PARTICULATE PHOSPHORUS SPECIATION AND PHOSPHATE RELEASE IN STREAMS AND DITCHES OF DUTCH AGRICULTURAL LOWLAND CATCHMENTS

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ABSTRACT

Phosphorus (P) enrichment by agricultural input on land increases problems associated with eutrophication in the adjacent surface waters like ditches and streams. Phosphorus in surface water is mainly present in particulate form and its transport strongly correlates with suspended matter (SM) dynamics. Most of this particulate P (PP) is assumed to be iron-bound (Fe-P), but this is not extensively studied in agricultural lowland catchments. Moreover, PP becomes bioavailable when it releases orthophosphate (o-PO_4) to the water column, which is mainly induced by the reduction of Fe-P in anoxic conditions. In this study, water samples were collected to quantify the P fractions in SM of Dutch polders and experimental set-ups were developed to examine the potential bioavailability of Fe-P in SM.

The SM concentration, P content and PP speciation in streams and ditches of Dutch polders were examined in relation to spatial and temporal variance. One study area showed higher SM concentrations at the first sampling moment compared to the following moments, but no clear difference was seen in a different study area. The variation in SM concentrations of sampling locations is most likely determined by local hydrological processes rather than seasonal changes. The Fe-P fraction was found to be the main contributor (32-96%) to the total PP pool, which is in line with previous studies on this topic. Organic P was the overall second largest proportion (2%-49%). Also, a logarithmic relation between SM concentration and P content was found, where high SM concentrations had a low P content and vice versa. Seasonal variability in PP speciation was seen in the fraction contributions from one of the areas. The Fe-P was decreasing until March while Org-P was decreasing, although this occurred earlier than expected. The reduction rates from the microbially induced experiment were 7 and 12.5 μmol Fe l^{-1} day^{-1}. The chemical reduction experiments showed faster rates (3.9, 12.1 and 70 μmol Fe^{2+} l^{-1} h^{-1}), but the biological experiment is probably more representative of the field situation. The results from this study could be used to manage the P loads and eutrophication potential in agricultural-dominated catchments.

CONTENTS

ABBREVIATIONS

CIP	Colloidal Inorganic Phosphorus
DP	Dissolved Phosphorus
DIP	Dissolved Inorganic Phosphorus
DRP	Dissolved Reactive Phosphorus
EXAFS	Extended X-ray Absorption Fine Structure
Fe-P	Iron-bound Phosphorous
FP	Ferric Phosphates
HFO	Hydrous Ferric Oxides
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
NMR	Nuclear Magnetic Resonance
P	Phosphorus
PIP	Particulate Inorganic Phosphorus
o-PO4	Orthophosphate
POP	Particulate Organic Phosphorus
PP	Particulate Phosphorus
SEDEX	A sequential extraction method developed by Ruttenberg (1992)
SM	Suspended Matter
TP	Total Phosphorus
XANES	X-ray Absorption Near Edge Structure Spectroscopy

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1. INTRODUCTION

Phosphorus (P) is an essential element for all life forms and plays an important role in the biological productivity of freshwater ecosystems. Long-term input of P on agricultural lands as fertilizer and animal waste has resulted in an increased P content of the soil. Phosphorous runoff from these lands is an important pollution source and may enhance eutrophication in adjacent ditches and streams. This eutrophication may lead to low oxygen levels, algae growth and biodiversity loss and thereby affect the water quality (Correll, 1998; King et al., 2015). Non-point inputs are difficult to measure and regulate due to the spatial dispersion of activities and the consequences vary in time due to effects of weather and hydrological processes. Detailed knowledge is required on the transport and retention of P in these systems in order to control the P loads and eutrophication potential in agricultural-dominated catchments (Reddy et al., 1999).

The two main forms of P that can be distinguished are dissolved phosphorus (DP) and particulate phosphorus (PP). Particulate P is associated with sediment or small living organisms and is not available for uptake but first needs to be transformed, while DP is directly bioavailable (Reddy et al., 1999). The transport of P in water systems like rivers and streams is found to be strongly correlated with the transport of suspended matter (SM) (Kronvang et al., 1997; Beusen et al., 2005). Once in the water column, PP can be transported over long distances before it deposits again more downstream. Surface- and subsurface runoff increase the amount of SM in the water column, but erosion and resuspension of bed sediment also create higher concentrations. A minimum shear flow is needed for erosion processes to occur (Reddy et al., 1999). The flow velocity in drainage ditches is possibly lower than this threshold, unless storm events and high discharges significantly increase the water flow. Some studies state that the majority of the SM is transported during infrequent storm events (Kronvang et al., 1997; Ballantine et al., 2008; Stutter et al., 2008; Vidon & Cuadra, 2011) and influenced by hydrological and biological changes on a seasonal scale (Jarvie et al., 2002). Authigenic production due to exfiltrating groundwater also contributes to the SM concentration in agricultural catchments and should not be underestimated as a PP source (Baken et al., 2013; Vanlierde et al., 2007). Oxidation of iron at the (sub)surface-water interface is known as the main production process of authigenic P-containing SM, which explains the large iron-bound PP (Fe-P) fraction of about 50-90% found by Van der Grift et al. (2016).

The effect that PP has on eutrophication in the water column depends on the physical and chemical characteristics of the fractions (Poulenard et al., 2008). Phosphorus speciation was already examined in SM and sediment of rivers and streams (Poulenard et al., 2008; Pacini & Gächter, 1999; Coelho et al., 2004; Boström et al., 1988), but results in agricultural lowland catchments is limited. Only Nguyen & Sukias (2002) studied P speciation in agricultural areas in New-Zealand, specifically of sediment in drainage ditches. Their findings showed that about 50% of P in sediment was bound to Al-, Fe- and Ca particles.

Particulate P studied by Ballantine et al. (2008) showed spatial variation in and between catchments in terms of the amount of organic, inorganic and algae available P. Following the findings of Van der Grift et al. (2016) with respect to the Fe-P pool of P, it is expected that similar results will be found in other Dutch catchments. Groundwater in the Netherlands is typically Fe-rich and anoxic (Griffioen et al.., 2013), so exfiltration of this groundwater may result in this large suspended Fe-P fraction in surface water.

As mentioned, transportation of PP depends on the water flow in the stream or ditch and if the flow rate is little, SM will deposit on the waterbed until it is remobilized again. This way, sediment and soil have the capacity to retain P (Reddy et al., 1999). Deposited PP may be released back into the water column as bioavailable orthophosphate (o-PO_4) by hydrological and biological changes. Changing redox conditions are mentioned as a main explanation of the release of o-PO_4, especially in relation to Fe dynamics. In short, P may be bound by Fe^{3+} compounds when the water is in an oxidized state, while anoxic conditions may allow Fe^{3+} reduction to Fe^{2+} and consequently the release of o-PO_4 (Correll, 1998). Although in theory this process seems straightforward, in the field it is more complex. The formation of P-bound colloids and $Fe^{2+}PO_4$ minerals like vivianite for instance may occur as well after reduction of Fe^{3+}. Besides the oxygen level of the sediment surface layer, also Fe-reducing microorganisms induce this reduction process (Søndergaard et al., 2003). These are expected to be more present in summer when conditions are more favourable for algae growth.

It is evident that SM dynamics plays an important role in P transport. The P-content of SM and speciation of PP, but also the release process of bioavailable o-PO_4 from these particles, determines the potential effect on eutrophication. Research on PP fractionation in agricultural lowland catchments is limited and does not take into account seasonal variability. Moreover, o-PO_4 release from waterbed sediment is extensively studied, although no distinction is made for the role of SM in this process. Therefore, the purpose of this study is to:

- determine the SM concentration, P content of SM and PP speciation in streams and ditches of different agricultural polders in the Netherlands to see if there is spatial variance;
- collect data on SM concentration, P content of SM and PP speciation a to explore seasonal variability;
- investigate the release of o-PO_4 and Fe^{2+} from SM by Fe-P reduction to make a statement about the short-term availability of suspended PP.

The first hypothesis when looking at literature is that *the SM concentrations are higher in winter,* due to more hydrodynamic forcing like high discharges and rain events. Second, *Fe-P is expected to be the largest pool in the total amount of PP*, since ferrous particles have a high P binding potential. At last, *the Fe-P fraction will decrease and the Org-P fraction will increase in spring*, due to a higher biological productivity resulting in the reduction of Fe^{3+} particles.

The following main research question is used in order to test the hypotheses:
"How does the particulate P content and speciation of suspended matter in a stream or drainage ditch of Dutch lowland catchments differ when studied in time and place and what is the P release rate of this suspended matter?"

To answer this question, it is subdivided into the next sub-questions:

1. *What is the P content and P speciation of the suspended matter in surface- and drainage water?*
2. *What is the P content and P speciation of the bed sediment?*
3. *Is there a difference in P content and/or P speciation of the suspended matter in time?*
4. *How fast can the bound P and Fe particles in suspended matter be mobilized by a chemically or microbially induced reduction process?*

2. THEORY

2.1 Phosphorus sources and transport pathways

The P input on agricultural land in lowland catchments is mainly derived from fertilizers and manure which are used for increased land productivity. Erosion and (sub)surface runoff are pathways for P to export from agricultural land to surface water (Sharpley et al., 1994). Phosphorus needs to be extracted from the soil, crop residues, applied fertilizer and manure in order to be able to be transported to surface water. This extraction process occurs when water, like rainfall or seepage, interacts with the soil before it moves to surface water as runoff. When P is being flushed away by water it can be exported in dissolved as well as in particulate form, due to sorption and desorption on soil particles (Sharpley et al., 1994). According to Sims et al. (1998) subsurface runoff is an important component of the total P (TP) export from agricultural land. These P losses in subsurface flow seem to be more evident in areas with high P concentrations and low sorption capacities of P in the soil. The P is moved via groundwater flow or preferential flow through macropores in the soil. Surface runoff is predominant in sloping, poorly drained and/or frozen soils (Grant et al., 1996), where runoff and erosion potentials are influenced by land management. Ulén et al. (2007) found that between few north-western European countries the forms, amounts and timing of P loss from agricultural watersheds are different due to variances in climate, soil, hydrological conditions and agricultural activity.

Transformations can take place between DP and PP when P has entered the water in dissolved or particulate form. This depends on the relative concentrations of these P forms and the absorption capacity of particles in the water column. The latter is also important in terms of the bioavailability and transportation of P (Grant et al., 1996). In terms of PP, there is a consensus in literature on the practically linear relation with SM concentration in surface water (Kronvang et al., 1997; Russel et al., 2001; Beusen et al., 2005), so this fact is taken into account in studies on P transport. Quantifying the SM and associated PP loss from catchments is difficult, because of the large spatial variation of PP concentration and the different delivery pathways as well as the large temporal variety of SM transport. The SM concentration in the water column is a function of the mobilization of fine particles and the sedimentation rate. The main mechanisms controlling this SM concentration are deposition, erosion, resuspension, drain discharge and (sub)surface runoff (Krongvang et al., 1997; Reddy et al., 1999). Bank erosion and resuspension are mostly triggered by hydrodynamic forces, like precipitation, storm events and high discharges. Mobilization of sediment in the water column can ensure these fine particles to be transported over long distances as long as the flow velocity is too high for sedimentation. For these processes to occur a minimum shear flow is needed (Reddy et al., 1999). When the flow velocity is lower than this shear flow the sedimentation flux downward will be higher, resulting in a lower concentration of SM in the water. The abiotic fluxes and in-stream processes influencing P transport in surface water are shown in *figure 2.1* with presence of Fe- and Ca particles.

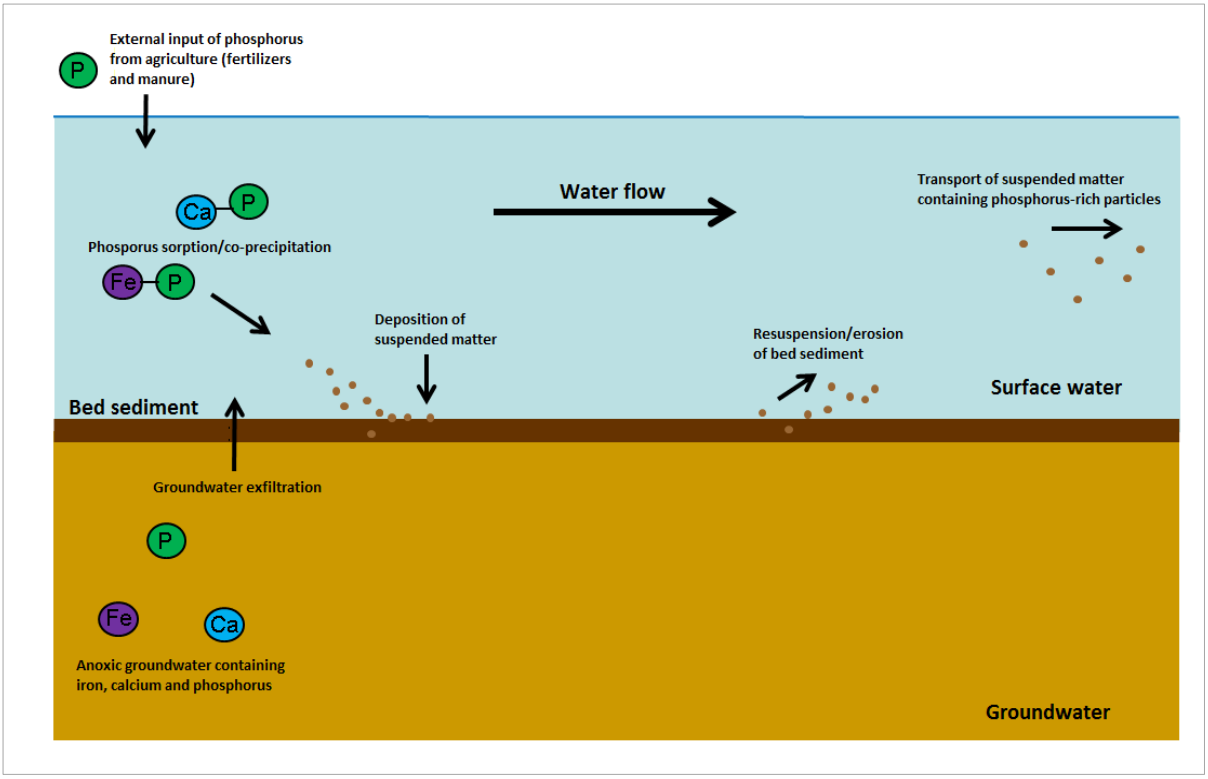

Figure 2.1. Conceptualized diagram of abiotic in-stream processes influencing P transport in surface waters.

2.2 Phosphorus forms and bioavailability

During the movement towards surface water it is unlikely that the P remains in the same form, since a lot of processes (physical and biological) can modify these fractions. In literature, the forms of P are distinguished by physical characteristics (dissolved, colloidal and particular) and whether it is organic or inorganic (Reddy et al., 1999). Dissolved inorganic P (DIP) or o-PO_4 and colloidal inorganic P (CIP), referred to as dissolved reactive P (DRP), are considered to be the fractions bioavailable for organisms, like algae and aquatic plants. Due to the rapid uptake, concentrations of DRP are highly variable. This can precipitate with solutes like Ca, Fe, Mn and Al, adsorb to organic material or mineral surfaces like clays, Fe- and Al oxides and carbonates as particulate organic- or inorganic P (POP or PIP). Dissolution and desorption of these fractions can release o-PO_4 back into the water column (Reddy et al., 1999). The total bioavailable P-pool includes not only o-PO_4, but also the transformable forms. The availability of PP depends on three factors which are (i) the time the particle is accesible for algae, (ii) the possibility of mobilized PP to reach the sites of primary production and (iii) the chemical environment like pH and redox potential (Boström et al., 1988).

2.3 Phosphorous and iron dynamics

Iron-rich, anaerobic (ground)water input provides a continuous source of dissolved Fe^{2+} in freshwater systems by subsurface flow, exfiltration or drain discharge (*figure 2.1*). The effect of Fe on nutrient availability in these systems is mostly determined by its strong potential to react with P. The relation between Fe^{2+} and P in surface water is studied by Baken et al. (2013) who describe that the process

begins when Fe^{2+} enters oxygenated surface water and precipitates to hydrous ferric oxides (HFO) and ferric phosphates (FP). The HFO's are characterized by the ability to absorb or incorporate P. Formation of FP's is put in motion when there is a shift from anoxic to oxygenated conditions at the sediment-surface interface with presence of Fe^{2+} and P. The ferric colloids produced are termed authigenic, because they are produced in the water column in contrast to allochtonous material which has a different source, like surface runoff or sediment erosion. A change in redox potential may in turn ensure the reductive dissolution of FP into dissolved Fe^{2+} and o-PO_4. Baken et al. (2013) sampled groundwater, surface water and suspended sediment in a Belgian catchment with iron-rich groundwater exfiltration. Fresh authigenic material was produced by oxidizing filtered ground- and surface water and contained about 44% Fe and also C, P and Ca in smaller concentrations. Binding of P by HFO's and also the formation of FP's resulted in a decrease of DRP in the water column. The influx of Fe precipitates due to groundwater seepage contributed significantly to the composition, concentration and fluxes of SM (Baken et al., 2013). The authigenic part of the total SM load is studied by Vanlierde et al. (2007) who found a contribution of 43-100% according to theoretical calculations. Model predictions estimated an annual contribution of 58 up to 96%. A smaller range (31-59%) is found by Baken et al. (2013), but it is also evident that authigenic production is an important source of SM and PP in surface water.

2.4 Phosphorous speciation of suspended matter

Particulate P is an overall term for P attached to sediment, compounds or organic material, but it does not make a distinction between the different fractions. The fate of PP in the water column depends on the physical and chemical characteristics of the different particles, which determines the mobility and environmental effects of PP (Poulenard et al., 2008). Phosphorus speciation, also known as P fractionation, of PP has been applied in several studies (Poulenard et al., 2008; Pacini & Gächter, 1999; Coelho et al., 2004; Boström et al., 1988), mostly in aquatic sediments, rivers and streams. Sequential chemical extraction methods are named as tools for determination of the various P fractions in particulate matter. One method is developed by Ruttenberg (1992), which is called the SEDEX method and commonly used for P speciation. It consists of five chemical treatments separating the major fractions of particulate P into five groups, which are respectively: (i) exchangeable P, (ii) Fe-P, (iii) Ca-bound P, (iv) detrital P and (v) organic P. Liu et al. (2014) and Li et al. (2014) used other techniques for the determination of P species, which are X-ray absorption near edge structure spectroscopy (XANES), extended X-ray absorption fine structure (EXAFS) and nuclear magnetic resonance (NMR). The various methods can have a different application and outcome, so a combination of methods will provide the most comprehensive information.

Limited studies have focused on P speciation of SM. Nguyen & Sukias (2002) found that SM in drainage ditches in agricultural areas (New-Zealand) contains a significant amount of P. Approximately 42-57% of P in drainage sediment was present as Al/Fe-P and Ca-P, which are loosely bound fractions. These sediments thus temporarily store P and eventually release this P into the overlying drainage water and surface water. Poulenard et al. (2008) sampled two rivers during a low flow period. Results showed that PP was mostly associated with Al, Fe, Ca and Si with P contents of 10-30%. Also, a difference was found

between the P content of particles upstream and downstream. Sediment and SM downstream contained more PP and showed a higher diversity of carrier phases. The latter is attributed to the increased contribution of clays, increase in Fe-P, decrease in Ca-P and Al-/Fe minerals which were not found upstream. Ballantine et al. (2008) identified spatial variation of P content in SM in and between catchments, although they only distinguished TP, inorganic P, organic P and algae available P.

2.5 Temporal variability in phosphorus transport

Many studies state that P transport in water systems has a temporal variability, on the short-term as well as on the long-term. Short-term variability is described in terms of weather, where precipitation and storm events can generate higher discharge and increased flow in streams and ditches. As mentioned (section *2.1*), the main cause for mobilization of SM is the increased flow velocity and the associated induced shear stress on sediment. The majority of the SM is transported during infrequent storm events (Kronvang et al., 1997; Ballantine et al., 2008). In agricultural polders, pumping regimes often limit the amount of discharge to maintain a proper water level. Particulate P sampling during rain events revealed changes in P concentrations and in P species distribution (Pacini & Gächter, 1999; Stutter et al., 2008), which can be assigned to changing sources of PP and flow-related differences in particle size. Pacini & Gächter (1999) also concluded that at least 25% and at most 70% of allochtonous PP transported during a single rain event may become bioavailable after ending up in a reservoir. Another research of Stutter et al. (2008) examined SM concentrations and P loads during 5 storm events in two lowland catchments in Scotland. The results show that increase in water flow during events induced rapid transport of PP and to a lesser extent DP. In addition, the PP fraction in drain discharge is found to be specifically high during storm events (Vidon & Cuadra, 2011).

The SM- and PP concentrations may also change on a seasonal scale, besides short-term variations due to weather events. Stutter et al. (2008) stated that DRP is mobilized faster from summer to autumn. Phosphorus solutes that are accumulated during summer are expected to be flushed away by soil water flow when hydrological activity increases. The difference in PP is attributed to retention of material in summer to autumn, which is flushed away during events from winter to spring due to erosion and resuspension. Jarvie et al. (2002) also concluded from average seasonal concentrations that SM concentrations were higher in winter corresponding with high river flows. Accumulation of sediment occurs during low summer flows. Higher concentrations of PP in autumn and winter can as well be attributed to high river flows and sediment mobilization. Ballantine et al. (2008) also found the seasonal variation although an annual trend could not be found.

3. METHODS & MATERIALS

The research questions will be answered with fieldwork and laboratory experiments. Section *3.1* describes the study areas were fieldwork was done. Water samples were collected for the PP speciation, ion concentrations and experiments. Filters from another area (Flevopolder) were also used for the examination of P fractions, but these were taken from a different study on SM. Therefore, this area is not extensively described. Fieldwork and laboratory methods are explained in sections *3.2* and *3.3*, respectively. Two experimental set-ups were developed to see if Fe^{2+} and o-PO_4 can be released through biological (section *3.4.1*) or chemical reduction (section *3.4.2*). This chapter concludes with a description of the data analysis in section *3.5*.

3.1 Study areas

Fieldwork was conducted in three agricultural areas in the Netherlands which locations are shown in *figure 3.1*. First, the Quarles van Ufford polder has a total surface area of about 12.000 ha of which 80% is used for agricultural purposes. These agricultural lands are mainly being used as grasslands with maize and fruit cultivation to a lesser extent. It is bordered in the northwest and south by dikes next to the Waal and Maas Rivers. Water discharge from the region mostly flows freely through water courses westwards into the river Maas. However, the water flow is controlled by pumping station "Quarles van Ufford" when discharges are high. There are three water inlets directly coming from the Maas, but also two culverts under the highway are letting water in from the eastern adjacent area. The region consists mainly of river clay soils (Siderius et al., 2011).

Figure 3.1. Location map of Quarles van Ufford (A), Langbroek (B), the Noordplaspolder (C) and the Flevopolder (D) in the Netherlands.

The area was chosen because it is predominantly occupied by agriculture, so almost all water courses are influenced by agricultural practices and fertilizing. Moreover, earlier studies on P speciation in lowland catchments (Ballantine et al., 2008; Nguyen & Sukias, 2002; Van der Grift, 2016-a) do not cover areas with river clay soils as present in Quarles van Ufford. Previous research in the area showed that a very small part of the surface water consists of inlet water in winter. Only 18% of the discharge water originates from the Maas River inlets and the adjacent area. However, the discharge is for 74% explained by inlet water in summer and it comes all the way to the smaller water courses (Siderius et al., 2011). Therefore, it was hard to select locations where surface water consists only of local water throughout the year, which is preferable for this study. Chosen sampling locations are scattered across the area with the majority located in ditches, meaning that the surface water was as much as possible influenced by local water (groundwater and seepage). This did not apply to Q5 and Q6 where measuring took place in the large watercourse "Grote Wetering". Specific locations and details of the sampling points are shown in *figure 3.2* and *appendix A.*

Figure 3.2. Map of Quarles van Ufford with measuring locations Q1-Q8.

Second, the area Langbroek is situated east of Utrecht at the transition from the elevated sandy region of the '"Utrechtse Heuvelrug" to the lower river clay grounds along the Kromme Rijn River. When the area began to be used for agricultural purposes, digging of the Langbroekerwetering canal across the region started to ensure drainage. A regular pattern of narrow stretched agricultural plots was developed from this watercourse, which is now a characteristic of the landscape. The area is used for the cultivation of maize and fruit, but mainly cattle farming and about 30% is defined as natural area. Rainwater that infiltrates in the elevated sandy zone may flow to the deep subsurface causing seepage at the foot of the hill or locally in the western region. The rain-, seepage and inlet water is directly and indirectly discharged into the Kromme Rijn River through a system of watercourses. Regulation by weirs, pumps and inlets is needed due to differences in altitude and surface water levels (Klaarenbeek et al, 2008). Langbroek is relevant for this study because the area is mainly used for agricultural purposes and eutrophication is therefore an important concern. According to the water board the P concentrations in

surface water are exceeding the legal thresholds, which is mainly caused by run-off and leaching from agricultural land (Klaarenbeek et al, 2008). Sampling points are scattered in the region with LB1 and LB2 in the lower region and LB3-6 on the other side of the Kromme Rijn, of which some correspond to monitoring locations of the water board. Locations LB4 and LB6 are situated in the main watercourse Langbroekerwetering. Specific locations and details of the sampling points are found in *figure 3.3* and *appendix A.*

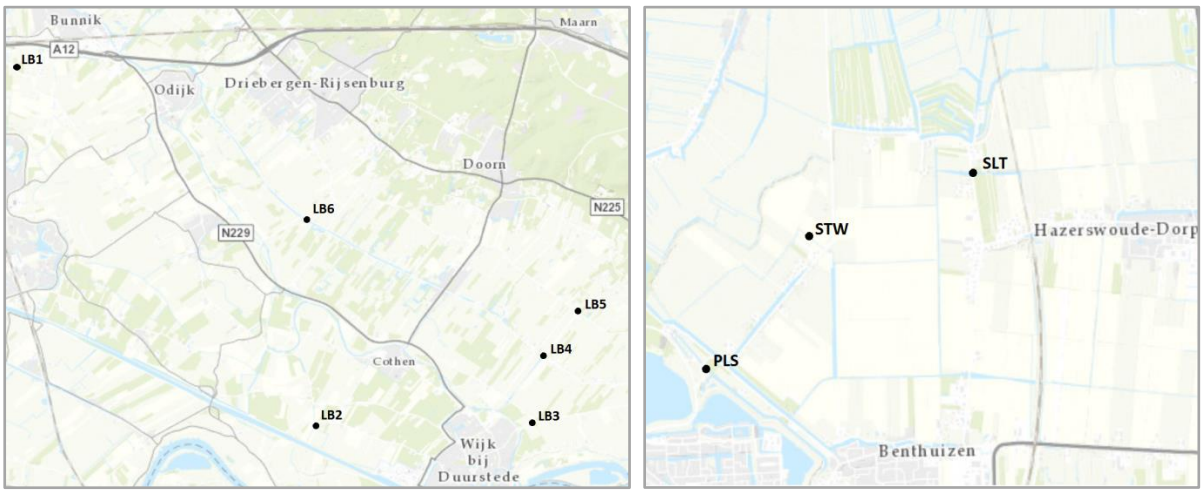

Figure 3.3. Map of Langbroek (left) with measuring locations LB1-LB6 and the Noordplaspolder (right) with measuring locations PLS, STW and SLT.

The Noordplaspolder is a reclamation area, a former lake, which mainly consists of croplands and pastures. Groundwater seepage is typical in the area, since it is lower than the adjacent northern and eastern polders. This results in the presence of inlets and pumping stations to regulate water levels, although the inlets are only important during dry summer periods (De Louw et al., 2004). According to De Louw et al. (2004) flushing with inlet water is also necessary due to seepage of brackish water which causes salinization. Moreover, the Noordplaspolder is characterized by marine clay soils which are in general calcareous. The relevance of this area is derived from the agricultural use of land as well as the frequent occurrence of groundwater exfiltration with high concentrations of Cl, P and Fe (De Louw et al., 2004). Three locations were sampled which were already selected for the purpose of another study: PLS in the main watercourse near the pumping station, STW upstream of a weir and SLT in a ditch. Measuring locations and details are shown in *figure 3.3* and *appendix A.*

The filters of the Flevopolder originated from the study of Van der Grift et al. (2016-b) in which water samples were taken every two to four weeks (January-August) from the “Lage Vaart” main channel. The area consists of clay soils and at upward groundwater seepage is common due to low altitudes. These samples were considered useful, because they came from an agricultural polder and the frequent sampling was convenient when looking at seasonal variability.

3.2 Fieldwork

Surface water samples were taken with Eijkelkamp peristaltic pumps and polyethylene tubes. Water was pumped through the tubes for few seconds before taking samples, so there is no contamination with previously pumped water. A container attached to a stick was useful for the collection of drainage water flowing out of a drainage tube. All containers, bottles and vials were rinsed with surface water before filling. Some samples required filtration, which was done in the field by connecting the pump outlet tube to a tripod filtration unit with 0.45 µm membrane filters. When required, acidification of the samples was done by adding a 68%-containing HNO_3 liquid (10 µL liquid/1 ml sample). *Table 3.1* shows an overview of the samples taken per location.

Table 3.1. Water samples taken per location.

Sample container	Volume	Treatment	Analysis
HDPE vial	60 ml	None	Total P
HDPE vial	60 ml	Filtration and acidification	Cations
PE vial	100 ml	Filtration	Anions, pH, alkalinity and PO_4
Glass bottle	2 l	None	SM concentration and P speciation

Since a lot of SM was needed for the reduction experiments, large water tanks of 20-50 l were filled at location Q5. When the water in these tanks was settled the upper excessive water was pumped off until a small layer of SM concentrated water remained. This remaining water and SM was transported to 2 l bottles and subsamples were used for the experiments.

Bed sediment samples were taken with a 2 m Van der Staay suction corer. Its principle is based on a vacuum suction resulting in the extraction of soil cores. This only works beneath the groundwater level, because the soil needs to be saturated (Van de Meene et al., 1979). The corer consists of an outer tube with handle and an inner tube with leather cup (*figure 3.4*). This leather cup needed to be sufficiently wet, so it was laid in the water for 10 minutes before use. The procedure (*figure 3.4*) started with placement of the corer in the soil and loosening of the inner tube with the screw. Sediment was sucked into the outer tube by pressing it downwards (inner tube stayed at the same height). Then the inner tube was fixed again with the screw before the corer was taken out entirely. The sediment core was pushed out by pressing the inner tube downwards. Only the top (about 5cm) was cut of the core and placed in a bag for analysis, since the research focuses on the upper part of the bed sediment that has the potential to be mobilized.

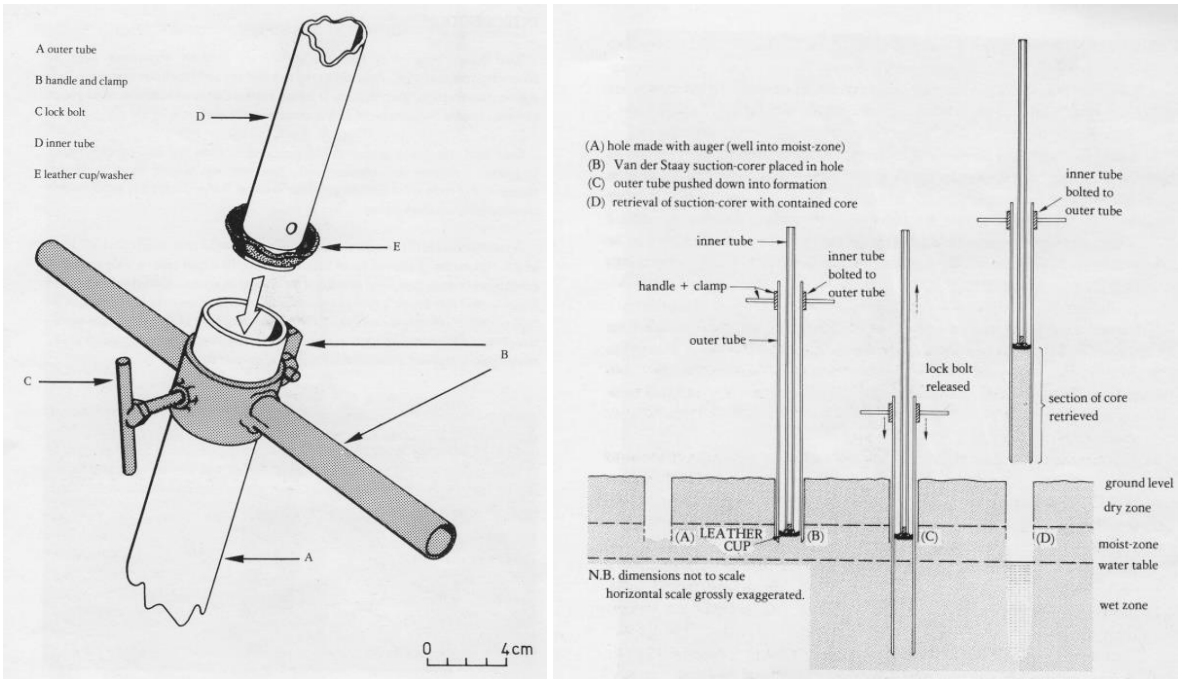

Figure 3.4. The components (left) and method (right) of the Van der Staay suction corer.

3.3 Laboratory methods

3.3.1 Filtration procedure

Well-mixed water from the 2 l glass bottles was filtered through 47 mm Whatman GF/F glass microfibre filters with a vacuum pump. Empty filters were dried, placed in labelled petri dishes and weighted beforehand. In order to get as much material on the filter, a maximum amount of water was used (until the filter is clogging for 10-30 minutes). Multiple filters, ranging from 3-6, were obtained from the bottles of each location. The reservoir of the filtration unit, which collected the water, was weighted before and after the procedure to determine the amount of filtered water. The weights in grams were translated to litres by stating that 1 g of water is equal to 1 l. The used filters were then again dried, weighted and stored in an excitator until further analysis.

3.3.2 Sequential extraction procedure (SEDEX)

The bed sediment samples were stored in a freezer after collection in the field. Later, the frozen samples were placed in a freeze dryer for 72 hours, so no moisture was present when using them for the SEDEX procedure. About 50-60 mg of the sediment sample was put in a 50 ml greiner tube. The dry filters were folded two times and put in 15 ml greiner tubes. The tubes were labelled and weighted without and with sample. The complete protocol for the SEDEX procedure is found in *appendix B*. When all the extractions were carried out, colorimetric analysis with use of a spectrophotometer determined the amount of P in the filtrates which corresponds with the various P fractions (APHA-AWWA-WPCF, 1989). Ultraviolet-visible spectrophotometry is based on the principle that the concentration of a substance can be determined by the amount of light absorption at a certain wavelength. The o-PO_4 that is present in the samples reacts with an added reagent and is then reduced to a blue colored compound. If no (or little) o-

PO_4 is present then there will be no coloration. The light absorbance of the samples corresponds with their o-PO_4 concentrations.

For each location at least one and at most two filters were used for the SEDEX. Not all filters could be included due to the limited sample capacity for conducting the extraction procedure. Selection criteria consisted of smallest deviation from the mean sediment concentration and amount of filters per location. A duplicate was allowed when more than three filters were available for a location. In this case a duplicate means that a second filter from the same sample was used even though SM concentrations varied between filters from the same location. Only one subsample from the bed sediment samples was used for the SEDEX, since they were homogenized.

3.3.3 General sample analysis

The total P concentration of water samples and filters was determined with colorimetric analysis after sample sterilization with an autoclave. Cation concentrations were analysed by ICP-OES. A part of the 100 ml filtered subsample (~50 ml) was used to determine pH and alkalinity with a titration device and 15 ml was used from the same subsample for analysis of anion concentrations by ion-chromatography. The amount of o-PO_4 was determined with the remaining water by colorimetric analysis. One or two filter samples per location and the bed sediment samples were analysed on the ICP-OES for TP concentration, after these samples were total destructed with strong acid.

3.4 Reduction experiments

3.4.1 Biological reduction

The first experimental set-up consisted of water and SM containing microcosms in which Fe-reducing organisms were injected with the aim to reduce the Fe particles. Orthophosphate and Fe^{2+} ions were expected to be released in the water over time during this experiment. The microorganisms needed to be grown first before injection in the experiment. Therefore, a 250 ml glass bottle with a plug of butyl rubber was filled with 10 mg from the upper layer of waterbed sediment sample and 200 ml water from the same location, assuming that the bed sediment already contained Fe-reducing organisms. Subsequently, acetate and ferrihydrite were added to stimulate microorganism growth. About eight times more moles of ferrihydrite than acetate was added, due to the 8 electrons that are transferred during the reduction reaction:

$$C_2H_4O_2 + 8FeOOH + 2H_2 \rightarrow 2CO_2 + 8Fe^{2+} + 16OH^-$$

Ferrihydrite was made according to the method of Lovley and Phillips (1986) by neutralizing a 0,4M $FeCl_3$ solution to a pH of 7 with NaOH. Afterwards the ferrihydrite was washed a few times to remove most of the NaCl. At last, a Tris buffer solution was made and added to the bottle content to minimize pH changes. Since anaerobic conditions were required, the bottle was bubbled with nitrogen for 2.5 hours before it was closed. The growth was given a time of minimal two weeks. It is preferable for all the acetate and

ferrihydrite to react by that time to minimize the risk that they were inoculated in the microcosms and possibly influencing the experiment. Additional acetate was added when an orange-brown colored liquid on top of the sediment indicated that there was still some ferrihydrite present. When all the acetate and ferrihydrite had reacted, the bottle was shaken after which the sediment deposited again. The upper water layer, assumed to contain sufficient micro-organisms, was used for the experiments.

Next, five microcosms were created in 250 ml glass bottles with a plug of butyl rubber. Ditch water (250 ml) with a high amount of SM was poured in each microcosm and was injected with water (20 ml) from the microorganism growth. Addition of a pH buffer, sample shaking and temperature were conditions that varied between the batches in order to examine the influence of these factors. Exact treatments of the experiment batches are presented in *table 3.2*. Water samples were periodically taken in order to verify if the organisms indeed reduced the Fe in SM and subsequently released o-PO_4 in the water. These samples were taken by pricking a needle through the rubber to take up water (2-3 ml). This way the anaerobic gas phase above the water in the bottle remained unaffected. The water was filtered in 15 ml greiner tubes with 0.45 µm syringe filters. The samples were analysed for o-PO_4 and Fe by colorimetric analysis.

Table 3.2. Conditions per batch for the biological reduction experiment.

Bottle #	SM	Micro-organisms	pH buffer	Shaking	Temperature °C
1	x	x	x	x	20°C
2	x	x	x	x	20°C
3	x	x	-	x	20°C
4	x	x	x	-	20°C
5	x	x	x	-	4/5°C

3.4.2 Chemical reduction

The following experiment investigated the possibility of P release by chemical reduction. The set-up for this experiment (*figure 3.5*) consisted of a glass airtight column in which anaerobic conditions could be created. A sample with a high amount of SM or filter was added to this column in which a gas phase remained. After filling up the column with UHQ (600-800 ml) it was closed and by bubbling with nitrogen the water was made anoxic. Ascorbic acid, also referred to as vitamin C, is known in chemistry as a potent reducing agent. Research shows that the rate of dissolution of Fe^{3+} is independent of the ascorbic acid concentration (Debnath et al., 2010), therefore an excess of acid was added (2-5 g). A stirrer enabled a continuous movement of water during the experiment. Just as with the biological experiment, water samples were taken periodically and filtered in 15 ml greiner tubes with 0.45 µm syringe filters. The o-PO_4 and Fe^{2+} concentration of the samples was determined with colorimetric analysis.

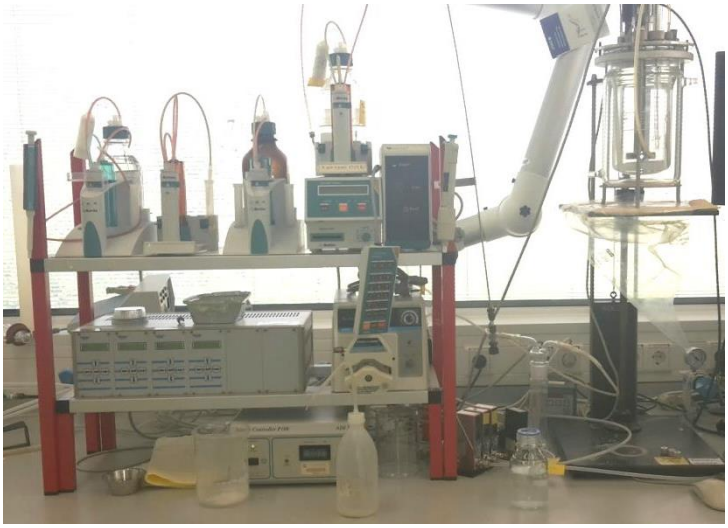

Figure 3.5. Experimental set-up for the chemical reduction experiments

3.5 Data analysis

The SM concentration (mg/l) per filter was calculated with the amount of material (mg) obtained on each filter and the amount of water filtered (l):

$$SM\ conc.(filter) = \frac{(dry\ weight\ used\ filter) - (dry\ weight\ empty\ filter)}{(weight\ used\ reservoir) - (weight\ empty\ reservoir)}$$

The SM concentration (mg/l) per location was determined by taking the average of all filter concentrations of that location:

$$SM\ conc.(location) = \frac{\sum(SM\ conc.filter\ 1, SM\ conc.filter\ 2, \dots)}{number\ of\ filters}$$

Furthermore, the P content of SM (mg/g) per fraction can be determined with the amount of material (mg) and the extracted P fraction (µg) per filter or sediment sample:

$$P_{content}(SM) = \frac{Extracted\ P_{fraction}}{(dry\ weight\ used\ filter) - (dry\ weight\ empty\ filter)}$$

At last, the P fraction contribution (%) to the total PP pool is calculated with the extracted P fraction (µg) and the sum of all the extracted fractions (µg) per filter or sediment sample:

$$\%PP_{\ fraction} = \frac{Extracted\ P_{fraction}}{\sum(fraction\ 1, fraction\ 2, \dots)}$$

The average of the P content and P fraction contribution of some samples are taken as a result when their measuring location is the same.

4. RESULTS

In this chapter the results from the fieldwork are presented separately for each location after some general observations are pointed out (section *4.1*). The SM concentrations of the locations of respectively Quarles van Ufford, Langbroek and the Noordplaspolder (section *4.2* to *4.4*) are shown first followed by the P content, PP speciation and water quality parameters. Only PP speciation results were available from the Flevopolder (section *4.5*). The last section *4.6* presents the results of the reduction experiments.

4.1 General observations

Pumped water was very clear in Quarles van Ufford indicating that the amount and composition of SM in the water caused little turbidity. Water height in the ditches was also not excessively high, at most 1 m since it was possible to stand in the water with hip waders if needed. This does not account for Q5 and Q6 located in the main watercourse "Grote Wetering". The soil of the waterbed was mostly dark colored, loose clay with no vegetation. Orange-brown precipitate was visible on locations Q4 and Q7 (*figure 4.1*), especially around the ends of drainage pipes and on the waterbed. This observation could indicate the presence of HFO's, since Baken et al. (2013) states that "the presence of HFO's is often witnessed by reddish brown sediment at the bottom of e.g. drainage ditches or small brooks". There was some scattered rainfall and hail during fieldwork although this did not cause a visible increase in water flow or surface runoff. Only in the main watercourse water was noticeably flowing towards the pumping station.

Figure 4.1. Orange brown precipitate at location Q4 (left) and Q7 (right).

Similar observations were made in Langbroek with no precipitation on the day of sample collection. However, water in the ditch of LB1 was visibly more turbid than other locations in the area were the water was clear. The water level was also higher in Langbroek than in Quarles van Ufford, because it was in general not possible to stand in the water. Water flow was most noticeable in the Langbroekerwetering in which LB4 and LB6 are situated.

No differences were observable between water taken from the locations, because it was all very clear. The SM, however, was different in color and structure between locations which was visible on the filters (*figure 4.2*). Further analysis will show whether or not these differences can be explained by the PP speciation.

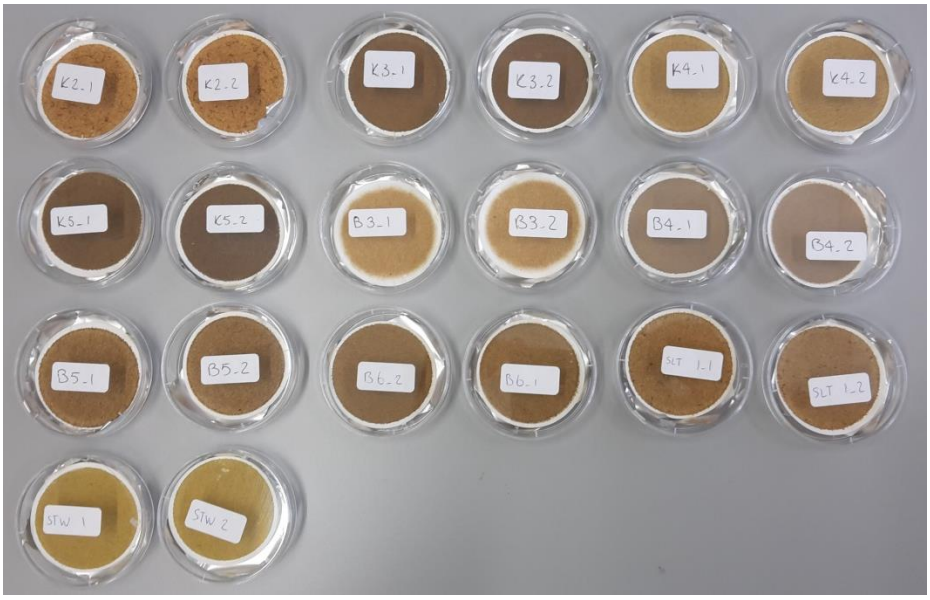

Figure 4.2. Dried filters after filtration of the water collected in June.

As for the biological reduction, culturing of the microorganisms was successful since all of the orange-brown colored ferrihydrite on top of the sediment was reduced within two weeks. Only a thick layer of dark, black sediment remained in the bottle. Moreover, the o-PO_4 and Fe^{2+} concentrations were checked each week and both showed an increase which indicated that the microorganisms were active. The color of SM and water in the microcosms did not visibly change during the experiment. The filters used for the chemical reduction experiments contained less sediment and were much lighter after the experiment.

4.2 Quarles van Ufford

Drainage water samples from Quarles van Ufford were named DQ2, DQ3 and DQ4 and correspond to the locations where they were taken which are Q2, Q3 and Q4 respectively. The average SM concentrations illustrated in *figure 4.3* (and presented in *appendix* C) show a large variation in results, with a minimum of 2 mg/l at Q4 and a maximum of 86.3 mg/l at DQ2 in February/March. Considering surface water, Q3 and Q7 located in ditches have the highest concentrations followed by Q5 and Q6 from the main watercourse. Since the other ditch locations have the lowest values, no clear difference can be seen between ditches and larger streams. Moreover, drainage water at Q2 is more than four times higher compared to surface water at the same location, although this difference does not exist for water types at locations Q3 and Q4. The SM concentrations are lower in April while comparable to the results from June. Now Q5 has the highest value which is located in the main watercourse. Location Q3 shows a large decrease from the first measuring moment in February, going from 65.9 mg/l to 3.7 (April) and 10.76 mg/l (June). Moreover,

high average concentrations correspond with high standard deviations which designate a large variability of values.

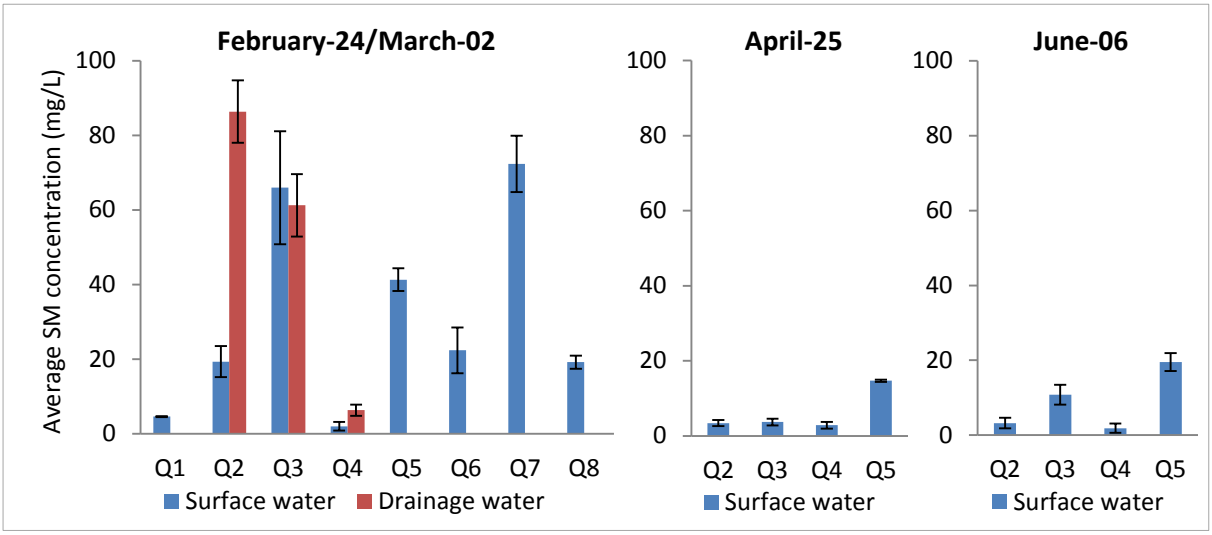

Figure 4.3. Average suspended matter concentrations per sampling time for Quarles van Ufford. The error bars depict the standard deviation.

Results from the SEDEX demonstrate that the largest proportion of the P content in SM is made up off Fe-P as depicted in *figures 4.4-4.5* and *appendix D*. Organic P is the overall second largest proportion of PP. The total P content of SM does not have an influence on these proportions, since between high and low P contents there is no visible difference in fraction distribution. However, this total P content is varying considerably between locations and sampling moments. Highest P contents in SM are found at locations Q1, DQ4 and Q4 in February. The maximum P content is lower in April compared to February, however, it is increasing again in June. Fluctuations between P content values are not proportional between the locations at different measuring moments. Bed sediment in Quarles van Ufford contains significantly less P compared to suspended matter at the same locations. The range of values for sediment has a minimum of 0.6 and maximum of 2.47 for the total P content (*figure 4.5*).

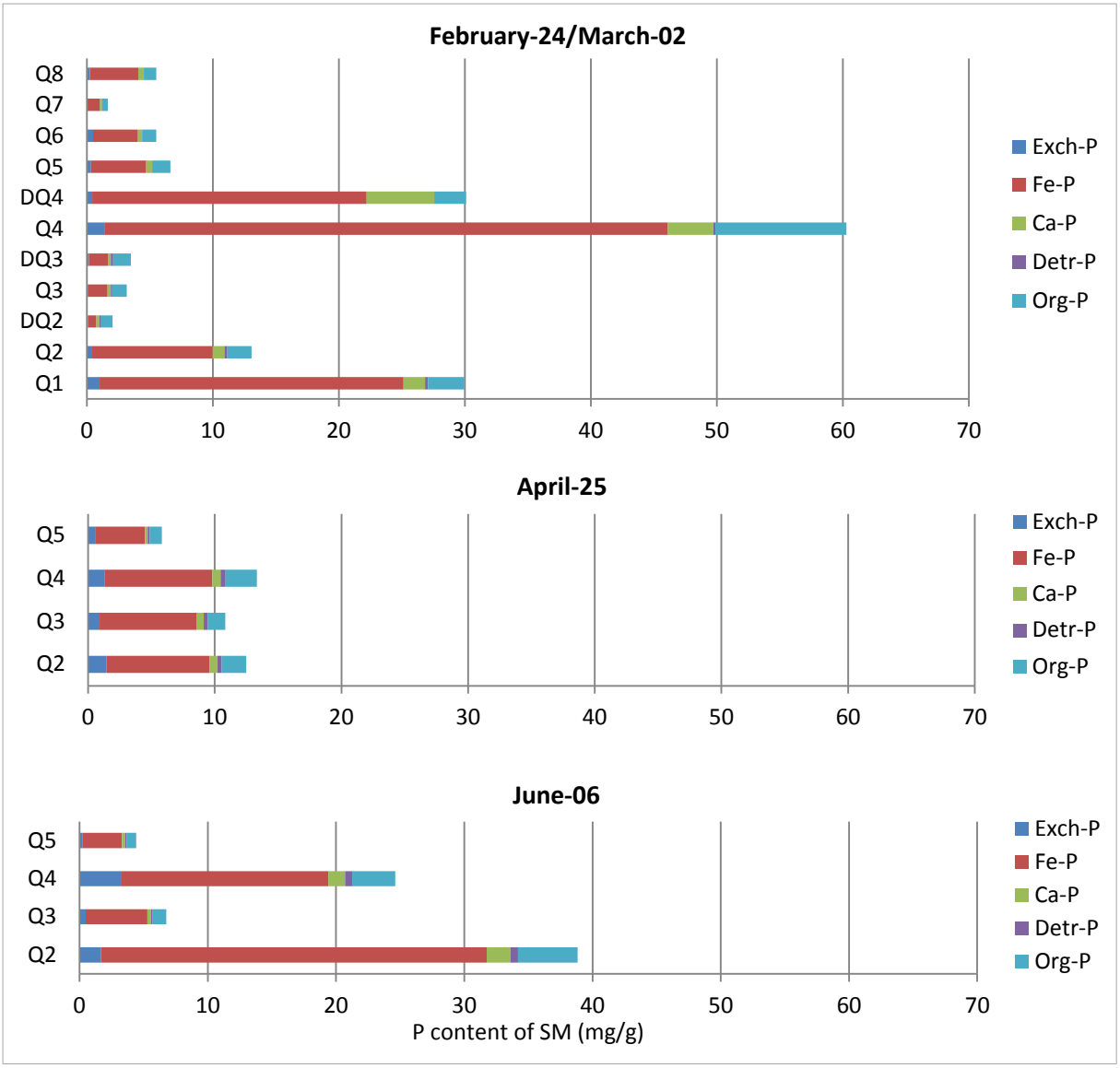

Figure 4.4. Phosphorous content of suspended matter per sampling time for Quarles van Ufford.

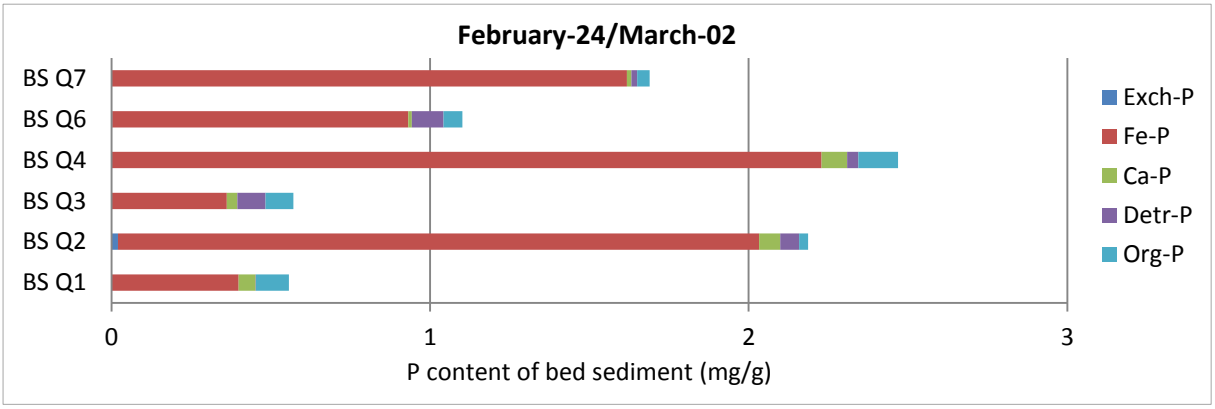

Figure 4.5. Phosphorus content of bed sediment sampling time for Quarles van Ufford. The BS on the vertical axis stands for "bed sediment". Note that the maximum value on the horizontal axis is different than the one of figure 4.4.

Data of fraction contributions to the total PP pool demonstrate that in general the largest part is represented by the Fe-P fraction. With few exceptions, Org-P has the second largest contribution to the total amount of PP. No clear trend between the different months is visible in Quarles van Ufford (*figure 4.6*). Locations DQ2, Q3 and DQ3 have a large Org-P fraction compared to other measuring points in February/March. Moreover, the bed sediment values reveal that Exch-P is not present in the soil.

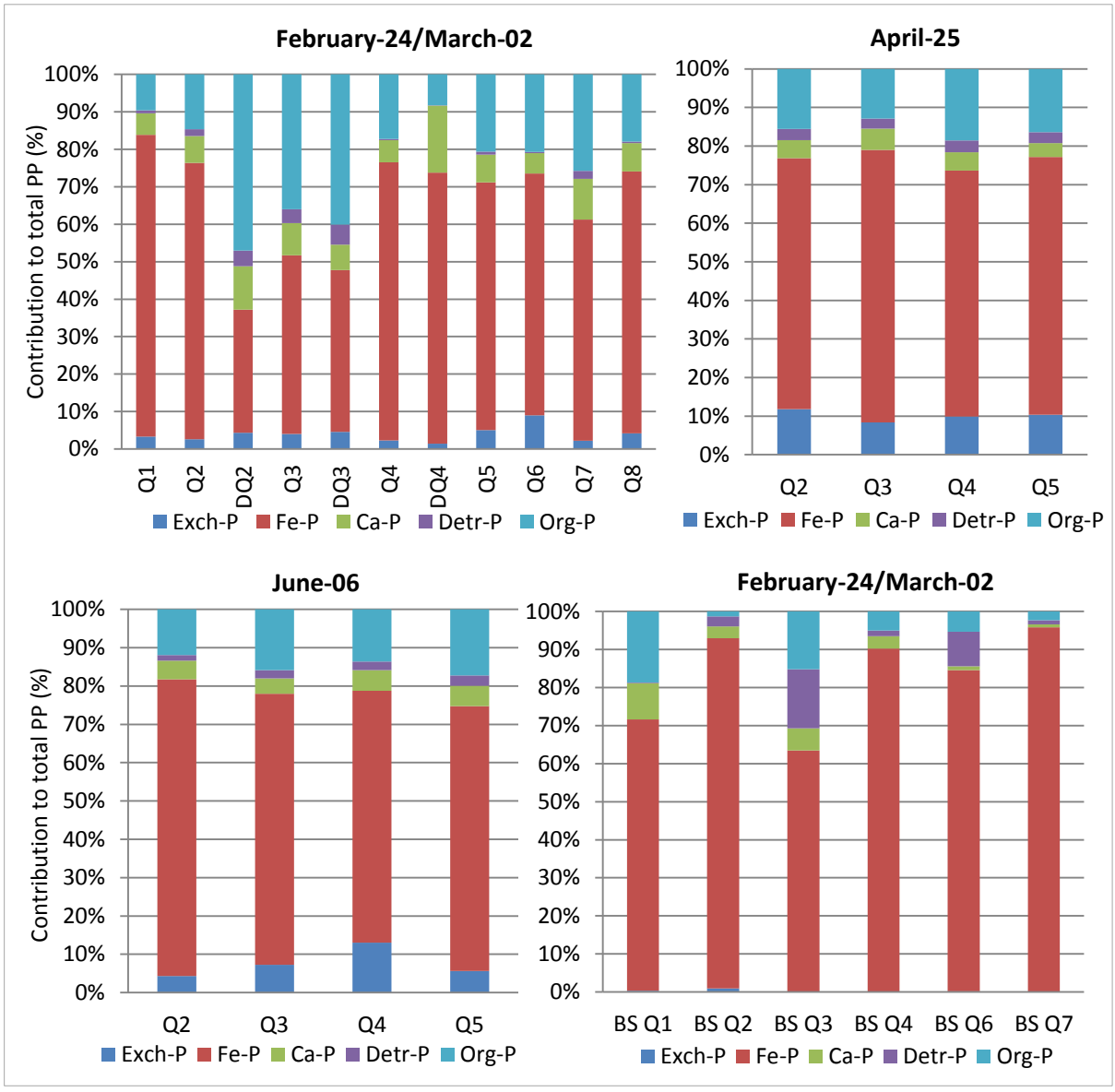

Figure 4.6. Fraction contribution to the total particulate phosphorous pool per sampling time for Quarles van Ufford.

The water quality parameters that are expected to be important are pointed out in this paragraph (*figure 4.7*) and a more detailed table of all measured parameters is found in *appendix E*. The cation and anion concentrations of February/March reveal fluctuating values. Exceeding concentrations are noticeable for Q4, DQ4, Q1, which show an evident $CaHCO_3$ abundance in the water. The soil at these locations is likely rich in calcium and the surface water origin is determined by groundwater seepage with has taken up Ca on its way to the surface. This is also, to a lesser extent, the case for Q2, Q7 and Q8. Higher SO_4 and Cl

concentrations are measured at Q4-Q8. Locations Q4, Q7 and Q8 are situated close to the dikes near the Maas and Waal River. Here, the SO_4 and Cl concentrations may come from river seepage water which has passed underneath the dikes. Locations Q5 and Q6 are located in the main watercourse, so the water origin is probably a combination of inlet water and discharge of polder water. Surface water at location Q3 and drainage water at Q2 consists probably for the most part of rainwater, as evidenced by the low ion concentrations. The DP varied from 0 to 0.1 mg/l and NO_3 from 0.7 to 6.8 mg/l at locations Q2-Q8. The NO_3 concentration of Q1 was remarkably high with 16.9 mg/l. Data from June does not show much variation, although Q3 and Q4 have higher Ca and alkalinity values compared to the other two locations for that sampling time. Also, the DP values are slightly higher (0.2-0.4 mg/l) and the NO_3 concentration of Q5 is exceeding with 14.9 mg/l.

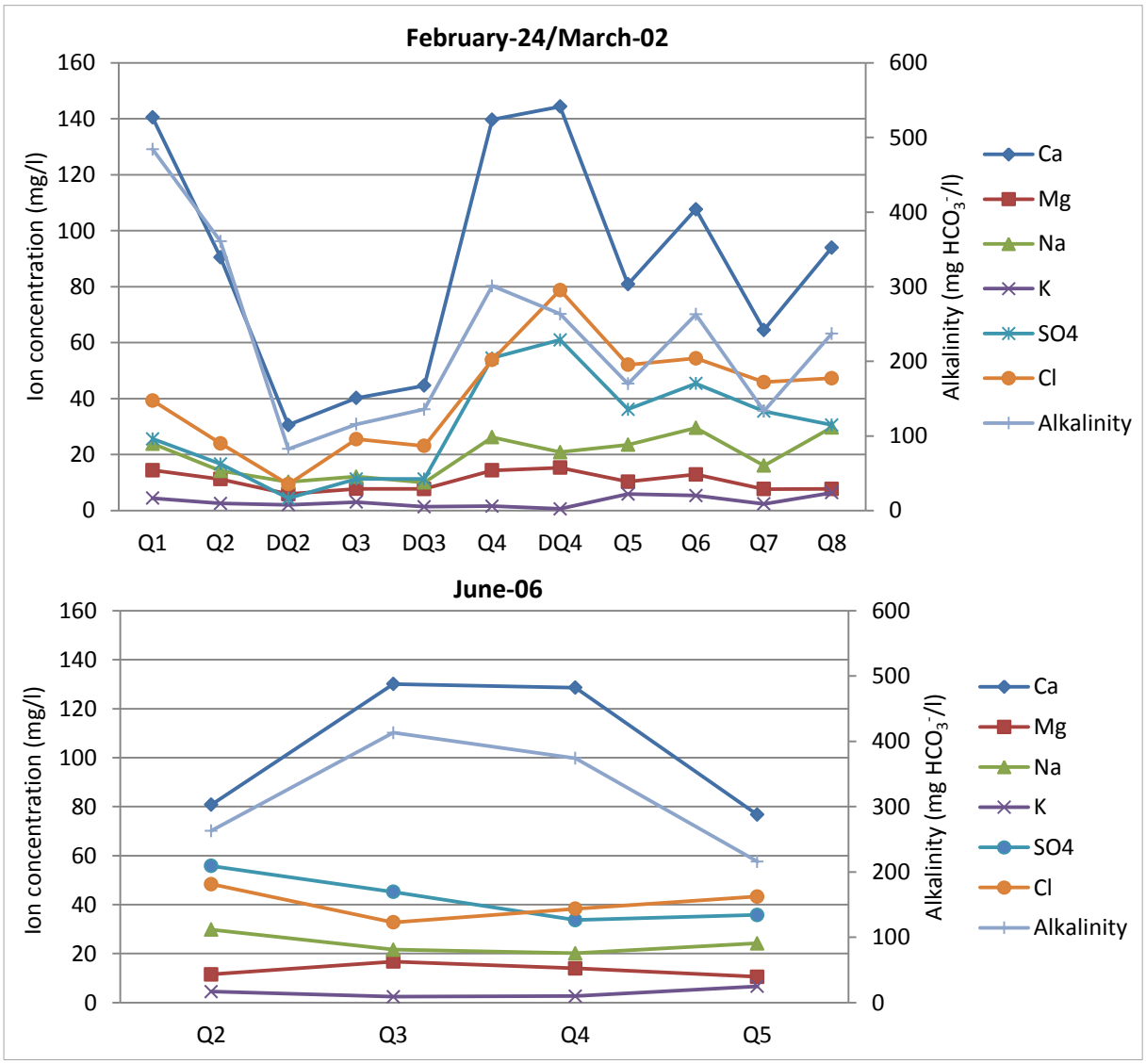

Figure 4.7. Water quality parameter per sampling time for Quarles van Ufford.

4.3 Langbroek

The SM concentration results from Langbroek (*figure 4.8* and *appendix C*) in March show a variation from 0.9 to 7.9 mg/l for LB2- LB6 with a deviant value for LB1 with 26.1 mg/l. The range in values is generally lower than the range for Quarles van Ufford in the same sampling period. Considering the results for June, the concentrations of LB4-LB6 are higher where now LB4 has the deviating concentration of 21.4 mg/l. This varies a lot with the minimum value for that period which is 0.7 mg/l for LB3.

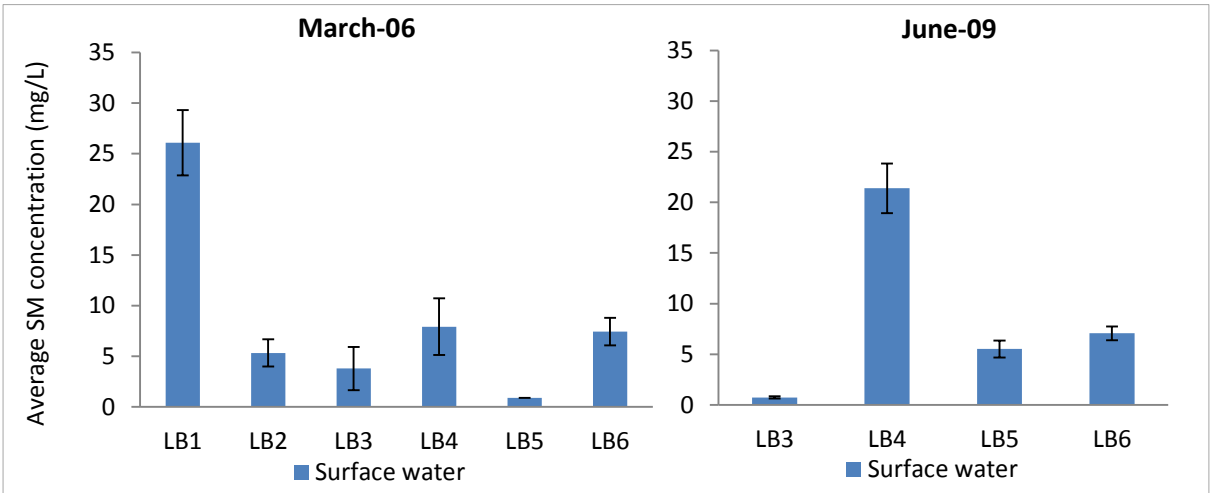

Figure 4.8. Average suspended matter concentrations per sampling time for Langbroek.

The hypothesis that Fe-P is the largest fraction followed by Org-P also accounts for Langbroek which results are shown in *figure 4.9* and *appendix D*. Locations LB3 and LB5 have the highest P content in SM. However, the total P content of location LB3 is going up (from 31.1 to 55.7 mg/g) and the one of location LB5 is going down (from 96.6 to 24.6 mg/g) between the two sampling times. The values of the other locations are varying below a P content of 20 mg/g.

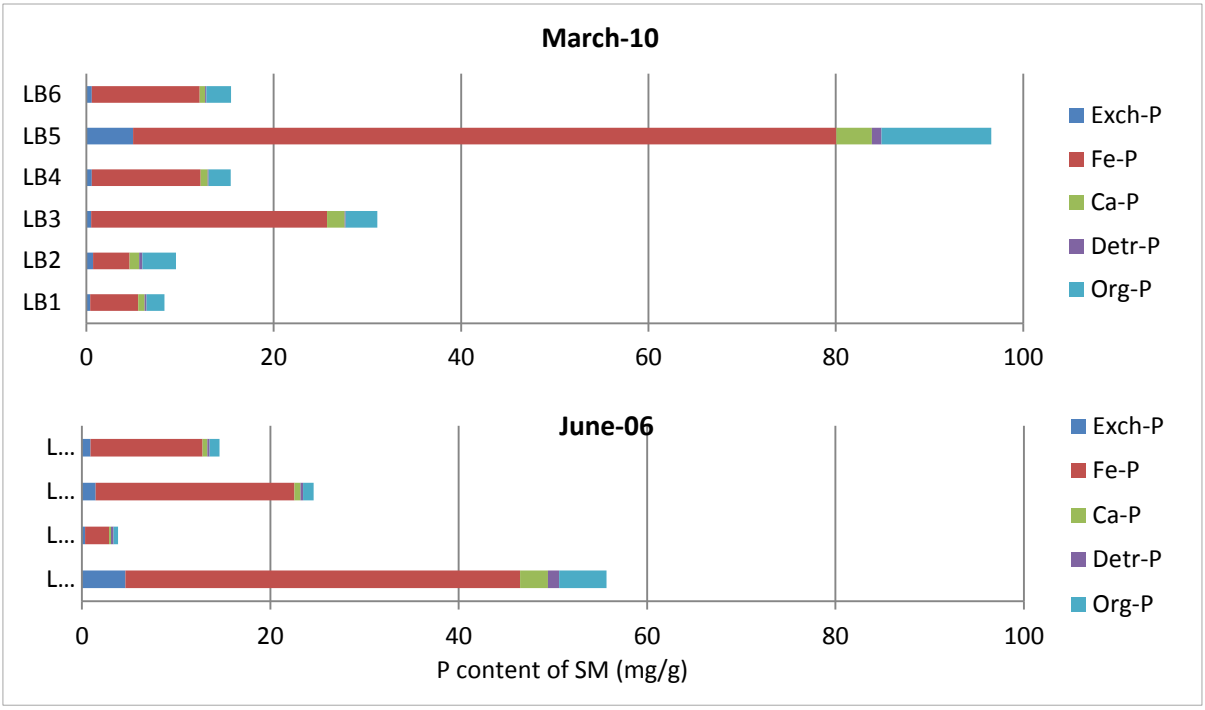

Figure 4.9. Phosphorus content of suspended matter per sampling time for Langbroek.

Fraction distribution outcomes from Langbroek (*figure 4.10)* do not show significant temporal or spatial differences between locations. The large Fe-P contribution is clearly visible with occasionally also a considerable Org-P fraction: the Org-P fraction is similar to the one of Fe-P at location LB2.

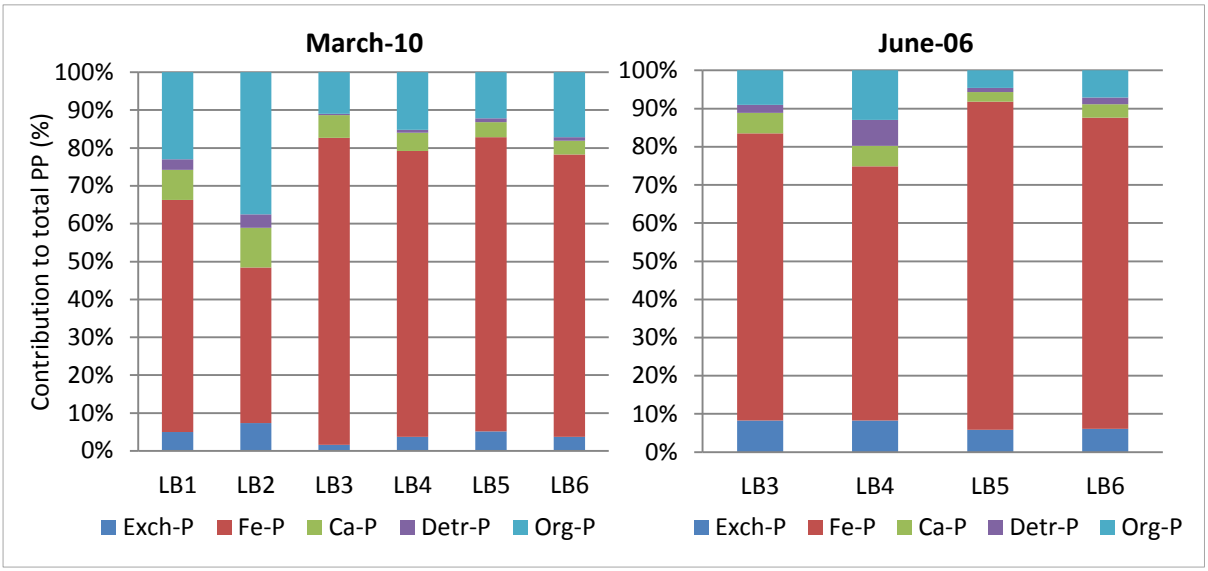

Figure 4.10. Fraction contribution to the total particulate phosphorous per sampling time for Langbroek.

Cation and anion concentrations of Langbroek (*figure 4.11* and *appendix E*) illustrate a high $CaHCO_3$ abundance at ditch locations L1-LB3 and LB5. This may be explained by groundwater seepage from Ca rich soils. The Ca and HCO_3 concentrations are slightly lower at locations LB4 and LB6, which are located in the main watercourse Langbroekerwetering. Here, the surface water may be mixed with rain water and water from the Kromme Rijn resulting in a lower presence of $CaHCO_3$. The Cl concentrations are slightly higher in ditch locations LB1-LB3. These measuring points are much closer to the Kromme Rijn than the other locations, so the infiltration of water from this stream may explain the higher Cl concentrations. The DP is varying from 0.04 to 0.1 mg/l in March and 0.4 to 1.5 mg/l in June. Regarding the NO_3 concentrations, it is highest in LB5 with 15 mg/l in March whereas the other locations have concentrations between 1.2 and 8.2 mg/l. The NO_3 values are fluctuating between 1.6 and 7.9 in June. In general, large fluctuations between measuring points are not as evident as in Quarles van Ufford. It is also notable that water quality parameters have barely changed over a period of three months.

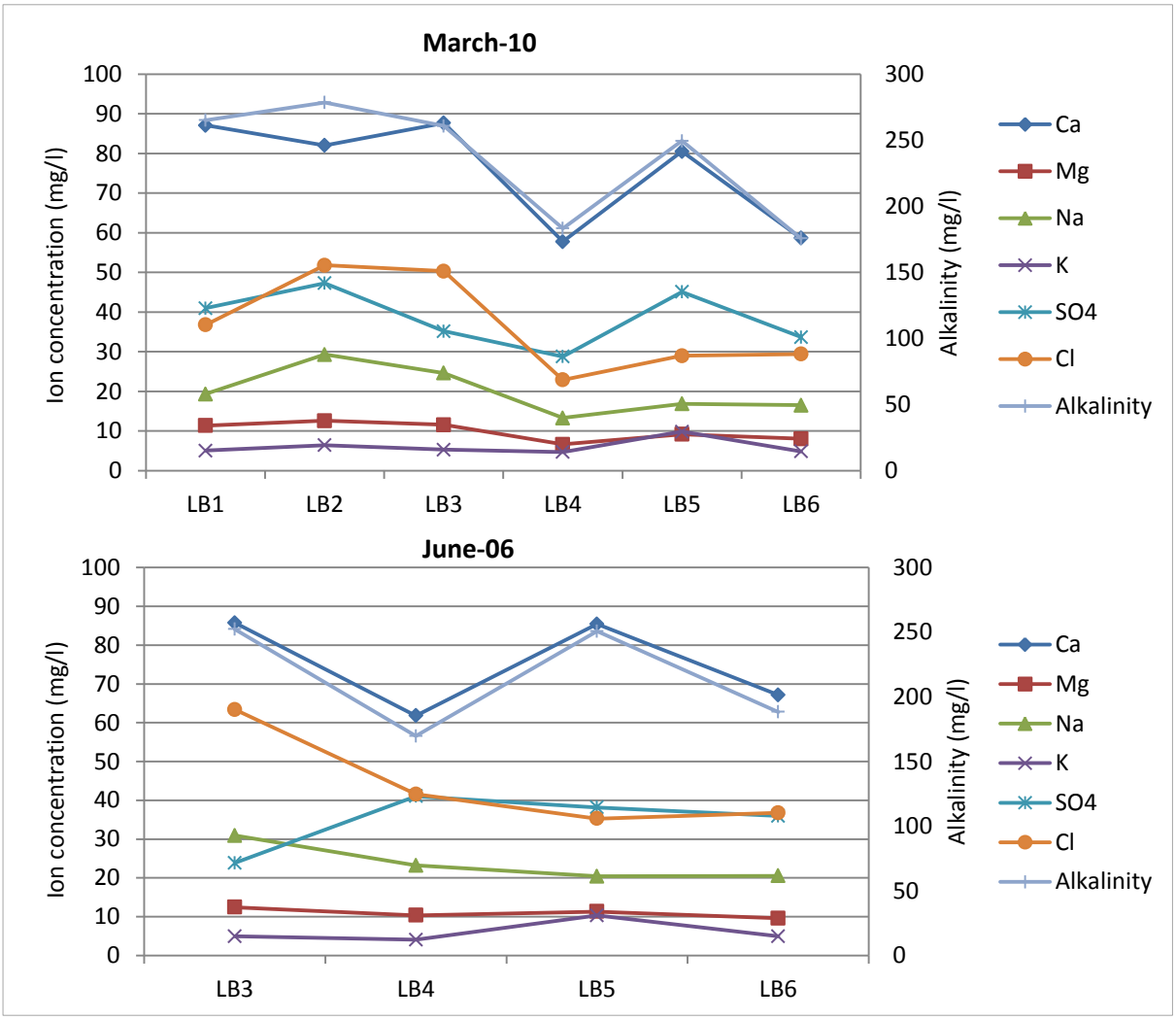

Figure 4. 11. Water quality parameters per month of Langbroek.

4.4 Noordplaspolder

The SM concentrations of the three locations from the Noordplaspolder are shown in *figure 4.12* and *appendix C*. Location PLS has a more than twice as high result (26.7 mg/l) than SLT and STW (9.1 and 9.6 mg/l). The measuring point PLS is situated before the pumping station and is therefore more influenced by changes in water flow caused by activity of the pumping station. Locations SLT and STW in side ditches have similar SM concentrations.

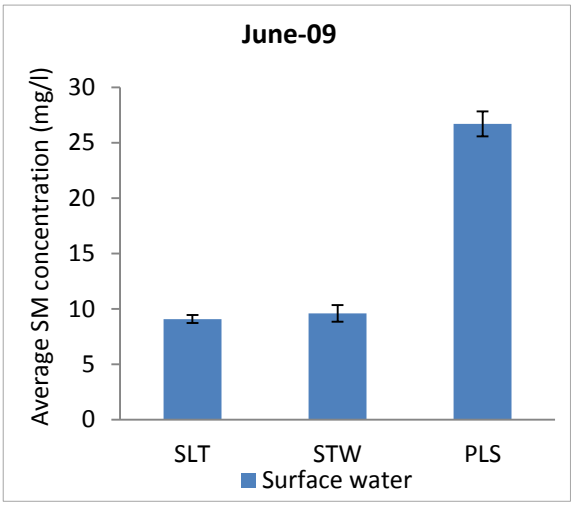

Figure 4. 12. Average suspended matter concentrations for the Noordplaspolder.

In the Noordplaspolder the PLS location has the lowest P content (6.6 mg/g) in relation to STW and SLT (18.4 and 19.6 mg/g) as seen in *figure 3.13* and *appendix D*. The proportions of the fractions are comparable for the locations and the Fe-P again predominates in the distribution. The same observations are made for the fraction contributions, since there are no differences between locations and the main fraction is Fe-P (*figure 4.14*).

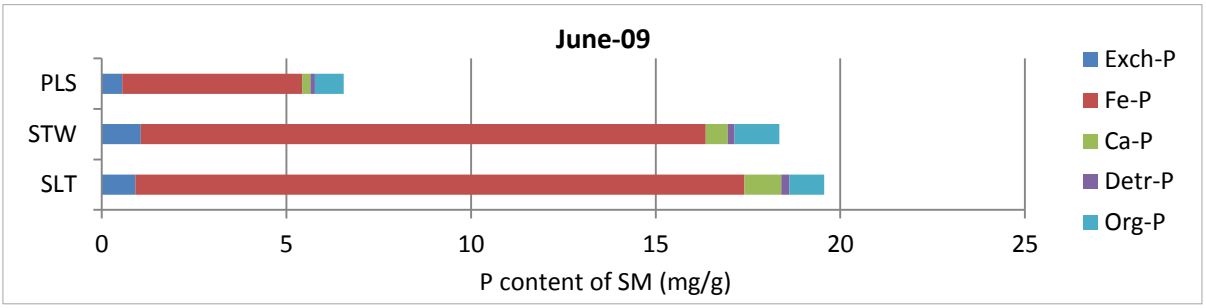

Figure 4. 13. Phosphorus content of suspended matter for the Noordplaspolder.

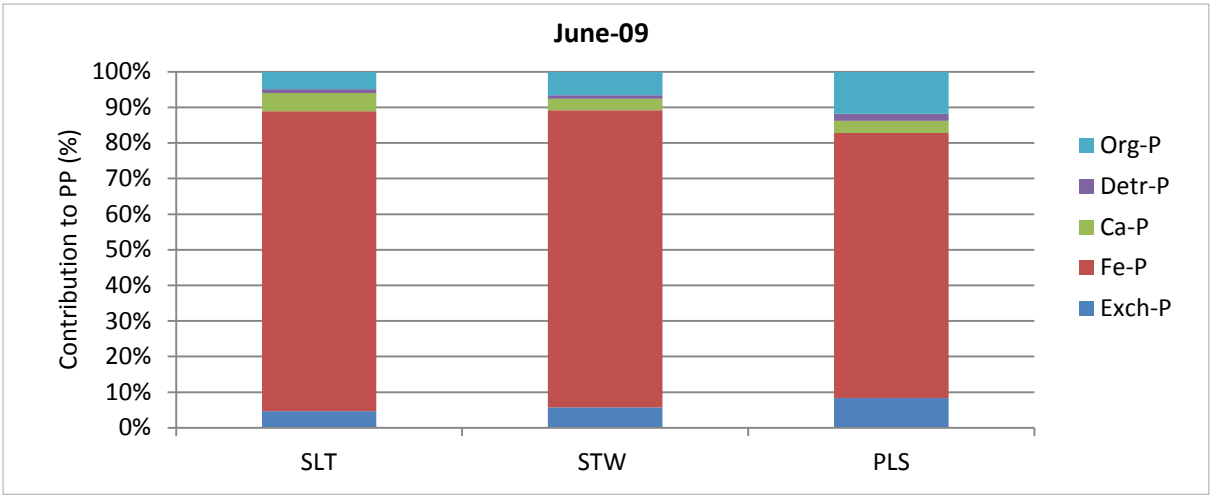

Figure 4.14. Fraction contribution to the total particulate phosphorous for the Noordplaspolder.

4.5 Flevopolder

Another study by Van der Grift et al. (2016) performed a high-frequency monitoring programme at the Flevopolder using the same SM filtration procedure as this research. Those filters were incorporated in the SEDEX procedure of this study to get a clearer picture on seasonal variances of P fractions in SM. The findings are shown in *figure 4.15* and *appendix D* with a measuring period from January to August, so winter data is missing. First, from January to February Fe-P is decreasing while Org-P as well as Exch-P is increasing. The measurement at March 12 shows a large Org-P contribution of almost 50% together with a sudden drop of Exch-P from 19 to 2% within a month. Afterwards, a more or less stable state follows with Org-P values around 27% and those of Exch-P around 18%. At August 24, the Exch-P fraction is higher again whereas the Org-P is smaller. Throughout the measuring period Fe-P varies from 58 to 41%, with a peak value on Jan 15 of 68%.

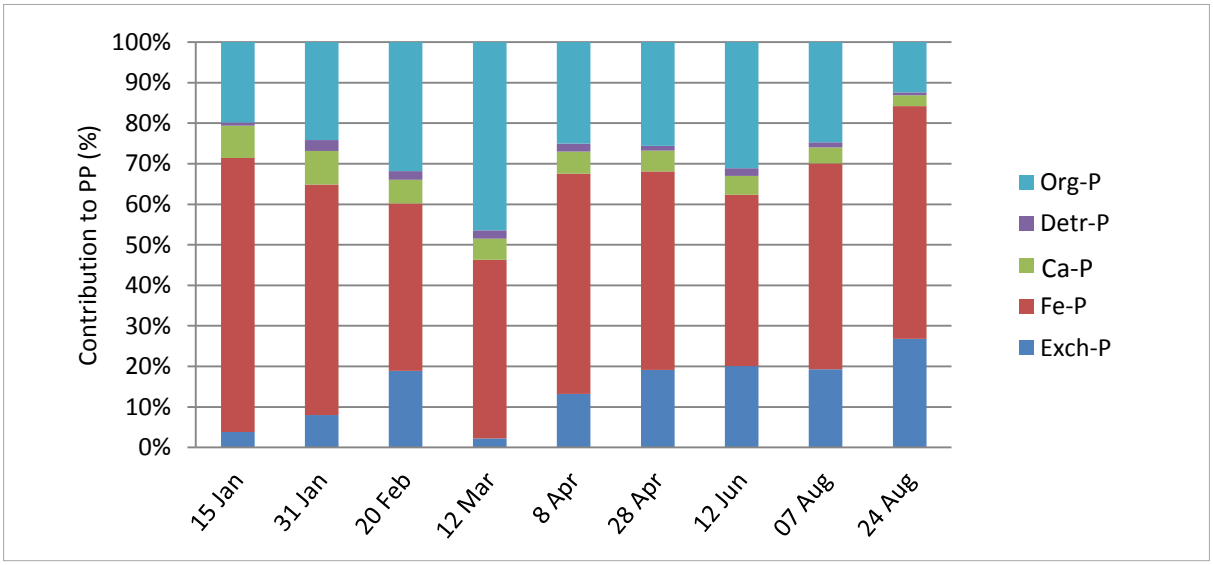

Figure 4.15. Fraction contributions to the total particulate phosphorous per month in the Flevopolder.

4.6 Reduction experiments

Multiple samples were taken from the five batches during the first two weeks of the experiment. The observation that there were no visible changes in the SM color of all the batches (*figure 4.16*) is explained by the results from all the samples giving o-PO_4 and Fe^{2+} concentrations of zero, revealing that no reduction had taken place.

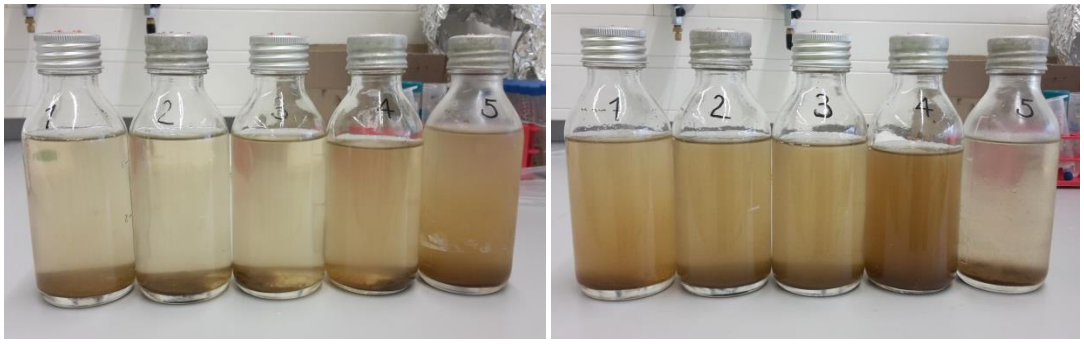

Figure 4.16. The five experimental batches on the 1st day (left) and on de 3rd day (right).

Initial growth of the micro-organisms was stimulated by adding acetate during preparation. Therefore, 5 ml of 1M Na-acetate was added in the first two experimental batches as well in order to see if organism activity can be stimulated. Concentrations were measured a few times afterwards within 1.5 week and resulted in an increase of Fe^{2+}, fluctuating o-PO_4 values and a visible color change to more dark green (*figure 4.17*).

Figure 4.17. The experimental batches after adding acetate at from left to right the 6th, 8th and 13th of July.

A noticeable aspect of the graph (*figure 4.18*) is the sudden drop in P concentrations at July 8, because the Fe^{2+} concentrations do seem to follow a gradual increase. This upward trend is going faster for batch 2 with a Fe concentration of 5.5 mg/l at July 8 while batch 1 had a concentration of 2.1 mg/l at that moment. Eventually, both batches have a Fe^{2+} concentration of about 5.1 mg/l on the last sampling moment at July 13. The P concentration stayed between a range of 0 to 0.3 mg/l.

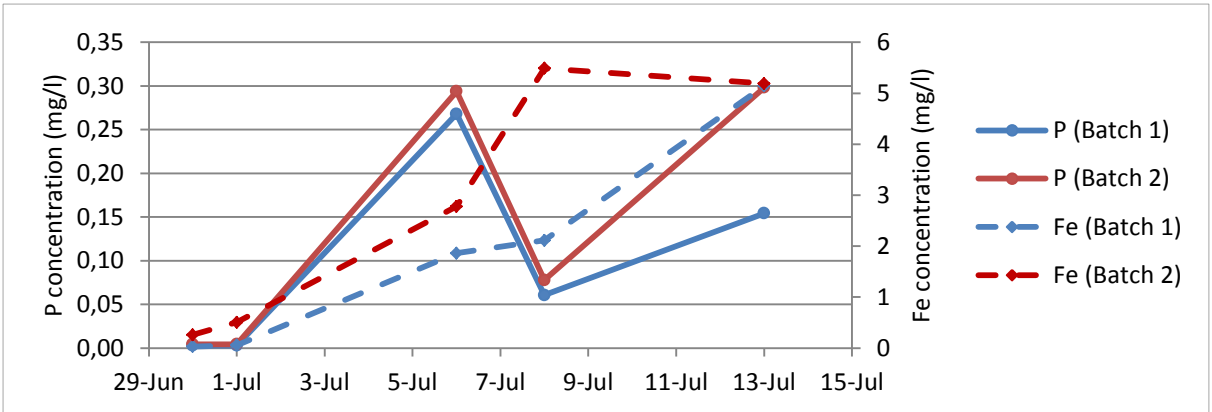

Figure 4.18. Phosphorous and iron(II) concentrations from the biological reduction experiments.

The reduction rate most likely corresponds to the increase in Fe^{2+} in the batches. The Fe concentration increases from 0 to 5.1 mg/l in 13 days in batch 1 which translates to a reduction rate of 0.4 mg l^{-1} day^{-1}. Or, when incorporating the molar mass of Fe (55.8 g/mol) the rate will be 7.0 µmol l^{-1} day^{-1}. The second batch already had a Fe^{2+} concentration of 5.5 mg/l after 8 days. This leads to a rate of 0.7 mg l^{-1} day^{-1} which is equal to 12.5 µmol l^{-1} day^{-1}. Thus, the reduction process seems to have gone faster in batch 2..

Chemical reduction experiments were conducted with one SM sample and two filter samples. The first experiment (Exp 1) with a SM sample resulted in o-PO_4 concentrations of zero (*figure 4.19*). However, the Fe^{2+} concentration increased within 1.5 hours to 5.95 mg/l and stays relatively stable during the following hours of the experiment which translates to a reduction rate of 4 mg l^{-1} h^1 (or 70 µmol l^{-1} day^{-1}). For experiment 2 (Exp 2) the o-PO_4 in the water rises during the first hours to 0.08 mg/l. Hereafter, the bubbling of nitrogen was stopped and the o-PO_4 value was decreased to zero in the next morning (*figure 4.19*). The Fe^{2+} concentration increased to a maximum of 1.3 mg/l in 6 hours resulting in a reduction rate of 3.9 µmol l^{-1} day^{-1}. In experiment 3 (Exp 3) the o-PO_4 remained low during the measuring time. The Fe^{2+} concentration increased to 1.7 mg/l in 2.5 hours with a reduction rate of 12.1 µmol l^{-1} day^{-1} and afterwards is decreased again to 0.8 mg/l. Therefore, the reduction process seems to have gone faster in Exp 3 compared to Exp 2 for the filter samples. Results of the reduction experiments are presented in *appendix F*.

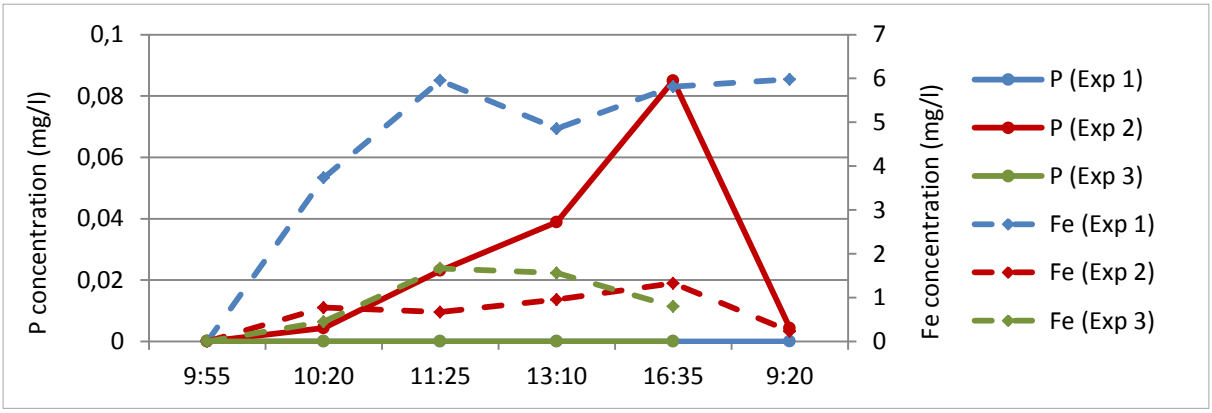

Figure 4.19. Phosphorus and iron(II) concentrations from the chemical reduction experiments.

5. DISCUSSION

The main purpose of this research was to identify the temporal and spatial variability of SM concentrations as well as the PP speciation in agricultural lowland polders. Methods that were used in this research have proven to give usable results to draw conclusions about this subject. First, the SM concentrations and the corresponding P content and PP speciation will be discussed in section *5.1* in relation to literature and other data. Second, seasonal variability in PP speciation is debated in section *5.*2. Subsequently, experiments to mimic the reduction of Fe-P in the field are discussed in section *5.3*. The used SEDEX method is discussed (section *5.4*) before there will be concluded with recommendations for future research (section *5.5*).

5.1 Analysis of suspended matter

5.1.1 Suspended matter concentrations

Large variations of SM concentrations between study areas as well as locations are seen, like in Quarles van Ufford. Spatial variety between locations is most likely characterized by local processes rather than regional features. The SM concentrations in February/March are in general higher compared to the other measuring moments. Studies on surface water quality recognize weather conditions as a major driver for variations in nutrient concentrations (Jordan et al. 2007). As mentioned, precipitation events can increase soil erosion and subsurface runoff resulting in higher amounts of SM in surface water (Reddy et al., 1999). Precipitation numbers from the KNMI weather station in Tiel (KNMI, 2016) show that 27.5 mm of rain had fallen in the region 4 days prior and on the day of sampling as shown in *figure 5.1*. Only 4.4 mm rain was recorded on the days before the sampling moment in April and only 0.4 mm before the sampling moment in June, which could explain the overall lower SM concentrations at these moments. The higher concentration at Q5 could be explained by the fact that it is situated in the main watercourse where flow velocity is higher and water from elsewhere in the area is flowing to this watercourse. The SM in the ditches will more likely deposit on the waterbed, but overall lower SM concentrations on these locations are not found in the results. Variation in SM between the ditch locations is probably induced by local hydrological differences. Inlet water from the Maas and the adjacent eastern may reach some of the ditches, since that is an important factor in Quarles van Ufford, especially in summer (Siderius et al., 2011). This may explain the high peaks found at locations Q3 and Q7.

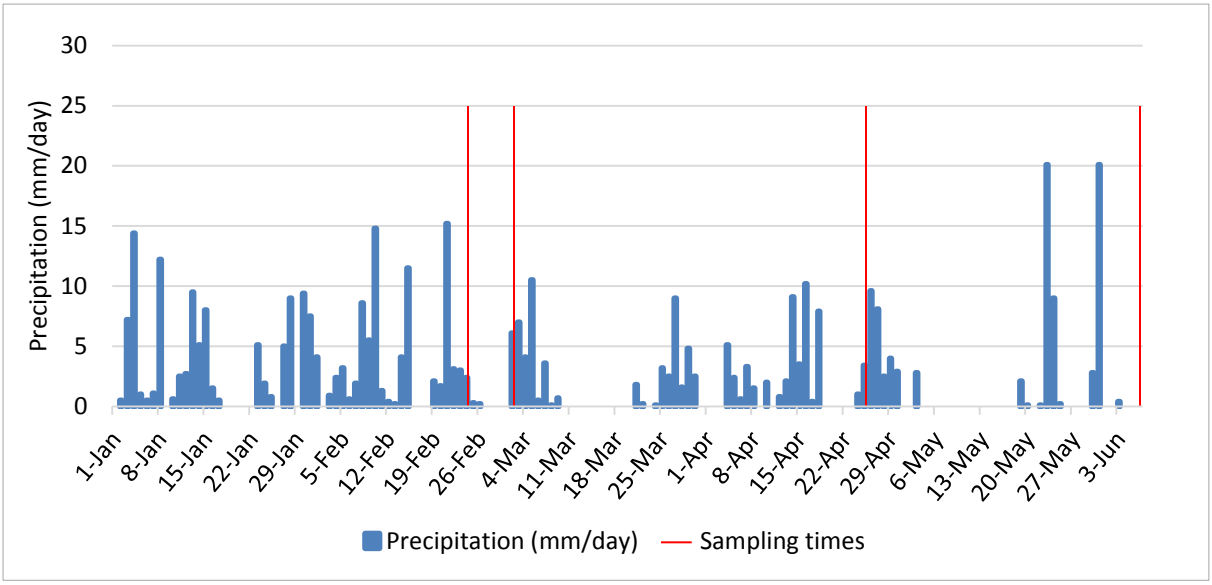

Figure 5.1. Precipitation measured in Tiel from the 1st of January to the 6th of June.

The place of sampling may have an effect on the relatively high drainage water concentrations. Drainage water samples were taken at the end of a drainage pipe just before the water reached the surface. Concentrations of Fe-P precipitates can be high, since oxidation of Fe^{2+} may already took place in the pipe resulting in the formation of these precipitates. However, the P content of SM in drainage water was low meaning that P particles are not the main part of the SM. This implies that other sources and processes, rather than Fe-P formation, explain the high SM concentration in drainage water.

Compared to Quarles van Ufford, the concentrations in Langbroek are generally lower. The SM concentration of LB1 is very high compared to the other locations in Langbroek. This is possibly due to the geographical location, since it is more distant from the "Utrechtse Heuvelrug" and on the other side of the "Kromme Rijn". For that reason it may be less affected by rainwater seepage originating from the hillside and more influenced by the stream itself. As where the other locations are "rinsed" by the connected water system and rainwater, LB1 is at the end of the catchment nearby the "Kromme Rijn" where all the water eventually ends up (Klaarenbeek et al., 2008). Higher concentrations at LB4 and LB6 in June can be explained by the fact that they are situated in the main watercourse "Langbroekerwetering" where higher flow velocities occur.

The water quality parameters are characterized by higher ion concentrations where less SM is measured. The ionic composition with a lot of dissolved particles typically does not reflect rainwater, but water from another origin. For example, groundwater that has taken up a lot of ions before exfiltration or surface water that comes from elsewhere in the catchment. As mentioned, locations with lower SM concentrations (Q1, Q2 and Q4) are likely to be influenced more locally. Therefore, the assumption is that exfiltration of mineralized groundwater result in the high $CaHCO_3$ abundance. When the authigenic formed Fe-P due to exfiltrating groundwater can deposit rapidly, it can result in the large Fe-P contribution found in bed sediment. Another possibility could be the formation of colloids rather than

solid particles. These colloids may pass through during the filtration procedure causing high ion concentrations instead of SM concentrations.

5.1.2 Particulate phosphorus content

There is a consensus in literature about the correlation between the SM- and PP concentration (Kronvang et al., 1997; Beusen et al., 2005). In this study however, this correlation is not clearly visible. The downward trends (black lines) of the concentrations showed in *figure 5.2* appear to go parallel next to each other. This means that the locations with higher SM concentrations also have higher PP values and vice versa, which is plausible when looking at other studies. Yet this does not seem to apply when the concentrations are plotted against each other in a graph (*figure 5.2*) and points are randomly scattered (R^2 = 0.2526) rather than linear. The concentrations are highly variable and susceptible to small changes in time and place, like hydrodynamic forcing and changes in P binding. Moreover, sampling was done at different locations and only at two moments. Validating the outcomes can be improved by sampling more frequently.

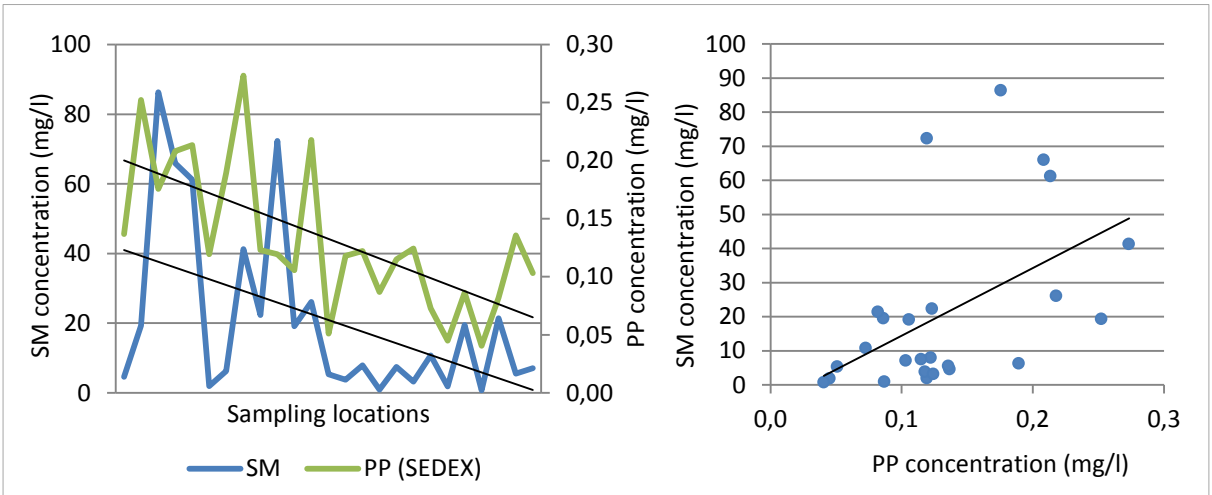

Figure 5.2. Correlation graphs between suspended matter and particulate phosphorus concentrations

The results on the P content of SM demonstrate that this ratio is high for locations with small SM concentrations and vice versa. This relation is illustrated in *figure 5.3* with on the right side the natural logarithm of both variables showing a linear correlation (R^2 = 0.8393). Now the assumption emerges that P content of SM does not change with changing SM concentrations. When the amount of SM increases and the P amount remains the same, the P content of SM will decrease. Thus, the SM concentration does not reflect the PP amount in the surface water. So, an increase in SM is determined by an increase in other kinds of particles rather than PP. Bed sediment contained a lot less PP compared to SM at the same location with a maximum of 2.4 mg/g. Two explanations can be used to clarify this finding. First of all, bed sediment consists of more material other than PP what will decrease the P pool in the waterbed. This is plausible since 1 cm^3 bed sediment consists of much more material than 1 cm^3 water with SM. Second, it is possible that most of the PP is in suspended form rather than deposited on the waterbed. This could be the case when mobilization of P particles is ensured by a sufficient flow velocity and the PP flux into

the surface water is higher than the downward sedimentation flux (Reddy et al., 1999). Phosphorus particles could also be less prone to deposition compared to other particles. Moreover, the method of waterbed sampling could also have affected the results. The upper few centimetres of the sediment core are taken and homogenized before taken subsamples. The composition of the sediment can, however, vary between these few centimetres giving uncertainty of the results.

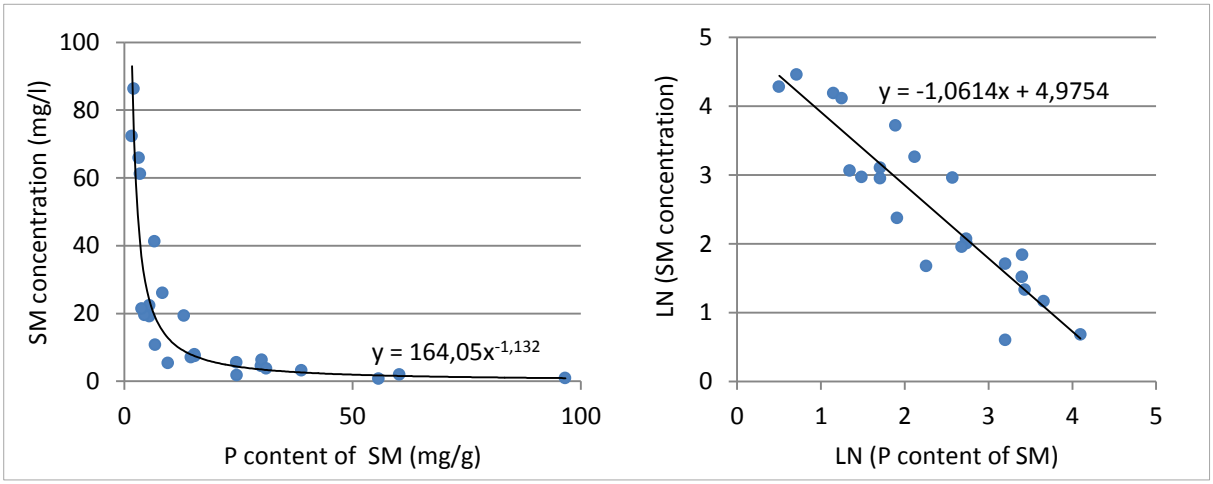

Figure 5.3. Correlation graph between suspend matter concentration and phosphorus content

5.1.3 Particulate phosphorous speciation

Results from all of the four areas share the outcome that Fe-P is in general the largest PP fraction (32%-96%). This is consistent with the observation that after exfiltration of Fe-rich groundwater, oxidation of Fe^{2+} to Fe^{3+} takes place due to the influence of oxygen. At the same time, o-PO_4 present will be immobilized by the authigenic formation of HFO's and FP's (Vanlierde et al., 2007; Baken et al., 2013). Considering Dutch polders, groundwater is indeed most often characterized by anaeroob, Fe-rich groundwater (Griffioen et al., 2013). Organic P is the overall second largest proportion of PP (2%-49%) as seen from the SEDEX extractions. The large range of contribution percentages for Fe-P and Org-P are explained by deviating values for single samples. *Figure 5.4* shows the fraction contributions for all results taken together, where the large Fe-P fraction is evident. The difference between extracted Fe-P and Org-P (µg/mg) in relation to the total PP (µg/mg) is also depicted in this figure. Again, the Fe-P dominance is displayed clearly by the higher increase of this fraction with increasing PP. The combination of a higher Fe-P fraction contribution with increasing PP could be explained by a higher authigenic production of HFO's and FP's (Baken et al., 2013).

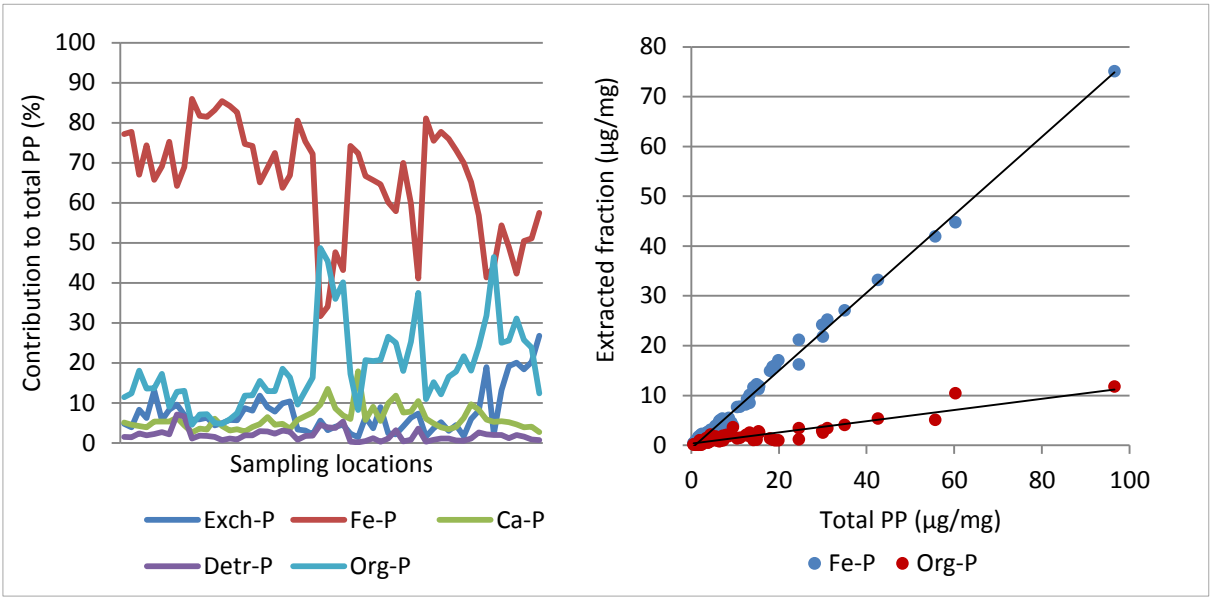

Figure 5.4. Fraction contributions (left) and extracted P to the total extracted PP (right) for all locations.

5.2 Seasonal variability

Results from the Flevopolder give the most frequent data on P distribution and has moreover less influence of external water throughout the sampling period. The latter is the case for Quarles van Ufford where water from the Maas River is influencing the area and Langbroek where the Kromme Rijn River affects water in the region. A trend is visible in the Flevopolder results which show a decrease in Fe-P contribution until March and at the same time Org-P is decreasing (*figure 5.5*). Hereafter, the Fe-P fraction is increasing again while Org-P is decreasing. This could be explained by the increase in biological productivity (algae growth) resulting in the reduction of Fe-P (Søndergaard et al., 2003). However, algae growth in January and February is early in case of the Netherlands, since it mostly occurs in spring. This year was characterized by a mild winter what might induce an early increase in biological productivity. The same trend is depicted from April to August for Fe-P, but Org-P is eventually not decreasing from June to August. Another notable finding is the drop of Exch-P in March before it slightly increases again from April to August. The changing conditions in the surface water due to an increase in organic particles could result in the release of loosely bound P. To conclude, the hypothesis that an increase in biological productivity corresponds with a reduction of Fe-P seems acceptable when looking at the Flevopolder.

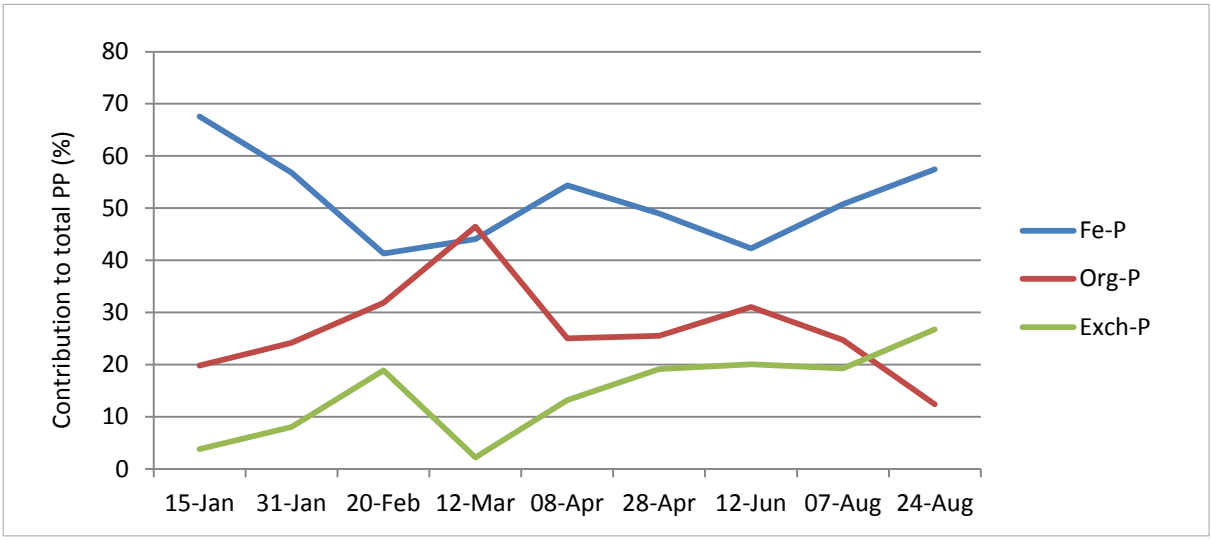

Figure 5.5. Fraction contributions to the total extracted P for the Flevopolder.

5.3 Reduction experiments

5.3.1 Biological reduction

The initial biological reduction experiment was unfortunately not successful due to inactivity of the Fe-reducing organisms. As seen in the results the addition of acetate has led to reduction of Fe en mobilization of o-PO_4. The first conclusion that is made is that the microorganisms need organic compounds (in this case acetate) in order to initiate the reduction process. However, for practical reasons it was not feasible to repeat the whole experiment with adding acetate in all the batches. Therefore, this was only done in batches 1 and 2 which were sampled five times in 1.5 week. The results showed an increase in Fe^{2+} in both batches with an end point of 5.1-5.2 mg/l. A Fe concentration of 5.49 mg/l was already measured after eight days in batch 2, as for the first batch the increase is more gradual. The rather stable concentration in the last five days of batch 2 and the similar end concentrations could indicate that the maximum reduction potential was reached in both batches. This assumption needs to be validated with a longer time-span of the experiment. The reduction rate of batches 1 and 2 are respectively 7 µmol l^{-1} day^{-1} and 12.5 µmol l^{-1} day^{-1}. This difference in rate cannot be explained by the method, because similar steps were taken and conditions are the same for both batches. It is most likely explained by batch conditions. Fewer microorganisms might be injected in the first batch or there is some variation in the SM composition between the two set-ups. Also the o-PO_4 concentration shows an increase for both batches, although there is a remarkable downward peak after 8 days. A reversal in P-binding due to oxidation is not possible due to the anoxic state of the experimental set-up. It could be explained by a measurement error or an influence of other processes, for example P-binding to particles in the water other than Fe. The P concentration goes up again after 13 days, so eventually o-PO_4 is released in the water. However, a reduction rate of the P concentration is not calculated since the data is disputable. The lack of results (n=5 for both batches) ensures that no clear statement can be made.

5.3.2 Chemical reduction

The experiment with SM showed an increase of Fe^{2+}, especially in the first 1.5 hours. The anaerobic conditions in combination with the ascorbic acid ensured the Fe^{2}+ release into the water. The SM should contain more than 35 µg of P which is bound to Fe, regarding the results from the SEDEX. However, no o-PO_4 is measured in all water samples although the expectation was that Fe^{2+} and o-PO_4 would increase simultaneously. Since o-PO_4 was not released into the water, it could still be attached to sediment particles other than Fe. In the CDB step of the SEDEX the Fe-P is measured, so it has to be present in the SM used for the experiment as well. The conclusion is that reduction with ascorbic acid does not resemble the process as described in the field.

The filter experiments have different outcomes. The first filter experiment (Exp 2) demonstrates an increase in both Fe^{2+} and o-PO_4 as hypothesized. The decrease of the last measuring point is explained by stopping nitrogen bubbling, which indicates that the anaerobic condition is required for reduction. According to the SEDEX outcome of a filter from the same location the filter in this experiment should contain about 0.1 mg/l P bound to Fe. The o-PO_4 concentration of 0.08 mg/l measured in the experiment indicates that after six hours the Fe-P might not be completely reduced. Filter experiment 3 (Exp 3) shows an increase in Fe^{2+}, but no increase in o-PO_4. However, the SEDEX reveals that the filter should contain about 0.06 mg/l P which is bound to Fe. Although Fe^{3+} reduction seem to took place (due to the increase of Fe^{2+}), the o-PO_4 concentrations indicate otherwise. It is possible that the released P was undergoing secondary processes so it could not be found in solution, like the binding on other particles at the filter. In general, the Fe^{3+} in the SM and on the filter can be chemically reduced within a few hours (1-6, possibly more) due to the reducing capacity of ascorbic acid. However, this is seen in the found Fe^{2+} concentrations rather than the o-PO_4 concentrations, because the latter showed some inexplicable results. The large variance of Fe^{2+} concentrations between the SM and the filters is explained by the increased concentration of the SM in the water prior to the experiment, resulting in a higher Fe-P content.

5.4 Sequential chemical extraction method

Although sequential chemical extraction is a widely used method to determine the distribution of different PP forms, it also comes with uncertainties. For each extraction step, a certain amount of liquid is added to the greiner tube with sample and poured off. It is inevitable that some liquid remains in the tube giving a deviant concentration measured by colorimetric analysis. This uncertainty is minimized by recalculating the concentration and thereby incorporating the remaining liquid (and remaining P) from the previous extraction step. Other known limitations of the SEDEX are the possibility of overlooking some PP fractions (Jordan et al., 2008) and that several P forms are extracted during one step which leads to an incorrect estimation of the fraction. For example, vivianite extraction during the CDB step, a reduced Fe mineral which is not expected to be important for SM in surface water. Except for the MgCl steps, some P is measured for the blank filters during the SEDEX analysis, but this measured amount of P is negligibly small. The reliability of the SEDEX results was checked by determining total PP with an aqua regia extraction on remaining filters and bed sediment samples. These concentrations are depicted in *figure 5.6* and show that the PP content is generally similar between the SEDEX and aqua regia extraction per

location. However, few expectations are showed which could be explained by variance between filters and sediment samples per location.

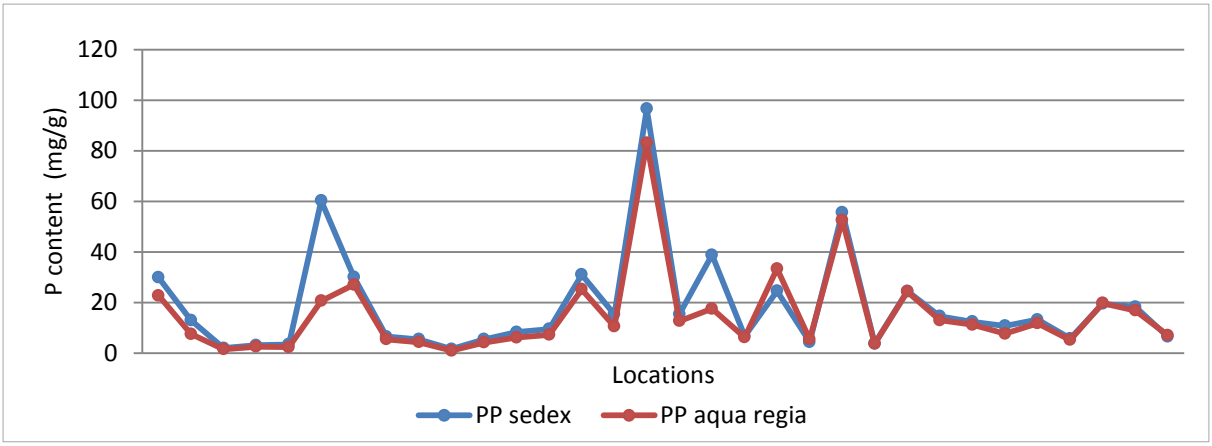

Figure 5.6. Phosporus content of SM and bed sediment from the SEDEX procedure and aqua regia extractions of all locations.

5.5 Recommendations for further research

As for this topic, it is recommended for the future that field samples are taken more frequently to create a more detailed result of seasonal variability. The influence of single events like rain storms and land fertilizing can this way be better recognised. This can be combined with a measurement of biological productivity in the ditches and streams as it is proven to be a main driver for Fe-P reduction. Spatial variety between the measuring points was also visible, so a more extended study on the hydrological processes of a specific location should create more understanding in SM dynamics. In the case of reduction experiments, biological reduction in particular reflects more the process in the field rather than chemical reduction. The experimental set-up of biological reduction has proven to work, so those results could be expanded with more batches and a longer time-span of the experiment. More batches with different conditions are needed to investigate the influence of other factors, like temperature and pH, on the reduction rate of Fe-P in SM.

6. CONCLUSION

The aim of this study was to determine SM concentration, P content and PP speciation in streams and ditches of Dutch polders in relation to spatial and temporal variance. Moreover, the availability of Fe-P in SM was studied with chemically and microbially induced reduction experiments. The SM concentrations from February/March in Quarles van Ufford were generally higher compared to the concentrations from April and June, but no clear differences between sampling moments were visible in Langbroek. There is also a lot of variety between sampling locations which is most likely determined by local hydrological rather than seasonal processes. Therefore, the first hypothesis that *SM concentrations are higher in* winter cannot be accepted. The large Fe-P fraction (32-96%) is evident in all study areas, so the second hypothesis that *Fe-P is expected to be the largest pool in the total amount of PP* is accepted. Organic P is the overall second largest proportion of PP (2%-49%). Also, a logarithmic relation between SM concentration and P content is found, where high SM concentrations have a low P content and vice versa. Regarding the PP speciation from the Flevopolder, Fe-P is decreasing until March while Org-P is increasing which means that the third hypothesis, saying that *the Fe-P fraction will decrease and the Org-P fraction will increase in spring*, is accepted. The decrease of Fe-P occurs earlier than expected, which could be explained by the mild winter of this year. Regarding the experiments, the biological reduction rates are 7 and 12.5 µmol Fe^{2+} l^{-1} day^{-1}. This is lower than the reduction rates of the SM sample (70 µmol Fe^{2+} l^{-1} h^{-1}) and the filters (3.9 and 12.1 µmol Fe^{2+} l^{-1} h^{1}) in the chemical experiments. However, the biological experiment is probably more representative of the field situation. Recommended for future research is more frequent sampling at locations, incorporating biological productivity measurements and expanding the biological reduction experiment (with including other factors like temperature and pH).

7. ACKNOWLEDGEMENTS

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Emma van Popta

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APPENDIX A: Details of measuring locations

Table A.1. Details of measuring locations per sampling time.

Month	Location	Sampling date	Surface water samples	Drainage water samples	Suspended matter	Bed sediment
February	Q1	Feb 24, 2016	x	-	x	x
	Q2	Feb 24, 2016	x	x	x	x
	Q3	Feb 24, 2016	x	x	x	x
	Q4	Feb 24, 2016	x	x	x	x
	Q5	Feb 24, 2016	x	-	x	-
March	Q6	Mar 02, 2016	x	-	x	x
	Q7	Mar 02, 2016	x	-	x	x
	Q8	Mar 02, 2016	x	-	x	-
	LB1	Mar 10, 2016	x	-	x	-
	LB2	Mar 10, 2016	x	-	x	-
	LB3	Mar 10, 2016	x	-	x	-
	LB4	Mar 10, 2016	x	-	x	-
	LB5	Mar 10, 2016	x	-	x	-
	LB6	Mar 10, 2016	x	-	x	-
April	Q2	Apr 25, 2016	-	-	x	-
	Q3	Apr 25, 2016	-	-	x	-
	Q4	Apr 25, 2016	-	-	x	-
	Q5	Apr 25, 2016	-	-	x	-
June	Q2	June 6, 2016	x	-	x	-
	Q3	June 6, 2016	x	-	x	-
	Q4	June 6, 2016	x	-	x	-
	Q5	June 6, 2016	x	-	x	-
	LB3	June 6, 2016	x	-	x	-
	LB4	June 6, 2016	x	-	x	-
	LB5	June 6, 2016	x	-	x	-
	LB6	June 6, 2016	x	-	x	-
	SLT	June 9, 2016	-	-	x	-
	STW	June 9, 2016	-	-	x	-
	PLS	June 9, 2016	-	-	X	-

Table A.2. Coordinates of measuring locations for Quarles van Ufford and Langbroek.

	Coordinates			
Location	**N**	**E**	**X**	**Y**
Q1	51.877.130	5.648.560	172997	432098
Q2	51.873.050	5.559.860	166890	431626
Q3	51.860.622	5.513.461	163666	430167
Q4	51.863.260	5.454.480	159634	430524
Q5	51.821.260	5.429.270	157900	425850
Q6	51.858.430	5.533.600	165085	429995
Q7	51.841.205	5.597.596	169492	428089
Q8	51.821.656	5.530.919	164908	425903
LB1	52.056.293	5.183.108	141002	452018
LB2	51.984.077	5.280.663	147681	443969
LB3	51.983.664	5.357.011	147507	443969
LB4	51.997.277	5.359.272	153082	445433
LB5	52.006.458	5.371.665	153933	446454
LB6	52.025.595	5.280.776	147695	448588

APPENDIX B: SEDEX procedure

Solutions:

- 1M $MgCl_2$ rinse (hexahydrate)
- 0.3M Na-citrate/1M $NaHCO_3$ buffer (add 12g dithionite to create CDB rinse on the day of use)
- 1M HCl rinse
- 1M Na-acetate/1M CH_3COOH (acetic acid) buffer

Step 1: Extraction of exchangeable P

- Add 10 ml $MgCl_2$ to each sample and shake the samples (30 min, 100 rpm)
- Weigh the tubes with solution, centrifuge (20 min, 2800 rpm) and pour the solution in a syringe
- Filter solution into another tube (labeled $MgCl_2$ 1) and store filtrate at 5°C

Step 2: Extraction of Fe-bound P

- Add 10 ml CDB solution to each sample and shake the samples (8 hours, 100 rpm)
- Weigh the tubes with solution, centrifuge (20 min, 2800 rpm) and pour the solution in a syringe
- Filter solution into another tube (labeled CDB) and store filtrate in the freezer at -20°C
- Add 10 ml $MgCl_2$ to each sample and shake the samples (30 min, 100 rpm)
- Weigh the tubes with solution, centrifuge (20 min, 2800 rpm) and pour the solution in a syringe
- Filter solution into another tube (labeled $MgCl_2$ 2) and store filtrate at 5°C

Step 3: Extraction of authigenic Ca-bound P

- Add 10 ml acetate buffer to each sample and shake the samples (6 hours, 100 rpm)
- Weigh the tubes with solution, centrifuge (20 min, 2800 rpm) and pour the solution in a syringe
- Filter solution into another tube (labeled ACETATE) and store filtrate at 5°C
- Add 10 ml $MgCl_2$ to each sample and shake the samples (30 min, 100 rpm)
- Weigh the tubes with solution, centrifuge (20 min, 2800 rpm) and pour the solution in a syringe
- Filter solution into another tube (labeled $MgCl_2$ 3) and store filtrate at 5°C

Step 4: Extraction of detrital P

- Add 10 ml HCl to each sample and shake the samples (24 hours, 100 rpm)
- Weigh the tubes with solution, centrifuge (20 min, 2800 rpm) and pour the solution in a syringe
- Filter solution into another tube (labeled HCl 1) and store filtrate at 5°C
- Add 10 ml UHQ to each sample, centrifuge (20 min, 2800 rpm) and remove the solution
- Repeat previous UHQ rinse a second time

Step 5: Extraction of organic P

- Dry the samples in the oven (24 hours, 50°C)
- Transfer sediment/filters from the tubes to (labeled) ceramic crubicles and ash samples (2 hours, 550°C) in a muffle oven
- Add 10ml HCl to each sample shake the samples (24 hours, 100 rpm)
- Weigh the tubes with solution, centrifuge (20 min, 2800 rpm) and pour the solution in a syringe
- Filter solution into another tube (labeled HCl 2) and store filtrate at 5°C

The PO_4 content of the filtrates is determined with colorimetric analysis (*appendix B*), apart from the CDB filtrate which is diluted five or ten times with UHQ before analysis with ICP-OES. The executed extractions are summarized in *table 2*.

Table B.1. Overview of phosphorous extractions during the SEDEX procedure.

Extraction step	P fraction	Filtrate	Analysis
1	Exchangeable P	$MgCl_2$ 1	Colorimetric analysis
2	Fe-bound P	CDB	ICP-OES
		$MgCl_2$ 2	Colorimetric analysis
3	Authigenic Ca-bound P	ACETATE	Colorimetric analysis
		$MgCl_2$ 3	
4	Detrital P	HCl 1	Colorimetric analysis
5	Organic P	HCl 2	Colorimetric analysis

APPENDIX C: Filtration results

Table C.1. Suspended matter concentrations per sampling time for Quarles van Ufford.

		February/March										
Location		**Q1**	**Q2**	**DQ2**	**Q3**	**DQ3**	**Q4**	**DQ4**	**Q5**	**Q6**	**Q7**	**Q6**
Filters	#	3	6	6	6	6	3	3	5	5	6	6
Average SM concentration	mg/l	4.56	19.31	86.33	65.93	61.22	1.98	6.29	41.29	22.35	72.31	19.16
Standard deviation	mg/l	0.14	4.16	10.38	15.16	8.38	1.16	1.50	3.06	6.13	7.56	1.76

		April				June			
Location		**Q2**	**Q3**	**Q4**	**Q5**	**Q2**	**Q3**	**Q4**	**Q5**
Filters	#	6	6	6	3	5	6	5	6
Average SM concentration	mg/l	3.43	3.70	2.85	14.69	3.20	10.76	1.83	19.51
Standard deviation	mg/l	0.80	0.92	0.88	0.27	1.43	2.65	1.25	2.39

Table C.2. Suspended matter concentrations per sampling time for Langbroek.

		March						June			
Location		**LB1**	**LB2**	**LB3**	**LB4**	**LB5**	**LB6**	**LB3**	**LB4**	**LB5**	**LB6**
Filters	#	6	5	6	6	2	6	4	6	6	5
Average SM concentration	mg/l	26.09	5.34	3.80	7.93	0.90	7.44	0.73	21.39	5.52	7.07
Standard deviation	mg/l	3.21	1.34	2.13	2.79	0.01	1.37	0.12	2.45	0.83	0.68

Table C.3. Suspended matter concentrations per sampling time for the Noordplaspolder.

		June		
Location		**SLT**	**STW**	**PLS**
Filters	#	6	5	6
Average SM concentration	mg/l	9.10	9.61	26.70
Standard deviation	mg/l	0.35	0.75	1.13

APPENDIX D: SEDEX results

Table D.1. Phosphorus content of suspended matter and sediment per sample.

Sampling month	Sample	Exch-P	Fe-P	Ca-P	Detr-P	Org-P	Total
		mg/g	mg/g	mg/g	mg/g	mg/g	mg/g
February	Q1	1.00	24.13	1.72	0.24	2.87	29.95
	Q2	0.34	9.64	0.93	0.24	1.91	13.06
	DQ2	0.09	0.67	0.24	0.09	0.95	2.03
	Q3	0.13	1.51	0.27	0.12	1.14	3.16
	DQ3	0.16	1.51	0.24	0.19	1.40	3.48
	Q4	1.37	44.75	3.59	0.17	10.38	60.27
	DQ4	0.43	21.78	5.38	0.03	2.48	30.10
	Q5	0.33	4.38	0.50	0.06	1.36	6.62
March	Q6	0.49	3.56	0.30	0.02	1.14	5.51
	Q7	0.04	0.97	0.18	0.03	0.43	1.65
	Q8	0.23	3.85	0.42	0.02	0.99	5.51
February	BS Q1	0.00	0.40	0.05	0.00	0.10	0.56
	BS Q2	0.02	2.01	0.07	0.06	0.03	2.19
	BS Q3	0.00	0.36	0.03	0.09	0.09	0.57
	BS Q4	0.00	2.23	0.08	0.03	0.13	2.47
March	BS Q6	0.00	0.93	0.01	0.10	0.06	1.10
	BS Q7	0.00	1.62	0.01	0.02	0.04	1.69
March	LB1	0.41	5.12	0.66	0.23	1.92	8.35
	LB2	0.70	3.92	1.00	0.34	3.58	9.55
	LB3	0.50	25.18	1.88	0.10	3.40	31.06
	LB4	0.57	11.63	0.75	0.12	2.34	15.40
	LB5	5.00	75.07	3.77	1.04	11.72	96.59
	LB6	0.57	11.52	0.57	0.14	2.65	15.45
April	Q2	1.47	8.13	0.59	0.36	1.94	12.49
	Q3	0.91	7.63	0.60	0.28	1.40	10.82
	Q4	1.32	8.49	0.63	0.41	2.47	13.33
	Q5	0.60	3.89	0.21	0.16	0.96	5.82
June	Q2	1.67	30.09	1.86	0.56	4.65	38.83
	Q3	0.49	4.80	0.27	0.15	1.06	6.76
	Q4	3.21	16.17	1.32	0.55	3.36	24.61
	Q5	0.25	3.05	0.24	0.12	0.76	4.42
	LB3	4.61	41.89	2.98	1.17	5.04	55.69
	LB4	0.32	2.55	0.21	0.26	0.50	3.83
	LB5	1.43	21.13	0.64	0.26	1.12	24.58
	LB6	0.89	11.91	0.50	0.26	1.04	14.60
	SLT	0.91	16.49	1.00	0.21	0.95	19.56
	STW	1.05	15.31	0.60	0.18	1.22	18.35
	PLS	0.55	4.87	0.22	0.13	0.78	6.55

Table D.2. Fraction contributions of the total particulate phosphorus per sample.

Sampling month	Sample	Exch-P	Fe-P	Ca-P	Detr-P	Org-P
		%	%	%	%	%
February	Q1	3.33	80.54	5.73	0.81	9.60
	Q2	2.60	73.77	7.16	1.81	14.66
	DQ2	4.37	32.83	11.56	4.20	47.03
	Q3	4.03	47.68	8.59	3.71	35.99
	DQ3	4.53	43.20	6.84	5.32	40.10
	Q4	2.28	74.24	5.96	0.29	17.23
	DQ4	1.42	72.37	17.87	0.11	8.24
	Q5	5.02	66.19	7.37	0.82	20.60
March	Q6	8.97	64.58	5.47	0.28	20.70
	Q7	2.23	59.02	10.85	2.12	25.77
	Q8	4.14	69.96	7.55	0.40	17.95
February	BS Q1	0.34	71.29	9.52	0.19	18.66
	BS Q2	0.93	92.04	3.05	2.70	1.28
	BS Q3	0.00	63.45	5.84	15.54	15.17
	BS Q4	0.00	90.26	3.26	1.41	5.07
March	BS Q6	0.20	84.35	1.06	9.04	5.35
	BS Q7	0.00	95.81	0.80	1.09	2.30
March	LB1	5.01	61.28	7.95	2.74	23.02
	LB2	7.37	41.06	10.47	3.59	37.50
	LB3	1.61	81.07	6.05	0.32	10.95
	LB4	3.69	75.50	4.84	0.76	15.21
	LB5	5.18	77.72	3.90	1.07	12.13
	LB6	3.71	74.56	3.69	0.88	17.17
April	Q2	11.78	65.07	4.71	2.92	15.53
	Q3	8.38	70.62	5.50	2.58	12.92
	Q4	9.93	63.71	4.76	3.07	18.53
	Q5	10.38	66.81	3.58	2.81	16.41
June	Q2	4.35	77.44	4.83	1.45	11.93
	Q3	7.27	70.69	4.06	2.16	15.82
	Q4	13.06	65.72	5.35	2.23	13.65
	Q5	5.66	69.06	5.33	2.69	17.25
	LB3	8.28	75.21	5.35	2.11	9.05
	LB4	8.31	66.55	5.35	6.86	12.92
	LB5	5.83	85.95	2.59	1.07	4.55
	LB6	6.09	81.58	3.46	1.77	7.11
	SLT	4.64	84.28	5.13	1.09	4.86
	STW	5.72	83.42	3.26	0.97	6.64
	PLS	5.72	83.42	3.26	0.97	6.64

Table D.3. Fraction contributions to the total particulate phosphorus per sample from the Flevopolder.

Date	Exch-P	Fe-P	Ca-P	Detr-P	Org-P
	%	%	%	%	%
15-Jan	3.82	67.58	7.95	0.81	19.84
31-Jan	8.04	56.83	8.31	2.65	24.17
20-Feb	18.91	41.32	5.78	2.15	31.84
12-Mar	2.22	44.06	5.26	2.01	46.45
08-Apr	13.19	54.38	5.44	1.96	25.03
28-Apr	19.14	48.96	5.17	1.18	25.55
12-Jun	20.04	42.30	4.61	1.96	31.08
07-Aug	19.27	50.77	4.01	1.20	24.75
24-Aug	26.77	57.46	2.66	0.69	12.41
15-Jan	3.82	67.58	7.95	0.81	19.84
31-Jan	8.04	56.83	8.31	2.65	24.17
20-Feb	18.91	41.32	5.78	2.15	31.84

APPENDIX E: Water quality parameters

Table E.1. Water quality parameters for Quarles van Ufford in February/March.

		Q1	Q2	DQ2	Q3	DQ3	Q4	DQ4	Q5	Q6	Q7	Q8
DP	mg/l	0.03	0.02	0.00	0.04	0.11	0.00	0.00	0.12	0.07	0.03	0.05
pH	-	7.39	7.51	7.50	7.08	7.05	7.13	7.04	7.49	7.9	7.35	7.8
Alkalinity	mg/l	484.16	361.01	82.56	115.75	135.73	301.01	263.48	169.95	262.85	133.45	237.2
F	mg/l	0.16	0.21	0.21	0.25	0.21	0.09	0.14	0.36	0.13	0.11	0.15
Cl	mg/l	39.3	24.0	9.4	25.5	23.1	53.8	78.8	52.1	54.4	45.9	47.3
Br	mg/l	0.04	0.06	0.03	0.08	0.07	0.11	0.22	0.12	0.11	0.1	0.14
NO_3	mg/l	16.85	3.32	0.73	0.69	0.75	1.63	0.98	6.81	5.04	0.52	3.36
SO_4	mg/l	25.6	16.7	4.40	11.3	11.3	54.5	61.0	36.2	45.4	35.5	30.6
Al	mg/l	0.00	0.00	0.91	6.45	3.86	0.00	0.00	1.28	0.22	0.4	0.37
Ca	mg/l	140.48	90.55	30.61	40.21	44.64	139.71	144.38	80.86	107.68	64.54	93.96
Fe	mg/l	0.03	0.02	0.86	4.99	3.46	1.28	0.82	2.59	1.13	2.51	1.21
K	mg/l	4.43	2.53	2.06	3.04	1.39	1.58	0.61	5.89	5.37	2.37	6.36
Mg	mg/l	14.42	11.22	5.87	7.79	7.72	14.34	15.33	10.29	12.89	7.69	7.75
Mn	mg/l	0.2	0.88	0.05	0.29	0.17	1.11	1.35	0.5	0.48	1.78	1.52
Na	mg/l	23.9	14.18	10.25	12.17	10.04	26.23	20.87	23.53	29.54	16.1	29.7
S	mg/l	9.12	5.95	1.23	3.05	3.03	18.16	19.26	11.97	15.59	12.54	10.78
Si	mg/l	3.82	4.2	3.25	14.18	10.31	4.4	4.67	6.71	3.85	6.79	7.42

Table E.2. Water quality parameters for Quarles van Ufford in June.

		Q2	Q3	Q4	Q5
DP	mg/l	0.37	0.19	0.18	0.42
pH	-	7.33	7.3	7.38	7.55
Alkalinity	mg/l	263.07	413.18	374.14	215.95
F	mg/l	0.13	0.19	0.17	0.13
Cl	mg/l	48.35	32.75	38.3	43.32
Br	mg/l	0.1	0.1	0.08	0.1
SO_4	mg/l	55.78	45.22	33.66	35.79
Al	mg/l	0	0	0	0
Ca	mg/l	80.79	130.1	128.6	76.76
Fe	mg/l	1.02	1.03	0.44	1.15
K	mg/l	4.47	2.39	2.65	6.65
Mg	mg/l	11.55	16.77	13.99	10.53
Mn	mg/l	0.07	0.35	0.08	0.46
Na	mg/l	29.82	21.59	20.13	24.23
S	mg/l	10.34	16.37	12.35	13.16
Si	mg/l	3.08	6.73	3.84	4.22

Table E.3. Water quality parameters for Langbroek in March.

		LB1	LB2	LB3	LB4	LB5	LB6
DP	mg/l	0.14	0.04	0.10	0.10	0.06	0.09
pH	-	7.77	8.02	7.52	7.47	7.57	7.49
Alkalinity	mg/l	265.14	278.59	260.87	183.30	249.55	175.8
F	mg/l	0.15	0.15	0.12	0.09	0.10	0.10
Cl	mg/l	36.8	51.8	50.3	22.9	29.0	29.4
Br	mg/l	0.09	0.12	0.12	0.08	0.10	0.08
NO_3	mg/l	5.20	1.20	8.20	7.00	15.10	6.90
SO_4	mg/l	41.0	47.3	35.2	28.8	45.1	33.7
Al	mg/l	1.52	0.69	0.23	0.36	0.2	0.5
Ca	mg/l	87.09	82.03	87.68	57.76	80.51	58.65
Fe	mg/l	2.26	0.72	1.99	1.39	0.74	1.12
K	mg/l	5.05	6.43	5.32	4.73	9.86	4.89
Mg	mg/l	11.39	12.6	11.56	6.64	9.2	8.05
Mn	mg/l	0.74	0.2	0.66	0.19	0.17	0.19
Na	mg/l	19.34	29.28	24.64	13.31	16.86	16.51
S	mg/l	14.18	16.03	12.29	9.29	15.44	11.72
Si	mg/l	6.04	1.94	5.17	4.93	3.36	4.57

Table E.4. Water quality parameters for Langbroek in June.

		LB3	LB4	LB5	LB6
DP	mg/l	0.37	0.56	1.53	1.04
pH	-	7.39	7.4	7.3	7.3
Alkalinity	mg/l	252.25	169.63	250.7	188.26
F	mg/l	0.11	0.1	0.05	0.07
Cl	mg/l	63.36	41.57	35.28	36.77
Br	mg/l	0.14	0.09	0.11	0.09
NO_3	mg/l	1.59	7.91	6.83	3.66
SO_4	mg/l	23.85	41.05	38.15	35.96
Al	mg/l	0	0	0	0
Ca	mg/l	85.75	61.79	85.4	67.13
Fe	mg/l	0.38	0.53	0.8	0.75
K	mg/l	4.95	4.06	10.3	4.92
Mg	mg/l	12.43	10.36	11.29	9.58
Mn	mg/l	0.16	0.13	0.5	0.28
Na	mg/l	30.91	23.21	20.41	20.54
S	mg/l	8.75	14.99	14.14	13.3
Si	mg/l	2.09	2.73	5.99	4.29

APPENDIX F: Reduction experiment results

Table F.1. Orthophosphate and iron(II) concentrations from the biological reduction experiment.

	Sample date	Sample name	P (µmol/l)	P (mg/l)	Fe (µmol/l)	Fe (mg/l)
Batch 1	30-Jun	BR 1_13	0.09	0	0.57	0.03
	1-Jul	BR 1_14	0.09	0	0.97	0.05
	6-Jul	BR 1_15	8.65	0.27	33.35	1.86
	8-Jul	BR 1_16	1.95	0.06	37.84	2.11
	13-Jul	BR 1_17	4.98	0.15	92.11	5.14
Batch 2	30-Jun	BR 2_13	0.14	0	4.66	0.26
	1-Jul	BR 2_14	0.14	0	9.03	0.5
	6-Jul	BR 2_15	9.49	0.29	49.77	2.78
	08-Jul	BR 2_16	2.51	0.08	98.30	5.49
	13-Jul	BR 2_17	9.63	0.3	92.96	5.19

Table F.2. Orthophosphate and iron(II) concentrations from the chemical reduction experiments.

	Sampling time	P (µmol/l)	P (mg/l)	Fe (µmol/l)	Fe (mg/l)
EXP 1	09:55	0	0	0	0
	10:20	0	0	66.82	3.73
	11:25	0	0	106.59	5.95
	13:10	0	0	86.93	4.85
	16:35	0	0	104.04	5.81
	09:20	0	0	107.11	5.98
EXP 2	09:40	0	0	0	0
	10:40	0.14	0	13.81	0.77
	11:45	0.74	0.02	11.99	0.67
	13:25	1.26	0.04	17.1	0.96
	15:50	2.74	0.08	23.75	1.33
	10:00	0.14	0	4.15	0.23
EXP 3	13:05	0	0	0	0
	14:15	0	0	8.07	0.45
	15:55	0	0	29.83	1.67
	09:50	0	0	27.96	1.56
	13:30	0	0	14.26	0.8