



Universitetet  
i Stavanger

FACULTY OF SCIENCE AND TECHNOLOGY

## MASTER'S THESIS

Study programme/specialisation: <b>Environmental Engineering/ Water science and technology</b>	Spring semester, 2018  Open
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Title of master's thesis:  <b>Phosphorus retention in a mature constructed wetland under base flow and storm flow conditions</b>	
Credits: <b>30</b>	
Keywords: <b>Leikvollbekken, constructed wetland, phosphorus, phosphate, iron, storm flow, base flow, agricultural runoff</b>	Number of pages: 90  + supplemental material/other: 11  Stavanger, 15 <sup>th</sup> June, 2018

## Abstract

The main objective was to monitor a mature constructed wetland, Leikvollbekken, with respect to phosphorus retention, both over long term and during short storm events. The hypothesis was that the wetland would have a positive retention over time, but that short periods with intense precipitation would cause wash-out of accumulated phosphorus due to high water flow. To evaluate this, weekly flow proportional composite samples were analysed for phosphorus, iron and suspended solids, as well as turbidity measurements. Two storm events, Storm A and Storm B, were monitored with time dependent composite samples and analysed for TP,  $\text{PO}_4^{3-}$  and TSS. Flow in and out of the wetland was monitored with a 15-minute interval during the whole thesis period.

Weekly measurements showed that Leikvollbekken retained TP and pTP (11.9 kg and 15.4 kg), while washing out sTP and  $\text{PO}_4^{3-}$  (-3.5 kg and -3.0 kg). No clear connection between average weekly flow and weekly retention efficiency was observed. The monitoring showed a great fluctuation in measured turbidity, TSS, phosphorus and iron concentrations. A distinct connection between flow and phosphorus concentrations was observed during the storm events. Storm A washed out phosphorus and solids (-5.7 kg TP, -17.3 kg  $\text{PO}_4^{3-}$ , 1.2 kg TSS), thus supporting the theory that heavy rain would produce great wash-out situations. Storm B retained phosphorus and solids (70.6 g TP, 9.9 g  $\text{PO}_4^{3-}$ , 183.7 kg TSS), showing that not all storms cause washout situations.

In general, empirical data supporting the theory for wash-out situations of phosphorus during high flow, and data supporting the assumed dependency of flow and concentrations, were obtained.

## Acknowledgments

I want to thank my supervisor, Assoc. Prof. Roald Kommedal, for the opportunity to work on the phosphorus project and for guidance through the year. The thesis could not have been written without his guidance.

I also want to thank Assist. Prof. Espen Enge for help with the practicalities in the lab and his help with analysing samples during the last storm, as well as answering any questions during the year.

A big thanks to all the people at the laboratories at UiS, for practical help and for always making the days in the lab joyful. A special thanks to Hans Kristian Brekke for help with endless small problems and always doing it with a smile.

Thanks to my roomie for support and especially for feeding me the weeks the thesis demanded long days in the field or at the laboratories.

Finally, I want to thank my family for IT-help, proofreading and for supporting me through the year with endless phone calls.

Stavanger June 2018

Liva M. Luth-Hanssen

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## Abbreviation list

CW = Constructed Wetland

FWS = Free Water Surface

PP = Particulate Phosphorus

SRP = Soluble Reactive Phosphorus

DP = Dissolved Phosphorus

TP = Total Phosphorus

sTP = Soluble Total Phosphorus

pTP = Particulate Total Phosphorus

P-load = Phosphorus load

TotFe = Total Iron

sTotFe = Soluble Total Iron

TSS = Total Suspended Solids

FSS = Fixed Suspended Solids

VSS = Volatile Suspended Solids

EPC = Equilibrium Phosphate Concentration

FTW = Floating Treatment Wetlands

NTU =Nephelometric Turbidity Unit

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# 1. Introduction

More surface waters have become eutrophic since the 1800s due to increased anthropogenic nutrient input (Smith, 1998). Surplus of fertilizer in agricultural fields leak phosphorus into surrounding surface waters (Lægreid, Kaarstad, Bøckman, & Norsk hydro, 1999), leading to eutrophic surface waters. Quantitative studies on low phosphorus concentrations are important to perform since even phosphorus concentrations negligible in an economical and agricultural aspect can have a significant effect on primary productions in surface waters (Lægreid et al., 1999). Multiple constructed wetlands have been established in Norway the last 20 years with an aim to treat diffuse water pollution, such as phosphorus runoffs from agricultural fields (Miljødirektoratet, 2014). Consequently, studies of constructed wetlands (CWs) performances are important to ensure optimal phosphorus retention and thus prevent eutrophication.

There has been much focus on use of CWs the last decades, both in Scandinavia and in the rest of the world. Relative reduction by wetlands have been reported as high as 88 % but also as a negative reduction (Adyel, Oldham, & Hipsey, 2017; B. C. Braskerud et al., 2005; Dong, Wiliński, Dzakpasu, & Scholz, 2011; Geranmayeh, Johannesson, Ulén, & Tonderski, 2018; Kao, Wang, Lee, & Wen, 2001; Kynkäänniemi, Ulén, Torstensson, & Tonderski, 2013) A total of 9 151 results appear when searching for CWs on Scopus. The number of results is reduced drastically to 2 172 when the search is limited to articles containing the keywords “phosphorus”, “phosphor” or “phosphate”. Previous studies focus on both abiotic and biotic phosphorus retention, and during long study periods. When narrowing the search to include the key words “storm water”, “storm peaks” or “pulses”, the number of results reduced to less than 50. This shows that there are not many published articles on how storm peaks effect CWs treating phosphorus.

The objective of this thesis is to evaluate Leikvollbekken, a mature wetland, with respect to phosphorus retention under base flow and storm events. The hypothesis is that storm peaks wash out accumulated phosphorus. This effect can have produced a false retention efficiency because previous sampling methods, consisting of time dependent composite samples over larger intervals, may not have captured this effect.

Methods for collecting water samples vary in earlier studies (Table 1-1). Some studies are based on single grab samples assumed to represent the concentration for a whole week, while other studies use automatic samplers to get continuous sampling. Another difference in sampling

methods used are whether flow measurements are included. Studies where flow measurements are not included, cannot estimate mass flux and hence cannot determine nutrient load.

*Table 1-1 Presentation of different types of sampling strategies used for monitoring CWs.*

<b>Sampling method</b>	<b>Flux</b>	<b>Examples of studies</b>
Grab without flow measurements	No	Hijosa-Valsero, Sidrach-Cardona, and Bécares (2012)
Grab with flow measurements	Yes	Kohler, Poole, Reicher, and Turco (2004), Miklas Scholz and Lee (2005), Maniquiz, Lee, Choi, Jeong, and Kim (2011)
Time dependent composite without flow measurements	No	-
Time dependent composite with flow measurements	Yes	Dzakpasu, Scholz, McCarthy, and Jordan (2015), Wadzuk, Rea, Woodruff, Flynn, and Traver (2010),
Flow dependent composite	Yes	B. C. Braskerud et al. (2005), Raisin and Mitchell (1995), Merriman and Hunt III (2014), Bent Christian Braskerud (2001),

Limited numbers of grab samples represent the sampling method providing the most limited representation of concentration changes in wetlands. Concentration peaks will not be represented with grab samples unless the frequency is high, which is very time consuming. Time dependent composite sampling is a method where samples are collected after a given time interval. This method can produce a composite sample with several subsamples, but can underestimate storm events. Flow dependent sampling collects samples after a given amount of water passing, hence producing a composite sample with higher sampling frequency during high flow.

Two different sampling methods were therefore used to achieve composite samples representative for Leikvollbekken. Flow dependent composite samples were used for the weekly measurements, while 1h time dependent composite samples were analysed during storm events.

## 2. Background

The background section consists of a general introduction to phosphorus and wetlands, before explaining the different sources for phosphorus and mechanisms for phosphorus retention. The section ends with a model for flux retention to explain the complex picture of phosphorus retention, prior to a statement of the objectives of the thesis.

### 2.1. Eutrophication and phosphorus

Phosphorus is known as the limiting nutrient for primary production in many freshwater systems (Dodson, 2005). Concentrations of 0.01 mg/L soluble phosphorus are expected to cause eutrophic waters, but eutrophication potentials are better determined by considering phosphorus loads (Smil, 2000). Excessive nutrient input in surface waters leads to increased productivity in every level in food chains (Lægneid et al., 1999). Primary producers grow out of their means and reduce water clarity, which leads to less light emitting through the water column. Lack of light decrease photosynthesis which give low oxygen concentration. This, combined with respiration and degradation of organic matter, produces an unhealthy, anoxic environment for living organisms.

Since the 1980s, the Norwegian Government has monitored the state of surface waters, showing that there are problems with eutrophic lakes all over Norway (Norwegian Institute for Water Research (NIVA), 2008). In general, human activity is considered to cause increased phosphorus flows in nature. Main sources are increased erosion due to less vegetation, organic waste unevenly distributed in the environment, centralized wastewater treatment with release into waters and use of inorganic fertilizers (Smil, 2000). Production of inorganic phosphorus fertilize started in the 1840s (Lægneid et al., 1999). Phosphate rocks were treated to produce ordinary superphosphate (7 -10% P) and later triplet superphosphate (20% P) (Smil, 2000), which caused a relocation of phosphorus bound to minerals to the bioavailable fraction. Norwegian Institute for Water Research (NIVA) and Norwegian Institute for Air Research (NILU) (2012) stated that 21% of Norway's land area was added more fertilize than needed. Since 1994, a total of 1000 CWs have been constructed in Norway (Miljødirektoratet, 2014) which can help prevent phosphorus from the fields reaching surface waters.

## 2.2. Definition of a wetland

There exist many definitions for wetlands (Kadlec & Wallace, 2008; Mitsch & Gosselink, 2015). The intergovernmental treaty named the Ramsar Convention, contributes to the wetland definitions with this broad definition:

*“areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt, including areas of marine water the depth of which at low tide does not exceed six metres”*

Marine wetlands, estuarine wetlands, wetlands in connection to lakes, rivers and streams, as well as swamps are all included in the Ramsar Convention.

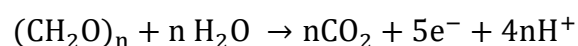
Bugs, birds and other small animals thrive in the wetlands. Thus, wetlands are considered a very important habitat for biological diversity by the Norwegian Environment Agency (Miljødirektoratet, (2016)).

## 2.3. Wetland environment

Wetlands can be called the kidneys of nature because of effective transformation of pollutants to harmless compounds due to high biological active (Mitsch & Gosselink, 2015). This transformation, combined with the low cost of maintenance, makes wetlands good for industrial and populated areas where pollutants of different classes are released.

In general, water enters wetlands as precipitation, surface runoff, groundwater infiltration and rivers flooding. A flood peak into wetlands enriches with both oxygen and nutrients for growth (Mitsch & Gosselink, 2015). Wetlands have a characteristic oxygen profile comprising of both aerobic and anaerobic compartments, and subsequently environments for both oxidation and reduction (Mitsch & Gosselink, 2015). Coupled oxidation-reduction reactions for various nitrogen components, manganese, iron and organic matter occur at different redox potentials (Dodson, 2005). For example, does oxidation of organic matter occur when the redox potential falls lower than  $-200$  mV (Reddy & DeLaune, 2008) (Equation 2-1). See subchapter “2.8 Internal phosphorus loading” for more information about iron and redox potential.

*Equation 2-1 Oxidation of organic matter creating increased redox potential.*



A thin upper layer of aerobic soil is often observed in wetlands and represents a source for oxidized ions. This layer is present simultaneous with anaerobic conditions in the deeper sediment layers due to water saturated soil having a low oxygen diffusion rate, combined with

microbial respiration and oxygen demand by reductants (Mitsch & Gosselink, 2015). Therefore plants use morphological and physiological adaptations, as well as whole plant strategies, to overcome the anaerobic conditions developed around root systems (Kadlec & Wallace, 2008). Such plants are commonly called macrophytes and include aquatic vascular plants, aquatic mosses and some large algae (Brix, 1997).

#### 2.4. Different types and use of constructed wetlands

CWs are made for specific purposes, which include retaining, transforming and removing different type of pollutions. Nutrients, heavy metals, petroleum waste and pathogens all represent possible pollutions in an environment. Studies show that CWs have been created to treat agricultural run off by nutrient retention (B.C. Braskerud, 2002; Fink & Mitsch, 2004; Kynkäänniemi et al., 2013), airport runoff (Thorén, Legrand, & Herrmann, 2003), urban runoff (Ko et al., 2010; Kohler et al., 2004; Scholes, Shutes, Revitt, Purchase, & Forshaw, 1999), highway runoff (Pontier, Williams, & May, 2004; Åstebøl & Hvitved-Jacobsen, 2014) and runoff from industry as metal production (Overall & Parry, 2004) and dairy production (O’neill, Foy, & Phillips, 2011). Further reading in this chapter focuses on CWs created for phosphorus removal.

Different designs are used to achieve phosphorus removal. Plants in strategic places is one method. Emerged and submerged plants in open water surfaces increase the hydraulic retention time by decreasing wind spreading of water and thus reducing water movements. Decreased water movement will again reduce resuspension of settled solids, as well as inducing settling of suspended solids. Plants also stabilize the bed surface and contribute with physical filtration of water by providing surfaces for adsorption of soluble phosphate (Brix, 1994). Vymazal (2013) stated *Typha ssp.*, *Scripus ssp.* and *Pharagmites* to be the most common CW plants world-wide out of 150 different plant species found. In Europe *P. australis* is the dominant plant, but different species of *T. latifolia*, *Carex*, *Iris pseudacorus* L. and *Glyceria Maxima* are also common.

CWs are designed to work in all seasons and under various weather conditions. To analyse wetlands performances under different hydrological fluctuations, flow is distinguished between base flow and storm flow. Base flow represents water flow when there is little rain and is the most common flow rate. Storm flow occurs during heavy rain. These two flow conditions have great impact on a wetland’s performance. A base flow should not be so small that plants dry up, but at the same time low enough to achieve a hydraulic retention time high enough for

sufficient settling of suspended particles. If a CW receives a storm flow much bigger than its maximum capacity, the high flow can produce a too high water velocity and wash out accumulated particles with adsorbed nutrients. A too big storm flow can also remove plants and constructions created due to friction between the water and plants (Ko et al., 2010). It is therefore important to design CWs as correct as possible according to both base flow and storm flow. This makes an interesting dilemma. A storm flow can be much bigger than base flow. Consequently, CWs are difficult to construct to work perfect under both base and storm flow.

Fink and Mitsch (2014) observed that a TP peak measured at the inlet of a wetland could be measured leaving the wetland after some time. The measured TP peak was smaller by the outlet, but observable. A concentration movement like this supports the idea of plug flow in wetlands.

M Scholz, Sadowski, Harrington, and Carroll (2007) stated that the wetland-farmyard area ratio needs to be more than 1.3 for a CW to achieve optimal phosphate removal. They also stated that each “cell” in a CW had to be less than 1 width to every 2.2 length.

Common types of CWs are free water surface, horizontal subsurface flow and vertical flow. All three types are constructed with different preferred use (Kadlec & Wallace, 2008).

#### 2.4.1. Free surface wetlands

Free water surface (FWS) wetlands (Figure 2-1) are identified with areas of open water containing floating and/or emerging plants. This type of CWs is more comparable with natural wetlands than other types of CWs. FWS treat water with processes as sedimentation, filtration, adsorption, absorption and precipitation of unwanted substances (Kadlec & Wallace, 2008).

Due to the free surface water, a wide range of wildlife is attracted to this type of wetland. A downside of a rich animal wildlife is increased risk of infection when treating wastewater containing pathogens, opposed to the goal of removing harmful pathogens (Kadlec & Wallace, 2008). Animals can also affect hydrological paths in the wetland. Fink and Mitsch (2004) observed a significant, stable drop in measured TP and SRP concentrations at a specific sampling point and assumed that a muskrat tunnel had altered the hydrological path causing the change.



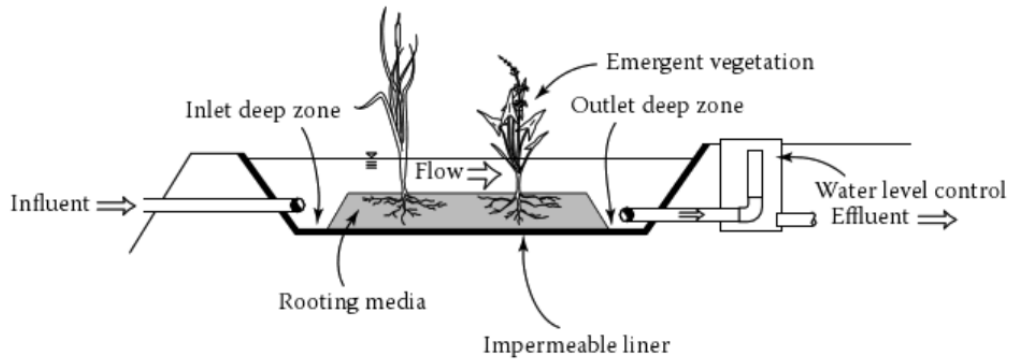


Figure 2-1 Drawing of a free water surface CW. (Kadlec & Wallace, 2008)

FWS wetlands work under different climates, but are affected by cold temperatures (Kadlec & Wallace, 2008). As temperature falls during winter, rates of biological and chemical reactions are reduced. An ice layer on free surface water will also reduce oxygen transfer into the water, which will in turn reduce the rate of oxygen dependent reactions and increase TSS removal due to more quiescence conditions.

A novel type of CWs is floating treatment wetlands (FTW). This type of CW consists of floating mats with emergent macrophytes, where the root zone extends into the waterbody (Tanner & Headley, 2011). The submerged roots provide a greater surface area for biofilm attachments and can also entrap suspended solids (Tanner & Headley, 2011).

#### 2.4.2. Horizontal subsurface flow and vertical flow wetlands

Horizontal subsurface flow and vertical flow wetlands are without open water surface and have a wetland body filled with pebbles, sand and rocks. These types of CWs are generally more expensive than free surface water wetlands, but have other positive applications as for instance treatment of pathogens without exposure to the surface. Consequently, this leaves the surroundings without risk of infection. (Kadlec & Wallace, 2008)

Vertical flow wetlands are special because they can have an aerobic top layer simultaneously as the bottom layer is anaerobic. This combination of anaerobic and aerobic conditions gives the wetlands a higher reduction of nutrients. (Kadlec & Wallace, 2008)

## 2.5. Phosphorus in wetlands

The phosphorus cycle (Figure 2-2) presents different phosphorus compounds naturally present in a typical wetland. The cycle shows how phosphorus moves in nature, and hence is important to be aware of when evaluating a wetlands performance for phosphorus retention.

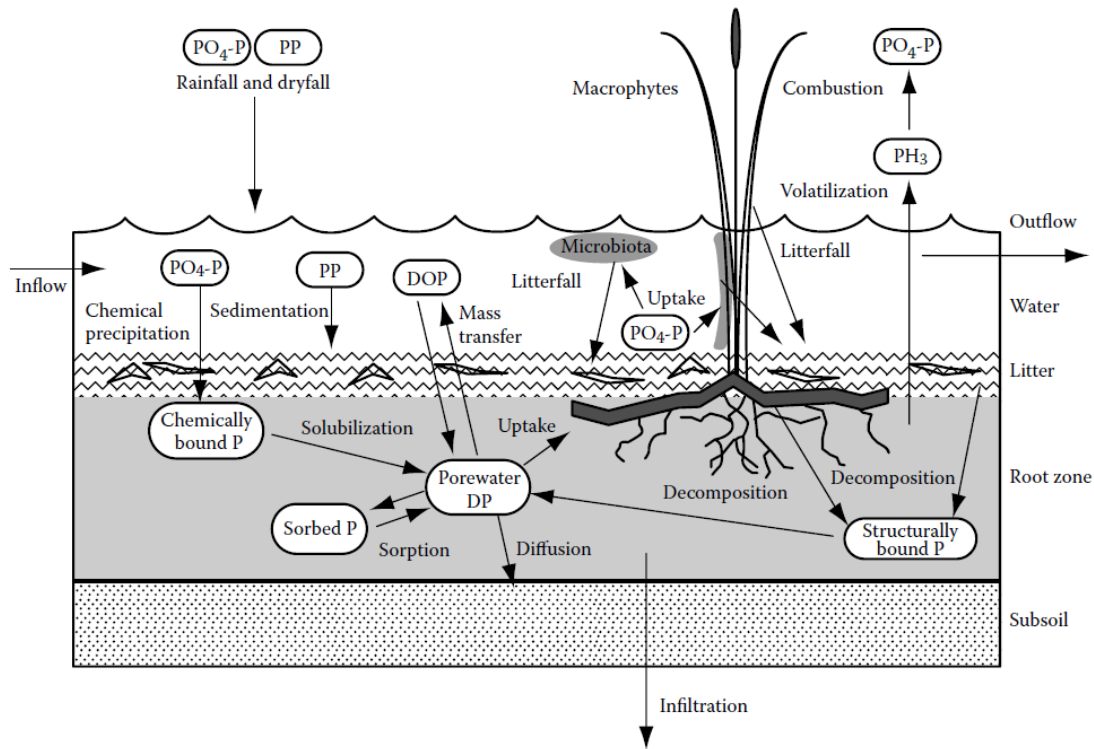


Figure 2-2 Drawing of the phosphorus cycle in a wetland. (Kadlec & Wallace, 2008)

Particulate phosphorus (PP) and dissolved phosphorus (DP) are distinguished between, when analytically determining phosphorous concentrations. The two fractions are generally separated by filtration of 0.45  $\mu\text{m}$ . In general, particulate phosphorus is both organic and inorganic particles with adsorbed or absorbed phosphate (Kadlec & Wallace, 2008).

The simplest form of soluble phosphorus is orthophosphate (Figure 2-3 a) which is an ester of the triprotic acid, phosphoric acid. Dominant forms of phosphoric acid in natural waters are  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  (Snoeyink & Jenkins, 1980). The acid is made up of inorganically bound phosphorus and oxygen. Only the oxygen atoms are able to react with other molecules (Brezonik & Arnold, 2011). The phosphoric acids,  $\text{HPO}_4^{3-}$ ,  $\text{HP}_2\text{O}_7^{3-}$  and  $\text{HP}_3\text{O}_{10}^{4-}$ , have a higher complex forming tendency than other phosphate species (Snoeyink & Jenkins, 1980). Polyphosphates (Figure 2-3 b and c) are made up of two or more orthophosphate molecules condensed together in a linear structure (Brezonik & Arnold, 2011).

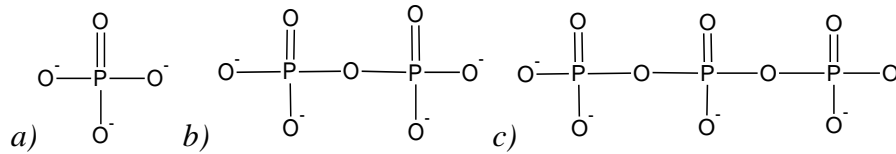


Figure 2-3 Structure of orthophosphate (a) and polyphosphate (b) and (c), pyrophosphate and tripolyphosphate accordingly.

Different forms of particulate phosphorus are chemically bound P, sorbed P, structurally bound P and PP suspended in waterbodies (Figure 2-2). In contrast to particulate phosphorus, dissolved phosphorus represents soluble species as orthophosphate and polyphosphates. An important classification of dissolved phosphorus is soluble reactive phosphorus (SRP). Different definitions of SRP exists. Reddy and DeLaune (2008) define SRP as only dissolved inorganic phosphate (DIP), while Dodson (2005) includes both organic and inorganic phosphorus that are taken up and used by plants and macrophytes. Kadlec and Wallance (2008) on the other hand define SRP as all phosphorus which is easily hydrolysed by soil enzymes. For this thesis SRP is defined as all dissolved easily reactive phosphorus, meaning phosphate that reacts with a colorimetric reagent without prior digestion or hydrolysis. Another phosphorus parameter is total acid hydrolysable phosphorus. This fraction includes all dissolved and particulate condensed phosphate, which can be transformed to orthophosphate by acid hydrolysis (Clesceri et al., 1998).

## 2.6. External phosphorus loading

CWs receive phosphorous from multiple sources (Figure 2-4). Most common sources are fertilizers used in agriculture on land above the wetland and leakage of wastewater, as well as animal waste and biosolids deposits (Smil, 2000).

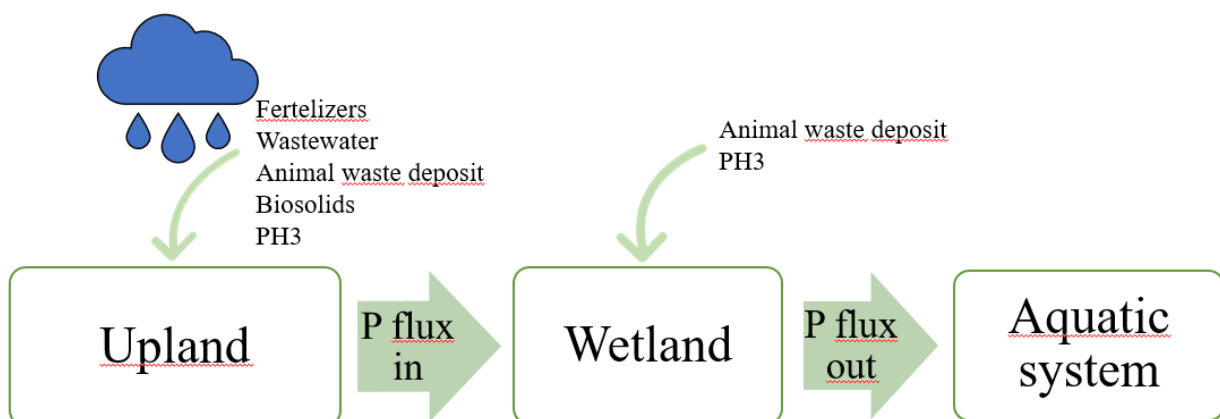


Figure 2-4 Schematic presentation of the connection between external phosphorous loadings, wetlands and connecting aquatic systems.

A catchments soil composition is important when assessing external phosphorus loadings. Phosphate minerals, such as apatite (Brezonik & Arnold, 2011), in soil will leach when heavy rain occurs (Raisin & Mitchell, 1995). Phosphorus is mobilized by water, transported and produces a concentration peak when the water reaches wetlands. Storm events can produce the phenomenon first-flush, with a higher concentration in the first water peak leaving catchment areas (Kadlec & Wallace, 2008). In general, sandy soils have less phosphate binding capacity than clay soils (Lægneid et al., 1999). Johannesson, Tonderski, Ehde, and Weisner (2017) studied seven different CWs and stated that a higher clay content in a catchment area would in fact contribute to higher phosphorus input. Thus, this indicates that catchment areas with clay do assimilate more phosphate over time and will release the phosphate taken up when heavy rain occur.

Another important factor is agricultural use of phosphorus. A surplus of fertilizers with high phosphorus content over many years, will create legacy phosphorus in soil and contribute to high runoff concentrations (Nair, Clark, & Reddy, 2015). Correct use of fertilizers is therefore very important. Enough fertilizers must be applied for the crop to thrive, but not so much that legacy phosphorus increases.

A theoretically possible external source is atmospheric deposits. Phosphine ( $\text{PH}_3$ ) and diphosphine ( $\text{P}_2\text{H}_4$ ) are two known gasses found in wetlands. Deposits from atmosphere to wetlands are assumed to contribute with little or no phosphorous (Kadlec & Wallace, 2008). Studies have focused more on release from wetlands and lakes to the atmosphere (Chao Han, Geng, Zhang, Wang, & Gao, 2011; Chao Han et al., 2010).

## 2.7. Mechanisms for phosphorus storage in wetlands

Different mechanisms can retain phosphorus in a wetland. All of them have in common that they do not remove phosphorus but retain it. Figure 2-5 shows different types of phosphorus storage with typical phosphorus content. The further subchapters in this section contain explanations of the main mechanisms.

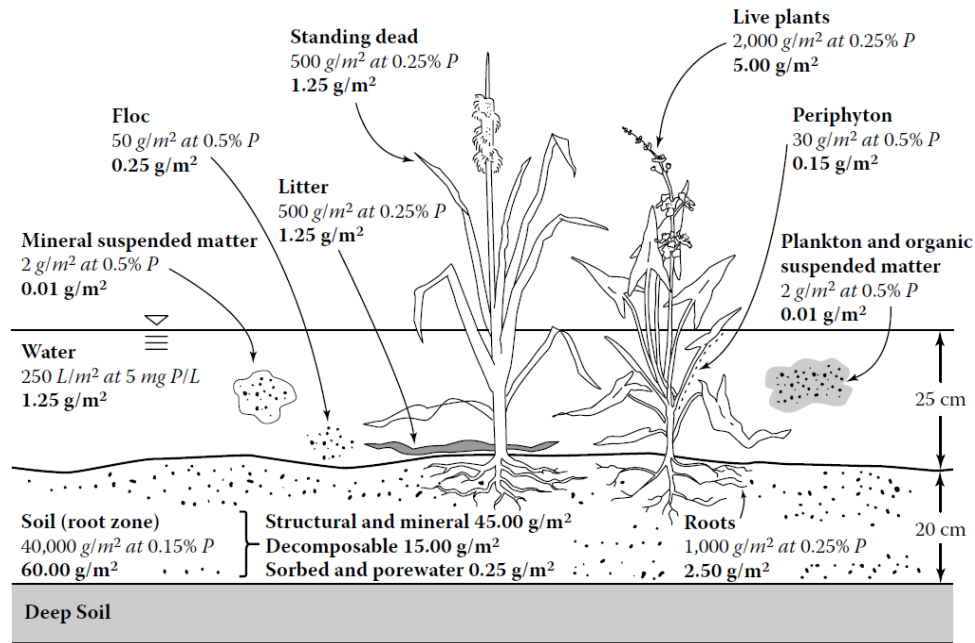


Figure 2-5 Different types of phosphorus storage. (Kadlec & Wallace, 2008)

### 2.7.1. Sorption to soil, plants and suspended particles

Wadzuk et al. (2010) published a study over several years where 19 storm water events were compared with the general base flow situation. During fall and winter, reduction of SRP was observed, even though these seasons generally are dominated by plant decay, which releases phosphorus. Thus, Wadzuk et al. (2010) stated that there must exist different mechanisms for SRP retention than plant uptake, and hence support the general theory of sorption of soluble forms of phosphorus on to sediments and plants. Suspended particles, sediment soil and plants are all possible adsorption sites. The mechanism of adsorption has been used to treat lakes with high phosphate concentrations (Changseok Han, Lalley, Iyanna, & Nadagouda, 2017; Schütz, Rydin, & Huser, 2017).

Sorption is considered a two-step process with adsorption from phosphoric water, through a liquid and on to surfaces as the first step. Adsorption is then followed by absorption where

phosphate enters the particles. Adsorption is often categorized as rapid, while absorption is categorized as slow. (Dunne & Reddy, 2005)

Brezonik and Arnold (2011) explain adsorption to particles by three different forces and mechanisms. Ionized functional groups on hydrophilic surface like natural organic matter, as well as inorganic iron and aluminium hydroxides, can adsorb phosphate by chemical reactions between the functional groups and phosphate. The charge of these particles depends on the degree of ionization. A low pH will give more ionization and stronger positive surface charge, which will adsorb more phosphate than a weaker surface charge (Figure 2-6). Because of this, a wetlands pH is important when aiming to alter the adsorption efficiency. Isomorphic substitution is the second mechanism, where a switch in the metal centre of hydrous oxides gives particles a charged surface. Aluminium oxide layers of clay minerals are examples of isomorphic substitutions, giving the particles a positive charge to attract negatively charged phosphate. The third mechanism is surface complexation reactions on particles, called specific adsorption. Phosphate ions can replace a hydroxide group on the surface of iron and aluminium hydroxides, thereby be adsorbed to the surface. A theoretical method for increased adsorption is to coat the surface of rocks or soil with hydroxide groups before filling the wetland with water (Rhue & Harris, 1999).

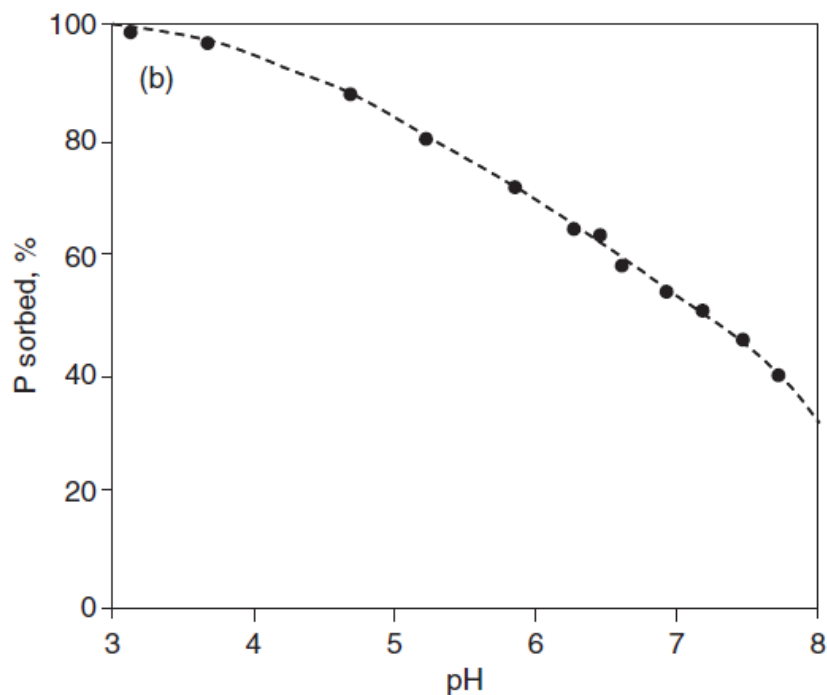


Figure 2-6 An illustration of how phosphate sorption for ferrihydrite is affected by different pH. Illustration published by Gustafsson (2003) and collected from Brezonik and Arnold (2011).

Adsorption of phosphate to suspended and non-suspended particles follows the Langmuir model, with a rapid adsorption rate in the beginning followed by saturation after a given time (Brezonik & Arnold, 2011). A factor that can complicate the use of the Langmuir model are already saturated soil with less available adsorption sites. Soil in recently constructed CWs has not been saturated with phosphate and therefore can have a higher fraction of adsorption sites available, while mature wetlands have been saturated with phosphate.

A parameter for determining a wetland's tendency for net adsorption or desorption is the equilibrium phosphate concentration (EPC) (Reddy & DeLaune, 2008). When the phosphate concentration is stable over time, equilibrium is achieved. If phosphate concentrations in waterbodies are lower than the determined EPC, phosphate will desorb back into the water (Brezonik & Arnold, 2011).

A small lake needs tons of adsorbent chemicals to have an effect on the eutrophication level (Dodson, 2005). Addition of chemicals only removes phosphate already present and does not reduce external phosphate loadings. Consequently, it is often considered a one time fix. Since phosphate also can desorb from the adsorbent, phosphate concentrations can increase over time due to desorption. Ooi et al. (2017) stated that there are many different adsorbents for phosphate today, but there have not been studies of them under the same conditions. Out of 63 different kinds of inorganic adsorbents, the Fe-containing adsorbent and MgAl layered double hydroxides were found to be most effective. Ooi et al. (2017) emphasize the importance of further study to improve the reusability of adsorbents. By improving reusability, adsorbents can be used multiple times and thus represent more sustainable, long lasting solutions.

### 2.7.2. Sedimentation of solids

Phosphate adsorbed to suspended particles, as well as precipitates, needs to settle in the wetland to obtain retention. Braskerud et al. (2005) stated that CWs in Norway generally retain a large fraction of particulate phosphorus. Consequently, sedimentation processes are important to achieve the best utilization of CWs.

Particles settling in quiescence water go through two phases, one with acceleration and one with constant velocity. Particles reach a terminal fall velocity when the buoyant, gravitational and drag force are in equilibrium (Geankoplis, 2013). Still, in an FWS CW there is always water movement and suspended particles do not settle in a quiescence environment. Sediments and suspended particles are transported by hydraulic flow, often distinguished as bed load and

sediment load. Bed load represents all sediments that are moved by rolling along the bed, while suspended load is moved in suspension. Sediment load represents the total transported material, both bed load and suspended load (Holden, 2005). The Hjulströms curve (Figure 2-7) is a well-known graph made by Filip Hjulström in 1935, used to calculate at what hydraulic flow a stream will erode, transport or deposit sediments (Hjulstrom, 1935). Water pulling on particles is the most essential force resulting in sediment transport and affects the sedimentation regime in a wetland (Geankoplis, 2013).

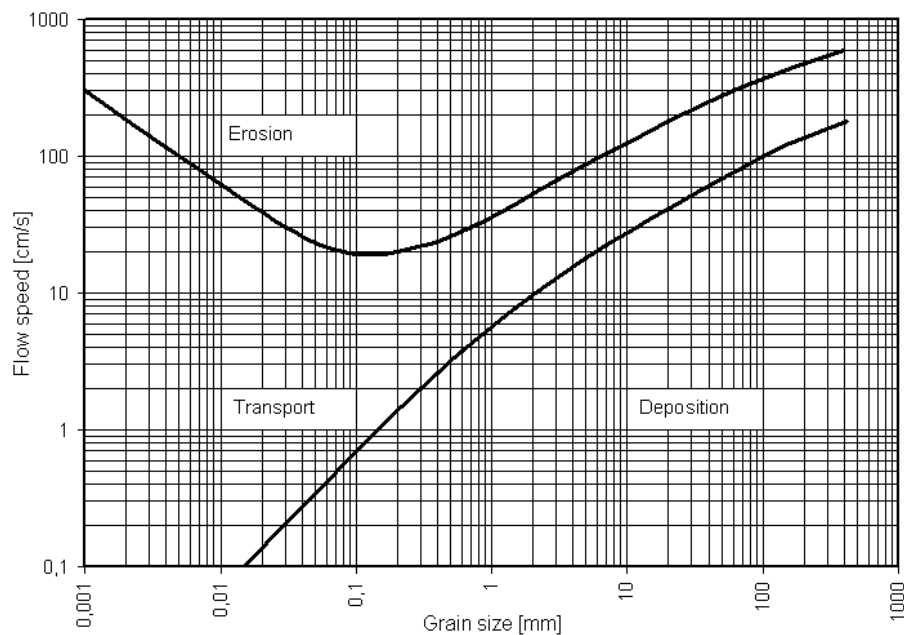


Figure 2-7 The Hjulström curve describing erosion, transport and deposition in streaming water (Hjulstrom, 1935).

Different flow patterns give different settling tendencies. In general, flow patterns are divided into laminar and turbulent flow. Laminar flow is characterized with a fluid layer which flows seamlessly without any swirls. Turbulent flow is the opposite, with swirls and a fluctuating tendency. The two types are distinguished by the Reynolds number (Geankoplis, 2013). Fine particles tend to settle in laminar flow patterns, and not in turbulent flow patterns (Chanson, 2004). In a constructed wetland the flow regime will be both laminar and turbulent, depending on hydraulic input.

Sedimentation is often considered as discrete settling, where particles settle separate, in order to describe the sedimentation process (Metcalf & Eddy, 2014). Stokes law (Equation 2-2) is the well-known equation used to determine terminal velocities for settling of spherical particles in a laminar flow.



Equation 2-2 Stokes law for terminal velocity. Where  $v_p$  is the terminal velocity (m/s),  $g$  is gravitation ( $m^2/s$ ),  $D_p$  is diameter of the particle (m),  $\delta$  is density of the water ( $kg/m^3$ ),  $\delta_p$  is density of the particle ( $kg/m^3$ ) and  $\mu$  is viscosity of the fluid ( $kg/m\cdot s$ ).

$$v_p = \frac{gD_p^2(\delta_p - \delta)}{18\mu}$$

Since particles are not perfectly spherical by nature, a sphericity factor ( $\psi$ ) is applied in calculations to correct for the impact the shape has on the terminal velocity (Metcalf & Eddy, 2014). A non-spherical shape will give particles lower settling velocity compared to if they were perfectly spherical. Difference in settling velocity occurs because the irregular shape increases the friction between the water and the particle (Jiménez & Madsen, 2003).

To ensure sufficient settling, sinking velocities of particles need to be greater than the upward water velocity. Thus, the particles' retention time ( $\tau_p$ ) must be greater than the hydraulic retention time ( $\tau_H$ ), giving a critical relationship (Equation 2-3).

Equation 2-3 The critical relationship between particle retention time and hydraulic retention time.

$$\tau_H \leq \tau_p$$

The two retention times are defined by different physical factors. Hydraulic retention time (Equation 2-4) is a function of volume ( $V$ ) and flow ( $Q$ ), while particle retention time (Equation 2-5) depends on the depth of the water column ( $H$ ) and particles' sinking velocity ( $v_p$ ).

Equation 2-4 Hydraulic retention time presented as a function of volume and flow. The equation can be derived to include length ( $L$ ), depth ( $H$ ) and width ( $W$ ) of a wetland instead of volume.

$$\tau_H = \frac{V}{Q} = \frac{L \cdot H \cdot W}{Q}$$

Equation 2-5 Particle retention time presented as a function of water column depth and particle sinking velocity.

$$\tau_p = \frac{H}{v_p}$$

Physical design parameters of a wetland are linked by combining hydraulic and particle retention time. This produces an equation where the depth of a wetland is irrelevant for particles' sinking velocity and thereby irrelevant for a wetland's ability for sedimentation (Equation 2-6 and Equation 2-7).

Equation 2-6 Presentation of the equilibrium of hydraulic and particle retention time.

$$\frac{L \cdot H \cdot W}{Q} = \frac{H}{v_p} \rightarrow \frac{L \cdot W}{Q} = \frac{1}{v_p}$$

*Equation 2-7 The equation for particle sinking velocity independent of water column depth.*

$$v_p = \frac{Q}{L * W} = \frac{Q}{A}$$

Braskerud (2001) suggested that wetlands should be constructed shallow with vegetation to create a short sedimentation distance and therefore achieve a higher removal efficiency. Geranmayeh et al. (2018) argued against Braskerud (2001) by emphasising that a lower settling distance with a fixed wetland width would increase the velocity of the water at high flowrates and therefor increase the risk for resuspension.

Another type of settling in wetlands is flocculent settling, where particles coalesce amid sedimentation, increasing particle density and thus increasing settling velocity (Metcalf & Eddy, 2014). Flocculent sedimentation depends on particle interaction and the extend of flocculent sedimentation is consequently determined by particle concentration. A higher particle concentration gives a greater tendency for flocculent settling. Kadlec and Wallace (2008) define flocs as unconsolidated material with a low density, which are easy disturbed. Phosphorous content in such material is typically between 0.1 to 0.4 % dry weight/cm<sup>3</sup> (Kadlec & Wallace, 2008). Metal hydroxides flocs of iron and aluminium entrap fine phosphoric particles, functioning as a surface for phosphate adsorption (Metcalf & Eddy, 2014) and removing phosphorus from the waterbody by flocculent settling (Snoeyink & Jenkins, 1980).

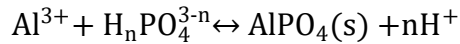
### 2.7.3. Chemical precipitation

Phosphate species act as ligands making complexes, both soluble and insoluble, with metals present in water. The complexes are reversible and represent a minor part in the complex picture of natural water chemistry (Brezonik & Arnold, 2011), but when manipulated correctly insoluble complexes can be good mechanisms for phosphate removal (Jernelov, 1970; Lindstrom & White, 2011; Welch & Schriever, 1994).

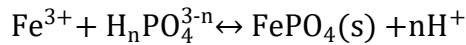
In general phosphate makes complexes with aluminium or iron under acidic conditions, where strengite (FePO<sub>4</sub>), vivianite ((Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) and variscite (AlPO<sub>4</sub>) are of significance in wetlands (Dunne & Reddy, 2005). Strengite is commonly observed in the upper part of a water column due to high oxygen concentrations. This is because phosphate precipitation is highly dependent on redox potential as well, as pH (Dunne & Reddy, 2005). Complexes with calcium and magnesium dominate under alkaline condition (Kadlec & Wallace, 2008), where beta

tricalcium phosphate ( $\text{B-Ca}_3(\text{PO}_4)_2$ ) and hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) are common precipitates in wetlands (Dunne & Reddy, 2005).

*Equation 2-8 Precipitation of variscite under acidic conditions.*



*Equation 2-9 Ferric phosphate precipitation under acidic conditions.*



The two reactions for variscite (Equation 2-8) and ferric phosphate (Equation 2-9), seem straight forward and easy to predict. But experience from the wastewater industry shows that the relationship is not as easily described, because alkalinity, redox condition, pH and trace elements affect precipitate formation (Metcalf & Eddy, 2014). Hydrogen sulphide produced by microorganisms in waters can inhibit precipitation of  $\text{FePO}_4$  due to formation of ferrous sulphide (Dunne & Reddy, 2005). More complex reactions have been described to give a better prediction of aluminium and iron reactions, but there are no descriptions that can predict the exact chemical dosage necessary for precipitation (Metcalf & Eddy, 2014). Computer models are therefor usually used to estimate equilibrium conditions for these reactions (Kadlec & Wallace, 2008). Even though addition of alum and iron for phosphate precipitation have been successfully used with respect to phosphate retention in lakes, the total ecological repercussion of such additions are not known (Lin et al., 2017).

B. C. Braskerud et al. (2005) stated that the presence of macrophytes affect precipitation rate because of their ability to create a higher pH by photosynthesis, as precipitation is pH dependent. This makes the iron and aluminium precipitates more soluble. The effect is most prominent in temperate areas as Florida, and not in cold temperate areas such as Norway due to shorter plant seasons, and thus a photosynthetic pH increase, which is not long-lasting.

#### 2.7.4. Biotic uptake

Biotic uptake includes plants and microbial uptake. Presence of plants does not only create a better environment for sedimentation (Bent Christian Braskerud, 2001; Peticrew & Kalff, 1992), but also retains phosphorus by uptake as phosphorus is known to be an important nutrient. An essential factor for biotic uptake is the seasons. Plants and microorganisms use phosphorus to grow during spring and summer, while they release phosphorus during fall and winter (Kadlec & Wallace, 2008).

Dissolved forms of phosphorus are more easily utilized than particulate phosphorus (Kadlec & Wallace, 2008). Plants primarily take up phosphate in the root zone, but also through stems and leaves surrounded by water (Brix, 1997). Usually plants utilize more phosphate than necessary and store it for future use (Dodson, 2005; Dunne & Reddy, 2005). The surplus of phosphate is stored as polyphosphate. This utilization and storing of phosphorus is known as the luxury consumption (Reddy & DeLaune, 2008). This was observed by Krahner and Kommedal (2017) where roots, stems and leaves of *Iris pseudacorus* and *Glyceria maxima* were analysed for TP during a one-year study. The plant species showed different trends for storage of phosphorus, but both showed a higher TP concentration in the root zone during non-growth seasons and higher concentrations in the stem and leaves during growth season. This observation supports the idea of P-storage in the root zone for use during growth.

Biological treatment of wastewater uses microorganisms' ability to assimilate phosphorus for enhanced biological phosphorus removal. Wastewater is treated under anaerobic and aerobic conditions to achieve growth of specific phosphorus accumulating organisms, which can obtain up to 80 % P-retention (Metcalf & Eddy, 2014). Although phosphorus concentrations in CWs are not as high as in wastewater, the microorganisms that assimilate phosphorus can be present and contribute to phosphorus retention.

## 2.8. Internal phosphorus loading

The term internal phosphorus loading includes phosphorus retained in wetlands released back into the waterbody (Figure 2-8). Mechanisms for such release are explained in this subchapter. Internal release will contribute to external phosphorus loadings, and effect if a wetland retains or release phosphorus.

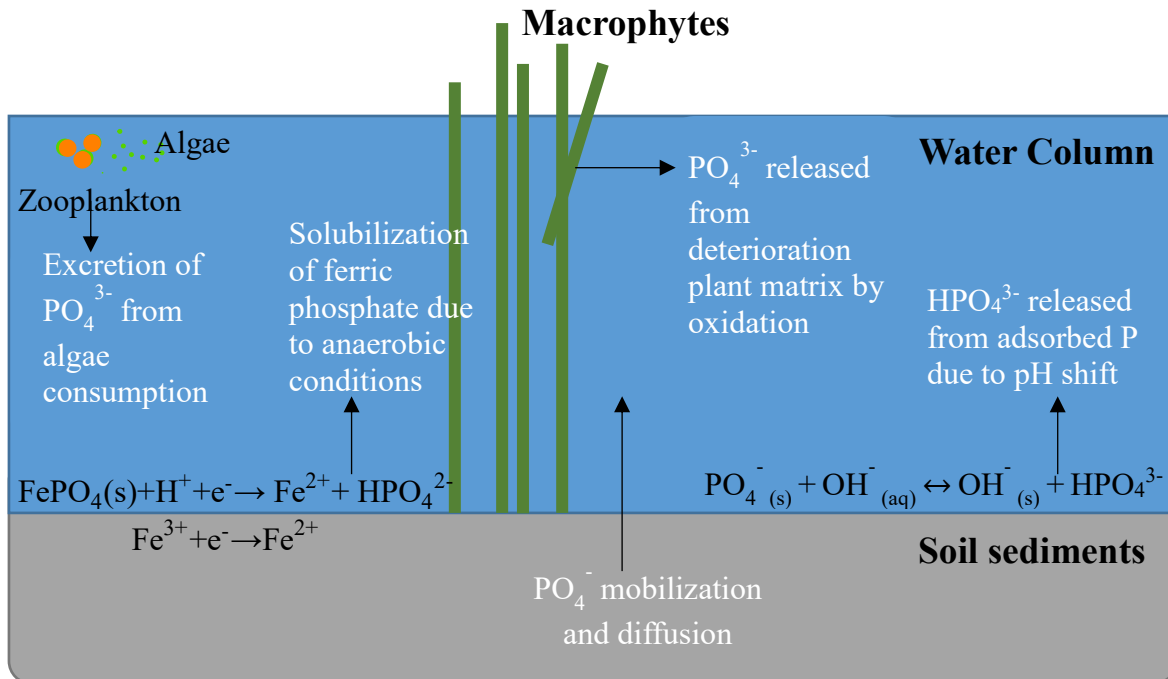


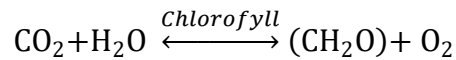
Figure 2-8 Sketch of mechanisms for internal phosphorus release in a wetland.

Phosphate is embedded in soil in various forms, such as apatite, adsorbed to hydroxides or associated with ion exchange sites (Brezonik & Arnold, 2011). Soil will leach phosphate if phosphate concentrations are lower in water than in soil (Dunne & Reddy, 2005). High iron or aluminium levels in sediments can decrease phosphorus leaching by increasing adsorption sites for phosphorus (Nair et al., 2015).

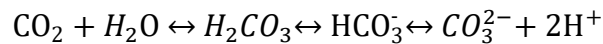
Another internal source is deterioration of plant matrix which releases phosphorus by oxidation (Kadlec & Wallace, 2008). In general, release from plant tissue occurs rapidly the first hours and decreases drastic over time. The rate of leaching is usually higher around a plant's root zone than around the leaves of plants (Dunne & Reddy, 2005). Because of phosphate release from plant matrix, plant removal before deterioration is crucial, if phosphorus retention by biomass is a goal.

Adsorbed phosphate can also be released back into the water during intense photosynthesis. When a large quantity of algae fixes CO<sub>2</sub> (Equation 2-10), pH in waters increases due to a shift in the bicarbonate equilibrium (Equation 2-11) (Dodson, 2005).

*Equation 2-10 Production of organic matter by photosynthesis with the use of light energy.*

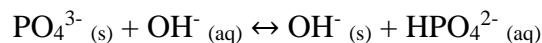


*Equation 2-11 The bicarbonate equilibrium in natural waters.*



Increased pH in water turns adsorbed phosphate into soluble hydrogen phosphate (HPO<sub>4</sub><sup>3-</sup>) by an ion exchange with OH<sup>-</sup> (Equation 2-12) (Dodson, 2005). Soluble hydrogen phosphate diffuses back into water, giving a higher phosphate concentration for growth.

*Equation 2-12 Ion exchange reaction between phosphate and OH<sup>-</sup>, releasing phosphate as HPO<sub>4</sub><sup>3-</sup>.*



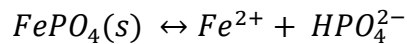
Understanding iron reactions are essential to understand internal phosphorus loads. High content of ferric iron produces a brownish-red colour in the sediments, while ferrous iron gives a greenish-grey colour . (Mitsch & Gosselink, 2015). When sediments in wetlands turn anaerobic, phosphorus is released back into waters as ferric phosphate dissolves due to coupled reduction-oxidation reactions (Ann, Reddy, & Delfino, 1999). Consequently, redox potential is important to understand as it indicates which chemical reactions occurs in a wetland (Dodson, 2005). Redox potential in waters is largely determined by the amount of dissolved oxygen (Howard, 1998) and indicates the intensity of redox reactions for both chemical reactions and microbiological systems (Mitsch & Gosselink, 2015). In general, large amounts of oxygen give the highest redox potential and inhibit other reactions as oxygen strongly reduces the abundance of electrons available (Dodson, 2005). Microbiological oxygen consumption reduces redox potential until the environment is anaerobic. When oxygen is depleted, other reactions in need of high electron activity can occur, as for instance nitrification, methane production and iron reduction (Dodson, 2005). This creates an opportunity for reduction of (Fe<sup>3+</sup>) to ferrous iron (Fe<sup>2+</sup>) (Equation 2-13), making solubilisation of ferric phosphate possible.

*Equation 2-13 Coupled redox reaction converting iron from ferric to ferrous.*



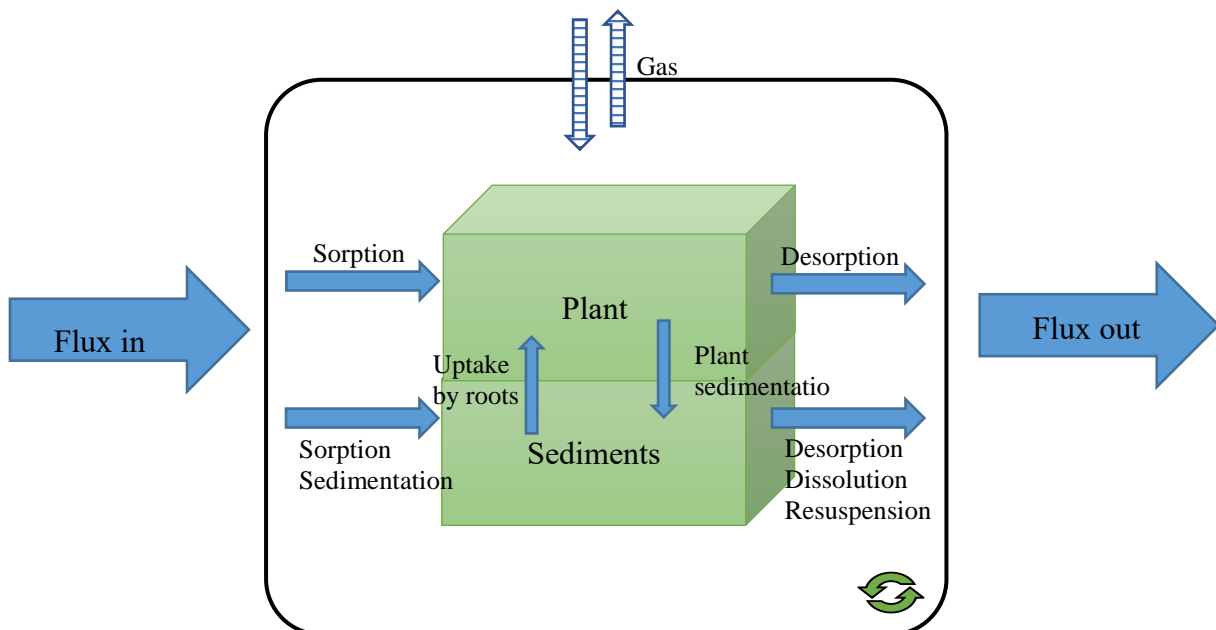
Ferric phosphate has a low solubility with a pH between 5 and 8 combined with a redox potential of around 300 millivolts (Dunne & Reddy, 2005). The solubility increases for all pH levels as redox potentials decreases down to -250 millivolts, and are in general high with low pH and low redox potentials (Dunne & Reddy, 2005). The combination of the correct redox potential and pH results in iron reduction (Equation 2-13), which again turns ferric phosphate precipitate soluble (Equation 2-14).

*Equation 2-14 Solubilisation of ferric phosphate because of reduction of iron.*



## 2.9. Wetland conceptual flux retention model

Phosphorus flux in a CW draws a complex picture with multiple factors affecting the overall phosphorus retention. The model presented in this subchapter is therefore created with the aim to illustrate the connections between the different loadings and mechanisms explained in subchapters: “2.6 External phosphorus loading”, “2.7 Mechanisms for phosphorus storage in wetlands” and “2.8 Internal phosphorus loading”.



*Figure 2-9 A cell of the conceptual flux retention model showing the different flux pathways as blue arrows with corresponding retention mechanisms in a wetland.*

The cell presented in Figure 2-9 focuses on flux around a single plant and the sediments. A CW can be considered a black box with external phosphorus loads going in and phosphorus loads going out, represented in the largest blue arrows named “Flux in” and “Flux out”. Inside the black box several mechanisms work to retain phosphorus, in unknown rates. The blue

arrows inside the green boxes illustrate phosphorus fluxes between plants and soil, while the blue arrows pointing onto the box illustrate mechanisms between water and plants/soil. Soluble phosphorus adsorbs onto plants and sediments and absorb into the sediments over time. Adsorbed phosphorus can desorb from both plants and soil if concentrations are smaller in the water than on surfaces. Phosphorus attached to suspended particles settle if the environments are calm enough, and resuspend if the hydraulic flow increases enough. Phosphorus leaving as gas is marked with the blue and white striped arrow, and is believed to be negligible when looking at the big picture, due to the size of the other mass fluxes. The recycling symbol in the right corner symbolizes complete water mixing.

A CW works often as a plug-flow as illustrated in Figure 2-10. This means that several cells, as the one presented in Figure 2-9, work simultaneously as the water passes from the inlet of a wetland to the outlet. Blue arrows between the cells represent phosphorus flux travelling from one cell to another. The phosphorus flux will increase or decrease depending on the different mechanisms presented in Figure 2-10.

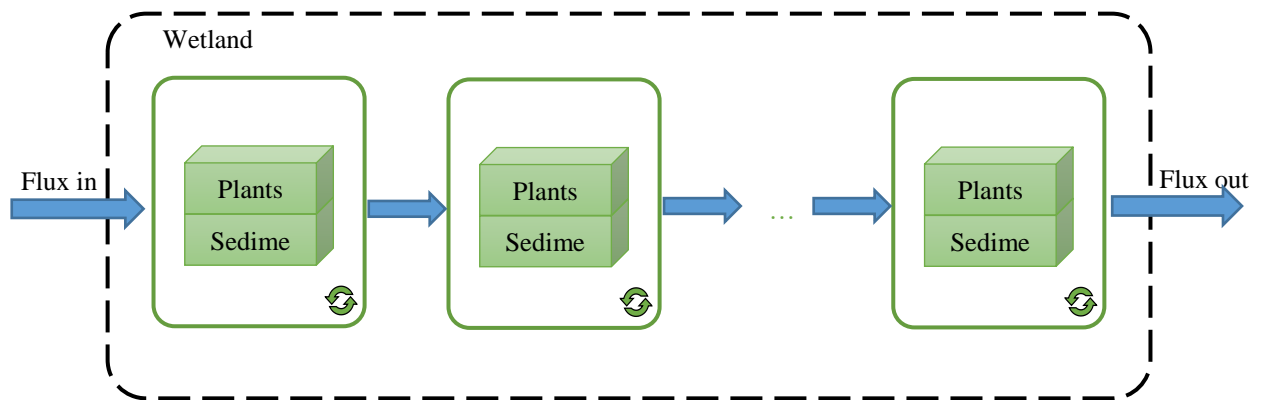


Figure 2-10 Wetland conceptual flux retention model demonstrated with multiple cells.



## 2.10. Knowledge gap and objectives

The objective of this thesis is to assess a mature CWs phosphorus retention efficiency under two different conditions, base flow and storm flow.

Long-term monitoring was performed with weekly sampling of phosphorus, suspended solids and iron. Leikvollbekken has been monitored for approximately 3.5 years. Several theses have been written about the wetland, both master and bachelor theses. The previous theses have estimated an overall TP retention at 31% (July 2016 - June 2017) and 18% (2015 – 2017). It is therefore assumed, that the wetland will have a positive retention this year too.

Storm flow monitoring consists of a detailed monitoring of two storm events, storm A and storm B, which provide empirical data for how Leikvollbekken responds to heavy flow peaks. Storm A occurred in the fall while Storm B occurred during spring. The hypothesis is that heavy precipitation causes high water flow, and thus washes out accumulated phosphorus.

There have been written many books and been performed a lot of studies on the performance on wetlands over the years, but the focus has been on newly constructed wetlands. Therefore, the efficiency of mature wetlands, as Leikvollbekken, is less known including how the efficiency changes with years. There have also been limited focus on how storm events effect the overall retention efficiency. The two storm events captured in this study can contribute to this knowledge gap by providing detailed, empirical data on how different sized storms can affect a mature wetland. The two storms also represent a spring storm and a fall storm, consequently providing information on how the effect of storms may differ depending on the seasons.

### 3. Methods

This section includes a site description and a description of the quantitative analysis used. The aim of the analysis studied herein was to determine the concentration of phosphorus parameters and other important water quality parameters, all essential for understanding phosphorus retention in Leikvollbekken. The wetland was equipped with two ISCO 6712 Full-Size Portable Samplers placed in a sampling house next to pond 2 (Figure 3-2 and Figure 3-15) The inlet and outlet suction tubes were placed in the pipeline connecting Pond 1 and Pond 2 and next to the sampling house, respectively. Quantitative analysis was performed once a week at the laboratories at UiS from 24<sup>th</sup> of August 2017 to 10<sup>th</sup> of Mai 2018. Weekly samples were analysed for TP, sTP, PO<sub>4</sub><sup>3-</sup>, TotFe, sTotFe, TSS and FSS. Samples collected during Storm A and Storm B were analysed for TP PO<sub>4</sub><sup>3-</sup> and TSS. Conductivity, pH and nitrate were included in the monitoring for Storm B.

#### 3.1. Leikvollbekken

Leikvollbekken is a constructed wetland made in 1993/1994 by Stavanger municipality. The wetland lays between “Haalandsvatnet” and “Stokkavannet”, where the latter is the drinking water reserve for the region. Stavanger municipality constructed Leikvollbekken, and other wetlands in strategic places, with the aim to improve the water quality of the lake. Prior to construction of the wetlands, Stokkavannet contained a high number of algae and hence had a poor water quality. The area surrounding Stokkavannet consists of private gardens, industry and agriculture, including greenhouses (Figure 3-1) which all release nutrients and pollutants.

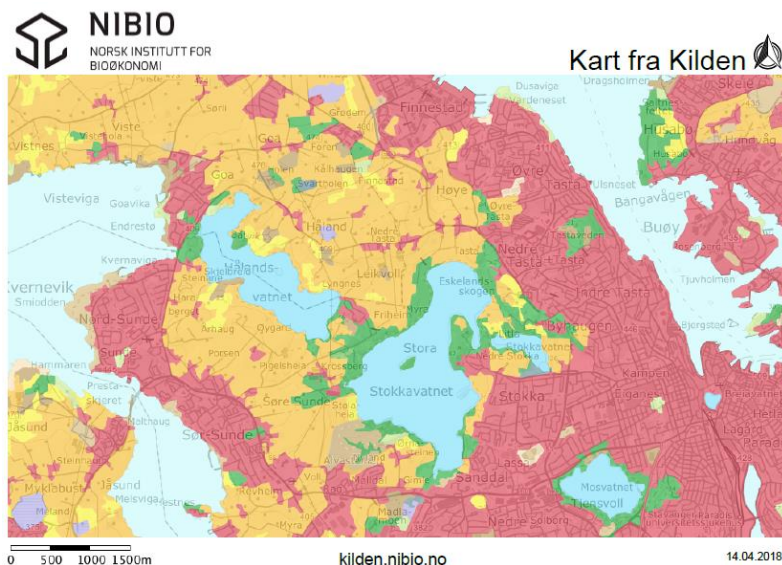


Figure 3-1 Use of area surrounding Store Stokkavannet and Leikvollbekken. Urban areas marked in red, forest areas marked in green, agricultural areas marked in orange/yellow, scanty vegetation in brown and open wetlands marked in purple.

Leikvollbekken was built with three dams and two ponds to control the water flow (Figure 3-2). Each of the dams were constructed using different sized rocks. Dam 1 and 3 were intended to spread the water flowing coming into the wetland, and thereby utilize the whole area, while dam 2 was designed to regulate the water flowing into pond 2 and thus control the water level in the pond.

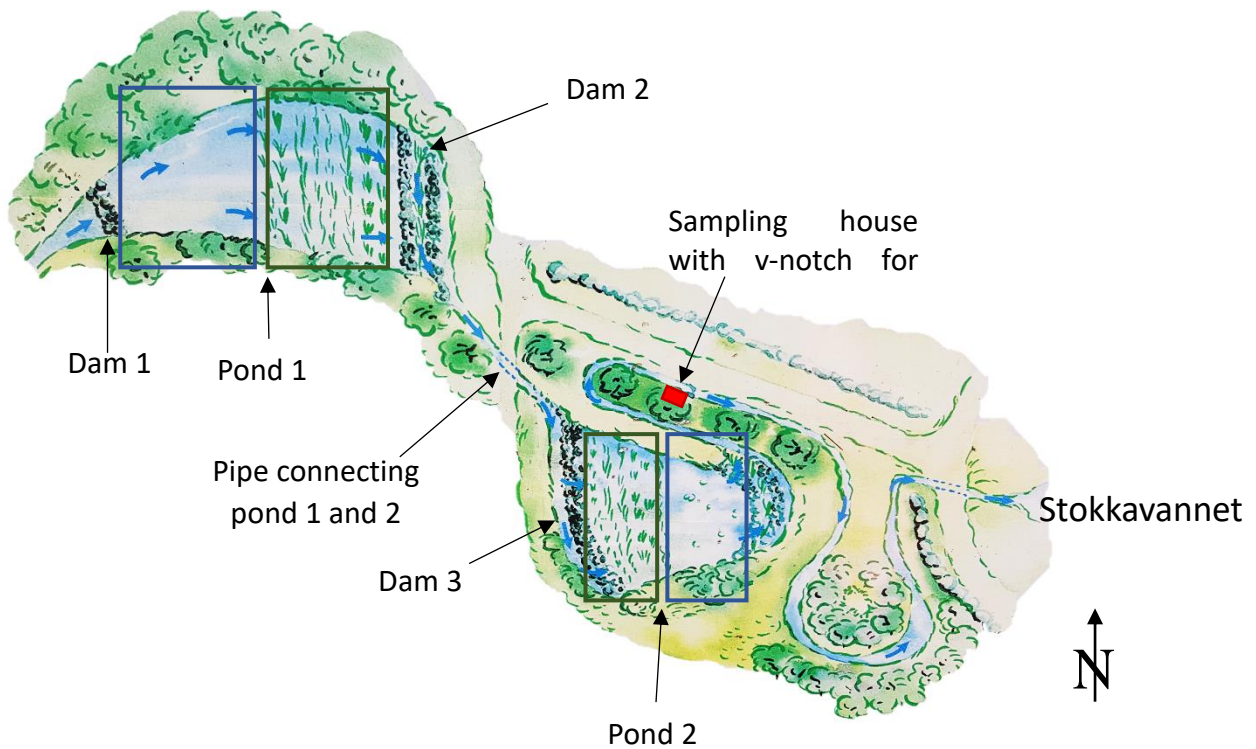


Figure 3-2: Drawing of how Leikvollbekken was when it was first constructed. Blue arrows in the drawing represents the direction of the water. The drawing is modified from the information board produced by Stavanger municipality, present next to the wetland.

Sediment load has over time filled the dams in both Pond 1 and 2. Consequently, it has reduced their ability to spread water and hence produced a preferred water path in Pond 1 (Figure 3-3) and Pond 2 (Figure 3-4). Water saturates the whole ponds, but the velocity of the water is much higher in the open surface area than in the snow-covered parts with high plant coverage and little water movement.

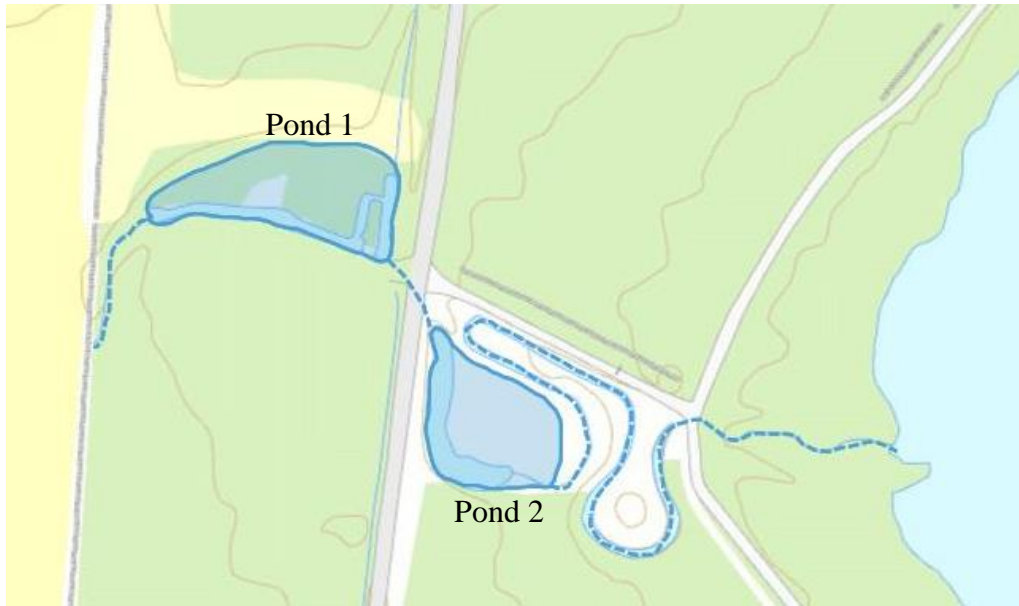


*Figure 3-3: Pond 1 covered with snow. The picture shows the outlet in the south-eastern corner of the pond towards west. Inlet to the pond is marked with a red circle. (18<sup>th</sup> of January 2018)*



*Figure 3-4: Pond 2 covered with snow. The picture was taken positioned over the inlet of the pond in the north-western corner of the pond towards east. (18<sup>th</sup> of January 2018)*

The two ponds were constructed with a deeper area for sedimentation, followed by a shallow area with macrophytes. The original sedimentation zone is marked with a dark, blue square and the macrophyte zone is marked with a dark, green square in Figure 3-5. Previously open, deeper areas are now shallow and filled with macrophytes (Figure 3-3 and Figure 3-4), due to plant growth over time. There is no clear boarder between the sedimentation area and the macrophyte area except from the preferred water path flowing through Pond 1 and 2.



*Figure 3-5 Assumed, present size of Leikvollbekken with the saturated areas marked see-through blue. The striped line represents the stream from the agricultural fields, through the CW and to Stokkavannet. Agricultural areas are marked in light yellow, forest areas in green and Stokkavannet in light blue.*

Pond 1 is the largest of the two ponds with an estimated saturated area of 813 m<sup>2</sup> and a free water surface of 208 m<sup>2</sup> (Figure 3-5). Pond 2 is estimated to be 611 m<sup>2</sup>, where 197 m<sup>2</sup> is open surface water. Therefore, it produces different hydraulic retention time between the two ponds. Estimates of retention times with a flow of 10 L/s, given water flows over the whole area in both ponds and a depth of 0.5 meter, are found to be 11.3 h for Pond 1 and 8.5 h for Pond 2. These estimated retention times are only theoretical, and the real-life retention time is assumed to be smaller. The real hydraulic retention time is not known, since no measurements have been performed.

The municipality has maintained the wetland by removing sediments sporadically. Such maintenance was observed after a large area of the Pond 1 had accumulated particles close to the ponds maximum capacity (Figure 3-6). Accumulated particles were dug up by the municipality, creating an open surface water channel from the inlet to the outlet of the pond (Figure 3-7). The dimensions of the channel are approximately 2 m width, 70 m length and 0.5-1 meter depth.



*Figure 3-6 Pond 1 filled with accumulated particles. (23<sup>rd</sup> of March 2018.)*



*Figure 3-7 Picture of Pond 1 in Leikvollbekken after sediment removal by Stavanger municipality. Removed sediments were placed next to the wetland, marked by a red circle. (5<sup>th</sup> of April 2018)*

Bedrock surrounding Leikvollbekken consists mostly of a combination of phyllite and some layer of quartzite and arkose (Figure 3-8). There have been no analytical measurements for iron in the sediments surrounding Leikvollbekken, but there are visual and measurable amounts of iron in Leikvollbekken. Phyllite contains iron in the form of biotite (Selbekk, 2018), and is therefore considered to be the iron source for Leikvollbekken.

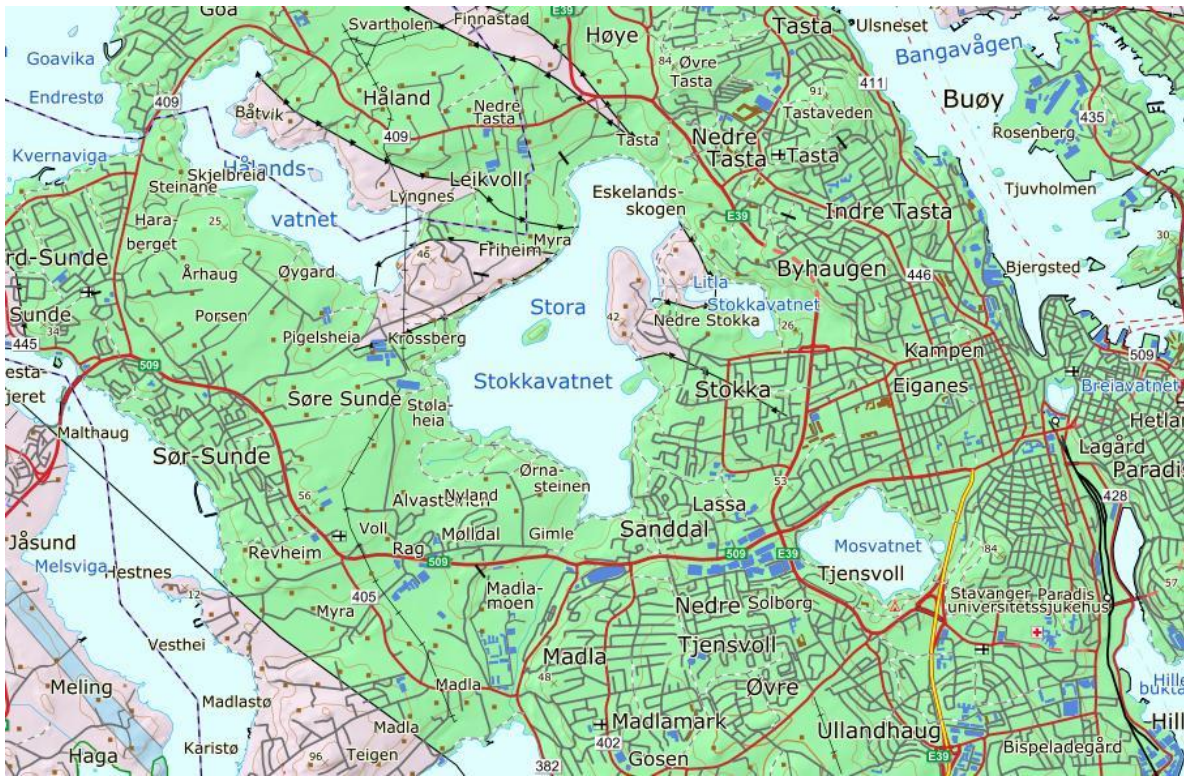


Figure 3-8: Map of the different types of bedrock present bedrock surrounding Leikvollbekken and Stakkavatnet (Norges Geologiske Undersøkelse (NGU)). Green represents a combination of fyllitt and some layers of quartzite and arkose. Light brown areas consist mostly of granodiorite, granite and “tonalitt”, as well as patchy areas of gneiss.

A brownish-red colour was observed in both Pond 1 (Figure 3-10) and Pond 2 (Figure 3-9). The colour was observed over the whole sampling period but seemed to be more prominent during the spring. An oily substance was often observed on the water next to areas with intense brownish-red colour (Figure 3-10).



*Figure 3-9 Picture of sediments with ferric iron in the stream after Pond. (15th of March 2018)*



*Figure 3-10 A brown-reddish stream (marked in a circle) observed from an old filling to Pond 1, including an oily surface. (15th of March 2018)*

Direct observation of algae bloom was made in Pond 1 (Figure 3-11) and Pond 2 in the end of May 2018. The large quantity of algae grew in 1-2 weeks and is considered to contribute with high  $\text{PO}_4^{3-}$  uptake.



*Figure 3-11 Algae observed in Pond 1. (23<sup>rd</sup> of May 2018)*



### 3.2. Precipitation data

The presented data has been measured at Våland weather station in Stavanger, situated 72 meters above sea level approximately 3-4 km from Leikvollbekken. The weather station was used to collect data, because of problems with the rain gauge installed in Leikvollbekken. Stavanger experiences many rainy days each year, with variable rain intensity. Months with most rain are usually October/November and February/March. This trend was seen with increased precipitation intensity from August to mid-October before it decreased to mid-January (Figure 3-12). The months following mid-February to mid-May were unusually dry with a maximum accumulated precipitation of 11 mm/day.

Two storm events have been analysed in this thesis named Storm A and Storm B, both marked in Figure 3-12 with arrows. The storm situations happened with dry periods prior to heavy rain. Storm A had 7 dry days with no precipitation, while Storm B happened with 6 dry days prior (Meterologisk institutt & NRK, 2007 - 2018). It is worth mentioning that the two months before Storm B were generally dry, even though some rain occurred.

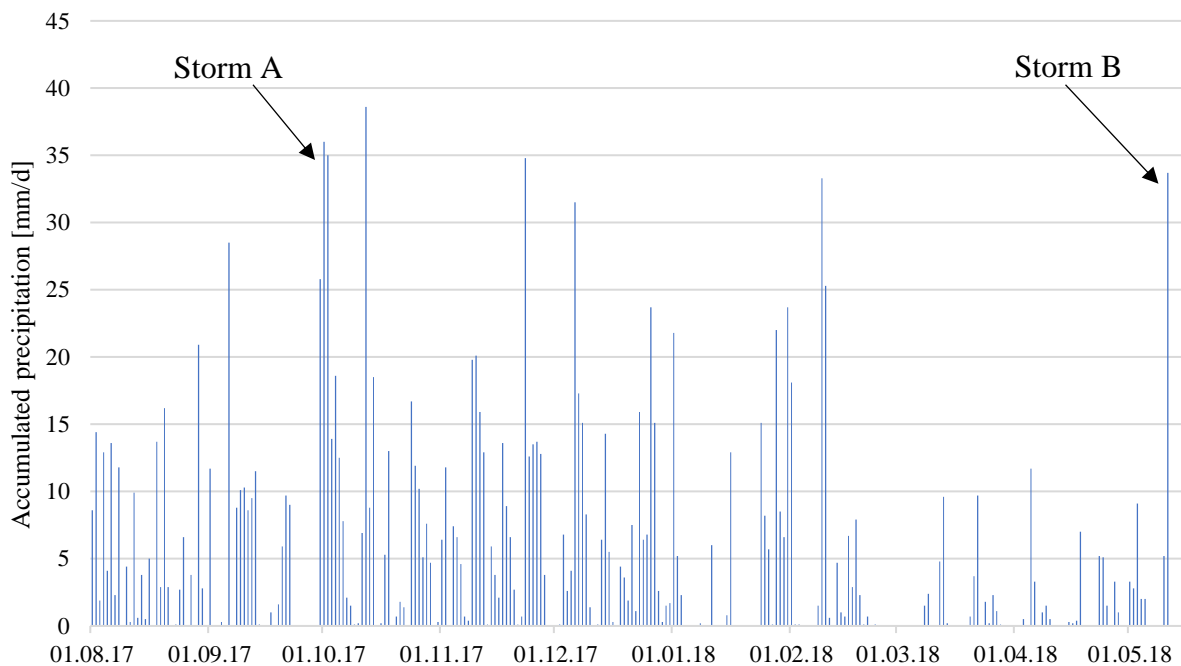


Figure 3-12 Accumulated precipitation measured at Våland weather station from 1st of August 2017 to 10<sup>th</sup> of May 2018 (Meterologisk institutt & NRK, 2007 - 2018).

Storm A was monitored between the 29<sup>th</sup> of September and the 2<sup>nd</sup> of October 2017 (Figure 3-13). The storm consisted of several peaks. Rain started falling around midnight 29<sup>th</sup> of September and continued in a fluctuating manner. The greatest peak was observed at 03:00 and measured to 8.3 mm/h. The whole storm consisted of 104 mm of precipitation.

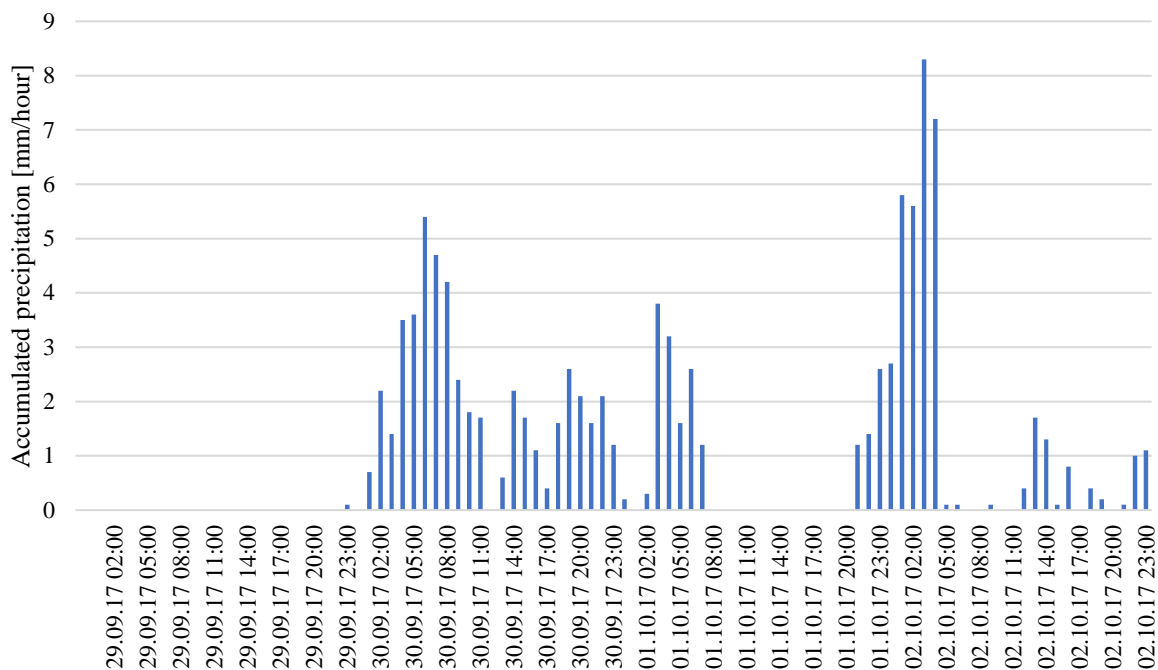


Figure 3-13: Accumulated precipitation measured at Våland weather station during Storm A from 29<sup>th</sup> of September 2017 to 2<sup>nd</sup> of October 2017 (Meterologisk institutt & NRK, 2007 - 2018).

Storm B took place between the 10<sup>th</sup> and 11<sup>th</sup> of May 2018 (Figure 3-14). Precipitation started at around 07:00 and ended around 22:00. The storm consisted of one large peak with a single subpeak at 08:00. The subpeak had the maximum precipitation rate of the whole storm with a rate of 4.5 mm/h.

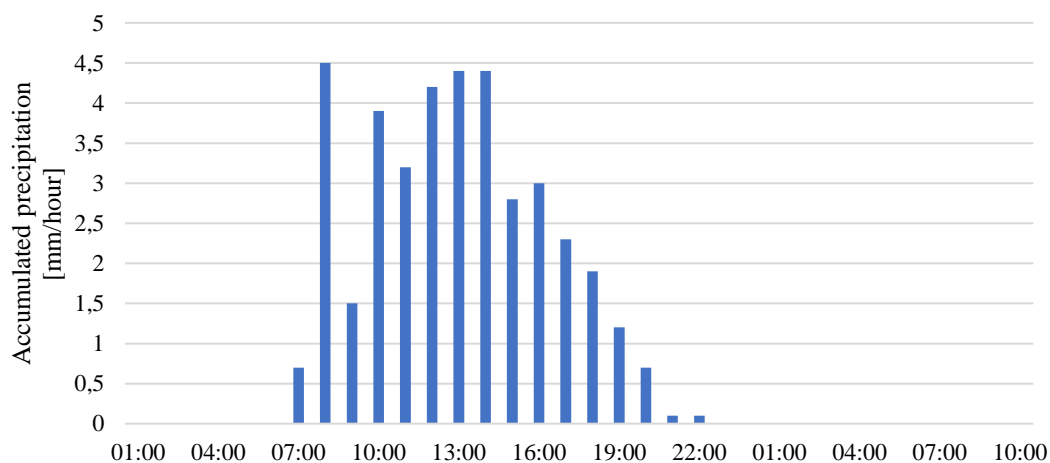


Figure 3-14 Accumulated precipitation measured at Våland weather station during Storm B between the 10<sup>th</sup> and 11<sup>th</sup> of May 2018 (Meterologisk institutt & NRK, 2007 - 2018).

### 3.3. Weekly water samples

The automatic samplers were programmed to follow a flow proportional program. A sample is taken after  $n$  pulses equal to  $10^n \text{ m}^3$  of water measured by an external flow meter. The samplers were programmed to collect samples after 7-8 pulses during weeks with much expected rain and hence high water flow. During weeks with low expected water flow, they were programmed to take samples after 2-3 pulses.

Subsamples of 50 mL were taken over a period of 6 to 8 days and stored in a 11L plastic container in refrigerators for conservation (Figure 3-16). The plastic containers were cleaned with a brush every week to remove organic matter adsorbed to the container. A 2L homogenous, composite water sample was collected from the inlet and outlet sampler.



*Figure 3-15 The sampling house positioned in Leikvollbekken equipped with two ISCO 6712 Full-Size Portable Samplers and one Teledyne ISCO Signature Flow Meter.*



*Figure 3-16 The ISCO 6712 Full-Size Portable Samplers placed inside house. Each of the samplers are placed on a refrigerator with the 11 L plastic containers inside.*

### 3.4. Storm water samples

During the two storms, an extra ISCO 6712 Full-Size Portable Sampler was placed over the inlet to pond 1 (Figure 3-17). The suction tube was placed in an open surface area with visual water movement close to the inlet and strapped to a metal pole to ensure it would stay in place during the storm (Figure 3-18). Water samples for the inlet of Pond 1 were included to get a better understanding of how Pond 1 is affected of a storm with high water flow. The two stationary automatic samplers for the inlet and outlet of pond 2 were also included in the storm water sampling.



*Figure 3-17 The automatic sampler placed over the inlet to pond 1. A car battery was placed with the sampler to provide electricity. The suction tube is marked with a red circle.*



*Figure 3-18 Close-up of the suction tube placed in the inlet to pond 1. The tube was placed in an open area with most visual water movement.*

All three samplers were equipped with a carousel arrangement with multiple plastic bottles of 1L (Figure 3-19). Each of the samplers was programmed to take time proportional samples, producing composite samples of given time intervals.

During Storm A, inlet samples of Pond 1 were collected as four subsamples of 200 mL in every bottle over one hour, for 24 hours. Sampler 2 and 3 for the inlet and outlet of pond 2 respectively, were programmed to take 4 samples of 200 mL over 7 hours and 4 hours respectively the first 24 hours. After the first 24 hours the inlet and outlet sampler collected 200 mL samples for 1,5 hours and 1 hour respectively.

During Storm B, inlet of Pond 1 and outlet of Pond 2 collected four 200 mL subsamples in each container over 24 hours. Samples were collected over 1.5 hour for the inlet of Pond 2.



*Figure 3-19 Carousel arrangement inside the portable automatic sampler placed at the inlet of pond 1.*

### 3.5. Teledyne ISCO Signature Flow Meter

A Teledyne ISCO Signature Flow Meter, with accessories, was used to measure flow of the inlet and outlet of Pond 2 every 15 minutes. Inlet flow was measured with a Teledyne ISCO TIENet 350 Area Velocity Sensor positioned inside the fully submerged pipeline between Pond 1 and 2. The sensor serves as the secondary device, measuring the average velocity with use of continuous ultrasonic waves. The fixed pipeline area serves as the primary device. Average flow was calculated by the Signature Flow Meter with the use of average velocity and a defined fixed pipeline area. Measurements by the Area Velocity Sensor are unstable when particle concentrations get too low for the ultrasonic waves to detect, which results in flow data that are unchanged in periods with low TSS. Because of this effect, outlet flow was used to determine flux. Outlet flow was measured with an ISCO TIENet 330 Bubbler module placed in the open channel before the v-notch. The Bubbler module serves as the secondary device and can determine the amount of pressure equal to the open channel liquid level. With the measured pressure, the Signature Flow meter converts pressure to flow by known relationships-between liquid level and flow rate. The Bubbler module was positioned in the open channel according to ISCO standards.

### 3.6. Analytical water analysis

In total, eight different parameters were measured during the study (Figure 3-20). This subchapter describes the materials and methods for the execution, as well as an explanation for why the method was performed the way it was.

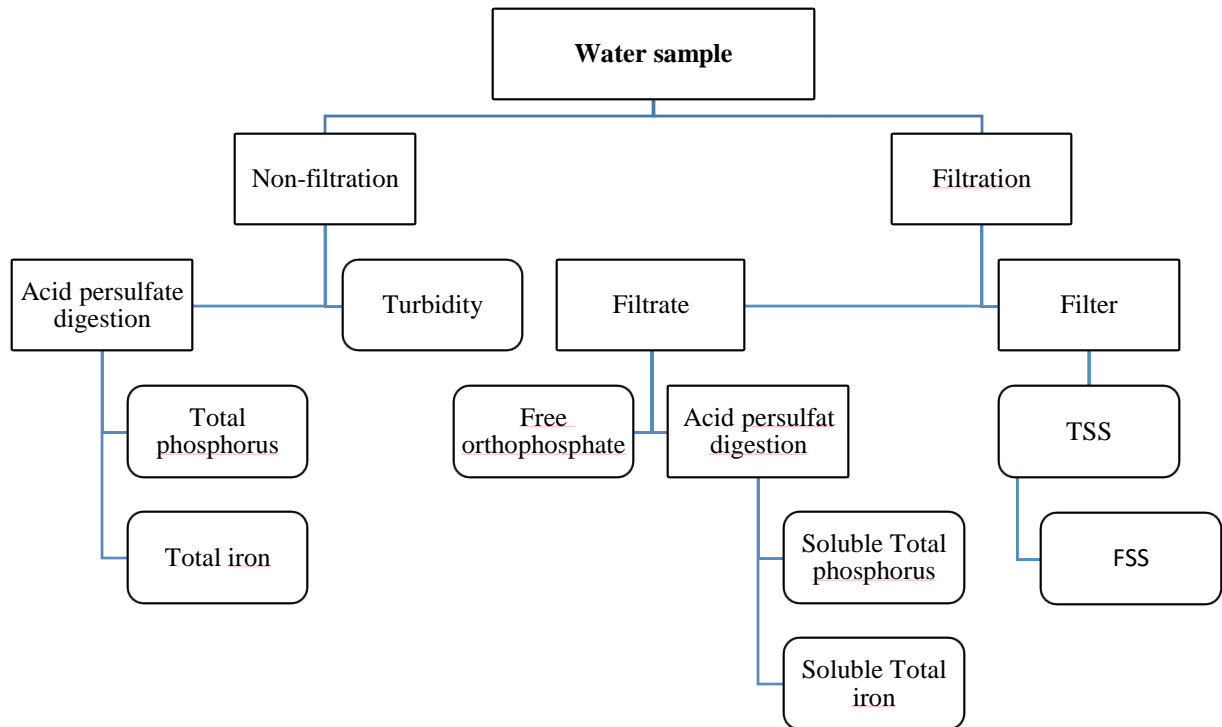


Figure 3-20 Schematic presentation of the analyses performed during the sampling period. Boxes with round edges represents parameters used in the result in this thesis.

#### 3.6.1. Phosphorus parameters

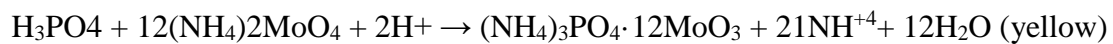
The following analysis described in this chapter was performed according to Standard Methods of Examination of Water and Wastewater 4500-P (Clesceri et al., 1998), with some exceptions. All glassware used during analysis was soaked in 0.5 N sulfuric acid over a period of 1 week to remove any phosphorus residue, with exception of glassware used for the digestion step. The glassware was filled with 0.5 N sulfuric acid and autoclaved. Preliminary filtration was carried out according to Standard Method 4500-P B.1. Filtered samples were measured to determine free orthophosphate and dissolved TP, while unfiltered samples were used to determine total phosphorus (Figure 3-20).

Samples for determining TP and sTP were digested prior colorimetric measurements. Digestion was performed by autoclavation (Panasonic MLS-3781L) with persulfate under acidic conditions according to Standard method 4500-P B.5, Persulfate Digestion Method. Persulfate

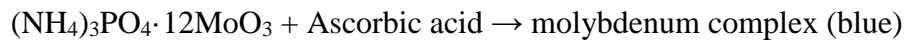
oxidizes particulate and condensed phosphorus under low pH and high temperature to release chemically bound phosphorus as orthophosphate.

Phosphorus concentrations were analysed according to Standard Method 4500-P E, the Ascorbic Acid Method with the range 0.1 to 6 mg P/L. Ammonium molybdate and potassium antimony tartrate, react with orthophosphate and form a yellow phosphomolybdate complex (Equation 3-1). Ascorbic acid reduces the acid formed and produces a blue coloured molybdenum complex (Equation 3-2) (Brezonik & Arnold, 2011).

*Equation 3-1 Formation of yellow phosphomolybdate complex.*



*Equation 3-2 Reduction of a phosphomolybdate complex by ascorbic acid to a blue molybdenum complex.*



Absorbance was measured at 880 nm with a spectrophotometer (SHIMADZU, UVmini -1240) and 4-mL glass-clear polystyrene cuvetts (Ratiolab®, path length 10 mm, wavelength range 340 to 900 nm). Calibration curves were constructed according to the standard method.

For further details on the execution of the analysis, see Appendix or Standard Methods of Examination of Water and Wastewater 4500-P.

### 3.6.2. Iron

5-mL removed from autoclaved TP and sTP samples, prior to colorimetric analysis, was used to measure total iron and total dissolved iron concentration respectively. This was done due to practicality in the lab as a full execution of the Modified Thiocyanate Method (Goswami & Kalita, 2013) would consume too much time. The Modified Thiocyanate Method oxidizes ferrous iron by ceric ammonium sulphate, before a ferric thiocyanate colour complex with potassium thiocyanate is formed. A spectrophotometer (SHIMADZU, UVmini -1240) and 4-mL glass-clear polystyrene cuvetts (Ratiolab®, path length 10 mm, wavelength range 340 to 900 nm) was used for absorbance measurements at 480 nm. For further information about the method, see Goswami and Kalita (2013) .

### 3.6.3. Total suspended solids and Fixed/Volatile suspended solids

Homogenized samples were filtered through glass microfiber filters (GE Healthcare Lifescience, 55mm) according to Standard Methods 2540 D, Total Suspended Solids Dried at 103 – 105 °C (Clesceri et al., 1998). Fixed/Volatile suspended solids were determined from 11<sup>th</sup> of January 2018 to 25<sup>th</sup> of Mai 2018 according to Standard Method 2540 E, Fixed and Volatile

Solids ignited at 550 °C (Clesceri et al., 1998). Glass microfiber filters used to determine TSS were placed in a muffle furnace (Nabertherm B170) and ignited at 550 °C for 30 minutes before cooling to room temperature in a desiccator to remove water residue. See Standard Methods 2540 D and E for further information.

Glass fiber filters were rinsed with DI water prior analysis before being dried in an oven (Termaks A/S) at 110 °C over minimum 24 hours. The filters were then placed in a desiccator for 24 hours and ignited in the muffle furnace at 550 °C for 30 minutes before stored in a desiccator until use.

#### 3.6.4. Turbidity

Raw samples, without filtration, of the inlet and outlet of pond 1 were measured each week with a turbidimeter (HACH 2100N Laboratory Turbidimeter) according to Standard Method 2130 B., the Nephelometric Method. Intensity of light scattered by the liquid analysed are compared with the scattering produced by a standard reference suspension under equal conditions. A turbid liquid has a higher scatter intensity than a non-turbid liquid. Air bubbles and dirty sampling glass represent interference sources, as well as vibrations that disturb the surface visibility. True colour is also listed as a possible interference, which will give lower measured turbidity, but the effect is known to not be significant (Clesceri et al., 1998).

#### 3.7. Data analysis

Measured concentrations were used to determine mass flux ( $M_F$ ) both for weekly measurements and for the two storm peaks (Equation 3-3). Mass fluxes were determined to get a better understanding of phosphorus, iron and suspended solid loadings.

*Equation 3-3: Mass flux equation used for weekly measurements.*

$$M_F = \bar{Q} * \bar{C} * \Delta t$$

$\bar{Q}$  = average flow over the week [L/h]

$\bar{C}$  = measured concentration [g/L]

$\Delta t$  = the time the automatic sampler sampled the given week [h/week]

The wetlands weekly retention performance was measured by subtracting determined outlet mass fluxes from the inlet mass fluxes for each week.

Total mass flux over the year-long monitoring was determined by adding all weekly mass fluxes together. Phosphorus retention in Leikvollbekken was determined as an area-specific retention



( $R_{Area}$ ) (Equation 3-4) and a relative retention ( $R_{Relative}$ ) (Equation 3-5). Area-specific retention was presented per year for the long-term monitoring and per day for Storm A and Storm B. A negative retention represents a wash-out situation, while a positive retention represents accumulation.

*Equation 3-4: Area specific retention in Leikvolbekken.*

$$R_{Area} = \frac{\text{g P retention}}{\text{m}^2 * \text{period}}$$

*Equation 3-5: Relative retention in Leikvolbekken.*

$$R_{Relative} = \frac{\text{g P retention}}{\text{g P load}} * 100$$

### 3.8. Statistical method

Simple regression was performed with Microsoft Excel. Such statistical analysis explores the relationship between the two variables and reveals if the connection is significant. Concentrations of the different parameters were analysed for the storm samples, while weekly retentions were analysed for the weekly monitoring. A level of 0.05 was chosen as the significance threshold.

### 3.9. Error analysis

Random errors are represented in the standard deviations determined based on two parallel analyses for TP, sTP, PO4<sup>3-</sup>, TotFe and sTotFe. Percentile standard deviations were calculated to get a better overall impression of the deviation taking change in variation into account.

## 4. Results

The results are divided into three main sections. The first being a year-long monitoring of nutrient retention, the second being a three days evaluation of Storm A and the third being the one day evaluating of Storm B.

### 4.1. Long-term monitoring of nutrients

Results of weekly samples are presented in this subchapter and represent the efficiency of Pond 2. Sampling occurred as planned during the fall, but some problems arose from mid-December. Samples from the dates 20<sup>th</sup> of December, 11<sup>th</sup> of January and 15<sup>th</sup> of March stand out with odd results. Samples from the 20<sup>th</sup> of December were rejected due to unreliable results and is therefore not included in the result section. Small amounts of water, less than 2L, were collected by the inlet automatic. These samples had a significant higher particle concentration, and visual plant leaves and insects of 1 cm in length. A few weeks are monitored without an inlet sample. Cold weather caused the pipeline for the inlet sampler to freeze, leaving the plastic container empty on the 8<sup>th</sup> of March. Stavanger municipality carried out maintenance of Leikvollbekken between 28<sup>th</sup> of March and 5<sup>th</sup> of April and pulled the inlet sampling tube out of position. Because of this, there are no inlet samples after the 5<sup>th</sup> of April.

Phosphorus parameters, iron parameters, suspended solids and turbidity were measured the whole sampling period. FSS, and thus VSS, were only analysed from 11<sup>th</sup> of January to 3<sup>rd</sup> of May due to problems with combustion of the filters.

#### 4.1.1. Hydraulic load

Flow varied over the sampling period, from under 2.5 L/s to over 200 L/s (Figure 4-1).

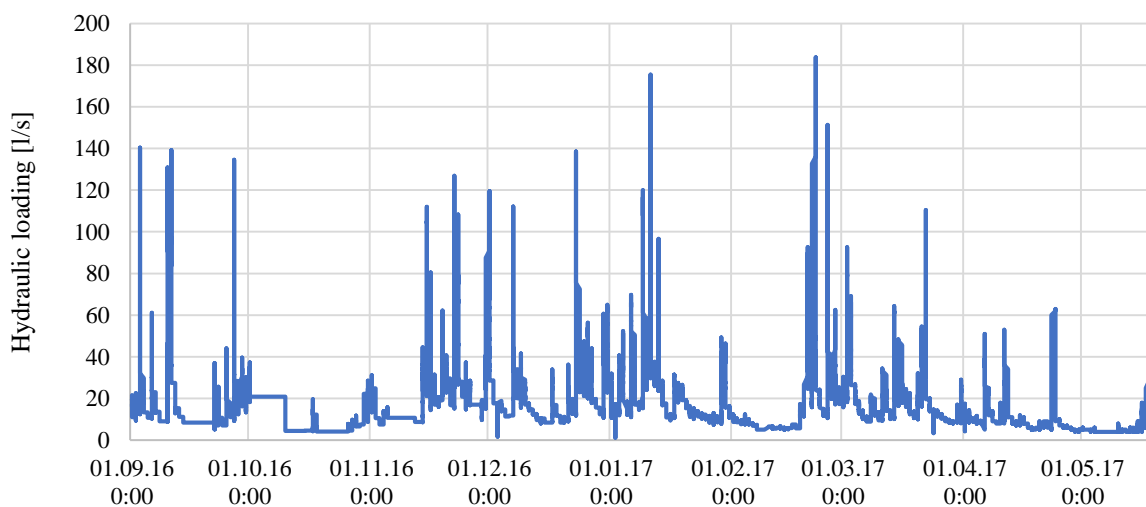


Figure 4-1 Flow [L/s] measured at the outlet of Pond 2 every 15 minutes.

### 4.1.2. Phosphorus

TP, sTP and  $PO_4^{3-}$  were analysed, while pTP were determined by subtracting sTP from TP. Concentrations of the soluble fractions showed less fluctuations compared to the particulate fraction, for both the inlet and outlet (Figure 4-2 and Figure 4-3). Average flow is plotted in a separate axis for presentation purposes.

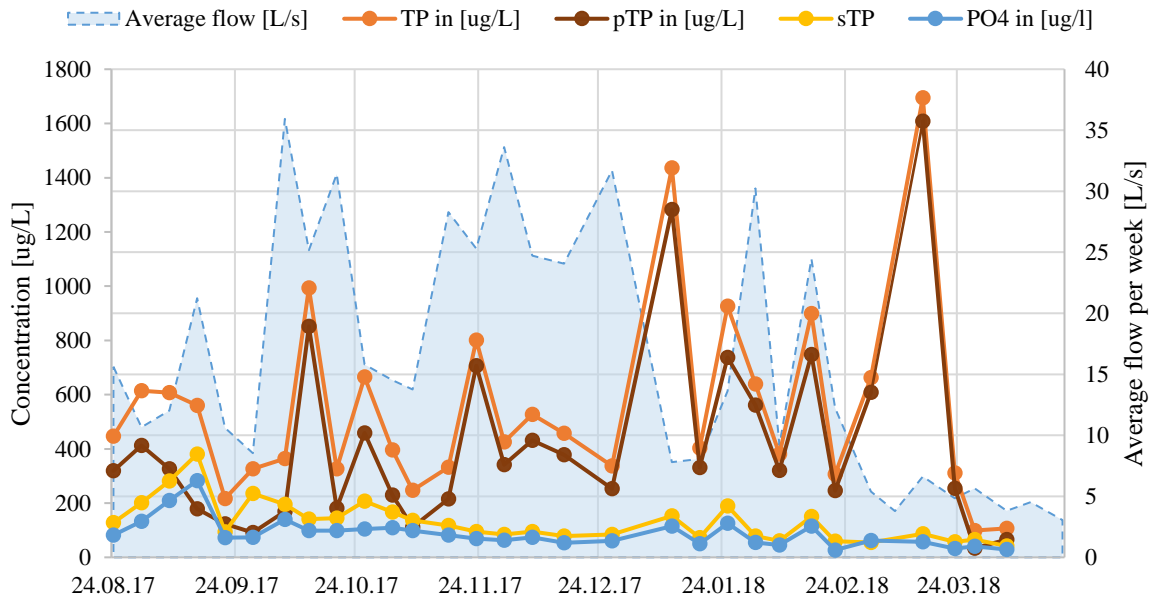


Figure 4-2 Concentrations of TP, sTP, pTP and  $PO_4^{3-}$  measured at the inlet of Pond 2.

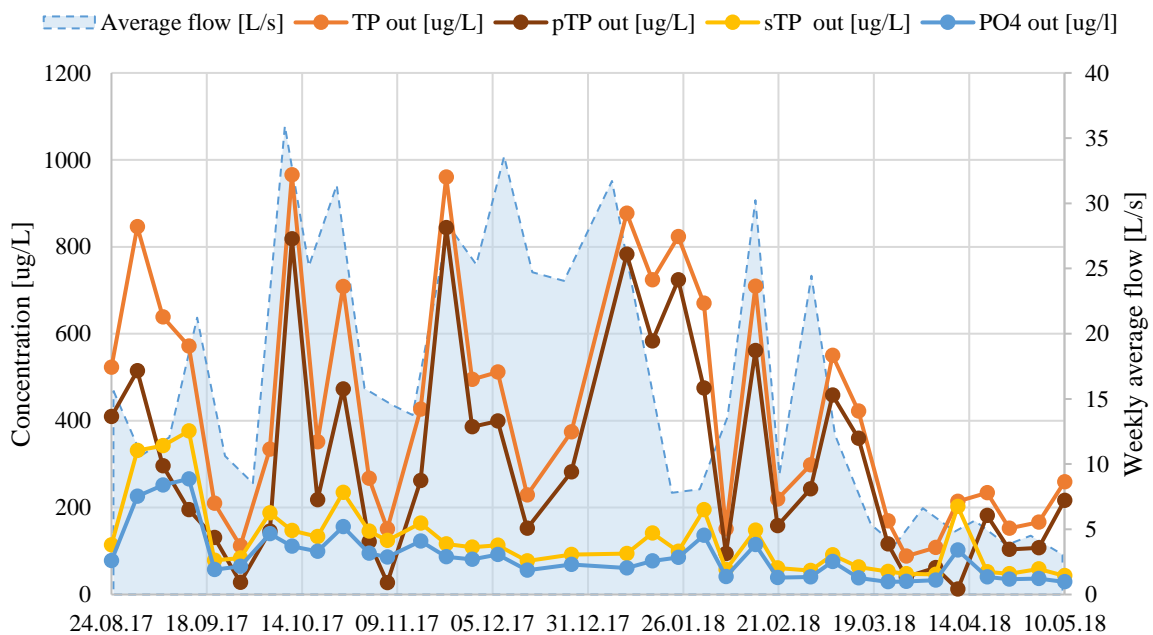


Figure 4-3 Concentrations of TP, sTP, pTP and  $PO_4^{3-}$  concentrations measured at the outlet of Pond 2.

Phosphorus retention varied over the year (Figure 4-4). Total particulate and soluble phosphorus are presented in black and yellow blocks. Total phosphorus retention is marked with a red line, because total phosphorus consists of particulate and soluble phosphorus. Phosphate retention is marked in green since it represents a fraction of the total soluble phosphorus.

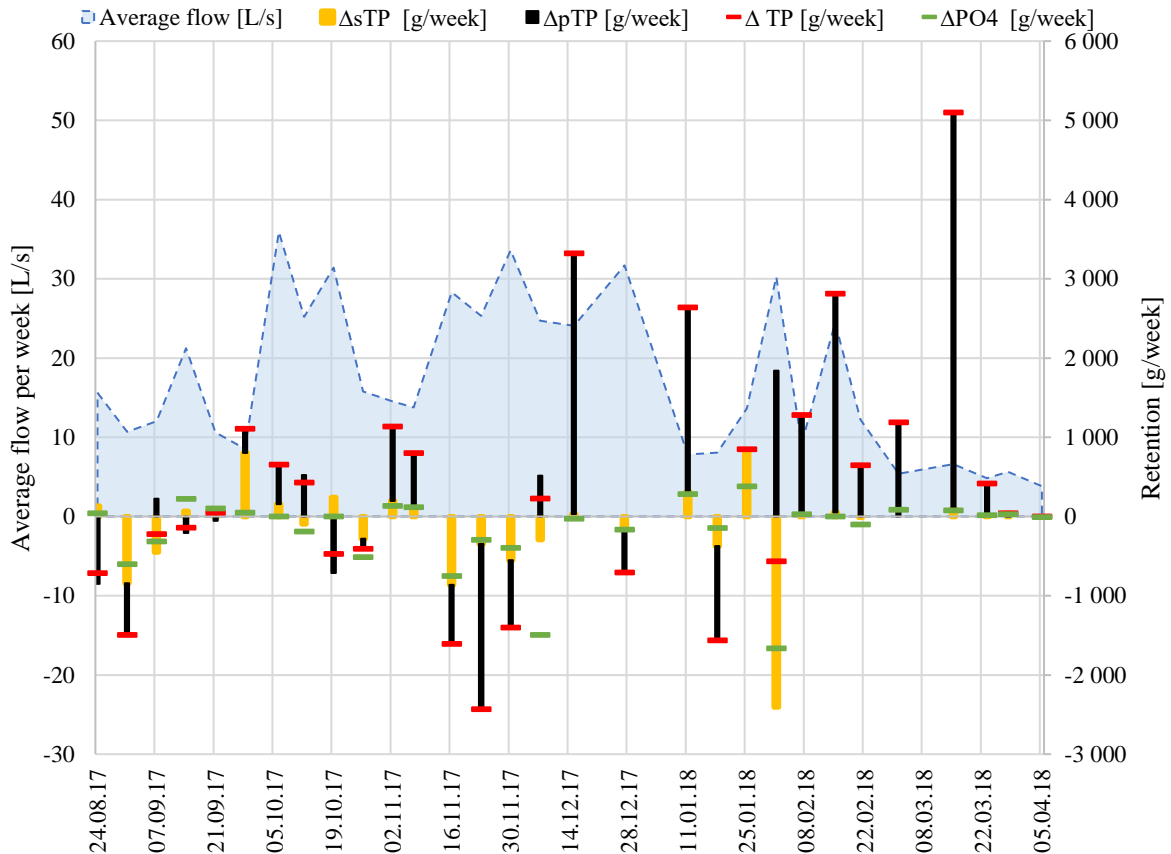


Figure 4-4 Weekly determined phosphorus retention for Pond 2.

The particulate fractions had a positive total retention, while the soluble fractions had a negative retention (Table 4-1).

Table 4-1 Retention phosphorus measured from August 2017 to May 2018.

	<b>Retention</b>	<b>Area specific retention</b>	<b>Relative retention</b>
TP	11.9 kg	32 g/m <sup>2</sup> ·year	7%
sTP	-3.5 kg	-9 g/m <sup>2</sup> ·year	-8%
pTP	15.4 kg	41 g/m <sup>2</sup> ·year	11%
PO <sub>4</sub> <sup>3-</sup>	-3.0 kg	-8 g /m <sup>2</sup> ·year	-10%

### 4.1.3. Iron

TotFe had higher weekly concentration variation compared to sTotFe and were measured up to 13.9 mg/L (Figure 4-5). Concentrations of sTotFe were never higher than 2.3, including both inlet and outlet samples.

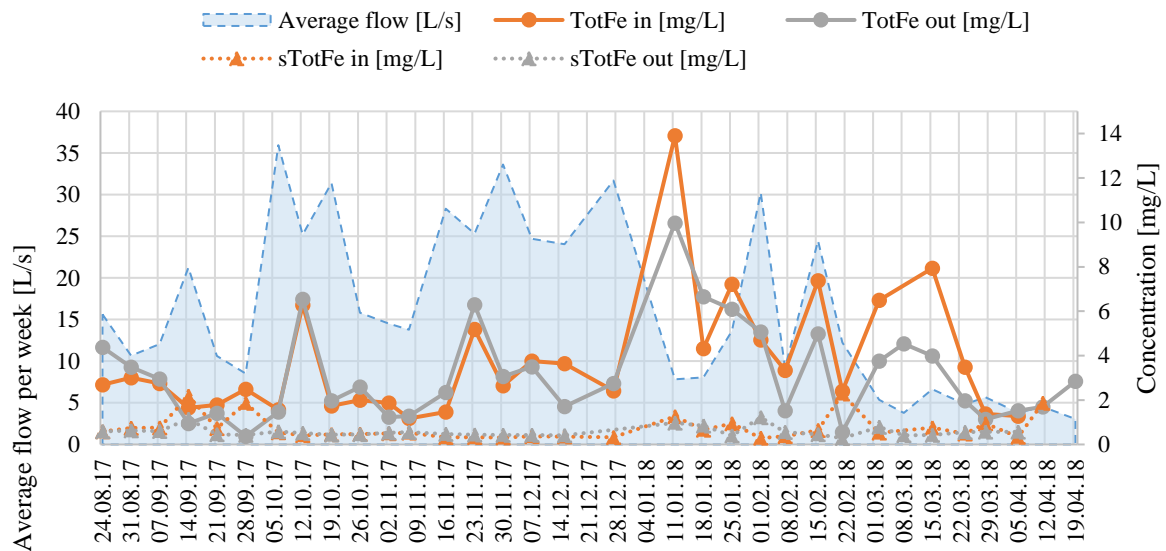


Figure 4-5 Variation in iron concentrations measured at the inlet and outlet of Pond 2.

Retention of iron varied over the year ( Figure 4-6). Particulate and soluble iron is presented in black and yellow blocks. Total iron retention is marked with an orange line, because total iron consists of particulate and soluble iron. In general, accumulation situations were greater in size than washouts. The largest positive retention observed was 40 kg TotFe /week, while the greatest washout was observed to be around 2 000 kg TotFe/week.

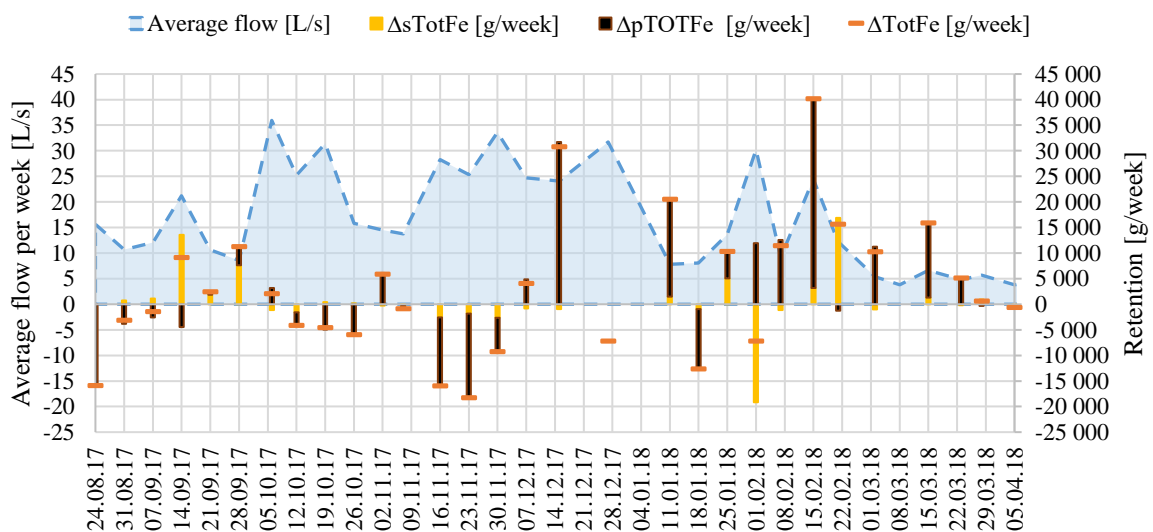


Figure 4-6 Retention of iron parameters for each week.

Overall iron retention was positive for both the particulate and soluble fraction (Table 4-2).

Table 4-2 Retention of iron parameters from August 2017 to May 2018

	Retention	Area specific retention	Relative retention
<b>sTotFe</b>	50 kg	134 g/m <sup>2</sup> *year	22%
<b>pTotFe</b>	127 kg	339 g/m <sup>2</sup> *year	12%
<b>TotFe</b>	177 kg	473 g/m <sup>2</sup> *year	13%

4.1.4. Suspended Solids

Measured TSS was more stable for fall-samples than spring-samples (Figure 4-7). Lowest TSS concentration found was 5 mg/L and the highest was 252 mg/L.

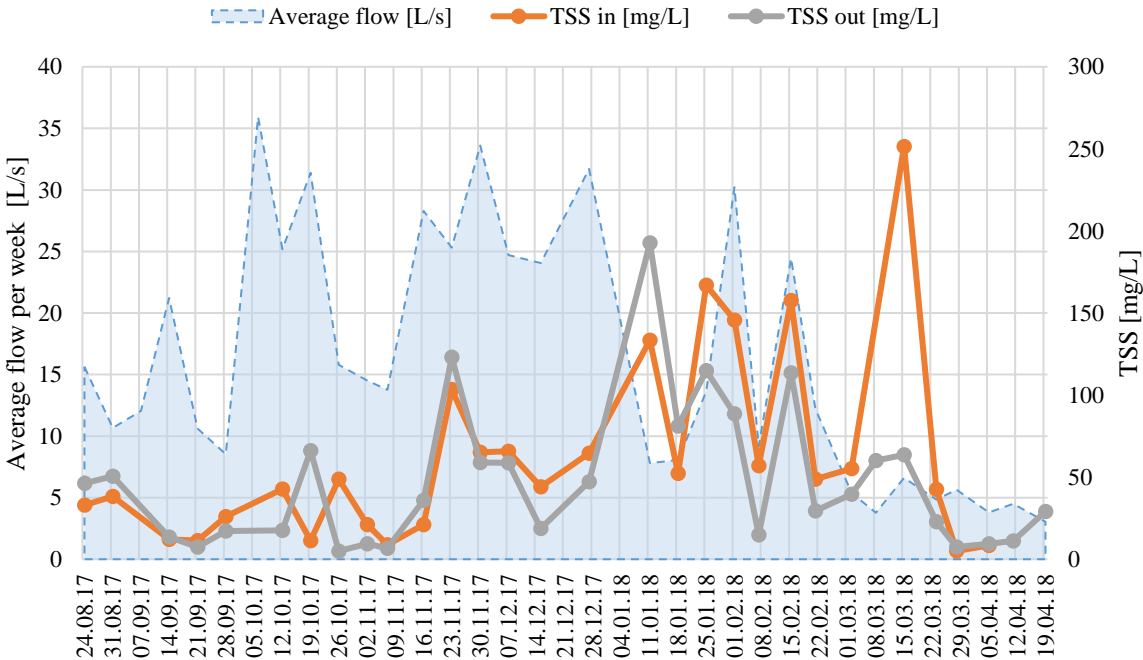


Figure 4-7 TSS concentrations [mg/L] for the inlet and outlet of Pond 2

FSS was determined analytically in the laboratory, while VSS was determined by withdrawing FSS-concentrations from TSS-concentrations. Inlet and outlet concentrations followed the same pattern as the average flow, except from the sample collected 15<sup>th</sup> of March 2018 (Figure 4-8).

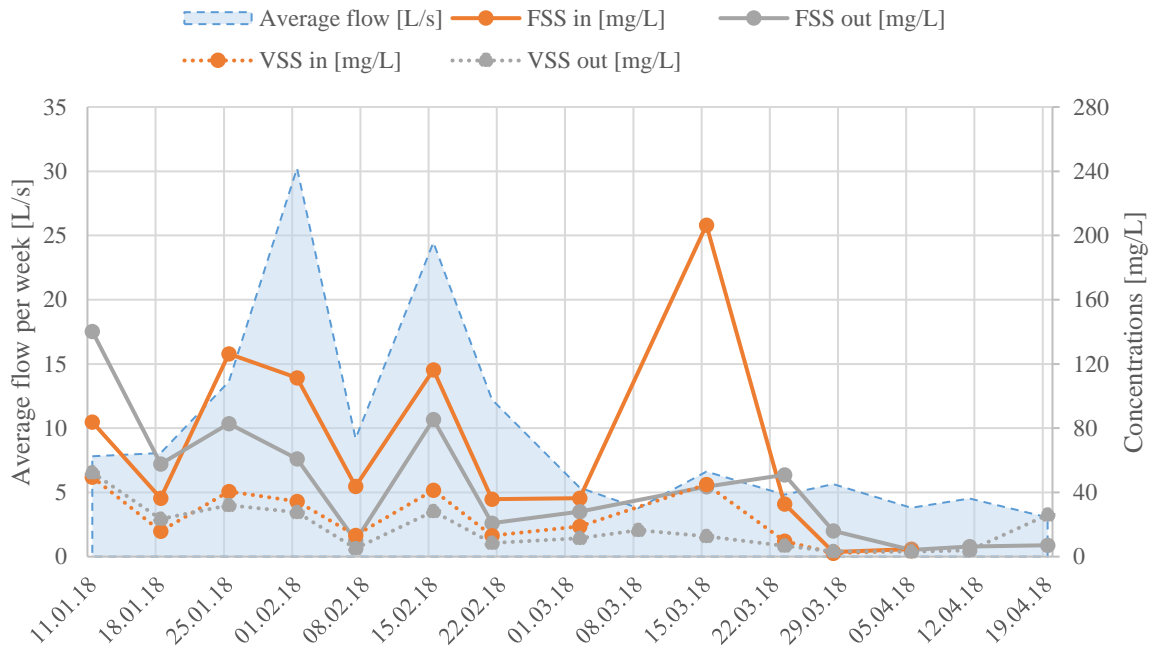


Figure 4-8 FSS and VSS concentrations [mg/L] for the inlet and outlet of Pond 2.

TSS and FSS were determined analytically in the lab, while VSS values were calculated by subtracting FSS from TSS. Retention of FSS represents a small fraction of TSS in weeks with large negative retention. Wash-out situations were greater in size than accumulation periods (Figure 4-9), leading to an overall washout of 60 kg TSS. This gives an area specific retention of  $-159 \text{ kg/m}^2 \cdot \text{year}$  and a relative retention of  $-304\%$ .

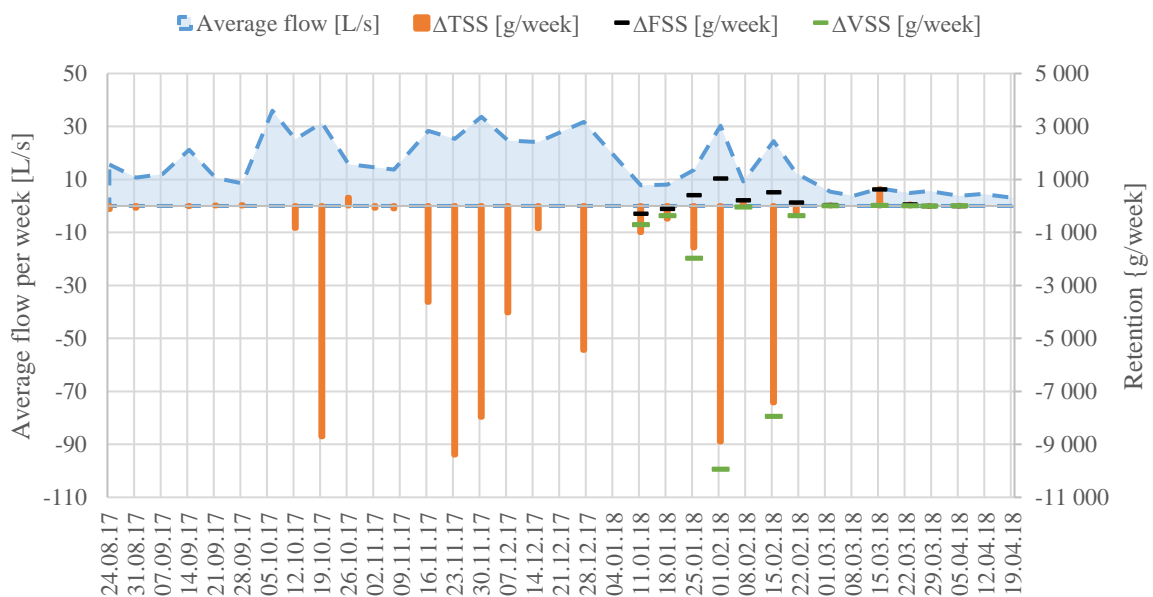


Figure 4-9 Retention of TSS [g/week], VSS [g/week], FSS [g/week] plotted over time, including the average flow per week [L/s].

#### 4.1.5. Error analysis

Mean standard deviations for TP, sTP, PO<sub>4</sub><sup>3-</sup>, TotFe and sTotFe were generally low (Table 4-3). All weekly phosphorus samples were analysed with two parallels, while iron samples were only analysed with two parallels from the 21<sup>st</sup> of February to the 3<sup>rd</sup> of May 2018. The two parallels were projected as a mean for the total standard deviation for each parameter.

Table 4-3 Mean standard deviation and mean percentile standard deviation estimated for TP, sTP, PO<sub>4</sub><sup>3-</sup>, TotFe and sTotFe.

	<b>Standard deviation</b>	<b>Percentile standard deviation</b>
TP	11 ug/L	2%
sTP	5 ug/L	2%
PO <sub>4</sub> <sup>3-</sup>	4 ug/L	3%
TotFe	0.06 mg/L	3%
sTotFe	0.01 mg/L	2%

Problems with the automatic sampler at the inlet of Pond 2 represent a source of error. Water samples collected varied greatly in solids, which is assumed to be caused by the sampling tube being out of position. The sampling tube was assumed to have been partly imbedded into the sediments, hence pulling in more solids. It is worth mentioning that this varied weekly and that some weeks did not show high TSS levels.

#### 4.1.6. Statistical analysis

Regression analysis was performed for different combinations of parameters. Relationships between flow and the other parameters are believed to be dependent. These kinds of relationships require a more complex statistical analysis to reveal true relationships. Such statistical analysis is beyond the scope for this thesis and is therefore not included. Mass fluxes have not been correlated against each other, since they are based on the same flow, and will therefore always have some degree of correlations. Because of this, the retention of the parameters has been analysed. The most relevant relationships are presented in Table 4-4.

Table 4-4 Results from regression analysis performed on long-term retention of phosphorus, iron and suspended solid variables.

	<b>R<sup>2</sup></b>	<b>Significance</b>	<b>P-value</b>	<b>n</b>
Retention of variables				
TP [g/week] vs. TotFe[g/week]	0.71	Yes	1.2*10 <sup>-8</sup>	28
pTP [g/week] vs. pTotFe [g/week]	0.73	Yes	4.5*10 <sup>-9</sup>	28
sTP [g/week] vs. sTotFe [g/week]	0.13	No	0.06	27
TP [g/week] vs. TSS [kg/week]	0.16	Yes	5.9*10 <sup>-5</sup>	28
PO <sub>4</sub> <sup>3-</sup> [g/week] vs. TSS [kg/week]	0.03	No	0.37	28
pTP [g/week] vs. TSS [kg/week]	0.07	No	0.31	29
pTP [g/week] vs. FSS [kg/week]	0.37	Yes	0.04	10



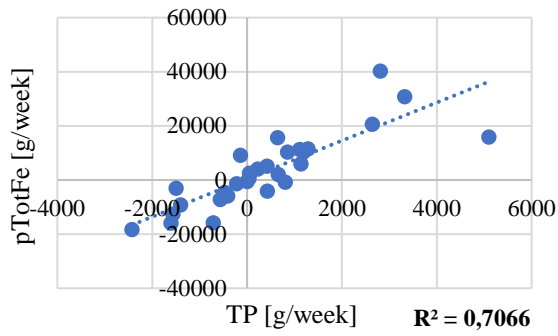


Figure 4-10 Scatter plot for the retention of TP and retention of TotFe.

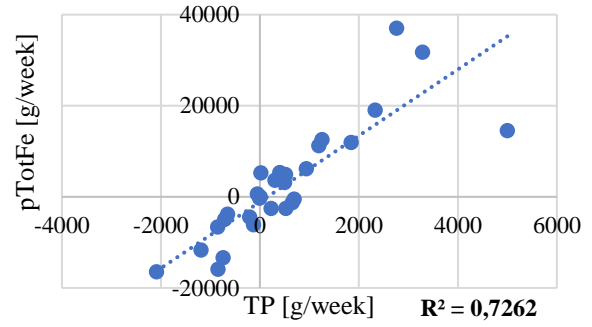


Figure 4-11 Scatter plot for the retention of pTP and retention of pTotFe.

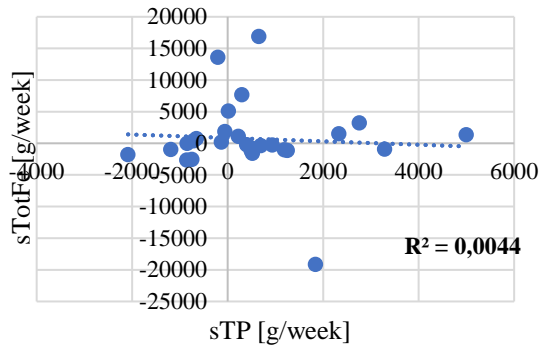


Figure 4-12 Scatter plot for the retention of sTP and retention of sTotFe.

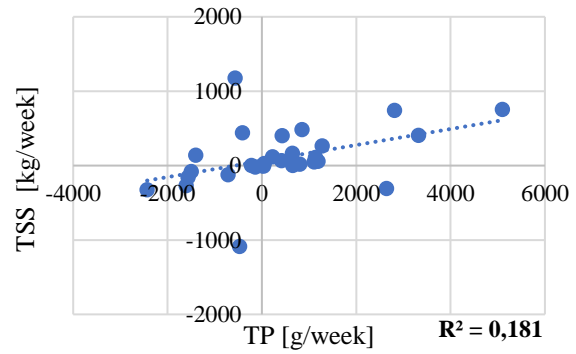


Figure 4-13 Scatter plot for the retention of TSS and retention of TP.

## 4.2. Storm A

Storm A lasted from 29<sup>th</sup> of September to 2<sup>nd</sup> of October 2017. A limited number of parameters were analysed because of smaller sampling volume (250 mL) transported to the laboratory due to practicalities during sampling. TP, PO<sub>4</sub><sup>3-</sup> and TSS were prioritized and determined for each of the 113 water samples collected.

### 4.2.1. Hydrological load

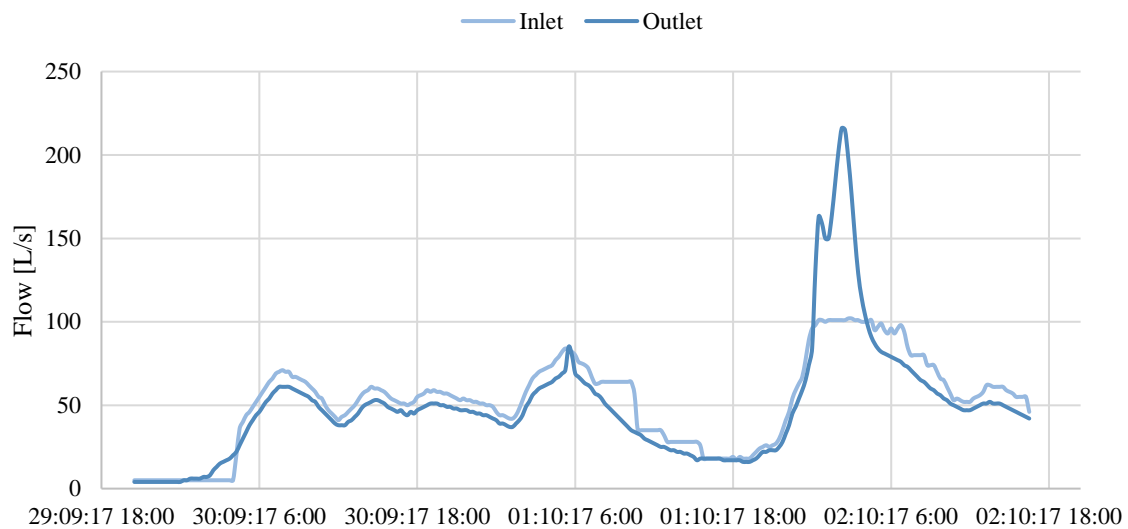


Figure 4-14 Hydraulic load measured by the flowmeters situated at the inlet and outlet of Pond 2.

Flow in and out of the wetland was measured continuously every 15 minutes during the storm. Inlet and outlet measurements were similar in values, with inlet flow generally measured to be higher than outlet flow (Figure 4-14), indicating the wetland to accumulate water.

It is important to mention that the inlet flow did not increase over 100 L/s due to limiting capacity of the pipeline connecting Pond 1 and Pond 2. Water bypassed the pipeline and Pond 2, hence flowing directly to the outlet.

The three precipitation peaks presented in Figure 3-13, are viewable in Figure 4-14. Two of the three peaks were relatively small, with a flow of under 80 L/s, while the flow of the last peak was higher than 200 L/s at most.

Average outlet flow per hour was estimated and used for further calculations, as the outlet is considered to be more reliable. See subchapter “3.5 Teledyne ISCO Signature Flow Meter” for detailed explanation on why the outlet is more reliable.

#### 4.2.2. Concentration variations

Concentration variations for the inlet of Pond 1, inlet of Pond 2 and the outlet of Pond 2 are presented in graphs below. When looking at the graphs, be aware that TSS is presented as mg/L while TP and  $\text{PO}_4^{3-}$  are presented as  $\mu\text{g/L}$ . Average flow is plotted in a separate axis for presentation purposes.

The automatic sampler placed at the inlet of Pond 1 collected 48 water samples in two sets, the first 24 hours and the last 24 hours, capturing two clear concentration peaks. No samples were collected in the period between 19:30 at the 3<sup>rd</sup> of September to 17:30 at the 1<sup>st</sup> of October due to programming of the automatic sampler. The concentrations into Pond 1 showed a trend of following the flow pattern. TP and TSS declined and rose according to decreased and increased flow, respectively (Figure 4-15). This was also observed for  $\text{PO}_4^{3-}$  during the two first storm peaks., but  $\text{PO}_4^{3-}$  concentrations stabilized around 300  $\mu\text{g/L}$  during the last peak.

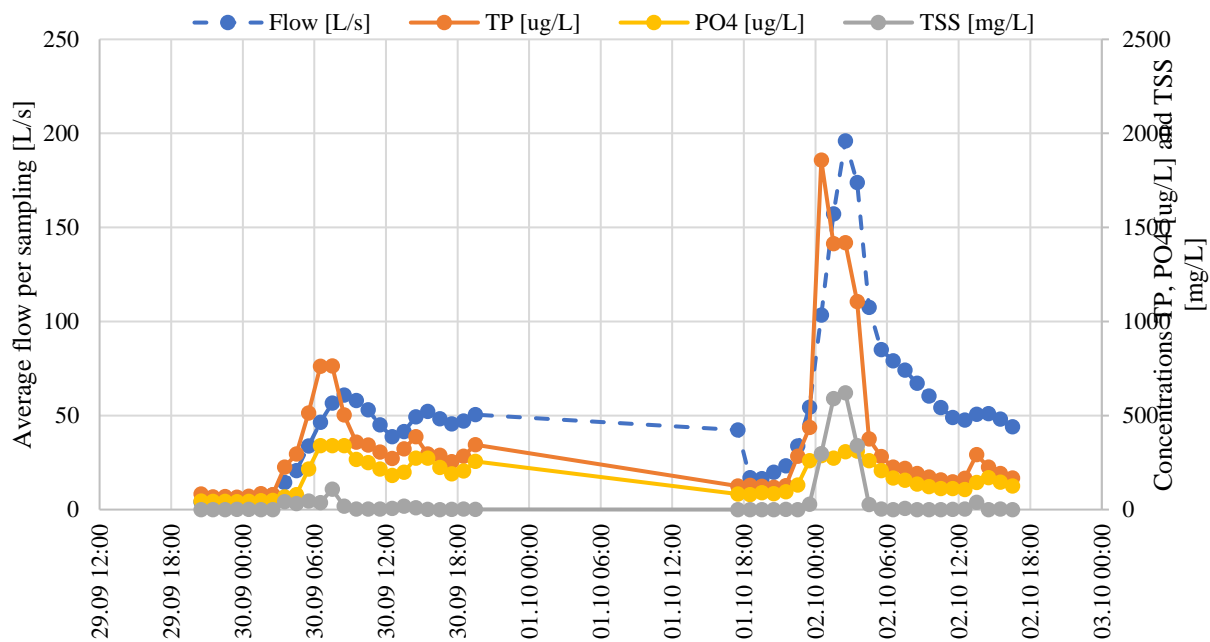


Figure 4-15 Concentrations measured at the inlet of Pond 1 and average flow of Storm A.

A limited number of water samples were collected at the inlet of Pond 2 due to shortage of plastic bottles for the carousel. 22 samples were collected in total, and each sample represents a greater time interval than samples collected at the inlet of Pond 1. Increased TP and TSS concentrations are observed simultaneously with flow peaks (Figure 4-16). The first flow peaks are not as easily seen due to average flow being determined over periods of 9 hours. The last storm peak was captured with a higher sampling frequency, 1.5 hour per sample. The second peak represents a 65% higher TP concentration and a 272% higher TSS concentration than the first peak. Limited variations were observed for  $\text{PO}_4^{3-}$  concentrations, compared to TP and TSS.

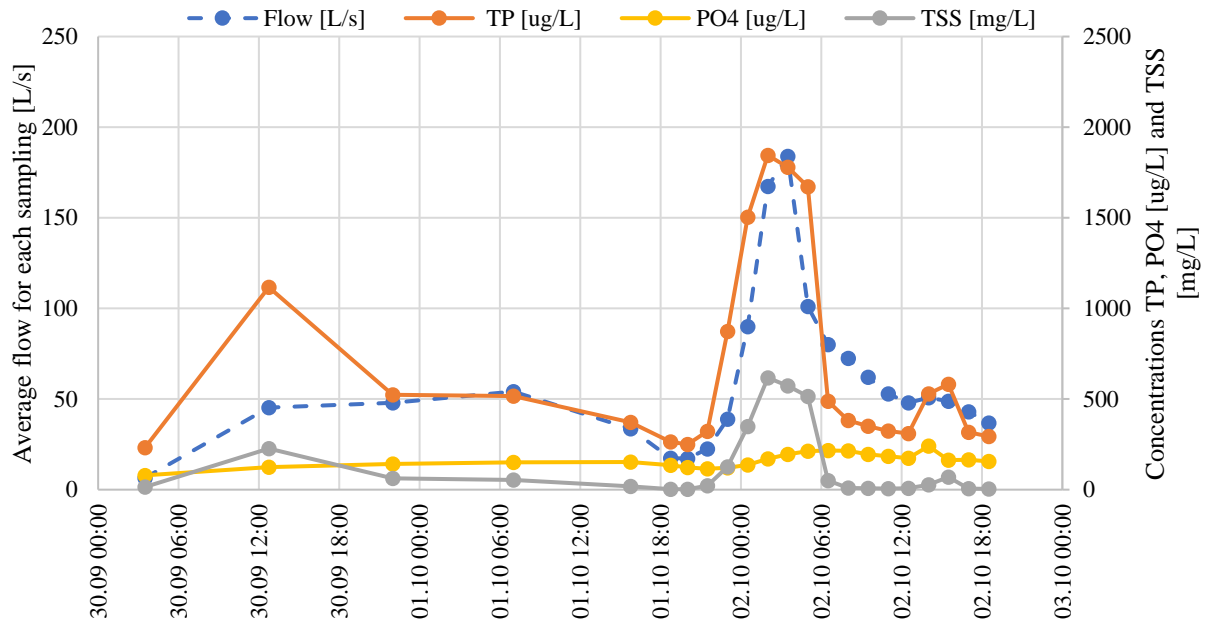


Figure 4-16 Concentrations measured at the inlet of Pond 2 and average flow of Storm A.

Concentrations measured at the outlet of Pond 2 (Figure 4-17) follow the same trends as the inlet of Pond 1 (Figure 4-15) and Pond 2 (Figure 4-16), where a flow peak was accompanied with concentration peaks for TP and TSS. The first 11 samples were collected over a four hours period producing a smoother graph than Figure 4-15. A drop in TP and TSS concentrations were observed amid the greatest peak, at 03:15 the 2<sup>nd</sup> of October. It is worth mentioning that the drop starts at the same time as water bypasses Pond 2, as explained in subchapter 4.2.1. PO<sub>4</sub><sup>3-</sup> showed the same tendency as the inlet of Pond 1 and inlet of Pond 2, with less variation than TP and TSS concentration.

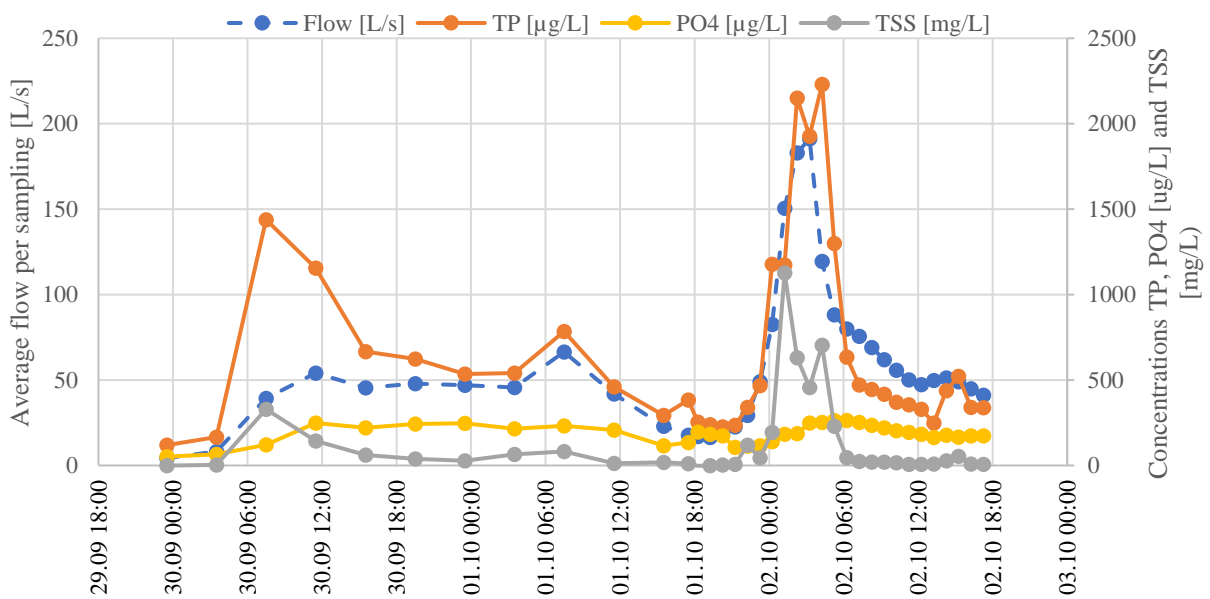


Figure 4-17 Concentrations measured at the outlet of Pond 2 and average flow of Storm A.

### 4.2.3. Retention

Mass flux per hour for the inlet of Pond 1, inlet of Pond 2 and outlet of Pond 2 were calculated to determine the retention for each of the ponds, as well as total retention of Leikvollbekken. Hourly mass flux for the composite samples representing more than 1 hour, was estimated by multiplying the mean concentration for the sample with the mean hourly flow. Hourly retention was determined by subtracting mass flux out from mass flux in.

A general negative retention of TP and TSS was observed (Figure 4-18), with a tendency for higher negative retention simultaneous with high flow. Positive TP and TSS retentions were observed during the last peak. Positive retentions were in general observed for  $\text{PO}_4^{3-}$ , except of the flow peak around 05:30 at the 1<sup>st</sup> of October with a retention of maximum -18  $\mu\text{g/L}$ .

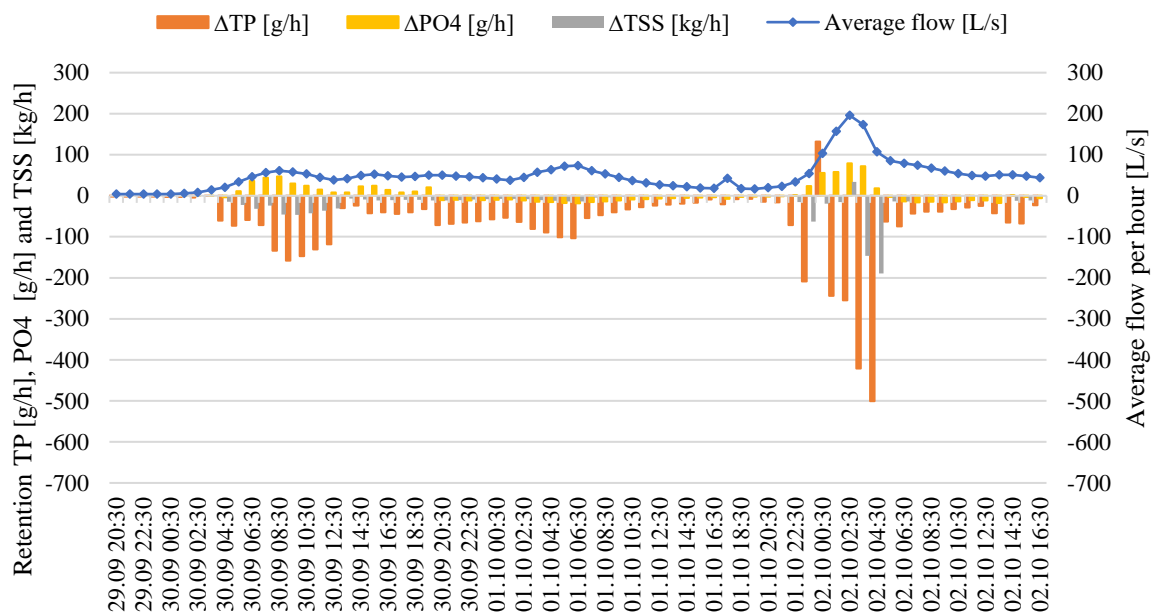


Figure 4-18 Retention of TP,  $\text{PO}_4^{3-}$  and TSS in Pond 1 from 29<sup>th</sup> of September to 2<sup>nd</sup> of October 2017.

In general, negative retentions of  $\text{PO}_4^{3-}$  dominated in Pond 2 (Figure 4-19). The greatest wash-out situation was during the last peak and had a size of -37  $\mu\text{g PO}_4^{3-}/\text{h}$ . TP showed a greater tendency for negative retention than positive retention. Retention varied for both TP and TSS from -283 g TP/h to 144 TP/h, and from -291 kg TSS/h to 110 kg TSS/h.

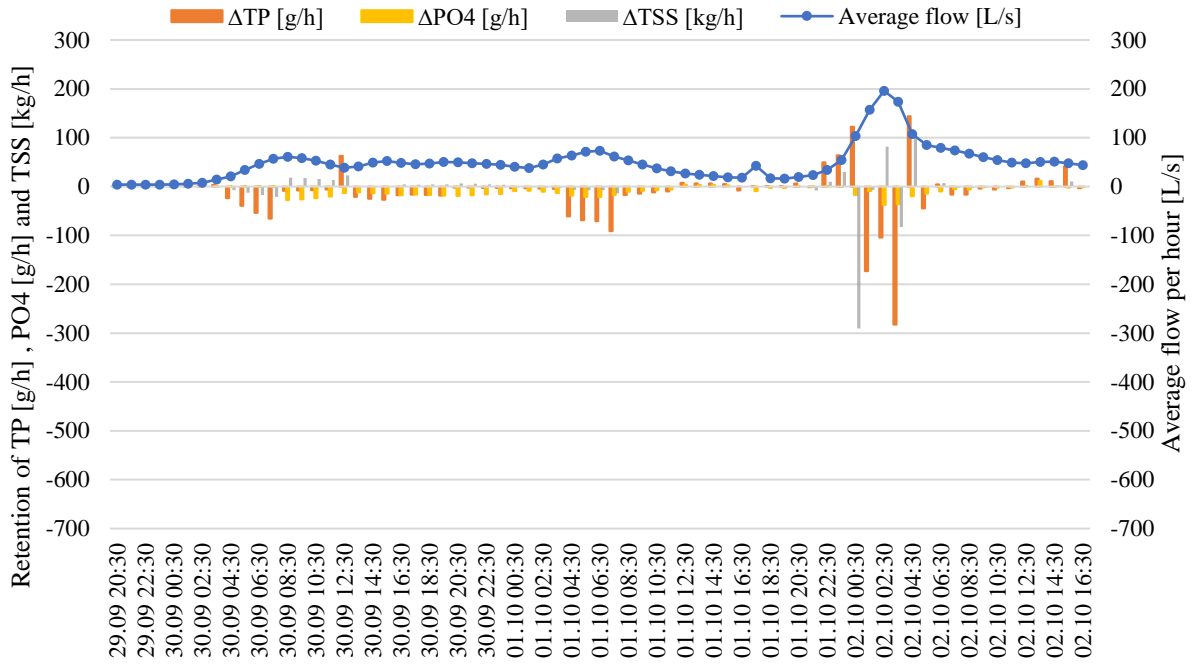


Figure 4-19 Hourly retention of TP, PO<sub>4</sub><sup>3-</sup> and TSS in Pond 2 during Storm A.

Retention of Pond 1 and 2 combined showed the wetland to release TP, TSS and PO<sub>4</sub><sup>3-</sup> most of the time (Figure 4-20). The greatest negative retention was observed during the last peak, showing a maximum of -704 g TP/h and -310 kg TSS/h. TSS was never observed greater than -50 kg TSS/h. A 404% higher wash-out of TP and a 260% higher wash-out of TSS was observed during the greatest flow peak, compared with the two previous peaks. PO<sub>4</sub><sup>3-</sup> was retained during flow peaks and washed out in between peaks.

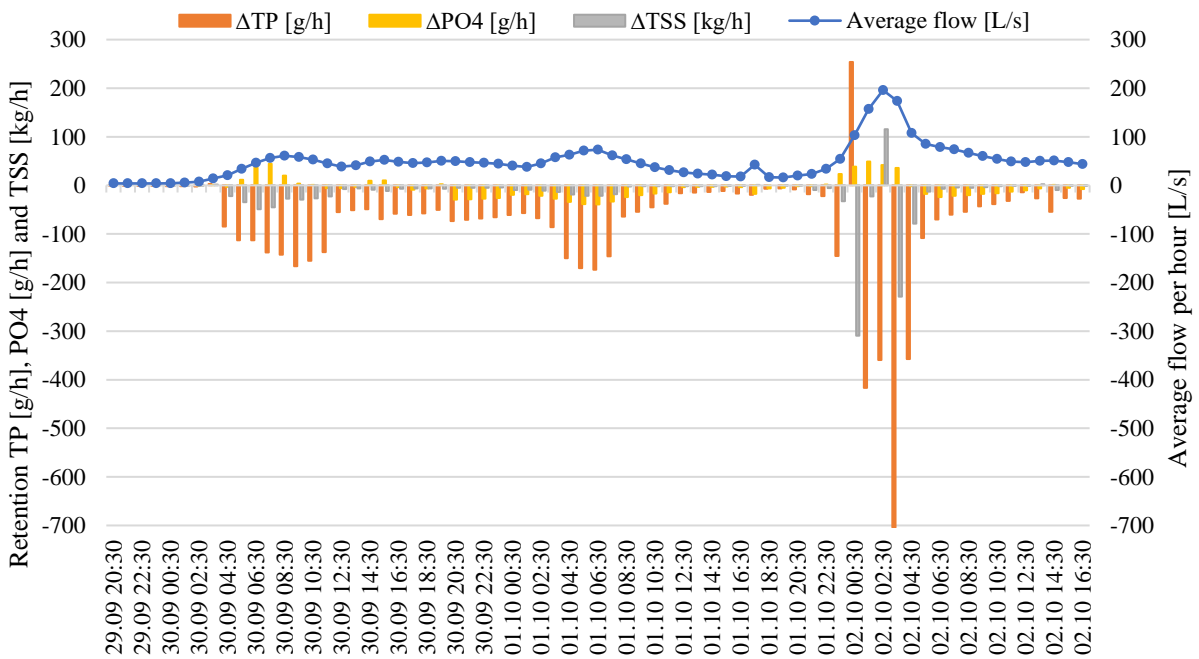


Figure 4-20 Hourly retention of TP, PO<sub>4</sub><sup>3-</sup> and TSS in the whole wetland during storm A.

Overall retentions, including area specific and relative retention, were mostly negative (Table 4-5).  $\text{PO}_4^{3-}$  in Pond 1 stood out as the only positive retention. But since Pond 2 washed out more than Pond 1 retained, the overall retention was negative.

Table 4-5 Overall retention of TP,  $\text{PO}_4^{3-}$  and TSS during Storm A.

	<b>Retention</b>	<b>Area specific retention</b>	<b>Relative retention</b>
<b>Pond 1</b>			
<b>TP</b>	-4 519 g	-1.95 g/m <sup>2</sup> ·day	-81%
<b>PO<sub>4</sub><sup>3-</sup></b>	257 g	0.11 g/m <sup>2</sup> ·day	12%
<b>TSS</b>	-980 kg	-0.42 kg/m <sup>2</sup> ·day	-84%
<b>Pond 2</b>			
<b>TP</b>	-816g	-0.35g/m <sup>2</sup> ·day	-8%
<b>PO<sub>4</sub><sup>3-</sup></b>	-591g	-0.26 g/m <sup>2</sup> ·day	-30%
<b>TSS</b>	-112 kg	-0.05 kg m <sup>2</sup> ·day	-5%
<b>Pond 1 and Pond 2</b>			
<b>TP</b>	-5 336 g	-2.31 g/m <sup>2</sup> ·day	- 96%
<b>PO<sub>4</sub><sup>3-</sup></b>	- 335g	-0.14 g/m <sup>2</sup> ·day	-15%
<b>TSS</b>	-1 092 kg	-0.47 kg/m <sup>2</sup> ·day	- 93%

#### 4.2.4. Statistical analysis

Regression analysis was performed on concentrations from the inlet of Pond 1 and outlet of Pond 2. Concentration parameters were analysed, since mass fluxes were calculated using flow and will therefore always have a positive correlation. Hence concentrations have been analysed in an attempt to bypass this connection.

Table 4-6 Results from regression analysis performed on phosphorus and suspended solid concentrations and average flow during Storm A.

	R <sup>2</sup>	Significance	P-value	n
Inlet of Pond 1				
TP [ug/L] vs. Average flow [L/s]	0.60	Yes	1.2*10 <sup>-10</sup>	48
TP [ug/L] vs. PO <sub>4</sub> <sup>3-</sup> [ug/L]	0.47	Yes	6.3*10 <sup>-8</sup>	48
TP [ug/L] vs. TSS [ug/L]	0.74	Yes	4.0*10 <sup>-15</sup>	48
TSS [mg/L] vs. PO <sub>4</sub> <sup>3-</sup> [ug/L]	0.19	Yes	0.001	48
Outlet of Pond 2				
TP [ug/L] vs. Average flow [L/s]	0.69	Yes	4.4*10 <sup>-10</sup>	36
TP [ug/L] vs. PO <sub>4</sub> <sup>3-</sup> [ug/L]	0.14	Yes	0.02	36
TP [ug/L] vs. TSS [ug/L]	0.61	Yes	1.7*10 <sup>-8</sup>	36
TSS [mg/L] vs. PO <sub>4</sub> <sup>3-</sup> [ug/L]	0.14	Yes	0.02	36

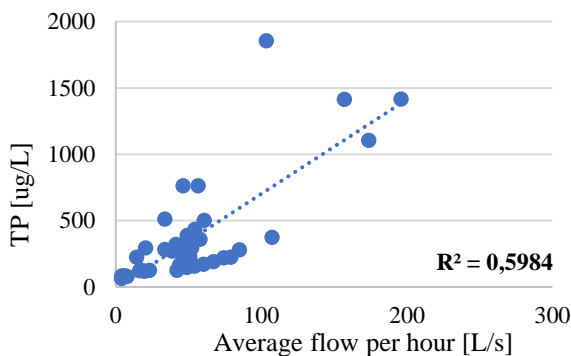


Figure 4-21 Scatter plot of TP and average flow for the inlet of Pond 1 during storm A.

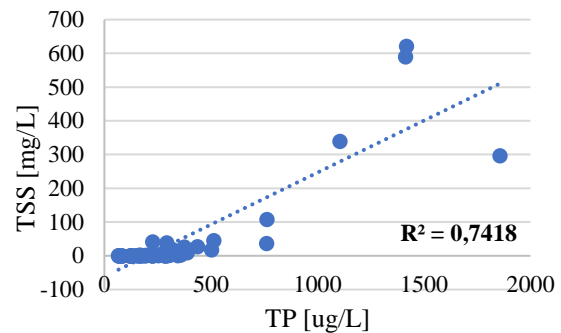


Figure 4-22 Scatter plot of TSS and TP for the inlet of Pond 1 during storm A.

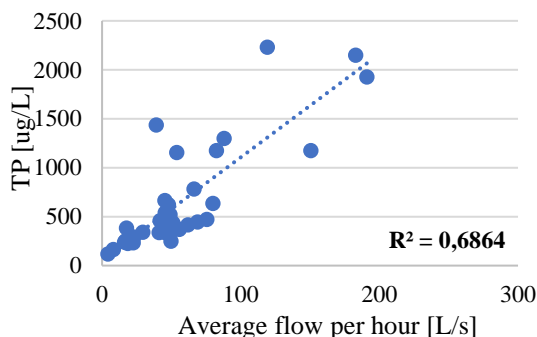


Figure 4-23 Scatter plot of TP and average flow per hour for the outlet of Pond 2 during storm A.

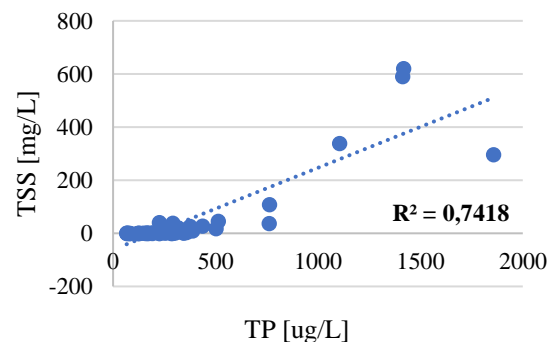


Figure 4-24 Scatter plot of TSS and TP for the outlet of Pond 2 during storm A.

Scatter plots of PO<sub>4</sub><sup>3-</sup> versus TSS, and TP, are presented in “Appendix D. Scatterplots”.



### 4.3. Storm B

A total of 66 water samples were collected and analysed for TP,  $\text{PO}_4^{3-}$  and TSS. The automatic samplers were started 03:00 at the 10<sup>th</sup> of May and stopped 04:00 at the 11<sup>th</sup> of May 2018.

#### 4.3.1. Hydrological load

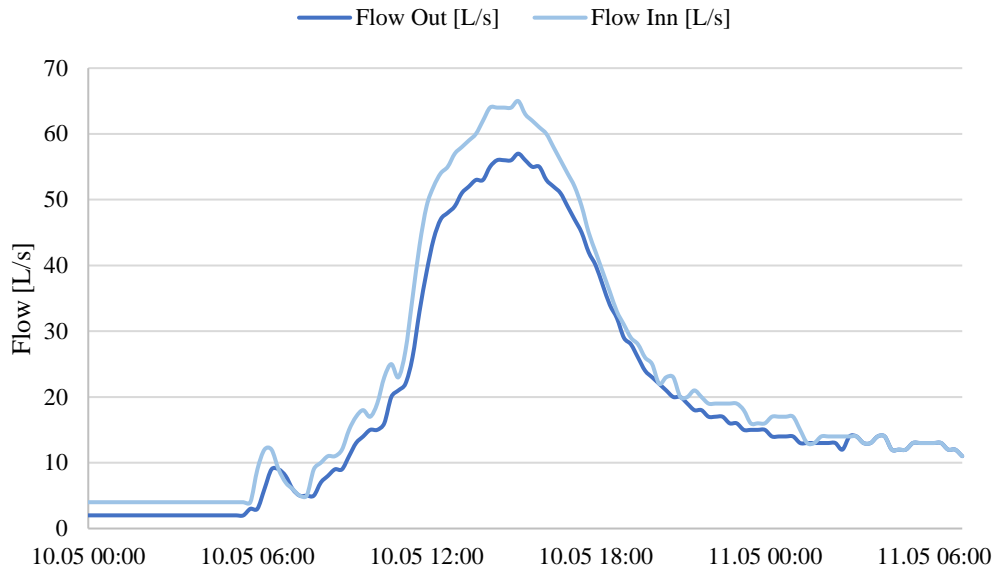


Figure 4-25 Hydraulic load between 03:00 at the 10<sup>th</sup> of May and 04:00 at the 11<sup>th</sup> of May 2018 measured by the flowmeters situated at Pond 2.

The flowmeters situated in the wetland monitored flow every 15 minute during the storm. Inlet measurements were in general greater than outlet measurements (Figure 4-25), indicating a rising water level. A small peak was observed around 07:00 followed by the main peak around 16:00. The flow went from 2 L/s to 57 L/s.

#### 4.3.2. Concentration variations

Concentration variations for the inlet of Pond 1, inlet of Pond 2 and outlet of Pond 2 are presented in graphs below. Average flow is plotted in a separate axis for presentation purpose.

Two clear concentration peaks were observed (Figure 4-26). The first peak occurred at 08:00 only one hour after the precipitation began. Measured concentrations presented a 4359% TP increase, a 5025% TSS increase and a 4489%  $\text{PO}_4^{3-}$  in one hour. The next measurement fell drastic for both TP and  $\text{PO}_4^{3-}$ . The second peak increased over five hours and had lower concentrations for TP and  $\text{PO}_4^{3-}$  than the first peak, while TSS was greater during the second peak.  $\text{PO}_4^{3-}$  decreased as the flow rose during the second peak.

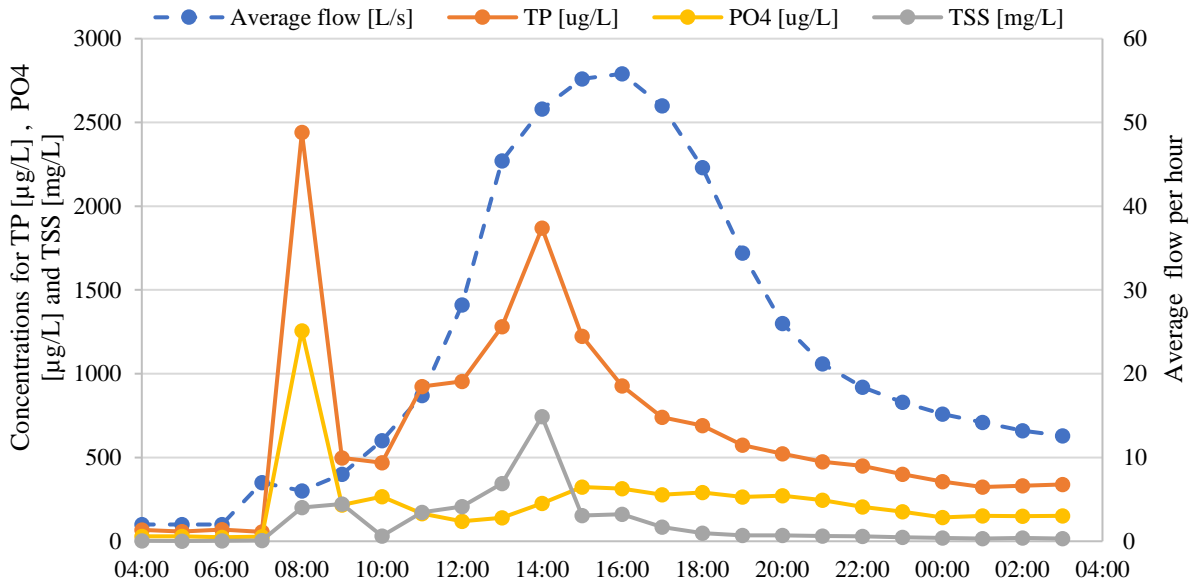


Figure 4-26 Concentrations measured at the inlet of Pond 1 and average flow during Storm B.

18 samples were collected and analysed for the inlet of Pond 2 (Figure 4-27). The composite samples were taken over a period of 1.5 hour. A small peak in TP and  $\text{PO}_4^{3-}$  can be observed at 10:00, three hours after precipitation started. Increased TSS is first observed at 13:30, simultaneous as the highest concentrations were observed. Final peaks for both TP and  $\text{PO}_4^{3-}$  were observed at 00:00.

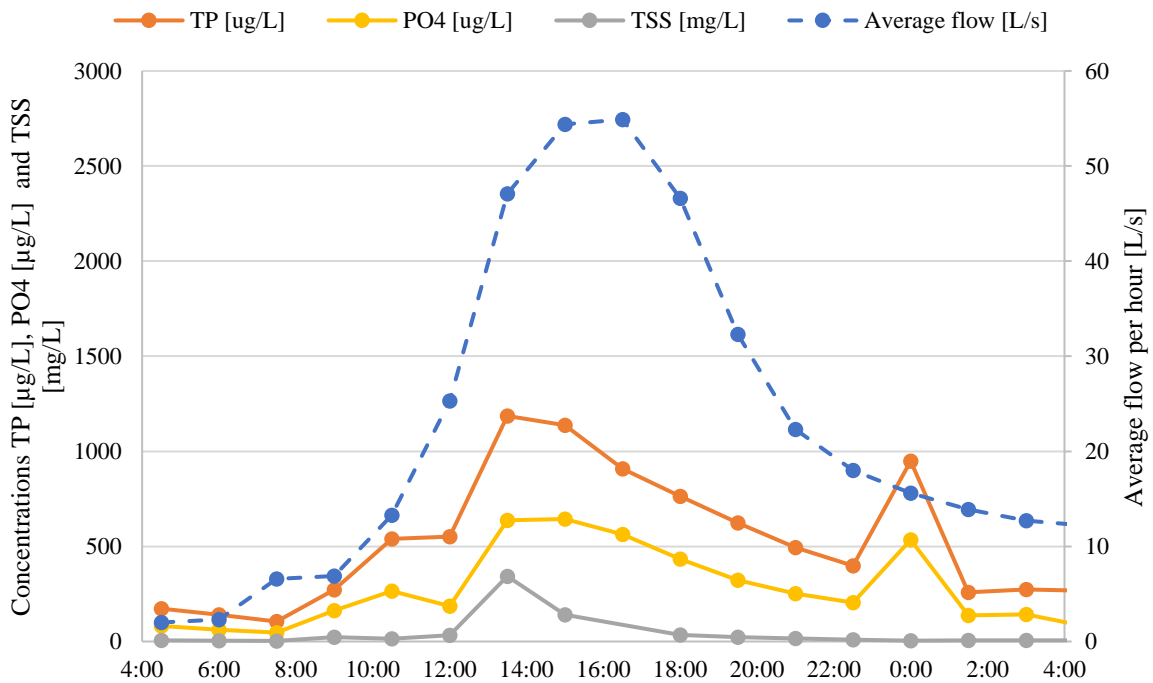


Figure 4-27 Concentrations measured at the inlet of Pond 2 and average flow during Storm B.

24 samples were collected at the outlet of Pond 2 (Figure 4-28). A distinct TP peak was observed 09:00, followed by a second TP peak at 14:00. Both TP peaks were accompanied with increased TSS.  $\text{PO}_4^{3-}$  does not follow the same pattern as TP or TSS. A stable increase for  $\text{PO}_4^{3-}$  was observed before rising drastically at 15:00.  $\text{PO}_4^{3-}$  later showed a stable decrease.

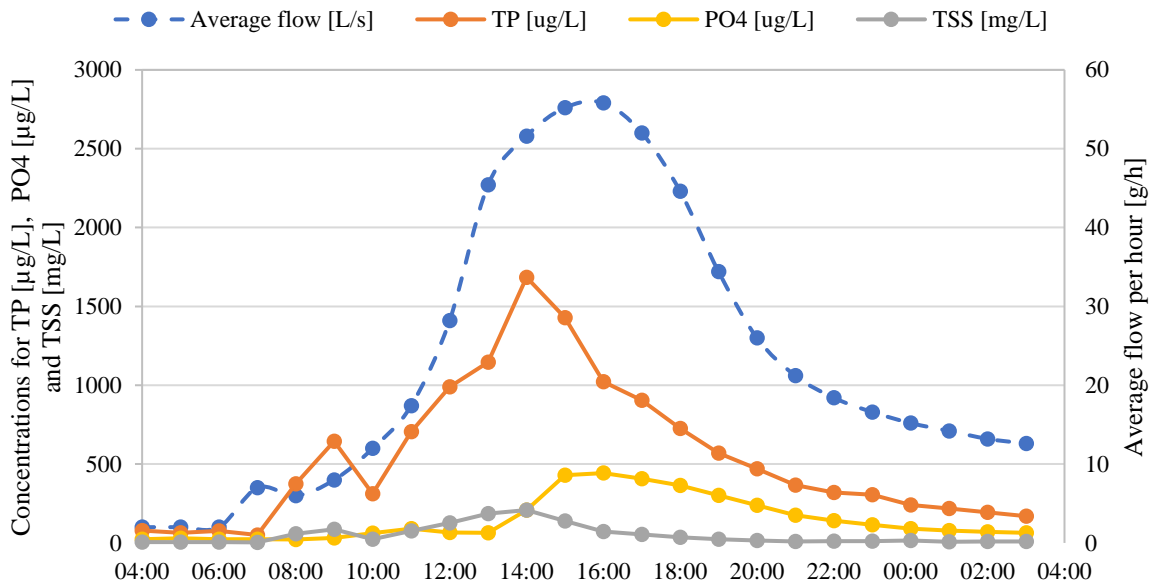


Figure 4-28 Concentrations measured at the outlet of Pond 2 and average flow during Storm B.

Conductivity, pH (Figure 4-29) and nitrate were analysed by Espen Enge (UiS) and determined with an ion- selective electrode (Enge, E.). Data for conductivity and nitrate are presented in Appendix A.

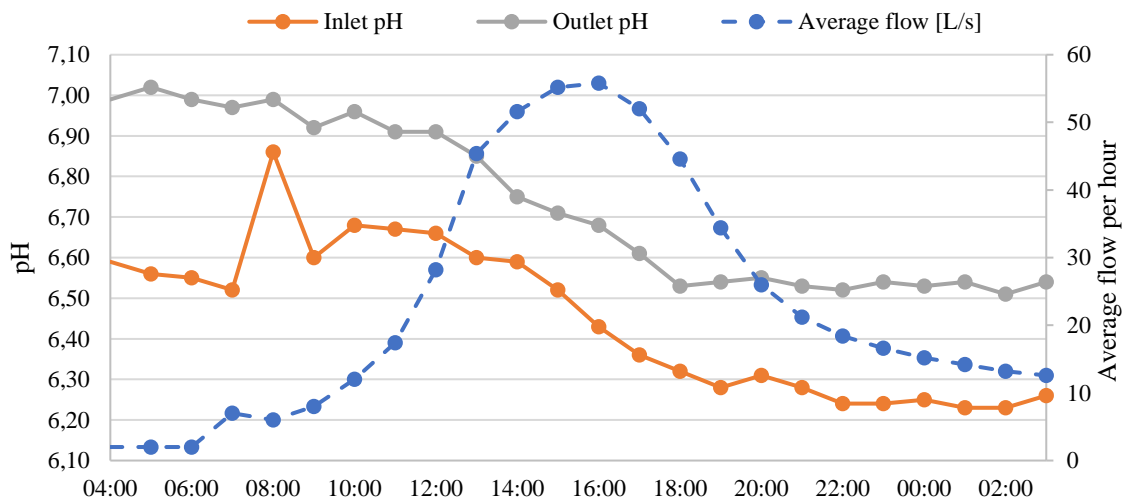


Figure 4-29 Change in pH measured for the inlet of Pond 1 and the outlet of Pond 2 during storm B and average flow per hour.

Measurements showed generally higher outlet pH than inlet pH, but both were reduced as waterflow increased. Outlet pH decreased with 0,46, while inlet pH decreased with 0,35.

### 4.3.3. Retention

Hourly retention was determined for Pond 1, Pond 2 and the whole wetland. Determined hourly mass flux for the outlet was subtracted from the hourly inlet mass flux to measure retention of the parameters.

Pond 1 had a trend of positive TP and TSS retention, and negative  $PO_4^{3-}$  retention (Figure 4-30)

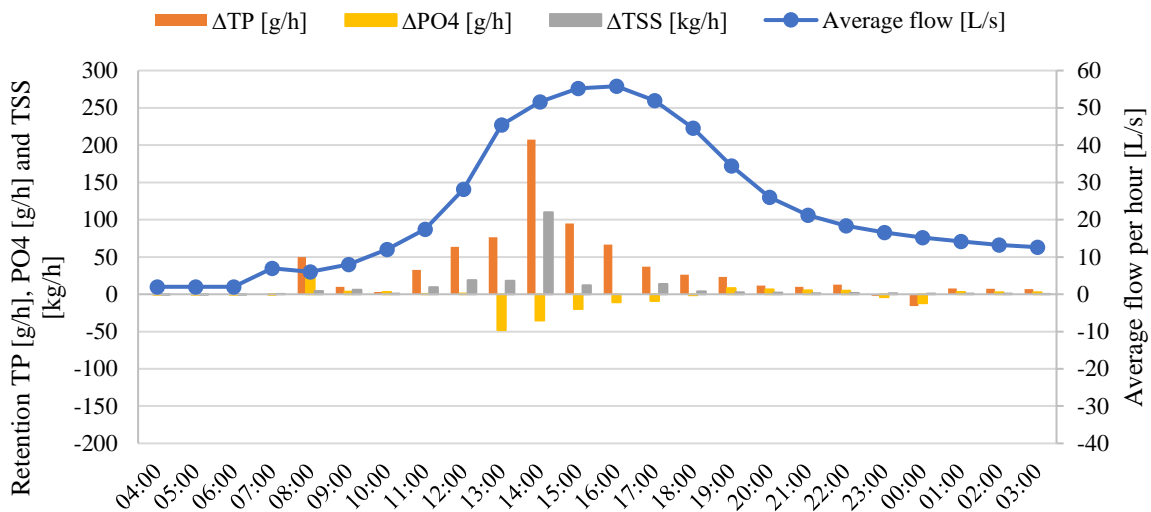


Figure 4-30 Hourly retention of TP,  $PO_4^{3-}$  and TSS in Pond 1 during Storm B.

Pond 2 shows the opposite trends of Pond 1, with negative TP and TSS retentions and positive  $PO_4^{3-}$  retentions.

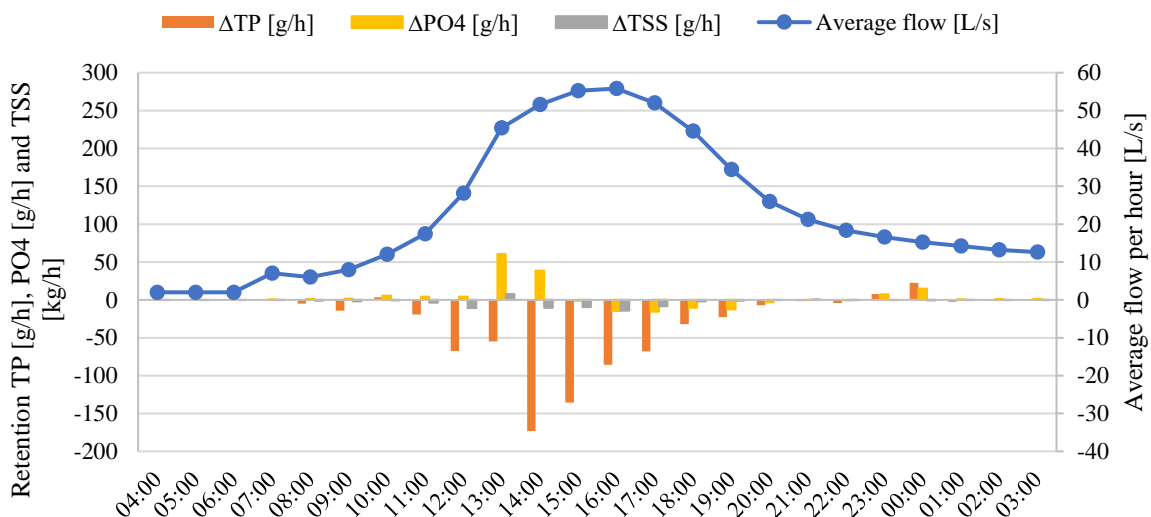


Figure 4-31 Hourly retention of TP,  $PO_4^{3-}$  and TSS in Pond 2 during Storm B.

The whole wetland experienced in general positive retention from precipitation started until 15:00 (Figure 4-32). The greatest hourly retention for TP and  $PO_4^{3-}$  was at 08:00, and was measured to 44.6 g TP/h and 26.7 g  $PO_4^{3-}$ /h. A negative TSS retention was never observed

during the storm, contrary to TP and  $\text{PO}_4^{3-}$ . Negative retentions for TP and  $\text{PO}_4^{3-}$  were observed from the flow peak at 15:00 to 19:00. After 19:00, the wetland had a stable positive retention for all three parameters.

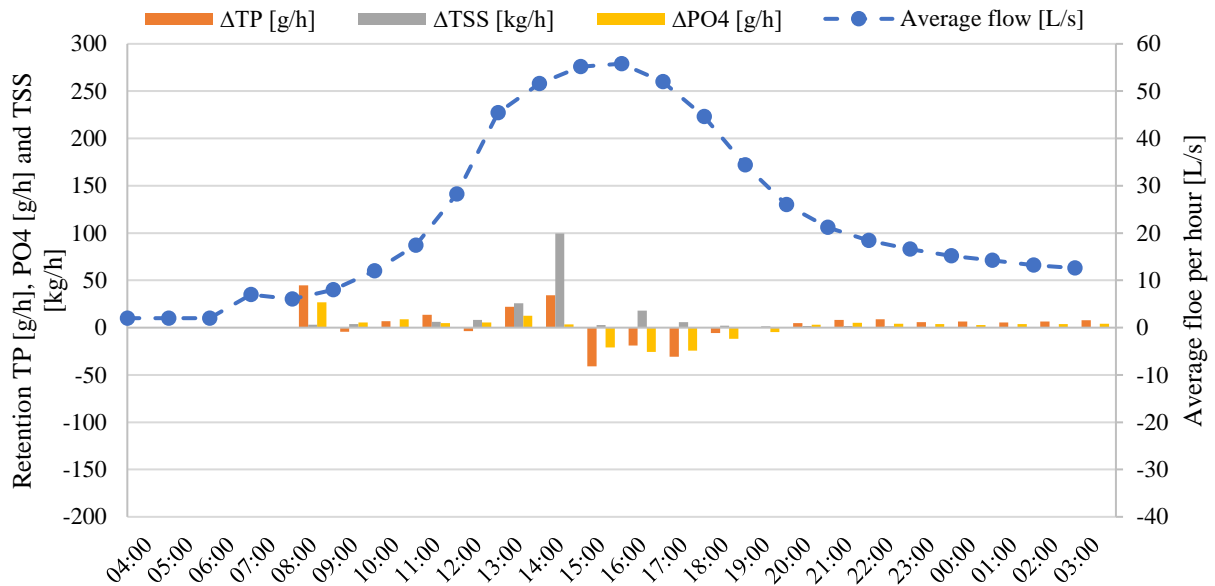


Figure 4-32 Retention of TP,  $\text{PO}_4^{3-}$  and TSS in the whole wetland.

Leikvollbekken had an overall positive retention for all three parameters during Storm B (Table 4-7).

Table 4-7 Area specific and relative retention for TP,  $\text{PO}_4^{3-}$  and TSS determined for Storm B.

	Retention	Area specific retention	Relative retention
<b>Pond 1</b>			
<b>TP</b>	728.7 g	0.90 g/m <sup>2</sup> ·day	42%
<b>PO<sub>4</sub><sup>3-</sup></b>	-73.9 g	-0.09 g/m <sup>2</sup> ·day	-15%
<b>TSS</b>	209.6 kg	0.26 kg/m <sup>2</sup> ·day	61%
<b>Pond 2</b>			
<b>TP</b>	-658.1 g	-1.1 g/m <sup>2</sup> ·day	-64%
<b>PO<sub>4</sub><sup>3-</sup></b>	83.9 g	0.1 g/m <sup>2</sup> ·day	15%
<b>TSS</b>	-58.3 kg	-0.1 kg/m <sup>2</sup> ·day	-58%
<b>Pond 1 and Pond 2</b>			
<b>TP</b>	70.6 g	0.05 g/m <sup>2</sup> ·day	4%
<b>PO<sub>4</sub><sup>3-</sup></b>	9.9 g	0.01 g/m <sup>2</sup> ·day	2%
<b>TSS</b>	183.7 kg	0.13 kg / m <sup>2</sup> ·day	54%

#### 4.3.4. Statistical analysis

Regression analysis was performed for concentrations at the inlet of Pond 1 and outlet of Pond 2 (Table 4-8). The same relationships were analysed for Storm B as during Storm A.

Table 4-8 Results from regression analysis performed on phosphorus and suspended solid concentrations and average flow during Storm B.

	R <sup>2</sup>	Significance	P-value	n
Inlet of Pond 1				
TP [ug/L] vs. Average flow [L/s]	0.22	Yes	0.02	24
TP [ug/L] vs. PO <sub>4</sub> <sup>3-</sup> [ug/L]	0.58	Yes	1.7 *10 <sup>-5</sup>	24
TP [ug/L] vs. TSS [ug/L]	0.54	Yes	4,3 *10 <sup>-5</sup>	24
TSS [mg/L] vs. PO <sub>4</sub> <sup>3-</sup> [ug/L]	0.04	No	0.37	24
Outlet of Pond 2				
TP [ug/L] vs. Average flow [L/s]	0.75	Yes	3.9*10 <sup>-8</sup>	24
TP [ug/L] vs. PO <sub>4</sub> <sup>3-</sup> [ug/L]	0.34	Yes	0.002	24
TP [ug/L] vs. TSS [ug/L]	0.83	Yes	4.8*10 <sup>-10</sup>	24
TSS [mg/L] vs. PO <sub>4</sub> <sup>3-</sup> [ug/L]	0.04	No	0.40	24

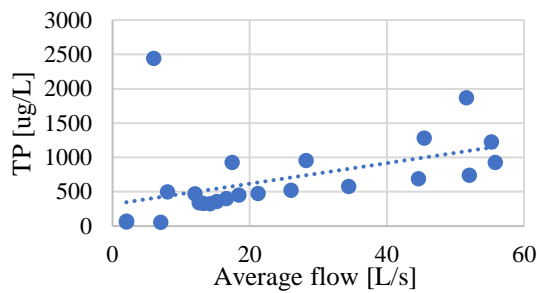


Figure 4-33 Scatter plot of TP and average flow for the inlet of Pond 1 during storm B.

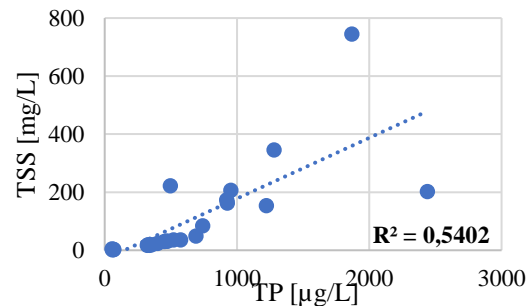


Figure 4-34 Scatter plot of TP and TSS for the inlet of Pond 1 during storm B.

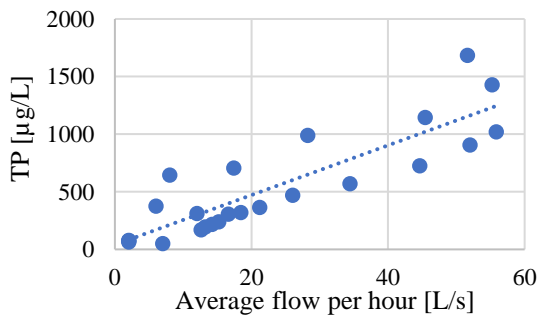


Figure 4-35 Scatter plot of TP and average flow for the outlet of Pond 2 during storm B.

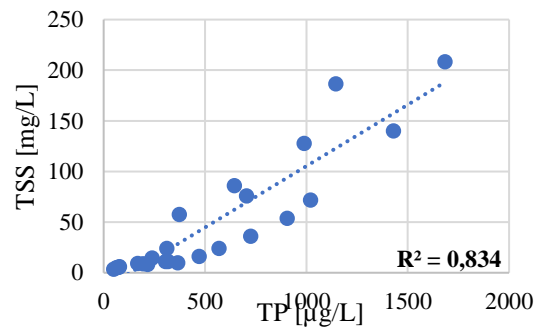


Figure 4-36 Scatter plot of TP and TSS for outlet of Pond 2 during storm B.

## 5. Discussion

The chapter is divided into four sections, starting with a section regarding phosphorus retention efficiency over the whole sampling period, based on the weekly samples. A detailed discussion of Storm A and Storm B follows, including comparison of the storms. The third section covers uncertainties in the thesis, and the last section involves thoughts about future aspects to study and future improvements of Leikvollbekken.

### 5.1. Phosphorus retention measured by weekly sampling

An overall positive relative TP retention of 7% was observed and is a lower retention compared to the estimated retentions in previous theses in this study, 31% (2016 - 2017) and 18% (2015 – 2017). The low relative retention may be a result of the sampling method used this year, opposed to previous theses. Weekly samples collected other years were mainly time dependent, while this year's samples were flow dependent. Consequently, the samplers collected more samples during storm peaks and thus had a larger fraction of storm peak water samples in the weekly composite samples. Therefore, the impact storm events had on Leikvollbekken have been better included in this year's retention efficiency. There may also have been more flow peaks during this study period, combined with many accumulated particles at the time of the peaks. A combination of high flow and accumulated particles cause wash-out of sediments, which often contain phosphorus, both suspended and rolling along the bed. High flow may also produce wash-out of accumulated soluble phosphorus.

A higher external P-load may be another explanation for the low relative retention. Relative retention is calculated by dividing retained kg by total phosphorus input, hence a higher input will give a lower relative retention, even if the wetland retains the same mass of phosphorus. The degree of phosphorus input in Leikvollbekken is mainly determined by how much fertilizer is spread on the fields. Large amounts of fertilizer added to the fields above the wetland increases the P-load into the wetland significantly, given that the farmers add more fertilizer than what is necessary for plant growth. Such practice may not be the case. The farmers in the area may be very precise, when calculating necessary amount of fertilizer. With that mentioned, there are other factors that affect how great phosphorus leaching will be and hence P-load. Fertilizers added to fields only hours before heavily precipitation may result in a high  $\text{PO}_4^{3-}$  concentration flush, since plants may not have absorbed  $\text{PO}_4^{3-}$ , leaving high amounts of  $\text{PO}_4^{3-}$  to run off.

Increased external P-loads over the years will not have the same influence on estimated amount of kgs retained, or on the area specific retention, as with the relative retention. These definitions of retention do not take P-input into account. Leikvollbekken had a positive retention of 11.9 kg and an area specific retention of 32 g/m<sup>2</sup>·year. These two estimations seem like likely retention values. Determined retention (kg) may be lower than the real retention due to one week monitored without an inlet samples, which was week 10. Retention calculations cannot be performed without an inlet sample, hence the overall retention may either be even more positive, or less positive. Weekly retentions were often around ±0.5 kg TP and ±1.5 kg TSS. The missed week may therefore be assumed to have had a limited effect on the total retention.

The area specific retention determined was almost twice as high as the year before. With that mentioned, area specific particulate phosphorus retentions of 26 – 71 g/m<sup>2</sup>·year have been estimated in other wetlands (B.C. Braskerud, 2002), indicating 32 g/m<sup>2</sup>·year to be a reasonable retention. A possible explanation for the difference, is different estimations of the wetland area and different area used in calculations. The area was found to be 655 m<sup>2</sup> in 2017 and 611 m<sup>2</sup> in 2018. A difference of 44 m<sup>2</sup> gives a difference of ±2 g/m<sup>2</sup>·year. The previous thesis in this study also estimated area specific retention over the total area of Leikvollbekken (Krahner & Kommedal, 2017). The results in this year's thesis have been calculated by dividing kg retained by the area of Pond 2, hence dividing the retention by a smaller area. These two factors combined are considered to explain the difference in the results in these two theses.

Particulate phosphorus was the only phosphorus fraction found to have a positive retention for the whole sampling period. Particulate retention therefore contributed with a high enough positive retention for Leikvollbekken to achieve a positive TP retention. Sedimentation in Leikvollbekken can therefore be viewed as an essential mechanism. Consequently, this supports previous statements of the importance of sediment removal. Previous theses have stated that Stavanger Municipality needs to remove sediments in Leikvollbekken. Pond 1 was filled with sediments after the winter (Figure 3-6), producing a small creak for water to flow, and thus creating higher velocity of the bulk flow, which again gives more resuspension and an assumed higher washout tendency. Maintenance with sediment removal was observed at the end of the sampling period (Figure 3-7). Unfortunately, the inlet sampler was not functioning the weeks post maintenance. Still the outlet sampler functioned, and outlet samples were analysed. Determined pTP concentration and mass flux the week post maintenance gave the lowest values during the sampling period, with 12 µg/L and 38 g/week respectively (Appendix B: Mass flux). TP measurements for the week was higher, 202 µg/L and 668 g/week (Appendix B: Mass flux),



with a high fraction of soluble phosphorus. Weeks following the record low values showed an average mass flux of 266 g/week, which is a significant reduction from 3894 g/week as an average for the weeks prior maintenance. Precipitation rates were generally low during the weeks post maintenance, resulting in an average low flow of 3 L/s. Consequently, the low flow may be a partial reason for the low particulate mass flux leaving the wetland and not solely sediment removal.

Overall negative retentions were observed for the soluble phosphorus parameters, both sTP and  $\text{PO}_4^{3-}$ . Accumulated soluble phosphate has therefore been released during the year. Consequently, this indicates that the mechanisms for internal phosphorus release must have been active in Leikvollbekken. Phosphate release from deteriorating plant matrix, microorganisms releasing phosphate from accumulated particulate phosphorus, iron phosphate solubilization or desorption due to pH shift are all possible mechanisms that can be responsible for such phosphate release. Fall and winter are known to be the seasons for plant deterioration, consequently releasing a lot of phosphate previously taken up by plants, and producing higher outlet concentrations. Another partial reason for no positive retention may be the sampling period, since the sampling period covered a limited period with growth, and hence biotic uptake may have contributed little to the overall retention. There would be some biotic uptake during early spring months. Still serious algae growth was first observed in the end of May 2018 (Figure 3-11), after the inlet of Pond 1 was out of function. Several weeks with assumed high rate of biotic uptake were therefore not included in the overall retention. Consequently, yearly soluble phosphorus retention is probably more positive than what is found in this study. Even though the overall soluble phosphorus retention was negative, some weeks were determined to have a positive retention. These weeks may be dominated by precipitation and sorption of soluble phosphorus, or the positive retention may be a result of the dilution effect when the inlet reaches Pond 2. A dilution effect may be probable due to the low positive retentions, which indicates small concentration differences between the inlet and outlet. No pH measurements were performed during the weekly monitoring, but the pH measurements during Storm B showed the outlet to have a higher pH compared to the inlet (Figure 3-10). If this observation is representative for the whole year, the pH change could affect the soluble phosphorus retention efficiency. Photosynthesis, as well as  $\text{CO}_2$  saturated soil water flowing into Leikvollbekken (Kommedal, R.), is considered to be the reason for the shift in pH. Both photosynthesis and input of  $\text{CO}_2$  saturated water lead to  $\text{CO}_2$  leaving the water, creating a shift in the bicarbonate equation and producing a higher pH at the outlet. A consequence of such pH shift may be

desorption of phosphate from particles when the particles are transported towards the outlet. Precipitation may also be less favourable by the outlet of Leikvollbekken, since a higher pH will make the precipitates more soluble. Therefore, the negative soluble phosphorus retention may be partly due to desorption and solubilization.

A significant relationship was found between retention of TP and TotFe. The relationship indicates that iron plays an essential role in Leikvollbekken. Weekly particulate iron concentrations varied more than the soluble iron concentrations. Further regression analysis showed retention of both particulate ( $p < 0.05$ ,  $R^2 = 0.73$ ) and soluble ( $p < 0.05$ ,  $R^2 = 0.46$ ) (Figure 5-1) parameters to be significant. The significant relationship between the soluble parameters was removed when an assumed outlier was removed from the data set, prior to the repetition of regression analysis was performed ( $p = 0.06$ ,  $R^2 = 0.13$ ) (Figure 4-12). Therefore the previously found significance can be seen as not significant.

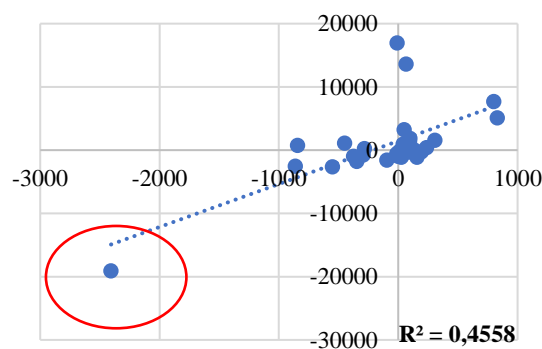


Figure 5-1 Scatter plot for retention of sTP and retention of sTotFe, before removal of what is considered to be an outlier (red circle).

Lack of a significant relationship between the soluble fractions may indicate that precipitation of  $\text{FePO}_4$  does not dictate retention of soluble phosphorus, since precipitation would cause retention in both soluble iron and phosphorus simultaneously. A significant relationship for the particulate, but not the soluble, may illustrate that retained phosphorus in connection with iron is already bound to iron when it enters the wetland, and is removed by sedimentation. This is interesting since Leikvollbekken experienced an overall positive pTP retention, even though 60 kg TSS was washed out. Suspended solid analysis performed from mid-January showed a tendency for retention of inorganic solids during washout of TSS (Figure 4-9). This combined with the significant relationship of pTP and pTotFe may indicate that much of the retained pTP is bound to iron, forming an inorganic compound.

Another interesting side of the TSS mass-balance is the high fraction of washed out VSS. Suspended organic matter is in general larger in size than inorganic particles and will

consequently have larger possible adsorption area. A reason for the overall negative  $\text{PO}_4^{3-}$  retention may therefore partly be adsorbed  $\text{PO}_4^{3-}$  washed out with VSS. The number of weeks with VSS measurements were limited, and any significant relationships found can therefore not be seen as proof due to a too small data set. Still,  $\text{PO}_4^{3-}$  and TSS concentrations had no significant relationship ( $p=0.37$ ,  $R^2=0.03$ ), thus indicating that the idea of VSS adsorption as a main mechanism for  $\text{PO}_4^{3-}$  may not be valid. With that mentioned, there was a significance relationship between TP and TSS retention ( $p<0.05$ ,  $R^2=0.16$ ). The relationship had a limited  $R^2$ , which states that the relationship is not linear. A significant relationship between these two parameters was predicted, since particulate phosphorus makes up a large fraction of TP, and particulate phosphorus is a part of TSS. Still, the regression analysis showed a significant relationship between the retention of the two parameters, supporting sedimentation of TSS to be a relevant mechanism for TP retention in Leikvollbekken. A significant relationship was also found between FSS and pTP ( $p<0.05$ ,  $R^2=0.37$ ), but not for TSS and pTP ( $p>0.05$ ,  $R^2=0.07$ ), thus supporting the idea that FSS sedimentation plays an important role. Still, it is worth mentioning that only 11 weeks were monitored for FSS and that the concentrations are based on different flowrates. Therefore, a conclusion cannot be made solely based on the data obtained in this study.

When discussing detailed retention mechanisms, like precipitation or adsorption, limitations of the method used are worth mentioning. A “black box”-analysis is not suitable to investigate microscale mechanisms. Still, the results of this “black box”-analysis contribute with knowledge about retention mechanisms and can be used as a pointer for further studies.

Water input, and hence flow, is obviously vital when exploring a wetland's ability for phosphorus retention. Higher flow transports more and larger particles, due to higher water velocity (Figure 2-7). Consequently, this makes washout situations more probable under high flow. The relationship of flow and inlet/outlet concentrations are complex. A specific flow, of for instance 75 L/s, does not produce a washout situation in a wetland every time. The number of accumulated particles is an important factor. Heavy rain producing high flow can cause great washouts, but flow peaks following that first flow peak may not wash out equal numbers of particles. This is due to less particles being present in the wetland, and means that the samples are dependent, as stated in subchapter “3.8 Statistical method”. Determinations of exact flow thresholds are therefore difficult. When analysing the two storm events, this sampling dependence became apparent. TP concentrations rose and declined in a clear, almost linear pattern, according to change in flow and showed the relationship between flow and

concentrations. Concentration plots also showed that a specific flow of for example 50 L/s during an increase period can have a higher concentration compared with the 50 L/s measurement during the decreasing period followed, due to less accumulated phosphorus left in the wetland. Scatter plots of TP concentrations and flow did not show this obvious connection (Figure 4-21, Figure 4-23, Figure 4-33, Figure 4-35). The plots seemed more random and chaotic, and showed at the same time a degree of relationship, as the significance levels supported. By only plotting the period with increased or decreased flow, the scatterplots showed a distinct relationship between TP and flow. Consequently, statistical analysis of flow and concentrations over a large timescale (weeks, months or years) will give a poor presentation of the connections.

## 5.2. Storm events

A common factor for both storms monitored, is the limited time for the concentrations to reach maximum before declining again. All concentration peaks lasted less than 7 hours, some even as short as 1 hour, as experienced for Storm B. Consequently, sampling techniques may miss these peaks, if the peaks are not considered and timed perfect. The rapid concentration peak observed at the inlet of Storm B is a good example. Here, TP and  $\text{PO}_4^{3-}$  concentrations increased by 4359% and 4489% respectively in one hour. A limited number of grab samples during the storm would not have produced the same concentration change as presented in the results in this thesis, since the samples may not have been taken at the necessary time for capturing the peaks. High frequency grab samples on the other hand, would most likely have been a better representation, but such sampling techniques require much manpower. Maniquiz et al. (2011) studied the retention efficiency of a CW, both under storm and base flow, based on grab samples taken during “daytime” under baseflow conditions and taken “within 6-12 h time frame for each storm”. The study concluded the efficiency to be higher during storm events due to low outlet concentrations post storms. Questions arise on how frequent the grab samples were collected, or if the storm samples consisted of only two inlet/outlet samples, with one at the beginning and one at the end of the storm. The study concluded based on reduction in concentrations following the storm, and does not take the mass flux into account, and thus disregards phosphorus released from the wetland during the storm. A lower concentration can be observed after heavy rain, as discussed in the section with sampling dependency, and may be the reason for the assumed higher removal efficiency. Yet, washed-out mass fluxes will still influence the recipient because the washed-out phosphorus previously accumulated in the wetland enters the recipient, hence producing a limited “real” CW efficiency. The study may therefore be

considered an example of how grab samples can give an incorrect picture of a wetland's performance. If the study included multiple, high frequency grab samples, a better monitoring of the concentration change would have been performed. Still, the study concludes solely based on reduced concentrations and will therefore not take phosphorus load into account, which is considered more correct for assessing eutrophication potential (Smil, 2000).

Other studies have used automatic samplers, both time and flow proportional, to achieve a better sampling profile. Dzakpasu et al. (2015), for example, stated 60% particulate phosphorus retention in a CW, but the conclusion was based on weekly composite samples with 12h between each subsample. Time proportional composite samples can give a good representation if the sampler is programmed with a high enough sampling frequency. Automatic samplers with 12h sequences may produce composite samples where concentration peaks are grossly underestimated, since a concentration peak can last less than 12h. Several samples can be collected without any of them representing a storm peak, if any should occur. Therefore, a study based on weekly time proportional samples can underestimate the wash-out situations that can occur during heavy rain. Still, the sampling technique can give a relatively good representation if the samples are collected over short intervals and with high enough frequency. Time dependent automatic sampling was used in this thesis for storm monitoring, not in the weekly sampling. The samplers were, most of the time, programmed to take 4 subsamples each hour every 15 minutes, and were therefore considered to have a high enough frequency for the composite sample to be a good representation of the mass flux passed for the respective hour.

Raisin and Mitchell (1995) stated flow proportional sampling to be a better method for wetland monitoring due to the effect heavy rainfall has on nutrient release in catchment areas. Flow proportional samplers correct for the underestimation of storm flow samples by collecting after a given pulse of water. Consequently, this provides correct concentrations with respect to the mass flux passed over a given time interval, if the total amount of water passed is multiplied with the determined concentration. Even though flow proportional sampling is regarded as a better technique for including storm peaks in long term monitoring, the method demands specific knowledge to optimize the technique. Predictions of expected flow levels are essential when programming a flow proportional automatic sampler. This is the case because the programmed pulse needs to be large enough to limit base flow samples, but also small enough for base flow samples to be included.

An interesting aspect of storm flow versus base flow, is how different flow affects the hydraulic path and retention time. In general, higher flow results in shorter hydraulic retention time, but

the hydraulic path is also affected. Water flows over larger areas of Leikvollbekken during base flow, while it flows the shortest distance during storm events producing a channeling effect (Figure 5-2). Consequently, using less of the CW's volume during storms, causes the hydraulic retention time to decrease greatly. This phenomenon was observed by direct observation during Storm A (Kommedal, R.). A heavy stream flooded through Pond 2, bending plants present and flowing over them.

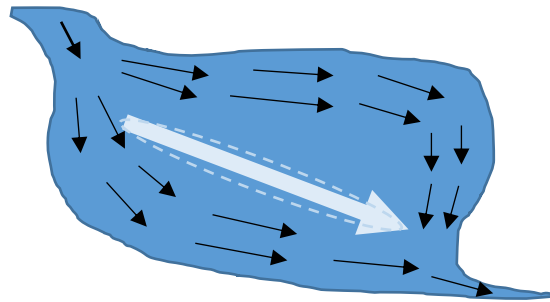


Figure 5-2 Sketch of the different hydraulic paths during base flow (black arrows) and storm flow (light blue arrow). The stripped area represents the area where most of the water will travel, hence reducing the wetland area dramatically.

### 5.2.1. Storm A

In general, negative retention was measured for Leikvollbekken during Storm A. Thus, supporting the hypothesis of high flow causing wash-out situations. Overall hourly retentions (Figure 4-20) show that the degree of negative TP retention follows the same pattern as the flow peaks. Pond 2 was expected to wash out accumulated phosphorus. This did occur, but Pond 1 washed-out more particles than Pond 2, 81% and 8% respectively. A possible reason for the difference in particle retention may be the channeling effect (Figure 5-2) forcing plants in Pond 2 towards the sediment, consequently sheltering particles from resuspension. Another possible reason for the low wash-out may partly be due to the water bypassing Pond 2 (Figure 4-14), hence not increasing the flow further in Pond 2, as well as producing a dilution effect approximately 10 meters before the sampling point. Drops in TP and TSS concentrations were observed simultaneous with the bypass situation, before increasing slightly (Figure 4-17), and so can be viewed as support of the idea of dilution. Still, the bypassing may not have influenced the mass flux greatly, since it only lasted a short period. Prior to Storm A, Pond 1 had a relatively larger number of particles and did not have any plants to hinder particle resuspension to the same degree as Pond 2. The preferred path for the water in Pond 1 (Figure 3-3) was also more in the form of a channel than a pond, as Pond 2. Consequently, a specific flow in Pond 1 will produce a higher water velocity and thus a higher degree of resuspension, compared with equal flow in Pond 2.

Samples measured at the inlet of Pond 1 showed that  $\text{PO}_4^{3-}$  concentrations was not influenced by flow to the same extent as TP and TSS (Figure 4-15). The two flow peaks resulted in approximately same  $\text{PO}_4^{3-}$  concentrations even though the last flow peak was around 2.5 times higher than the first. A possible explanation is the increased amount of water, which will dilute  $\text{PO}_4^{3-}$  concentrations to some extent. This dilution may be a theoretical explanation but is not considered to have had a significant effect on the concentrations. Another more probable reason for this may be that heavy rain on soil above Leikvollbekken mobilizes  $\text{PO}_4^{3-}$  in a steady manner and reaches a maximum leaching rate, where extra water not will result in higher leaching rates. And if a slightly higher leaching rate may occur, dilution caused by more water can reduce the rise in concentration, making the concentration unchanged.

A surprising finding was for Pond 1 to have an overall positive retention of 12%  $\text{PO}_4^{3-}$  despite the high flow. Leikvollbekken accumulated water during the high precipitation rates (Figure 4-14), thus elevating the water level in the wetland. Overflow from the preferred water creak (Figure 3-3) on to the dense vegetation area, described as the saturated area in the site description, may therefore be part of the reason for the positive retention. Most of the water flowing into Pond 1 will be transported directly to Pond 2 with high velocity and wash out phosphorus stored in the creak, while the overflow will “activate” the whole wetland. The water flowing over will have an increased area up to  $\sim 1020 \text{ m}^2$  and thus a higher hydraulic retention time. A higher hydraulic retention can increase the amount of  $\text{PO}_4^{3-}$  taken up by plants or adsorbed to surfaces. These mechanisms can be considered to have limited effect during high flow velocities, since contact time between  $\text{PO}_4^{3-}$  and surfaces would be limited. Water, which flowed over to the saturated wetland area, may have experienced a long enough retention time for the mechanisms to work. Another possible reason for the positive  $\text{PO}_4^{3-}$  retention may be reactions between iron and  $\text{PO}_4^{3-}$ , as Pond 1 consist of areas with viewable iron (Figure 3-10). A flow peak into the wetland can enrich the area with oxygen, hence producing a favourable redox potential for ferric phosphate precipitation. pH measurements during Storm B showed that the pH decreased as the water load increased. No pH measurements were performed during Storm A. Still, a more acidic environment would in theory support the idea of ferric phosphate precipitation, since the reaction favours acidic conditions.

Pond 2 washed-out 591 g  $\text{PO}_4^{3-}$ . There is no obvious wetland area in Pond 2, which can be “activated” by overflow as in Pond 1. Elevated water levels will instead cause a bypass situation, where water flows directly from the inlet to the outlet, bypassing Pond 2. Such water movement was observed during the storm. Consequently, the mechanisms for  $\text{PO}_4^{3-}$  retention

is assumed to have had too limited time to function. A factor worth mentioning, is a manhole, which pumps out water from an unknown source during heavy precipitation. Water from this manhole was observed to flow into the creak before the sampling point for the outlet of Pond 2. Since the source of the water is unknown, we cannot exclude the possibility for it to contain  $\text{PO}_4^{3-}$ . Consequently, this may produce a higher outlet concentration and thus a higher estimated wash-out situation. Whether or not the water contained large amounts of  $\text{PO}_4^{3-}$  cannot be determined, since no samples were collected from the manhole. Still, negative  $\text{PO}_4^{3-}$  measurements support the hypothesis of wash-outs during high flow.

### 5.2.2. Storm B

Storm B differed from Storm A in both degree of precipitation and duration, with 3.8 times lower maximum flow and only 24 h duration. Still, the storm had much of the characteristics of “the perfect storm”, with longer dry weather periods prior to heavy precipitation.

Extreme TP and  $\text{PO}_4^{3-}$  peaks were observed a short hour after precipitation (Figure 4-26). Both peaks had a concentration more than 430 times larger than the previous sample and were initiated by a relative low flow peak, approximately 8 L/s. Such low flow measurements would normally not result in such intense concentration peaks, but the fields above Leikvollbekken had experienced limited amount of precipitation over two months at the same time as regular additions of fertilizer. The theory is that phosphorus, mostly as  $\text{PO}_4^{3-}$ , had accumulated over time, hence leaving plenty ready to be mobilized by water and flushed into Leikvollbekken. This type of flush corresponds to a “first-flush”. A sampling method used when analysing storm events have been grab samples at the first flush, considering the concentration to be the highest peak for the storm. The method would have been more suitable for Storm B than Storm A, since the first flush into the wetland was the highest concentration peak for Storm B. A study that solely is based on this sampling method may therefore underestimate mass fluxes, if the storm is not a “perfect storm”. Kohler et al. (2004) is an example of such a study, reporting a 74% relative phosphorus retention. Another observation made was that the first flush for the inlet and outlet of Pond 2 was significantly lower than the concentration peak following. Consequently, a first flush grab sample would produce a grossly underestimation of the mass fluxes passing these sampling points. If first flush grab samples had been used for Storm B, the estimated phosphorus retention would be greater than the estimated value in this thesis, and the conclusion would have been that the wetland was more efficient than it really was.



Pond 1 had a surprisingly high positive retention of TP (42%) and TSS (61%). Maintenance of the pond, 4-5 weeks prior to the storm, removed large quantities of settled particles, producing larger volume for sedimentation. Such removal of sediments had not been done prior to Storm A, and is assumed to be the main reason for the difference in the pond's retention during the two storms. Not only did the maintenance produce room for particles to settle, but it also gave a higher hydraulic retention time due to larger volume. The maximum flow rate of Storm B was estimated to be 65 L/s producing a minimum hydraulic retention time of ~36 min. Storm A experienced a 3.77 times higher flow rate. If the channel had been constructed during Storm A, the hydraulic retention time would have been ~12 min. Still, the channel was not constructed prior to Storm A, and the hydraulic retention time would have been much lower. Therefore, sedimentation of settled solids contributed with positive phosphorus retention to a greater extent during Storm B than Storm A. Additionally, the general higher retention time during Storm B may also have created a more quiescence environment and thus reduced the degree of resuspension.

A negative  $\text{PO}_4^{3-}$  retention was observed in Pond 1 despite the relatively quiescence environment. Water entering Pond 1 prior to the wash-out contained much phosphorus (Figure 4-26). High phosphorus input combined with the high hydraulic retention time, before the flow increased drastically, may have provided long enough time for microbial phosphorus release. Hourly wash-outs were largest when the flow increased over a flow threshold, causing wash-out of accumulated  $\text{PO}_4^{3-}$ .

Pond 2 showed the opposite retentions to Pond 1, with a positive  $\text{PO}_4^{3-}$  retention and a negative TP and TSS retention. A factor worth mentioning is the dilution effect. Pond 2 consists of a larger volume than Pond 1, consequently, diluting the water entering. Such effects can give an impression of the pond retaining phosphorus, since the effluent concentration will be lower than the inlet concentration. Plant growth is a possible theoretical explanation for the positive retention, but several kgs of plant biomass would need to be produced to retain the same amount of  $\text{PO}_4^{3-}$ . No extreme growth was observed during the storm. Still, some uptake can have occurred, but is not seen as the main reason. Contrary to Storm A, the flow during Storm B was not great enough to force the plants to bend towards the sediments. Consequently, the plants did not hinder resuspension. In addition, there was no bypass situation causing dilution of the water right in front of the outlet sampler.

### 5.3. Errors and uncertainties

Sampling procedures represent the largest source for uncertainties. In general, flow proportional samples are better when analysing weekly composite samples, and have thus been used in this study. Predictions of future flow are essential, and problems occurred during the sampling period due to such predictions. The weather forecast was checked each week before programming the automatic samplers, but the amount of rain forecasted did not always occur. Some weeks the samplers were programmed with too high pulse, resulting in composite samples with less than 11L sample. This situation is assumed to not have a significant impact, since samples were collected the whole week. Other weeks the samplers were programmed with too high pulse. This situation is less preferred since the automatic sampler fills up the composite sample before the week has past, hence not collecting samples the last hours or days. Large concentration changes may occur during the days not captured and can produce a composite sample with lower concentrations than the “real” sample. Still, the days/hours left unsampled may not contain storm peaks, hence may the composite sample be a relatively well representative sample.

From mid-December the automatic samplers gave a signal of error. The samplers could not detect any liquid. This was most common for the inlet sampler. The specific reason for this error is not known, since the suction tubes were below ground, but multiple possible reasons are known. Air pockets and frozen water in the pipeline would trick the automatic sampler to assume no liquid was present. Heavy hydraulic flow may also have transported leaves onto the suction tube, thus preventing water from entering. During the period errors occurred, the inlet samples also consisted of an unnormal number of suspended solids, plant residues and insects. The characteristics of the inlet samples changed greatly from week to week. One week the sampler collected only around 0.5 L water, with an extreme number of solids. This change in characteristic may have occurred due to the suction tube being out of position. The suction tube was placed in the fully submerged pipeline between pond 1 and 2. Particles had accumulated inside the pipeline, giving plants opportunity for growth (Kommedal, R.). The suction line may therefore have been positioned closer to the sediments, or plants, than it should have been. Such positioning may have caused larger numbers of particles to enter the suction tube, consequently producing a composite sample with high TSS value. It is worth mentioning that this is only a theory, and that we have not gone into the pipeline, checking its position. Therefore, the high TSS values may be real values.

Accurate sampling is very important since the concentrations of the composite samples were multiplied with the average flow to determine mass fluxes, producing estimations of retention. Small concentration changes can result in great differences in estimated weekly retention. Estimated percentile standard deviation for the parameters analysed showed a general low variance (2-3%). The estimation will include this deviation, which represents a degree of uncertainty in the determined retention. A surprising finding was that  $\text{PO}_4^{3-}$  had a one percentile higher deviation compared to TP and sTP. The reason for this may be the low  $\text{PO}_4^{3-}$  concentrations, which will be more affected by pollution in the lab than the unfiltered samples with higher concentrations. In general, deviations for  $\text{PO}_4^{3-}$  was 1-2  $\mu\text{g/L}$  which are very small amounts, and may thus be regarded as insignificant. The degree of homogenization for the unfiltered samples is assumed to have a greater influence on the standard deviation than pollution in the lab. Situations with low turbidity and high TSS result in relatively fast settling of suspended particles, producing a lower concentration in the upper layer of the container and thus making it difficult to transfer only homogenized samples.

Another source of error was found in the analytical procedure. TP concentrations were determined for samples without colorimetric reagent added (Figure 5-3) and plotted against measured turbidity. Particle residue after autoclavation produced turbid samples, which produced higher TP concentrations compared to the real value. The correlation plot did not produce a relationship with high fitting ( $R^2$ ), suitable for adjusting the determined TP concentrations for this error. Still, this is not considered to represent a large error in the estimated retention since the inlet and outlet samples often had similar turbidity, hence approximately the same error which would be removed when the retention was determined.

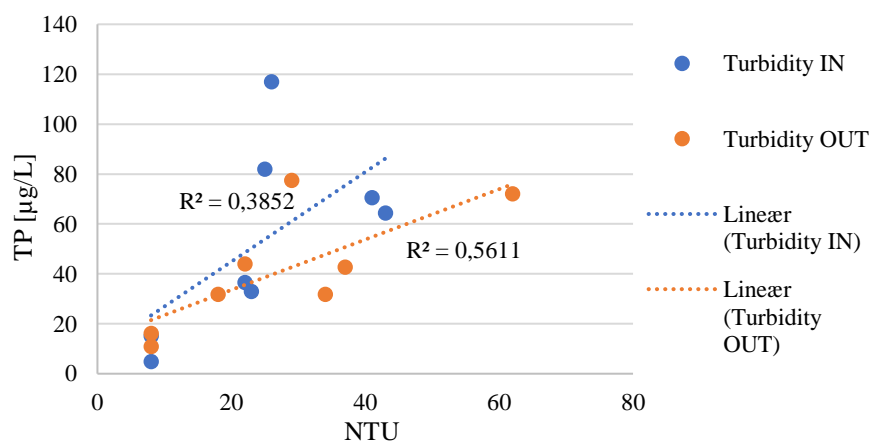


Figure 5-3 TP concentrations [ $\mu\text{g/L}$ ] found in samples, without reagent added, plotted against corresponding turbidity measurements.

#### 5.4. Future perspective

Multiple interesting findings were discovered during the study. The “black box” method only states that something has occurred with the parameters monitored. The method does not provide enough information to determine microscale connections. Consequently, the study does not provide enough information to determine if ferric phosphate precipitation is a dominant mechanism, or if ferric phosphate enters the wetland already fixed. Therefore, detailed analysis with iron speciation and partition of the soil should be performed on samples collected at the inlet of Pond 1, and at the inlet and outlet of Pond 2. Iron speciation and partition could indicate if phosphate in the soil is primarily fixed with iron, and if the composition in the soil changes further into Leikvollbekken.

A tendency for FSS retentions was observed during the weekly measurements, even though the wetland had a negative TSS retention. Further weekly samples should therefore include FSS/VSS-analysis each week to see if this tendency is constant over the seasons. There is a possibility for the positive retention of FSS to be a coincidence, or a spring phenomenon.

Turbidity in the TP-samples after autoclavation was found to be a source of error, producing a higher phosphorus concentration. This error should be considered and if possible reduced by filtering the samples post autoclavation or determining exactly how much extra phosphorus the turbidity represents each week and subtract the concentration from the real sample.

Trace studies of the hydraulic flow in Leikvollbekken should also be performed. Leikvollbekken is assumed to have a poor spreading of the water and to experience a channelling effect. Still, the degree of channelling during base flow and storm flow is not known and thus the hydraulic retention time is not known. Concrete measurements of the hydraulic retention time of the two ponds would provide further useful information for improvements of Leikvollbekken.

Several possible improvements can be executed on Leikvollbekken. Regular maintenance, with plant and sediment removal, should be performed. Settled particles need to be removed if particulate phosphorus settling in the ponds is going to represent a sustainable mechanism for phosphorus removal. Structural improvements on Leikvollbekken should also be conducted to reduce the impact of wash-out situations. In general, the hydraulic retention time during storm flow situations needs to be higher. A possible solution is to increase the wetland’s area, but this will only be a temporary solution, since particles will accumulate, producing a lower volume and hence a shorter retention time. Another possible solution is to install a bypass during

extreme flow. This could be a good solution, since Leikvollbekken proved to have a positive retention efficient during Storm B and not during Storm A. Leikvollbekken can thus retain phosphorus during relative high flow, if maintenance has been performed prior, but needs help when the flow increases too much. Areas north and south of Leikvollbekken consist of light dense forest with a relative flat surface. Hence, an overflow from Leikvollbekken onto these areas could be a possibility. Three hypothetical bypass positions are presented: the inlet of Pond 1, the outlet of Pond 1 and on the south-west corner of Pond 2 (Figure 5-4). Location A may be the easiest to execute, but may not represent the most efficient bypass location, since the water level increases further down the channel. Location B may be one of the more efficient locations, since the water level increases dramatically here. A bypass construction would need to go under the road, since the area north is located higher than the water, hence making the bypass construction complex and costly. A bypass in this position could remove the dilution effect overflow from Pond 1 to Pond 2 may have produced, and thus contribute to more accurate retention estimates during extreme rainfalls. A last possible bypass location is the south-west corner of Pond 2, location C. Direct observation of overflow from Pond 2 onto the creek following Pond 2 was observed in the two weeks post Storm A. A possible bypass in the south-west corner would reduce this effect and ensure the water to not flush directly into Stokkavannet, which may cause high phosphorus release. These bypass constructions do not have to release the water on top of the soil of bordering areas but can release the water in to the soil creating subsurface flow. By creating subsurface flow, increased hydraulic retention time is achieved. Still, subsurface flow saturates the area and how such saturation would affect the vegetation is not known.



Figure 5-4 Possible locations for bypass constructions in Leikvollbekken.

## 6. Conclusion

The main objectives of the study was to asses Leikvollbekken's phosphorus retention efficiency over several months and to assess how storm events affect the retention. Several mechanisms work together to achieve phosphorus retention, and the estimated retention is highly dependent on the sampling techniques used.

Conclusions based on weekly monitoring are presented in bullet points below:

- Leikvollbekken retained TP during the sampling period. A positive retention was found for particulate phosphorus and all iron parameters, simultaneous with a negative retention for soluble phosphorus and TSS.
- Weekly phosphorus retention varied with no obvious connection to average weekly flow.

Conclusions based on storm event monitoring:

- Storm A washed out phosphorus, both soluble and particulate, while Storm B had a total positive retention. Consequently, this showed that storm events can wash out accumulated phosphorus, depending on produced hydraulic velocity and retention time, and thus the degree of resuspension and transport.
- Leikvollbekken will benefit from a bypass construction to prevent accumulated phosphorus to reach Stokkavannet during storm events, and thus contribute to the eutrophication potential in Stokkavannet.
- Water samples collected in a CW are dependent, hence making a numerical flow threshold difficult to determine without including sediment level.

In general, weekly monitoring of Leikvollbekken confirmed that Leikvollbekken still retains phosphorus. The hypothesis of wash-out situations, produced by intense precipitation, was confirmed by Storm A. Consequently, this indicates previous sampling methods underestimate the effect storm events can have on a wetlands phosphorus retention.

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## Appendix A. Nitrate and conductivity change during Storm B

Nitrate and conductivity was analysed by Espen Enge (Uis).

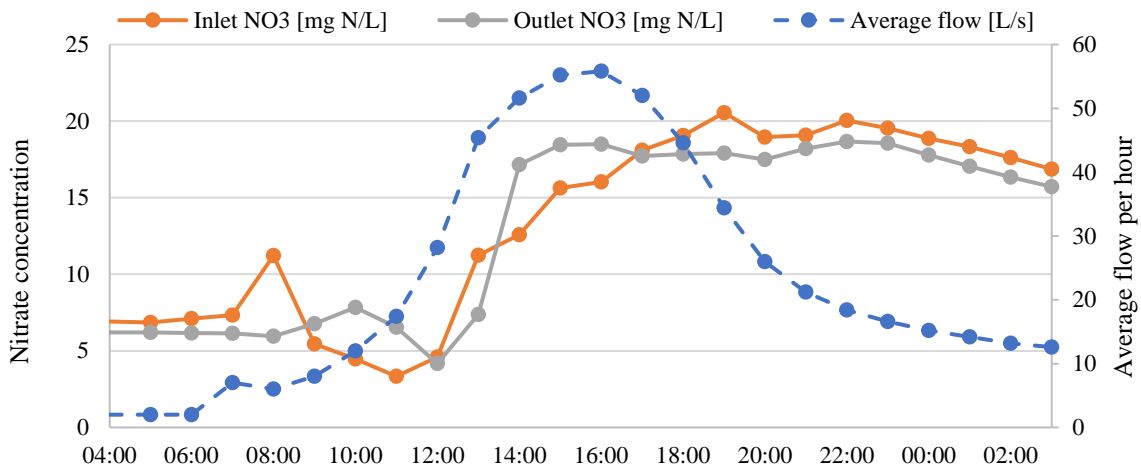


Figure 0-1 Change in nitrate concentration measured the inlet of Pond 1 and the outlet of Pond 2 during storm B and average flow per hour.

Nitrate showed a rapid increase as water flow increased. The inlet and outlet followed the same trend with a dip in concentrations prior to a rapid increase. What separated them apart was how fast the nitrate boost was. The outlet increased from 4.2 mg N/L to 17.2 mg N/L over two hours, while it took five hours for the inlet to reach 18.2 mg N/L.

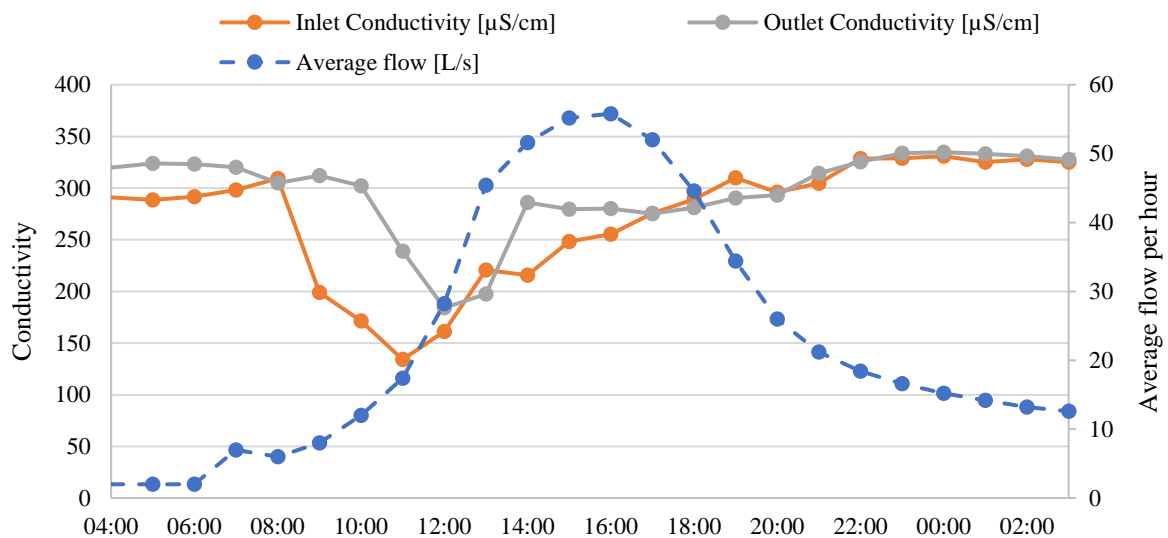


Figure 0-2 Change in conductivity measured for the inlet of Pond 1 and the outlet of Pond 2 during storm B and average flow per hour.

A rapid conductivity decrease was observed when precipitation started. Inlet conductivity experienced an earlier and greater decrease compared with outlet measurements. Both inlet and outlet conductivity stabilized around 330 µS/cm.

# Appendix B: Mass flux

## B.1. Weekly samples

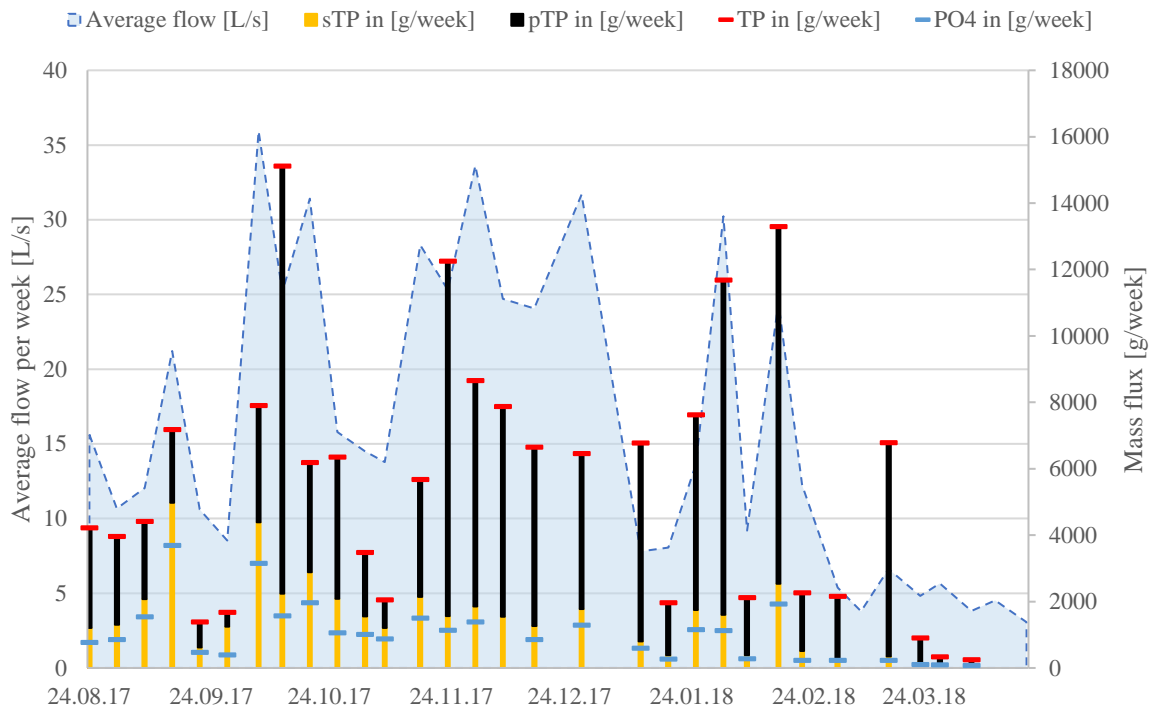


Figure 0-1 Phosphorus mass flux for the inlet of Pond 2 for each week in the sampling period.

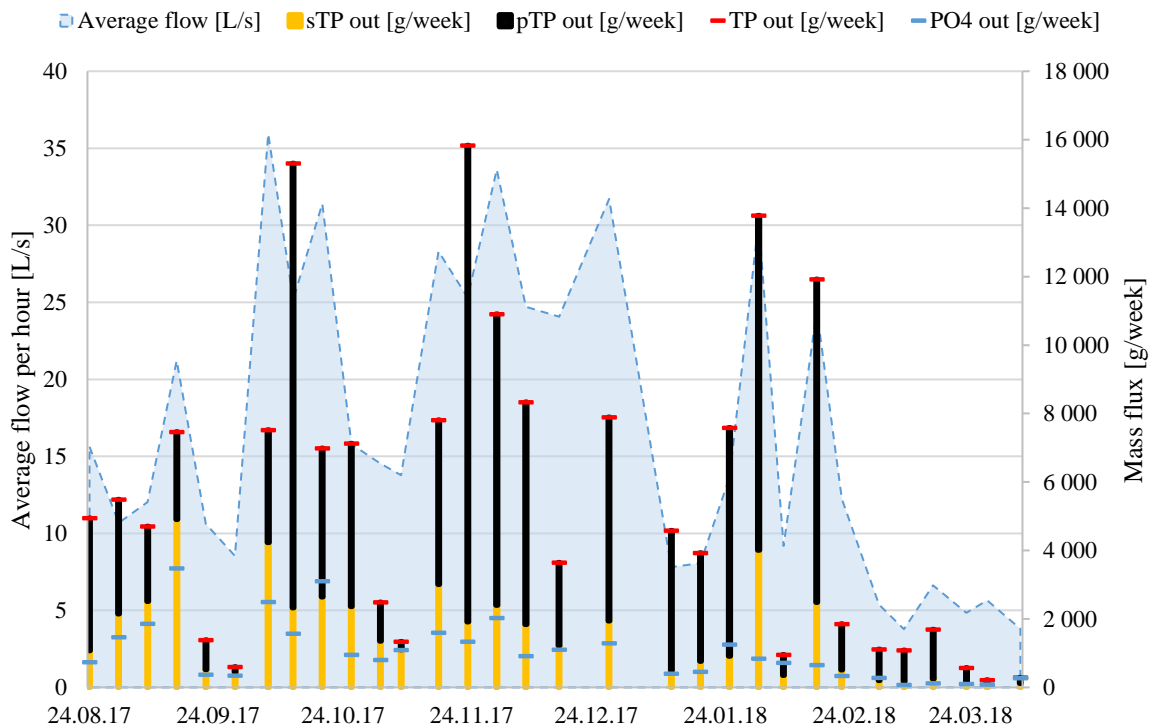


Figure 0-2 Phosphorus mass flux for the outlet of Pond 2 for each week in the sampling period.

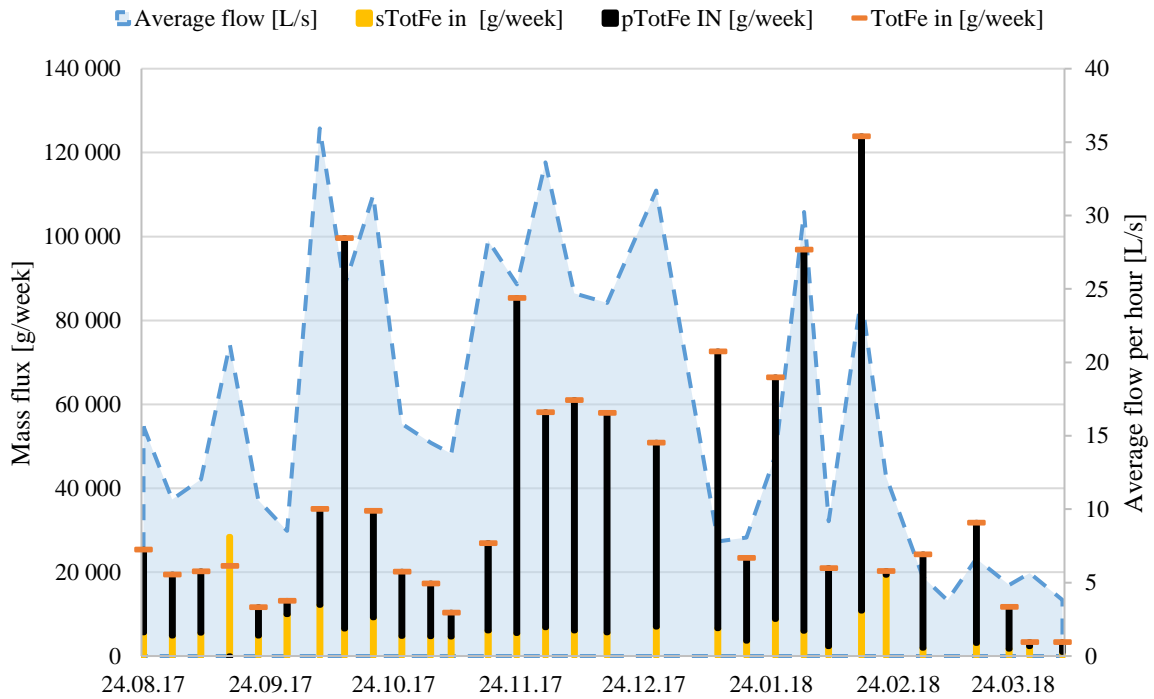


Figure 0-3 Iron mass flux for the inlet of Pond 2 for each week in the sampling period.

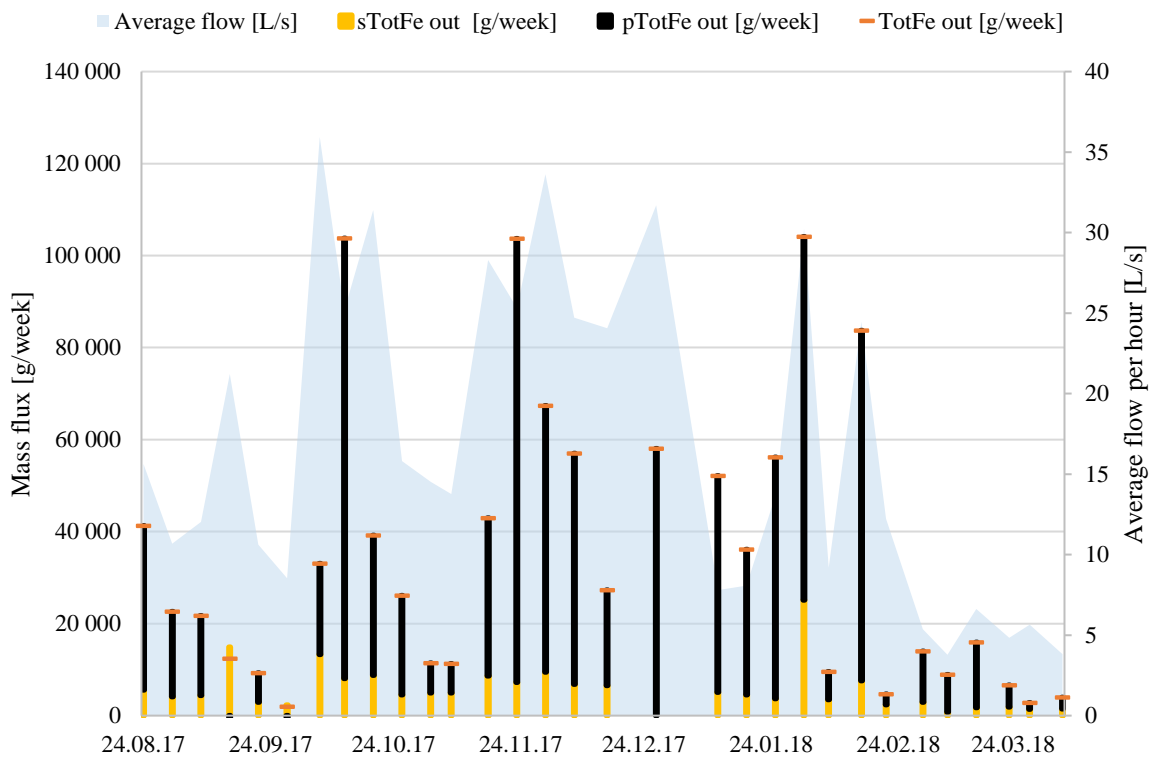


Figure 0-4 Iron mass flux for the outlet of Pond 2 for each week in the sampling period.

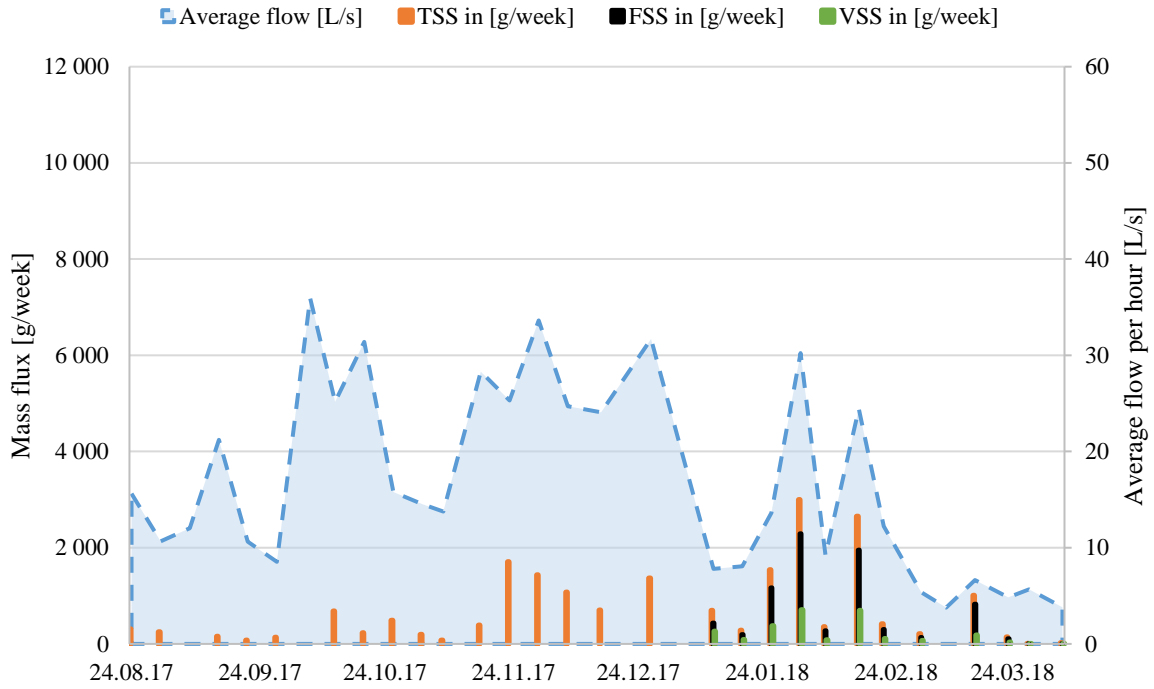


Figure 0-5 Suspended solid mass flux for the inlet of Pond 2 for each week in the sampling period.

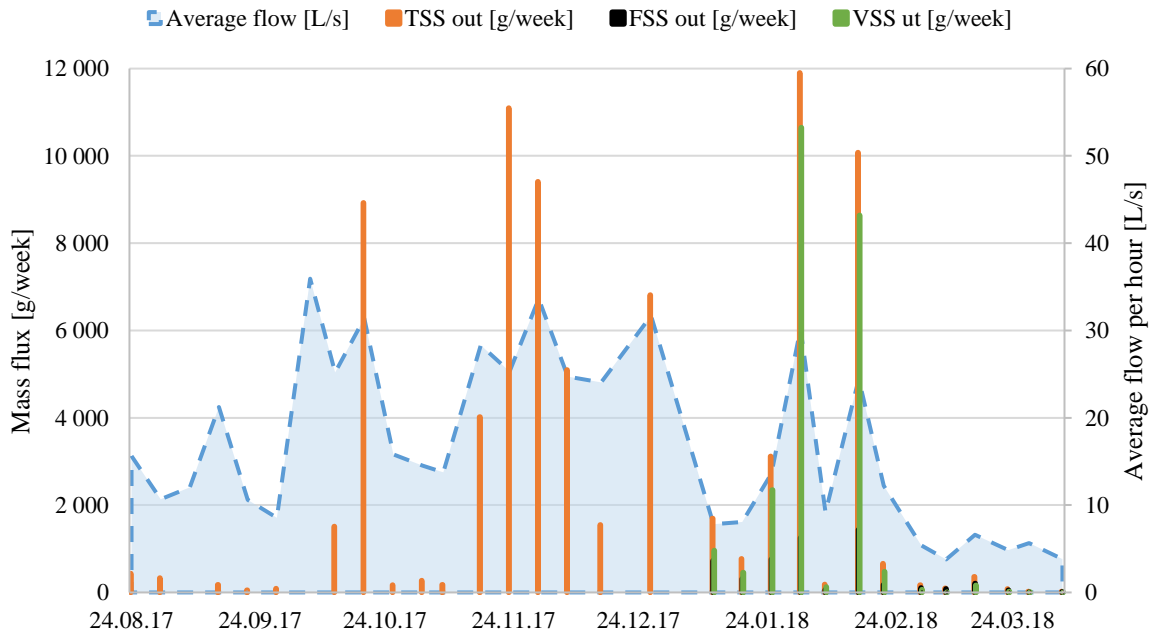


Figure 0-6 Suspended solid mass flux for the outlet of Pond 2 for each week in the sampling period.

## B.2. Mass flux measured during Storm A

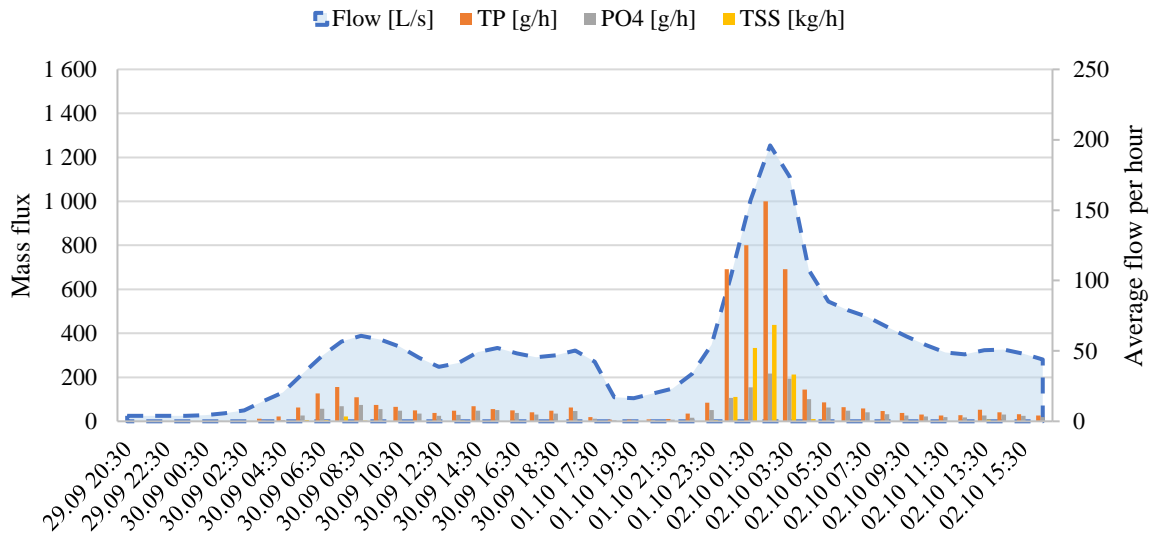


Figure 0-7 Mass flux and average flow at the inlet of Pond 1.

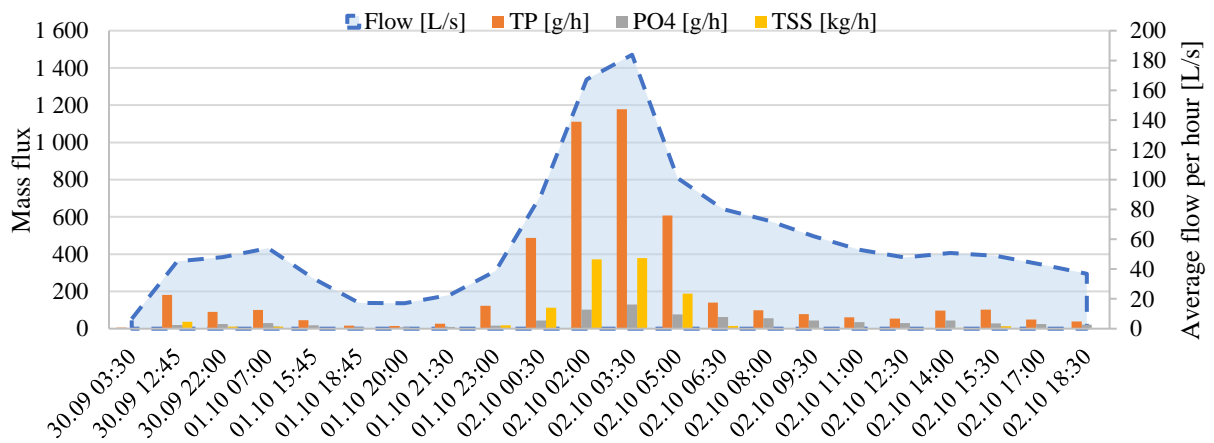


Figure 0-8 Mass flux and average flow at the inlet of Pond 2.

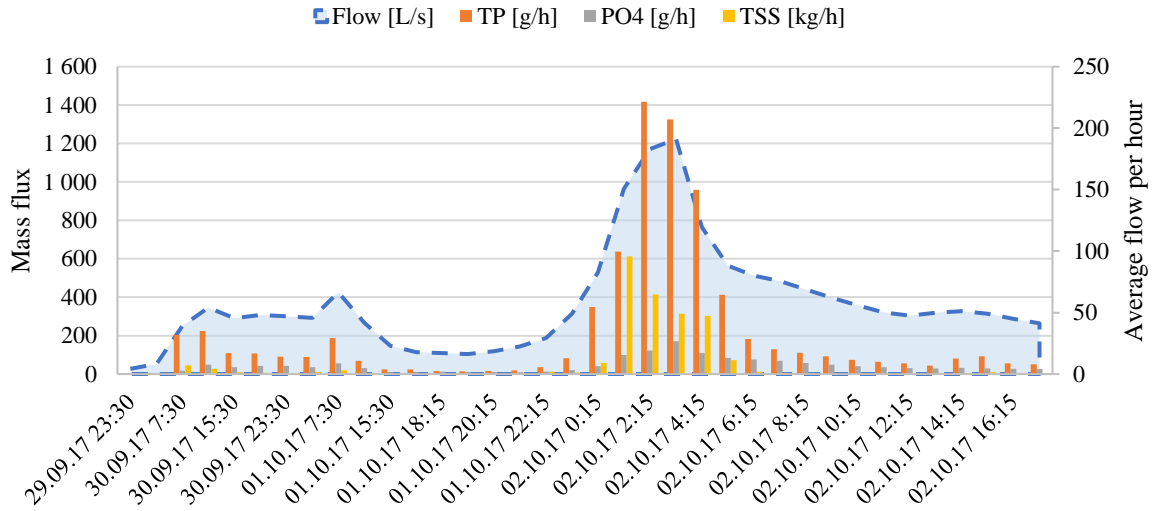


Figure 0-9 Mass flux and average flow at the outlet of Pond 2.

### B.3. Mass flux measured during Storm B

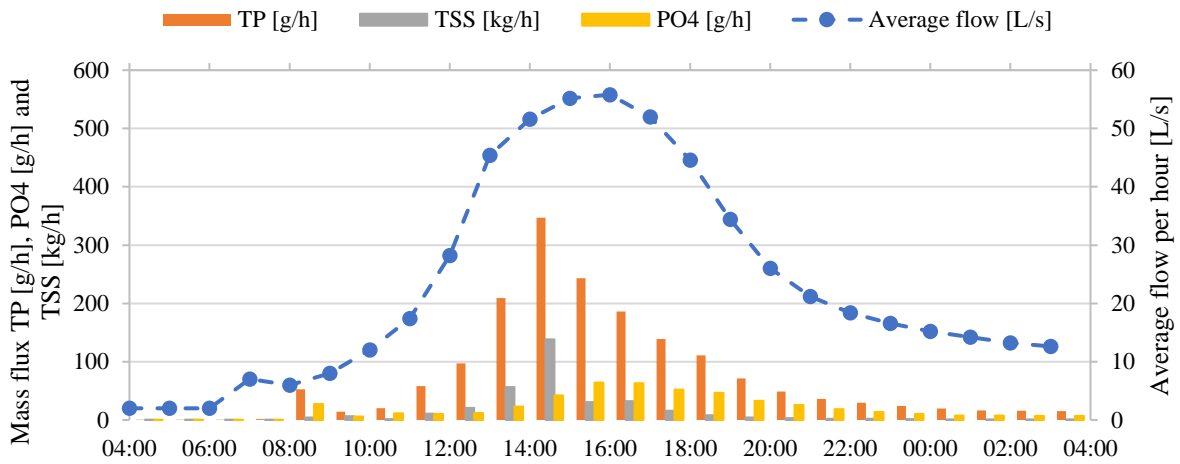


Figure 0-10 Mass flux for TP,  $PO_4^{3-}$  and TSS for the inlet of Pond 1 and average flow per hour.

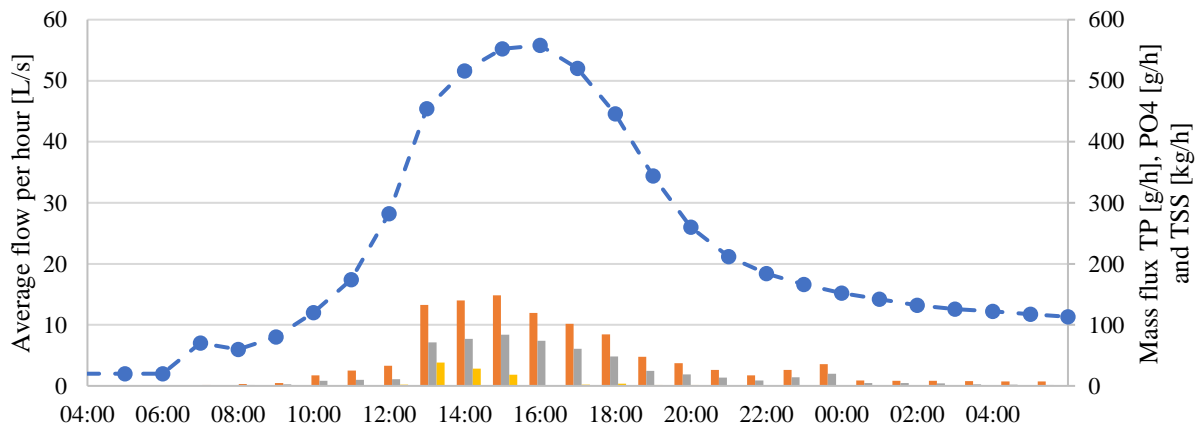


Figure 0-11 Mass flux for TP,  $PO_4^{3-}$  and TSS for the inlet of Pond 2 and average flow per hour.



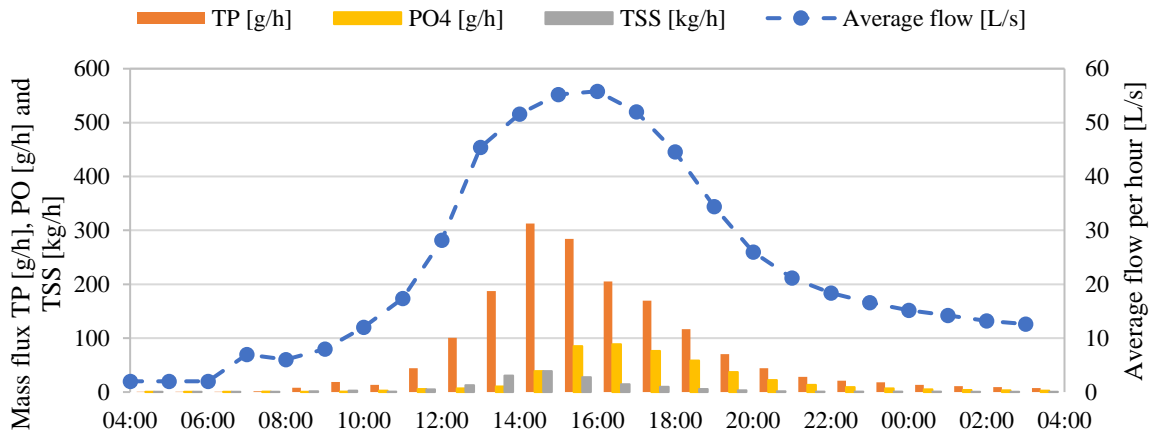


Figure 0-12 Mass flux for TP, PO<sub>4</sub><sup>3-</sup> and TSS for the outlet of Pond 2 and average flow per hour.

## Appendix C. Calibration curves

A calibration curve was made each week for the phosphorus analysis. An example of such curve is presented (Figure 0-1).

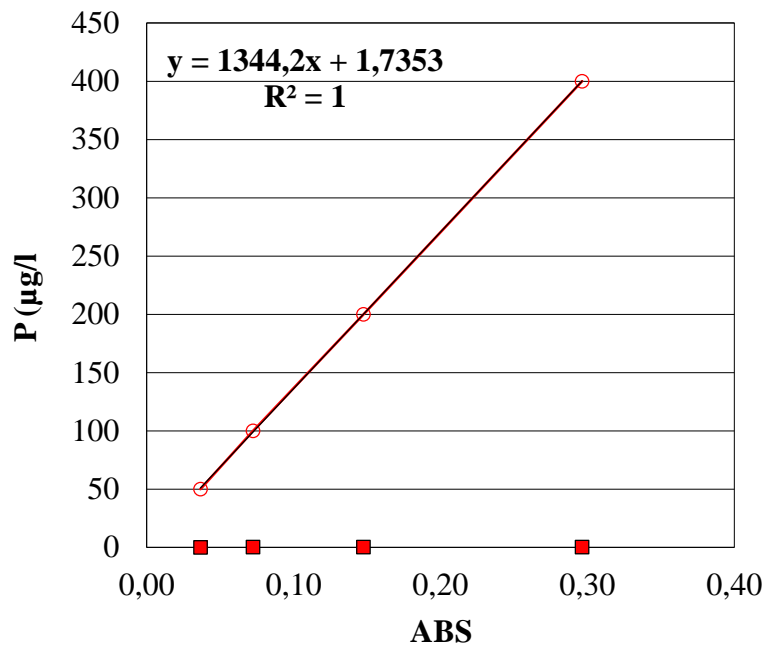


Figure 0-1 Calibration curve made the 15<sup>th</sup> of March (1344.2, 1.7353) for the phosphorus analysis.

A pre-made calibration curve from 1<sup>st</sup> of January 2015 (7.70, 0.00) was used for the iron analysis. Control samples were analysed and confirmed the curve to be accurate.

# Appendix D. Scatterplots

## D.1. Weekly samples

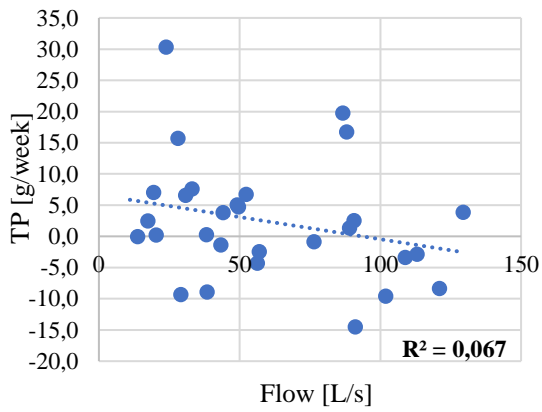


Figure 0-1 Scatter plot for weekly retention of TP and weekly average flow [L/s].

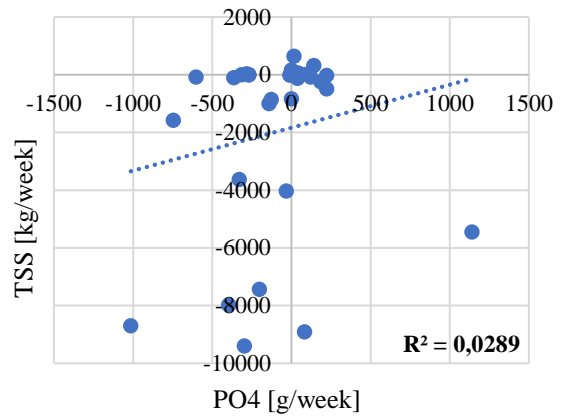


Figure 0-2 Scatter plot for the retention of TSS and retention of PO<sub>4</sub><sup>3-</sup>.

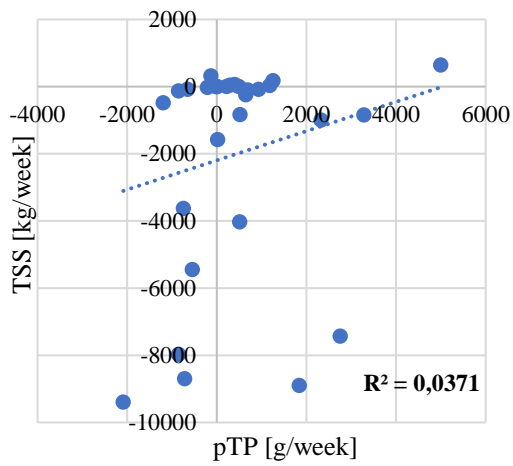


Figure 0-3 Scatter plot for the retention of TSS and retention of pTP.

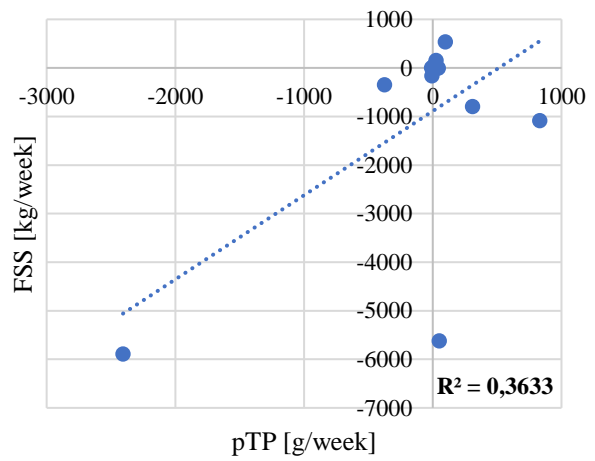


Figure 0-4 Scatter plot for the retention of FSS and retention of pTP.

## D.2. Storm A

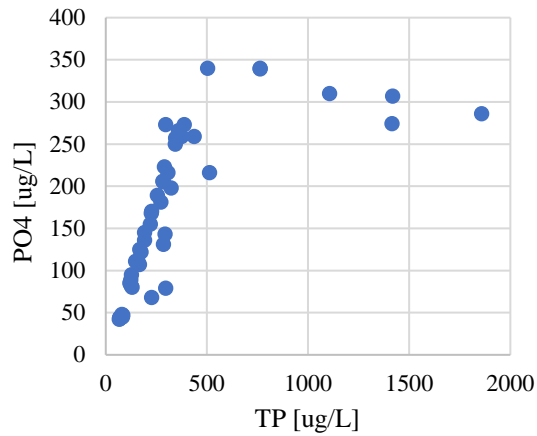


Figure 0-5 Scatter plot of TP and  $PO_4^{3-}$  for the inlet of Pond 1 during storm A.

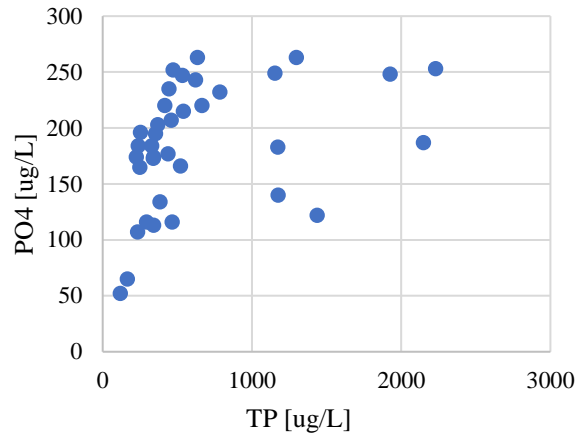


Figure 0-6 Scatter plot of TP and  $PO_4^{3-}$  for the outlet of Pond 2 during storm A.

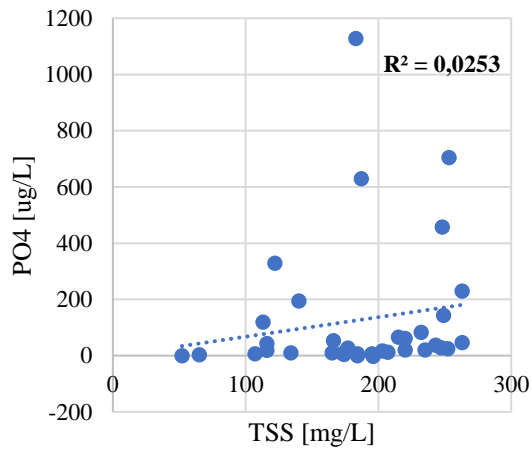


Figure 0-7 Scatter plot of TSS and  $PO_4^{3-}$  for the inlet concentrations of Pond 1 during Storm A.

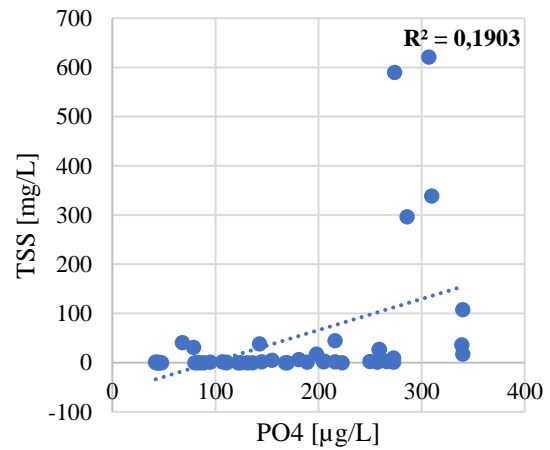


Figure 0-8 Scatter plot of TSS and  $PO_4^{3-}$  for the outlet concentrations of Pond 2 during storm A.

### D.3. Storm B

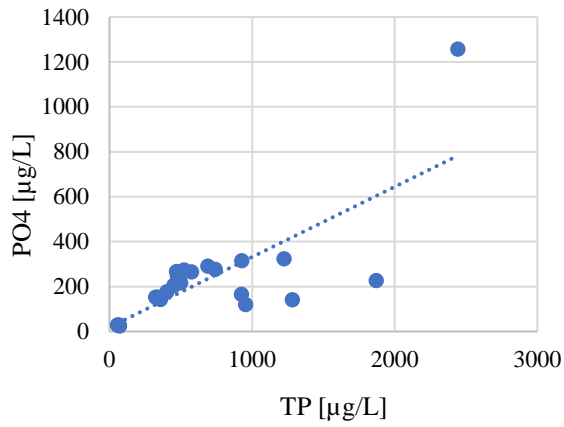


Figure 0-9 Scatter plot of TP and PO<sub>4</sub><sup>3-</sup> for the inlet of Pond 1 during storm B.

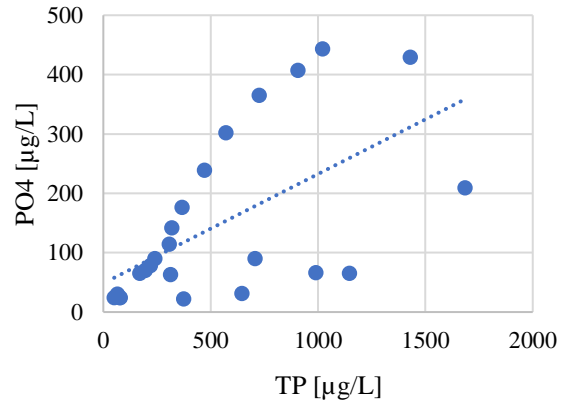


Figure 0-10 Scatter plot of TP and PO<sub>4</sub><sup>3-</sup> for the outlet of Pond 2 during storm B.

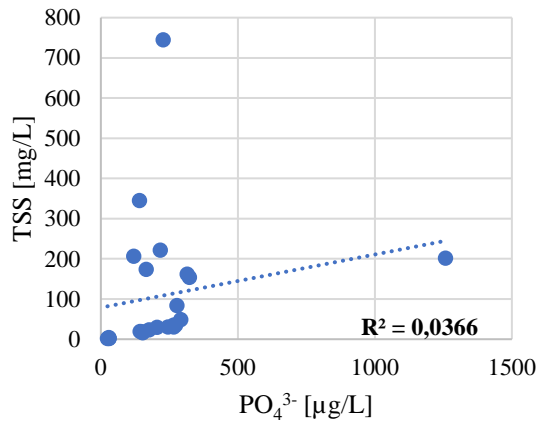


Figure 0-11 Scatter plot of TSS and PO<sub>4</sub><sup>3-</sup> for the inlet concentrations of Pond 1 during Storm B.

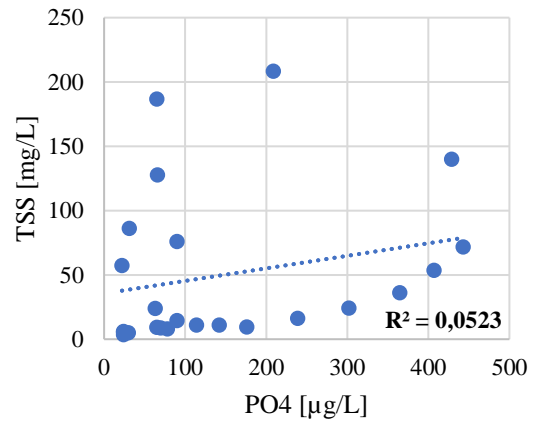


Figure 0-12 Scatter plot of TSS and PO<sub>4</sub><sup>3-</sup> for the outlet concentrations of Pond 2 during storm B.