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 Implication of forms and distribution of phosphorous in sediments of three Stavanger lakes and ponds of constructed wetland on the potential for sedimentary phosphorous release and future eutrophication.

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Abstract

Excess of bioavailable phosphorus in fresh-water systems results in algal blooms and subsequent biogeochemical activities which in turn as positive feedback can escalate eutrophication and significantly reduce water quality. The forms of sedimentary phosphorus is major factor determining internal release of this nutrient. Knowledge about phosphorous forms and distribution can contribute in prediction of potential lake response to nutrient enrichment and other biochemical changes in the water systems, and it can guide in planning of measures to maintain good water quality. This study is focused on phosphorous forms and dynamics in sediments of three urban lakes: Mosvatnet, Hålandsvatnet and Stora Stokkavatnet, which are geographically close, but have different morphological and trophical features. The study has the aim to assess potential for sedimentary phosphorus release and future eutrophication development.

The results showed differences in phosphorus distributions both vertically with sediment depth and laterally between locations in the lakes. Relations to a number of factors such as mixing regime, presence of oxygen, water temperature and pH level were observed. It was determined that the dominant forms of phosphorus in the all studied lakes sediments were bound with iron (oxyhydr)oxides which is a redox sensitive form and potentially mobile, and bound to organic matter which can be released by biological mineralization. Eutrophic lake Hålandsvatnet currently has the highest sedimentary phosphorous concentrations of the three lakes. Due to anoxic conditions phosphorous is released from deep-water sediment and circulates into epilimnion maintaining high productivity. Since phosphorous is depleted in lower sediment layers because of long-term diagenetic release, the sediment may be capable only to sustain high release rates over limited time periods, and faster response to reduction of external nutrient load may in this case be expected. Neighboring mesotrophic lake Stora Stokkavatnet seems to be highly vulnerable to increase in external phosphorus load, because it can contribute to develop anoxic conditions in hypolimnion and trigger similar internal anaerobic release of iron bound phosphorus as in Hålandsvatnet. Furthermore, phosphorous in the sediment of a wetland pond constructed to protect Stora Stokkavatnet is dominantly in potentially mobile form and is capable to be released and transported into the lake water. Removal of pond sediment can therefore be a recommendation to protect the water quality in Stora Stokkavatnet. Mosvatnet can also be expected as sensitive to increase in external phosphorus load. Other factors than anoxic conditions can facilitate subsequent internal phosphorous release in this lake, and any acceleration of internal water fertilization may have strong eutrophication impact due to very small water volume compared to the sediment area, and because of direct contact between these two compartments that implies little limitation of transport for released phosphorus to be available for algal uptake.

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Abbreviations

AP	apatite phosphorus
BD	bicarbonate dithionite
CDB	citrate dithionite bicarbonate
DGT	the diffusive gradients in thin films
NAIP	non-apatite inorganic phosphorus
NTA	nitrilotriacetic acid
OP	organic phosphorus
P	phosphorus
P_{tot}	total phosphorus
SEDEX	sequential extraction method
SMT	Standard Measurements and Testing Program

1 Introduction

This paper is focused on phosphorus content and its fractions analyzed in lake sediments and on possible mechanisms and impacts of its release. The understanding of phosphorus accumulation and transformation is important for protection of freshwater resources against eutrophication, which is the combined process of increased fertilization and productivity. The increase of agricultural activity and population density around water bodies has had adverse effects on their ecosystems, structure and functioning leading to dominance of nuisance cyanobacteria and anaerobic microbial processes. Urban lakes are especially subject to high level disturbance and this kind of ecosystem impact. This is an unwanted development since the urban lakes have high recreational values and may also serve as active or reserve sources of drinking water.

The major limiting nutrient responsible for eutrophication of fresh-water systems is phosphorus. As component of fertilizers, manure and other animal waste the part of phosphorus, not removed by plants and crops, is washed out from watersheds in soluble and particulate forms and transported to natural sinks such as lakes. In the lake water the bioavailable fraction of the nutrient is rapidly consumed by microorganisms (phosphorous overload results in algal bloom), while less bioavailable forms are sorbed to particles (clay minerals, iron and aluminum oxides and hydroxides) or transformed by reactions to insoluble forms (reprecipitation as calcium-, iron-, aluminum phosphates). Particulate forms and planktonic debris sink to the bottom and enrich the sediment with phosphorus (Holtan, Kamp-Nielsen, & Stuanes, 1988). Lake sediment is a storage and at the same time a potential internal source of phosphorus within reservoir systems. However, the total phosphorus content in the sediment is not a determining factor for potential remobilization and release by itself. It depends on the forms in which it is present in sediment and changing biogeochemical conditions. The transformation and transportation of phosphorus at the sediment-water interface occur continuously, but the direction in which it proceeds - retention or dissolution, is influenced largely by physical/chemical conditions at this interface, sediment characteristics and microbial processes (Hupfer & Lewandowski, 2008).

Reduction of external phosphorus load is a common measure for recovery of eutrophicated inland lakes and reservoirs. However, often such an approach alone has low efficiency due to phosphorus release from sediments (Ding et al., 2016). In some cases up to 80% of total phosphorus input is provided by internal sediment release when the bottom waters become anoxic during summer periods (Søndergaard, Jensen, & Jeppesen, 2003). Internal phosphorus release can be so intense and persistent that water quality of lakes has in several cases not improved for many years even after significant reduction of external phosphorus load has been achieved (Granéli,

1999). Since sediment is one of the main phosphorus sources, the understanding of its characteristics and composition is important for prediction of lake ecosystems behaviour.

1.1 Objectives

The main objective of this thesis has been to gain better understanding of potential phosphorus dynamics in sediment of freshwater lakes with focus on accumulation, transformation, remobilization and release, as well as the influence of various external and internal factors to these processes. The study objects have been three urban lakes: Hålandsvatnet, Stora Stokkavatnet and Mosvatnet in Stavanger (Norway). It has been conducted by means of measuring total phosphorus content and its fractions (loosely bound P, Fe-, Al- bound P, Ca-bound P) in lake sediment samples from deep and shallow sites and along vertical profiles of the lakes. These three lakes are geographically close to each other and thereby share some similar natural conditions, but are also very different in other respects, such as trophic state. Correlation of sediment analyses and natural factors, particularly lake morphology, trophic level and mixing regime are observed and regarded, and a part objective has been based on these correlations to evaluate the roles and importance of antropogenic and natural factors in the future eutrophication development in the lakes.

An additional part objective has been to evaluate the effectiveness of phosphorus accumulation and retention in the sediment of a constructed protective wetland system within Stokkavatnet's catchment based on analysis of sampled pond sediment from this system.

2 Theoretical background

2.1 Forms and origin of phosphorus in sediment

Phosphorus occurs in nature almost exclusively as phosphate (Holtan et al., 1988). A great part of agricultural phosphates is sorbed to soil particles or is incorporated into soil organic matter. Falling into lakes, dissolved phosphorus is usually quickly consumed by microorganisms, or sorbed on sediment surface, or accumulated in the interstitial water (Holtan et al., 1988). Particulate fraction of phosphorus in lake sediment is composed from allochthonous and autochthonous sources. Allochthonous P primarily consists of organic matter from drainage area, grains of phosphorus containing minerals or other mineral particles with sorbed phosphate. A major fraction of the total phosphorus carried out from watersheds by streams is in form of particulate matter delivered during a relatively short period of time when discharge rate increased, and hence the flood velocity is sufficient to transport particles of varying sizes and densities (Holtan et al., 1988). Autochthonous phosphorus is presented in dead or alive planktonic organisms, excretion products, organic detritus, humic substances and in some cases co-precipitates with carbonates (calcium phosphate, dicalcium phosphate, beta-tricalcium phosphate, octacalcium phosphate, and hydroxyapatite) (Di Luca et al., 2017). Fallen down matter undergoes various transformations depending on the chemical, physical and biological conditions on the lake bottom.

The study of vertical profiles of lake sediment can reveal sedimentation and diagenesis features of reservoirs. Decreasing trend of water content and phosphorus concentration per gram of dry matter with depth can be created either by external processes (increased P load or sedimentation rate) or internal transformations such as accumulation of P in surface layer transported by diffusion from deeper parts, or by combination of both (Mortimer, 1942).

Boström et al. (1982) tried to compare data of surficial sediments from different lakes (oligotrophic to eutrophic) and concluded that usually content of inorganic phosphorus is higher than organic P. Certainly, there are large variations from lake to lake and it is preferable to evaluate calcareous sediment separately.

2.2 Sediment-water phosphorus exchange

The solubility of phosphates is controlled by processes such as sorption–desorption and dissolution–precipitation depending on conditions in sediments. Sorption-desorption reactions are decisive in sediments with high content of iron and aluminum hydroxides (Holtan et al., 1988). In nature relationships between different components within sediment are quite complex, so, for

simplicity, the phosphate sorption is usually represented on individual clay minerals or metal oxides and hydroxides.

Surface charge of iron and aluminum hydroxides complexes depends on pH of environment. At low pH they are positively charged and at high pH - negatively. pH level at which hydroxides have no net surface charge is called a point of zero charge and it varies for different complexes. Specific sorption of phosphate can proceed in two ways: ligand exchange either with aqua groups or with hydroxy groups (Holtan et al., 1988). Exchange with aqua groups results in an increase of negative charge of hydroxide surface as shown in equation 2.1.

$$[Fe(H_2O)_4(OH)_2]^+ + H_2PO_4^- \rightleftharpoons [Fe(H_2O)_3(OH)_2(H_2PO_4)]^0 + H_2O \qquad 2.1$$
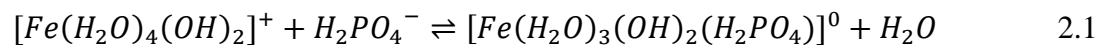
The exchange of phosphate with hydroxy groups does not affect the surface charge, but releases equivalent amounts of hydroxyl ions into the solution (equation 2.2).

$$[Fe(H_2O)_3(OH)_3]^0 + H_2PO_4^- \rightleftharpoons [Fe(H_2O)_3(OH)_2(H_2PO_4)]^0 + OH^- \qquad 2.2$$
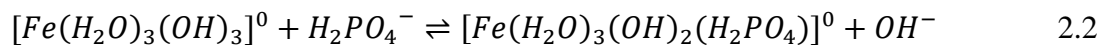
The reaction proceeds in both directions and phosphate release is expected at high pH. This simplified sorption mechanism seems to be the same for clay minerals in lake sediments (Holtan et al., 1988). These finely-grained deposits have high adsorption potential due to their large surface area. In general, ligand exchange process is pH dependent and can occur both in oxic and anoxic environments. Several authors have observed aerobic phosphorus release at high pH levels (Drake & Heaney, 1987; Furumai & Ohgaki, 1988). In contrast, it is possible that decreasing pH leads also to mobilization of some phosphorus fractions (carbonate-bound P or/and sorbed P) since pH strongly controls also their solubility (Eckert, Nishri, & Parparova, 1997).

Reduction resulting in dissolution of iron (oxyhydr)oxides bearing phosphorus is main mechanism of phosphorus release in sediment (Mortimer, 1942). In the middle of the 20th century it was only hypothesis, however recently it was proved *in situ* by observation with the aid of modern technologies (Ding et al., 2016; Wu & Wang, 2017). A special binding gel was developed for simultaneous uptake of dissolved Fe(II) and phosphorus. The experiments were conducted with millimetre spatial resolution according to diffusive gradients in thin films theory (DGT). The results demonstrated simultaneous release of phosphorus following reduction and dissolution of iron (oxyhydr)oxides. The main binding phase for labile phosphorus prior to its release was determined as ferrihydrite, probably due to its high sensitivity to redox conditions. Rydin (2000) conducted release experiments and determined that the loosely sorbed-P and Fe-bound P are the main potentially mobile phosphorus pools in surface lake sediments. Also, he concluded that the primary source for Fe-bound P pool is underlying organic phosphorus. About 60% of organic-P in the deep anoxic layers is mobilized and diffuse to upper layer during sediment diagenesis. Baldwin

(2002) suggested that phosphate ions bound to iron minerals in the sediment can be solubilized under anaerobic conditions directly by iron-reducing bacteria which reduce ferric minerals to dissolved ferrous ions. Also, sulfate-reducing bacteria indirectly are involved in phosphorus release. This produces sulfide that is a strong reducing agent sufficient to also reduce ferric minerals (Boström, Persson, & Broberg, 1988). In case of oxic conditions in overlaying water dissolved phosphate either becomes bound to Fe(III) or can be taken up by aerobic microorganisms (Gächter & Meyer, 1993) and remain in surface sediment. In anaerobic environment on water-sediment interface there are no barriers preventing phosphorus release to overlying water. This stream of easily available phosphate supports primary production and thus enhance the further development of hypoxia (Sulu-Gambari et al., 2017).

Dissolved phosphorus release from sediment is strongly associated to hypolimnetic anoxia (Petticrew & Arocena, 2001). However, phosphorus mobilization is a complex process which is controlled not only by oxygen presence and redox conditions but also by a number of other factors: various sediment features (Driscoll, Effler, Auer, Doerr, & Penn, 1993), character of organic matter decomposition (Moore, Reddy, & Graetz, 1992), pH, temperature, microbial activity and other variables alone or in combination (Hupfer & Lewandowski, 2008). Prairie et al. (2001) reported many cases of lakes in North America where P release was not observed or was extremely low after anoxia was established in hypolimnion. It seems that the role of decomposition and bacterial mineralization of organic matter mechanisms has been historically underestimated. Formerly, phosphorus cycle at sediment-water interface was presented as primarily abiotic process (Gächter, Meyer, & Mares, 1988). Several modern studies have demonstrated bacterial impact being more important than redox driven Fe (oxyhydr)oxide mobilization.

2.3   Methods of sediment phosphorus determination

Different variations of sequential extractions schemes are usually used to determine forms of sediment phosphorus (**Table 2.1**).

A single standard is not applicable to all types of sediments, and methodology should by selected depending on deposits composition. A literature analysis was conducted in order to select a procedure for objects of this study. In the middle of the 20th century the scheme of Williams was primarily used (Williams, Syers, & Walker, 1967). Williams with colleagues was the first scientists who adapted procedure of Chang and Jackson used in soil science to lake sediments. Sequential extraction schemes are developed for removing step by step phosphorus forms with different strength or binding energy in sediment samples (Pettersson, Boström, & Jacobsen, 1988).

In the latest versions of William's scheme sediment phosphorus was separated into non-apatite P (NAIP, reductant soluble and hydroxide soluble dissolved reactive P), apatite P (AP, dissolved reactive P hydrochloric acid extraction) and organic P (OP, difference between dissolved unreactive P and dissolved reactive P in sequential extracts at extremely low and high pH). Organic P was supposed to be completely extracted by hydrochloric acid (0.5 mol/l) and sodium hydroxide (1 mol/l). Total phosphorus and molybdate reactive phosphorus were measured in the pooled extracts (Williams, Jaquet, & Thomas, 1976). From bioavailability point of view the NAIP fraction is potentially available but the AP and OP are not readily available (Broberg & Persson, 1988). Boström et al. (1988) reviewed this conclusion and tried to evaluate and correlate results of sequential chemical extractions with algal-available P fraction.

Table 2.1 Extraction schemes for determining the fractional composition of sediment phosphorus (Pettersson et al., 1988).

Authors and year		Extraction	Proposed fraction	Shortcomings
1. Chang and Jackson (1957)	a.	NH_4Cl 1 mol/l	labile P	extraction of Fe-P by NH_4F
	b.	NH_4F 0.5 mol/l pH 8.2	Al-bound P	resorption by CaF_2
	c.	NaOH 0.1 mol/l	Fe-bound P	precipitation of phosphate
	d.	HCl 0.5 mol/l	Ca-bound	with iron
	e.	CDB	reductant-soluble P	
	f.	NaOH	refractory P	
2. Williams et al. (1971)	a.	NaOH/NaCl 0.1/1.0 mol/l	non-occluded Fe-, Al-P	resorption by carbonates in calcareous sediments
	b.	CDB 85°C	reductant-soluble P	Ca-P released by CDB
	c.	HCl 0.5 mol/l	apatite P	
3. Williams et al. (1976)	a.	CDB 0.22/1.0 g/0.1 M	non-apatite P	resorption by carbonates in calcareous sediments
	b.	NaOH 1 mol/l		Ca-P and org-P released by CDB
	c.	HCl 0.5 mol/l	apatite P	
4. Hieltjes and Lijklema (1980)	a.	NH_4Cl 1 mol/l pH 7	labile P	dissolution of small amount of Fe-P and Al-P by NH_4Cl
	b.	NaOH 0.1 mol/l	Fe- and Al-bound P	
	c.	HCl 0.5 mol/l	Ca-bound P	
5. Psenner et al. (1985)	a.	H_2O	water-soluble P	resorption by carbonates in calcareous sediments
	b.	DB 0.11 mol/l 40°C	reductant-soluble P	
	c.	NaOH 1 mol/l	Fe- and Al-bound P	
	d.	HCl 0.5 mol/l	Ca-bound P	
	e.	NaOH 1 mol/l 85°C	refractory P	

Eventually Hieltjes and Lijklema updated Williams scheme (Hieltjes & Lijklema, 1980). The key point of their study is differentiation of phosphorus forms depending on behavior in lake sediment in terms of exchange processes occurring on water-sediment interface. They have emphasized an importance of removing calcium carbonate (on the first step by NH_4Cl) if it is present in sediment to separate Fe-, Al-bound phosphorus (NaOH extraction) and Ca-bound P (HCl extraction) because in this way phosphorus can be resorbed on carbonate on the step of extraction by NaOH. They also observed that a significant part of Ca-bound phosphorus was

dissolved by CDB-reagent in Williams's scheme. Today Hieltjes and Lijklema procedure is most commonly used.

In order to determine loosely bound P which is also probably the most bioavailable, chelators can be used (Pettersson et al., 1988). For example, Golterman (1982) suggested using NTA chelator agent (nitrilotriacetic acid) as a sensitive separation of calcium- and iron-bound phosphorus, pointing out that strong acid and alkaline solutions are too aggressive. Unfortunately, the NTA often interferes with the determination of phosphorus. Chelator extractions are not commonly used and have to be tested more.

Psenner and his coworkers (1984) developed procedure of P fractionation where he determined water-soluble phosphorus (H_2O-RP), P adsorbed to iron and manganese hydroxides or reductant soluble P (BD-RP), iron- and aluminium-bound P (NaOH-RP), calcium-bound P (HCl-RP) and refractory P ($NaOH_{85°C}$-RP). The authors claimed that this fractionation scheme is more applicable for estimation of water-sediment exchange processes. Pettersson (1988) presented a good comparison of these four extraction methods mentioned above. He recommended schemes similar to Hieltjes and Lijklema (1980) and Psenner (1984) as the most reliable. The first one is technically simple and allows to gain all significant information about inorganic fractions of sediments. On the other hand, second, Psenner´s technique is more relevant for estimation of sediment-water phosphorus exchange.

Results of Hieltjes and Lijklema´s procedure from surface sediment of around 16 different lakes were compared by Pettersson (1988). The total phosphorus content of the sediments varied from 0.55 mg/g dw to 6.49 mg/g dw. He concluded that labile phosphorus (NH_4Cl-RP) was generally low, from 0.4% to 7.6% of total phosphorus. At the same time, up to 60% of most lakes sediment consist of iron- and aluminium-bound P or non-apatite inorganic phosphorus (NaOH-RP). However, Pettersson's study showed that more than half of total phosphorus content is generally organic P, up to 90% in the sediment of the oligotrophic and acidified lakes.

In recent decades, some others modern schemes have been developed. For example, SEDEX (sequential extraction method) is widely applied in biochemical studies mostly for marine environment (Sulu-Gambari et al., 2017). Based on Williams's method, the SMT (Standart Measurements and Testing Program of the European Commission) protocol was developed. It is simple and easily reproducible method that provides comparable data for water management and routine investigations (Ruban et al., 2001).

2.4 Lake ecosystem, balance and recovery

There is a common opinion that all lakes, their conditions and characteristics are quite different and should be observed individually. In 1957 Hutchinson (1957) claimed that lakes are sophisticated self-regulated systems. For example, a single short-term increase in phosphorus load, no doubt, will lead to an increase in lake's productivity. However, a lake is capable to return to its former state if nutrient stress stops. In water systems phosphate is nearly insoluble and tends to be captured in sediment due to precipitate formation, sticking to rocks, minerals, organic matter, and to mineral colloids (such as ferric hydroxide). Therefore, the highest amount of phosphorus is stored in sediment (Dodson, 2005). Many studies show that eutrophication can be reversed, but not in cases of favorable conditions for internal loading from sediment (Granéli, 1999). Internal phosphorus loading can be reduced by removal of phosphorus-rich surface sediment layer or by addition of iron or aluminum sulfate (alum) to increase sediment's sorption capacity (Søndergaard et al., 2003). Alum acts as colloidal iron particles and significantly improves water quality. It forms insoluble colloids which slowly sink, adsorb phosphate ions, and deposit phosphate on a lake's bottom (Dodson, 2005). However, it takes tons of alum to treat even a small lake and needs to be repeated periodically about every 5 years (Welch & Schrieve, 1994).

One of the major restoration method today is aeration i.e. improvement of oxygen conditions in the hypolimnion which is suitable not for all lakes and its effectiveness is questionable (Tammeorg, Möls, Niemistö, Holmroos, & Horppila, 2017). A recent study by Katsev and Dittrich (2013) was based on reaction-transport model and showed that aeration of Lake Sempach (Switzerland) had only short-term effect on phosphorus retention and leaded to a temporary decrease of iron-bound phosphorus release. The amount of oxidized iron was not sufficient to adsorb enough P. Authors concluded that long term restriction of external P inputs into the lake should be the major phosphorus-controlling restoration measure.

An addition of nitrate as an electron acceptor instead of oxygen so called "Riplox Method" was proposed by Ripl in 1976. This method is at least 80% more expensive than the treatment by iron/alum (Foy, 1986), however faster and technically easier to perform than the oxygenation (Ripl, 1976; Søndergaard, Jeppesen, & Jensen, 2000). The technique application is limited only water systems where phosphorus release is dependent mostly on redox conditions. In addition, there is a risk of obtaining an extremely high level of nitrate in sediment, which causes pH decrease and dramatic consequences (Ripl, 1976). Knowledge about sediment nitrate dosing is currently limited and needs further investigations.

In general the majority of eutrophic lakes treatments described in studied literature is either expensive, or temporary and ineffective, or can lead to severe consequences. Prevention of excessive sediment phosphorus release is regarded as safer and more effective measure than treatment. A small disturbance on a water system may induce positive feedback leading to rapid eutrophication. Increased biological activity, establishment of hypoxic conditions, drop in Eh are the main triggers of sediment phosphorus liberation. Estimation of phosphorus release potential and understanding of its mechanisms, which depend on distributions of phosphorus in different fractions and various conditions in lake sediments, are crucial for maintenance and treatment of water reservoir.

3 Materials and methods

3.1 Area of the study

Figure 3.1 Orthophotomap of the lakes location with marked sampling sites.

The objects of this study are three lakes located almost in the center of Stavanger city (Western Norway): Hålandsvatnet, Stora Stokkavatnet and Mosvatnet (**Figure 3.1**). These lakes are the largest natural fresh water bodies in the area, important recreation sites for the residents and habitats for abundant bird species. From 1863 to 1931 Mosvatnet was the main drinking water source for the city. From 1931 to 1959 this role was taken over by Stora Stokkavatnet reservoir. Now Stora Stokkavatnet is the Stavanger back-up water supply. Hålandsvatnet is considered to be one of the best place for fishing in Rogaland area. However, this lake has algae bloom regular which makes water poisonous (Molversmyr, 2010).

Table 3.1 Morphometric data of lakes: Hålandsvatnet, Stora Stokkavatnet and Mosvatnet (Holtan, 1985; NVE, 2018).

Parameters	Hålandsvatnet	Stora Stokkavatnet	Mosvatnet
Area (km^2)	1.07	2.134	0.5
Volume (mill. m^3)	10.084	23.8	0.849
Average depth (m)	9	10.6	2
Maximum depth (m)	25	42	3.5
Residence time (years)	1.32	5.5	0.39
Catchment area (km^2)	7.92	10.37	2.2

The smallest lake, Mosvatnet, is surrounded by a walking route, buildings and large roads. Lake area is approximately 0.5 km^2. Its watershed zone is 2.2 km^2 (NVE, 2018) and completely urbanized. Morphometric data for all three lakes is shown in Table 3.1. Mosvatnet is a shallow lake with maximal depth about 3.5 m (**Figure 3.2**) thus it is easily stirred by the wind and most of

Figure 3.2 Depth contours (m) and volume/area to depth relationships for Mosvatnet lake (NVE, 2018).

the time non-stratified. Around 30 years ago Mosvatnet was highly eutrophic and was treated by biomanipulation (rotenone) which gave successful results at least for the first years (Sanni & Wærvågen, 1990). Today the external phosphorus load is less than in 1980-s partly due to the establishment of constructed wetland in 1991 on Madlabekken (Molversmyr, 1992). The lake has status of moderate eutrophic (Molversmyr, 2016).

Figure 3.3 Depth contours (m) and volume/area to depth relationships for Hålandsvatnet lake (NVE, 2018).

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Hålandsvatnet is the second largest lake in the Stavanger region, closest to the sea and highly wind exposed (Molversmyr, 2006). It is 25 m deep (NVE, 2018), narrow with steep banks (**Figure 3.3**). The catchment area of lake is mainly agricultural farmlands (78%) which provide significant phosphorus input and facilitate high primary production (Molversmyr, 2006). The lake eutrophication began in 1980s and remains relatively unchanged to this day despite the decrease in external nutrient load. Hålandsvatnet is a dimictic lake and has water stagnation periods in summer and winter. During warm periods, from June to October, in hypolimnion (below 13-15 m depth) anoxic condition develops due to active bacterial degradation processes (Molversmyr, 2010).

Stora Stokkavatnet is the largest lake in Stavanger city with surface area around 2.13 km^2. Catchment area is relatively small – 10.37 km^2. It is represented mainly by cultivated lands on the northern and western side, and by residential areas on the east and south. A small forest belt stretches along the perimeter of the lake. The deepest part of the lake is located in the central and southern parts with maximal depth of 42 m, the northern area is quite shallow and not deeper than 6 m (**Figure 3.4**). Stora Stokkavatnet is a mesotrophic lake with medium primary productivity and moderately oxic conditions in hypolimnion in the summer. As Hålandsvatnet this lake has cold and warm stagnation periods. Hypolimnion is commonly observed below 13-15 m depth (student field observations in 2015 and 2017).

Four constructed wetlands were built in late 1980s and early 1990s around Stokkavatnet in order to maintain good water quality by reducing the nutrients load from farmlands runoff to the lake. One of them, near the shore on the north-west, is called Leikvollbekken and it is represented by a system of two artificial ponds with depth not more than 50 cm and surface area around 700 m^2 each (**Figure 3.1**). This area has dense vegetation which act as filters, chain of barriers and meandering water streams providing cleaner water flow into the lake. In this study sediment from a constructed wetland near the lake Stora Stokkavatnet was sampled and analysed along with lakes sediments. Three short sediment

Figure 3.4 Depth contours (m) for the lake Stora Stokkavatnet. Equidistance 5 m (Ibrekk, 1985).

cores from the bottom of two Leikvollbekken ponds were taken for tests (**Figure 3.1**).

3.2 Field work

All sediment samples (42 in total) from the lakes and wetland ponds were collected by the author during one week in September, before autumn overturn in 2017. Sampling spots are marked in **Figure 3.1**. Sediment from lake bottoms were collected from a boat by sediment core sampler in core tube with diameter 6 cm and length 60 cm (**Figure 3.5**). In total, there were collected 8 cores from the lakes and 3 cores from constructed wetlands, sampling depths are shown in **Table 3.2**. An overview of water parameters in the upper and bottom zones of the lakes is presented in **Table 3.3**. Since sediments are exposed to different water conditions (temperature, pH, oxygen concentration etc.) above and below hypolimnion depth in stratified lakes such as Stora Stokkavatnet and

Figure 3.5 Sediment core sampler (a), collected core from Stora Stokkavatnet (b) and vertical extrusion system for the slice and remove sediment section (c).

Hålandsvatnet, two cores of sediment were collected from deep locations of these lakes and one sample from shallow sites closer to the shore. Two duplicates of core samples were taken from south-east area of Mosvatnet. At the same day of sampling, from the upper, middle and lower parts of each core 4-5 samples were sliced with thickness 1 cm and average weight 25 g. Samples were stored in polyethylene boxes, frozen for 3 months until they were analysed in laboratory.

Table 3.2 The water depths of sediment sampling sites. H – Hålandsvatnet, S – Stora Stokkavatnet, M – Mosvatnet, L – Leikvollbekken constructed wetland ponds (L1, L3 – pond 1, L2 – pond 2).

Name	Depth (m)	Name	Depth (m)	Name	Depth (m)	Name	Depth (m)
H1	24	S1	34	L1	0.4	M1	2.4
H2	24	S2	34	L2	0.3	M2	2.4
H3	8	S3	8	L3	0.4		

Changes in phosphorus fractions are not expected during this time of frozen conditions. Previously by Molversmyr (2010) sediment samples were already analysed in Hålandsvatnet at the same places as H1, H2, and H3 and in Mosvatnet (M1, M2) in 1999 (Molversmyr, 2000).

Sediment cores from constructed wetland ponds were short (max. 6 cm) due to thin sediment layer and dense mass of macrophyte roots (especially in pond 2, L2) which prevented deeper sampling. Bottom of pond 1 (L1 and L3) was dug up couple years ago and some quantities of small fragments of bedrocks were mixed up with soft organic rich sediment. Whole cores were taken for

Figure 3.6 Sampling of sediment in pond 1 of constructed wetland. (a) Pond 1. (b) Core from the bottom.

analyses and divided into 1 - 4 cm thick sections and frozen in polyethylene boxes for 3 months. The sediment in ponds and streams of the study area is characterized by a red colour due to high content of iron (hydro)oxides. Iron is released here by weathering of iron rich bedrock – phyllite (NGU, 2018).

Table 3.3 Lakes water physicochemical parameters in the euphotic and bottom zones of sediment cores sampling. September 2017. Student field observations.

Water parameter	Zone	Hålandsvatnet (H1, H2)	Stora Stokkavatnet (S1, S2)	Mosvatnet (M1, M2)
Temperature (°C)	Euphotic	15.5	15.6	15.0
	Bottom	8.9	6.8	14.8
Oxygen (mg/l) [saturation (%)]	Euphotic	9.8 [98]	9.5 [96]	9.8 [97]
	Bottom	0.03 [0]	2.5 [20]	9.1 [90]
pH	Euphotic	7.4	7.5	7.8
	Bottom	6.9	7	7.8

3.3 Analytical methods

In December 2017 sediment samples were unfrozen, and following procedures were carried out in laboratory: drying at 110±5°C and water content determination (ASTM D2216-05, 2005), ignition at 550°C and measuring volatile components content (SM 2540 E, 2000), acid digestion of dried sediment for total phosphorus analysis (Standard Norge, 2005). Following

recommendations from Pettersson's paper (1988) extraction scheme of Hieltjes and Lijklema (1980) was selected for this study. This scheme is not only one of the technically easiest to implement but also one of the most commonly used. It was used for studying of similar objects by previous authors, so using this scheme allows more accurate comparison of results Ammonium molybdate spectrometric method was used for determination of phosphorus concentrations in obtained solutions and extractions (NS-EN ISO 6878, 2004).

Standard test method for laboratory determination of water (moisture) content of soil and rock by mass (D2216-05)

Materials and equipment: evaporating porcelain dishes 120 mm diameter; drying oven (Termaks); desiccator; analytical balance, readability 0.01 g.

Figure 3.7 Wet sediment samples in porcelain dishes before evaporation.

Method D2216-05 is used commonly for soil samples and appropriate for sediments testing with minimum mass 20 g. In this method water content is calculated from total weight loss of a sample at 110±5°C. Water is considered to be the only saturating fluid (ASTM D2216-05, 2005).

Unfrozen sediment samples (average weight 25 g) were transferred to porcelain dishes (**Figure 3.7**). The weight of dishes and dishes with wet sediment were noted. Samples were placed in the oven for 24 hours to dry out until they obtained a constant mass. Dried and cooled samples were kept in desiccator and weighed a first time to control that there was no additional loss of mass. To determine sufficient drying period 8 (out of 42) samples were additionally dried and weighted twice with two hours difference. Any additional weight loss was not observed during this extra two hours. Thus, it was concluded that drying for 24 hours is appropriate time for the given sediment.

Standard method for determination of fixed and volatile solids ignited at 550°C (SM 2540 E)

Materials and equipment: small porcelain dishes; muffle furnace; desiccators; analytical balance, readability 0.001 g.

Dried (after method D2216) samples were grinded well and 0.2 g of each sample were ignited in porcelain dishes at 550°C until achieving a constant weight. The loss in weight is considered to be volatile sediment content representing organic matter (SM 2540 E, 2000), and remaining fixed solids is inorganic matter.

To determine a sufficient burning period a half of the samples was ignited twice for 30 min, and no difference in weight was observed between the first and second ignitions. Thus it was concluded that 30 min at 550°C is sufficient for 0.2 g samples of studied sediment.

Determination of total phosphorus (NS-EN 14672)

Materials and equipment: kjeldahl tubes; heating device (digestion system 6, 1007 Digester); pipettes; glass filters 1.5 µm; volumetric flasks 100 ml.

Reagents: concentrated sulfuric acid, $\rho = 1.84$ g/ml (18 mol/l); concentrated nitric acid, $\rho = 1.42$ g/ml (15 mol/l); sodium hydroxide, (5 mol/l); phenolphthalein indicator solution; distilled water.

This European Standard is mostly used for characterization of sludge (Standard Norge, 2005). This method is based on dissolution of test material in concentrated nitric and sulphuric acids at temperatures around 150-170°C. This leads to oxidation of organic matter and conversion of all forms of phosphorus into dissolved orthophosphate. Digester is used to maintain high temperature in tubes with acidified samples. During this procedure, a small amounts of concentrated nitric acid are added regularly to support the process since nitric acid is consumed on oxidation and is boiled down. With nitric acid lost the boiling temperature rises and any organic matter is digested by concentrated sulfuric acid, causing the mixture to char. Oxidation is considered complete when the test mixtures is no longer fumed. Resulted solutions are then cooled and their pH is adjusted for the next phosphate analysis.

In this procedure, dried sediment samples with weight around 0.2 ± 0.01 g were treated. The representative mass was tested by comparison with results of the same method but applied for 0.5 ± 0.01 g test portions collected from Lake Årungen and analysed in 2016. These sediment samples and previous results for them were provided by Steinar Sanni (Li, 2016). Difference in results was less than 0.1 g P/kg dw for triplicates of 3 samples. The standard deviation is 5% of the mean. Small coefficient of variations indicates the reliability of the obtained results.

At least two replicates were tested for all sediment samples. Acidic digesting was conducted in accordance to Standard Method (Standard Norge, 2005). The 0.2 ± 0.01 g of dried and homogenized sediment samples were transferred into Kjeldahl tubes in digester and then added 2.0 ml of sulfuric acid and 1.0 ml of nitric acid. Mixtures were heated to 150-170°C temperature under proper exhaust ventilation until brown/yellow fumes ceased (around 10-15 min). Then additional 0.5 ml of nitric acid was added into the tubes. Such nitric acid addition was repeated 4-5 times until no brown fumes were produced. Afterwards mixtures were cooled, mixed with 10 ml of distilled water and heated in digester for 10-15 min. This operation was conducted twice. After

solutions were cooled, 25 ml of distilled water were added along tubes sides to wash down any remaining solutions and particles.

The last step of the procedure was neutralizing the resulting solutions for the following spectrometric analysis of phosphate concentrations. For two replicated samples pH was adjusted in two different ways. In the first trial, the resulting solutions were neutralized to alkaline state (pH = 12-13). Digestion tests were repeated independently for 13 duplicates out of 42 samples. With 3 drops of phenolphthalein indicator solution, 25 ml of sodium hydroxide was added to tubes. The colour of mixtures was changed from yellow to brown/red and brown flocks were formed (**Figure 3.8**). In addition, for all samples digestion test was repeated but, after oxidation, resulting acidic solutions were minimally neutralized (pH = 1 or less). Not more than 10 ml of sodium hydroxide was added to prevent formation of any precipitate. Digestion tests were repeated independently for 7 duplicates out of 42 samples. Final solutions were filtrated to flat-bottom flasks and diluted to 100 ml. One reagent blank without addition of any sediment sample was following the whole procedure in every session.
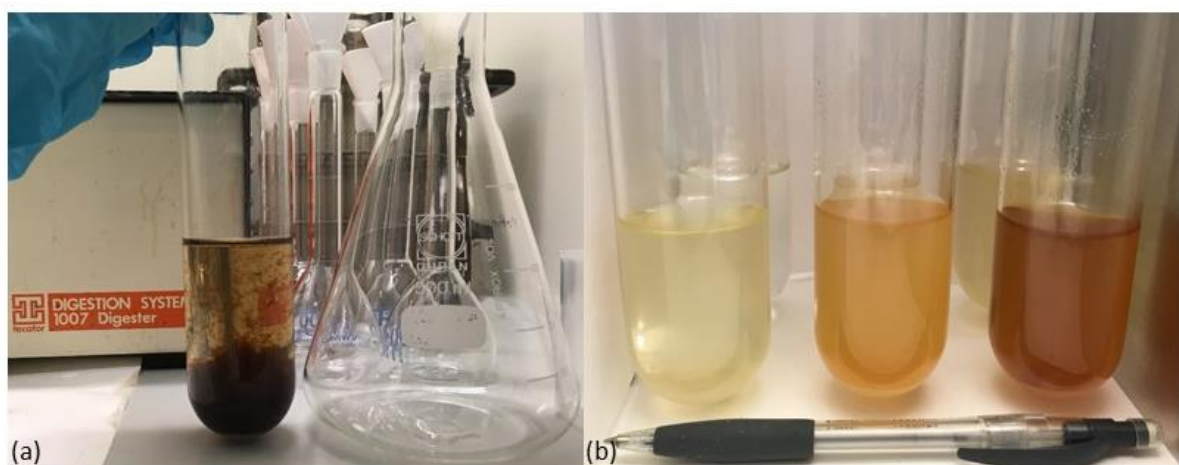
Figure 3.8 Digestion solutions of lake sediment. (a) alkaline, pH = 12, (b) acidic, pH = 1

Fractionation of phosphorus in lake sediment based on Hieltjes and Lijklema scheme (1980).

Materials and equipment: centrifuge tubes 50 ml; centrifuge (5804R); laboratory shaker; glass filters 1.5 µm; volumetric flasks 100 ml, 50 ml; pipettes.

Reagents: 1M solution of NH_4Cl; 0.1M solution of NaOH; 0.5M solution of HCl; concentrated sulfuric acid, $\rho = 1.84$ g/ml (18 mol/l); activated carbon; saturated solution of NaCl; distilled water.

Fractionation scheme of Hieltjes and Lijklema consist of three stages which are shown in **Table 3.4**. Dried sediment samples with weight 0.2 ± 0.1 g were analysed. Reliability of samples

mass was checked in the same way as it was done for total phosphorus analysis. The extraction results were compared with results for Lake Årungen. The comparison with previous results shows minor discrepancy of 0.2 g P/kg dw for three procedure steps for 3 samples. The coefficients of variations for loosely bound, iron bound and calcium bound phosphorus were 12%, 19% and 16%, respectively. This is a fairly low values and results were considered to be reliable. A reagent blank sample with the addition of distilled water instead of sediment was taken through the all stages.

Table 3.4 Fractionation scheme based on Hieltjes and Lijklema method (1980). Dried samples with mass 0.2 ± 0.1 g were extracted in procedure.

Phosphate form	Stage description
Loosely bound	25 ± 1 ml of 1M NH_4Cl was poured into a centrifuge tube with sample. The mixture was shaken for 2 hours in the shaker, then centrifuged for 10 min at the speed of 3500 rpm. Solution was filtrated and poured off into 50 ml flat-bottom flasks. Solution was not further diluted.
Fe -, Al – bound	The sediment residue was mixed with 25 ± 1 ml of 0.1M NaOH and shaken for 17 hours. Then solution was centrifuged, filtrated in the flat-bottom flask and mixed with 0.5 ml of concentrated H_2SO_4 and 0.2-0.5 g of activated carbon to coagulate humic acids and to remove colour of fulvic acids. After 20 min solution was filtered into 100 ml flat-bottom flask and diluted. In order to remove mechanically deposited fluoride solution in the extract, 25 ± 1 ml of saturated NaCl was added into the centrifuge tube with the residues of sediment. Solution was centrifuged for 10 min and liquid was thrown away.
Ca - bound	The washed sediment residue was mixed with 25 ± 1 ml of 0.5M HCl and shaken for 24 hours. Then tube was centrifuged and solution filtrated into 100 ml flat-bottom flask and diluted.

Determination of phosphorus. Ammonium molybdate spectrometric method (NS-EN ISO 6878, 2004).

Materials and equipment: UV-VIS spectrophotometer (at 880 nm); volumetric flasks 50 ml; pipettes.

Reagents:

Ascorbic acid solution, $\rho = 100$ g/l. Note: the solution is stable for 2 weeks if stored in amber glass bottle in a refrigerator and should be colorless.

Acid molybdate, Solution I. Mixture: 13 g ± 0.5 g of ammonium heptamolybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$, 200 ml ± 5 ml distilled water, 0.35 g ± 0.05 g of antimony potassium

tartrate hemihydrate [K(SbO)C$_4$H$_4$O$_6$·1/2H$_2$O] and 300 ml ± 5 ml of 9 mol/l sulfuric acid. Note: the reagent is stable for at least 2 months in amber glass bottle.

Acid molybdate, Solution II. Mixture: 230 ml ± 0.5 ml of 9 mol/l sulfuric acid, 270 ml ± 5 ml of distilled water, 13 g ± 0.5 g of ammonium heptamolybdate tetrahydrate [(NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O], 0.35 g ±0.05 g of antimony potassium tartrate hemihydrate [K(SbO)C$_4$H$_4$O$_6$·1/2H$_2$O]. Note: the reagent is stable for at least 2 months in amber glass bottle.

Turbidity-color compensation solution. Mixture: on a volume/volume basis, two parts of 4.5 mol/l sulfuric acid and one part of ascorbic acid solution.

Orthophosphate standard solution ρ_P = 2 mg/l. 1 ml of this standard solution contains 2 µg P. Solution was prepared and used at the same day.

Distilled water

Spectrophotometric method was chosen as an inexpensive, fast and accurate procedure for large number of samples. This method is based on measurement of the absorbance of the coloured molybdenum blue complex which is bounded with dissolved forms of phosphorus. Colour intensity is determined by spectrophotometer. The accuracy is highly dependent on phosphorus concentration in tested samples. This very sensitive method is applicable only for low concentrated solutions up to 0.8 mg/l, and above this level the linear relationship between absorbance data and phosphorus concentrations disappears. Most of the solutions of the lake sediments were phosphorus-rich and was diluted up to 50 times.

Before testing calibration graph was plotted based on orthophosphate standard solutions with range of concentrations from 0 mg/l to 0.72 mg/l. The graph was verified every time when new chemicals were used, about once a month. Blank test was carried out in parallel with the determination. One example of calibration curve is presented in Appendix A

The small volume of tested solution (from 2 ml to 20 ml, depends on phosphorus concentration) was transferred to 50 ml flat-bottom flask. Then 1 ml of ascorbic acid was added followed by 2 ml of acid molybdate. Two solutions of acid molybdate were used: solution I was used in analyses after fractionation stages, and solution II was used for highly acidic mixtures after sediment digestion. Then distilled water was poured to make up to the mark of flask. Absorbance of solution was measured using spectrophotometer at 880 nm wave length in period between 10 to 30 min after mixing reagents.

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Initial colour of tested solutions was considered negligible due to strong dilution. For slightly diluted turbid and/or coloured solutions the absorbance with compensation reagent was measured in parallel to tested sample. The final value of absorbance was determined as difference of results for tested sample and compensation.

The total phosphorus content (P_{tot}) of the original sample was calculated by equation 3.1:

$$P_{tot} = \frac{C \times V}{m_D \times 1000}$$
3.1

where

P_{tot} is the total phosphorus content in [g/kg];

C in [mg/l] is the phosphorus concentration in the initial solutions (in 100 ml flasks) after digestion or extraction steps. The calculation of this concentration, taking into account the blank concentration, turbidity and dilution, is described in Appendix B;

V is the volume of initial solution in flat-bottom flasks in [ml]. Here it is mostly 100 ml, only for NH$_4$Cl-P fractions volume of 50 ml was analysed;

m_D is the dry mass of sample taken for the analyses in [g].

Statistical analysis

Possible relationships between concentrations of total phosphorus and its fractions are analysed by linear regression using standard Microsoft Excel tool. Only one reliable correlation is found and described in next chapter.

Due to lack of sample material for total phosphorus analysis of upper layers (0 – 2 cm) in core H1 the total phosphorus value is estimated from duplication core H2 by comparison of P fractions content. Since quantitatively the content of dominant Fe-bound P and Ca-bound P fractions is similar (±0.1 g P/kg dw) in core H1 to core H2 the total phosphorus concentrations are assumed to be also equal.

4 Results

4.1 General sediment cores characteristic

Sediment cores from lakes Mosvatnet, Hålandsvatnet and Stora Stokkavatnet and also from the two ponds of constructed wetland belonging to Stokkavatnet watershed were taken in the 12-15th September 2017. The length of lake cores is from 26 to 43 cm, samples from constructed wetland ponds represent the first 4-8 cm sediment from the bottom. In general, a common pattern of stratification is observed in the lake sediment. In all cores the upper part consists of fine black, dark-brown material as gyttja which lies on more bright, yellow or grey coloured bases. In Mosvatnet a yellow claylike layer is observed from the core depth around 38 cm. In Stokkavatnet's cores the grey fine-grained material is under 10-20 cm of dark brown sediment. In Hålandsvatnet's deep area an upper black layer is 20 cm and covers yellow-brown sandy sediment. Near the shore, at the depth of 8 m, the black layer is much thinner – only the first 2-3 cm. The cores do not have any remarkable smell. However, in sediment from a depth of 24 m in Hålandsvatnet gas bubbles appeared in about 20 min after lifting to the surface.

Water content estimated in dried at 110±5 °C sediment samples is in the range of 51 - 97%. In **Figure 4.1** there is a clear trend of decreasing water saturation with core depth. A similar tendency is observed in thin sediment sections of Leikvollbekken ponds (**Table 4.1**). For all samples there is a positive correlation between water and organic matter fraction. The most saturated surficial sediment (up to 97% water content) of deep Hålandsvatnet area is, at the same time, the most organic-rich (almost 43% of organic content). On the other hand, the sandy bottom layer of core from this lake almost completely consists of inorganic material and has the lowest portion of water (58%). **Figure 4.1** reveals that the content of organic matter generally decreases with core depth, although some fluctuations within core are observed due to stratified sediment structure. The mean of organic fraction is around 23.5% in all samples. Deepwater sediment of Lake Hålandsvatnet has significantly higher organic matter proportion (about 32.5%) comparing to the other lake sediments (**Figure 4.2**). The whole detritus-rich sample from pond 2 of Leikvollbekken has around 33.5% of organic matter.

Table 4.1 The fractions of water and organic matter in ponds sediment of constructed wetland Leikvollbekken.

	Pond 1			Pond 2
Core depth (cm)	0-1	1-2	2-6	0-4
Water content (%)	83.5	77.6	51.3	96.6
Organic matter (%)	21.4	21.1	12.4	33.5
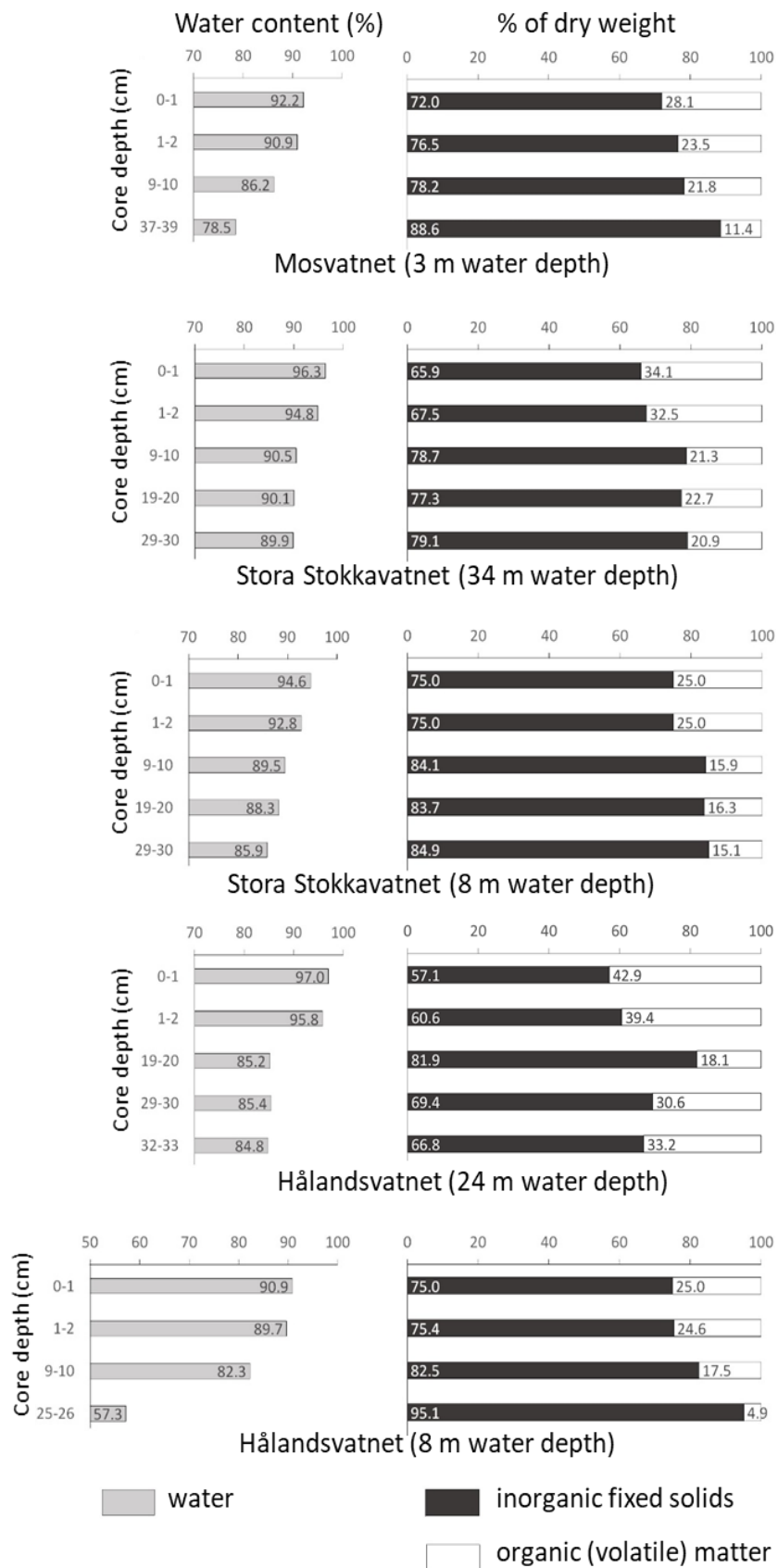
Figure 4.1 Water (weight loss after drying) and organic matter (weight loss after ignition of dried samples) content in lakes sediment profiles.
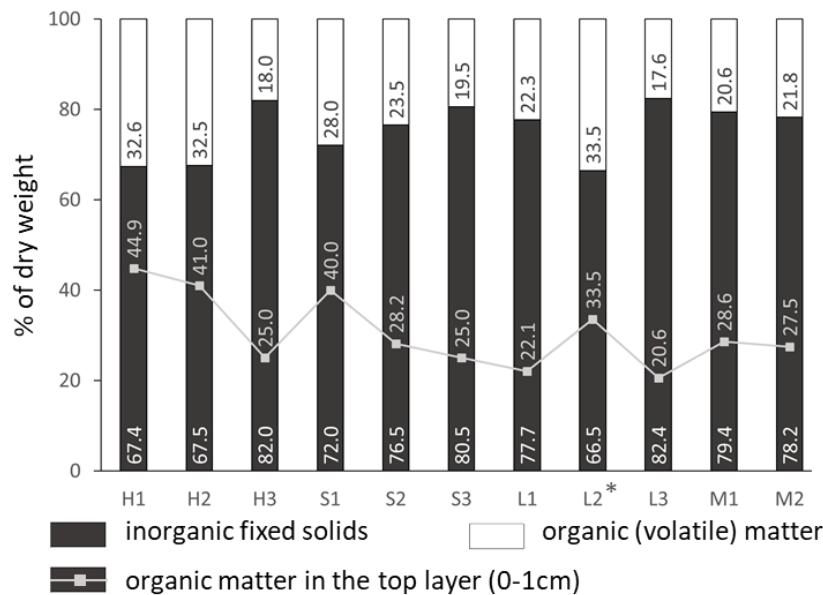
Figure 4.2 The average content of organic matter in the collected samples from the sediment cores of lakes and ponds. The linear graph represents the portion of organic material in the first centimetre of sediment cores. * - for the sediment from pond 2 (L2) of constructed wetland data is given for the whole 4 cm core sample.

In contrast, the sediments from shallow areas of Stora Stokkavatnet and Hålandsvatnet have the lowest organic proportions, around 18% and less (**Figure 4.2**). In general, inorganic material predominates over the organic matter in all sediment samples.

4.2   Total phosphorus content and its fractions

For this study, the acid digestion procedure (Standard Norge, 2005) was used to determine the totality of elemental phosphorus in the samples. This method is commonly used for determination of phosphorus content in sludge. It is expected that this method is appropriate for natural sediment samples. Also three phosphorus fractions were extracted (Hieltjes & Lijklema, 1980): loosely-bound P (NH_4Cl-extractable-P), Fe-bound (NaOH-extractable-P) and Ca-bound (HCl-extractable-P). It is assumed that the difference between total phosphorus value and the sum of three fractions is an organic phosphorus content. Currently there is no standard method for P speciation in aquatic sediment (Turner, 2005). Extraction scheme developed by Hieltjes and Lijklema is the most commonly used. Samples preparation is important for correct fractionation. There are two main differences of this study from previous. First, this study is conducted on dry sediment samples, in contrary to wet samples used for previous works. Second, fractionation procedure is recommended to conduct under N_2 atmosphere conditions (Dittrich et al., 2013; Paludan & Jensen, 1995), and for current study conditions were oxic. Because of this measured content of oxygen sensitive fractions (Fe-bound P and probably labile-P) can differ from natural distribution.

Deviations

In the first attempts of the total phosphorus determination solutions, obtained after strong oxidation, were neutralized to approximately pH = 12. The standard deviation is calculated for this total phosphorus analysis based on results of two independent sediment sample tests. Repeated independent studies were conducted for 13 samples out of 42 (25% of all samples). The mean of the coefficient of variation for total-P in alkaline solutions is relatively small - 5.20%, that indicates low variations and sufficient precision of estimations (**Table 4.2**). Method reproducibility was also pre-tested on three samples from Lake Årungen (Li, 2016) where total phosphorus was analysed in the same way in alkaline solutions. Low variability is obtained for these two independent results with average coefficient of variation of 4.35% ($SD = 0.05$).

Spectrophotometric reproducibility is very high. The standard deviation for the same repeated samples ($n = 10$) is less than about 2.12% of the mean. The calibration graph example used for phosphate determination is presented in Appendix A. The relationship between absorbance and phosphorus concentrations is linear with slope around 0.7 and R^2-value from 0.9944 to 1.0.

Table 4.2 Average standard deviations of total phosphorus results and P-fractions. Total phosphorus is calculated from the results in alkaline and acidic solutions. Lab – P, Fe – P and Ca – P are based on phosphorus concentrations in extracts with NH_4Cl, NaOH and HCl respectively.

		Total P (alkaline) (n = 13)	Total P (acidic) (n = 7)	Total P (n = 39)	Lab – P (n = 6)	Fe – P (n = 10)	Ca – P (n = 10)
Mean	(g/kg)	4.37	2.53	3.33	0.01	2.13	0.61
Standard deviation	(g/kg)	0.22	0.09	0.19	0.001	0.14	0.04
Coefficient of variation	(%)	5.20	3.67	6.93	6.35	8.95	6.78

For several samples total phosphorus measurement was lower than sum of phosphorus fractions. A possible reason for such underestimation is precipitation of phosphate during neutralization step. Therefore, to estimate influence of this effect dissolved phosphate analysis was repeated in acidic solutions with pH ≤ 1. In this repeated test solutions were translucent and did not have any precipitate except grains of resistant minerals, presumable, colourless quartz grains and other sand components). Repeated test was conducted for two duplicates for 7 samples out of 42 and results show low coefficient of variation of 3.67%. Comparison of results in alkaline and acidic solutions did not reveal any significant difference. Standard deviation was 6.93% of the mean (**Figure 4.3**). Based on this small difference it was concluded that phosphate loss at high pH

is negligible and total phosphorus measured in alkaline solution are correct and can be used for further analysis.

In order to solve an issue with underestimated total phosphorus content experimental procedures were reviewed for the tests of uncertain samples. Experimental errors were revealed in fractionation extraction steps. These steps were redone correctly on replicates of uncertain samples. Based on new results all data set was analysed using Dixon's Q-test. Q (gap/range) value was calculated for P fraction concentrations, outliers outside of 95% confidence range and results of incorrect fraction extraction series were excluded from further study. New average phosphorus fraction concentrations in sum does not exceed corresponding total phosphorus content. It is highly recommended to conduct fractionation procedure at least for three duplicates of all tested samples.
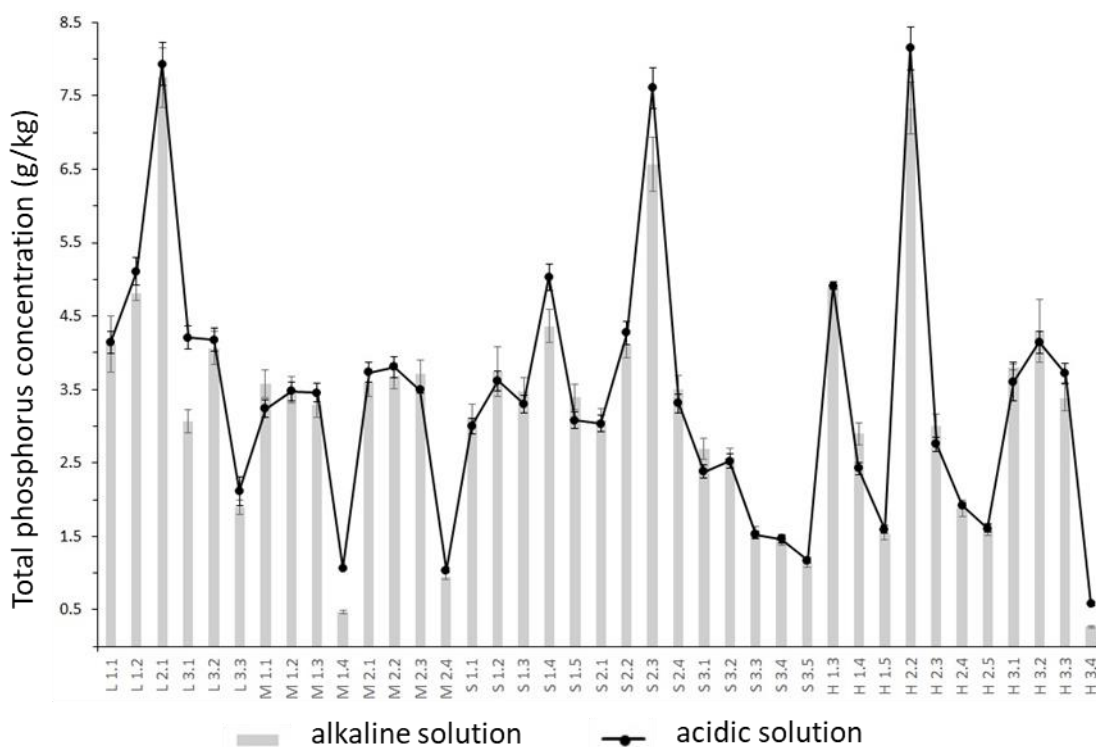
Figure 4.3 Total phosphorus concentrations determined independently in alkaline and acidic solutions. Error bars show duplicate standard deviation.

The standard deviations of phosphorus fractions are given in **Table 4.2**. At the first stage of extraction procedure, labile phosphorus concentrations are very low (less than 1 g P/kg dw) or are not detected (in 12% of NH_4Cl extracts). In general, the coefficients of variation are the highest for NaOH extraction (Fe-, Al-bound P) (8.95% of mean). This fraction is less reproducible because NaOH solution extracts most organic bound P together with P adsorbed onto Fe-(oxihydr)oxides (Psenner et al., 1984). Subsequently, the extract is acidified and the organic P fraction is isolated by filtration, but this procedure can increase the probability of errors and fluctuations. All extraction results are presented in Appendix C.

Phosphorus distributions in sediment profiles

In general studied sediments are phosphorus rich, especially the upper layers with maximum content of 8 mg/kg dw for deep part of Lake Hålandsvatnet. The same high content is in the four upper centimetres of organic-rich sediment from constructed wetland pond 2 (**Table 4.3**). In **Figure 4.4** a comparison of total P content and its fraction distributions is shown for tested intervals of lake vertical profiles.

There is a clear trend for Stora Stokkavatnet and Hålandsvatnet, that the total P content is higher in the lake sediment from the deepwater parts (34 and 24 m water depth, respectively) than from the shallow areas (8 m water depth for both).

Table 4.3 Total phosphorus and fractions content in sediment cores of the constructed wetland ponds 1 and 2 in Leikvollbekken. The residual phosphorus contents were calculated by subtracting the sum of fractions from the total P. The fraction percentage of total P is given in parentheses.

	Pond 1			Pond 2
Core depth (cm)	0-1	1-2	2-6	0-4
Labile P, g/kg	0.008±0.003	0.001±0.001	0.008±0.001	0.022±0.001
(%)	(0.21)	(0.03)	(0.4)	(0.29)
Fe-, Al-bound P, g/kg	2.31±0.58	2.88±0.37	1.5±0.15	5.66±0.14
(%)	(58.8)	(64)	(73.5)	(72.2)
Ca-bound P, g/kg	0.46±0.01	0.52±0.03	0.38±0.03	0.63±0.05
(%)	(11.8)	(11.6)	(18.6)	(8)
Residual P, g/kg (%)	1.15 (29.2)	1.1 (24.4)	0.15 (7.5)	1.53 (19.5)
Total phosphorus, g/kg	3.93±0.52	4.51±0.47	2.04±0.18	7.84±0.13

In Hålandsvatnet the phosphorus concentration is four-fold higher in the first centimetres of sediments comparing to 25–30 cm core depth. Similar tendency is observed only for the shallow sediment of Stora Stokkavatnet where the surficial total phosphorus concentration decreases by up to two times comparing to sample from 30 cm core depth. The large intervals between samples on vertical profiles does not allow making more accurate estimation. In the deepwater sediment of Stora Stokkavatnet the P content is almost at the same level (about 3 g/kg) over the entire 30 cm core. In the shallow lake Mosvatnet the total P content remains at the same level at least witin the first 10 cm (3.5 g/kg) and is up to three-fold lower at the 37 cm core depth.

In short sediment core of pond 1 constructed wetland Leikvollbekken total phosphorus content decreases to a half below 2 cm sediment depth and it is covarying with the decrease of Fe-, Al-bound P and organic P (residual fraction) (**Table 4.3**). In the sediment of pond 2, extremely high phosphorus content is found, and mainly in the form of iron-bound P (72.2% of total).
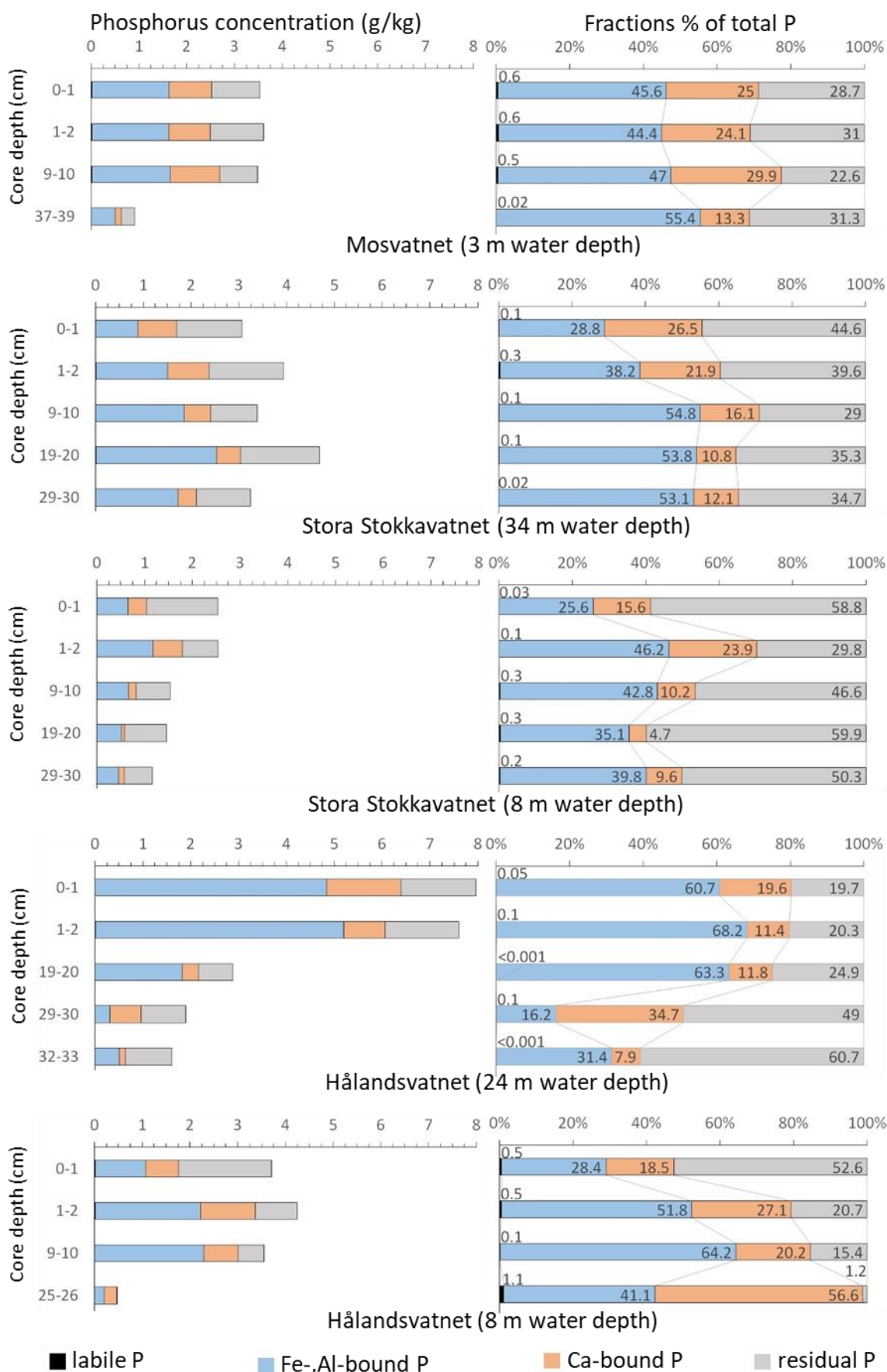
Figure 4.4 The vertical distribution of total phosphorus and its fractions (in g P/kg dw and % of total P) in sediments of lakes Mosvatnet, Stora Stokkavatnet and Hålandsvatnet. The residual phosphorus contents were calculated by subtracting the sum of fractions from the total P.

In general, the proportion of loosely adsorbed P (labile fraction extracted by NH$_4$Cl) is relatively low (around 0.3% of total P) and therefore does not show in most graphs. Overall, NaOH-extractable P fraction (Fe-, Al-bound P) is the prevalent and decisive form (in average 45%) of phosphorus accumulation in sediment. Strong linear relationship and positive correlation is found only between total P content and iron-bound P (R^2 = 0.87, p-value = 0.05, n = 35). Less than a fifth of total P is bound with carbonate. And the calculated range of inert and organic residual fraction varies around 10-45%.

In the upper 10 cm layer of Mosvatnet the average ratios of P forms are 2:1:1 for iron-bound, carbonate-bound and residual fraction, respectively. Phosphorus associated with carbonate is a hardly soluble form and expected to be quite stable and fixed in sediment with sediment depth. However, in sediment interval 37-39 cm the carbonate-bound P content is around one half of the content of upper samples.

In the upper layers of deepwater sediment of Stora Stokkavatnet, the residual fraction dominates over iron-bound P form in approximately 42% versus 34%. In addition, in the surface layers carbonate-bound P content is twice higher than in lower layers. Below 9 cm of sediment depth the distribution of P is quite homogeneous and more than 50% of phosphorus is iron-bound. Sediment from shallow water areas of Stora Stokkavatnet, in general, contains higher residual fraction than deepwater sediment: in average 49% for shallow water samples comparing to 36% in deepwater samples. In average, in the first two centimetres portions of iron-bound and residual P are comparable (36% and 44%). Carbonate phosphorus shows similar vertical pattern of Ca-P distribution as in deepwater lake area with the decrease from 20% in upper layers to 8% in lower layers. Below 9 cm of sediment depth the ratios of fractions are 4:1:5 for Fe-P, Ca-P and residual form respectively, with small fluctuations. The proportion of carbonate-bound P decreases and residual-P slightly increases from top to bottom samples and organic form is predominant for the lower sediment levels.

In the deepwater sediment of Hålandsvatnet, while the total phosphorus content decreases with depth, the percentage of fractions is uniform to at least 20 cm sediment depth: 5:1:2 for Fe-P, Ca-P and residual-P, respectively. Samples were collected when bottom environment was anoxic. It is favourable conditions for release of iron-bound phosphorus. Nevertheless, the concentration of this fraction in the surface sediment layer is highest (5 g P/kg dw) comparing to other lakes where oxygen is present in bottom water. Phosphorus in samples from sediment profile below 29 cm is mostly in inert organic form (around 55%). In the interval 29-30 cm the high carbonate-bound portion of phosphorus (34.7% of total) is found coupled with the decrease of iron-bound fraction. On the depth of 32-33 cm organic-P fraction is dominant (60.7%). In the first

10 cm of shallow sediment of Hålandsvatnet there is a sharp fall of residual organic P fraction with the depth from almost 53% to 15.4% and significant increase in the portion of Fe-P form from 28.4% to 64.2%. In the lower sandy sample from depth interval 25-26 cm organic P is almost completely absent (1.2%) and P is distributed between Fe-bound and Ca-bound fractions as 41.1% and 56.6%, respectively.

In the short sediment profile of pond 1 of Leikvollbekken the highest portion of phosphorus was extracted with NaOH (P associated with Fe-, Al (oxihydr)oxides) from all tested levels (**Table 4.3**). In the interval below first 2 cm of core this fraction and organic-bound P content are lower in 2 and 8 times, respectively, comparing to surficial layer. At the same time, there is no difference in concentration of carbonate associated P in vertical profile.

The first two centimetres of sediment play the most important role in phosphorus exchange processes between sediment and water. Pie chart (**Figure 4.6**) presents an overview of phosphorus pools in percentages for surface sediment layers of lakes and Leikvollbekken pond 1 (0-2 cm). Inorganic P fractions are dominant in the

Figure 4.6 Average percentages of phosphorus fractions in the upper 2 cm of sediments of lakes and Leikvollbekken pond 1.

upper layers and mostly phosphorus is bounded with iron (oxyhydr)oxides. The comparison of phosphorus fractions in upper layer from the different sampling sites is presented in **Figure 4.5**.
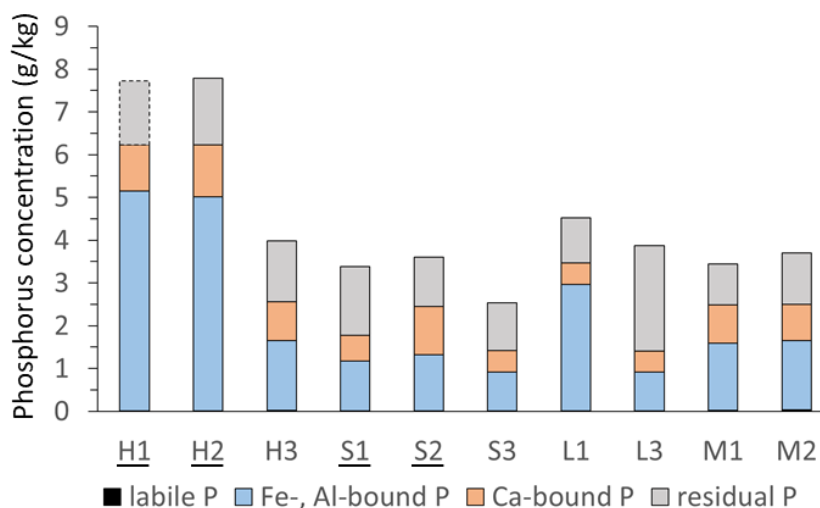
Figure 4.5 The phosphorus content and its forms present in the first two centimeters (0 - 2 cm core interval) of sediments at sampling points. Names of deepwater cores are underlined. The dashed line of the residual P at the sampling site H1 is approximation for the duplicate core H2, since the total phosphorus was not determined here due to a shortage of material.

Results for pond 2 sediment in Leikvollbekken were excluded due to its sample volume was not comparable to others.

Among all sampling points shown in the **Figure 4.5**, upper layer of sediment from deepwater location of Hålandsvatnet (H1 and H2) has twice as high total phosphorus content comparing to all other sampling sites, including its own sediment from shallow part (H3). In addition, this increase associated with the increase of Fe-, Al-bound fraction of P (**Figure 4.7**). The percentage of the Ca-bound fractions is quite similar for all upper layers of the lakes, however in surficial sediment of pond 1 of constructed wetland this fraction is in 10% lower. In deep (S1, S2) and shallow (S3) areas of Stora Stokkavatnet top sediments have different total P concentration and different carbonate associated P fraction (slightly lower in shallow zone), but the ratios of fractions are similar (**Figure 4.7**).

	Mosvatnet [3m]	Stokkavatnet [34m]	Stokkavatnet [8m]	Hålandsvatnet [24m]	Hålandsvatnet [8m]	Pond 1 [0.4m]
Residual P (%)	29.9	41.8	44.3	20	35.5	26.7
Ca-bound P (%)	24.5	23.9	19.8	15.6	23.1	11.7
Fe-, Al-bound P (%)	45	34	35.9	64.4	40.9	61.5
Labile P (%)	0.6	0.2	0.1	0.1	0.5	0.1

Figure 4.7 Stacked column chart of relative content of the different phosphorus pools in the upper sediment layers (0-2 cm) of lakes and constructed wetland ponds. Water depth of sampling spot is shown in square brackets.

5 Discussions

The three studied lakes Mosvatnet, Stora Stokkavatnet and Hålandsvatnet are located relatively close to each other and have quite a lot of similarities (for instance, bedrock substrate, water chemistry, climate impact). However, lakes are different in a number of parameters such as morphology, exposure to wind and trophic level. Mosvatnet is polymictic and the shallowest of the studied lakes with practically flat bottom, at the same time dimictic lakes Hålandsvatnet and Stora Stokkavatnet have noticeable depth difference. Stokkavatnet is a mesotrophic lake and other two lakes are eutrophic. Hålandsvatnet is located close to the sea and exposed to stronger wind influence comparing even to the nearest Stokkavatnet. These differences play significant role in phosphorus distribution in bottom sediment, its release into water and aspects of eutrophication process.
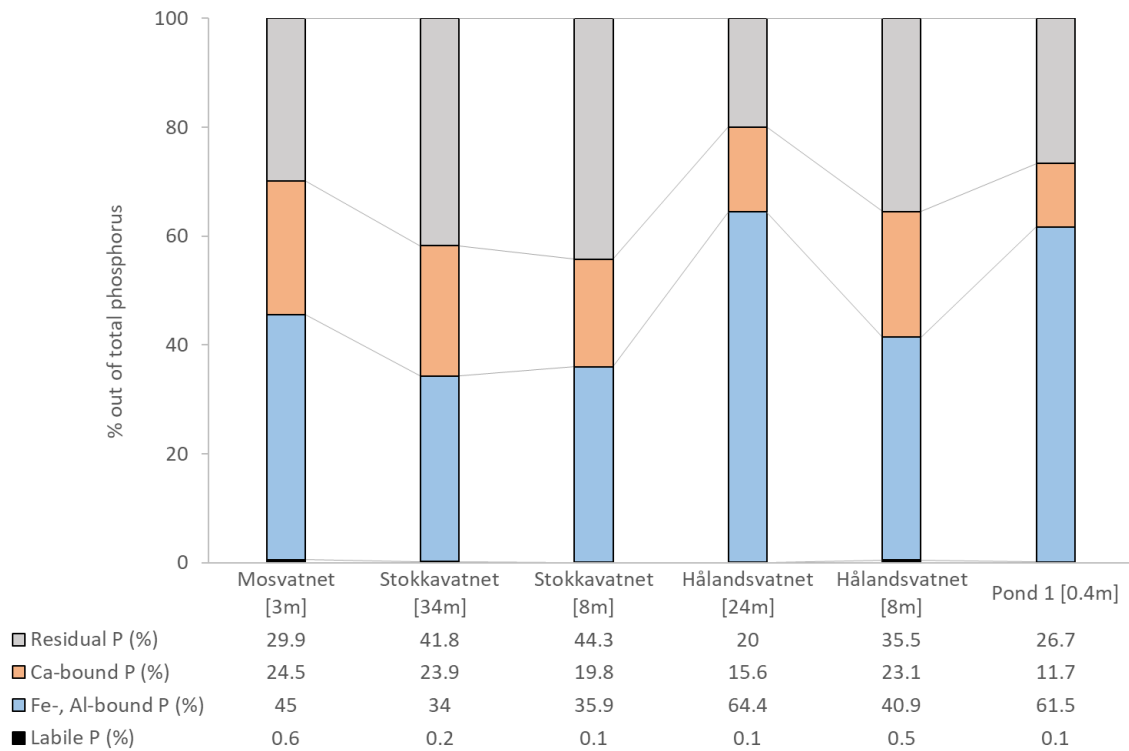
The results in the present study is discussed with emphasis on the two primary aims: To investigate phosphorus dynamics and to assess the potential for sedimentary phosphorus release. In addition, the influence of lakes features on the possible future eutrophication developments is discussed. The present study is focused specifically on bottom sediment because it is both a main sink for phosphorus and an important internal source of this nutrient. Molversmyr (2000) emphasised that the first upper millimetre layer can contain more total phosphorus than the entire water body. Particles and precipitates, containing phosphorus in different forms and stored on bottom of lakes and ponds, can be transformed significantly by biological and/or chemical processes. Dynamic phosphorus transfer can proceed in both directions across the interface between water and sediment. The net phosphorus migration can be reflected in pattern of nutrient distribution in sediment profile.

Phosphorus distribution in vertical sediment profiles

Measured total phosphorus content is in general noticeably higher in deepwater sediment samples comparing to those from shallow water sites (**Figure 5.1**). This trend is explained by combination of three factors: exposure to wind, presence of oxygen and water temperature differences. Shallow water sediment is exposed to more intensive resuspension due to wind and wave activity (Håkanson & Jansson, 1983). This regime leads to washing out of fine material with high content of phosphorus either included into particles or sorbed on its surface (Dodson, 2005). Higher temperature and presence of oxygen result in more intense biological activity which in turn facilitates phosphorus transformation, consumption and transporting into water column.

In addition, effect of these three factors can be seen on distribution of organic matter. Combination of warm temperature, presence of oxygen and appropriate mixing results in fast
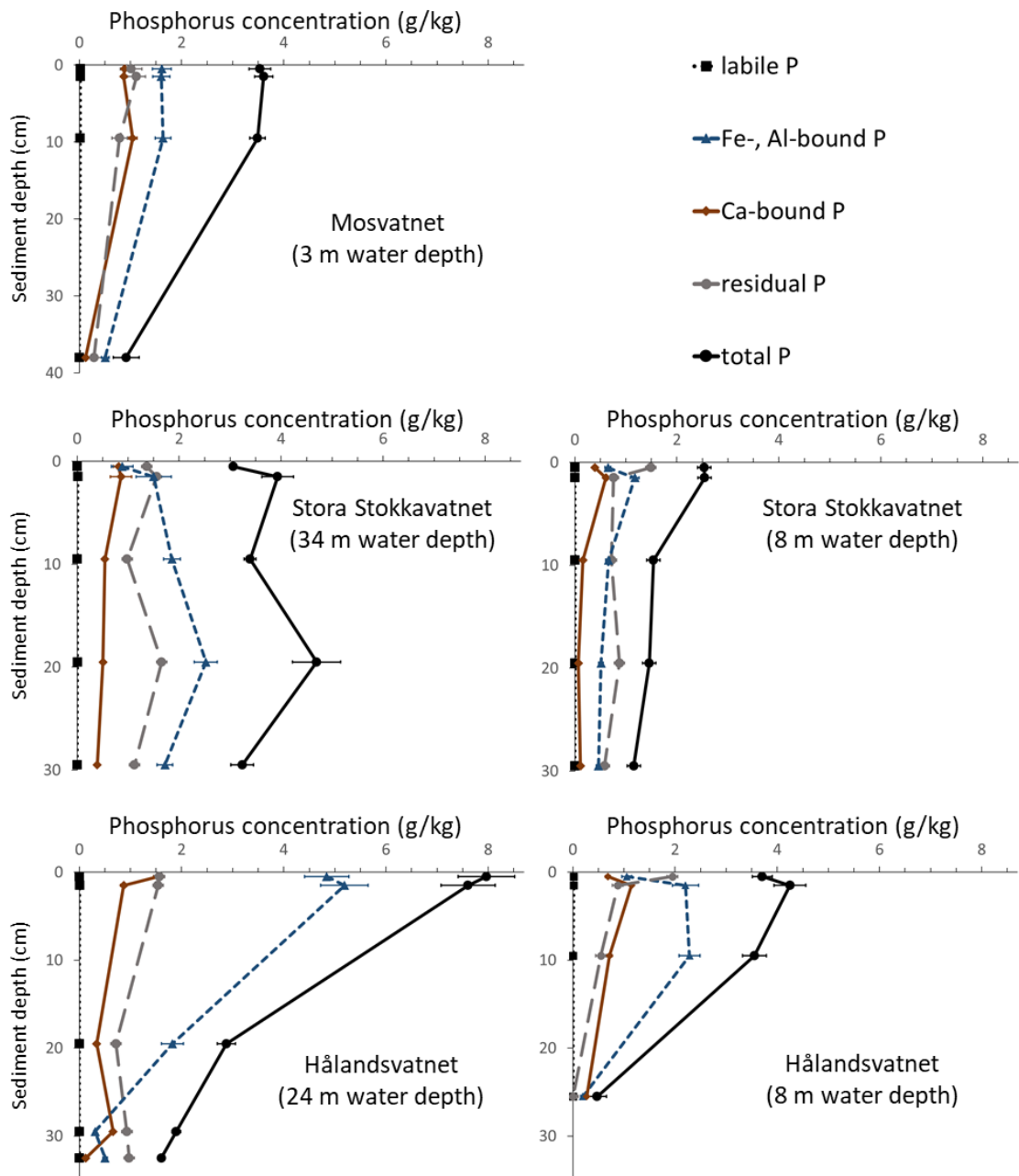
Figure 5.1 Approximate depth profiles of phosphorus forms and total phosphorus content in sediment of three studied lakes.

degradation of organic matter and liberation of phosphorus from sediment. This pattern is demonstrated by lower organic matter content in shallow water sites of Stora Stokkavatnet and Hålandsvatnet comparing to their deepwater zones. Moreover, samples from 8 m depth of Hålandsvatnet, which is exposed to stronger wind influence, have thinner organic layer comparing to samples from the same depth of Stora Stokkavatnet which is more covered from winds.

Pattern of total phosphorus distribution in vertical sediment profiles depend on lake trophic level and presence of oxygen in water on the interface with sediment. For all sampling sites, except deepwater part of Stora Stokkavatnet, total phosphorus concentration decreases with sediment

depth (**Figure 5.1**). Such distribution, according to literature study, is the most common for majority of lake sediments (Dittrich et al., 2013; Granéli, 1999; Holtan et al., 1988; Łukawska-Matuszewska, Vogt, & Xie, 2013; Søndergaard et al., 2003). However, distribution in deepwater sediment of Stora Stokkavatnet is opposite – total phosphorus content and its specific fractions are either constant or even increase with sediment depth. At the same time Stora Stokkavatnet is the only sampling site with mesotrophic state where oxygen is present in bottom water during the whole year. Similar tendencies depending on trophic level were observed by Dittrich et al. (2013). Sediment of eutrophic lakes tend to have profile of phosphorus reduction with depth. And oligotrophic lakes in contrary have constant or increasing with sediment depth phosphorus content. In sediment of Stora Stokkavatnet the relatively uniform distribution of phosphorus fractions may indicate that there is no significant phosphorus net accumulation or releasing trends, which is typical for mesotrophic lakes. It has been suggested for oligotrophic lakes that increasing phosphorus content with depth may indicate relative tolerance of such lakes to nutrient enrichment (Dittrich et al., 2013). However mesotrophic lakes have a limited capability to adsorb additional phosphorus load.

The decrease of total phosphorus concentration is mainly caused by the decrease of redox sensitive Fe-bound fraction. It indicates that this fraction is dissolved in deep horizons and transport into upward layers representing long-term phosphorus release. In case of anoxic conditions on sediment-water interface there is no appropriate barrier for phosphorus trapping in sediment. The decrease of organic matter, organic-bound and carbonate-bound phosphorus fraction also confirms diagenetic long-term release of phosphorus in Mosvatnet, Hålandsvatnet and shallow areas of Stora Stokkavatnet (**Figure 5.1**). This decrease of phosphorus with sediment depth can have a positive effect on rate of water quality improvement in case of decreasing external nutrients load (Molversmyr, 2010) because of low potential for internal phosphorus release.

In opposite, in deep area of Stora Stokkavatnet the high amount of stored organic-bound and Fe-bound phosphorus is a potentially mobile phosphorus pool. Lake Stora Stokkavatnet is vulnerable to escalation of external nutrient input, which intensifies biological activity and fast consumption of oxygen. Current student field observations show worryingly low oxygen content in hypolimnion (2.5 mg/l). If anoxia establishes in stratified bottom water of Stora Stokkavatnet, redox sensitive Fe-bound phosphorus will be liberated. Because of high phosphorus content accumulated in lower levels such internal release may cause positive feedback, leading to rapid eutrophication, which results in even faster phosphorus release. This released phosphorus will be accumulated in hypolimnion and transported into upper water levels during mixing periods leading to higher productivity accelerating eutrophication. If anoxia establishes in bottom water of Stora

Stokkavatnet, the high potential for long-term internal fertilization of lake water may lead to delay in the response of a lake, despite even a substantial reduction in the external phosphorus load (Cullen & Forsberg, 1988).

Sediment of deep areas of highly productive lake Hålandsvatnet is organic rich (up to 40% in surficial layer, **Figure 4.1**). Samples were collected in the middle of September and results of total phosphorus content in Hålandsvatnet possibly match a trend of fast sediment accumulation. Here, on water depth of 24 m in the first 2 cm of sediment the highest total phosphorus concentration is observed (almost 8 mgP/kg dw) with dominance of Fe-bound P fraction (**Figure 5.1**). This relatively high phosphorus accumulation in the surficial layer is in agreement with Sanni and Hertzberg (1983) study, which explain increased sedimentation rate in Norwegian eutrophic lake Årungen by massive seasonal dying of algae in the end of September and intensive Fe-, Al-(oxihydr)oxides precipitation. It is therefore likely that, domination of iron (oxihydr)oxides associated phosphorus in sediment of Hålandsvatnet is caused by seasonal drop of this nutrient consumption by biota. This result is in accordance with Molversmyr (2010) previous observations of surficial sediment composition in Hålandsvatnet in 2010. Molversmyr concludes that internal anaerobic phosphorus release in Hålandsvatnet's hypolimnion has a little effect on general level of phosphorus in the lake water, however in mixing period this is a source of nutrient for algae bloom. It is likely that a sharp increase of iron associated phosphorus and total phosphorus is a result of two processes. First, the migration of redox sensitive fraction from the deeper sediment and its accumulation at the surface sediment due to regularly anoxic conditions. And second, continuous sedimentation of iron bound phosphorus. The domination of this fraction in the upper layer indicates the presence of the higher concentration of dissolved phosphorus in Hålandsvatnet water than in other studied sites.

Factors found to be influencing development of anoxic conditions in the hypolimnion have been explored by Nurnberg (2004). He examined the probability of anoxia development based on regression analysis of 55 stratified lakes with different trophic conditions and concluded that even in geographically close reservoirs, nutrient concentration and lake morphology (depth to area ratio) play the main roles.

Surface sediment

In the first 2 cm of all bottom sediment sample phosphorus is mainly in inorganic form with domination of potentially mobile iron associated P fraction (approximately 70% of total inorganic forms). In this study, content of the most bioavailable labile phosphorus is less than 0.05 gP/kg dw (**Figure 5.1**). However, these results may be underestimated because sample preparations and

extraction procedure were carried out under oxic conditions. In recent literature, the most common practice is to conduct NH_4Cl (labile P) and $NaOH$ (Fe-bound P) extraction steps of fractionation procedure for wet sediment samples under N_2 atmosphere with the aim to prevent any transformations. In this study sediment cores were cut in the presence of oxygen and dried before fractionation. However, significant deviations between results in oxic and anoxic conditions are not expected, because of very low concentration of labile phosphorus which is contained mainly in pore water. Also, the results of $NaOH$ extraction that are interpreted as iron associated phosphorus content may be slightly overestimated in terms of potential mobility due to presence of redox insensitive Al-bound phosphorus part. A further study of sediments using more specified fractionation procedure, for example Psenner's (1984), is therefore suggested.

Carbonate bound phosphorus fraction represents an immobilized P pool (Holdren & Armstrong, 1980) and is capable to release phosphorus in response to temperature increase or pH decrease. Such scenario is very unlikely in the near future for the studied lakes but possible as a result of climate change.

Distribution of phosphorus fractions in surficial sediment layer is an informative indicator of current phosphorus dynamics and reservoir condition. Total phosphorus content in shallow upper layer of Hålandsvatnet is higher in comparison to Stora Stokkavatnet upper layer at the same water depth (**Figure 5.1**). Along with this, sediment from both studied sites is not subjected to anoxic conditions and has similar fractions ratio (3:2:5, Fe-P, Ca-P, organic-P, respectively) (**Figure 4.7**). The uniform increase of phosphorus content in all fractions of Hålandsvatnet shallow sediment may be explained by higher trophic state of Hålandsvatnet compared to Stora Stokkavatnet production level.

Fraction distribution in the first 2 cm of shallow sediment of Stora Stokkavatnet and Hålandsvatnet is similar (**Figure 5.1**). Below 1 cm depth concentration of organic bound phosphorus drop is possibly connected to the increase of iron and carbonate associated phosphorus fraction. One of the possible explanations of these changes is fast diagenesis in the upper sediment (0-1 cm) due to oxic conditions in overlaying water (Dittrich et al., 2013). This hypothesis is confirmed by the magnitude of changes, for example in shallow sediment of Stora Stokkavatnet organic P decrease [0.7 g/kg] = Ca-bound P [0.2 k/kg] and Fe-bound P [0.5 g/kg] increase. In shallow sediment of Hålandsvatnet the change of Fe-bound P in the interval of 1-2 cm is too high to be explained only by diagenetic transformations: organic bound P decrease [1.1 g/kg]$_{(1-2 cm)} \neq$ Ca-bound P [0.5 g/kg]$_{(0-1 cm)}$ and Fe-bound P [1.1 g/kg]$_{(0-1 cm)}$ increase. It is possible that along with organic matter degradation, the Fe associated phosphorus release occurs on the sediment-water interface resulting in depletion of this fraction in the first centimetre sediment layer. Sanni and

Hertzberg (1983) shows that in oxic shallow areas (< 3-4 m water depth) of eutrophic Lake Årungen the main phosphorus releasing mechanism is pH dependent ligand exchange. Epilimnion pH level increases in warm season due to active biological respiration. It is experimentally observed that intense phosphorus release occurs at pH level around 10 (8<pH<11) (Sanni, 1982). High pH level in epilimnion water of eutrophic Lake Hålandsvatnet is often reported in summer periods (Molversmyr, 2010). Ligand exchange process mainly occurs on water-sediment interface, and diffusion on this border is quite high comparing to transport in pore water (Malmaeus & Rydin, 2006). Thus, higher depletion of iron associated phosphorus fraction in the first upper centimetre comparing to the layer below indicates a short-term phosphorus release from sediment in the shallow water area of Hålandsvatnet. In shallow areas of Stora Stokkavatnet little evidence of phosphorus liberation by ligand exchange is found, or at least in lesser magnitude than in Hålandsvatnet, because decrease of iron bound phosphorus is not observed in the upper sediment layer. Subsequently, released dissolved phosphorus partially is consumed by biota and washed off into deepwater areas of Hålandsvatnet. Here it bounds to organic material and iron (oxihydr)oxides and sinks down enriching deepwater surficial Hålandsvatnet sediment. Redox-sensitive phosphorus fraction may be partly dissolved again and released into overlying water during warm seasons in stratified lakes with developed anoxic conditions, but it will be retained in hypolimnion below thermal barrier (Sanni & Hertzberg, 1983). During the period of lake mixing, however, there is a high possibility that part of this dissolved nutrient may recirculate to the epilimnion. In Hålandsvatnet significant amount of mobile phosphorus circulates in water column during a year. There is a continuous cycle of processes of phosphorus precipitation, dissolution and migration in water column again. However only 22% of sediment area of Hålandsvatnet and 9% of lake water volume is on water depth below 15 m and exposed to anoxic conditions (**Figure 3.3**). Consequently aerobic shallow sediment is dominant source of phosphorus to water column (Molversmyr, 2010). Stora Stokkavatnet has two times higher water volume than Hålandsvatnet, however these two lakes are morphologically similar: 21% of sediment area and 9% of Stora Stokkavatnet water volume is located below 15 m water depth that is approximate hypolimnion border. Therefor consequences of eutrophication similar to processes of Hålandsvatnet are expected in Stora Stokkavatnet.

Fast release of pH dependant phosphorus is also expected in moderately eutrophic Lake Mosvatnet. It is quite productive lake (pH almost 8) with intense mixing regime. However, no changes are observed in the first upper 2 cm of sediment. One of the possible explanations of uniform phosphorus fractions distributions is the specific lake morphology. The lake bottom is flat and lake is shallow (max. depth 3.5 m) thus sedimentation occurs evenly over the entire bottom

surface. Molversmyr (2000) analysed sediment collected in May 1999. In general, the trend of phosphorus accumulation was detected in the first 3 cm of sediment. The total phosphorus concentration in the upper layer was 1.5 times higher than obtained in this study and was presented mainly by iron-bound fraction (80%). The thickness of sediment has increased by about 7 cm since this the last observation in 1999 as it can be estimated from the depth of marked yellow claylike layer. However, in this study total phosphorus content in the sediment depth of 9-10 cm is different from the previous results for upper layers. Sanni (1988) showed that in Mosvatnet wind-induced currents effectively mix and redistribute sediment. He reported, for example, that almost 14 cm of upper sediment was mixed during summer and autumn of 1986. Thus, sediment resuspension can be a reason for the relatively uniform phosphorous distribution in the upper sediment collected in September for this study. A combination of results from different studies suggests that this regime of regular sediment mixing and the seasonal increase of water pH level facilitates the sediment phosphorus release. Taking into account that the volume of lake water is relatively small in relation to sediment area, it is expected that even small internal phosphorus release may significantly increase the lake productivity (Molversmyr, 2000). However, based on the water monitoring data of Mosvatnet, Molversmyr (2000) pointed out that there is no evidence of sediment phosphorus liberation trend and this lake is highly vulnerable to external nutrient load. Increase of nutrients input in Mosvatnet can results in increase of biological activity, algae bloom and increase of water pH level that leads to sedimentary phosphorus liberation by mechanism of ligand exchange. This in combination with sufficient resuspension of lake sediment is expected to lead to high internal water fertilization and fast escalation of eutrophication in this shallow lake.

The role of constructed wetland Leikvollbekken is to retain the nutrients washed out from watershed of Stokkavatnet to the lake body to prevent water eutrophication. The sediment layer in ponds is quite thin and in average content of total phosphorus in the upper layer is approximately 1 gP/kg dw higher than in Stora Stokkavatnet. Decrease of organic and Fe-bound phosphorus with sediment depth indicates decomposition of sediment and transport of phosphorus upward to sediment-water interface. Previous study (winter 2016-2017) of retention capacity of the Leikvollbekken area demonstrated that this constructed wetland is efficient in retention of particulate phosphorus, however, readily bioavailable dissolved phosphate concentration decreases insignificantly without vegetation uptake (Krahner, 2017). The results of present sediment study show that more than 60% of sediment phosphorus is associated with iron (oxihydr)oxides that is short-term phosphorus sink. It is expected that this association is unstable in wetland environment. Intense biological activity and high possibility of anoxia developing in logged water can result in dissolution of Fe (oxyhydr)oxides and liberation of phosphorus.

Relatively small water volume, dense active microbial community and regular resuspension of sediment are also negative factors for phosphorus retention in sediment of ponds of constructed wetlands.

6 Conclusions

Measurement and comparison of total phosphorous content, its forms and distributions from different parts of three urban lakes: Hålandsvatnet, Stora Stokkavatnet and Mosvatnet in Stavanger (Norway), conducted in this study, reveals significant differences of phosphorous dynamics in these lakes, despite their close geographical location. Differences are also observed even within the same lake but depending on sampling site. These differences are determined by combination of several natural factors. Morphology of a reservoir is one of the main parameter that governs phosphorus cycle in lake's ecosystem and as a result phosphorus vertical and lateral distribution in a lake sediment. It is observed, that for lakes with significant depth difference phosphorus content is higher in deepwater sediment comparing to that from shallow water sites. Number of factors facilitates phosphorus transformations and release from sediment: exposure to wind and appropriate mixing regime, high water temperature, high pH level of water and presence of oxygen. These factors along with existing distribution and composition of phosphorous in sediment determine possible future behavior of lakes in case of changes in external nutrient load. In all studied lakes dominant forms of phosphorous are association with iron (oxyhydr)oxides and organic material. These fractions are potentially sources of internal phosphorous release from sediment into water column.

Hålandsvatnet is the most productive lake of all three, and it has the highest phosphorous content in sediment. High content of potentially bioavailable form of phosphorus is accumulated in upper layers of deepwater sediment. Shallow water areas of Hålandsvatnet are subjected to constant resuspension, caused by strong wind activity that in combination with intense biological activity, high pH level, warm water temperature and also presence of oxygen facilitates washing out of phosphorous from sediment. These areas serve as a main source of internal phosphorous release through the mechanism of ligand exchange and biological transformation of organic matter. Then released phosphorous is consumed by biota or sorbed on Fe (oxyhydr)oxides and precipitates in deepwater areas of the lake, accumulating in sediment. Due to anoxic conditions in deepwater zones phosphorous is then released from dominant redox-sensitive Fe-bound fraction into hypolimnion. During mixing periods phosphorous is circulated back to epilimnion, fertilizing it and maintaining high biological productivity of the lake. Distribution of phosphorous with sediment depth shows significant depletion of phosphorous in deeper layers. This may result in relatively fast response on reduction of external nutrient load, because internal source in upper sediment layers is capable to maintain only short-term phosphorous release.

Stora Stokkavatnet is significantly less productive than Hålandsvatnet, but due to similarity in their morphology development of eutrophication is also expected to be similar. Currently Stora Stokkavatnet is a mesotrophic lake and serve as a backup water source for Stavanger. A slight diagenetic long-term phosphorous release, similar to Hålandsvatnet, is observed in shallow water areas of Stora Stokkavatnet, but in deepepwater zones phosphorous release does not occur, due to mild biological activity and oxic conditions in hypolimnion. This relatively good state of the lake can easily be disturbed by creating anoxic conditions in deep-water areas, which will launch a chain reaction of positive feedback similar to Hålandsvatnet processes, leading to escalated eutrophication. Moreover, phosphorous distribution with sediment depth is different in Stora Stokkavatnet, lower layers contain as much phosphorous as upper sediment. Because of this, if internal release is launched in Stora Stokkavatnet, it has high potential to have a long-term character and will maintain eutrophic conditions in the lake for decades regardless to any external changes. One of the possible reasons for creating anoxic conditions, that should be avoided, is an increase of external nutrient load which leads to acceleration of biological activity and consumption of oxygen.

To reduce phosphorus input into Stora Stokkavatnet from watersheds a system of artificial wetlands is constructed. However, this study shows that sediment phosphorous of constructed wetland ponds is mostly in mobile iron-associated form. A proper trapping of phosphorous in sediment is not possible due to intense biological activity, regular resuspension and possibility of developing reducing conditions in sediment of constructed wetland ponds.

Mosvatnet has different morphology, it is the shallowest of the three lakes and has practically flat bottom. Its sediment is exposed to regular wind mixing and wave resuspension, warm overlaying water, oxic conditions and seasonal increase of pH level due to active biological respiration. All this factors facilitates sedimentary phosphorus release by intense biological degradation of organic matter and ligand exchange mechanism. Currently significant phosphorus leaching from sediment is not observed. Even a slight increase of external nutrients input can initiate rapid internal phosphorus release due to accelerating lake productivity which in turn increase water pH level. Taking in account a relatively small volume of water comparing to sediment area this launch of internal release possibly can drastically affect water quality by escalation of eutrophication.

Experience of previous studies shows that restoration of freshwater reservoirs is often very expensive and rarely effective. In general, current study shows that to improve or at least maintain water quality in the studied lakes it is vital to control and reduce external nutrient load. It is important to continue monitoring of phosphorous content and distribution in water and sediment.

Also it is necessary to maintain and monitor conditions in the lake protective systems such as constructed wetlands.

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Appendixes

Appendix A. The calibration curve for phosphate determination

Appendix B. Total phosphorus data

Appendix C. Results of phosphorus fractionation procedure

Appendix A.   The calibration curve for phosphate determination

Figure A.1 shows one example of calibration curve which was constructed on base of standard phosphate solutions of 0.12, 0.24, 0.36, 0.48, 0.60, and 0.72 mg/l. The absorbance was read at 880 nm. Δ A (*y*-axis) is a difference in the absorbance of the phosphate containing solution (*A*) and blank sample (A_b). All phosphorus analysis sessions included one blank sample. This relationship was obtained on the 31st of January 2018.
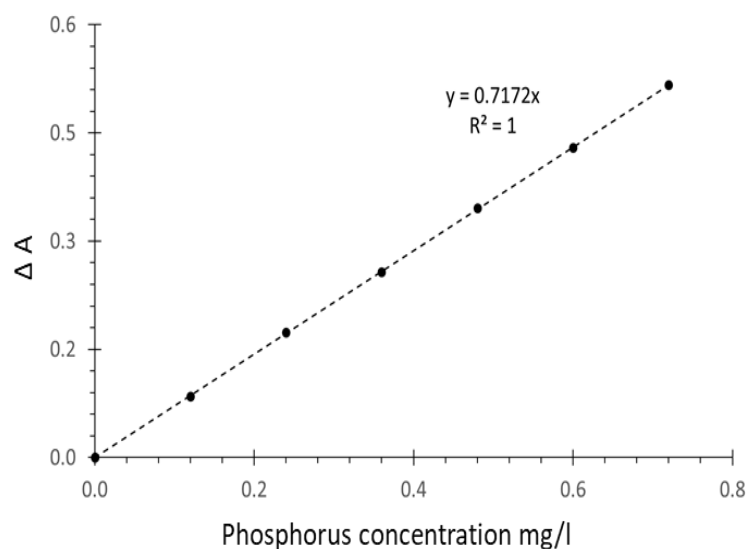

Figure A.1 Calibration graph for phosphorus analysis.

The phosphate concentration (C_{read}) measured by the spectrophotometer was calculated by equation B.1:

$$C_{read} = \frac{(A - A_b)}{f}$$

equation B.1

where

A is the absorbance of the test portion;

A_b is the absorbance of the blank test. In case of turbid samples, absorbance of sample duplicate with turbidity-colour compensation reagent (A_t) was measured. If $A_t > A_b$ then, instead blank absorbance, A_t was subtracted from the absorbance of the test portion.

f is the slope of the calibration graph in [l/mg] (Appendix A).

Initial phosphate concentration C in 100 ml flasks before dilution was calculated using proportion $C_1 \times V_1 = C_2 \times V_2$ (equation B.2):

$$C = \frac{C_{read}[\frac{mg}{l}] \times 50\ [ml]}{V_s\ [ml]}$$

equation B.2

where

V_s is a volume of tested solution diluted in 50 ml flasks.

In **Table B.1** the data of total phosphorus is presented in alkaline and acidic tested solutions. Index with numbers (for example, P_1) indicates the number of independent tests of phosphate determination. Standard deviation for single result is average deviation for session (alkaline tests - $\pm$ 5.20%, acidic - $\pm$ 3.67%, for both – 6.93%).

Table B.1 The total phosphorus data in alkaline and acidic solutions. Dried samples with mass 0.2±0.1 g were analyzed. The data is presented as mean±standard deviation g P/kg dw.

Sample name	P_{tot} [g/kg] in alkaline solution				P_{tot} [g/kg] in acidic solution			Mean
	P_1	P_2	P_3	P_{tot}	P_1	P_2	P_{tot}	P_{tot}[g/kg]
L 1.1	4.387	3.846	-	4.12±0.38	4.139	-	4.14±0.15	4.12±0.27
L 1.2	4.885	4.737	-	4.81±0.1	5.105	-	5.11±0.19	4.91±0.19
L 2.1	7.749	-	-	7.75±0.4	7.930	-	7.93±0.29	7.84±0.13
L 3.1	3.063	-	-	3.06±0.16	4.207	-	4.21±0.15	3.63±0.81
L 3.2	4.225	3.903	-	4.06±0.23	4.177	-	4.18±0.15	4.10±0.17
L 3.3	1.899	-	-	1.90±0.1	1.977	2.251	2.11±0.19	2.04±0.18
M 1.1	3.576	-	-	3.58±0.19	3.235	-	3.24±0.12	3.41±0.24

Sample name	P$_{tot}$ [g/kg] in alkaline solution				P$_{tot}$ [g/kg] in acidic solution			Mean
	P$_1$	P$_2$	P$_3$	P$_{tot}$	P$_1$	P$_2$	P$_{tot}$	P$_{tot}$[g/kg]
M 1.2	3.619	3.373	-	3.50±0.17	3.477	-	3.48±0.13	3.49±0.12
M 1.3	3.287	-	-	3.29±0.17	3.454	-	3.45±0.13	3.37±0.12
M 1.4	0.471	-	-	0.47±0.02	1.053	1.070	1.06±0.01	0.86±0.34
M 2.1	3.596	-	-	3.60±0.19	3.732	-	3.73±0.14	3.66±0.10
M 2.2	3.810	3.557	-	3.68±0.18	3.807	-	3.81±0.14	3.72±0.15
M 2.3	3.707	-	-	3.71±0.19	3.461	3.519	3.49±0.04	3.56±0.13
M 2.4	0.954	-	-	0.95±0.05	1.035	-	1.03±0.04	0.99±0.06
S 1.1	3.134	-	-	3.13±0.16	3.001	-	3.00±0.11	3.07±0.09
S 1.2	3.989	3.510	-	3.75±0.34	3.619	-	3.62±0.13	3.71±0.25
S 1.3	3.474	-	-	3.47±0.18	3.306	-	3.31±0.12	3.39±0.12
S 1.4	4.362	-	-	4.36±0.23	5.029	-	5.03±0.18	4.70±0.47
S 1.5	3.396	-	-	3.40±0.18	3.082	-	3.08±0.11	3.24±0.22
S 2.1	3.083	-	-	3.08±0.16	3.034	-	3.03±0.11	3.06±0.03
S 2.2	4.215	3.983	-	4.10±0.16	4.272	-	4.27±0.16	4.16±0.15
S 2.3	6.302	6.827	-	6.56±0.37	7.607	-	7.61±0.28	6.91±0.66
S 2.4	3.502	-	-	3.50±0.18	3.308	-	3.31±0.12	3.41±0.14
S 3.1	2.688	-	-	2.69±0.14	2.380	-	2.38±0.09	2.53±0.22
S 3.2	2.565	-	-	2.57±0.13	2.525	-	2.52±0.09	2.54±0.03
S 3.3	1.559	-	-	1.56±0.08	1.522	-	1.52±0.06	1.54±0.03
S 3.4	1.457	-	-	1.46±0.08	1.462	-	1.46±0.05	1.46±0.01
S 3.5	1.137	-	-	1.14±0.06	1.174	-	1.17±0.04	1.16±0.03
H 1.1					N/A*			
H 1.2					N/A*			
H 1.3	4.876	4.898	-	4.89±0.02	4.946	4.877	4.91±0.05	4.90±0.03
H 1.4	2.896	-	-	2.90±0.15	2.422	-	2.42±0.09	2.66±0.33
H 1.5	1.533	-	-	1.53±0.08	1.594	-	1.59±0.06	1.56±0.04
H 2.1	7.967	-	-	7.97±0.41		N/A*		7.97±0.55
H 2.2	7.086	7.583	-	7.33±0.35	8.147	-	8.15±0.3	7.61±0.53
H 2.3	3.002	-	-	3.00±0.16	2.753	-	2.75±0.1	2.88±0.18
H 2.4	1.762	1.991	1.881	1.88±0.11	1.948	1.903	1.93±0.03	1.90±0.09
H 2.5	1.601	-	-	1.60±0.08	1.609	-	1.61±0.06	1.61±0.01
H 3.1	3.833	3.781	-	3.81±0.04	3.419	3.794	3.61±0.27	3.71±0.19

Sample name	P_{tot} [g/kg] in alkaline solution				P_{tot} [g/kg] in acidic solution			Mean P_{tot}[g/kg]
	P_1	P_2	P_3	P_{tot}	P_1	P_2	P_{tot}	
H 3.2	4.600	4.002	-	4.30±0.42	4.143	-	4.14±0.15	4.25±0.31
H 3.3	3.388	-	-	3.39±0.18	3.718	-	3.72±0.14	3.55±0.23
H 3.4	0.272	-	-	0.27±0.01	0.562	0.597	0.58±0.02	0.48±0.18

* Samples were not analysed due to a lack of material for tests.

Appendix C.   Results of phosphorus fractionation procedure

Table C.1 The data of phosphorus content in extracts by the method Hieltjes and Lijklema (1980). Dried samples with mass 0.2±0.1 g were sequentially mixed with 25±1 ml solutions of 1M NH_4Cl, 0.1M NaOH and 0.5M HCl. The data is presented as mean±standard deviation g P/kg dw.

Sample name	NH_4Cl	NaOH	HCl	Sum of fractions	Mean P_{tot}[g/kg]
	g P/ kg dw				
L 1.1	0.01±0.001	2.72±0.24	0.47±0.03	3.20±0.28	4.12±0.27
L 1.2	0.003	3.2±0.1	0.52±0.01	3.72±0.11	4.91±0.19
L 2.1	0.022±0.001	5.66±0.14	0.63±0.05	6.31±0.19	7.84±0.13
L 3.1	0.006	1.9±0.17	0.46±0.03	2.36±0.2	3.63±0.81
L 3.2	<0.001	2.56±0.17	0.53±0.05	3.09±0.21	4.10±0.17
L 3.3	0.008±0.001	1.5±0.15	0.38±0.03	1.89±0.18	2.04±0.18
M 1.1	0.019±0.001	1.65±0.21	0.89±0.02	2.56±0.23	3.41±0.24
M 1.2	0.027±0.002	1.48±0.13	0.89±0.06	2.40±0.19	3.49±0.12
M 1.3	0.015±0.001	1.53±0.14	0.98±0.07	2.53±0.2	3.37±0.12
M 1.4	<0.001	0.56±0.05	0.09±0.01	0.65±0.06	0.86±0.34
M 2.1	0.025±0.002	1.51±0.13	0.86±0.06	2.39±0.19	3.66±0.1
M 2.2	0.046±0.003	1.72±0.15	0.85±0.06	2.61±0.21	3.72±0.15
M 2.3	0.021±0.001	1.75±0.16	1.1±0.07	2.87±0.23	3.56±0.13
M 2.4	<0.001	0.45±0.04	0.15±0.01	0.61±0.05	0.99±0.06
S 1.1	0.003	1.03±0.09	0.45±0.03	1.48±0.12	3.07±0.09
S 1.2	0.011±0.001	1.30±0.02	0.75±0.13	2.07±0.15	3.71±0.25
S 1.3	0.004	1.86±0.17	0.54±0.04	2.41±0.2	3.39±0.12
S 1.4	0.006	2.52±0.23	0.51±0.03	3.04±0.26	4.70±0.47
S 1.5	0.001	1.72±0.15	0.39±0.03	2.11±0.18	3.24±0.22
S 2.1	0.004	0.73±0.07	1.18±0.08	1.91±0.15	3.06±0.03
S 2.2	0.015±0.001	1.9±0.17	1.08±0.07	2.99±0.24	4.16±0.15
S 2.3	0.005	3.36±0.3	1.59±0.11	4.96±0.41	6.91±0.66
S 2.4	0.002	2.2±0.2	0.34±0.02	2.55±0.22	3.41±0.14
S 3.1	0.001	0.65±0.06	0.39±0.03	1.04±0.08	2.53±0.22
S 3.2	0.002	1.18±0.09	0.61±0.06	1.79±0.14	2.54±0.03
S 3.3	0.005	0.66±0.06	0.16±0.01	0.82±0.07	1.54±0.03
S 3.4	0.005	0.51±0.05	0.068±0.005	0.59±0.05	1.46±0.01
S 3.5	0.003	0.46±0.04	0.11±0.01	0.57±0.05	1.16±0.03
H 1.1	0.002	4.31±0.39	0.95±0.06	5.26±0.45	N/A

Sample name	NH₄Cl	NaOH	HCl	Sum of fractions	Mean P_{tot}[g/kg]
			g P/ kg dw		
H 1.2	0.007	5.97±0.53	1.21±0.08	7.19±0.62	N/A
H 1.3	0.005	3.96±0.35	0.56±0.04	4.52±0.39	4.90±0.03
H 1.4	0.001	1.43±0.13	0.14±0.01	1.57±0.14	2.66±0.33
H 1.5	0.001	0.73±0.07	0.06±0.004	0.79±0.07	1.56±0.04
H 2.1	0.004	4.84±0.43	1.56±0.11	6.4±0.54	7.97±0.55
H 2.2	0.008±0.001	5.19±0.46	0.87±0.06	6.06±0.52	7.61±0.53
H 2.3	<0.001	1.82±0.22	0.34±0.02	2.16±0.24	2.88±0.18
H 2.4	0.002	0.31±0.03	0.66±0.04	0.97±0.07	1.90±0.09
H 2.5	<0.001	0.5±0.05	0.13±0.01	0.63±0.05	1.61±0.01
H 3.1	0.019±0.001	1.05±0.09	0.68±0.05	1.76±0.14	3.71±0.19
H 3.2	0.019±0.001	2.2±0.26	1.15±0.02	3.37±0.28	4.25±0.31
H 3.3	0.004	2.28±0.2	0.72±0.05	3.01±0.25	3.55±0.23
H 3.4	0.005±0.001	0.2±0.04	0.27±0.01	0.47±0.06	0.48±0.18