm layer of Phoslock® was applied on two cores (nr. 4 and 5) as suspension. A mark was set on each tube. After the layers had time to settle, sediment-suspension was applied to have 5cm on top. The procedure was the same as it was for the core-experiment.

Phoslock® caused a visible resuspension of the sediment. This could explain the large distribution of lanthanum (core 6). In addition, the Phoslock® layer was larger than intended (2-3cm instead of 0.5-1cm). This could be explained by the expanding clay.

Pictures were taken before and right after the application of the sawdust/Phoslock® layer, after 5 days of sedimentation, right after the application of the sediment on top and 48 hours later. Appendix 9.7 shows the measured values and pictures. The sawdust layers were 0.4 to 0.7cm below the mark while the Phoslock® layers were 0.6-0.8cm below. The 3cm deeper laying Phoslock® cannot be explained completely by compression of the sediment on top.

This means that another long-time experiment of at least one year should be conducted with cores taken from a location in the lake where organisms are not present. Another important conclusion is that greatest caution must be exercised while applying Phoslock® and sediment. Finally, this experiment did not display lake conditions but laboratory conditions which means that relevant processes are missing. That is why the tracer should be further investigated under defined conditions and field conditions.

4.6 SOLUBILITY OF SUBSTANCES CONTAINING LANTHANUM

For each measured duplicate of a sample, the highest value was taken for the graphs. The detection limit was $<0.1\mu\text{g/l}$. If values were measured under the detection limit, $0.05\mu\text{g/l}$ was used.

4.6.1 WATER AS A BLANK VALUE

The lanthanum concentration in $\mu\text{g/l}$ is for water is both shown in Figure 24 and Figure 25.

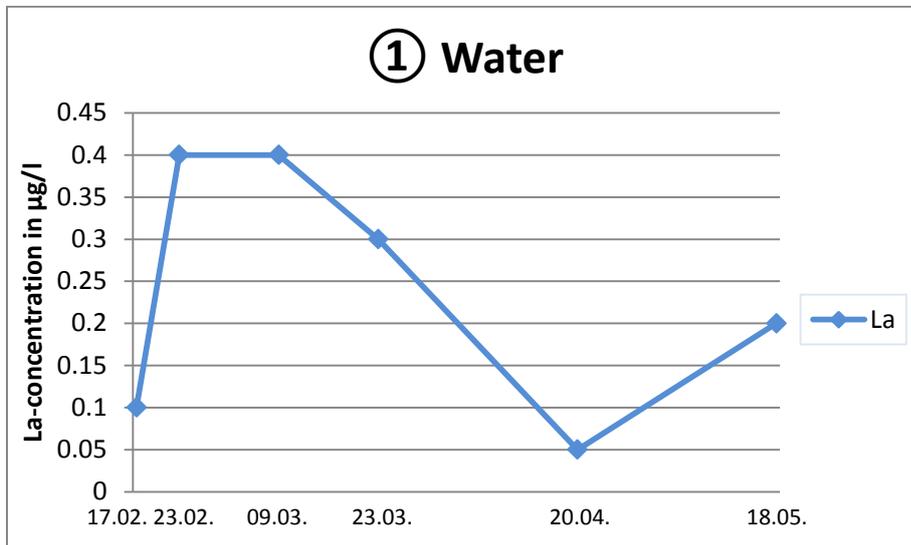


Figure 24 The graph shows the lanthanum concentration in $\mu\text{g/l}$ of 1l tap water of beaker ① over a period of 13 weeks.

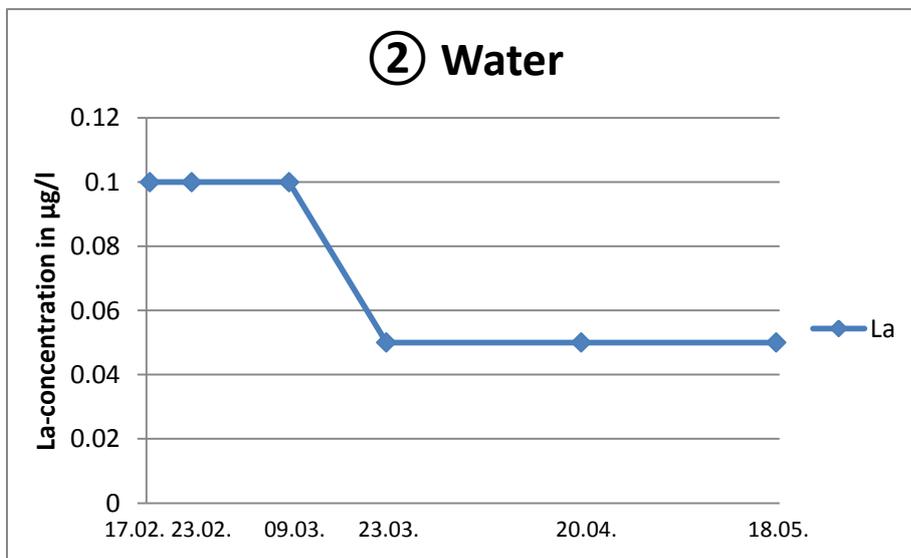


Figure 25 The graph shows the lanthanum concentration in $\mu\text{g/l}$ of 1l tap water of beaker ② over a period of 13 weeks.

According to the book “Geochemistry of European Bottled water”, there was no lanthanum found in German bottled and tap water (Reimann & Birke, 2010). The concentration found in the beaker filled with water ① has very small concentrations up to $0.4\mu\text{g/l}$ with the usual reservation of measurement inaccuracy. The concentrations for beaker ② are close to the detection limit ($0.1\mu\text{g/l}$).

4.6.2 PHOSLOCK® IN WATER

Figure 26 shows the lanthanum concentration of 20g Phoslock® while Figure 27 shows it for 50g.

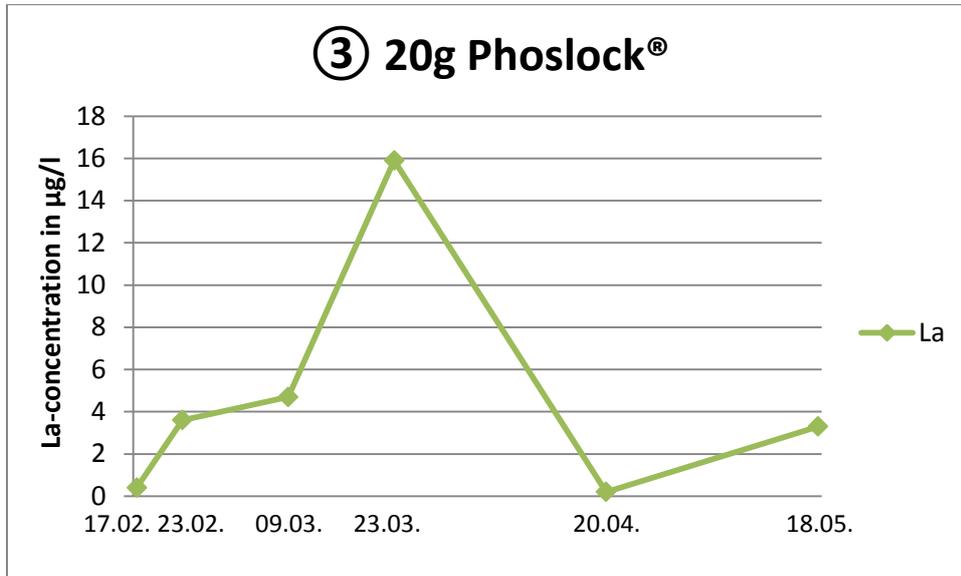


Figure 26 The graph shows the lanthanum concentration in µg/l in 1l tap water of beaker ③ filled with 20g Phoslock® over a period of 13 weeks.

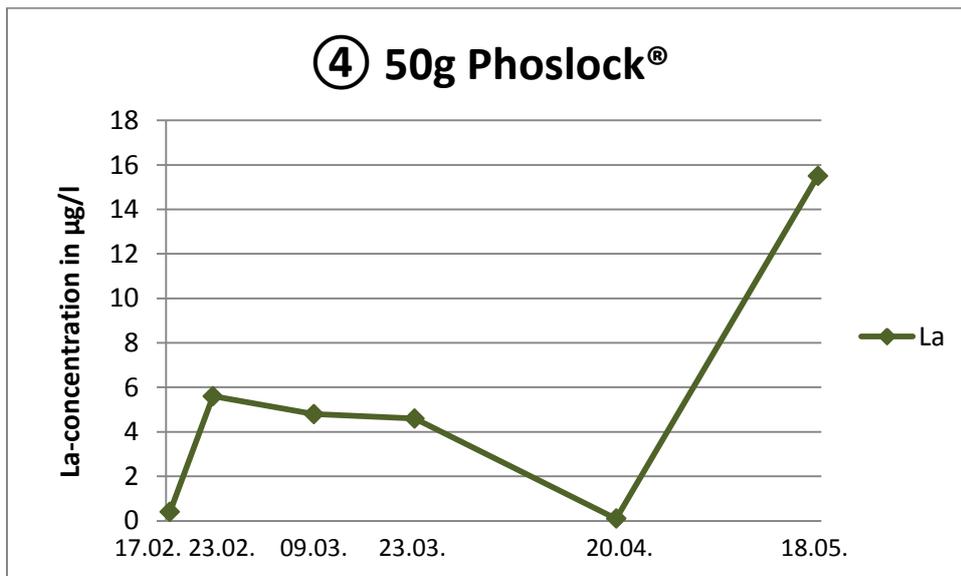


Figure 27 The graph shows the lanthanum concentration in µg/l in 1l tap water of beaker ④ filled with 50g Phoslock® over a period of 13 weeks.

The beaker filled with 20g Phoslock® ③ shows a peak at 15.9µg/l with a sharp decrease down to 0.2µg/l followed by a slight increase over the experiment time period. The beaker filled with 50g Phoslock® ④ rises up to 6µg/l followed by decrease down to 0.1µg/l at the same time as the decrease occurs for the beaker ③. In the last month of the experiment, the lanthanum concentration sharply increases in beaker ④ up to 15.5µg/l.

4.6.3 SEDIMENT MIXED WITH PHOSLOCK® IN WATER

Figure 28 shows the lanthanum concentration for 20g sediment mixed with 17mg Phoslock® while the same is shown in Figure 29 for 60g sediment and 5g Phoslock®.

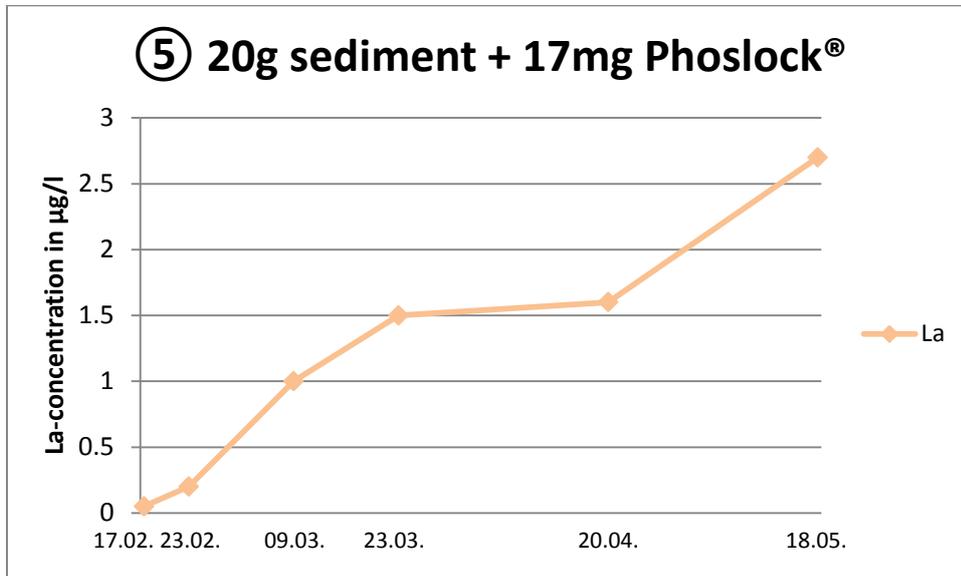


Figure 28 The graph shows the lanthanum concentration in µg/l in 1l tap water of beaker ⑤ filled with 20g sediment + 17mg Phoslock® over a period of 13 weeks.

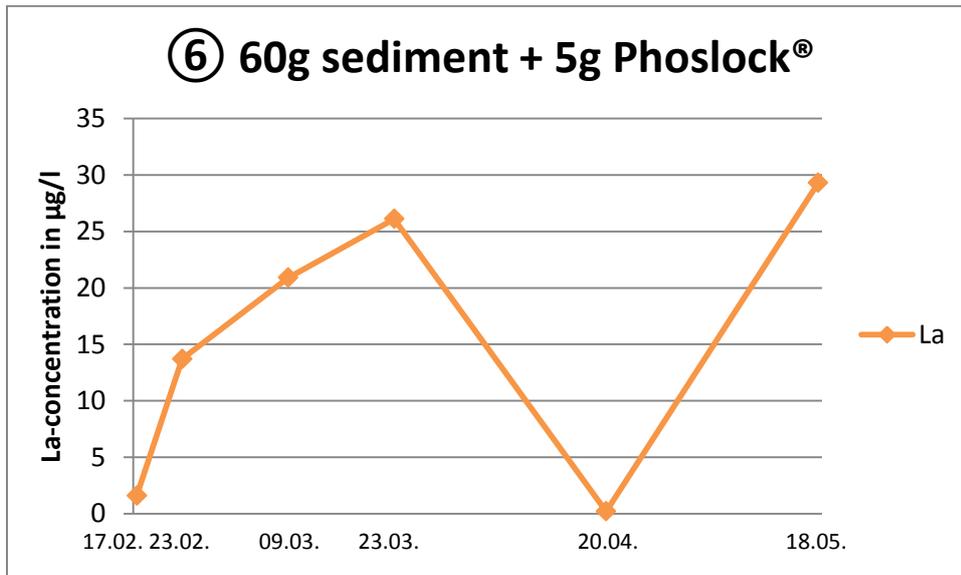


Figure 29 The graph shows the lanthanum concentration in µg/l in 1l tap water of beaker ⑥ filled with 60g sediment + 5g Phoslock® over a period of 13 weeks.

The lanthanum concentration for beaker ⑤ rises almost constantly up to 2.7µg/l. The concentration of beaker ⑥ increases during the first month of the experiment up to 26.1µg/l followed by a sharp decrease down to 0.2µg/l. The sharp decrease occurred at the same time as it did for ③ and ④. During the last month of the experiment, the concentration rises again up to 29.3µg/l.

The irregularity of the analysis done on the 20th of April 2015 can only be explained by technical measurement errors. Equilibrium was not reached for the beakers with Phoslock® and sediment mixed with Phoslock®.

4.6.4 END-ANALYSIS

Table 11 shows the measured values at the end of the experiment for the six beakers.

Table 11 Properties of the six beakers like DOC, pH, LF, SRP, TP and the acid capacity

Beaker	DOC in [mg/lC]	pH	Electrical conductivity in [mS/cm]	SRP in [mg/l]	TP in [mg/l]	Acid neutralisation capacity to pH 4.3 in [mmol/l]
① Water	3.23	7.8	0.56	0.003	0.013	2.53
② Water	3.11	8	0.57	0.008	0.019	2.46
③ 20g Phoslock®	2.18	7.5	0.99	<0.003	0.022	1.33
④ 50g Phoslock®	2.58	7.3	1.57	<0.003	0.076	0.62
⑤ 20g sediment + 17mg Phoslock®	2.90	5.7	0.60	0.032	0.090	0.12
⑥ 60g sediment (YRH) + 5g Phoslock®	2.89	5.7	0.64	<0.003	0.057	0.76

The Dissolved Organic Carbon DOC is the least for the beakers with only Phoslock®. This is because part of the DOC is most likely absorbed by the bentonite. This applies for the beakers filled with sediment and Phoslock® as well because the DOC is smaller than in the tap water. In addition, the sediment could have absorbed some as well. However, the sediment can also release DOC. This matter cannot be further determined.

The pH for the tap water is about 8. It decreases slightly in beaker ③ and ④ while it decreases significantly down to 5.7 for beaker ⑤ and ⑥ where the sediment was mixed with Phoslock®. This was expected because biological degradation processes in the sediment evidently happened and caused a formation of carbon dioxide which decreases the pH. This also explains why the acid neutralisation capacity is the lowest for beaker ⑤ and ⑥. The lower pH values for the beakers filled with Phoslock® ③ and ④ are most likely caused by the formation of lanthanum carbonate which extracts hydrogen carbonate from the water and consequently decreases acid capacity. However, this explains the lower value not completely. Other factors that could have played a role cannot be determined.

The electrical conductivity describes the concentration of dissolved ions, especially sodium and chloride. Clearly, Phoslock® released NaCl when in contact with water (see Table 12). It is assumed that this has something to do with the production process of Phoslock®. The electrical conductivity for all beakers except ④ is within the typical range for tap water (500-1000µS/cm) (Aqion, 2012-2015) while that of beaker 4 is higher.

The purpose of Phoslock® is to bind phosphate. That is why the amount of Soluble Reactive Phosphorus SRP is quite low except for beaker ⑤. The amount of added Phoslock® was obviously too small to bind all the phosphate available in the sediment.

The total amount of phosphorus TP describes the particulate phosphorus which Phoslock® is not able to bind. The TP is very high in beaker ⑤ as well as in ④. It looks like the particulate phosphorus

came from the sediment itself and maybe even from the Phoslock®. If it is released from the Phoslock® one can assume that this phosphorus will not be available for algae. This is supported by the SRP < 3µg/l.

Table 12 shows the elemental analysis of the six beakers.

Table 12 Elemental Analysis of the six beakers

Beaker	Element in mg/l					
	Ca	Cl	K	Mg	Na	SO ₄
① Water	86.9	33.25	2.42	5.87	18.1	98.53
② Water	86.6	32.63	2.32	5.76	18.2	98.6
③ 20g Phoslock®	72.1	153.19	3.02	7.42	106	105.21
④ 50g Phoslock®	69.5	330.53	4.66	6.24	215	117.11
⑤ 20g sediment + 17mg Phoslock®	84.8	33.29	2.36	6.61	18.5	208.86
⑥ 60g sediment (YRH) + 5g Phoslock®	69.7	59.77	2.3	7.29	40.3	156.46

As mentioned above, Phoslock® releases sodium and chloride.

It looks like calcium was taken up by Phoslock®. It cannot be determined if this happened by adsorption or ion exchange considering these measurements because the sediment most likely plays a role as well.

Phoslock® obviously releases potassium which can be expected from bentonite. The lower concentrations in beaker ⑤ and ⑥ can be explained by the added sediment. Sediment in general binds potassium.

Phoslock® also releases magnesium in very small amounts as well as the sediment most likely does. Small amounts of sulfate are most likely released by Phoslock® and the sediment as well. That the concentration is higher in beaker ⑤ than in ⑥ can be attributed to Phoslock®. However, this cannot be completely explained because the concentrations of ③ and ④ do not reflect this assumption.

What can be concluded from the experiment is that it should have been set up for a longer time period until the equilibrium of lanthanum would have been reached. In the beakers, Phoslock® can only interact with a limited amount of sediment. This is completely different in lake sediment conditions where no equilibrium is reached, diffusion continues and Phoslock® continues to release more and more La³⁺ ions. Among other parameters, the equilibrium concentration is needed to estimate with the help of a model calculation the diffusion of lanthanum in sediment.

During the internship, sediment and pore water samples of cores taken from two lakes (Eichbaumsee, Silbersee in Stuhr) were analysed (see Internship Report, Appendix 9.8). The highest La-concentrations found in the sediment of core I and II of the Eichbaumsee were 12454µg/g and 6729µg/g. The highest concentrations in the pore water were 8.8µg/l and 21.6µg/l respectively. The concentrations in the sediment of core I and II of the Silbersee in Stuhr were 844µg/g and 1204µg/g while the concentrations in the pore water were 11.9µg/l and 13.3µg/l respectively. It is very unlikely that lanthanum migrates in the pore water because the amount of released lanthanum in comparison to the amount of added Phoslock® and what therefore could be released is extremely small.

4.7 POSSIBLE APPLICATION OF THE TRACER IN THE FIELD

PROCEDURE

Based on 2.2.3, the company of Phoslock® already uses suitable techniques to apply Phoslock®. To get an even Phoslock®-suspension, it is important to mix it continuously and to have a pumping system to forward it to a spraying system that is mounted on a swimming platform. It is possible to bring the spraying system in depth right above the sediment (Figure 30) by fixing it with leashes under the swimming platform. The topography should be known for the lake where the tracer is supposed to be applied. With the help of a depth detection system, the spraying system is cautiously lowered until it hangs close to the sediment surface without disturbing it.



Figure 30 Spraying system used for Phoslock® applications. The spray bar can be hung in the hypolimnion or above the surface (Phoslock, 2015).

The spraying system should not be too close because of resuspension. An echo sounder can be used to apply Phoslock® in a consistent depth.

THE LOCATION OF THE TRACER

According to Håkanson (1977) and Bloesch (2004), the lake is divided into three zones: the erosion zone, the transportation zone and the accumulation zone. A tracer in the erosion zone would be useless because the tracer layer would not stay where it is supposed to. The erosion zone is characterised by coarse deposits of medium-sized silt, gravel and sand. Sediment resuspension occurs in frequent periods. The same applies for the transportation zone that is characterized by accumulation of fine grained sediment over a short period. The resuspended sediment is transported into accumulation areas. Both zones are too turbulent for a tracer. Fine grained sediments (< 63µm) accumulate at the deepest point of the lake, the accumulation zone. There, the greatest concentration of organic matter and different contaminants can be found. This means that also sediment varves can form without disturbance. This makes the accumulation zone the best suitable for a possible tracer application.

SIZE OF TRACED AREA

The size of the tracer as a time marker in the lake sediment depends on the size of the lake. Certain factors need to be considered:

- **Lake characteristics:**

Currents and the depth of the sampling location needs to be taken into account as well, because the deeper the location, the more complicated it gets to take samples.

- **Difficulty of taking sediment cores from a boat and finding already used sampling locations:**

The boat is anchored on a rope which is usually three times as long as the water depth. This means that the boat will be moving depending on the currents and on wind which will influence the accuracy of sample taking. There is also the four anchoring system but this will probably be too complex if sample taking is planned only every couple of years.

Finding already used sampling locations back will be difficult even with a GPS. There is the danger to get very close to the used sampling locations and get a useless sediment core.

- **Taking sediment cores will disturb the surrounding sediment:**

If sampling every once in a while is planned, one needs to get a larger picture of the space needed. Based on the assumption that sediment cores will be taken with the Mondsee Corer, a sediment tube with 9cm diameter plus the size of the Mondsee Corer will be lowered into the lakebed. This means that 0.5m around each sampling location will be useless due to disturbance of the surrounding sediment.

- **Need of multiple determinations:**

To guarantee heterogeneity of the Phoslock® layer, multiple determinations will be needed.

- **Form of the tracer:**

The question is also if the tracer should be applied in form of areas or stripes (Figure 31).

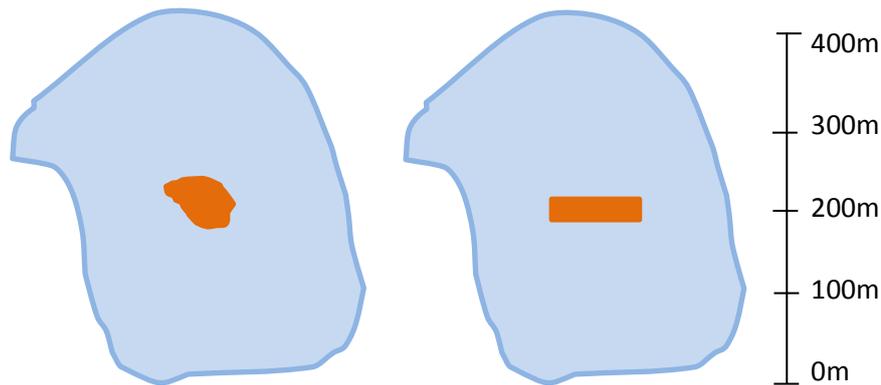


Figure 31 Sketch of a lake with Phoslock® applied as an area and in form of two stripes

If it is desired to take samples with Phoslock® parallel to lake sediment where no Phoslock® was applied, stripes might be better. It is disputable which is better suitable to take accurate samples and to avoid useless sediment cores taken instead though.

All these factors determine the size of the tracer. An area of 10x10m would result in theoretically 200 sediment cores. This amount is not realistic on account of the reasons above. Maybe 100 are more realistic. An area of 50x50m would result in theoretically 5000 sediment cores but in reality, less.

5 CONCLUSION

Considering the literature research and the outcomes of the internship and the bachelor thesis, Phoslock® is indeed retraceable because of high lanthanum levels. According to the natural lanthanum background concentrations which range from 8 to 40µg/g found by Prange & Tümpling (1997) and Yasseri & Nowak (2008) (see Introduction), Phoslock® as a tracer could be applied in these water bodies. Even if the tracer is supposed to have a 10 times as high concentration than naturally found, the amount of Phoslock® added is comparably small. This agrees for the most part with the ideal tracer definition from the Introduction. It occurs only in low quantities naturally in the labelled compartment of the environment, it is also clearly detectable, easy to quantify and not toxic or harmful for other reasons.

However, there are certain possible disturbances that have to be kept in mind to ensure the tracer stays where it was applied:

- Bioturbation
- Gas emission
- Location of the tracer: best in the accumulation zone
- Different lake processes (currents)
- Water and sediment characteristics: pH, hardness, alkalinity (La prefers carbonate), DOC (higher La³⁺, toxic effect)
- Complex interactions of bentonite and lanthanum with sediment and pore water elements: According to the ideal tracer definition (see Introduction), Phoslock® is not an ideal tracer due to its ability to bind phosphate. In addition, bentonite is also expected to have an impact in the sediment.

It is recommended to rethink the best method to prepare the cores and to set up another long time experiment of at least one year. The cores should be taken from a location in the lake where organisms are not present. Greatest caution must be applied while adding Phoslock® and sediment. It is also recommended to rethink a method to investigate the amount of La³⁺ ions which is released in the field to further examine if the lanthanum stays in the sediment or migrates into the pore water.

In addition, it is recommended to look further into the different processes bentonite and lanthanum will have on the sediment and the pore water. The best location for a time marker in the sediment and the best method to apply it must be further investigated as well.

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9 APPENDIX

9.1 OVERVIEW OF PHOSLOCK® APPLICATIONS

Table 13 This overview includes available information on Phoslock® applications such as lake depth, surface area and lake volume, Phosphorus (P) in sediment, in pore water and in the water column before and after the application, P precipitation in the water body, the P bound in sediment, the amount of applied Phoslock® and notes (Phoslock, 2015).

Location	Sur-face area in ha	Max depth in m	Min or average depth in m	Volume in m ³	P in sediment in mg/kg TS	P in water column before appli-cation in µg/L	P in water column after appli-cation in µg/L	P pre-cipita-tion in water body in kg	P bound in sediment in kg	First application/ potential post treatment (post) in t	Phos-lock® dosage in g/m ²	P in pore water in mg ortho-P/L	Notes
Germany Bärensee	6	Average 2.6		156.000	700 available: 140	84	25			11.5 post: 3 2 nd post: 3	183 post: 50 2 nd post: 50		- Efficient control of P
Behlendorfer See	63	16	Average 6.2	3.900.000	214	141.03	22.82	550	1440	214	340		- Application only in 7m depth - P conc. (C _p) decreased 80%
Blankensee	22.5	Average 1.65		371.250	66					66	294		- C _p decreased drastically - prevention of cyanobacteria bloom
Eichbaumsee	23	16			1.716.700						148	643.5	
Feuersee	0.95	2			12.500						9	947	
Otterstedter See	4.5	11				2900 available: 2030					11	244	
Silbersee	7	9	4.5	350.000	1000 available: 410	160 post: 53	35 post: 26			21.5 post: 4	307 post: 57		

3 Pond sewage treatment plant			2100 1500 1300						1 1 1			
Europe												
Austria												
Reithersee	1.5	7.7 Average 4	67.000				6		400			Used for swimming
Netherlands												
De Kuil	7									41.5	593	
Het Groene Eiland	5.6	Average 2.5	130.000			238462	31	110	11 post: 3.1	196 post: 55	0.02-0.39	Used for swimming
De Rauwbraken	4	12				4-944	< 10			18	450	- used for swimming - 2 tonnes of Poly Aluminium Chloride (PAC)
The UK												
Clatto Reservoir	9	Average 4	350.000	730					24	266		
Loch Flemington	15	Average 0.75	112.500						25	166		Alkaline
The Serpentine	16									66	412,5	Used for swimming
New Zealand												
Lake Okareka	330									60		Hypolimnion anoxia
Australia												
Emu Lake	10.5									Trial: 7 26 post: 22.2	Trial: 66 248 post: 21,4	
South Africa												
Hartbeespoort Dam	2.5	Average 3		200-800	15			6	240			
USA												
Maison Park	4				620	410						

9.2 SEDIMENT CORE PREPARATION CORES OVERVIEW

In Table 14, an overview is given about the ten sediment cores in total, the ones used for analysis and the ones used as a reserve core. This is important to show where the Phoslock® layer is expected to be in theory.

Table 14 Overview over the sediment cores, the sediment and water column in cm, the applied Phoslock® dosage, the sediment on top and notes

	Nr.	Sedi- ment in cm	Water column in cm	Phos. dosage in mg	Notes during sedimentation	Sedi. on top in cm
Pre- Analysis	PreA1	25				
	PreA2	23				
First analysis	1	27	28	56.0	Sediment on top maybe too early	5
	2	25.5	30.5	57.0	Sediment ice core sunk Sediment on top maybe too early as well	6.3
Second Analysis	3	25.5	30	57.4	Sediment on top quite early Uneven top layer	4-5
	4	25	31	57.3	Sediment on top quite early	5
Third Analysis	5	27.5	28	56.0		4
	6	27.5	28	58.9	Only 3cm on top; a second sedimentation step was needed	6
Sedi- ment core		30	26			
Reserve core	7	26	30	56.4		5

9.3 RESULTS AFTER ONE WEEK STORAGE

9.3.1 GRAIN SIZE

Table 15 Grain size results for the first analysis of core 1 and 2.

Depth in cm	Diameter 10% in μm	Diameter 50% in μm	Diameter 90% in μm
Core 1 0-1	≤4.08	≤19.09	≤54.78
Core 1 1-2	≤5.08	≤20.91	≤51.98
Core 1 2-3	≤5.30	≤21.88	≤52.99
Core 1 3-4	≤5.06	≤19.46	≤42.49
Core 1 4-5	≤4.61	≤17.48	≤38.19
Core 1 4.5-5	≤4.36	≤17.06	≤39.74
Core 1 5-5.5	≤4.39	≤16.78	≤38.59
Core 1 5.5-6	≤4.64	≤17.72	≤39.40
Core 1 6-6.5	≤4.56	≤17.36	≤37.99
Core 1 6.5-7	≤5.14	≤19.46	≤41.05
Core 1 7-8	≤4.80	≤18.72	≤41.93
Core 1 8-9	≤4.91	≤19.13	≤44.35
Core 1 9-10	≤5.75	≤22.33	≤49.70
Core 2 0-1	≤4.02	≤17.27	≤41.80
Core 2 1-2	≤5.02	≤19.10	≤43.43
Core 2 2-3	≤5.15	≤19.58	≤43.87
Core 2 3-4	≤5.28	≤20.26	≤44.42
Core 2 4-4.5	≤4.90	≤19.43	≤43.55
Core 2 4.5-5	≤5.40	≤20.71	≤44.76
Core 2 5-5.5	≤4.51	≤17.35	≤37.52
Core 2 5.5-6	≤3.69	≤17.39	≤34.77
Core 2 6-6.5	≤4.61	≤17.73	≤39.31
Core 2 6.5-7	≤4.69	≤18.30	≤39.84
Core 2 7-8	≤5.18	≤20.47	≤45.50
Core 2 8-9	≤5.38	≤21.53	≤48.95
Core 2 9-10	≤5.31	≤21.30	≤49.45

9.3.2 DRY WEIGHT, WATER CONTENT AND IGNITION RESIDUE AND LOSS

CORE 1 AND 2

Table 16 shows the results per layer of sediment core 1 concerning sample wet and dry weight in g, the water content in %, the ignition residue in g and the loss on ignition in %. The same is shown in Table 17 for sediment core 2.

Table 16 Results of the first analysis for core 1: sample weight, dry weight, water content, ignition residue and loss.

Depth	Sample wet weight	Sample dry weight	Water content	Ignition residue	Loss on Ignition
in cm	in g	in g	in %	in g	in %
0 - 1	61.69	10.14	83.6	8.67	14.5
1 - 2	51.17	11.42	77.7	9.94	13.0
2 - 3	59.53	14.43	75.8	12.43	13.9
3 - 4	59.43	12.96	78.2	11.09	14.4
4 - 4.5	24.27	5.05	79.2	4.33	14.3
4.5 - 5	21.75	4.51	79.3	3.79	16.0
5 - 5.5	27.08	5.77	78.7	4.96	14.0
5.5 - 6	20.96	4.48	78.6	3.86	13.8
6 - 6.5	27.83	6.01	78.4	5.14	14.5
6.5 - 7	25.46	5.67	77.7	4.83	14.8
7 - 8	49.66	11.19	77.5	9.54	14.7
8 - 9	52.99	12.33	76.7	10.45	15.2
9 - 10	52.49	12.24	76.7	10.52	14.1

Table 17 Results of the first analysis for core 2: sample weight, dry weight, water content, ignition residue and loss.

Depth	Sample wet weight	Sample dry weight	Water content	Ignition residue	Loss on Ignition
in cm	in g	in g	in %	in g	in %
0 - 1	56.57	9.11	83.9	7.78	14.6
1 - 2	47.72	9.8	79.5	8.39	14.4
2 - 3	64.86	14.46	77.7	12.49	13.6
3 - 4	64.8	15.14	76.6	13.1	13.5
4 - 4.5	22.46	5.19	76.9	4.51	13.1
4.5 - 5	28.45	6.63	76.7	5.64	14.9
5 - 5.5	25.72	5.7	77.8	4.9	14.0
5.5 - 6	21.25	4.69	77.9	3.89	17.1
6 - 6.5	26.41	6.09	76.9	5.09	16.4
6.5 - 7	27.46	6.62	75.9	5.68	14.2
7 - 8	49.51	11.78	76.2	10.12	14.1
8 - 9	51.1	12.64	75.3	10.9	13.8
9 - 10	51.38	12.96	74.8	11.17	13.8

9.4 RESULTS AFTER SEVEN WEEKS STORAGE

9.4.1 GRAIN SIZE

Table 18 Grain size results for the first analysis of core 3 and 4.

	Diameter 10% in μm	Diameter 50% in μm	Diameter 90% in μm
Core 3 0-1cm	4.89	19.07	47.94
Core 3 1-2cm	4.87	17.96	42.97
Core 3 2-3cm	4.85	18.08	43.09
Core 3 3-4cm	5.08	18.38	42.56
Core 3 4-4.5cm	5.22	20.03	47.69
Core 3 4.5-5cm	5.41	20.86	50.00
Core 3 5-5.5cm	5.91	22.70	52.00
Core 3 5.5-6cm	5.48	21.84	53.82
Core 3 6-6.5cm	5.75	22.77	54.14
Core 3 6.5-7cm	5.40	21.90	55.78
Core 3 7-7.5cm	5.82	23.32	56.18
Core 3 7.5-8cm	5.66	22.74	57.05
Core 3 8-8.5cm	6.26	24.69	58.20
Core 3 8.5-9cm	5.36	22.10	55.78
Core 3 9-9.5cm	5.41	22.09	53.11
Core 3 9.5-10cm	5.28	21.31	52.05
Core 3 10-10.5cm	5.17	20.66	50.02
Core 3 10.5-11cm	5.20	19.83	47.95
Core 3 11-11.5cm	5.15	19.36	44.82
Core 3 11.5-12cm	5.46	19.70	44.11
Core 4 0-1cm	4.44	17.52	41.50
Core 4 1-2cm	4.76	17.89	42.14
Core 4 2-3cm	4.74	18.38	42.37
Core 4 3-4cm	4.74	18.01	42.04
Core 4 4-4.5cm	4.75	18.58	43.85
Core 4 4.5-5cm	5.13	20.00	46.77
Core 4 5-5.5cm	5.93	22.44	51.12
Core 4 5.5-6cm	5.32	20.54	48.49
Core 4 6-6.5cm	5.27	20.77	49.73
Core 4 6.5-7cm	5.51	21.64	51.62
Core 4 7-7.5cm	5.39	21.49	52.67
Core 4 7.5-8cm	5.69	22.31	53.00
Core 4 8-8.5cm	5.71	23.24	56.22
Core 4 8.5-9cm	5.57	22.86	58.99
Core 4 9-9.5cm	5.68	23.08	57.78
Core 4 9.5-10cm	5.33	21.97	56.07
Core 4 10-10.5cm	5.37	21.89	53.04
Core 4 10.5-11cm	5.84	21.35	46.15
Core 4 11-11.5cm	5.20	19.10	43.80
Core 4 11.5-12cm	5.63	20.23	44.63

9.4.2 DRY WEIGHT, WATER CONTENT AND IGNITION RESIDUE AND LOSS

CORE 3

Table 19 shows the results per layer of sediment core 1 concerning sample wet and dry weight in g, the water content in %, the ignition residue in g and the loss on ignition in %.

Table 19 Results of the first analysis for core 3: sample weight, dry weight, water content, ignition residue and loss.

Depth	Sample wet weight	Sample dry weight	Water content	Ignition residue	Loss on Ignition
in cm	in g	in g	in %	in g	in %
0 – 1	91.1	16.96	81.4	14.52	14.4
1 – 2	45.54	9.79	78.5	8.4	14.2
2 – 3	59.67	13.2	77.9	11.34	14.1
3 – 4	54.29	12.16	77.6	10.43	14.2
4 – 4.5	29.76	6.73	77.4	5.75	14.6
4.5 – 5	17.05	3.9	77.1	3.34	14.4
5 – 5.5	25.99	6.01	76.9	5.19	13.6
5.5 – 6	26.27	6.17	76.5	5.35	13.3
6 – 6.5	21.27	5.19	75.6	4.51	13.1
6.5 – 7	18.86	4.52	76.0	3.9	13.7
7 – 7.5	41.18	10.46	74.6	8.81	15.8
7.5 – 8	17.17	4.26	75.2	3.67	13.8
8 – 8.5	26.56	6.84	74.2	5.85	14.5
8.5 – 9	18.74	4.76	74.6	4.08	14.3
9 – 9.5	33.82	9.12	73.0	7.88	13.6
9.5 – 10	23.17	6.23	73.1	5.44	12.7
10 – 10.5	24.89	6.65	73.3	5.8	12.8
10.5 – 11	22.1	5.45	75.3	4.77	12.5
11 – 11.5	22.1	5.02	77.3	4.35	13.3
11.5 – 12	29.2	6.61	77.4	5.69	13.9

CORE 4

The same is shown in Table 20 for sediment core 4.

Table 20 Results of the first analysis for core 4: sample weight, dry weight, water content, ignition residue and loss.

Depth	Sample wet weight	Sample dry weight	Water content	Ignition residue	Loss on Ignition
in cm	in g	in g	in %	in g	in %
0 - 1	80.56	15.33	81.0	13.19	14.0
1 - 2	48.17	10.71	77.8	9.21	14.0
2 - 3	61.2	14.08	77.0	12.16	13.6
3 - 4	54.1	13.01	76.0	11.22	13.8
4 - 4.5	22.71	5.34	76.5	4.6	13.9
4.5 - 5	26.45	6.19	76.6	5.3	14.4
5 - 5.5	25.38	5.99	76.4	5.14	14.2
5.5 - 6	21.4	5.06	76.4	4.31	14.8
6 - 6.5	29.11	7.03	75.9	6.03	14.2
6.5 - 7	23.18	5.82	74.9	5.03	13.6
7 - 7.5	20.4	5.2	74.5	4.47	14.0
7.5 - 8	28.83	7.39	74.4	6.37	13.8
8 - 8.5	24.75	6.43	74.0	5.51	14.3
8.5 - 9	19.65	5.11	74.0	4.42	13.5
9 - 9.5	23.48	6.38	72.8	5.49	13.9
9.5 - 10	26.92	7.38	72.6	6.38	13.6
10 - 10.5	22.3	6.1	72.6	5.28	13.4
10.5 - 11	25.14	6.74	73.2	5.82	13.6
11 - 11.5	17.53	4.57	73.9	3.96	13.3
11.5 - 12	30.86	7.64	75.2	6.63	13.2

9.5 RESULTS AFTER TEN WEEKS STORAGE

9.5.1 GRAIN SIZE

Table 21 Grain size results for the first analysis of core 5 and 6.

	Diameter 10% in μm	Diameter 50% in μm	Diameter 90% in μm
Core 5 0-1cm	4.30	17.99	43.76
Core 5 1-2cm	4.85	19.32	44.69
Core 5 2-3cm	5.28	20.93	49.42
Core 5 3-4cm	5.68	21.80	50.05
Core 5 4-4.5cm	5.19	20.75	51.35
Core 5 4.5-5cm	5.89	23.02	54.17
Core 5 5-5.5cm	6.05	23.95	54.50
Core 5 5.5-6cm	5.91	22.81	53.68
Core 5 6-6.5cm	5.31	21.11	50.21
Core 5 6.5-7cm	5.14	20.64	50.16
Core 5 7-7.5cm	5.86	23.03	53.35
Core 5 7.5-8cm	5.95	24.06	60.83
Core 5 8-8.5cm	5.53	22.92	59.45
Core 5 8.5-9cm	5.52	22.87	59.07
Core 5 9-9.5cm	5.67	23.36	58.85
Core 5 9.5-10cm	5.81	23.55	59.69
Core 5 10-10.5cm	5.25	22.15	57.51
Core 5 10.5-11cm	5.94	24.30	61.66
Core 5 11-11.5cm	5.35	22.90	59.89
Core 5 11.5-12cm	5.23	21.12	50.83
Core 6 0-1cm	3.98	15.72	39.28
Core 6 1-2cm	5.19	18.45	43.05
Core 6 2-3cm	5.20	18.84	44.32
Core 6 3-4cm	5.92	23.26	57.33
Core 6 4-4.5cm	5.70	23.11	57.73
Core 6 4.5-5cm	5.45	22.53	57.34
Core 6 5-5.5cm	5.75	23.34	59.00
Core 6 5.5-6cm	6.24	24.68	59.05
Core 6 6-6.5cm	5.23	21.57	55.71
Core 6 6.5-7cm	5.17	20.48	50.30
Core 6 7-7.5cm	5.69	22.63	53.35
Core 6 7.5-8cm	5.41	21.30	51.04
Core 6 8-8.5cm	5.59	21.80	52.19
Core 6 8.5-9cm	5.53	21.91	52.71
Core 6 9-9.5cm	5.45	21.78	52.87
Core 6 9.5-10cm	5.87	23.46	54.00
Core 6 10-10.5cm	5.71	22.56	53.45
Core 6 10.5-11cm	5.50	22.46	53.77
Core 6 11-11.5cm	5.67	22.58	54.36
Core 6 11.5-12cm	5.46	22.38	54.46

9.5.2 DRY WEIGHT, WATER CONTENT AND IGNITION RESIDUE AND LOSS

CORE 5

Table 22 shows the results per layer of sediment core 5 concerning sample wet and dry weight in g, the water content in %, the ignition residue in g and the loss on ignition in %.

Table 22 Results of the first analysis for core 5: sample weight, dry weight, water content, ignition residue and loss.

Depth	Sample wet weight	Sample dry weight	Water content	Ignition residue	Loss on Ignition
in cm	in g	in g	in %	in g	in %
0 - 1	70.27	13.55	80.7	11.56	14.7
1 - 2	55.79	13.14	76.4	11.33	13.8
2 - 3	51.04	12.6	75.3	10.83	14.0
3 - 4	45.78	11.42	75.1	9.81	14.1
4 - 4.5	38.16	9.04	76.3	7.73	14.5
4.5 - 5	28.14	6.75	76.0	5.77	14.5
5 - 5.5	13.27	3.21	75.8	2.73	15.0
5.5 - 6	23.13	5.69	75.4	4.91	13.7
6 - 6.5	21.7	5.34	75.4	4.61	13.7
6.5 - 7	25.8	6.55	74.6	5.58	14.8
7 - 7.5	25.34	6.46	74.5	5.59	13.5
7.5 - 8	30.16	7.82	74.1	6.68	14.6
8 - 8.5	19.2	4.93	74.3	4.23	14.2
8.5 - 9	23.18	6.03	74.0	5.15	14.6
9 - 9.5	21.92	5.82	73.4	4.96	14.8
9.5 - 10	26.49	7.15	73.0	6.14	14.1
10 - 10.5	29.51	7.97	73.0	6.81	14.6
10.5 - 11	19.69	5.37	72.7	4.57	14.9
11 - 11.5	28	7.55	73.0	6.44	14.7
11.5 - 12	20.16	5.92	70.6	5.13	13.3

CORE 6

The same is shown in Table 23 for sediment core 6.

Table 23 Results of the first analysis for core 6: sample weight, dry weight, water content, ignition residue and loss.

Depth	Sample wet weight	Sample dry weight	Water content	Ignition residue	Loss on Ignition
in cm	in g	in g	in %	in g	in %
0 – 1	57.34	7.39	87.1	6.35	14.1
1 – 2	53.32	9.3	82.6	8.11	12.8
2 – 3	63.57	12.65	80.1	10.79	14.7
3 – 4	45.93	10.5	77.1	9	14.3
4 – 4.5	25.2	6.18	75.5	5.35	13.4
4.5 – 5	25.3	6.43	74.6	5.55	13.7
5 – 5.5	29.67	7.82	73.6	6.76	13.6
5.5 – 6	24.16	5.79	76.0	4.99	13.8
6 – 6.5	22.24	5.85	73.7	4.97	15.0
6.5 – 7	25.74	6.32	75.4	5.4	14.6
7 – 7.5	26.48	6.28	76.3	5.35	14.8
7.5 – 8	26.91	6.42	76.1	5.51	14.2
8 – 8.5	29.26	7.08	75.8	6.11	13.7
8.5 – 9	27.35	6.38	76.7	5.5	13.8
9 – 9.5	30.75	7.56	75.4	6.53	13.6
9.5 – 10	22.2	5.58	74.9	4.7	15.8
10 – 10.5	25.97	6.68	74.3	5.76	13.8
10.5 – 11	27.76	7.37	73.5	6.37	13.6
11 – 11.5	36.22	9.75	73.1	8.41	13.7
11.5 – 12	30.1	8.1	73.1	7.01	13.5

9.6 OVERVIEW OVER CORE LENGTHS AND DIFFERENCES FOR THE CORE-EXPERIMENT

Table 24 Overview over the sediment cores with the expected Phoslock® layer and theoretical and real lengths after application and sectioning to show the possible difference that occurred.

	Nr.	Sediment column in cm	Sediment on top in cm	Expected Phoslock® in layer in cm	Real Phoslock® layer in cm	Theo. core length in cm	Core length after appli- cation in cm	Core length before section- ing in cm	Difference in cm	Theor. remaining sediment core length after sectioning in cm	Remaining sediment core length after sectioning in cm	Difference in cm
First analysis	1	27	5	4-5	7-9	32	-	-	-	22	25	3
	2	25.5	6.3	5.5-6.5	7-8	31.8	-	-	-	21.8	23	1.2
Second Analysis	3	25.5	4-5	3-5.5	4-5	29.5-30.5	31	-	+0.5-1.5	19	18	1
	4	25	5	4-5	4-5	30	30.5-31	-	+0.5-1	18.5-19	18	0.5-1
Third Analysis	5	27.5	4	3-4.5	4-4.5	31.5	32.5	31.5	-1	19.5	20	0.5
	6	27.5	6	5-6.5	6-8.5	33.5	34	33.5	-0.5	21.5	21.3	0.2

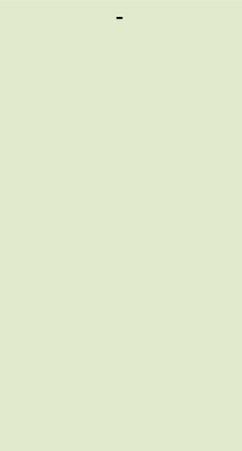
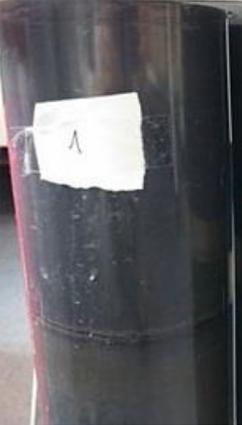
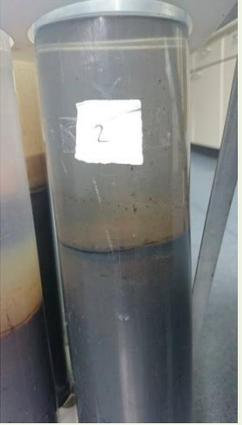
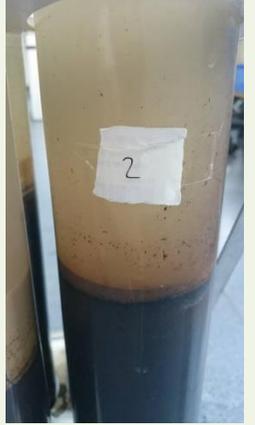
Table 24 shows the theoretical and real lengths of the sediment cores after application of Phoslock® and sediment and sectioning to show the possible difference that occurred between the expected Phoslock® layer and where it really was located.

There was an original amount of sediment in the tubes (“Sediment column”). Phoslock® was added and a mark was set on the tube. Then, sediment was applied on top of the Phoslock® layer (“Sediment on top”). It was tried to get 5cm on top. Based on the mark, the Phoslock® layer was calculated to be in a certain layer (“Expected Phoslock® in layer”). For comparison, the “Real Phoslock® layer” is shown next to the expected one. Based on the sediment column and the sediment on top, the theoretical core length (“Theo. Core length”) is calculated. The “Core length (right

after the application” was measured and is shown next to the theoretical one. For the third analysis, the sediment column was also measured before the sectioning (“Core length before sectioning”). This means that the sediment already had time to consolidate and compress the underlying sediment. There is a “Theoretical remaining sediment core length after (the) sectioning”. Because there is the hypothesis that the sediment is also compressed while sectioning, the “Remaining sediment core length after sectioning” was measured as well. In addition, the “Differences” are shown.

Unfortunately, not all values were measured for each core and measuring inaccuracy is likely because no consistent starting point for measuring was taken. It is recommended to use one for future experiments.

9.7 ADDITIONAL EXPERIMENT

Nr	Before application	Right after the sawdust/Phoslock® application	5 days after the sawdust/Phos. Application	Right after the application of sediment on top	48 hours after the application of sediment on top
1			 0.3-0.5cm below mark		 0.4-0.7cm below mark
2			 0.2-0.3cm below mark		 0.4-0.6cm below mark





All photos taken by Sylvia Schuster.

9.8 INTERNSHIP RESULTS: ANALYSIS OF SEDIMENT AND PORE WATER SAMPLES OF THE LAKES EICHBAUMSEE AND SILBERSEE IN STUHR

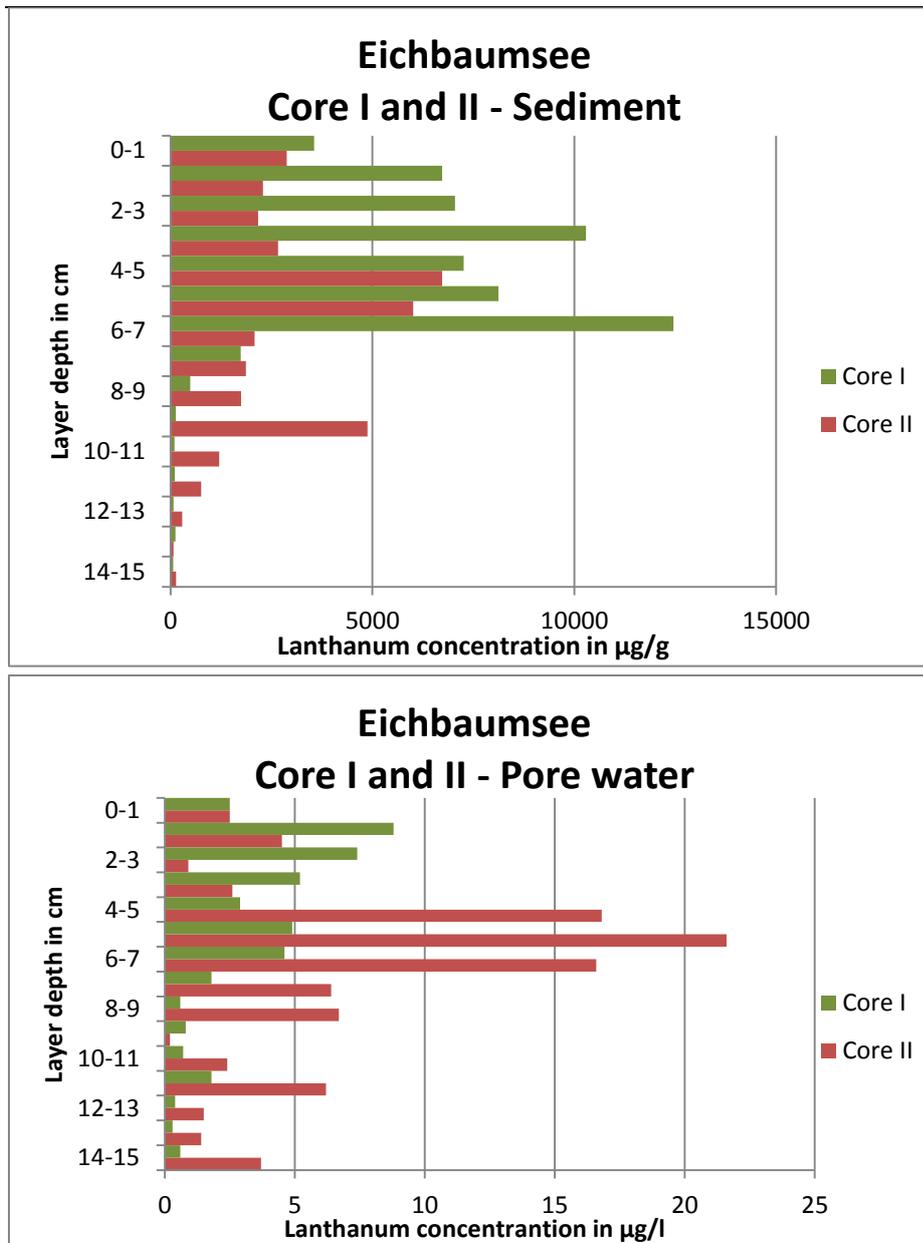


Figure 32 The graphs show the lanthanum concentration in the sediment (above) and the pore water (below) for core I and II of the Eichbaumsee. The sediment samples were analysed by ICP-OES and the pore water samples by ICP-MS.

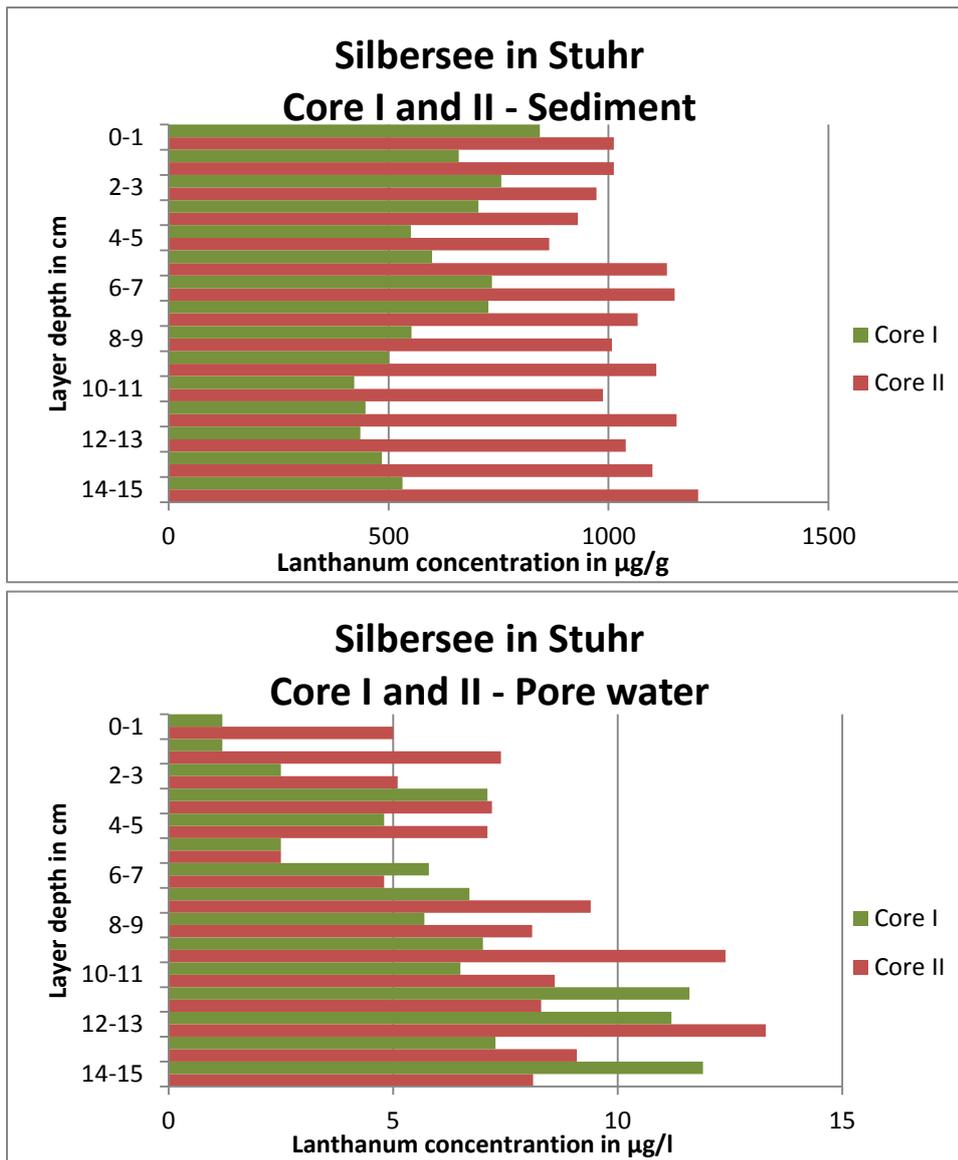


Figure 33 The graphs show the lanthanum concentration in the sediment (above) and the pore water (below) for core I and II of the Silbersee in Stuhr. The sediment samples were analysed by ICP-OES and the pore water samples by ICP-MS.