Reaching ultra low phosphorus concentrations by filtration techniques

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Summary

The wastewater treatment plants (WWTP) in the Netherlands mainly remove (suspended) solids, nutrients and decrease the chemical and biological oxygen demand of the water (WWTP effluent) before it is discharged into the surface water. When the biological and chemical oxygen demand in the WWTP effluent is too high for the receiving water, oxygen depletion may occur. This causes death to fishes and can also cause odour problems. When the concentration of nutrients (i.e. nitrogen and phosphorus) is too high, eutrophication will cause excessive growth of weeds and algae. This research mainly deals with the removal of phosphorus from WWTP effluent. One objective of this research is to obtain ultra low total phosphorus concentrations by filtration of wastewater treatment plant (WWTP) effluent. Ultra low total phosphorus concentrations are concentrations meant below 0.15 mg/L. Another related objective of this research is to investigate how these concentrations can be attained consistently in the filtrate water. Therefore, a measurement technique has been developed to compare different filter concepts and different process settings. The optimal floc formation, filtration technique and mechanisms and temperature influences are investigated.

Total phosphorus can be found in different forms in surface water and WWTP effluent. These forms can be divided into dissolved, colloidal and particulate phosphorus. These different phosphorus forms contain a large number of organic and inorganic phosphorus components. WWTP effluent consists to a great extent of orthophosphorus, which can be removed by precipitation, coagulation, flocculation and filtration when a metal salt is dosed as the coagulant. During precipitation, colloidal material forms. Coagulation is the process of destabilization of colloidal particles in a way that these particles can grow as a result of particle collision. Precipitation and coagulation require a good initial mixing to maximize

the binding of the metal salt with the available phosphorus and to minimize the competing reactions. The optimal initial mixing energy is between 500 – 1500 s^{-1}.

Flocculation is the process that follows after initial mixing and its purpose is to form flocs and aggregates from the fine particles and destabilized particles. The degree of flocculation is dependent on the combination of the velocity gradient and the retention time. Typical velocity gradients are between 25 – 200 s^{-1} in combination with a retention time of 2 – 10 minutes. The temperature has a major influence on the floc formation. Different techniques can be used for the filtration step, for example downflow depth filtration with a single of dual media filter bed, or continuous sand filtration. In a filter bed the shear rate may be sufficient to promote flocculation in the filter pores but, due to the accumulation of deposits, the shear rate will increase if a constant filtration rate is applied. When the shear force in the filter bed becomes too high, particles or flocs may detach and a breakthrough of the filter bed may occur.

Denitrification is the biological reduction of nitrate to nitrogen gas. Denitrification takes place when nitrate is used as an electron acceptor instead of oxygen. Denitrification requires the presence of nitrate (or nitrite), the presence of a substrate (methanol is frequently used) and the absence of oxygen. Nitrite is consumed at a rate twice that of the nitrate reduction rate; therefore, the rate-limiting step for denitrification is the reduction from nitrate to nitrite. Nitrite accumulation during denitrification can, however, be caused by many factors. When combining nitrogen and chemical phosphorus removal in a single sand filter, phosphorus limitation may occur. Low orthophosphorus concentrations may affect the denitrification conversion rate by inhibiting the rapid growth of heterotrophic microorganisms in response to increasing nitrate loads.

Pilot-plant investigations were conducted at the Horstermeer WWTP and the Leiden Zuidwest WWTP. The pilot-plant at the Horstermeer WWTP consists of a dual media filter and a “One Step Total Effluent Polishing filter” (i.e. 1-STEP®), operated for denitrification and simultaneous phosphorus removal. The pilot installation at the Leiden Zuidwest WWTP consists of small, full-scale installations. Continuous sand filtration and dual media filtration are combined to investigate separate denitrification and phosphorus removal and are compared for simultaneous denitrification and phosphorus removal. At both locations methanol is used as a carbon source. At the Horstermeer WWTP, poly aluminium chloride is used and at the Leiden Zuidwest WWTP ferric(III)chloride is used as a coagulant.

Knowledge of the different phosphorus forms in WWTP effluent is essential to reach ultra low concentrations in the WWTP effluent. Different techniques can be used to analyse phosphorus, but chemical analysis is widely used. The advantage of chemical phosphorus analysis is that it can be conducted on site and gives reliable and accurate information about the phosphorus content of a sample. The chemical principle is based on the molybdenum blue method. Different forms of phosphorus can be measured depending on the pre-treatment step of a sample. Interactions of components like silicate or arsenate can either give an underestimation or overestimation of the orthophosphorus concentration. Additionally, the filtration step through 0.45 μm introduces an error in the measured concentrations. This is caused by the colloidal phosphorus fraction. To what extent this overestimation or underestimation is, should be investigated per location.

The TU Delft phosphorus distribution has been developed to have an easy and quick method to determine orthophosphorus, metal-bound phosphorus, dissolved “organic” phosphorus and particulate organic phosphorus. To determine the TU Delft phosphorus distribution on-site, also referred to as phosphorus distribution, only four measurements need to be executed; namely, total phosphorus and orthophosphorus in an unfiltered sample, and total phosphorus and orthophosphorus in a filtered sample through 0.45µm. For this filtration step, a cellulose acetate filter is used to filter a sample volume of 10 ml under a limited pressure of 50 mbar. Phosphorus concentrations are measured with Hach Lange cuvette tests LCK349. This method uses ascorbic acid for the reduction step. Total phosphorus is analysed by a pre-treatment step of acid hydrolysis with sulphuric acid. To determine the size of the metal-bound phosphorus, a 10 ml sample is filtered with a vacuum of 50 mbar through filters with different pore sizes. Orthophosphorus concentrations are measured in the filtered samples and in the unfiltered samples. With these results the estimated floc size can be calculated by adding up the floc sizes proportionally, of course without the fraction <0.45 µm which is dissolved phosphorus. In order to be able to investigate removal mechanisms in the filter bed for phosphorus removal as well as for denitrification, profile measurements are made on a regular basis. For a profile measurement, samples are taken from the WWTP effluent, from the upper water layer of the fixed filter bed, every 10 or 20 cm in the filter bed and from the filtrate water of the filter. Profile measurements can be combined with phosphorus distributions. In this case a phosphorus distribution is made for every sample point.

The results of the characterisation of the WWTP effluent show that the phosphorus distribution is site specific. Temperature, seasonal and pH influences on the phosphorus distribution were not found. A linear relationship between the total phosphorus concentration and the unfiltered orthophosphorus (sum of orthophosphorus and metal-bound phosphorus) or the filtered orthophosphorus might be found. The initial mixing energy has no influence on the phosphorus size fractionation and phosphorus distribution in the upper water layer of a fixed bed filter. This means that the initial mixing energy of 300 s^{-1} is already sufficient. After coagulation, orthophosphorus is bound to metal ions and forms metal-bound phosphorus. The dissolved “organic” phosphorus decreases after coagulation and the particulate organic phosphorus increases, which suggests that part of the dissolved “organic” phosphorus may be colloidal or associated with colloidal material. The size of the formed flocs can be influenced by the coagulant dosage and the flocculation time. The results show that the estimated floc size with a flocculation time of 24 minutes is approximately 7 – 12 µm, which is larger than the size of flocs formed with a flocculation time of 10 minutes, these flocs are approximately 2 – 5 µm. But filtration experiments showed that these larger flocs do not result in higher removal efficiencies in the filter bed. Sometimes even the opposite effect was found.

During the filtration experiments, results showed that an increasing total phosphorus concentration in the feed water results in increased total phosphorus concentrations in the filtrate water. The coagulant dosage is a major influence on the filter runtime. With increasing coagulant dosage, the filter runtime decreases. For continuous sand filtration, an increase in the total phosphorus concentration in the feed water does not lead to higher total phosphorus concentrations in the filtrate water. 1-STEP® filtration reaches higher removal efficiencies compared to dual media filtration. Continuous sand filtration reaches the highest removal efficiencies for total phosphorus concentrations of 0.1 – 1.5 mg/L.

The temperature influence on phosphorus removal was also investigated during this research. The results show that the rate of metal-hydroxide precipitation (the transfer of orthophosphorus to metal-bound phosphorus) is not significantly inhibited by low temperatures, but flocs become larger with increasing temperatures. During filtration all tested filtration techniques contained the highest total phosphorus concentrations in the filtrate for water temperatures of < 13°C. For continuous sand filtration an increasing temperature leads to decreasing total phosphorus concentrations in the filtrate. This same trend is found for downflow depth filtration techniques, but for higher phosphorus concentrations (>0.8 mg/L) the optimal temperature range is between 13°C and 18°C and not ≥18°C. The turning point varies per installation and is probably influenced by the velocity (shear rate) in the filter bed and the floc strength.

Inhibition of denitrification, probably due to phosphorus limitation, might occur for PO_4-P/NO_x-N ratios below 0.055 mg/mg in the WWTP effluent. A newly developed coagulant dosage system decreases the risk of phosphorus limitation and, in addition, a reduction in the coagulant dosage was found.

It is to be concluded that phosphorus removal to an ultra low concentration can be achieved, but knowledge about the different phosphorus forms and their behaviour is of major importance.

Samenvatting

De rioolwaterzuiverinsinstallaties (rwzi's) in Nederland verwijderen vooral zwevende stof en nutriënten en verminderen het chemisch en biologisch zuurstofverbruik van het afvalwater (rwzi effluent) voordat het wordt geloosd op het oppervlaktewater. Wanneer het chemisch en biologisch zuurstofverbruik van het rwzi effluent te hoog is voor het ontvangende water, kan zuurstoftekort ontstaan. Dit zuurstoftekort in het oppervlaktewater veroorzaakt vissterfte en stank. Wanneer de concentratie aan nutriënten (stikstof en fosfaat) te hoog is, kan eutrofiëring leiden tot overmatige groei van wier en algen. Dit onderzoek gaat vooral in op fosfaatverwijdering uit rwzi effluent, ook wel afloop nabezinktank genoemd. Eén van de onderzoeksdoelen is om ultralage totaal-fosfaatconcentraties in het rwzi effluent te behalen door middel van filtratietechnieken. Ultralage totaal-fosfaatconcentraties zijn dit geval concentraties lager dan 0,15 mg/l. Een onderzoeksdoel is om te bepalen hoe deze concentraties zo stabiel mogelijk kunnen worden behaald. Voor het vergelijken van verschillende filterconcepten en instellingen is een meetmethode ontwikkeld. De optimale vlokvorming, filtratietechniek, mechanisme en temperatuurinvloeden zijn onderzocht.

In het oppervlaktewater en rwzi effluent komt totaal-fosfaat voor in verschillende vormen. Deze fosfaatvormen kunnen worden onderverdeeld in opgelost, colloïdaal en gebonden fosfaat. De verschillende fosfaatvormen bestaan uit een groot aantal organische en anorganische fosfaatverbindingen. Rwzi effluent bestaat voor een groot deel uit orthofosfaat dat met een coagulant (metaalzout) door middel van precipitatie, coagulatie, flocculatie en filtratie kan worden verwijderd. Tijdens precipitatie worden colloïdale deeltjes gevormd. Coagulatie is de stabilisatie van deze colloïdale deeltjes zodat de deeltjes kunnen groeien als ze met elkaar botsen. Precipitatie en coagulatie vereisen een goede initiële menging om de binding van metaalzout met orthofosfaat te vergroten en om het aandeel aan nevenreacties te minimaliseren. De optimale initiële menging is 500 – 1500 s^{-1}.

Flocculatie of vlokvorming beschrijft het proces dat volgt op de initiële menging. Het doel van vlokvorming is om vlokken en aggregaten te vormen van de kleine gedestabiliseerde deeltjes. De mate van vlokvorming hangt af van de combinatie van de mengenergie en verblijftijd. Een mengenergie tussen 25 – 200 s^{-1} in combinatie met een verblijftijd van 2-10 minuten wordt veel gebruikt. De temperatuur is van grote invloed op de vlokvorming. Voor de filtratiestap kunnen verschillende technieken worden gebruikt, bijvoorbeeld enkel- of dubbellaags vastbedfiltratie of continue filtratie. In een filterbed kan de afschuifspanning bijdragen aan een goede vlokvorming in de filterporiën, maar wanneer een vaste filtratiesnelheid wordt gehanteerd zal de afschuifspanning toenemen als gevolg van accumulatie van deeltjes. Als de afschuifspanning in het filterbed te hoog wordt, kunnen deeltjes en vlokken afbreken waardoor doorslag van het filterbed kan vóórkomen.

Denitrificatie is de biologische afbraak van nitraat naar stikstofgas. Het vindt plaats wanneer nitraat in plaats van zuurstof dient als elektronendonor dient. Voorwaarden voor denitrificatie zijn de aanwezigheid van nitraat (of nitriet), de aanwezigheid van een substraat (methanol is een veelgebruikt substraat) en de afwezigheid van zuurstof. Nitriet wordt in vergelijking met nitraat twee keer zo snel afgebroken, waardoor de afbraak van nitraat naar nitriet de bepalende factor is voor de totale reactiesnelheid. Nitrietaccumulatie kan door veel verschillende oorzaken ontstaan. Wanneer denitrificatie en chemische fosfaatverwijdering worden gecombineerd in één zandfilter, kan fosfaatlimitatie ontstaan. Lage fosfaatconcentraties kunnen de denitrificatiesnelheid beïnvloeden door de remming van de groei van heterotrofe organismen als gevolg van toenemende nitraatconcentraties.

Onderzoek op pilotschaal is uitgevoerd op de rwzi Horstermeer en de rwzi Leiden Zuidwest. De proeflocatie op de rwzi Horstermeer bestond uit een Multimedia filter en een “One Step Total Effluent Polishing filter”(1-STEP® filter) die beide werden ingezet voor simultane denitrificatie en fosfaatverwijdering. De proeflocatie op de rwzi Leiden Zuidwest bestond uit praktijkschaal installaties. Continue zandfiltratie en Multimedia filtratie zijn gecombineerd om gescheiden denitrificatie en fosfaatverwijdering te kunnen vergelijken met simultane denitrificatie en fosfaatverwijdering. Op beide locaties is methanol als koolstofbron gebruikt. Op de rwzi Horstermeer is polyaluminiumchloride als coagulant gebruikt en op de rwzi Leiden Zuidwest is ijzerchloride gebruikt.

Kennis over de verschillende fosfaatvormen die aanwezig zijn in het rwzi effluent, is essentieel voor het behalen van ultralage concentraties. Voor de analyse van fosfaat zijn verschillende technieken beschikbaar, maar chemische analyse is veelgebruikt. Het voordeel van chemische fosfaatanalyses is dat het op locatie kan worden toegepast en het direct betrouwbare informatie over het fosfaatgehalte in het monster geeft. Chemische fosfaatanalyses zijn veelal gebaseerd op de molybdeenblauw methode. Verschillende fosfaatvormen kunnen worden gemeten afhankelijk van de toegepaste voorbehandeling van het monster. Silicaat en arsenaat kunnen interfereren met de fosfaatmeting, hierdoor kan een over- of onderschatting van de fosfaatconcentratie worden veroorzaakt. Ook filtratie door 0,45 μm introduceert een meetfout in de gemeten fosfaatconcentratie. Dit wordt veroorzaakt door de colloïdale fosfaatfractie. De mate waarin een over- of onderschatting ontstaat, zal per locatie moeten worden bepaald.

De TU Delft fosfaatverdelingsmethode is ontwikkeld, zodat er een eenvoudige en snelle methode beschikbaar is voor de bepaling van orthofosfaat, metaalgebonden fosfaat, opgelost “organisch” fosfaat en gebonden organisch fosfaat. Voor het bepalen van de fosfaatverdeling zijn vier metingen nodig. Dit zijn totaal-fosfaat en orthofosfaat in een ongefiltreerd monster en in een monster gefiltreerd door 0,45 μm. Voor deze filtratiestap is een filter van celluloseacetaat gebruikt om 10 ml monster met behulp van 50 mbar onderdruk te filtreren. De fosfaatconcentratie is met behulp van Hach Lange kuvettentesten LCK349 gemeten. Deze methode gebruikt ascorbinezuur als reductiestap. Totaal-fosfaat is gemeten door toepassing van een hydrolysestap met zwavelzuur. Voor de bepaling van de vlokgrootte van het metaalgebonden fosfaat is steeds 10 ml monster gefiltreerd met een onderdruk van 50 mbar door filters met verschillende poriegroottes. Orthofosfaat is gemeten in de ongefiltreerde en gefiltreerde monsters. Door de resultaten proportioneel op te tellen kan een schatting worden gemaakt van de vlokgrootte. Natuurlijk wordt het opgeloste orthofosfaat niet meegenomen in de berekening. Voor de bepaling van de mechanismen voor de fosfaatverwijdering en de denitrificatie in het filterbed zijn profielmetingen gemaakt. Voor een profielmeting worden monsters genomen in de afloop nabezinktank, de bovenwaterstand van het filter, elke 10 – 20 cm in het filterbed en in het filtraat. Profielmetingen kunnen worden gecombineerd met fosfaatverdelingen. In dit geval kan een fosfaatverdeling voor ieder monsterpunt worden gemaakt.

Analyse van fosfaat, aanwezig in het rwzi effluent, laat zien dat de fosfaatverdeling locatiespecifiek is. Invloeden van temperatuur, seizoen en pH op de fosfaatverdeling zijn niet gevonden. Een lineaire relatie tussen de totaal-fosfaatconcentratie en de gefiltreerde of ongefiltreerde (som orthofosfaat en metaalgebonden fosfaat) orthofosfaatconcentratie kan per locatie mogelijk worden gevonden. De initiële menging heeft geen invloed op de fosfaatfractionering en ook niet op de fosfaatverdeling in de bovenwaterstand van een Multimedia filter. Dit betekent dat een initiële menging van 300 s^{-1} voldoende is. Na coagulatie is het orthofosfaat gebonden aan metaalionen en vormt zo metaalgebonden fosfaat. Na coagulatie neemt de concentratie opgelost “organisch” fosfaat af en de concentratie gebonden organisch fosfaat toe, dit suggereert dat een gedeelte van het opgeloste “organische” fosfaat colloïdaal is of gebonden aan colloïdaal materiaal. De grootte van de gevormde vlokken kan worden beïnvloed door de coagulantdosering en de flocculatietijd. Resultaten laten zien dat de geschatte vlokgrootte bij een flocculatietijd van 24 minuten gemiddeld 7 – 12 μm is, dit is groter vergeleken met de geschatte vlokgrootte van vlokken gevormd bij een flocculatietijd van 0 minuten, deze zijn namelijk 2 – 5 μm. Filtratie-experimenten laten zien dat grotere vlokken geen grotere verwijdering geven in het filterbed.

De resultaten van de filtratie-experimenten laten zien dat een toenemende totaal-fosfaatconcentratie in het voedingswater leidt tot een toename van de totaal-fosfaatconcentratie in het filtraat. De coagulantdosering is van grote invloed op de looptijd van het filter. Een toenemende coagulantdosering resulteert in een afnemende looptijd. Voor continue filtratie leidt een toename van de totaal-fosfaatconcentratie in het voedingswater niet tot een hogere totaal-fosfaatconcentratie in het filtraat. 1-STEP® filtratie geeft een groter verwijderingsrendement vergeleken met multimedia filtratie. Continue filtratie geeft het hoogste verwijderingsrendement binnen het totaal-fosfaatconcentratie bereik van 0,1 – 1,5 mg P-totaal/l.

De temperatuursinvloed op de fosfaatverwijdering is onderzocht. De resultaten geven weer dat de snelheid waarmee metaal-hydroxide neerslaat (de overgang van orthofosfaat naar metaalgebonden fosfaat) niet significant wordt geremd door de lage temperaturen, maar vlokken worden groter bij een toenemende temperatuur. Alle geteste filtratietechnieken geven de hoogste fosfaatconcentraties in het filtraat voor temperaturen <13°C. Continue filtratie geeft bij toenemende temperaturen afnemende totaal-fosfaatconcentraties in het filtraat. Dezelfde trend is gevonden voor vastbedfilters, maar voor hogere totaal-fosfaatconcentraties (>0,8 mg/l) is het optimale temperatuursbereik tussen de 13°C en 18°C en niet langer ≥18°C. Dit omslagpunt varieert per installatie en wordt waarschijnlijk veroorzaakt door de afschuifspanning van het filterbed in combinatie met de vloksterkte.

Remming van de denitrificatie, waarschijnlijk veroorzaakt door fosfaatlimitatie, kan voorkomen bij PO_4-P/NO_x-N verhoudingen in de afloop nabezinktank lager dan 0,055 mg/mg. Een nieuw ontwikkeld coagulant doseersysteem vermindert het risico op fosfaatlimitatie en vermindert de benodigde coagulantdosering.

Er kan worden geconcludeerd dat fosfaatverwijdering tot ultralage concentraties kan worden bereikt, maar daarbij is kennis van de verschillende fosfaatvormen van essentieel belang.

Table of contents

Abbreviations and symbols

1-STEP®	1-Step Total Effluent Polishing
Al^{3+}	Aluminium ion
ATP	Adenosine TriPhosphate
BOD	Biochemical Oxygen Demand
CFA	Continuous Sand Filter A
CFB	Continuous Sand Filter B
CFD	Computational fluid dynamics
COD	Chemical Oxygen Demand
bCOD	biodegradable COD
C-source	Carbon source
DMF	Dual media filter
DNA-P	Deoxyribonuclein-phosphorus
Fe^{3+}	Ferric ion
FHI	FrauenHofer Institute
GAC	Granular Activated Carbon
G-value	Velocity gradient
H	Hydrogen atom
LC_{50}	Lethal concentration
MBBR	Moving Bed Biofilm Reactor
MeOH	Methanol
MPR	Maximum Permissible Risk
NO_2-N	Nitrite
NO_3-N	Nitrate

NO_x-N	Total inorganic oxidized nitrogen (sum nitrate and nitrite)
N-total	Total nitrogen concentration
NTU	Nephelometric Turbidity Units
NW4	Vierde Nota Waterhuishouding, Dutch Directive
O	Oxygen atom
P	Phosphor atom
PACl	Poly aluminium chloride
PO_4-P	Orthophosphorus
P-ortho	Orthophosphorus concentration
P-total	Total phosphorus concentration
R	Carbon/Hydrogen molecule chain
rpm	rotations per minute
SBR	Sequencing Batch Reactor
SRT	Solids Retention Time
STOWA	Dutch Foundation for Applied Water Research
TOD	Total Oxygen Demand
TSS	Total Suspended Solids
TU Delft	Delft University of Technology
UWL	Upper Water Layer
VSS	Volatile Suspended Solids
WFD	Water Framework Directive
WWTP	WasteWater Treatment Plant
Y	Yield

μ	Dynamic viscosity [Ns/m^2]
A_p	Filter grain surface [m^2]
COD_{MeOH}	COD fraction of methanol (kg/kg)
D_p	Effective grain size [m]
g	Gravitational constant [m^2/s]
G_w	Shear rate within the filter pores [s^{-1}]
h_L	Head loss [m]
k	Resistance coefficient [-]
k_d	Endogenous decay rate per day [d^{-1}]
p	Porosity [-]
ϕ_s	Sphericity of the filter grain [-]
t	Retention time [s]
T	Temperature [°C]
v	Average filtration rate [m/s]
v_u	Flow velocity upstream [m/s]
V	Volume of the flocculation tank [m^3]
V_p	Filter grain volume [m^3]
x	Length where mixing takes place (7.5 times the diameter of the upstream pipe) [m]
Y_n	Net biomass yield [g VSS/g COD]
ρ	Unit weight of water [N/m^3]

1 Introduction

1.1 Wastewater treatment in the Netherlands

Wastewater is, according to the Oxford dictionary (2010), defined as used water that contains waste substances from homes, factories and farms. Tchobanoglous (2003) defines wastewater as a combination of the liquid or water-carried wastes removed from residences, institutes and commercial and industrial establishments, together with groundwater, surface water and storm water as may be present. Reading those two definitions it may be concluded that wastewater is used water which contains pollutants and therefore needs to be treated at a wastewater treatment plant (WWTP). The main goals of wastewater treatment are to protect public health and to prevent environmetal damage. The Netherlands had 352 wastewater treatment plants in 2008 (CBS, 2010). These plants mainly remove (suspended) solids and nutrients, and reduce the chemical and biological oxygen demand of the water (WWTP effluent) before it is discharged into the surface water. When the biological and chemical oxygen demand in the WWTP effluent is too high for the receiving water, oxygen depletion may occur. This causes death to fishes and can also cause odour problems. When the concentration of nutrients (i.e. nitrogen and phosphorus) is too high, eutrophication will cause excessive growth of weeds and algae.

This research mainly focuses on the removal of phosphorus from WWTP effluent. Figure 1.1 shows the yearly average phosphorus load per population equivalent for the Netherlands. The graph shows a decline in the total phosphorus load in the feed water between 1985 and 1990, this is due to the detergents, which no longer contain phosphorus. The graph also shows a slightly increasing total phosphorus load in the feed water of the wastewater treatment plants (WWTPs) for the last decade. But, in spite of this increase, the total phosphorus load has a decreasing tendency. This is probably the result of the increased knowledge about phosphorus removal and the application of specific treatment techniques, such as biological and chemical phosphorus removal.

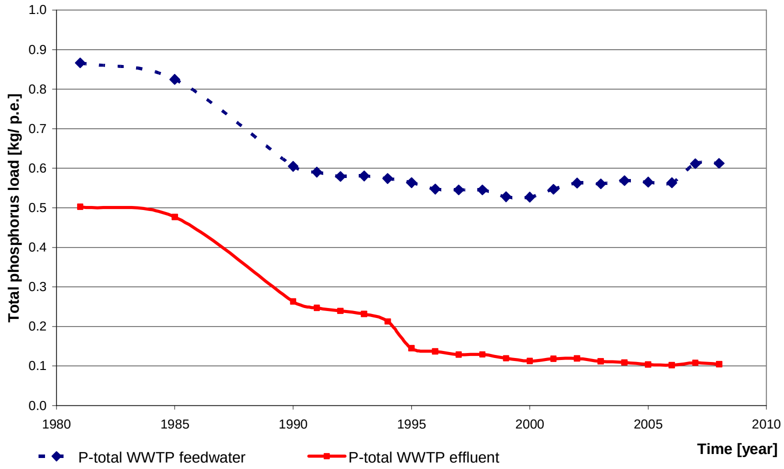

Figure 1-1 – Yearly average total phosphorus load in the WWTP feed water and WWTP effluent per p.e. (CBS, 2010)

The average quality of the effluent of the WWTPs in the Netherlands in 2008 is displayed in Table 1-1.

Table 1-1 – Average quality of the effluent of the WWTPs in the Netherlands in 2008 (CBS, 2010)

Parameter	Unit	Average concentration
Biochemocal oxygen demand	mg/L	4
Chemical oxygen demand	mg/L	39
Total phosphorus	mg/L	1
Total nitrogen	mg/L	9

The current discharge limits for WWTPs in the Netherlands are displayed in Table 1-2. A comparison of the discharge limits with the average concentrations in the WWTP effluent shows that the average concentrations are well below the discharge limits.

Table 1-2 – Current discharge limits for WWTPs in the Netherlands (WVO, 2010)

Parameter	Unit	Discharge limit	Remark
Biochemical oxygen demand	mg/L	20	
Chemical oxygen demand	mg/L	125	
Suspended solids	mg/L	30	
Total phosphorus	mg/L	1	> 100,000 p.e.
	mg/L	2	2,000 - 100,000 p.e.
Total nitrogen	mg/L	10	>20,000 p.e.
	mg/L	15	2,000 - 20,000 p.e.

1.2 Future changes in the legislation

In 1998 the Ministry of Transport and Water Management introduced the fourth Memorandum on Water Management (in Dutch: *Vierde Nota Waterhuishouding* or NW4) which contains the water policy for the Netherlands until 2006 (Van der Beesen, 1998). In the NW4, the norms for water quality are defined and discharge points, which need to be improved, are set out. The NW4 contains norms for Maximum Permissible Risk (MPR) (in Dutch: MTR, *Maximaal Toelaatbaar Risiconiveau*) and target values. The MPR values relate to the minimum water quality which needs to be reached by the end of 2015. The MPR values are preliminary and it is not known yet which final values will become effective. The target values are set as a norm to prevent negative ecological effects over a longer time scale (Scherrenberg, 2006).

In 2000 the European Union (European Commission, 2000) introduced the Water Framework Directive (WFD). The aim of the WFD is to achieve an ecological and biological balance for all surface waters, coastal waters, transitional waters and groundwaters in Europe by 2015. The ecological quality status of water bodies is based on the status of biological, hydromorphological and physicochemical quality elements (Borja, 2005). The European Commission identified 33 priority substances (European Commission, 2008) and their maximum allowable concentrations, FHI-values (Fraunhofer Institute) which are specified in the Annex of the WFD.

Since the introduction of the Dutch NW4 in 1998 and the European WFD in 2000, water authorities have been required to comply with more stringent discharge limits. To meet the deadline of 2015, water authorities in all river basin districts throughout Europe are obligated to adopt a coherent program of measures by 2009. In case a river basin district includes more than one member state, a trans-boundary management plan must be developed. The Netherlands is involved in management plans for four trans-boundary river basin districts: the Rhine, Meuse, Scheldt and Ems. In the meanwhile, the values identified in the NW4, the MPR values, are still being used, as well as the European guidelines for Swimming Water Quality and Dangerous Substances.

1.3 Objective of the research

The objective of this research is to find a way to obtain ultra low total phosphorus concentrations by filtration of wastewater treatment plant (WWTP) effluent. Ultra low total phosphorus concentrations are concentrations below 0.15 mg/L. The goal of this research is not only to reach these concentrations but to investigate how these concentrations can be reached consistently in the filtrate water. For this research, chemical phosphorus removal is generally combined with biological nitrogen removal. During this research only the phosphorus removal in the polishing step is investigated.

The following are the research objectives :

- developing a measurement technique to be able to compare different filter concepts and different process settings,
- finding the optimal floc formation (therefore investigation of the optimal coagulant dosage, the optimal initial mixing energy and the use of flocculation zones is required),
- investigating which filtration technique is best. Therefore investigating which filtration technique is required to reach ultra low total phosphorus concentrations in the filtrate water and whether phosphorus and nitrogen can be removed simultaneously,
- investigating the temperature influences on coagulation, flocculation and filtration,
- investigating how phosphorus is removed in a filter bed. Investigating the influence of a single layer filter bed like 1-STEP® filtration or a two layers filter bed like dual media filtration,
- finding the boundary conditions required for reaching ultra low total phosphorus concentrations in the filtrate water.

In order to investigate how these low total phosphorus concentrations in the filtrate water can be reached, pilot-plant investigations were initiated at two locations, namely the Horstermeer WWTP and the Leiden Zuidwest WWTP. The pilot research at the Horstermeer WWTP started in March 2005 in cooperation with Witteveen+Bos Consulting Engineers, Waternet and Delft University of Technology. The research continued until the end of 2009. The demonstration research at the Leiden Zuidwest WWTP started in October 2006 in cooperation with Witteveen+Bos Consulting Engineers, The Rijnland District Water Control Board and Delft University of Technology. This research ended in January 2009. The STOWA (Dutch Foundation for Applied Water Research) participated in this demonstration project. The project was financially supported by the LIFE program of the European Union. In May 2010 the project at the Leiden Zuidwest WWTP was announced as one of the five “Best of the Best” LIFE Environment projects of 2009.

1.4 Outline of the thesis

Chapter 2 starts with a description of the phosphorus forms that are present in the WWTP effluent. After this, the fundamentals of precipitation, coagulation, flocculation and filtration are presented. The principles of denitrification are considered because the experiments were mainly conducted during simultaneous nitrogen and phosphorus removal. The chapter ends with the experiences on granular activated carbon filtration. Chapter 3 introduces the pilot installations at the Horstermeer WWTP and at the Leiden Zuidwest WWTP. This chapter provides information about the analyses, the back wash programmes and chemical dosings. Chapter 4 describes in detail how the TU Delft Phosphorus distribution method was developed and what the applications of the method are. Chapter 5 is the first of four chapters that present results. Chapter 5 starts with a characterisation of the WWTP effluent phosphorus, followed by the results of conducted coagulation and flocculation experiments. Chapter 6 describes the results of the filtration experiments. During the experiments which are described in Chapter 5 and Chapter 6, temperature influences were found. These influences are presented in Chapter 7. During denitrifying phosphorus removal and sometimes nitrate removal, rates decreased and nitrite accumulation occurred. This was possibly due to phosphorus limitation. This is investigated and the results are shown in Chapter 8. The evaluation and discussion are presented in Chapter 9, followed by Chapter 10 which contains the final conclusions of this research.

1.5 References

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2 Experiences

This chapter contains a general exploration of the processes used for phosphorus and nitrogen removal. This chapter is divided into four subjects, namely chemical phosphorus removal, biological nitrogen removal (denitrification), biological activated carbon and the experiences of other research. At first chemical phosphorus removal is described for the different dissolved, colloidal and particulate phosphorus forms present in WWTP effluent (Section 2.1). Secondly, the binding of dissolved phosphorus to metal ions (coagulation) and the formation of particulate phosphorus (flocculation) are described in Sections 2.2 and 2.3. This is followed by the removal of particulate phosphorus by filtration in Section 2.4. The part about biological nitrogen removal, denitrification, which is described in Section 2.5, deals with the principles of denitrification, methanol dosage as a carbon source, nitrite accumulation and phosphorus uptake by denitrifying bacteria. Biological activated carbon is described in Section 2.6. The experiences of other research are described in Section 2.7.

2.1 Phosphorus compounds in WWTP effluent

Phosphorus can be found in different forms in surface water and WWTP effluent. These forms can be divided into dissolved, colloidal and particulate phosphorus, see Figure 2-1. Colloidal phosphorus is within the size range of 0.01 – 1.0 μm (Tchobanoglous et al., 2003). The different phosphorus forms contain a large number of different components which may even change between dissolved status and particulate status (Spivakov et al., 1999). For example, bacteria can mineralize dissolved and particulate organic phosphorus into dissolved orthophosphorus which can precipitate with metal salts and become particulate.

Figure 2-1 – Distribution of dissolved, colloidal and particulate material

This section is divided into two subsections, the first subsection describes the dissolved phosphorus forms which may be present in WWTP effluent (Section 2.1.1) and the second subsection describes the particulate phosphorus forms including colloidal phosphorus (Section 2.1.2).

2.1.1 Dissolved phosphorus

Soluble or dissolved phosphorus can be divided into dissolved reactive phosphorus (orthophosphorus), dissolved acid hydrolysable phosphorus and dissolved organic phosphorus. These three forms are shown schematically in Figure 2-2. Dissolved acid hydrolysable phosphorus can be polyphosphorus, pyrophosphorus, metaphosphorus (Stevens and Stewart, 1982a; Spivakov et al., 1999; Bratby, 2006). Dissolved acid hydrolysable phosphorus is converted into orthophosphorus by acid hydrolysis at 100°C.

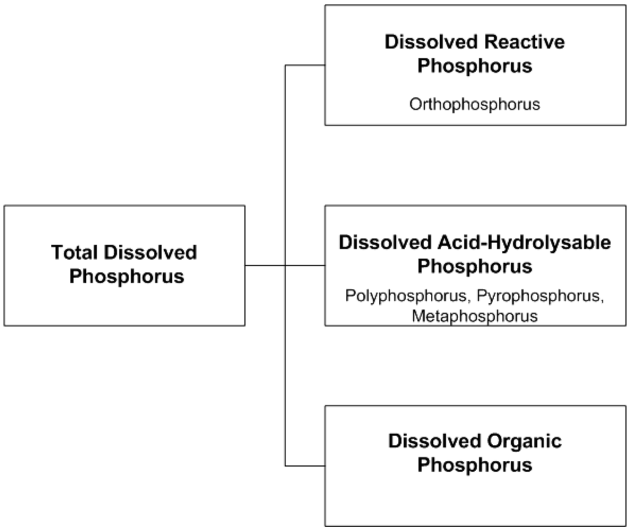


Figure 2-2 - Forms of dissolved phosphorus

These three forms of dissolved phosphorus are described separately. The next subsections contain molecule structures of the different phosphorus forms. In these molecule structures O stands for an Oxygen atom, P for a Phosphorus atom and H for a Hydrogen atom.

2.1.1.1 Dissolved reactive phosphorus

Dissolved reactive phosphorus or orthophosphorus, for example PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4, is available for biological metabolism without further breakdown and is the end product of many decomposition reactions (Ahlgren, 2006). A general molecule structure is given in Figure 2-3. From chemical precipitation with divalent or trivalent metals, orthophosphates will become particulate (STOWA, 1992; Spivakov et al., 1999).

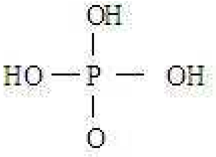


Figure 2-3 - General molecular structure orthophosphorus (Ahlgren, 2006)

Orthophosphorus is the only phosphorus form which is not considered completely biological because a large part of the sedimentary orthophosphorus has other sources than biological transformations (Ahlgren, 2006). The biological orthophosphorus is a decomposition product of larger organic phosphorus compounds.

2.1.1.2 Dissolved acid hydrolysable phosphorus

Dissolved acid hydrolysable phosphorus can be divided into four components (see Figure 2-4), namely polyphosphorus, pyrophosphorus, metaphosphorus and lower oxidation states.

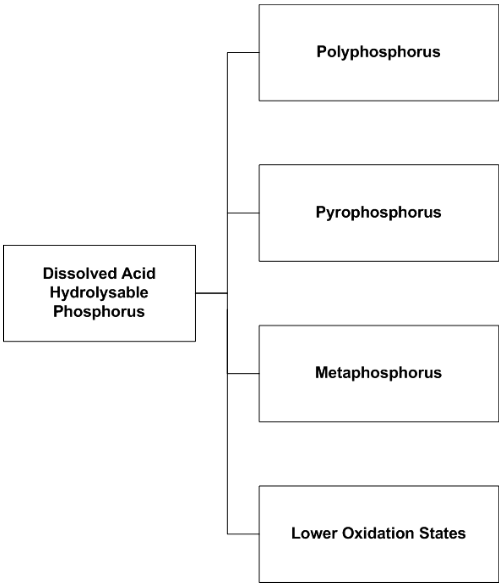


Figure 2-4 – Forms of dissolved acid-hydrolysable phosphorus

Polyphosphorus

Polyphosphorus is a generic name for a series of compounds which can be inorganic and organic. In this paragraph only the inorganic form is discussed. In Section 2.1.1.3, organic polyphosphorus is described.

Polyphosphates are linear condensed inorganic phosphates and complex molecules consisting of two or more phosphorus atoms, oxygen atoms and sometimes hydrogen atoms. A general molecular structure is shown in Figure 2-5; the amount of P groups can vary. Examples are (Spivakov et al., 1999) diphosphate ($H_4P_2O_7$), triphosphate ($H_5P_3O_{10}$) and tetraphosphate ($H_6P_3O_{13}$). Polyphosphates can hydrolyse in aqueous solutions to orthophosphate forms. This hydrolysis is very slow (Tchobanoglous, 2003). Polyphosphates can take part in precipitation reactions or can adsorb to particles (Bratby, 2006).

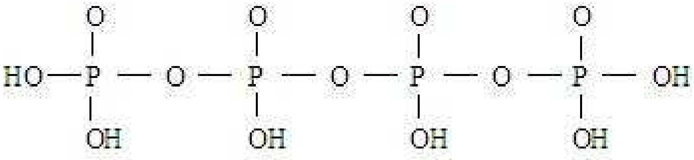


Figure 2-5 - General molecular structure polyphosphorus (Ahlgren, 2006)

A part of the polyphosphorus accumulated by activated sludge is located outside the cytoplasmic membrane and forms complexes with metal cations (Hill et al., 1989). A portion of the inorganic phosphorus which is released through enzymatic degradation of polyphosphorus may be involved in the transport of readily degradable organic material across the cytoplasmic membrane (Hill et al., 1989).

Pyrophosphorus

Pyrophosphorus (Ahlgren, 2006) is an inorganic molecule which consists of two phosphorus groups ($H_4P_2O_7$), as shown in Figure 2-6. Pyrophosphorus is the smallest form of polyphosphorus, but a distinction between the two is made because pyrophosphorus is a single inorganic compound and polyphosphorus, on the other hand, represents a group of compounds which is inorganic but might occur as an organic compound. Pyrophosphates can take part in precipitation reactions or can adsorb to particles (Bratby, 2006).

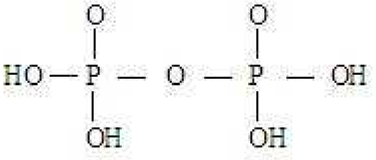


Figure 2-6 - General molecular structure of pyrophosphorus (Ahlgren, 2006)

Metaphosphorus

Metaphosphorus consists of cyclic condensed phosphates. Examples are trimetaphosphate ($H_3P_3O_9$) and tetrametaphosphate ($H_4P_4O_{12}$) (Spivakov et al., 1999). In Figure 2-7 the molecule structure of trimetaphosphorus is shown. Trimetaphosphorus was used in detergents until the negative effect on surface water was known (nowadays in many countries it has been replaced by sodium nitrilotriacetate).

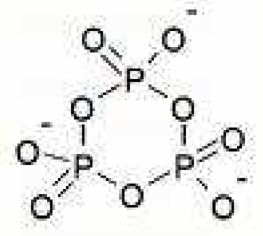


Figure 2-7 - Molecular structure of trimetaphosphorus

Lower oxidation states
The lower oxidation states of phosphorus containing molecules are detected in wastewater (Spivakov et al., 1999). These compounds are, for example, phosphinate (H_3PO_2), phosphonate (H_3PO_3), hypophosphate ($H_4P_2O_6$), diphosphate ($H_4P_2O_7$) and isohypophosphate ($H_4P_2O_6$).

2.1.1.3 Dissolved organic phosphorus

Dissolved organic phosphorus can include phosphosaccharides (adenosine monophosphate, adenosine diphosphate, adenosine triphosphate), nucleic acids, phospholipids, inosit-hexaphosphate (phytin) and organic phosphorus, which is bound to metal ions (Uhlmann et al., 1990). The characterisation, with nuclear magnetic resonance spectroscopy, of leachate from grassland soils (Toor et al., 2003) shows that 88% of the phosphorus is organic and 12% is inorganic. Further investigation of the organic phosphorus shows that it mainly consists of monoesters (67.4%) and diesters (20.2%).

Phosphorus can be an integral part of coloured organic matter, for example humic acids and fulvic acids (Stevens and Stewart, 1982a). The phosphorus content in humic acids is 0.9%; in fulvic acids the phosphorus content is higher (Stevens and Stewart, 1982b). Phosphorus may also be associated with humic acids by the formation of humic acid-metal-phosphorus complexes. Stevens and Stewart (1982a) showed that the coloured material contained organic phosphorus and that also the phosphorus content of the organic material decreased as the mol weight decreased.

If dissolved organic phosphorus takes part in a precipitation reaction, it may suggest that it is colloidal or associated with colloidal material (Stevens and Stewart, 1982a).

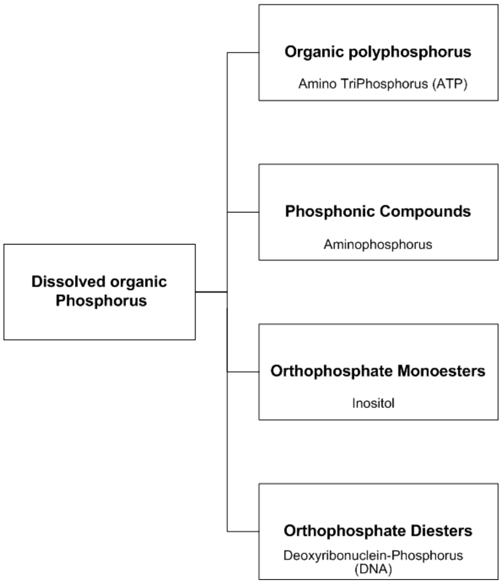


Figure 2-8 - Forms of dissolved organic phosphorus

The next paragraphs will explain that dissolved organic phosphorus is divided into four groups (see Figure 2-8) of compounds, namely organic polyphosphorus, phosphonic compounds, orthophosphate monoesters and orthophosphate diesters.

Organic polyphosphorus

Organic polyphosphorus is, for example, adenosine triphosphate (ATP). ATP plays an important role in the energy transfer in all organisms (Ahlgren, 2006). The presence of polyphosphorus in sediment can be an indication of biological and microbial activity (Ahlgren, 2006). This is due to bacteria which can accumulate orthophosphorus as polyphosphorus during aerobic conditions. The accumulated polyphosphorus is hydrolysed during oxic conditions to orthophosphorus and then released. In a WWTP the process of accumulation and release of orthophosphorus by bacteria is called biological phosphorus removal. Activated sludge mainly contains polyphosphates; under anaerobic conditions these polyphosphates are hydrolysed to orthophosphorus within 8 hours (Röske and Schönborn, 1993).

Phosphonic compounds

Phosphonic compounds or phosphonates occur widely in nature (Ingall et al., 1990; Ahlgren, 2006). Phosphonic compounds are unique because phosphorus is directly bound to an organic compound by a carbon-phosphorus bond, see Figure 2-9. In the figure, R stands for a carbon/hydrogen chain. Due to this stable bond, release of phosphorus from phosphonic compounds is difficult. A few marine microorganisms can break down aminophosphonic acids but this process is inhibited when orthophosphorus is present. The decomposition of orthophosphorus containing organic compounds enriches sedimentary organic matter with phosphonic compounds.

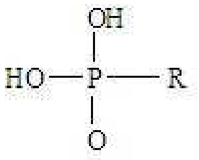
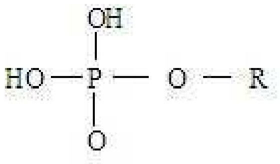


Figure 2-9 - General molecular structure of phosphonic compounds (Ahlgren, 2006)

Orthophosphate monoester

The orthophosphate monoesters are a large group of compounds that includes sugar phosphates, mononucleotides, phospholipids and inositol phosphate. Inositol phosphate is a molecule that consists of a six-carbon atom ring with varying numbers of phosphorus groups attached (Ahlgren, 2006); this is shown in Figure 2-10. Inositol is the most bound to sediments. Monoesters are supposed to be very stable in sediment but can degrade to orthophosphorus under anaerobic conditions (Ibid.).



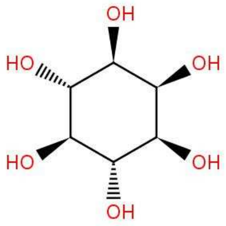


Figure 2-10 - Left: General molecule structure of orthophosphorus monoester (Ahlgren, 2006) and right: inositol phosphorus

Orthophosphate diester

The abundant fraction of orthophosphorus diesters is deoxyribonuclein-phosphorus (DNA-P or $C_2H_8NO_4P$) associated. This DNA-P is primarily bacterial (Ahlgren, 2006). Other fractions are teichoic acid phosphorus and microbial phosphor lipids (for example, Chephalin $C_7H_{12}NO_8P(2R)$). Phosphor lipids are important compounds of the cell membrane because phosphor lipids consist of a glycerol part with two fatty acid chains and a phosphate group which can be covalently bound to other compounds. Teichoic acids are negatively charged and are, for example, ribitol or glycerol molecule structures which are linked via a diester bond. Eighty-five percent of the cell wall is made up of teichoic acids (Ahlgren, 2006).

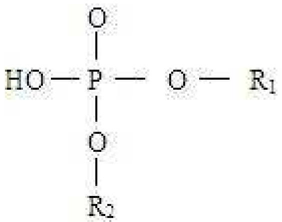


Figure 2-11 - General molecular structure orthophosphate diester (Ahlgren, 2006)

2.1.2 Particulate and colloidal phosphorus

Less information about particulate and colloidal phosphorus, compared to dissolved phosphorus, is available. Particulate phosphorus can be divided into particulate organic phosphorus and metal-bound (inorganic) phosphorus. Particulate phosphorus can be separated by filtration or centrifugation. The amount of particulate phosphorus is usually calculated by subtracting the filtered or centrifuged phosphorus concentration from the total phosphorus concentration (Stevens and Stewart, 1982a). According to the Standard Method (1998), filtrate which passes through a filter with a nominal pore size of 2.0 μm or less is classified as dissolved. In practice, the separation between dissolved and particulate fractions is usually made by filtration through a filter with a pore size of 0.45 µm.

Colloidal phosphorus is within the size range of 0.01 – 1.0 μm and therefore is measured as dissolved phosphorus (Tchobanoglous et al., 2003) when filtration through 2.0 μm is used for the separation between dissolved and particulate. This is schematised in Figure 2-12. The figure shows that by filtration through 2.0 μm, an overestimation of dissolved phosphorus concentration occurs and an underestimation of particulate phosphorus concentration occurs.

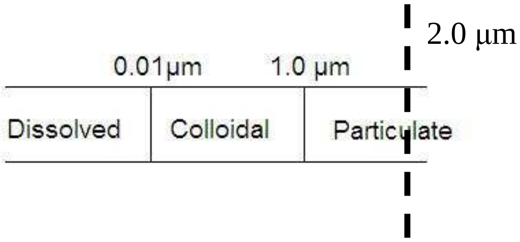


Figure 2-12 – Results for filtration through 2.0 μm, overestimation of the dissolved fraction

When filtration through 0.45 μm is used for the separation between dissolved and particulate as shown in Figure 2-14, an overestimation of dissolved phosphorus concentration and types of particulate phosphorus concentration occur. This is because the colloidal fraction is divided between the dissolved and particulate forms.

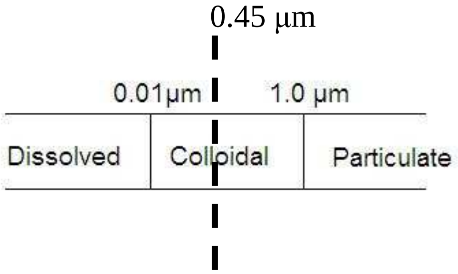


Figure 2-13 – Results for filtration through 0.45 μm, overestimation of the dissolved fraction and the particulate fraction

Metal-bound phosphorus is maybe one of the most known particulate phosphorus forms present in wastewater after metal salt addition. The formation of this particulate phosphorus form is described in Section 2.2. The size of metal-bound phosphorus varies within a wide range (0.01 - 50 μm) and is influenced by many factors, for example the shear rate and temperature (see Section 2.3). Colloidal metal-bound phosphorus can also be found in the wastewater. This phosphorus form gives an overestimation of the orthophosphorus concentration when filtered through 0.45 μm. Detailed information about the overestimation of orthophosphorus concentration caused by (colloidal) metal-bound phosphorus is described in chapter 4.

The presence of humic acids and organic phosphorus in particulate material must be due to the association with hydrous metal oxides, organic material and inorganic minerals (Stevens and Stewart 1982b). Reitzel et al. (2006) found an increased concentration of organic phosphorus when aluminium dosage was used. This can be explained by the adsorption of organic particles by aluminium flocs.

Particulate inorganic phosphorus occurs in mineral phases, adsorbed to particles (biotic and abiotic) and as intracellular storage products (orthophosphorus, pyrophosphorus and polyphosphorus) (Yoshimura et al., 2007).

2.2 Fundamentals of coagulation

Phosphorus can be removed biologically and chemically. When chemical phosphorus removal is employed, a combination of processes, namely precipitation, coagulation, flocculation and filtration is commonly used. Precipitation is the process in which an insoluble solid precipitate drops out of solution, thereby removing material from the solution (McMurry and Fay, 1998). During precipitation colloidal material forms. Coagulation is the process of destabilisation of colloid particles such that these particles can aggregate as a result of particle collision (Tchobanoglous, 2003). The precipitation step is often included when the coagulation process is mentioned. When coagulation is mentioned in this thesis, precipitation and coagulation are meant. For chemical coagulation, a coagulant, generally metal salt, is added to the wastewater which destabilises the particles. The particle size distribution entering the filter bed depends on both the chemical dosage and the initial mixing energy (Boller, 1984a). The size range of the formed particles is 0.01 to 1 μm (Tchobanoglous, 2003). After destabilisation, flocculation process takes place. This process is described in Section 2.3. Coagulation reactions are often incomplete and many competing reactions with other substances in the wastewater occur (Tchobanoglous, 2003). For coagulation, the commonly used coagulants are ferric(III)chloride , poly aluminium chloride (PACl), ferrous sulphate and aluminium chloride (Bratby, 2006). Aluminium and iron coagulants are popular because of their effectiveness, ready availability and relatively low costs (Bratby, 2006). The basic chemical reactions for phosphorus removal with aluminium and ferric salts are:

$$Fe^{3+} + H_nPO_4^{3-n} \rightarrow FePO_4 (\downarrow) + nH^+$$

$$Al^{3+} + H_nPO_4^{3-n} \rightarrow AlPO_4 (\downarrow) + nH^+$$

When aluminium and ferric salts are in solution, immediate dissociation will take place to form hydrated reaction products (Bratby, 2006; Thistleton et al., 2000). The theoretical metal/orthophosphorus dosage ratio is 1 mol/mol but in typical operating conditions for advanced treatment the metal/orthophosphorus dosage ratio is approximately 4 mol/mol. This is due to competing reactions, adsorption and the formation of a mixture of soluble ferric phosphorus, solid ferric phosphorus and ferric hydroxide complexes (Takács et al., 2006; Denham, 2007; Bratby, 2006). At low phosphorus concentrations, higher coagulant doses are required to reach low phosphorus residuals (Bratby, 2006). When the coagulant dosage is higher than the stoichiometric requirements, there will be an increased formation of mixed metal-hydroxide-phosphate (Ibid).

The solubility diagrams for aluminium (left diagram) and ferric (right diagram) salts are shown in Figure 2-14. Aluminium hydroxide and ferric hydroxide precipitate are formed within the grey areas, polynuclear and polymeric species (hydrolysed products) are outside the grey areas. The minimum solubility or iso-electrical point for aluminium is pH 6.3 and for ferric, pH 8.

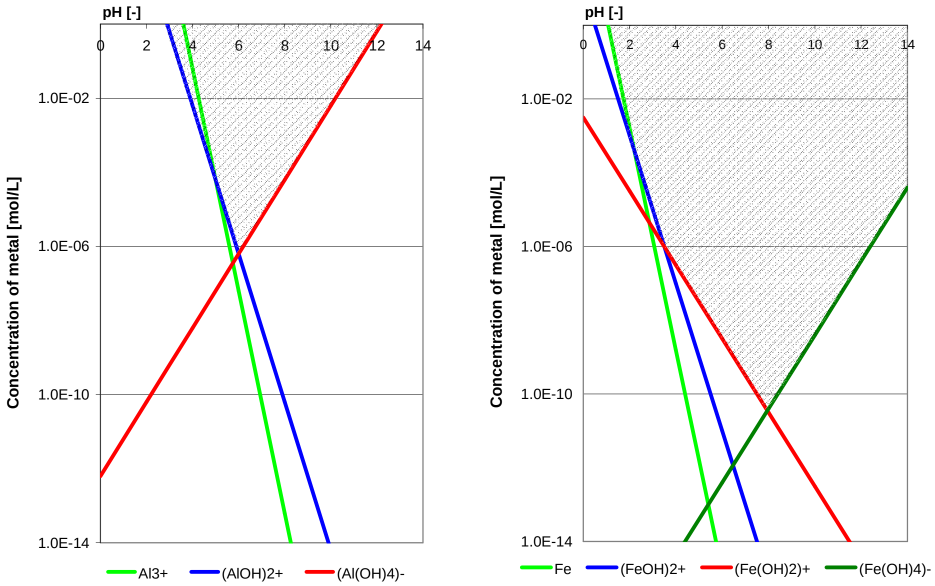


Figure 2-14 – Solubility diagram for aluminium (left) and ferric (right) (Tchobanoglous, 2003)

The most important coagulation mechanisms for wastewater treatment are adsorptive coagulation and precipitation coagulation; the latter is known as sweep coagulation (Miska-Markusch, 2009). Adsorptive coagulation is the adsorption and charge neutralisation of colloidal particles or ions by the positively charged hydrolysed products (Tchobanoglous, 2003). Sweep coagulation occurs when a sufficient amount of coagulant is dosed. In this case large amounts of metal hydroxide flocs will be formed, which will settle. When these flocs settle, they sweep through the water containing colloidal particles (Tchobanoglous, 2003).

PACl is a prehydrolysed coagulant. Prehydrolysed coagulants are formed by the addition of a base to a simple coagulant such as aluminium chloride (Exall and vanLoon, 2003). Prehydrolysed coagulants favour the formation of soluble polynuclear species, like dimers (Exall and vanLoon, 2003). The efficiency of prehydrolysed aluminium flocculants is, according to Boisvert and Jolicoeur (1999), related to its ability to form amorphous $Al(OH)_3$ instead of highly charged cationic species. Prehydrolysed flocculants are, compared to metal salts, less sensitive to temperature influences, operate efficiently over a wide pH range, require a lower dosage, do produce less chemical residuals (Bratby, 2006).

When the objective is to remove soluble, colloidal and quasi-colloidal phosphorus by coagulant addition, six different mechanisms play a role in phosphorus removal, according to Takács et al. (2006). These six mechanisms are:

- precipitation of orthophosphorus;
- co-precipitation (formation of amorphous complexes);
- formation of soluble phosphorus and hydroxide complexes;
- formation of organic side products and other wastewater components;
- adsorption of organic phosphorus ions and dissolved “organic” phosphorus to the hydroxide flocs;
- coagulation and flocculation of primary precipitate colloidal particles and colloidal organic phosphorus.

2.2.1 Initial mixing energy

For phosphorus removal by coagulation, as described in Section 2.2, metal salts are generally added to the water. To maximize the binding of the metal salt with the available phosphorus and to minimize the side reactions with other substances in the wastewater, a good initial mixing is necessary. The initial mixing must take place directly after the metal salt dosing. The initial mixing process is influenced by the characterisation of the wastewater, the temperature, the type of coagulant, the coagulant dosage, the mixing intensity and duration (Mhaisalkar, 1991). Insufficient rapid mixing may have two harmful effects, namely wastage of chemicals and a slower particle aggregation rate for a given dosage (Vrale and Jordan, 1971). However, according to Boller (1984b) too high mixing energies result in small colloidal neutrally charged precipitates that pass the filter bed. For a sufficient initial mixing, a certain initial mixing energy, or so-called velocity gradient (G-value), is required. To create this velocity gradient, static mixers or valves are commonly used.

In the literature contradictory G-values for optimal initial mixing energy are given. According to Tchobanoglous (2003), the optimal G-value for initial mixing is 500 – 1,500 s^{-1}. Bratby (2006) states that, when using a hydrolysing metal coagulant for inline initial mixing, the optimal G-value is between 1,200 – 2,500 s^{-1}. Thistleton et al. (2002) found with jar testing that the initial mixing has no effect on the orthophosphate removal rates and that orthophosphate removal rates remain high even when no initial mixing is used. According to Mhaisalkar (1991), the optimum G-value and mixing time are dependent on the turbidity of the water, and the mixing time increases with an increase in the water turbidity. For any water there exists an optimal combination of G-value and mixing time (Mhaisalkar, 1991).

The formulas to calculate the G-value within a pipeline are described below (Braty, 2006). First of all, the head loss (h_L) is calculated:

$$h_L = k \frac{{v_u}^2}{2g} \qquad \text{eq. 2.1}$$

h_L = head loss [m]
k = resistance coefficient [-]
v_u = flow velocity upstream [m/s]
g = gravitational constant [m^2/s]

The k-value or resistance coefficient for a 90° corner is 0.5. The resistance for a gate valve can be calculated using the following formula:

$$k = 2.8\left(1-\beta^2\right)\left(\frac{1}{\beta^4}-1\right) \text{ with } \beta = \frac{diameter\ \ gate\,valve}{diameter\ \ pipe\,upstream} \qquad \text{eq. 2.2}$$

The formula to calculate the G-value is:

$$G = \sqrt{\frac{\rho \cdot h_L}{t \cdot \mu}} \qquad \text{with } t = \frac{x}{v} \qquad \text{eq. 2.3}$$

G = initial mixing energy [s^{-1}]
ρ = unit weight of water [N/m^3]
t = retention time [s]
μ = dynamic viscosity [Ns/m^2]
x = length where mixing takes place [m]
(7.5 times the diameter of the upstream pipe)

The velocity gradient in a reservoir or basin used during the flocculation process, for example, can be calculated with comparable formulas. These are described in Section 2.3.

2.2.2 Temperature effect on the coagulation

Morris and Knocke (1984) conducted experiments to investigate the temperature effects on coagulation. They showed that a low temperature (1°C) does not significantly inhibit the rate of metal-hydroxide precipitation, and that precipitation occurs within a minute. With a decreasing water temperature, the minimum solubility of an aluminium hydroxide species shifts to a higher pH and, thus, the optimal operating pH shifts to a higher pH (Bratby, 2006). The influence of temperature on floc formation can be ascribed to the change in viscosity of the water and/or the change in hydrolysing reaction kinetics of the coagulant (Kang and Cleasby, 1995; Hurst et al., 2004; Bache and Gregory, 2007). For example, the rate of hydrolysis for Fe(III) salts accelerates with an increase in temperature and pH and the formation time of soluble polymeric iron species decreases rapidly (Kang et al., 1995).

2.3 Flocculation

Flocculation follows after initial mixing and coagulation. In wastewater treatment flocculation's main purpose is to form aggregates or flocs from finely divided particles and from chemically destabilised particles (Tchobanoglous, 2003). To destabilise and form larger aggregates, particles need to approach close enough and make contact. Two types of flocculation can be defined. These are perikinetic flocculation (microflocculation) and orthokinetic flocculation (macroflocculation). Perikinetic flocculation signifies the aggregation of particles by the random thermal motion known as Brownian movement. This flocculation is the main mechanism for particles between 0.001 and 1.0 μm (Tchobanoglous, 2003). Orthokinetic flocculation signifies the aggregation of particles between 1 and 2 μm. This type of flocculation requires a velocity gradient or differential settling. Due to the velocity gradient, particles will collide and form larger flocs. During flocculation by differential settling, larger particles will overtake smaller particles and form larger flocs when they collide (Tchobanoglous, 2003). Specially designed flocculation tanks or basins, mostly with mixers and baffles, are used for orthokinetic flocculation.

2.3.1 Velocity gradient and floc growth

The degree of flocculation is dependent on the combination of the velocity gradient (G-value), the retention time (Dharmappa et al., 1993) and the coagulant dosage. The formula to calculate the velocity gradient or G-value during flocculation is (Bratby, 2006):

$$G = \sqrt{\frac{P}{V \cdot \mu}} \qquad \text{eq. 2.4}$$

G = velocity gradient or G-value [s^{-1}]
V = volume of the flocculation tank [m^3]
μ = dynamic viscosity [Ns/m^2]

Typical velocity gradients used for flocculation in direct or contact filtration systems are between 25 s^{-1} and 200 s^{-1} in combination with a retention time of 2 – 10 minutes (Tchobanoglous, 2003). It should be noted that it is not the average velocity gradient in the flocculation tank that is determinative but the local velocity gradient of the mixer-affected zone (François, 1987).

Floc growth in a flocculation tank is determined by the velocity gradient referred to as the applied shear rate, the particle concentration and the collision efficiency (Yukselen and Gregory, 2004). The growth of flocs is restricted by the shear rate because flocs may break when the shear rate is too high, and by the collision efficiency which decreases when flocs become larger (Yukselen and Gregory, 2004). Thus, the breakage of flocs depends on floc strength and the applied shear rate, therefore an exact shear rate for which flocs break cannot be given. Boller and Blaser (1998) showed a strong dependency between the floc size and the floc strength and classified flocs into easily breakable flocs of 500 – 2000 μm and hardly breakable flocs smaller than 100 μm. Increased shear rates cause floc breakage; as a result of this, smaller but more compact flocs are produced (Spicer et al., 1998). When the shear rate is decreased after disruption of the flocs occurs, floc regrowth starts but for a limited extent: the floc size after regrowth is lower than the previous value (Yukselen and Gregory, 2004; Yukselen and Gregory, 2002). Regrowth can be improved by an increased concentration of suspended solids and by an increase in the shear rate (François, 1987). According to Yukselen and Gregory (2004, 2006) flocs that are formed with higher dosage ratios have a more open structure; because of this structure, flocs can easily fall apart.

Spicer et al. (1998) conducted experiments to compare floc characteristics produced with a continuous velocity gradient of 50 s^{-1}, a cycled velocity gradient (flocculation at 50 s^{-}1, floc breakage with 100 s^{-1}, 300 s^{-1}, 500 s^{-1} and regrowth at 50 s^{-1}), and a tapered velocity gradient (gradual reduction of 300 s^{-1} to 50 s^{-1}). The results showed that flocs formed with a cycled velocity gradient are slightly smaller, but denser and more compact compared to flocs formed at a constant velocity gradient of 50 s^{-1}. Flocs formed with a tapered reduction were also denser and more compact, but were smaller compared to flocs formed at a constant velocity gradient of 50 s^{-1}.

Polyaluminium chloride shows a more rapid flocculation and gives significantly larger flocs compared to alum, which is possibly due to the more rapid precipitation and the increased binding strength between particles (Yukselen and Gregory, 2004). Leentvaar and Rebhun (1983) showed that ferric chloride dosings in combination with a polymer lead to stronger flocs compared to coagulation and flocculation without a polymer addition.

2.3.2 Temperature and pH effect on flocculation

The water viscosity increases with a decreasing temperature, but the initial mixing energy is generally high enough to undo the negative effect of the higher water viscosity (Kang et al. (1995). Therefore, the influence of temperature on floc formation and reformation is mostly related to changes in the coagulant chemistry (Fitzpatrick et al., 2004). Hydrolysis constants and kinetic factors may be the cause of the negative effect caused by low temperatures. These negative effects are described by Fitzpatrick et al. (2004) as:

1. floc breakage increases with an increasing temperature,
2. floc recovery or reformation decreases with an increasing temperature,
3. the smaller the flocs, the less they break and the better their recovery or reforming.

Morris and Knocke (1984) showed during experiments without taking the pH into account that the temperature mainly affects the floc size. Flocs formed at 1°C are often smaller than flocs formed at 20°C. Thus, warmer temperatures produce larger flocs which break more easily and reform less well than lower temperatures (Fitzpatrick et al., 2004).

Hanson and Cleasby (2007) show that the solubility kinetics at 5°C and 20°C are nearly similar if the pOH is constant. When keeping the pOH constant, the Al/OH ratio is constant and thus provides constant conditions for the formation of hydroxides. The relationship between pH and pOH is described below:

$$pH + pOH = pK_w \qquad \text{eq. 2.5}$$

The pK_w is calculated as follows:

$$pK_w = -6,0875 + \frac{4470,99}{T} + 0,01706T \qquad \text{eq. 2.6}$$

From the formula it can be concluded that the pH needs to be decreased for higher temperatures. Hanson and Cleasby (1990) conducted experiments with a constant pOH and constant pH and concluded the following:

- Alum flocs under all tested conditions are significantly weaker than iron flocs,
- Ferric flocs formed at 20°C and 5°C are of similar strength as long as the pOH is constant,
- Ferric flocs formed at 5°C are weaker compared to flocs formed at 20°C when the pH is constant,
- Alum flocs formed at 5°C and a constant pOH are much stronger compared to flocs formed at 5°C with a constant pH,
- Alum flocs formed at 20°C with a constant pOH are stronger compared to flocs formed at 5°C, also with a constant pOH.

Temperature affects aluminium-based coagulants as well as ferric-based coagulants (Morris and Knocke, 1984; Haarhoff and Cleasby, 1988; Fitzpatrick et al., 2004) but aluminium-based coagulants produce flocs that are more influenced by temperature. When stable and similar-sized flocs are required all year round, ferric-based coagulants seem the best choice (Fitzpatrick et al., 2004). Fitzpatrick’s group compared polyaluminium chloride (PACl) with ferric sulphate and alum for different temperatures. The results showed that PACl coagulants produce the largest flocs for all experimented temperatures (7° - 27°C). The reduced influence of temperature on PACl coagulants can possibly be explained by the pre-polymerisation of the product. Due to the pre-polymerisation, the influence of temperature is smaller (Meijers et al., 1984). This could explain why PACl coagulants are mainly used during winter time (Bratby, 2006).

On an equimolar basis ferric(III)chloride removes turbidity more efficiently compared to aluminum sulfate at low temperatures (3°C) and low turbidity (<2 NTU), according to Haarhoff and Cleasby (1988). In 2004, Hurst et al. found similar results when comparing NTU removal at temperatures of 5°C and 15°C with ferric(III)chloride dosings. Results showed that the NTU removal was significantly impaired at 5°C. When the dosage rate increased, the NTU removal increased, but the NTU removal at 5°C was lower compared to the removal rate at 15°C, even at high dosages (> 10 mg Fe^{3+}/L).

The rate of hydrolysis increases with an increasing pH and an increasing temperature, which results in a shorter period of time needed for the formation of soluble polymeric iron species (Van der Woude and De Bruyn, 1983). When the pH is even a few tenths below the optimum pH, the growth rate of the flocs will decrease rapidly, leading to smaller flocs (Bache and Gregory, 2007).

2.4 Filtration

Granular media filtration, such as continuous sand filtration or fixed bed filtration, is commonly used for the removal of phosphorus precipitates formed during the coagulation and flocculation process. Less commonly used are for example synthetic medium filters, continuous backwash filters or pressure filters. Filtration is a process during which water flows through a porous filter media, which can be a membrane, a filter paper, synthetic meterial, or a sand layer. A sand filter (partly) retains suspended solids and ferric and aluminium precipitates, but can also contain biomass for the removal of dissolved substances like nitrate.

According to Tchobanoglous (2003) nine different removal mechanisms and phenomena contribute to the removal of material within a sand filter. These are straining, sedimentation, impaction, interception, adhesion, flocculation, chemical adsorption, physical adsorption and biological growth. The first five mechanisms are of importance for the removal of suspended particulate matter and are described below. Straining or sieving implies mechanical filtering of particles larger than the pore space of the filter medium. This mechanism is the principal one for particle removal but can result in a cake layer forming in the top layer of the filter bed. Sedimentation or internal impaction implies that particles settle on the filter medium within the filter bed. Interception is the removal of particles that move along the streamline and are removed as they come in contact with the filter medium. Graham (1988) investigated flocculation and removal of flocs within a filter bed and concluded that particle flocculation is the minority mechanism of enhanced particle removal with a cationic polymer. The mechanisms are mainly particle-grain attachment and the deposition of particles onto previously deposited particles.

2.4.1 Dual media filtration and continuous sand filtration

Downflow depth filtration with a single, dual or multi medium and deep bed upflow continuous backwash filtration, also called continuous sand filtration, are frequently used as filtration techniques for the treatment of wastewater treatment plant effluent. Figure 2-15 shows schematically both filtration techniques, with dual media filtration on the left side and continuous sand filtration on the right side.

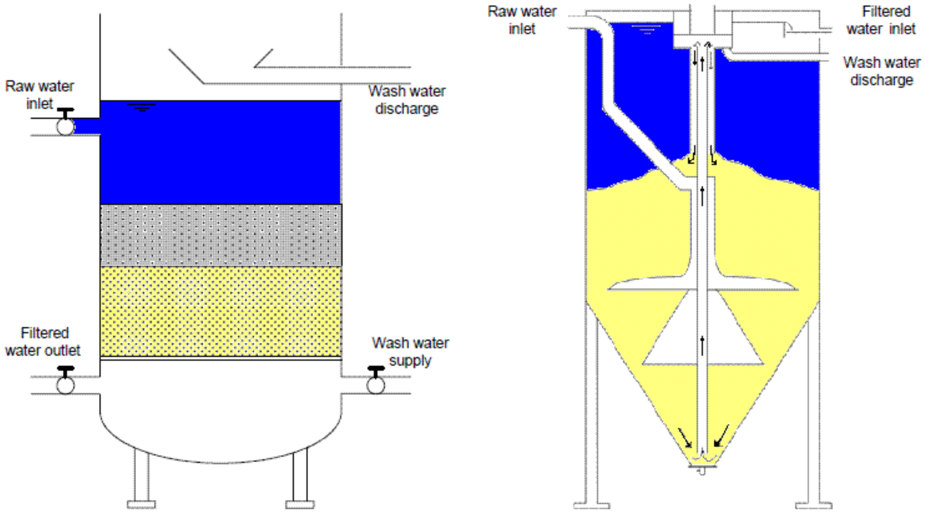


Figure 2-15 – Dual media filtration (left figure) and continuous sand filtration (right figure) (Van den Berg van Saparoea, 2008)

With downflow depth filtration the water which needs to be filtered is introduced at the top of the filter; this is called the raw water inlet in Figure 2-15. The water moves downwards through the upper water layer and the filter media, after which it is collected in the underdrain system. Via the filtered water outlet, the so-called filtrate water goes to filtrate storage tanks where this water is stored to be used parts for a backwash procedure. During the backwash of a filter, the accumulated material is removed by shear force created by the flow of the backwash water and is removed through the expanded bed (Tchobanoglous, 2003). A backwash is initiated when the upper water layer increases or when a breakthrough of the filter bed occurs. During a backwash, no filtrate is produced.

With continuous sand filtration the water is introduced into the filter bed through a series of riser tubes and is distributed evenly into the sand through an inlet construction (Tchobanoglous, 2003) in the middle of the sand layer. The water flows upwards through the downwards moving sand bed. The filtrate water overflows a weir at the top of the filter and is discharged. The sand and the removed particles are removed from the bottom of the filter bed by an airlift pipe. During the turbulent upflow, high velocity gradients are applied as a result of which the sand is washed and cleaned and falls back through a sand washer on top of the filter bed.

The used filter material for downflow depth filtration and continuous sand filtration influences the filtrate water quality and should be chosen with care. Especially the grain size, the uniformity, the pore size, and the adsorption capacity are of major importance. Frequently used materials are anthracite, hydro-anthracite, quartz sand, basalt and granate sand.

The optimal filtration rate depends on many aspects. These include the concentration of particulate matter in the feed water, the amount of chemicals dosed for coagulation, the shear force in the filter bed, the floc strength and the temperature of the feed water.

2.4.2 Filter runtime and filter loading

The filter runtime is the period between two backwashes. During this period the filter produces filtrate water. For downflow depth filtration the maximum filter runtime is dependent on the head loss over the filter bed and the filtrate quality. The head loss over the filter bed increases during the runtime mainly because of cake layer formation. As a result of the increasing head loss over the filter bed, the upper water layer will rise, until the maximum water level is reached. When this is reached a backwash will be initiated.

A cake layer on top of the filter bed or a clogged layer within the filter bed results in locally high water pressure gradient, but below this layer the pressure gradient will decrease. Figure 2-16 shows the pressure drop in a dual media filter.

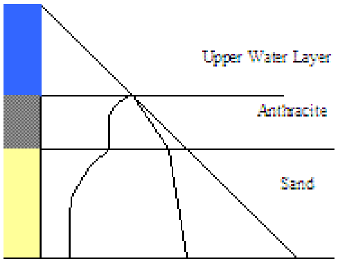


Figure 2-16 – Pressure curves in a filter bed (Miska-Markus, 2009)

Zouboulis et al. (2007) compared the filtrate water quality and the filter runtime for a dual media filter and a single media filter for the treatment of drinking water after coagulation/flocculation and sedimentation. The filter bed of the dual media filter contains sand (grain size 0.64 mm) and anthracite (grain size 1.0 – 1.1 mm). The filter bed of the single media filter contains a sand layer (grain size 0.64 mm). Both filters have a filter bed height of 1 m and a filtration rate of 9.4 m/h. The results show that the turbidity in the filtrate water is comparable for the two filter types, but the filter runtime for the dual media filter is 3 to 4 times longer compared to the single media filter. When coagulant (0.1 – 0.3 mg Al^{3+}/L) was dosed, the turbidity of the filtrate water increased and the filter runtime dramatically decreased for both filters. The dual media filter reached a filter runtime of 10 – 15 hours instead of 74 hours without coagulant dosage. But the filter runtime of the dual media filter was still approximately twice the filter runtime of the single media filter. This phenomenon is explained by the removal of larger particles in the coarse anthracite layer, whereas the smaller particles were trapped in the finer sand layer. This maximized the filter loading and therefore the filter runtimes are longer compared to single media filtration.

2.4.3 Velocity gradient in a filter bed

Two types of filtration can be distinguished: floc filtration, where flocs are formed in a flocculation tank or basin before entering the filter and flocculation filtration, and the so-called direct filtration, where flocs are formed in the top layer of the filter bed. In a flocculation tank, low velocity gradients are used to prevent floc breakage. The typical velocity gradients used for flocculation are between 25 s^{-1} and 200 s^{-1} (Tchobanoglous, 2003), as stated in Section 2.3.1. When the flocs enter the filter bed divergence flows occur within the first centimetres of the filter bed. Boller and Blaser conclude from mathematical models that floc rupture is dominated by the amount of straining or divergence flow. In a filter bed the shear rate may be sufficient to promote flocculation in the filter pores, but due to accumulation of deposits the shear rate will increase if a constant filtration rate is applied (Chuang and Li, 1997). When the shear force in the filter bed becomes too high, particles or flocs may detach and a breakthrough of the filter bed occurs. Polymeric coagulants or flocculant aids are frequently used to prevent breakthrough of the filter bed before the maximum head loss is reached. This is because polymeric coagulants form much stronger flocs compared to ordinary metal salts (Chuang and Li, 1997; Yukselen and Gregory, 2004; Leentvaar and Rebhun, 1983).

To calculate the shear rate within pores of the filter bed, Chuang and Li (1997) developed the following formula based on the Kozeny-Carman equation in which the filter bed is simplified as clustered capillary tubes:

$$G_w = 25\left(\frac{1-p}{p^2}\right)\frac{v}{\phi_s \cdot D_p} \text{ in which } \phi_s = \frac{\pi^{1/3}\left(6V_p\right)^{2/3}}{A_p} \qquad \text{eq.2.7}$$

G_w = shear rate within the filter pores [s^{-1}]
p = porosity [-]
v = average filtration rate [m/s]
ϕ_s = sphericity of the filter grain [-]
D_p = effective grain size [m]
V_p = filter grain volume [m^3]
A_p = filter grain surface [m^2]

According to this formula, the shear rate within the filter pores increases rapidly during filtration, see Figure 2-17. This figure shows the shear rate for an anthracite layer with grain size 1.70 - 3.35 mm when filtration with 5, 10, 15 and 20 m/h is applied. The porosity of the new anthracite is 0.5; this decreases to 0.35 due to the biomass which is attached to the anthracite. During filtration the porosity decreases even further, resulting in increasing shear rates (G-values).

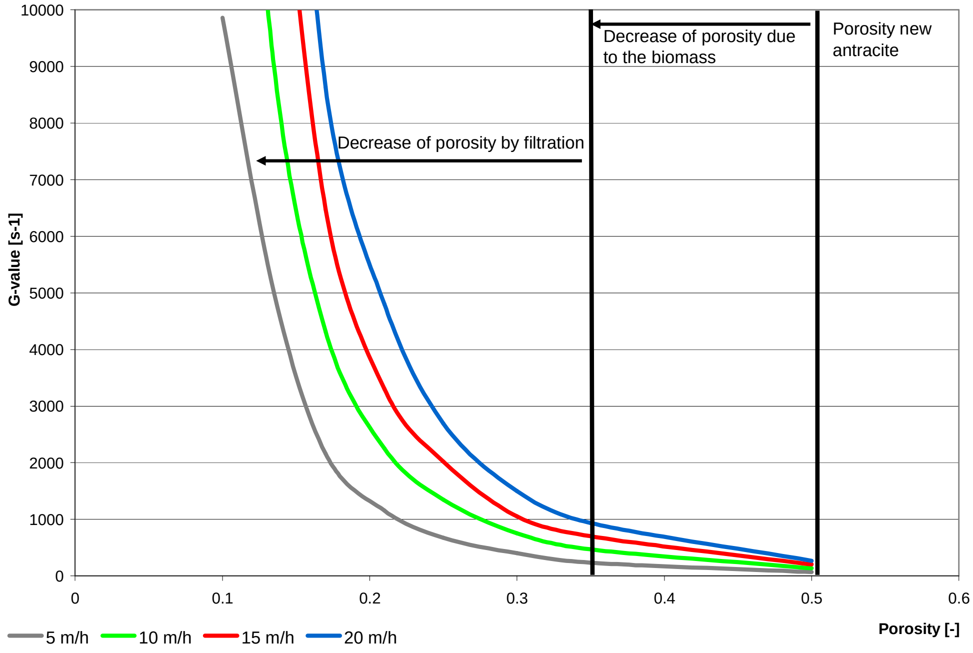


Figure 2-17 – The influence of the porosity on the shear rate (G-value) and the filtration rate for an anthracite layer with grain size 1.70 - 3.35 mm

2.5 Denitrification

Denitrification is the biological reduction of nitrate to nitrogen gas. Denitrification takes place when nitrate is used as an electron acceptor instead of oxygen (Gayle et al., 1989). The nitrate reduction reactions involve the following biological reduction steps (Tchobanoglous, 2003) of nitrate to nitrite, to nitric oxide, to nitrous oxide and to nitrogen gas:

$NO_3^- \text{ (aq)} \rightarrow NO_2^- \text{ (aq)} \rightarrow NO \text{ (g)} \rightarrow N_2O \text{ (g)} \rightarrow N_2 \text{ (g)}$

The denitrification process is an anoxic process but most of the denitrifying bacteria are facultative, meaning that also oxygen can be used when available (Gayle et al., 1989). According to Payne (1981) many different denitrifying bacteria are known including *Achromobacter*, *Bacillus*, *Hyphomicrobium*, *Pseudomonas* and *Thiobacillus*. Most of these bacteria are heterotrophic, *Paracoccus denitrificans* and *Thiobacillus* are autotrophic. For each denitrification step, a specific enzyme is used to catalyse the reaction. These enzymes are called nitrate reductase or nitrite reductase, for example.

The following circumstances are required for denitrification, (Van der Graaf, 1996):

- the presence of nitrate (or nitrite): the conversion rate is independent of the nitrate concentration when the nitrate concentration is > 1 mg NO_3-N;

- the presence of substrate: in theory 1 kg of nitrate or nitrate-N can oxidize 2.86 kg COD;
- the absence of oxygen: in practice an oxygen concentration < 0.5 mg O_2/L;
- good process conditions: an optimal pH range is pH 7 to pH 9, the optimal temperature is approximately 40°C, but denitrification can take place at lower temperatures, even as low as 5°C.

As an electron donor, one of these three sources is used

1. biodegradable soluble COD in the feed water;
2. biodegradable soluble COD produced during endogenous decay;
3. exogenous source, for example, methanol or acetate.

The third option is frequently used for post-treatment steps when biodegradable soluble COD is not available in the feed water.

2.5.1 COD demand

The theoretical COD requirements for denitrification can be calculated as follows (Tchobanoglous, 2003):

$$\frac{COD}{NO_3 - N} = \frac{2.86}{1 - 1.42 \cdot Y_n} \qquad Y_n = \frac{Y}{1 + k_d \cdot SRT} \qquad \text{eq. 2.8}$$

Y_n = net biomass yield [g VSS/g COD]
k_d = endogenous decay rate per day [d]
SRT = sludge retention time [d]

2.5.2 Methanol

Methanol usage as a carbon source for denitrification has the advantage that the costs are relatively low and the sludge production is low compared to other organic compounds (Koch and Siegrist, 1997). A disadvantage is the needed adaptation period for the bacteria which can take a few days up to several weeks. According to Timmermans and Van Haute (1983), a higher denitrification rate (25%) is measured with methanol as a carbon source in comparison to the denitrification rate which is obtained when wastewater carbon is used as a carbon source. The reaction stoichiometry for methanol is given below.

$5\ CH_3OH + 6\ NO_3^- \rightarrow 3\ N_2 + 5\ CO_2 + 7\ H_2O + 6\ OH^-$

Methanol systems are often enriched with *Hyphomicrobium* spp. (Sperl and Hoare, 1972; Lemmer et al., 1997). *Hyphomicrobium* spp. is capable of using nitrate, under anaerobic conditions, for assimilation and respiration (Nurse, 1980). The growth of these organisms is independent of the methanol and nitrate concentration, but is sensitive to temperature and pH. The optimal pH is 8.3 (Timmermans and Van Haute, 1983). During Lemmer et al.'s research (1997), taxonomic classification of the microorganisms in a denitrifying fixed filter bed with methanol dosage was conducted. Results showed that not only methylotrophs but also *Hydrogenophaga*, which are not able to use C_1-carbon sources like methanol, were found. Because these microorganisms are readily detected in activated sludge, it is likely that these organisms were washed out from the secondary clarifier.

The net biomass yield for methanol is 0.17 g VSS/g bCOD (10°C) and 0.18 g VSS/g bCOD (20°) (Tchobanoglous, 2003). Without methanol loss (Koch and Siegrist, 1997) the yield was 0.42 kg-COD_x/kg-COD_{me}^{-1} during wintertime and 0.39 kg-COD_x/kg-COD_{me}^{-1} during summertime.

To denitrify 1 kg NO_3-N, the following methanol dosage is required (Koch and Siegrist, 1997):

$$\frac{\Delta NO_3 - N \cdot 2.86}{(1-Y_n)\cdot COD_{MeOH}} = \frac{1.0 \cdot 2.86}{(1-0.4)\cdot 1.5} = 3.2\,\frac{kg\ MeOH}{kg\ NO_3 - N} \qquad \text{eq. 2.9}$$

COD_{MeOH} = COD fraction of methanol (kg/kg)

The efficiency of the denitrification depends on the oxygen concentration in the feed water. Oxygen decreases the denitrification rate and increases methanol consumption (Koch and Siegrist, 1997).

According to Koch and Siegrist (1997), the biofilm activity in the first 30-40 cm of the filter bed strongly depends on the filter runtime. This is caused by biofilm loss. In the central and lower parts of the filter bed, no significant increase in the denitrification rate can be found during the filter runtime. To prevent overdosing methanol, the dosage should be reduced in the first hours after the main backwash. During a methanol dosage break of one week, denitrification rates decreased but after restarting the methanol dosage the denitrification rate increased within a week to the level observed before the dosage break.

2.5.3 Nitrite accumulation

Nitrite is consumed at a rate twice the nitrate reduction rate; therefore, the rate-limiting step for denitrification is the reduction from nitrate to nitrite (Timmermans and Van Haute, 1983). Nitrite accumulation during denitrification can, however, be caused by many factors. Hunter (2003) summarises factors which can play a role in nitrite accumulation. These factors include the differential repression of nitrate and nitrite reductase, the competition of nitrate and nitrite reductase for electron donors, the presence of carbon sources that select nitrite producing bacteria, the increase of electrical conductivity and the presence of toxic substances. These toxic substances can be heavy metals, pesticides, etc. Nitrite accumulation, according to Koch and Siegrist (1997), depends on the water temperature during growth and not on the actual temperature. A temporary higher reduction rate for the reduction of nitrate to nitrite compared to the reduction of nitrite to N_2 (g) might be due to a microbial population shift from winter to summer; during summertime more microorganisms are present which reduce nitrate to nitrite.

Other reasons for nitrate accumulation can be the wash out of *Nitrobacter* from the secondary clarifier and the activity of facultative anaerobic bacteria (Lemmer et al., 1997).

This activity results in a lower pH value which inhibits nitrous oxide reductases or nitrate reductases.

When oxygen is present in the filter bed, nitrite reductase is strongly inhibited. Nitrate reductase, on the other hand, is not inhibited by oxygen or nitrite until a concentration of 0.1 mM. (Gayle et al. 1989). This can result in nitrite accumulation. After nitrite accumulates to sufficient concentrations, the activity of nitrite reductase increases and the denitrification process proceeds (Gayle et al. 1989).

The toxicity of nitrite to fresh water fish varies widely. For example, rainbow trout (*Salmo gaidneri*) show a lethal concentration (LC_{50}) of less than 1 mg/L, but largemouth bass (*Micropterus salmoides*) show an LC_{50} of 452.7 ±24.6 mg/L (Tomasso, 1986).

2.5.4 Phosphorus uptake by denitrifying bacteria

When combining nitrogen and chemical phosphorus removal in a single sand filter, phosphorus limitation may occur. Low orthophosphorus concentrations may affect the denitrification conversion rate by inhibiting the rapid growth of heterotrophic microorganisms in response to increasing nitrate loads (Husband and Becker, 2007). When chemical precipitation is used for the phosphorus removal, just a little amount of bio-available phosphorus remains in the water to support the growth of denitrifying bacteria. This can result in difficulties during operation but also the start-up period of a denitrifying filter is drastically increased and can even take up to six months (de Barbadillo et al., 2006).

Theoretically, phosphorus becomes a limiting factor when concentrations are below 0.04 mg P/mg NO_x-N, assuming 3 mg of methanol per mg NO_x-N (de Barbadillo et al., 2006; Husband and Becker, 2007). NO_x-N is the total amount of inorganic oxidized nitrogen, namely the sum of the nitrate and nitrite concentration. Research shows (de Barbadillo et al., 2006) that an orthophosphorus/NO_x-N ratio of approximately 0.02 mg/mg or higher does not appear to have any impact on the denitrification rate. When the orthophosphorus/NO_x-N ratio is too low, resulting in an increase of NO_x-N in the filtrate water, the orthophosphorus concentration needs to be increased, possibly by dosing phosphoric acid (deBarbadillo et al., 2006; Hanner et al., 2003; Hultman, et al., 1994) or potassium phosphate (Husband and Becker, 2007).

According to Nordeidet et al. (1994), the divergence of the found limitation ratios for nitrification is caused by the culture history with respect to the amount of accumulated polymetaphosphate in the cells, the carry-over of the elements in the inocula and/or the effect of phosphate on the pH of the medium. This might be applicable on denitrifying bacteria too.

At the Loudden treatment plant in Stockholm (Hultman et al., 1994), Sweden, biological treated and settled effluent was introduced into DynaSand filters where denitrification, phosphorus precipitation and filtration take place. Methanol was dosed as the carbon source and ferric chloride was used to precipitate orthophosphorus. Nitrate concentrations in the feed water of the filter, up to 20 mg NO_3-N/L, were tested in combination with phosphorus concentrations of 0.2 mg PO_4-P/L and 0.5 mg P-total/L. During the research, tests were conducted to find the minimum required phosphorus concentration in the feed water. The results of these tests indicate that the influence of the orthophosphorus concentration on the denitrification rate is small when the orthophosphorus concentration remains above 0.1 mg/L.

At the Sjölunda wastewater treatment plant in Malmö (Hanner et al., 2003), Sweden, a moving bed biofilm reactor (MBBR) is used for denitrification. Chemical phosphorus removal with ferrous sulphate is accomplished in an earlier stage of the treatment process. Methanol or ethanol is dosed as the carbon source; the dosage is not controlled. In periods with high nitrate concentrations in the feed water of the MBBR, simultaneous bleed-through of COD and high (6 mg NO_3-N/l or higher) nitrate concentrations in the WWTP effluent occurred. During these periods the concentration of orthophosphorus in the WWTP effluent was ± 0.05 mg PO_4-P/L. When dosage of phosphoric acid was started, the amount of available orthophosphorus increased and the nitrate concentration decreased. The orthophosphorus concentration remained low despite the higher amount of available orthophosphorus. An orthophosphorus concentration in the feed water of the MBBR of 0.10 mg/L was the minimum required to avoid phosphorus limitation. Although dosage of phosphoric acid solves the problem of phosphorus limitation, the strategy is to adjust the coagulant dosage more actively.

2.6 Biological activated carbon

In wastewater treatment, activated carbon is most commonly used as an adsorbent for the treatment of WWTP effluent. This can be in the form of powdered activated carbon (diameter <0.0074 mm) or granular activated carbon (diameter >0.1 mm). Activated carbon is prepared by making char from organic materials (Tchobanoglous, 2003) such as wood, coconut shell, walnut hulls. The type of material used influences the final pore sizes and regeneration characteristics. The char is pyrolised at about 700°C and then activated by exposure to oxidising gases at temperatures around 800°C to 900°C. The gases develop a porous structure. According to Tchobanoglous (2003), the pore sizes within the activated carbon can be divided into macropores (>25nm), mesopores (>1nm and <25nm) and micropores (<1 nm). The activated carbon needs to be regenerated when the maximum adsorption capacity is reached and a breakthrough occurs. Regeneration can be achieved by chemical oxidation, steam, solvents or biological conversion processes.

Mainly organic material but also inorganic compounds like nitrogen, sulphides and heavy metals are removed by activated carbon. According to Tchobanoglous (2003), adsorption takes place in four steps: bulk solution transport, film diffusion transport, pore transport and adsorption. Adsorption can occur on the outside of the activated carbon but also within the macro-, meso-, or micropores. The amount of organic material which can adsorb is a function of the characteristics and the concentration of the adsorbate in combination with the temperature (Tchobanoglous, 2003). Many different adsorption isotherms have been developed; most commonly used are the Freundlich and the Langmuir Isotherms.

Activated carbon is not frequently used as a filter medium for biological denitrification like anthracite and sand are (Sison et al., 2996). The activated carbon is surrounded by a biofilm containing bacteria in the macropores and exoenzymes in the micropores (Scholz and

Martin, 1997). This form of filtration is called biological activated carbon filtration. Biological activated carbon is more effective and has an extended lifetime compared to granular activated carbon (Ibid.). This extended lifetime is probably the result of the uptake of previous adsorbed organic material by the biomass. This results in the reopening of adsorption sites (Sison et al., 1996). Even during high shear stress which occurs during a backwash of the filter bed, no significant reduction of the biomass is observed (Scholz and Martin, 1997). When peak loadings of toxic substances are in the feed water, activated carbon protects and dampens the effects (Ibid.).

Sison et al. (1996) conducted research to investigate whether granular activated carbon can function as a temporary storage for the supplied external carbon source which is required during denitrification. The denitrifying bacteria consume the carbon source, which results in desorption of the granular activated carbon. This principle was tested by intermittent dosings of a carbon source. Results showed that the removal rates for total nitrogen were higher during the period of carbon source dosing compared to the starvation period when no carbon source was dosed and the biomass had to utilize organic carbon from the granular activated carbon. During the starvation period, the total nitrogen removal declined over time which implies that the available adsorbed carbon source lessened. Nevertheless, the overall total nitrogen removal during the experiments varied between 80% and 95%. A comparison of granular activated carbon with anthracite as the filter medium shows a clear difference during the starvation period. During this period the total nitrogen removal efficiency dropped to 29% for anthracite compared to 90% during filtration with granular activated carbon. The mechanism of desorption of the carbon source from the activated carbon by the denitrifying biomass also becomes effective when NO_x-N concentrations in the feed water fluctuate and, as a result of this, an insufficient carbon source is supplied. This may lead to higher overall total nitrogen removal rates and steadier filtrate concentrations compared to filtration with anthracite.

2.7 Experiences from other research

Filtration techniques for the filtration of wastewater have been in use for many years. This probably is the reason for thinking that chemical phosphorus removal to low concentrations by filtration techniques has already been researched enough. But when searching the literature, just a few studies can be found which are comparable with this current research, especially for dual media filtration. This is, therefore, proof that everything is not already known about this topic. Examples of the found research are described in this section.

The first full scale multi media filtration plant was built at the Hochdorf WWTP in Switzerland in 1979. Results of the experimental research on phosphorus removal are described in Boller (1984b). Ferric(III)chloride and aluminiumchoride in combination with polymers were tested. The results showed that total phosphorus concentration in the filtrate water of 0.05 – 0.2 mg/L could be reached for a filtration rate of 10 m/h and filter runtimes of 15 to 30 hours. Flocculant aids were necessary to prevent solids breakthrough especially for filtration rates above 7 m/h.

Hultman et al. (1994) initiated research to investigate simultaneous nitrogen, phosphorus and suspended solids removal with a DynaSand filter, which is a continuous sand filter. The cross-sectional area of the filter used was 4.7 m^2. The bed heights used were, for most of the time, 3.5 m and 4.6 m. The grain size of the sand was 1.2 – 2.0 mm. The filter treated the WWTP effluent of the Loudden WWTP located in Sweden. Filtration rates varied between 10 m/h and 22 m/h. At the feed of the filter, methanol was added as a carbon source and ferric chloride as a coagulant. A control loop for the methanol addition was installed and the metal/orthophosphorus ratio varied between 1.2 mol/mol and 3.3 mol/mol. The results show that nitrate concentrations decreased from 7.3 – 20 mg/L to 0.5 – 2.2 mg/L and the total phosphorus concentration decreased from 0.6 – 5 mg/L to 0.1 – 0.5 mg/L. Therefore, it is concluded that ultra low phosphorus concentrations are not reached during their research.

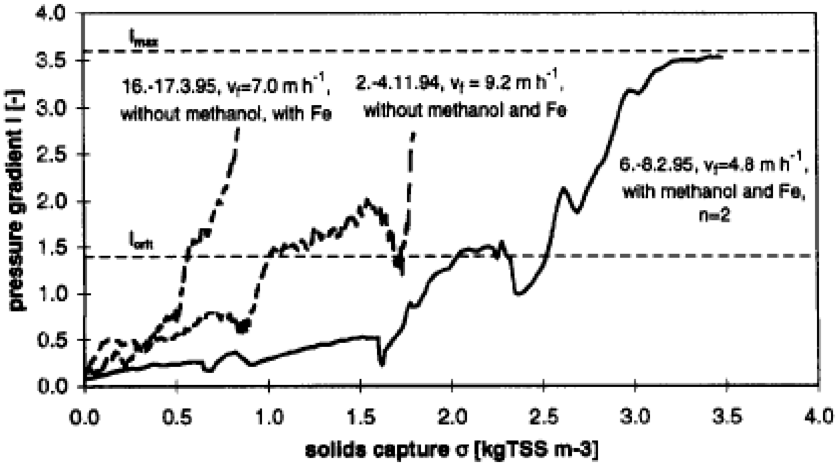


Figure 2-18 - Pressure gradient as a function of solids captured under different operating conditions adopted from Koch et al. (1997)

At the Zurich-Werdhölzli WWTP in Switzerland, tertiary filtration with single layer downflow depth filtration was used for simultaneous nutrients removal (Koch et al., 1997). The aim of the research was to investigate the feasibility and performance of denitrification in a sand filter in a cold climate. Experiments were conducted on a rectangular filter with a surface area of approximately 84 m^2. Filtration rates of 5 – 10 m/h were used. The filter bed height was 0.3 m made of quartz sand with a grain size of 1.0 mm. Methanol was used as a carbon source and was added to the feed water of the filter. Ferric chloride was added to the water for phosphorus removal. The paper is mainly about the denitrification parameters but also shows some results on the solids captured during filtration for ferric chloride dosage, for methanol dosage, and for the situation where both chemicals are dosed. These results are shown in Figure 2-18. The lowest solids capture was found for ferric chloride (Fe) dosage, without methanol. This improves for the situation where methanol is added and no ferric chloride. However, the highest solid capture was found for the combination of methanol dosage and ferric chloride dosage.

In the Washington DC area, USA, effluent phosphorus requirements are extremely stringent to protect the Chesapeake Bay (Takács et al., 2006). The total phosphorus discharge limits are usually below 0.2 mg/L. The Blue Plains advanced WWTP discharges in this area. This treatment plant is one of the largest nutrient removal plants of North America and consist of primary settling, a step-feed Biological Nutrient Removal (BNR) system followed by clarifiers and gravity filters for chemical phosphorus removal with iron. Takács et al. (2006) conclude that ultra low orthophosphorus concentrations can be achieved with the addition of iron salts using a combination of simultaneous and tertiary precipitation.

At the Konoike WWTP in Osaka, Japan, Hidaka et al. (2003) conducted pilot research to remove phosphorus and nitrogen from raw sewage by a pre-coagulation and bio-filtration process. The bio-filtration consisted of a denitrification filter, a nitrification filter with side stream to the denitrification filter, and a polishing filter with anoxic and aerobic part. Ferric(III)chloride was dosed for the chemical phosphorus removal. Hidaka et al. (2003) concludes that orthophosphorus was completely removed in the pre-coagulation step and the residual phosphorus was removed by immobilisation into biomass in the following biological treatment. Total phosphorus concentrations in the effluent of the pilot installation were steady around 0.2 mg/L. The removal efficiency was 90 – 95%.

Husband and Becker (2007) conducted demonstration testing of denitrification effluent filters to achieve limit of technology for total nitrogen and phosphorus. The experiments took place at the Arlington County Wastewater Pollution Control Plant, which is located in the southern part of Arlington County, USA. The facility consists of influent screening, vortex grit removal, primary treatment, off-line equalization tank, step-feed activated sludge with final settling tanks, lime reaction tanks/tertiary clarifiers (LRTs) originally installed as a two stage chemical precipitation process for phosphorus removal, gravity sand filters, carbon filters, chlorine disinfection and post aeration. For the chemical phosphorus removal ferric(III)chloride is added in the primary and tertiary clarifiers. Effluent polishing filters used for the demonstration testing reduced TSS, nitrate and the total phosphorus concentration. The discharge limit for total phosphorus is 0.18 mg/L. A down flow depth filter and a continuous sand filter were compared. Based on the results conclude Husband and Becker (2007) that the maximum average total phosphorus concentration in the feed water of a deep bed denitrification filter may be 0.6 mg/L to be able to fulfil the discharge limit of 0.18 mg P-total/L in the effluent.

Ditterich et al. (1996) conducted research of effluent treatment with microfiltration. The goal of this research was to meet the European microbiological standards of the European Union for bathing water and to reduce the total phosphorus concentration to levels below 0.05 mg/L tp avoid eutrophocation. Microfiltration with a pore size of 0.2 μm were used in combination with ferric(III)choride dosage. Three microfiltration membranes were tested, DOW, Starcosa and Memcor. DOW and Sarcosa were cross-flow, DOW was a flat sheet and membrane, Starcosa was a hollow-fibre membrane. Memcor was a dead-end module with a hollow-fibre membrane. Without ferric(III)chloride dosage a considerable reduction of the total phosphorus concentration was achieved. The effluent of the Memcor and DOW membranes contained 0.06 mg P-total/L and for the Starcosa membrane 0.09 mg P-total/L. With a ferric(III)chloride dosage of 0.014 mol/m^3 prior to microfiltration all three installations fulfilled the target value of 0.05 mg P-total/L.

2.8 Summary

Total phosphorus can be found in different forms in surface water and WWTP effluent. These forms can be divided into dissolved, colloidal and particulate phosphorus. These different phosphorus forms contain a large number of organic and inorganic phosphorus components. WWTP effluent consists, for a large part, of orthophosphorus which can be removed by precipitation, coagulation, flocculation and filtration when a metal salt is dosed as the coagulant. During precipitation, colloidal material forms. Coagulation is the process of destabilization of colloidal particles in a way that these particles can grow as a result of particle collision. Precipitation and coagulation require a good initial mixing to maximize the binding of the metal salt with the available phosphorus and to minimise the side reactions. The optimal initial mixing energy is between 500 – 1500 s^{-1}. Flocculation is the process which follows after initial mixing and has the purpose of forming flocs and aggregates from the fine particles and the destabilised particles. The degree of flocculation is dependent on the combination of the velocity gradient and the retention time. Typical velocity gradients are between 25 – 200 s^{-1} in combination with a retention time of 2 – 10 minutes. Temperature has a major influence on floc formation. Different techniques can be used for the filtration step, for example downflow depth filtration with a single or dual media filter bed, or continuous sand filtration. In a filter bed, the shear rate may be sufficient to promote flocculation in the filter pores but, due to the accumulation of deposits, the shear rate will increase if a constant filtration rate is applied. When the shear force in the filter bed becomes too high, particles or flocs may detach and a breakthrough of the filter bed occurs.

Denitrification is the biological reduction of nitrate to nitrogen gas. Denitrification takes place when nitrate is used as an electron acceptor instead of oxygen. Denitrification requires the presence of nitrate (or nitrite), the presence of substrate (methanol is frequently used) and the absence of oxygen. Nitrite is consumed at a rate twice the nitrate reduction rate; therefore the rate-limiting step for denitrification is the reduction from nitrate to nitrite. Nitrite accumulation during denitrification can, however, be caused by many factors. When combining nitrogen and chemical phosphorus removal in a single sand filter, phosphorus limitation may occur. Low orthophosphorus concentrations may affect the denitrification conversion rate by inhibiting the rapid growth of heterotrophic microorganisms in response to increasing nitrate loads.

From the experiences of other research can be concluded that ultra low phosphorus concentrations can be reached but require a lot of effort. When the discharge limits are below 0.15 mg P-total/L is membrane filtration a good option.

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3 Pilot-plants

Pilot-plant investigations are conducted at the Horstermeer WWTP and the Leiden Zuidwest WWTP. The pilot-plant at the Horstermeer WWTP consists of a dual media filter and a “One Step Total Effluent Polishing filter” i.e. 1-STEP®, operated for denitrification and simultaneous phosphorus removal. The pilot installation at the Leiden Zuidwest WWTP consists of small full-scale installations. Continuous sand filtration and dual media filtration are combined to investigate separate denitrification and phosphorus removal and are compared for simulations of denitrification and phosphorus removal.

This chapter contains a description of the pilot-plant at the Horstermeer WWTP in Nederhorst den Berg (Section 3.1) and of the demonstration installation at the Leiden Zuidwest WWTP in Leiden (Section 3.2). Schemes of the installations are given and the dosage of chemicals, the initial mixing, the backwashes, and (hand) analyses are described in subsections. Section 3.3 describes the protocol for the jar tests which are used to investigate the type of coagulant and the dosage ratio which should be used for the experiments. Section 3.4 describes the method for pressure readings and the construction of Lindquist diagrams. A summary of this chapter is given in Section 3.5.

It has to be clear that this research was part of the extensive investigation programs at the two locations. The results of these investigation programs are only partly used for this research. The results of the research programs can be found in STOWA (2009a) and STOWA (2009b).

3.1 The Horstermeer WWTP

3.1.1 Operation of the Horstermeer WWTP

The Horstermeer WWTP is a treatment plant of Waternet, a Dutch water company which is responsible for drinking water, waste water, surface water and safety behind the dykes in the Amsterdam region. The Horstermeer WWTP treats the wastewater of 140,000 population equivalents (per p.e. 136 g Total Oxygen Demand, TOD) living in the areas of Naarden-Bussum, Hilversum-West and Nederhorst den Berg. The main flow of the WWTP is 26,000 m^3/day. The treatment plant consists of grit removal, primary sedimentation, aeration and final sedimentation. In Figure 3-1 a schematisation of the Horstermeer WWTP is given.

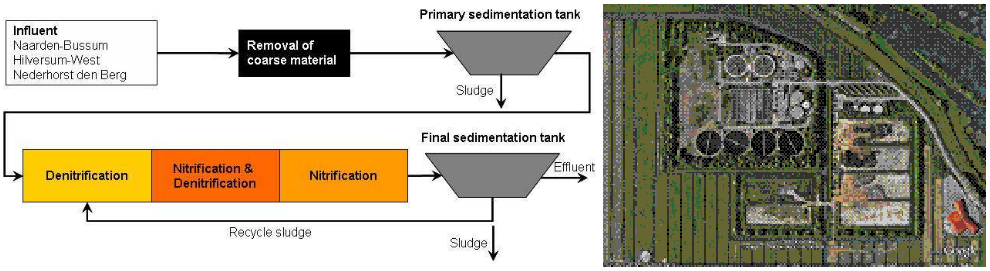

Figure 3-1 – Scheme (left side) and photograph (right side) of the Horstermeer WWTP

The plant was originally designed for nitrification only, but after implementation of on-line analysers and the introduction of a denitrification zone, a considerable improvement of effluent quality was achieved. N-total decreased from 30 mg/L to <15 mg/L. Poly aluminium chloride (PACl) is added in the aeration tanks just before the final sedimentation tanks, with a metal/total phosphorus ratio of 0.65 mol/mol. PACl is dosed to prevent filamentous sludge bulking in the final sedimentation tanks and to enhance the phosphorus removal. Ferric chloride sulphate is dosed at the primary sedimentation tank with a metal/total phosphorus ratio of 0.38 mol/mol and at the outlet of the aeration tanks with a metal/total phosphorus ratio of 0.25 mol/mol. Ferric chloride sulphate is dosed for phosphorus removal only. With these dosing conditions, the effluent concentrations fulfil the current discharge limit of 1.0 mg P-total/L.

Effluent quality and legislation for the Horstermeer WWTP

The Horstermeer WWTP effluent is discharged into the river Vecht, which is part of the Rhine River Basin District. The Horstermeer WWTP has to improve the effluent quality, due to the actual Vecht River reduction program, from a yearly average concentration for total nitrogen from 14 mg/L to less than 5 mg/L, and for total phosphorus from 1 mg/L to 0.5 mg/L, by the end of 2009. Probably in a later stage, the effluent quality needs to be improved further to MPR quality. In Table 3-1 the main effluent quality parameters of the Horstermeer WWTP effluent for the year 2008 are given.

Table 3-1 - Effluent quality of the Horstermeer WWTP compared with concentrations based on the Vecht River reduction program and the MPR concentrations in 2007, 2008 and 2009.

Parameter	Average 2007 [mg/L]	Average 2008 [mg/L]	Average 2009 [mg/L]	Discharge Permit [mg/L]	Vecht River reduction program [mg/L]	MPR Value [mg/L]
COD	35	32	37			
BOD	4	4	5			
N-total	14.1	13.5	13.6	14.0	5.0	2.2
Nkj	10	2.9	4.4			
NO_3-N	3.7	10.3	8.4			
P-total	1.0	0.8	0.9	1.0	0.5	0.15
P-ortho	0.57	0.4	0.4			
TSS	12	11	12.6			

3.1.2 Pilot installation at the Horstermeer WWTP

The research program at the Horstermeer WWTP is started to investigate how 2.2 mg N-total/L and 0.15 mg P-total/L in the filtrate can be reached. The pilot-plant consists of a dual media filter and a “One Step Total Effluent Polishing filter” (i.e. 1-STEP®) operated for denitrification and simultaneous phosphorus removal. The feed water of the filters, WWTP effluent, passes a 450 μm screen and is collected in the feed water buffer tank. In the filtrate buffer tank the orthophosphorus (PO_4-P) and the total inorganic oxidised nitrogen (NO_x-N) concentrations are measured. The orthophosphorus measurement is pre-filtered over a 0.45 μm filter. The doses of methanol and coagulant depend on the measured concentrations in the feed water buffer tank. After the feed water buffer tank, the water is divided between the two filtration installations.

Dual media filtration

The feed water is pumped from the buffer tank into the dual media filter (DMF). A scheme of the dual media filter is shown in Figure 3-2 and a photograph is shown in Figure 3-3. Turbidity is measured on-line. In the pipeline to the filter, a coagulant and a carbon source are dosed. The dual media filter has a filtration surface of 0.8 m^2 and a filter bed height of approximately 120 cm. During the experiments, a flow rate of 8 m^3/h is used, which results in a filtration rate of 10 m/h.

When the feed water enters the filter system it first enters the upper water layer (UWL) of approximately 120 cm. The retention time is approximately 7 minutes. In the UWL flocculation can take place. The UWL rises at the end of the filter runtime to a maximum of 145 cm as the filter bed resistance increases, and the level regulation valve is already completely open. A backwash with filtrate water from the filtrate buffer tank is initiated when 145 cm is reached. The filter bed of the dual media filter contains two filtration layers:

- top: anthracite, 80 cm height, 2.0 – 4.0 mm grain diameter, 1,400 kg/m^3 density;
- bottom: quartz sand, 40 cm height, 1.25 – 1.5 mm grain diameter, 2,600 kg/m^3 density.

The retention time in the filter bed is 8-9 minutes. After filtration, the filtrate is collected in a filtrate buffer tank, where unfiltered orthophosphorus (PO_4-P), total phosphorus (P-total) and total inorganic oxidised nitrogen (NO_x-N) in the filtrate water are measured continuously by on-line analysers. Turbidity is measured in a side stream from the filtrate pipeline.

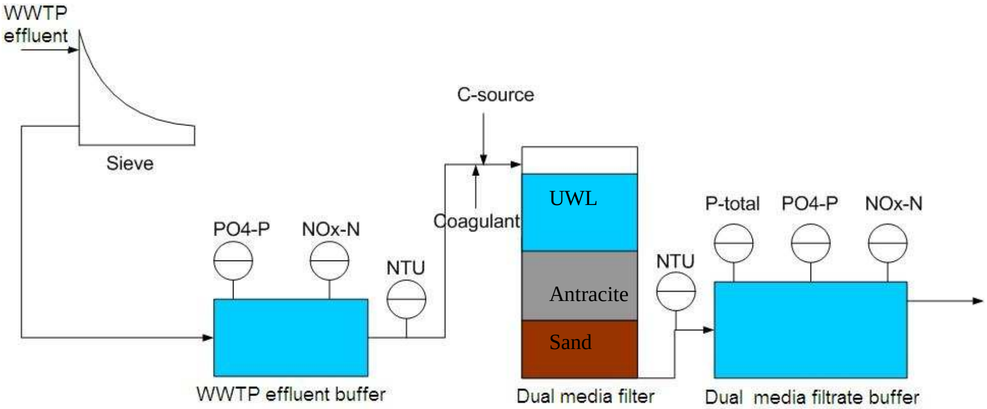

Figure 3-2 - Scheme of the dual media filter at the Horstermeer WWTP

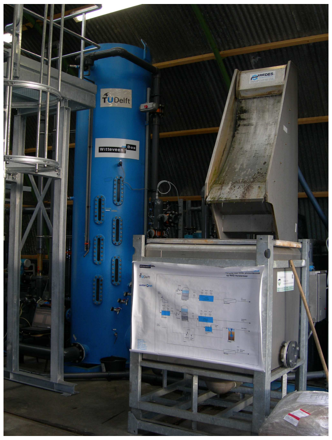

Figure 3-3 - Photograph of the dual media filter at the Horstermeer WWTP

1-STEP® filtration

The feed water of the 1-STEP® filter is pumped from the feed water buffer tank. A scheme of the 1-STEP® filter is shown in Figure 3-4 and a photograph is shown in Figure 3-5. Turbidity is measured in-line. In the pipeline to the filter, a coagulant and a carbon source are dosed. Initial mixing of the chemicals with the feed water takes place with a gate valve. The 1-STEP® filter has a filtration surface of 1 m^2 and a filter bed height varying between experiments of 100-190 cm. During the experiments a flow rate of 10 m^3/h was used, which resulted in a filtration rate of 10 m/h.

When the feed water is introduced in the filter system, it first enters the upper water layer (UWL) of 120 cm (100 cm filter bed height) to 210 cm (190 cm filter bed height). The retention time varies from approximately 7 minutes to a maximum of 11 minutes. In the UWL flocculation can take place. The UWL increases at the end of the filter runtime to a maximum 160 cm as the filter bed resistance increases. A backwash with filtrate water from the filtrate buffer tank is initiated when 160 cm is reached. The retention time in the filter bed, when 190 cm height, is 5 minutes.

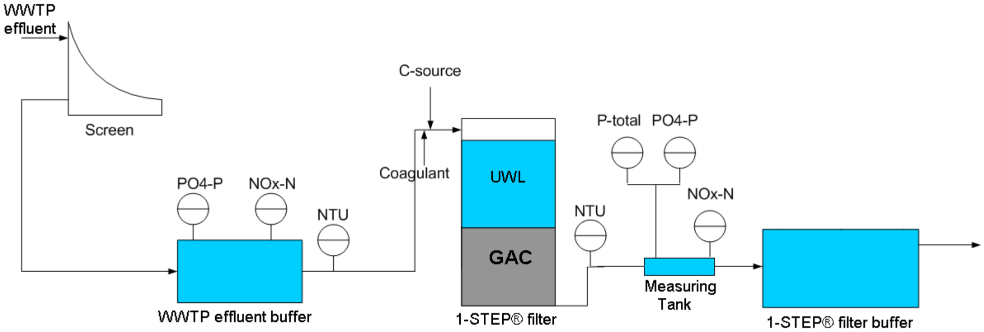

Figure 3-4 - Scheme of the 1-STEP® filter at the Horstermeer WWTP

For 1-STEP® filtration, granular activated carbon (GAC) is used. Important aspects which should be taken into account when choosing a granular activated carbon for WWTP effluent filtration (STOWA, 2009) are the grain size, the mechanical strength, the pore structure, purity and the reactivation possibilities. In cooperation with Norit (supplier of activated carbon), a specific type of granular activated carbon was chosen. The 1-STEP® filter contains 190 cm granular activated carbon with a grain size of 1.70-3.35 mm, 610 kg/m^3 density.

Figure 3-5 - Photograph of the 1-STEP® filter at the Horstermeer WWTP

After filtration, turbidity was measured on-line. Unfiltered orthophosphorus (PO_4-P), total phosphorus (P-total) and inorganic oxidised nitrogen (NO_x-N) are continuously measured by on-line analysers in a separate measuring tank. The filtrate water is collected in a filtrate buffer tank.

3.1.3 Initial mixing

At the Horstermeer WWTP three different methods for initial mixing/coagulant dosage are tested, namely dosage before a gate valve, dosage with an injection ring 0.5 m after a 90° bend, and dosage with an injection ring 1.0 m after the 90° bend. The inner diameter of the pipe where coagulant is dosed is 80 mm, which corresponds with a flow area of 5,026 mm^2.

Gate Valve

The coagulant was dosed on-line just after a 90° bend (see Figure 3-7) and 0.10 m before a gate valve which made it possible to vary the initial mixing energy. The minimum initial mixing was reached when the gate valve was completely open. A fully open gate valve and a flow rate of 8 m^3/h gave an initial mixing energy of ±120 s^{-1}. Closing the valve for 70% with a flow rate of 8 m^3/h gave an initial mixing energy of ±1,300 s^{-1}, see Figure 3-6.

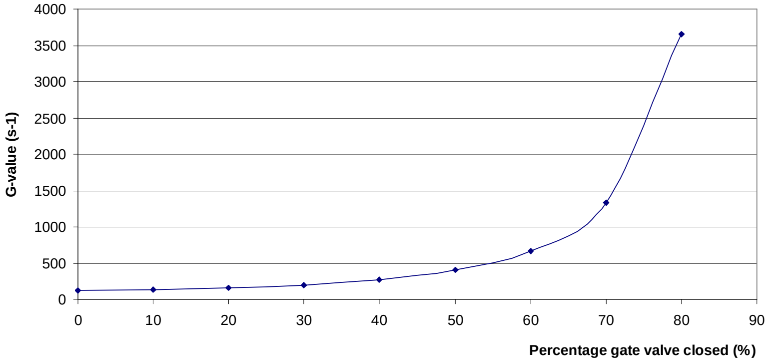

Figure 3-6 - Influence of the gate valve on the G-value for the dual media filter at the Horstermeer WWTP with a flow rate of 8 m^3/h

Figure 3-7 – Photograph of the initial mixing with a gate valve at the Horstermeer WWTP

Injection ring

Using the injection ring (see Figure 3-8), coagulant can be dosed simultaneously at three points, at the most. By replacing an injection point for a cap, two injection points or even one injection point can be used. The injection point can be placed in the centre of the pipe or along the side wall. When the injection ring is used, the gate valve is fully open. The injection ring was initially placed 0.5 m after the 90° bend. In a later stage of the research, the injection ring was 1.0 m after the bend.

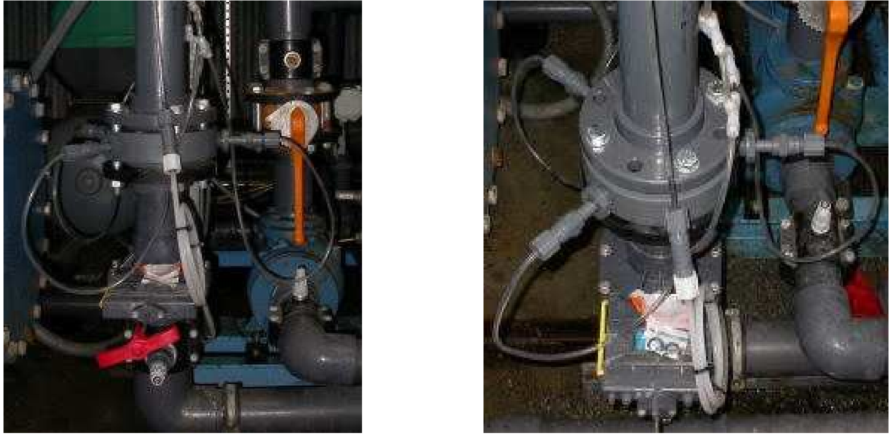

Figure 3-8 – Photograph of the initial mixing with an injection ring at the Horstermeer WWTP

3.1.4 Dosage ratios

For simultaneous removal of phosphorus and suspended solids, PACl is dosed into the filter feed water. PACl was chosen because in preliminary jar tests it showed higher removal efficiency regarding phosphorus removal in comparison to ferric(III)chloride (Miska-Markusch, 2009). This was probably due to the low pH of the WWTP effluent, which is pH 6.8 on average. The research started with Aqualenc (PACl), but from January 2008 the research continued with PAX-11 because Aqualenc was no longer available. The ratios used, of Al^{3+}/orthophosphorus for Dual Media filtration, were 3-5 mol/mol depending on the orthophosphorus concentration in the feed water. The Al^{3+}/orthophosphorus ratios used for the 1-STEP® filter were 5 mol/mol for orthophosphorus concentrations in the WWTP effluent of <0.25 mg/L and 4 mol/mol for orthophosphorus concentrations > 0.25 mg/L.

For denitrification, methanol dosage was based on the actual nitrate and free oxygen-concentrations in the feed water. After the screen, the free oxygen concentration was approximately 4 mg/L. COD/NO_3-N ratios of 4.0-6.0 g/g were applied.

3.1.5 Backwash

Both filters are back-flushed with air and filtrate water collected in the filtrate buffer tank. A backwash is started when the upper water layer exceeds a maximum level or when the maximum filtration runtime has passed. The maximum filtration runtime for both filters is

12 hours. As described in subsection 2.4.2 (filter runtime and filter loading) bump cleaning is needed to release nitrogen gas formed during denitrification. A bump cleaning is conducted automatically every 3 hours. Table 3-2 and 3-3 show the parameters of the backwash and the bump cleaning for the dual media filter and the 1-STEP® filter. Every backwash starts with a 1-minute pause to lower the upper water layer to prevent filter media to be washed out.

Table 3-2 – Parameters for backwash and bump cleaning for the dual media filter

Backwash				**Bump cleaning**			
Phase	Time [minutes]	Flow rate [m/h]	Water/Air	Phase	Time [minutes]	Flow rate [m/h]	Water/Air
1	2	-	-	1	6	25	water
2	4		air	2			
3	2	37.5	water	3			
4	2	62.5	water	4			
5	7	50	water	5			
Total	17			**Total**	6		

Table 3-3 – Parameters for backwash and bump cleaning for the 1-STEP® filter

Backwash				**Bump cleaning**			
Phase	Time [minutes]	Flow rate [m/h]	Water/Air	Phase	Time [minutes]	Flow rate [m/h]	Water/Air
1	1	-	-	1	8	15	water
2	6		air	2			
3	2	40	water	3			
4	5	60	water	4			
5	5	40	water	5			
Total	19			**Total**	8		

3.1.6 Hand analysis

Grab samples were used to evaluate the removal mechanisms of denitrification and phosphorus removal. All grab samples were tested with Hach Lange cuvette tests. The cuvette tests used were the following:

- COD	LCK314	range	15	–	150 mg/L O_2
- NO_2-N	LCK341	range	0.015	–	0.6 mg/L NO_2-N
- NO_2-N	LCK342	range	0.6	–	6.0 mg/L NO_2-N
- NO_3-N	LCK339	range	0.23	–	13.5 mg/L NO_3-N
- NH_4-N	LCK304	range	0.015	–	2.0 mg/L NH_4-N
- N-total	LCK138	range	1.0	–	16.0 mg/L N-total
- PO_4-P	LCK349	range	0.05	–	1.5 mg/L PO_4-P
- P-total	LCK349	range	0.15	–	4.5 mg/L P-total

For Al^{3+} measurements MERCK tests were used, product number 1.14825.0001 with a measuring range of 0.02 – 1.20 mg Al^{3+}/L.

Frequently, the turbidity [NTU], the oxygen concentration [mg/L], the pH and the temperature [°C] were measured by hand analysers.

3.1.7 On-line analysers

For the Horstermeer WWTP on-line analysers were used to control the methanol and coagulant dosage.

Total phosphorus, orthophosphorus, NO_x-N, turbidity, temperature are measured on-line (see Table 3-4). It should be taken into account that an orthophosphorus measurement without a pre-filtration step of 0.45 µm, measures metal-bound phosphorus together with orthophosphorus. Only the orthophosphorus measurement in the WWTP effluent is pre-filtered. The concentrations given by the on-line analysers are checked by analysing grab samples twice a week.

Table 3-4 – On-line analysers at the pilot installation of the Horstermeer WWTP

	WWTP Effluent	**Filtrate DMF**	**Filtrate 1-STEP®**
P-total		x	x
P-ortho	x1)	x	x
NO_x-N	x	x	x
Oxygen			
Turbidity	x	x	x
Temperature	x		
pH			

1) Pre-filtered through 0.45 µm

3.2 The Leiden Zuidwest WWTP

3.2.1 Operation of the Leiden Zuidwest WWTP

The Leiden Zuidwest WWTP is a treatment plant of Hoogheemraadschap van Rijnland and treats the water of 126,000 population equivalents (per p.e. 136 g TOD) from the areas of Leiden Zuidwest, Voorschoten, Hazerswoude-Groenendijk and Zoeterwoude-Rijndijk. The average daily flow is 24,000 m^3. At the WWTP, removal of coarse solids takes place first, followed by activated sludge with nitrification and denitrification combined with chemical phosphorus removal, and finally sedimentation. In Figure 3-9 a photograph of the Leiden Zuidwest WWTP is given.

Figure 3-9 – Photograph of the Leiden Zuidwest WWTP

Effluent composition at the Leiden Zuidwest WWTP

In Table 3-5 the yearly average effluent composition of the Leiden Zuidwest WWTP of 2007 is compared with the MPR values and the restrictions of the Rijnland District Water Control Board. The parameters are nitrate (NO_3-N), Kjeldahl nitrogen (N_{Kj}), total nitrogen (N-total), total suspended solids (TSS), total-phosphorus (P-total), chemical oxygen demand (COD) and biochemical oxygen demand (BOD).

Table 3-5 - Effluent composition of the Leiden Zuidwest WWTP compared with the restrictions set by the Rijnland District Water Control Board and the MPR values in 2007 and 2008

Parameter	Unit	Average concentration in effluent 2007	Average concentration in effluent 2008	Restrictions Rijnland	MPR value
Flow	m^3/d	29,300	28,098		
NO_3-N	mg/L	1.4	1.45		
NH_4	mg/L	0.9			
N_{Kj}	mg/L	2.2	2.6		
N-total	mg/L	3.6	4.0	10	2.2
TSS	mg/L	6.0	20	12	
P-total	mg/L	0.73		0.6 $^{1)}$	0.15
COD	mg/L	24	36	125	
BOD	mg/L	2	6	8	

1) Moving average over the last 10 measurements

3.2.2 Pilot installation at the Leiden Zuidwest WWTP

The goal of the research program at the Leiden Zuidwest WWTP is to gain knowledge, operational experience and to determine the design criteria for sand filtration. The pilot installation at the Leiden Zuidwest WWTP consists of small full-scale installations. Before the WWTP effluent enters the WWTP effluent buffer tank, it passes a submerged 3 mm screen which is cleaned daily. From this WWTP effluent buffer tank, the water is divided into two filtration streets. Street A consists of two flocculation tanks and a continuous sand filter (CFA) for simultaneous denitrification and phosphorus removal. Street B consists of a continuous sand filter (CFB), two flocculation tanks and a dual media filter. Street B is designed for separate denitrification and phosphorus removal. CFB can be bypassed for experiments with simultaneous denitrification and phosphorus removal with DMF.

A side stream of the feed water entering the pilot installations flows through a continuously circulating measuring buffer tank. In this buffer tank the total inorganic oxidised nitrogen (NO_x-N), orthophosphorus, total phosphorus, oxygen, turbidity, and pH are measured with on-line analysers. The on-line analysers for total phosphorus and orthophosphorus measure every 6 minutes, alternating between the PO_4-P concentration and the P-total concentration. The sample is not filtered through 0.45 µm, which means that the measured concentrations for orthophosphorus are the sum of PO_4-P and metal-bound phosphorus. These on-line analysers are applied to control the carbon source and coagulant dosage.

Street A - Continuous sand filter

The continuous sand filter in Street A was designed for simultaneous denitrification and phosphorus removal. A scheme of the continuous sand filter is shown in Figure 3-10 and a photo is shown in Figure 3-10. In the feed water of the filter, a carbon source and coagulant were dosed. The dosage of a carbon source depended on the measured NO_x-N and oxygen concentration in the feed water; the coagulant dosage depended on the orthophosphorus concentration. Initial mixing took place by a gate valve. For flocculation, flocculation tanks can be used. The total residence time in the flocculation tanks can be varied between 0 minutes and 25 minutes. The mixing energy can be varied between 40 s^{-1} and 200 s^{-1}.

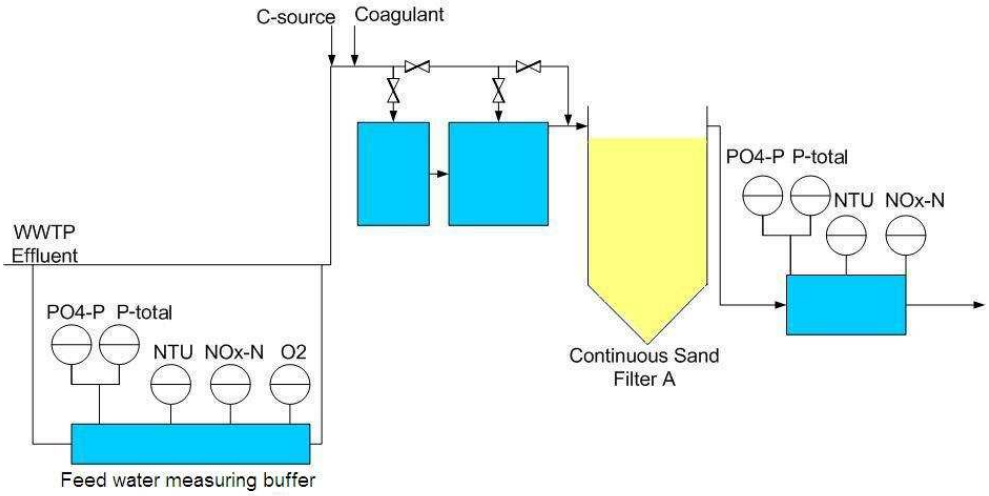

Figure 3-10 – Continuous sand filtration for simulations of denitrification and phosphorus removal at the Leiden Zuidwest WWTP

Figure 3-11 – Photograph of the continuous sand filter A at the Leiden Zuidwest WWTP

After the flocculation tanks, the water entered the continuous sand filter with a filtration surface of 3 m^2. During the experiments, the flow rate was varied up to a maximum of 60 m^3/h which resulted in a maximum filtration rate of 20 m/h. The filter bed height was 2 meters and consisted of quartz sand with a grain size of 1.2 mm – 2.0 mm (density 2,600 kg/m^3).

After filtration, on-line analysers for total phosphorus (P-total), orthophosphorus (PO_4-P), turbidity, total inorganic oxidized nitrogen (NO_x-N) and oxygen were placed in the filtrate water measuring buffer tank. The on-line analysers for total phosphorus and orthophosphorus, measured every six minutes, alternating between the PO_4-P concentration and the P-total concentration. The sample was not filtered through 0.45 µm, which means that the measured concentrations for orthophosphorus were the sum of PO_4-P and the metal-bound phosphorus.

Street B – Continuous sand filtration followed by dual media filtration
The continuous sand filter in Street B was designed for denitrification only. In the feed water of the filter, a carbon source was dosed, followed by a gate valve for initial mixing. The dosage of the carbon source depended on the measured NO_x-N and oxygen concentration in the feed water. After dosage the water entered the continuous sand filter with a filtration surface of 3 m^2. During the experiments, the flow rate was varied up to a maximum of 60 m^3/h, which resulted in a maximum filtration rate of 20 m/h. The filter bed height was 2 meters and consisted of quartz sand with a grain size of 1.2 mm – 2.0 mm (density 2,600 kg/m^3). After filtration, turbidity was measured.

The filtrate of the continuous sand filter B was used as feed water for the dual media filter (see Figure 3-12). Coagulant was dosed for chemical phosphorus removal. The dosage of the coagulant depended on the orthophosphorus concentration measured in the feed water measuring buffer tank. Initial mixing took place with a gate valve. For flocculation, flocculation tanks can be used. The total residence time in the flocculation tanks can be varied between 0 minutes and 25 minutes. The mixing energy can be varied between 40 s^{-1} and 200 s^{-1}.

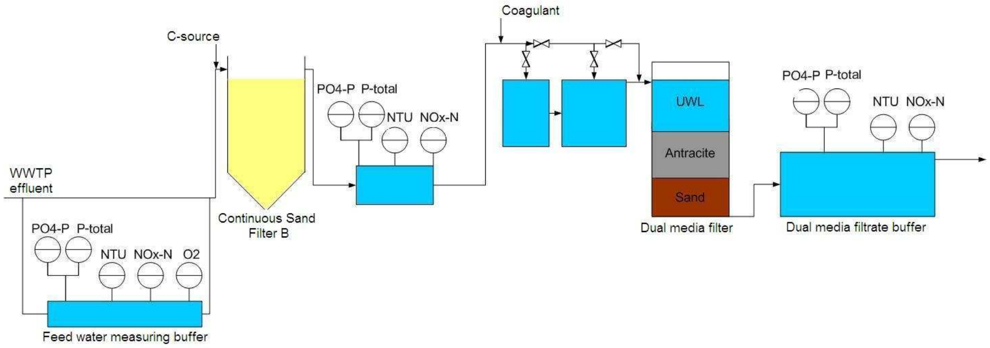

Figure 3-12 – Continuous sand filtration for denitrification and dual media filtration for phosphorus removal at the Leiden Zuidwest WWTP

After the flocculation tanks, the water entered the dual media filter with a filtration surface of 3 m^2. The flow rates were varied between 30 m^3/h, 45 m^3/h and 60 m^3/h, which resulted in filtration rates of 10 m/h, 15 m/h and 20 m/h. When the feed water entered the dual media filter, it first entered the upper water layer (UWL) of approximately 180 cm. The retention time was approximately 11 minutes for a flow rate of 30 m^3/h. In the UWL, flocculation can take place. The UWL increased at the end of the filter runtime to maximum of 220 cm when the filter bed resistance increased and the level regulation valve was already completely open. A backwash with filtrate water from the filtrate buffer tank was initiated when 220 cm was reached.

For dual media filtration two different filter beds were tested: a coarse filter bed and a fine filter bed.
The coarse filter bed of the dual media filter contains two filtration layers:

- the top layer is anthracite, 800 mm height, 2.0 mm – 4.0 mm grain diameter and a density of 1,400 kg/m^3;
- the bottom layer is quartz sand, 400 mm height, 1.50 mm – 2.25 mm grain diameter and a density of 2,600 kg/m^3.

The fine filter bed of the dual media filter contains two filtration layers:

- the top layer is anthracite, 600 mm height, 1.4 mm – 2.0 mm grain diameter and a density of 1,400 kg/m^3;
- the bottom layer is quartz sand, 900 mm height, 0.71 mm – 1.25 mm grain diameter and a density of 2,600 kg/m^3.

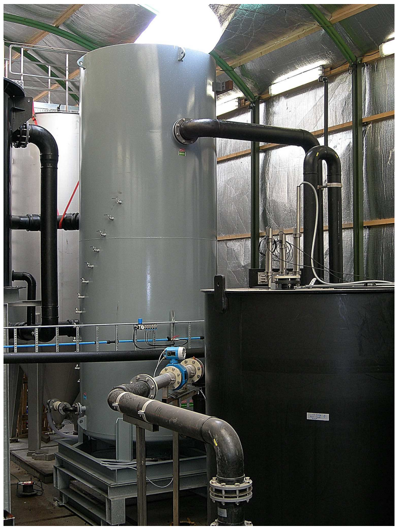

Figure 3-13 – Photograph of the dual media filter at the Leiden Zuidwest WWTP

After filtration on-line analysers for total phosphorus (P-total), orthophosphorus (PO_4-P), turbidity, total inorganic oxidised nitrogen (NO_x-N) were placed in the filtrate water buffer tank. The on-line analysers for total phosphorus and orthophosphorus, measured every six minutes, alternating between the PO_4-P concentration and the P-total concentration. The sample was not filtered through 0.45 µm, which means that the measured concentrations for orthophosphorus were the sum of PO_4-P and the metal-bound phosphorus.

Street B –Dual media filtration
In this situation continuous sand filter B is bypassed (see Figure 3-14). Dual media filtration was used for simultaneous denitrification and phosphorus removal. In the feed water of the filter, a carbon source and coagulant were dosed. The dosage of a carbon source depended on the measured NO_x-N and oxygen concentration in the feed water; the

coagulant dosage depended on the orthophosphorus concentration. Initial mixing took place with a gate valve. For flocculation, flocculation tanks can be used. The total residence time in the flocculation tanks can be varied between 0 minutes and 25 minutes. The mixing energy can be varied between 40 s^{-1} and 200 s^{-1}.

After the flocculation tanks the water entered the dual media filter with a filtration surface of 3 m^2. When the feed water entered the dual media filter it first entered the upper water layer (UWL) of approximately 180 cm. The retention time was approximately 11 minutes for a flow rate of 30 m^3/h. In the UWL flocculation can take place. The UWL increased at the end of the filter runtime to a maximum 220 cm as the filter bed resistance increased and the level regulation valve was already completely open. A backwash with filtrate water from the filtrate buffer tank was initiated when 220 cm was reached. The flow rates were varied between 30 m^3/h and 60 m^3/h, which resulted in filtration rates of 10 m/h to 20 m/h. The coarse filter bed of the dual media filter contains two filtration layers:

- the top layer is anthracite, 800 mm height, 2.0 mm – 4.0 mm grain diameter and a density of 1,400 kg/m^3;
- the bottom layer is quartz sand, 400 mm height, 1.50 mm – 2.30 mm grain diameter and a density of 2,600 kg/m^3.

The fine filter bed of the dual media filter contains two filtration layers:

- the top layer is anthracite, 600 mm height, 1.4 mm – 2.0 mm grain diameter and a density of 1,400 kg/m^3;
- the bottom layer is quartz sand, 900 mm height, 0.7 mm – 1.3 mm grain diameter and a density of 2,600 kg/m^3.

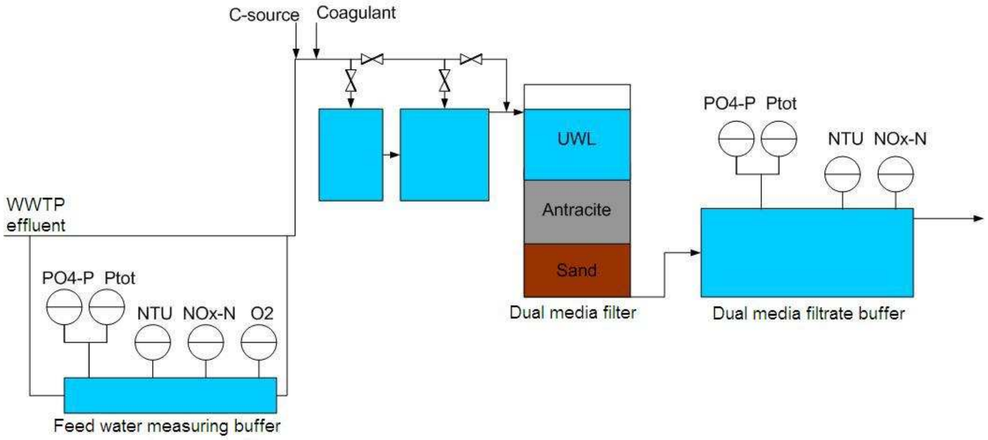

Figure 3-14 – Schematisation of the dual media filter at the Leiden Zuidwest WWTP used for simultaneous denitrification and phosphorus removal

After filtration on-line analysers for total phosphorus (P-total), orthophosphorus (PO_4-P), turbidity, total inorganic oxidized nitrogen (NO_x-N) were placed in the filtrate water buffer tank. The on-line analysers for total phosphorus and orthophosphorus, measured every six minutes, alternating between the PO_4-P concentration and the P-total concentration. The sample was not filtered through 0.45 µm, which means that the measured concentrations for orthophosphorus were the sum of PO_4-P and the metal-bound phosphorus.

3.2.3 Initial mixing

Coagulant was dosed in-line before a gate valve which made it possible to vary the initial mixing energy. The situation of coagulant dosage was not exactly the same for both streets. In Street A (Figure 3-10) the dosage of coagulant took place 0.67 m before the gate valve. There were several meters of straight pipe before the dosage point, and 1.57 m after the dosage point was a 90° bend. In Street B the coagulant (Figure 3-15) dosage took place 0.30 m before a 90° bend, and 0.1 m after the bend was a gate valve. Two 90° bends were situated just before the dosage point.

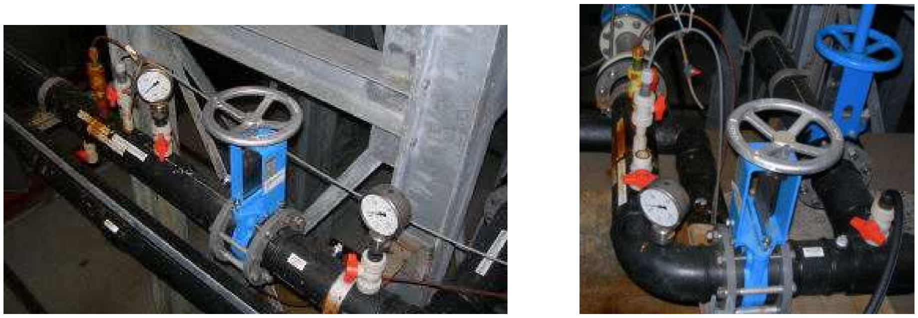

Figure 3-15 – Photograph of the initial mixing for Street A (left) and Street B (right)

The diameter of the valve was 100 mm which corresponds with a flow area of 7,854 mm^2. Figure 3-16 gives the influence of the gate valve on the G-value for 30 m^3/h and 50 m^3/h.

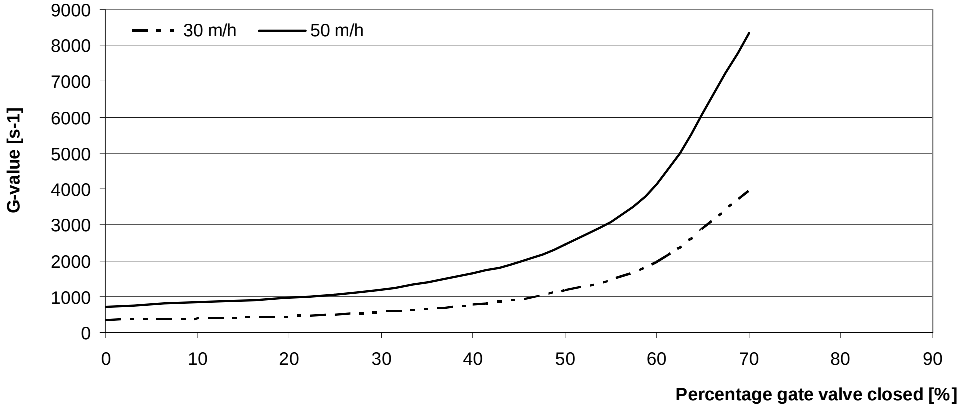

Figure 3-16 - Influence of the gate valve on the G-value with a flow rate of 30 m^3/h and 50 m^3/h for the Leiden Zuidwest WWTP

3.2.4 Flocculation tanks

Each filtration street ontained two flocculation tanks, which are used in series. The tanks contain baffles to prevent short-circuiting. The flow patterns of the tanks were tested and were ideal. The maximum flocculation time when both flocculation tanks are in series was 24 minutes, see also Table 3-6. The G-value in the flocculation tanks can vary between 40 s^{-1} – 200 s^{-1}.

Table 3-6 – Flocculation time (hydraulic) retention time for the flocculation tanks

	Volume [m^3]	Flocculation time [min]		
		10 m/h	15 m/h	20 m/h
Tank 1	4.1	8.2	5.5	4.1
Tank 2	7.9	15.8	10.5	7.9
Total	12	24	16	12

3.2.5 Dosage ratios

Preliminary jar tests gave the best results for ferric(III)chloride ($FeCl_3$). As for the coagulant dosage, Fe^{3+}/orthophosphorus ratios of 2-8 mol/mol were used.

Both continuous sand filters were denitrifying filters; methanol (MeOH) was used as an additional carbon source. The MeOH dosage varied between 3 kg - 5 kg MeOH/kg NO_x-N.

3.2.6 Backwash program dual media filter

During the experiments, the filtration runtime was up to 24 hours. The filter bed was backwashed when the upper water layer exceeded a maximum level, the maximum filter runtime had passed, or when the turbidity or the orthophosphorus concentration in the filtrate water became too high (breakthrough of the filter bed). The dual media filter was back-flushed with air and filtrate water which was collected in a filtrate buffer tank. Every backwash started with a 90-second pause to lower the upper water layer to prevent the filter media from being washed out. Every three hours a bump cleaning took place.

Table 3-7 – Parameters for the backwash and bump cleaning for the dual media filter

Backwash				**Bump cleaning**			
Phase	Time [s]	Flow rate [m/h]	Water/Air	Phase	Time [s]	Flow rate [m/h]	Water/Air
1	90	-		1	120	20	water
2	90	30	air	2			
3	200	50	water	3			
4	60	30	water	4			
5	120	30 → 0	water	5			
Total	560			**Total**	120		

3.2.7 Hand analysis

Grab samples were used to evaluate the removal mechanisms of denitrification and phosphorus removal. All grab samples were tested with Hach Lange cuvette tests. The cuvette tests were:

- Fe^{3+} LCK321 range 0.2 – 6.0 mg/L Fe^{3+}
- COD LCK314 range 15 – 150 mg/L O_2
- NO_2-N LCK341 range 0.015 – 0.6 mg/L NO_2-N
- NO_2-N LCK342 range 0.6 – 6.0 mg/L NO_2-N
- NO_3-N LCK339 range 0.23 – 13.5 mg/L NO_3-N
- NH_4-N LCK304 range 0.015 – 2.0 mg/L NH_4-N
- N-total LCK138 range 1.0 – 16.0 mg/L N-total
- PO_4-P LCK349 range 0.05 – 1.5 mg/L PO_4-P
- P-total LCK349 range 0.15 – 4.5 mg/L P-total

Frequently, the turbidity [NTU], the oxygen concentration [mg/L], the pH and the temperature [°C] were measured by hand analysers.

3.2.8 On-line analysers

The on-line analysers were used to control the methanol and coagulant dosage. Total phosphorus, orthophosphorus, NO_x-N, turbidity, temperature, pH and oxygen were measured on-line (see Table 3-8). It should be taken into account that an orthophosphorus measurement without a pre-filtration step of 0.45 µm, measures metal-bound phosphorus together with orthophosphorus. The concentrations given by the on-line analysers were checked by analysing grab samples twice a week.

Table 3-8 – On-line analysers at the pilot installation of the Leiden Zuidwest WWTP

	WWTP Effluent	Filtrate CFA	Filtrate DMF
P-total	x	X	x
P-ortho	x	X	x
NO_x-N	x	X	x
Oxygen	x		
Turbidity	x	X	x
Temperature	x		
pH	x		

3.3 Jar tests

Jar tests have proven to be a useful tool to investigate the type of coagulant and the dosage ratio which should be used for an advanced treatment step. Besides this, jar tests can also be used to investigate temperature influences on floc formation. The protocol for jar tests is described in this section.

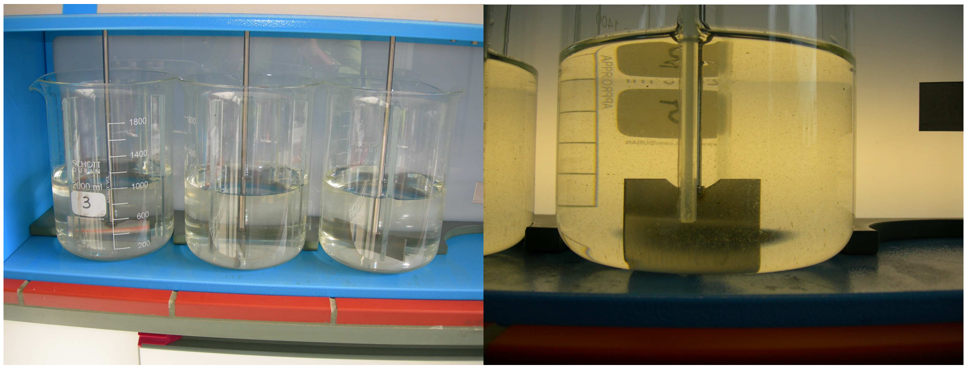

Figure 3-17 – Photographs of the jar tester

Before every jar test, the coagulant used was diluted with ultra pure water to avoid too small and inaccurate volumetric dosages. Due to the dilution, the pH of the coagulant increased. When the pH increases, ferric(III)chloride can form flocs and the performance of the coagulant will deteriorate (Hong-Xiao and Stumm, 1987). For PACl, the higher pH caused by dilution resulted in a decrease of $AlSO_4^+$ and dimers, but the amount of tridecamer in the pre-hydrolysed coagulant increased (Exall and vanLoon, 2003).

The jar apparatus contained six jars. The stirring velocity can be adjusted equally for all jars. The maximal number of revolutions is 300 rpm. Every jar was filled with 1 litre of WWTP effluent. All jars contain four baffles to increase the energy gradient during stirring. Figure 3-18 illustrates the specific relationship between the energy gradient (G-value) and the rpm of the stirrers for this jar tester.

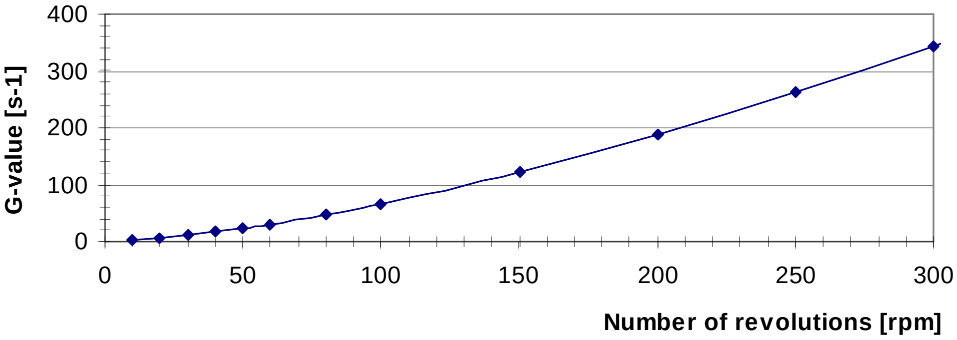

Figure 3-18 – Mixing energy for the jar tester

Dosage of the coagulant was conducted during a stirring velocity of 300 rpm. After a mixing time of 30 seconds, the stirring velocity was decreased to 20 rpm for 10 minutes. During this period, floc formation took place. All jars were observed visually, and after the flocculation period samples were taken for analyses. All samples were filtered through 0.45 µm and analysed for orthophosphorus and total phosphorus to investigate the binding of orthophosphorus. An example of the results after a jar test with Q-pus (a poly aluminium chloride) and ferric(III)chloride conducted with metal/orthophosphorus ratios of 0, 2, 4, 6, 8 and 10 mol/mol is given in Figure 3-19. In this case, the results show a higher removal of P-total and P-ortho for ferric(III)chloride. The optimal metal/orthophosphorus ratio for ferric(III)chloride is 8 mol/mol.

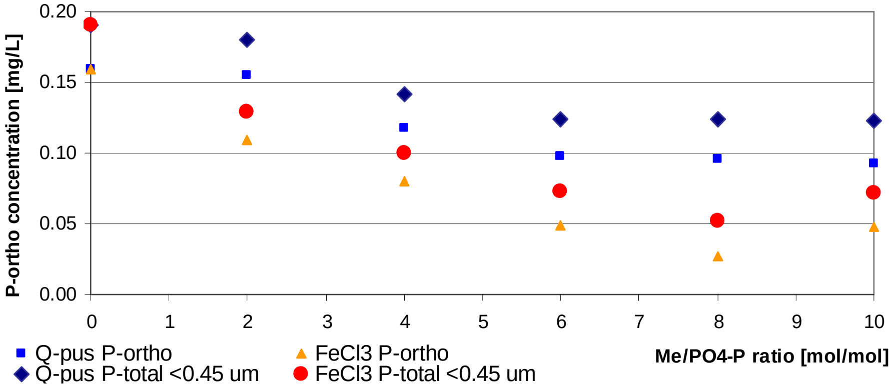

Figure 3-19 – Results of a jar test used to determine the optimal dosage ratio, and a comparison between Q-pus (PACl) and $FeCl_3$. Experiments conducted at the Leiden Zuidwest WWTP 7 November 2006

When floc sizes need to be investigated, for example to determine the temperature influences on floc formation, filtration through 0.45 µm, 2 µm, 5 µm and 10 µm is conducted. In all the filtrates and in the unfiltered sample, the total orthophosphorus concentration (orthophosphorus with metal-bound phosphorus) was measured. In all jars the pH was measured at the end of the experiment. An example of a jar test which is used to determine the influence of coagulant dosage is shown in Figure 3-20. In this case ferric(III)chloride was dosed at a metal/orthophosphorus ratio of 4 mol/mol. The results show that the WWTP effluent (blue bars) mainly contains orthophosphorus <0.45 µm. After coagulant dosage (green bars) the orthophosphorus concentration which is of course metal bound shifts from the fraction <0.45 µm to the fractions 0.45 – 2 µm, 2 – 5 µm, 5 – 10 µm, and >10 µm.

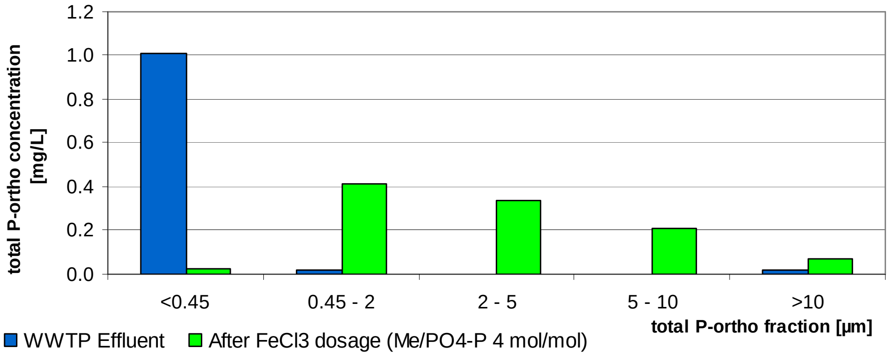

Figure 3-20 – Results of a jar test to investigate the shift in size fractions after ferric(III)chloride dosage with a metal/orthophosphorus ratio of 4 mol/mol. Experiment conducted at the Leiden Zuidwest WWTP 18 February 2008

3.4 Lindquist diagrams

The filter bed resistance increases during filtration. The cause of this pressure increase is the accumulation of suspended solids, the accumulation of colloid substances and biological growth (STOWA, 2006). The accumulation of these solids and substances together with the biological growth will lead to clogging and/or a breakthrough of suspended solids. Accumulation of solids of the filter bed will be on top of the filter bed or throughout the whole filter bed, depending on the water quality, the grain size, the water temperature and the filtration rate (STOWA, 2006). Accumulation of solids which is distributed over the complete filter bed is called deep bed filtration. When accumulation only occurs at the top of the filter bed it is called cake filtration.

The increase of filter resistance during filtration, for a fixed filter bed, is measured with pressure readings. These pressure readings are displayed using Lindquist diagrams. At the Leiden Zuidwest WWTP and the Horstermeer WWTP, pressure readings were observed for the dual media filters and the 1-STEP® filter. The pressure along the filter bed heights was observed by pressure gauges installed on the side of the filters. The pressure gauges for the dual media filter at the Horstermeer WWTP are shown in Figure 3-21. The pressure is measured in mbar of cmWC (cm Water Column).

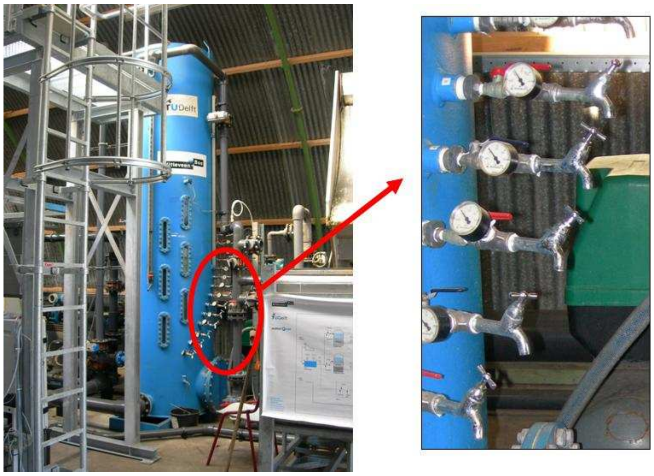

Figure 3-21 – Photograph of the pressure gauges and taps along the dual media filter at the Horstermeer WWTP

An example of a pressure reading for the dual media filter at the Horstermeer WWTP is presented in Figure 3-22. On the vertical axis the filter bed height is given and on the horizontal axis the pressure is given. In this figure the total runtime is given, meaning that the bump cleaning, which is every three hours, is not specified. The figure shows a pressure drop with an increasing runtime.

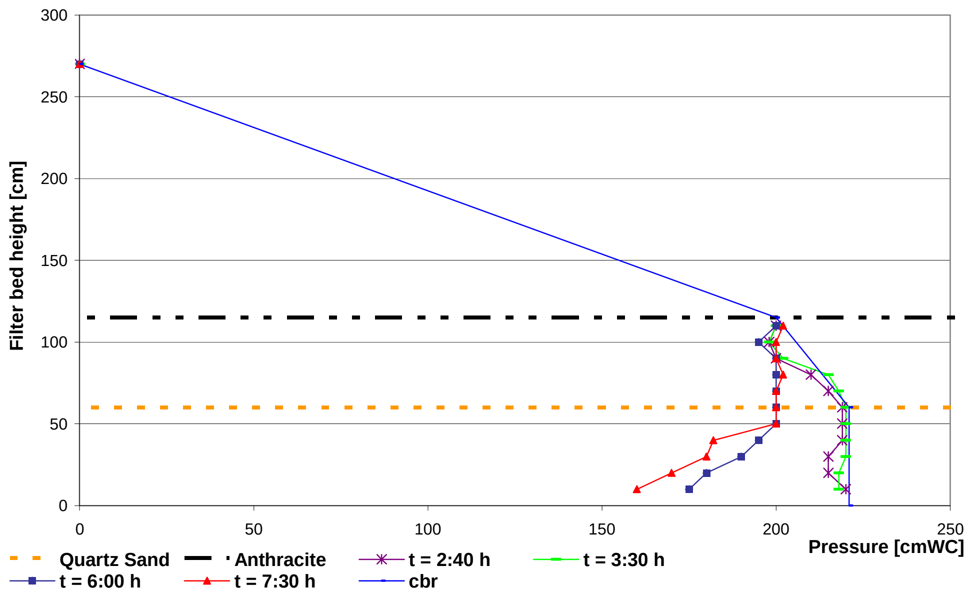

Figure 3-22 – Example of a Lindquist diagram in [cmWC] for the dual media filter at the Horstermeer WWTP. t = total runtime in hours [h].

3.5 Summary

Pilot-plant investigations were conducted at the Horstermeer WWTP and the Leiden Zuidwest WWTP. The pilot-plant at the Horstermeer WWTP consists of a dual media filter and a “One Step Total Effluent Polishing filter”(i.e. 1-STEP®) operated for denitrification and simultaneous phosphorus removal. The pilot installation at the Leiden Zuidwest WWTP represents a small full-scale installations. Continuous sand filtration and dual media filtration were combined to investigate separately denitrification and phosphorus removal and were compared for simulations of denitrification and phosphorus removal. The dosage of a carbon source and coagulant were discussed as well as the initial mixing and flocculation tanks. This chapter gave a description of the installations, process conditions and the methods which were used during this research.

3.6 References

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4 Analysing phosphorus in filtration processes

A literature overview of research conducted at WWTPs to reach ultra low concentrations for total phosphorus (Hultman et al., 1994; Hidaka et al., 2003; Takács et al., 2006; Husband and Becker, 2007) shows mainly information about soluble phosphorus (orthophosphorus) and total phosphorus. Only a few studies (e.g. Spivakov et al., 1999; Shand et al., 2000; Miska-Markusch, 2008) describe colloidal phosphorus and different forms of phosphorus as well.

During the first period of this current research, it already became clear that knowledge of the different forms of phosphorus is essential to reach ultra low phosphorus concentrations in WWTP effluent. The TU Delft phosphorus distribution method was developed to be able to measure the different phosphorus forms present in WWTP effluent, filtrate water and other water samples. Knowledge about phosphorus distribution can be used to optimise phosphorus removal in post-treatment techniques. A distribution of phosphorus also enables a comparison of filter concepts and enables optimisation of the initial mixing energies, residence times in flocculation chambers and filter concepts.

This chapter describes the background of chemical phosphorus analysis (Section 4.1) and the phosphorus components which are measured (Section 4.2). Measurement errors and the interaction between compounds are described in Section 4.3. The development and evaluation of the TU Delft phosphorus distribution method is described in Section 4.4.

Fractionation of phosphorus sizes and profile measurements are discussed in Sections 4.5 and 4.6.

4.1 Chemical phosphorus analysis

Chemical phosphorus analysis is widely used but it is not the only way of determining the phosphorus content of a sample. Other techniques, for example Nuclear Magnetic Resonance (NMR) spectroscopy, can also be used. NMR spectroscopy is a spectroscopic technique based on the magnetic properties of atomic nuclei (Lens and Hemminga, 1998). NMR spectroscopy can be used to differentiate between phosphorus as orthophosphorus, monoesters, diesters, pyrophosphorus, polyphosphorus and phosphanates (Reizel et al., 2006). Although this information is very useful, the analysis is time consuming and too complicated to be used at a WWTP on daily basis. Therefore, the main focus of this Section is on chemical phosphorus analysis which can be conducted on-site to generate reliable and accurate information about the phosphorus content of a sample.

4.1.1 Orthophosphorus analysis

The chemical determination of orthophosphorus, as either orthophosphorus or total phosphorus, depends in all cases on a good analytical orthophosphorus method (Broberg and Pettersson, 1988). The most common method for such determination is the method described by Murphy and Riley (1962). This method is based on the formation of molybdenum blue. A year after their work, Stephens (1963) increased the sensitivity of the method developed his predecessors by only increasing the concentration of ascorbic acid.

The chemical principle of the molybdenum blue method contains two phases, which are described by Korn, 2002. The first phase is the reaction of orthophosphorus with molybdate ions in an acid medium. Murphy and Riley (1962) prescribed sulphuric acid as a medium. In this way molybdophosphoric acid $(PMo_{12}O_{40})^{3-}$ is formed. If the acidity is too low ($pH < 0.7$) in this phase, a non-linear colour will develop and molybdate will be reduced, causing an error (Crouch and Malmstadt, 1967; Broberg and Pettersson, 1988). If the acidity is too high, the colour development will decrease.

The second phase is the reduction of the blue heteropoly acid by a reducing agent. For this reducing agent Murphy and Riley (1962) prescribed ascorbic acid, but also stannous chloride and hydrazine sulphate have been used in the past (Broberg and Pettersson, 1988; Chamberlain and Shapiro, 1969). According to Broberg and Pettersson (1988), the use of ascorbic acid has some advantages and disadvantages when compared with other reducing agents. The advantages are that it is less sensitive to high salt concentrations, the colour development is relatively independent of temperature, and the colour is more stable. The disadvantage is that the development of the colour is rather slow. This slow colour development can be accelerated by the introduction of antimony as a catalyst. The intensity of the blue colour after the reduction stage is proportional to the amount of orthophosphorus incorporated into the formed complex (Sjösten and Blomqvist, 1997). The intensity, or optical density, of the solution is measured with a spectrophotometer after a fixed time because the formation of the molybdenum blue is time dependent and somewhat unstable (Korn, 2002). The wave length used differs: Murphy and Riley (1962) prescribed 882 nm, but Crouch and Malmstadt (1967) measured at 650 nm during their research, and Korn et al. (2002) measured at 680 nm. Stephens (1963) claims that the extract has two absorption maxima, namely at 690 nm and 810 nm. The reaction time is 5 (Stephens, 1963) or 10 minutes (Murphy and Riley, 1962).

Improvement of the analytical molybdenum blue method will continue. One of the developments is the application of ultrasonic waves to enhance the sensitivity of the molybdenum blue method (Korn et al., 2002). By using ultrasonic waves, the degradation of molybdate in an acidic medium is increased, resulting in a larger amount of orthophosphorus able to react with the molybdate which increases the sensitivity of the measuring method. The estimated detection limit for this method is 27 μg/L.

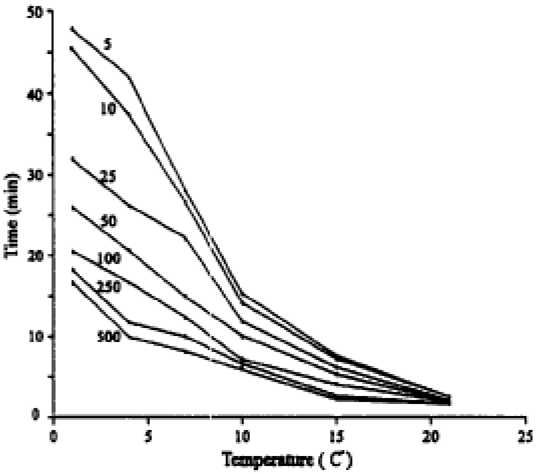

Figure 4-1 – Reaction time needed for complete development of the molybdenum blue method (Sjösten and Blomqvist, 1997). Results are shown for orthophosphorus concentrations of 5, 10, 25, 50, 100, 250 and 500 μg/L.

Sjösten and Blomqvist conducted research in 1997 to estimate the influence of the orthophosphorus concentration and the temperature on the molybdenum blue method. The experiments were conducted for seven different orthophosphorus concentrations in the range of 5 μg/L to 500 μg/L. One of the conclusions for water samples with the same temperature is that samples which contain low orthophosphorus concentrations need a longer reaction time compared to samples with higher orthophosphorus concentrations. For samples with the same orthophosphorus concentration but different temperatures, it can be concluded that the reaction rate decreases with decreasing temperatures. These results comply with the results found by Harvey already in 1948. The results of the temperature influences are shown in Figure 4-1. For treatment of WWTP effluent at, temperatures between 9° C and 22° C (minimum temperature and maximum temperature of effluent at the Horstermeer WWTP in 2008) with a standard reaction time of 10 minutes, an incomplete reaction occurs when the temperature drops below 10° C in combination with orthophosphorus concentrations below 0.1 mg/L.

4.1.2 Pre-treatment steps

By using different pre-treatment steps before conducting orthophosphorus analysis, different forms of phosphorus can be measured. Acid hydrolysis at 100° C during one hour, referred to as digestion, is a pre-treatment step which is very common. During this step the organic phosphorus content of the sample is converted into orthophosphorus (Tchobanoglous et al., 2003). After cooling and the addition of molybdate, molybdenum blue is formed and the orthophosphorus concentration can be measured. The orthophosphorus concentration measured in the sample after acid hydrolysis at 100° C is then called total phosphorus concentration, which is the sum of organic phosphorus and orthophosphorus.

Another pre-treatment step which can be used is filtration of the sample before orthophosphorus is measured. Determination of orthophosphorus or total phosphorus without filtration includes, in addition to dissolved phosphorus, also colloidal and particulate phosphorus. When filtration is used, depending on the pore size of the filter, a distinction can be made between dissolved, colloidal and particulate phosphorus. According to Tchobanoglous et al. (2003) the size range of colloidal material is 0.01 μm up to 1.0 μm.

4.2 Phosphorus components

Phosphorus can be found in different forms in surface water and in WWTP effluent, which was described in Section 2.1. Summarised, these phosphorus forms can be divided into dissolved and particulate phosphorus. The separation between dissolved and particulate fractions is usually made by filtration through a filter with a pore size of 0.45 μm. This means that a part of the colloidal phosphorus (0.01 – 1.0 μm) is measured as dissolved phosphorus.

Figure 4-2 shows (Spivakov et al., 1999; Bratby, 2006) that dissolved phosphorus can be subdivided into dissolved reactive phosphorus (orthophosphorus including colloidal metal-bound phosphorus), dissolved acid-hydrolysable phosphorus (polyphosphorus, pyrophosphorus, metaphosphorus, lower oxidation states) and dissolved organic phosphorus (orthophosphate monoesters, organic polyphosphorus, orthophosphate diesters, phosphonic components). Polyphosphorus and dissolved organic phosphorus can take part in a precipitation reaction with metal salts or can adsorb to particles or carrier material. Dissolved organic phosphorus can be bound to humic and fulvic acids. Particulate phosphorus can be separated into particulate organic phosphorus and metal-bound phosphorus. Dissolved reactive phosphorus is measured by an orthophosphorus measurement (Ahlgren, 2006).

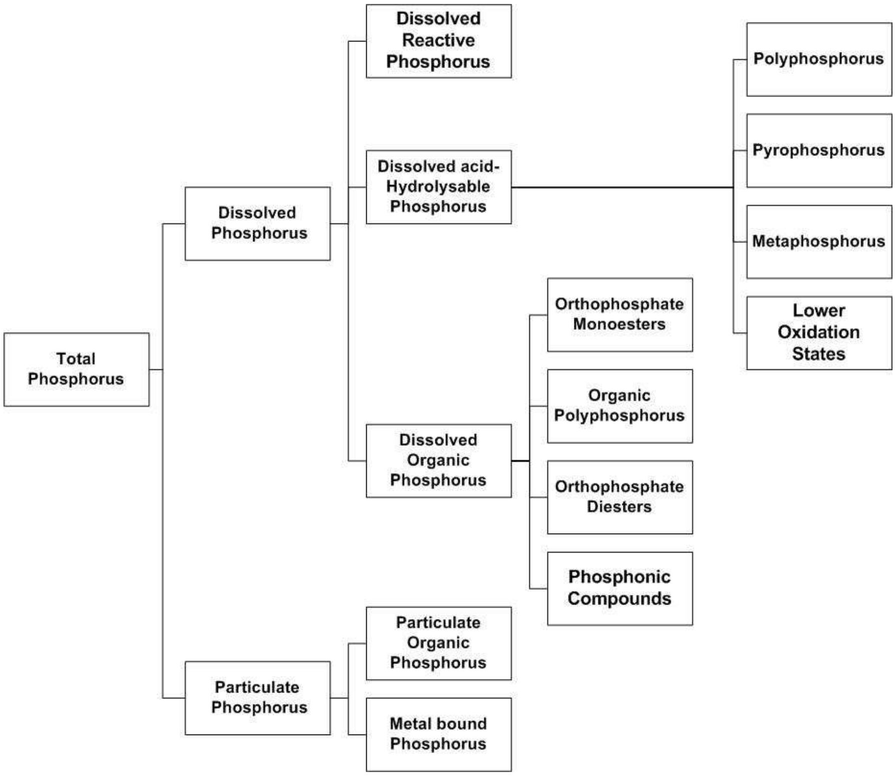

Figure 4-2 - Total overview phosphorus distribution

4.3 Interactions of components and measuring errors

Measuring orthophosphorus with the molybdenum blue method has some drawbacks which should be taken into account when analysing the result. Broberg and Pettersson described the two major problems in 1988. These problems are, firstly, the hydrolysis of acid liable phosphorus components, like orthophosphate monoesters. Some of these orthophosphate monoesters, like adenosine monophosphate (5’-AMP) and phosphorylcholine chloride, are hydrolysed within 30 seconds to nearly 100% orthophosphorus when acid is added (Baldwin, 1998; Broberg and Pettersson, 1988; Chamberlain and Shapiro, 1969; Burton, 1973). This means that the concentration of orthophosphorus can be overestimated. Several possibilities to decrease the interaction of these components have been developed over the years, for example decreasing the reaction time (Chamberlain and Shapiro, 1969) or decreasing the acidity, but none of these modifications have been widely used (Broberg and Pettersson, 1988).

The second problem, described by Broberg and Pettersson (1988) and Blomqvist and Westin (1998), is the interaction of simultaneously formed complexes between molybdate and chromate, tungstate, vanadate, silicate, arsenic, germanate and arsenate. The effects of these substances (Blomqvist and Westin, 1998) can either be an overestimation or an underestimation of the orthophosphorus concentration. Measuring a low orthophosphorus concentration increases the importance of the possible interactions from other ions, such as arsenic in pesticides. In the WWTP effluent, silicate is the only one of these components that can occur in concentrations that could interfere with the orthophosphorus measurement. To minimise the effect of the presence of silicate, it is important to use an acid/molybdate ratio of 4:1 which is also recommended by Murphy and Riley (1962).

Dissolved acid hydrolysable phosphorus, including higher molecular weight species like hexametaphosphate, are converted into orthophosphorus by acid hydrolysis at 100°C (Broberg and Pettersson, 1988; Spivakov et al., 1999). This conversion occurs during the determination of organic phosphorus and implies that the amount of organic compound might be overestimated.

Not only soluble components may interfere with the molybdenum blue method. Stainton (1980) claims that the significance of the overestimation of orthophosphorus by the molybdenum blue method depends on the ratio between the present colloidal phosphorus and the orthophosphorus. In his article, different molybdenum blue methods were tested and all of them degraded a part of the colloidal phosphorus fraction to orthophosphorus. Therefore, it can be deduced that phosphorus present in the colloids reacted with molybdate and was measured as orthophosphorus.

In this research the distinction between dissolved and particulate phosphorus is made by filtration through 0.45 μm. The use of filters with this porosity is very common and widely used (Danielsson, 1982; Spivakov et al., 1999; Shand et al., 2000; Gregory, 2006). The filters can be of different materials, for example cellulose acetate, cellulose nitrate, glass fiber or polyethersulphon. It should always be taken into account that a measuring error might occur when adsorption of phosphorus or desorption of phosphorus or heavy metals takes place (Danielsson, 1982). This can result in extremely low or high phosphorus concentrations in the filtered water. These problems can be resolved by rinsing or soaking the filter with demineralised water or with acid. It is advisable to test if adsorption or desorption took place before using any filter material.

When the distinction between dissolved and particulate is made by filtration through 0.45 μm, very fine particulate phosphorus may be measured as dissolved, and dissolved phosphorus may be retained by adsorption or occlusion (Burton, 1973). Besides this, the colloidal fraction is not taken into account. This colloidal fraction can be colloidal phosphorus or phosphorus which is associated with colloidal material (Stevens and Stewart, 1982). The range of colloidal material is 0.01 μm to 1 μm according to Tchobanoglous et al. (2003). This means that a part of the colloidal phosphorus is measured as dissolved phosphorus and a part as particulate phosphorus. Actual dissolved orthophosphorus is thus measured after filtration through a pore size of 0.01 μm.

During filtration through 0.45 μm, cake filtration may occur when the sample contains too much colloidal or particulate material or when too large a quantity of the sample is filtered. Danielsson (1982) conducted experiments with 0.45 μm Millipore and 0.40 Nucleopore membrane filters to estimate the maximum filter load. The results of these experiments showed that large errors may occur when membrane filters are used for the removal of large particles due to a change in the effective pore size. Shand et al. (2000) reported when using an increasing sample volume an increasing amount of organic phosphorus and orthophosphorus which is retained in the filter deposit. To avoid these errors, investigations should be made to estimate the maximum filter load for a specific sample (Sheldon and Sutcliffe, 1969).

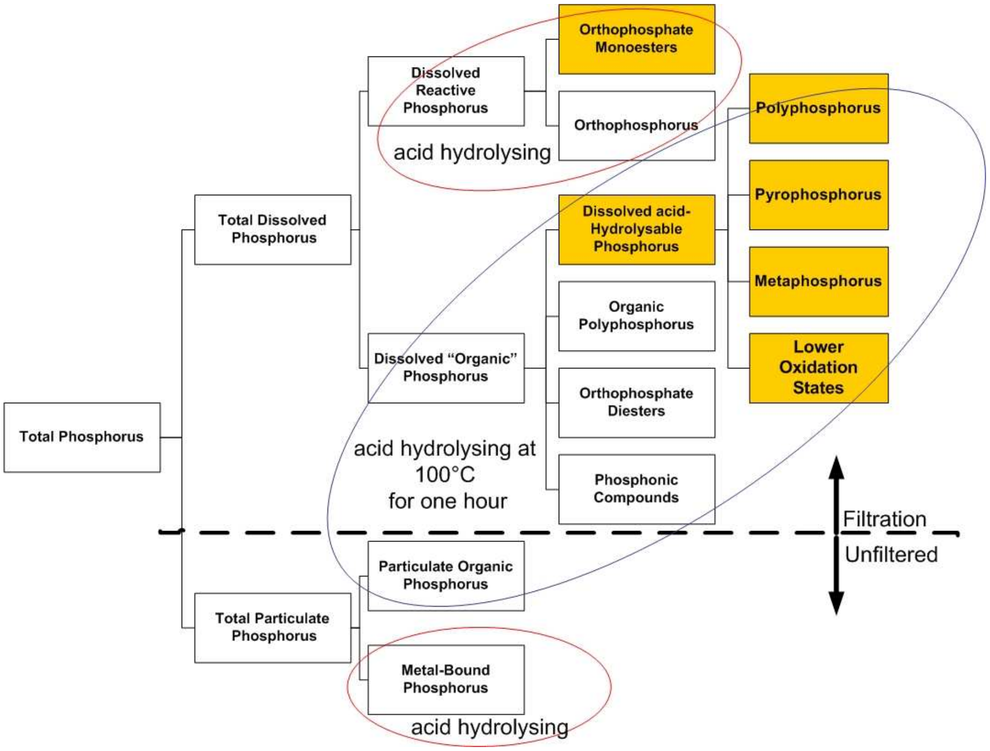

Figure 4-3 - The measured distribution of phosphorus, including the measured phosphorus components. The orange areas show the measuring errors caused by orthophosphate monoesters, which are organic and not measured as organic phosphorus, and dissolved acid hydrolysable phosphorus, which is measured as dissolved organic phosphorus while it is not organic.

When taking into account the analytical methods and all the described measuring errors which occur using the molybdenum blue method, the scheme presented in Figure 4-2 should be rearranged. In Figure 4-3 the phosphorus distribution is shown to provide an overview of the phosphorus forms which are actually measured. The components which are measured at the “incorrect” place are indicated with an orange colour. The figure also shows, besides the measuring errors, the analytical method which should be applied to measure a certain component or a group of components. Dissolved reactive phosphorus is measured after filtration by acid hydrolysation which takes place within the molybdenum blue method. The dissolved “organic” phosphorus is written between quotation marks because during the digestion step also the dissolved acid hydrolysable phosphorus, which is inorganic, is converted into orthophosphorus. Dissolved “organic” phosphorus is measured after filtration by a total phosphorus measurement which includes the dissolved reactive phosphorus. To calculate the concentration of dissolved “organic” phosphorus, the dissolved reactive phosphorus needs to be subtracted. Particulate organic phosphorus is measured in a digested unfiltered sample. This measurement will include all phosphorus components which need to be subtracted to calculate the particulate organic phosphorus concentration. Metal-bound phosphorus is converted into orthophosphorus by acid hydrolysation. When using the molybdenum blue method for an unfiltered sample without digestion, the metal-bound phosphorus concentration including the dissolved reactive phosphorus concentration is measured. After subtracting the dissolved reactive phosphorus concentration, the metal-bound phosphorus is given.

4.4 The TU Delft phosphorus distribution method

As stated before in Section 4.1, the focus is on chemical phosphorus analysis which can be conducted on site. This applies also for determination of the phosphorus distribution. Determination has to be easy, quick and should not make use of complex measurements or pre-treatment steps. With these restrictions in mind, the TU Delft phosphorus distribution method has been developed.

4.4.1 Determination of the TU Delft phosphorus distribution

To determine the TU Delft phosphorus distribution, also referred to as phosphorus distribution, on site, only four measurements need to be executed: namely, total phosphorus (P-total) and orthophosphorus (P-ortho) in an unfiltered sample, and total phosphorus and orthophosphorus in a filtered sample through 0.45 µm. For this filtration step, a cellulose acetate filter is used to filter a sample volume of 10 ml under a limited pressure of 50 mbar. Phosphorus concentrations are measured with Hach Lange cuvette tests LCK349. This method uses ascorbic acid for the reduction step. Total phosphorus is analysed by a pre-treatment step of acid hydrolysis with sulphuric acid (Murphy and Riley, 1962).

Figure 4-4 is made using knowledge about the chemical orthophosphorus analysis in combination with the available pre-treatment steps and the knowledge of the different forms of phosphorus. The figure shows the information gained with each phosphorus measurement in combination with a pre-treatment step and shows how these results can be used to calculate the concentrations of the different phosphorus forms. The figure is an intermediate figure used for the construction of Figure 4-5.

Figure 4-5 shows how the four phosphorus fractions are related to each other. Total phosphorus (P-total unfiltered) is divided into total dissolved phosphorus (P-total < 0.45 µm) and total particulate phosphorus (P-total unfiltered – P-total < 0.45 µm). Total dissolved phosphorus is divided into orthophosphorus (P-ortho < 0.45 µm) and dissolved “organic” phosphorus (P-total < 0.45 µm – P-ortho < 0.45 µm). Total particulate phosphorus is divided into particulate organic phosphorus (total particulate phosphorus – metal-bound phosphorus) and metal-bound phosphorus (P-ortho unfiltered – P-ortho < 0.45 µm).

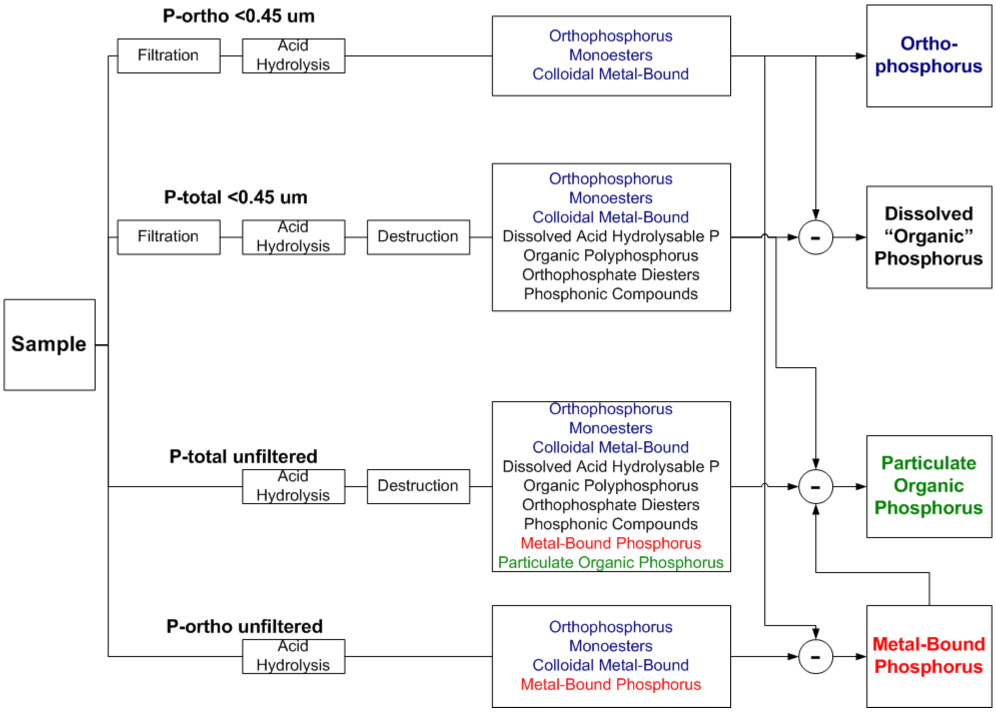

Figure 4-4 – Intermediate figure of the TU Delft phosphorus distribution method

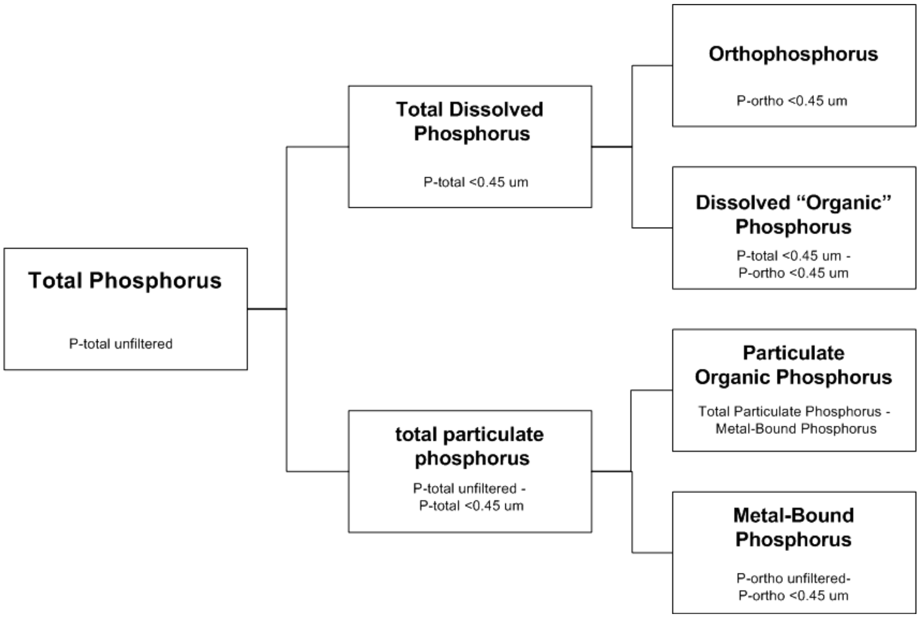

Figure 4-5 – TU Delft phosphorus distribution method (Scherrenberg et al., 2008)

When information is required about the colloidal phosphorus fractions, filtration through 0.1 μm filters needs to be conducted. Orthophosphorus and total phosphorus need to be measured in the filtrate. The colloidal fractions shown in Figure 4-6 can be calculated using the same method as described in Figure 4-5.

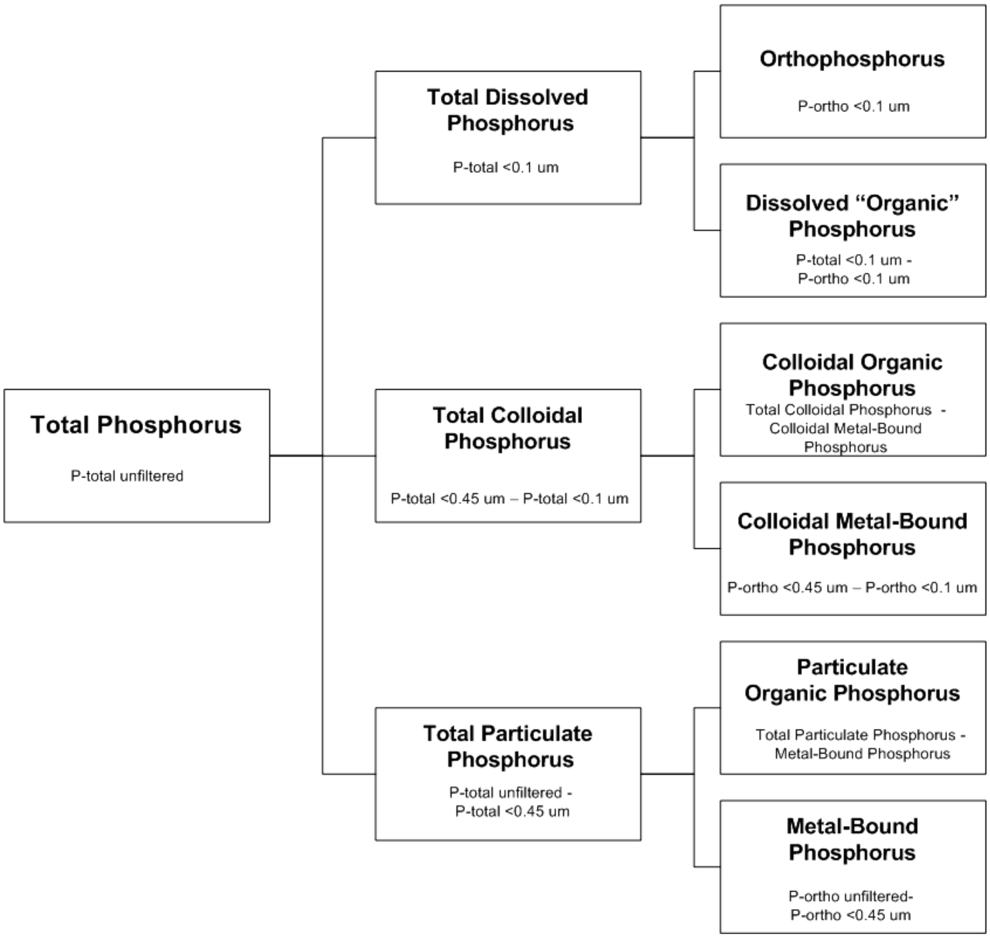

Figure 4-6 - Distribution of phosphorus including the colloidal fractions

4.4.2 Evaluation: analysis of the errors

Construction of the on-site TU Delft phosphorus distribution method as shown in Figure 4-5 introduces inaccuracies caused by the molybdenum blue method and the filtration step. It should be kept in mind that this practical method has been developed to determine the phosphorus distribution on site without making use of highly specialised laboratory equipment.

The phosphorus concentrations were analysed with Hach Lange cuvette tests (LCK349) based on the phosphorus molybdenum blue method. The relative analytical precision of LCK349 (0.05 – 1.5 mg P-total/L) and the 95% confidence interval are shown in Figure 4-7. The relative precision decreases with decreasing total phosphorus concentrations. For a total phosphorus concentration of 0.15 mg/L, the 95% confidence interval is ± 0.0068 mg/L, meaning that the total phosphorus concentration is in the range of 0.143 – 0.157 mg/L. When different phosphorus measurements are subtracted or added up, the 95% confidence interval becomes ± 0.0136 mg/L.

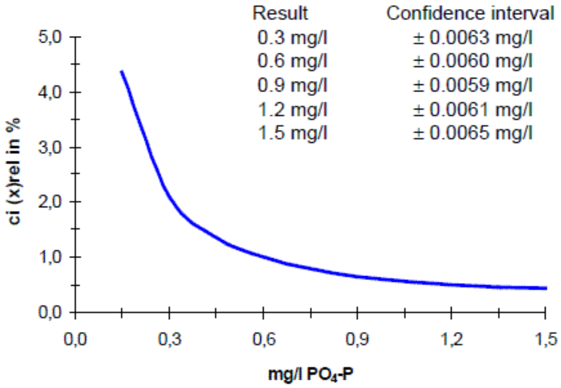

Figure 4-7 – Relatively analytical precision of LCK349 and the 95% confidence interval (Hach Lange, 2009)

As discussed in Section 4.3, the molybdenum blue method also introduces an error caused by dissolved acid hydrolysable phosphorus and orthophosphate monoesters. Based on available information, the concentrations of these components in WWTP effluent in the Netherlands is estimated to be less than 0.01 mg/L.

To give an estimation of the error which is introduced when the colloidal fraction is not taken into account, phosphorus distributions are made with 0.45 μm and 0.1 μm filters. The phosphorus distributions are calculated using Figure 4-5 and 4-6 for nine samples taken at the Horstermeer WWTP. The results are shown in Figure 4-8 and 4-9. Figure 4-8 shows that total phosphorus concentration mainly consists of orthophosphorus (64%). Metal-bound phosphorus represents 21% of the total phosphorus; dissolved “organic” phosphorus represents 7%, and particulate organic phosphorus represents 8%. Figure 4-9 shows that only a small part (4% of the total phosphorus concentration) of the orthophosphorus, measured with the standard phosphorus distribution, is actually colloidal metal-bound phosphorus. This results in an overestimation of the orthophosphorus concentration of 7%, on average, for these samples taken at the Horstermeer WWTP.

The dissolved “organic” phosphorus concentration measured with the standard phosphorus distribution also contains colloidal organic phosphorus, specifically 4% of the total phosphorus concentration is colloidal “organic” phosphorus and just 3% of the total phosphorus concentration is really dissolved “organic” phosphorus so, the colloidal fraction causes a rather high overestimation for the dissolved “organic” phosphorus measurement with the standard phosphorus distribution of more than 100% on average for the samples taken at the Horstermeer WWTP.

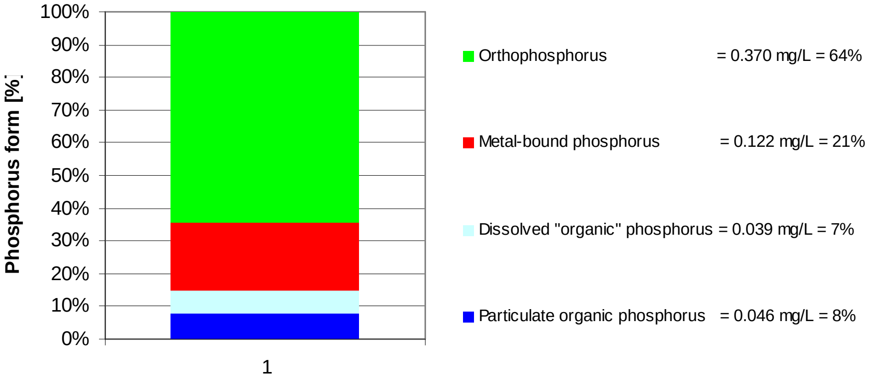

Figure 4-8 – Average (9 samples) phosphorus distribution (standard phosphorus distribution) for the effluent of the Horstermeer WWTP

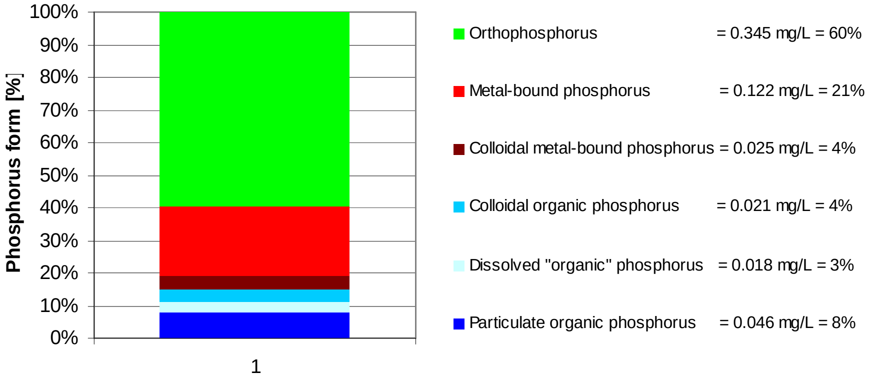

Figure 4-9 – Average (9 samples) phosphorus distribution including the colloidal fractions for the effluent of the Horstermeer WWTP

Regarding the practical application, Figure 4-10 shows an example of the TU Delft phosphorus distribution method (Scherrenberg et al., 2008). This phosphorus distribution was made on January 15, 2008, for continuous sand filter A (CFA) at the Leiden Zuidwest WWTP, with a filtration rate of 17 m/h, a coagulant dosage ratio of 4 mol Me^{3+}/mol PO_4-P, initial mixing of 1,000 s^{-1} and a flocculation time of 4 minutes. The graph shows the phosphorus distribution into orthophosphorus, metal-bound phosphorus, dissolved “organic” phosphorus and particulate organic phosphorus for the WWTP effluent, after flocculation and in the filtrate water of continuous sand filter A (CFA).

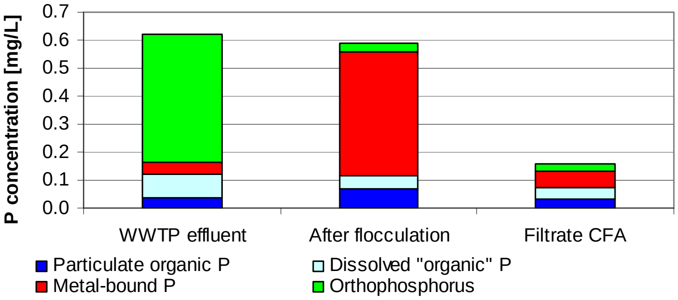

Figure 4-10 - Results of the phosphorus distribution of WWTP effluent, after flocculation and of the filtrate of continuous sand filter A (Filtrate CFA) into particulate organic P, dissolved “organic“ P, metal-bound P and orthophosphorus. 15 January 2008

The results show that almost all (>90%) available orthophosphate (green bar, first column) is bound by metal ions after flocculation and is entrapped in flocs after flocculation (remaining green bar, second column). The dissolved ‘organic’ phosphorus decreased after flocculation and the particulate organic phosphorus increased, which suggests that part of the dissolved “organic” phosphorus may be colloidal or associated with colloidal material (Stevens, 1982). About 50% of the particulate organic phosphorus was removed in the filter bed. This is shown by the dark blue bar in filtrate CFA which is half of the dark blue bar after flocculation. The orthophosphorus which is not bound after flocculation will remain dissolved orthophosphorus and will pass through the filter bed. In this case, 12% of the formed metal-bound phosphorus is not removed during filtration; this could be due to a small initial floc size or because of scouring of flocs in the filter bed. Scouring will decrease the floc size which can lead to a breakthrough of metal-bound phosphorus.

A frequently seen phenomenon is a lightly increased total phosphorus concentration in the upper water layer compared to the concentration in the feed water. The cause of this increase is not clear. Hach Lange states in the product information (Hach Lange, 2009) that Fe^{3+} and Al^{3+} do not cause interference for concentrations up to 50 mg/L. The concentrations used for Fe^{3+} and Al^{3+} never exceeded 50 mg/L, therefore, the increase, which was measured after coagulation, was most likely not caused by the coagulant dosage. A cause, which is most likely responsible for the increase of the total phosphorus concentration in the upper water layer, may be a form of accumulation. The upper water layer of a fixed bed filter can be compared with a continuously stirred tank reactor, eventhough the motions are very low. A sample taken from the upper water layer will therefore represent the situation after coagulation and flocculation.

4.5 Phosphorus size fractionation

To determine the size of the metal-bound phosphorus, a 10 ml sample is filtered with a vacuum of 50 mbar through a filter with a pore size of 10 µm (polycarbonate), a pore size of 5 µm (polycarbonate), a pore size of 2 µm (polycarbonate) and through a pore size of 0.45 µm (cellulose acetate). The use of different filter materials is inevitable because polycarbonate filters are not available with a pore size of 0.8 µm, and cellulose acetate filters have a maximum pore size of 0.8 µm. Orthophosphorus concentrations are measured in the filtered samples and in the unfiltered samples. The orthophosphorus concentrations are measured with Lange cuvette tests LCK349 (Murphy and Riley, 1962). The results gained with this method show the size of the metal-bound phosphorus flocs and show which part of the orthophosphorus remains dissolved. With these results, the estimated floc size can be calculated by adding up the floc sizes proportionally, of course without the fraction <0.45 µm, which is dissolved phosphorus. Equetion 4.1 shows the cacluation.

$$\frac{\sum\left(average\ \ filter\ \ pore\ size \bullet [PO_4 - P]\right)}{\sum[PO_4 - P]} = estimated\ \ floc\ size \qquad \text{eq. 4.1}$$

Figure 4-11 shows the results of a phosphorus size fractionation which was made for the dual media filter at the Horstermeer WWTP on the 17th of March, 2008. The filtration rate was 10 m/h, the dosage ratio used was 4 mol Me^{3+}/mol PO_4-P, and the initial mixing energy was 1,000 s^{-1}. The flocculation time was approximately 7 minutes. The phosphorus size fractionation was made with 0.45 µm, 2 µm and 10 µm filters.

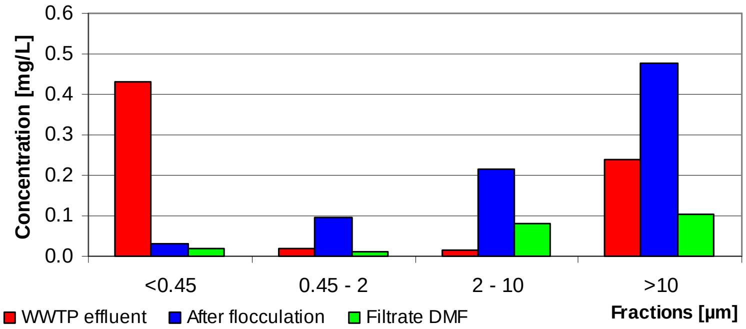

Figure 4-11 – Results of the phosphorus size fractionation of WWTP Effluent (red bars), After flocculation (blue bars) and the filtrate water of the dual media filter (green bars) at the Horstermeer WWTP. 17 March 2008

The phosphorus size fractionation of the WWTP effluent shows that most of the phosphorus present is orthophosphorus (red bar < 0.45 µm). Another significant amount of the WWTP effluent phosphorus is > 10 µm (red bar >10 µm). This was probably caused by metal-bound phosphorus which was washed out from the secondary sedimentation tanks. After flocculation (blue bars), orthophosphorus is bound, which is shown by the decrease of phosphorus <0.45 µm. The amount of phosphorus which decreased in the fraction to <0.45 µm is transferred to metal-bound phosphorus, which can be seen by the increase in all fractions above 0.45 µm. In the filtrate water of the dual media filter (green bars), a decrease of phosphorus can be seen for all the fractions. Phosphorus below 2 µm is almost completely removed in the filter bed and large parts of the fractions 2 – 10 µm and > 10 µm are removed. Since no filters with a pore size >10 µm are used is the average floc filter pore size estimated. For the smaller fractions is the average pore size 3 times the minimum pore size. Therefore, an average pore size of 30 µm is used for the fraction >10 µm. The estimated floc size in the filtrate water is:

$$\frac{\left(\frac{0.45+2}{2}\right)\bullet 0.01\,mg/L+\left(\frac{2+10}{2}\right)\bullet 0.079\,mg/L+30\bullet 0.105\,mg/L}{0.01+0.079+0.105}=18.7\,\mu m$$

4.6 Profile measurements

In order to be able to investigate removal mechanisms in the filter bed for phosphorus removal as well as for denitrification, profile measurements are made on a regular basis. For a profile measurement samples are taken of the WWTP effluent, the upper water layer of the fixed filter bed, every 10, 20 or 40 cm in the filter bed (by taps which are placed in the wall of the filter) and in the filtrate water of the filter. Orthophosphorus (<0.45 µm), nitrate, nitrite and COD are measured in the samples with Hach Lange cuvette tests. Additionally, the oxygen concentration is measured.

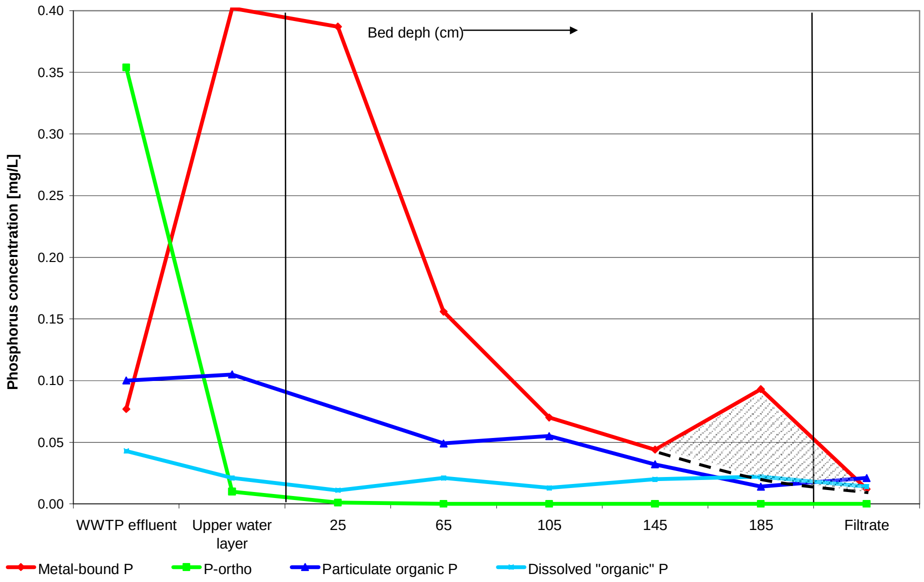

Figure 4-12 – Profile measurement combined with phosphorus distribution for the 1-STEP® filter 19 November 2008

Profile measurements can be combined with phosphorus distributions. In this case a phosphorus distribution is made for every sample point. Figure 4-12 shows an example of such a profile measurement made for the 1-STEP® filter at the Horstermeer WWTP. This profile measurement was made on the 19th of November, 2008. The Al^{3+}/PO_4-P ratio used was 4 mol/mol and the filtration rate was 10 m/h. The profile measurement shows the phosphorus distribution through the filter bed. The information provided from these results show which phosphorus forms are removed. The graphs show the orthophosphorus (green line), the metal-bound phosphorus (red line), the particulate "organic" phosphorus (dark blue line) and the dissolved "organic" phosphorus (light blue line) concentrations through the filter bed.

The graph shows that nearly all the orthophosphate (decreasing green line), which is available in the WWTP effluent, was transferred to metal ions after coagulation and flocculation (see the rising red line in the upper water layer). Metal-bound phosphorus and particulate "organic" phosphorus were removed in the filter bed. Dissolved "organic" phosphorus will pass the filter bed, despite the filter media of activated carbon. The graph also shows an increase in metal-bound phosphorus just before the bottom plate of the filter bed is reached (see the cross-hatched area in Figure 4-12). The cause of this increase is not absolutely clear yet, but it is probably caused by deposited metal-bound phosphorus or sludge. Care must be used when taking a sample because this deposited material might get into the sample due to the strong flow towards the tap. This will cause a measurement error for the particulate phosphorus forms especially for the metal bound phosphorus. Probably this overestimation will be occurring all over the filter; especially at places with a large accumulation of solids this might be the case. The effect might be minimised when the flow towards the tap is below the filtration rate.

4.7 Summary

Knowledge of the different phosphorus forms in WWTP effluent is essential to reach ultra low concentrations in the WWTP effluent. Different techniques can be used to analyse phosphorus but chemical analysis is widely used. The advantage of chemical phosphorus analysis is that it can be conducted on site and gives reliable and accurate information about the phosphorus content of a sample. The chemical principle is based on the molybdenum blue method. Different forms of phosphorus can be measured depending on the pre-treatment step of a sample. Interactions of components like silicate or arsenate can either give an underestimation or overestimation of the orthophosphorus concentration in a sample. Besides, the interaction caused by certain components in the filtration step through 0.45 μm introduces an error in the measured concentrations. This is caused by the colloidal phosphorus fraction. To what extent this overestimation or underestimation is made should be investigated per location.

The TU Delft phosphorus distribution was developed to have an easy and quick method to determine orthophosphorus, metal-bound phosphorus, dissolved "organic" phosphorus and particulate organic phosphorus. To determine the TU Delft phosphorus distribution, also referred to as phosphorus distribution, on site, only four measurements need to be executed, namely total phosphorus and orthophosphorus in an unfiltered sample and total phosphorus and orthophosphorus in a filtered sample over 0.45μm. For this filtration step a cellulose acetate filter is used to filter a sample volume of 10 ml under a limited pressure of 50 mbar. Phosphorus concentrations are measured with Hach Lange cuvette tests LCK349. This method uses ascorbic acid for the reduction step. Total phosphorus is analysed by a pre-treatment step of acid hydrolysis with sulphuric acid (Murphy and Riley, 1962).

To determine the size of the metal-bound phosphorus, a 10 ml sample is filtered with a vacuum of 50 mbar through filters with different pore sizes. Orthophosphorus concentrations are measured in the filtered samples and in the unfiltered samples. With these results the floc size can be calculated by adding up the floc sizes proportionally, of course without the fraction <0.45 μm which is dissolved phosphorus. In order to be able to investigate removal mechanisms in the filter bed for phosphorus removal as well as for denitrification, profile measurements were made on a regular basis. For a profile measurement samples were taken of the WWTP effluent, the upper water layer of the fixed filter bed, every 10 or 20 cm in the filter bed and in the filtrate water of the filter. An overestimation of the particulate phosphorus forms might occur due to accumulation of solids which will get out when taking a sample. Profile measurements can be combined with phosphorus distributions. In this case, a phosphorus distribution was made for every sample point.

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5 Characterisation, coagulation and flocculation

For the removal of phosphorus to ultra low concentrations, precipitation, coagulation and flocculation processes are used. During precipitation colloidal material is formed which is destabilised during coagulation in a way that these particles can grow as a result of particle collision. Precipitation and coagulation require a good initial mixing to maximise the binding of the metal salt with the available phosphorus and to minimise the side reactions. Flocculation is the process which follows after initial mixing and has the purpose to form flocs and aggregates from the fine particles and destabilised particles.

Chapter 5 illustrates the results of the characterisation of the WWTP effluent (Section 5.1). Results of different locations in the Netherlands are described in this section. The minimum initial mixing energy required for the coagulation process and the influence of the retention time on the flocculation process are investigated in Section 5.2. Results of temperature influences on the coagulation and flocculation process are described in Chapter 7.

5.1 Characterisation of WWTP effluent phosphorus

The results of the characterisation of the WWTP effluent are divided into two subsections, the first subsection, 5.1.1, deals with the results from the Horstermeer WWTP and the Leiden Zuidwest WWTP, the second subsection, 5.1.2, deals with the results of other locations where phosphorus distributions are also made.

5.1.1 Characterisation for the Horstermeer WWTP and the Leiden Zuidwest WWTP

During both researches conducted at the Horstermeer WWTP and the Leiden Zuidwest WWTP phosphorus distributions of the WWTP effluent are made on a regular basis. In total 90 phosphorus distributions are made at the Horstermeer WWTP in the period between October 2007 and November 2009. For the Leiden Zuidwest WWTP 36 phosphorus distributions are made in the period between October 2007 and November 2008. In this section the average results and the change of the distribution with increasing total phosphorus concentrations are shown for both locations.

Table 5-1 and Figure 5-1 show the average concentrations and percentages for orthophosphorus, dissolved “organic” phosphorus, particulate organic phosphorus and metal-bound phosphorus for the Horstermeer WWTP. The average results show that 59% of the total phosphorus is orthophosphorus (green areas), 25% is metal-bound phosphorus (red areas), 10% is particulate organic phosphorus (dark blue areas) and 6% is dissolved “organic” phosphorus (light blue areas).

Table 5-1 – Average (90 samples) phosphorus distribution for effluent of the Horstermeer WWTP. The average total phosphorus concentration was 0.70 mg/L.

Location	Unit	Ortho-phosphorus	Dissolved "organic" P	Particulate organic P	Metal-bound P
Horstermeer WWTP	mg/L	0.41	0.04	0.07	0.18

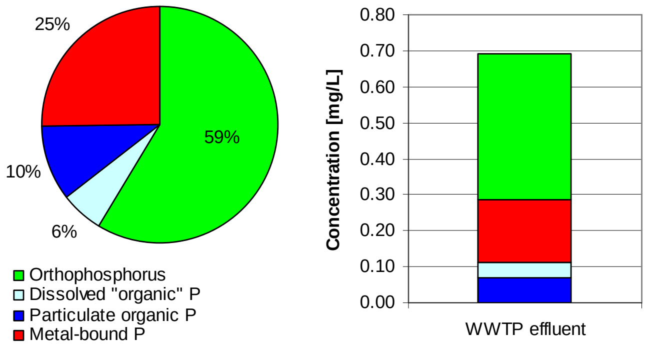


Figure 5-1 – Average (90 samples) phosphorus distribution for effluent of the Horstermeer WWTP given in percentages (left) and concentrations (right)

Table 5-2 and Figure 5-2 show the average concentrations and percentages for orthophosphorus, dissolved “organic” phosphorus, particulate organic phosphorus and metal-bound phosphorus for the Leiden Zuidwest WWTP. The average results show that 71% of the total phosphorus is orthophosphorus (green areas), 7% is metal-bound phosphorus (red areas), 7% is particulate organic phosphorus (dark blue areas) and 15% is dissolved “organic” phosphorus (light blue areas).

Table 5-2 – The average (36 samples) phosphorus distribution for effluent of the Leiden Zuidwest WWTP. The average total phosphorus concentration was 0.55 mg/L.

Location	Unit	Ortho-phosphorus	Dissolved "organic" P	Particulate organic P	Metal-bound P
Leiden Zuidwest WWTP	mg/L	0.39	0.08	0.04	0.04

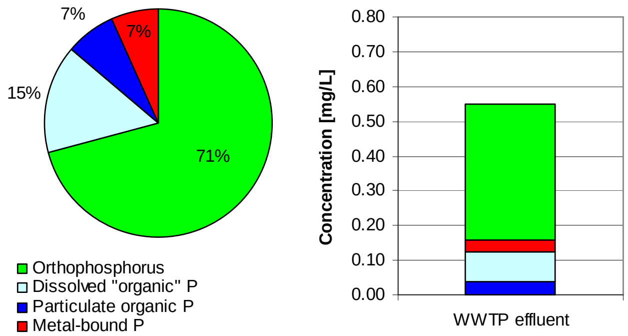


Figure 5-2 – The average (36 samples) phosphorus distribution for effluent of the Leiden Zuidwest WWTP given in percentages (left) and concentrations (right)

The results show different phosphorus distributions for the WWTP effluent. The most obvious difference between the two locations is the percentage and concentration of metal-bound phosphorus, which is much higher for the Horstermeer WWTP. The high metal-bound phosphorus concentration is probably due to the treatment process. The secondary sedimentation tanks are highly loaded and frequently discharging metal bound phosphorus. This is not the case for the Leiden Zuidwest WWTP. This results in variations of the total phosphorus concentration in the WWTP effluent between 0.3 mg/L and 2.7 mg/L. Temperature, seasonal and pH influences on the phosphorus distribution were not found to be significant.

In the effluent of the Horstermeer WWTP, the percentages of the organic phosphorus forms might give an incorrect image due to the higher concentrations of metal-bound phosphorus and orthophosphorus there. The sum of the particulate and dissolved organic phosphorus was almost the same for both locations: for the Horstermeer WWTP, 0.11 mg/L, and for the Leiden Zuidwest WWTP, 0.12 mg/L. Nevertheless, this does not automatically mean that the concentration of organic phosphorus is always in this size range. During a Dutch study (STOWA, 2009) about the biological availability of nitrogen and phosphorus, the dissolved “organic” phosphorus was measured at 23 WWTPs in the Netherlands. Most of the results were within the range of 0.03 - 0.16 mg/L, but peaks of 0.23 mg/L up to 0.59 mg/L were found.

For the Horstermeer WWTP and the Leiden Zuidwest WWTP, the measured phosphorus distributions were divided into concentration ranges for total phosphorus. The concentration ranges for total phosphorus were 0.0 mg/L – 0.5 mg/L, 0.5 mg/L – 1.0 mg/L, 1.0 mg/L – 1.5 mg/L and >1.5 mg/L. For each concentration range, the average phosphorus distribution was calculated. These distributions are shown in Figure 5-3. At the Leiden Zuidwest WWTP, no total phosphorus concentrations above 1.5 mg/L were measured. Referring to Figure 5-3, the difference between the two locations is obvious. An increasing total phosphorus concentration shows at the Horstermeer WWTP, an increase in orthophosphorus (green bars) and in metal-bound phosphorus (red bars), but shows for the Leiden Zuidwest WWTP only an increase in orthophosphorus. The total amount of organic phosphorus increased between the fractions 0.0 mg/L – 0.5 mg/L and 1.0 mg/L – 1.5 mg/L. The total increase for the Horstermeer WWTP was 0.07 mg/L, and for the Leiden Zuidwest WWTP 0.06 mg/L.

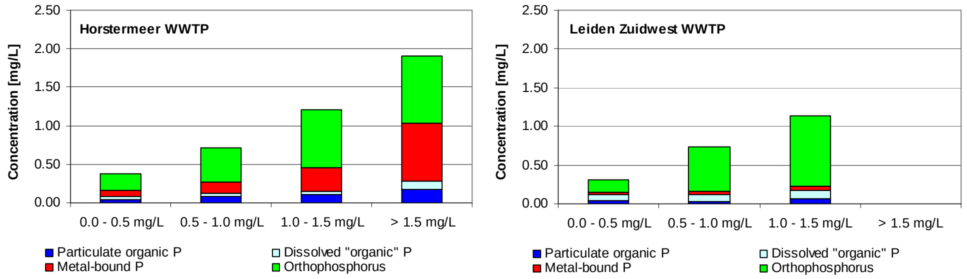


Figure 5-3 – Phosphorus distribution per concentration range for the Horstermeer WWTP (left) and the Leiden Zuidwest WWTP (right)

The results shown in Figure 5-3 lead to Figure 5-4, which shows, for the Horstermeer WWTP (left graph), a linear relationship between the total phosphorus concentration and the unfiltered orthophosphorus concentration (sum of orthophosphorus and metal-bound phosphorus). For the Leiden Zuidwest WWTP, a linear relationship between the total phosphorus concentration and orthophosphorus concentration (right graph) is shown. From this linear relationship it can be concluded that the organic phosphorus concentration is quite stable.

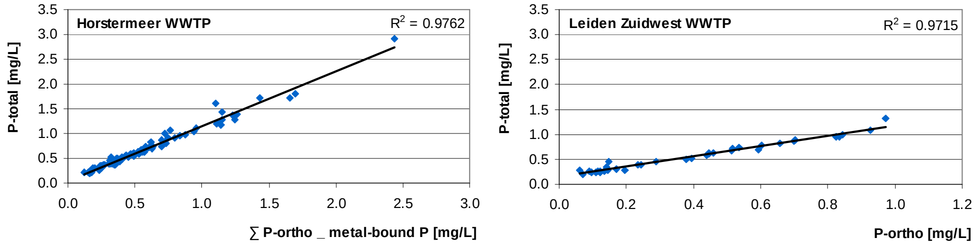


Figure 5-4 – Relationship between total phosphorus and the sum of orthophosphorus and metal-bound phosphorus for the Horstermeer WWTP (left graph) and the relationship between total phosphorus and orthophosphorus for the Leiden Zuidwest WWTP (right graph)

5.1.2 Characterisation for other locations

The WWTP Nieuw-Vossemeer, a treatment plant of Waterschap Brabantse Delta, treats the wastewater of 3,361 population equivalents (per p.e. 136 g TOD) living in the area of West-Brabant. The main flow of the WWTP is 730 m^3/day. The treatment plant consists of grit removal, an oxidation ditch and final sedimentation. Phosphorus is chemically removed with polyaluminium chloride. In the period July 2009 to February 2010, in total 8 phosphorus distributions were made. In this subsection the average results are described.

Table 5-3 and Figure 5-5 show the average concentrations and percentages for orthophosphorus, dissolved "organic" phosphorus, particulate organic phosphorus and metal-bound phosphorus for the WWTP Nieuw-Vossemeer. The average results show that 79% of the total phosphorus is orthophosphorus (green areas), 8% is metal-bound phosphorus (red areas), 5% is particulate organic phosphorus (dark blue areas) and 8% is dissolved "organic" phosphorus (light blue areas).

Table 5-3 – Average (8 samples) phosphorus distribution for effluent of the WWTP Nieuw-Vossemeer. The average total phosphorus concentration was 0.55 mg/L

Location	Unit	Ortho-phosphorus	Dissolved "organic" P	Particulate organic P	Metal-bound P
WWTP Nieuw-Vossemeer	mg/L	0.44	0.05	0.03	0.04

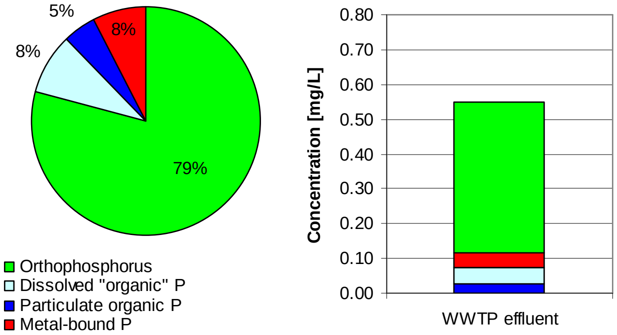


Figure 5-5 - Average (8 samples) phosphorus distribution for effluent of the WWTP Nieuw-Vossemeer

In July 2009 Waternet made phosphorus distributions according to the TU Delft phosphorus distribution method for all their wastewater treatment plants. Table 5-4 and Figure 5-6 display the results for the Westpoort WWTP, the Amsterdam West WWTP, the Blaricum WWTP, the Uithoorn WWTP and the De Ronde Venen WWTP. The treatment plants of Blaricum and Uithoorn make use of chemical phosphorus removal; the treatment plants of Westpoort, Amsterdam West and De Rond Venen make use of biological phosphorus removal. The dissolved organic phosphorus varies between 0.07 – 0.16 mg/L, which is comparable with the results found during the STOWA (2009) research.

Although the phosphorus distribution made for the treatment plants all consist of only one measurement, the results clearly show that a phosphorus distribution is site specific.

Especially for orthophosphorus and for particulate organic phosphorus, wide variations may be found between different locations.

Table 5-4 – Phosphorus distribution for the effluent of the WWTPs of Waternet

Location	Unit	Ortho-phosphorus	Dissolved "organic" P	Particulate organic P	Metal-bound P
Westpoort WWTP	mg/L	0.244	0.106	0.145	0.055
Amsterdam West WWTP	mg/L	0.169	0.161	0.076	0.034
Blaricum WWTP	mg/L	0.537	0.103	0.030	0.020
Uihoorn WWTP	mg/L	0.459	0.081	0.194	0.056
Ronde Venen WWTP	mg/L	0.210	0.070	0.192	0.078

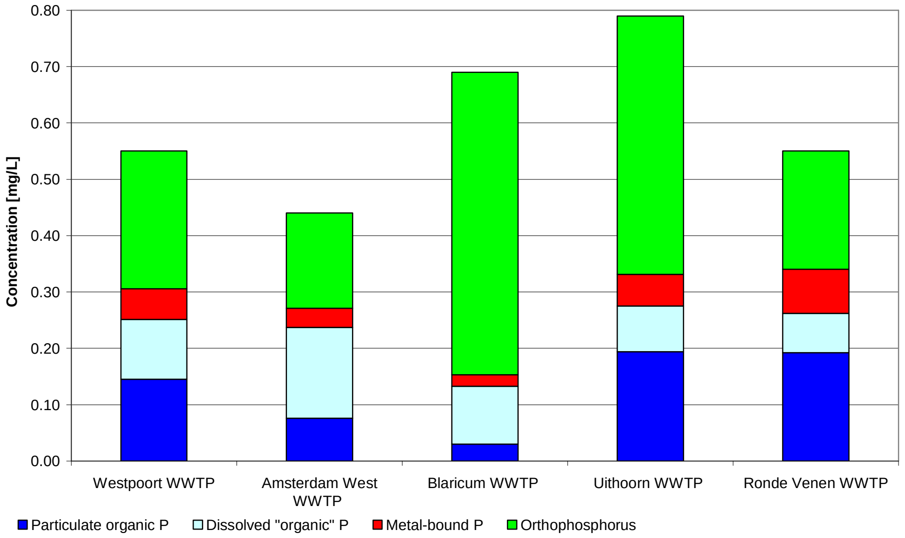


Figure 5-6 – Phosphorus distribution for the Westpoort WWTP, the Amsterdam West WWTP, the Blaricum WWTP, the Uithoorn WWTP and the Ronde Venen WWTP. All WWTPs of Waternet, July 2009.

5.2 Coagulation and flocculation

Before providing the results, an important remark needs to be made about the use of sample points or taps when taking samples for phosphorus distributions and fractionations to investigate, for example, on the influence of the minimum initial mixing energy. According to Bratby (2006), a sharp decline in a velocity gradient, for example from 1000 s^{-1} to 100 s^{-1}, can have a detrimental effect on the water quality. But a tap itself will have a high head loss leading to a high velocity gradient, which will be approximately 2100 s^{-1}. This is calculated for a fully open tap with a diameter of 10 mm, a flow of 0.18 m^3/h and a water temperature of 15° C. Due to this high velocity gradient, formed flocs will break down in the tap and, as a result, the outcome of a phosphorus size fractionation will give a distorted image. Therefore, the upper water layer was chosen as a sample point for all the experiments.

Futhermore the upper water layer can be regarded to be a more or less completely mixed tank. A disadvantage of using the upper water layer as a sample point is that the processes of coagulation and flocculation cannot be investigated as separate processes but are always combined.

This section is divided into 5 subsections. Subsection 5.2.1 describes the jar tests which were conducted. Subsection 5.2.2 describes the results of the experiments which were conducted to investigate the minimum required initial mixing energy. These experiments were conducted at the Horstermeer WWTP and at the Leiden Zuidwest WWTP. Changes in the phosphorus distribution due to coagulation and flocculation processes are described in Subsection 5.2.3 and the changes in the phosphorus size fractionation are described in Subsection 5.2.4. Finally, the floc growth and the minimum required flocculation time are described in Subsection 5.2.5.

5.2.1 Jar tests

As described in Subsections 3.1.4 for the Horstermeer WWTP and 3.2.5 for the Leiden Zuidwest WWTP, jar tests were conducted to estimate the type of coagulant. The results of the jar tests for the Horstermeer WWTP (Miska-Markusch, 2009) showed for polyaluminium chloride (PACl) higher removal efficiencies compared to ferric(III)chloride. This is probably due to the low pH of the WWTP effluent, which is pH 6.8 on average. For the Leiden Zuidwest WWTP, the preliminary jar tests gave the best results for ferric(III)chloride ($FeCl_3$). The pH of the WWTP effluent is on average pH 7.0.

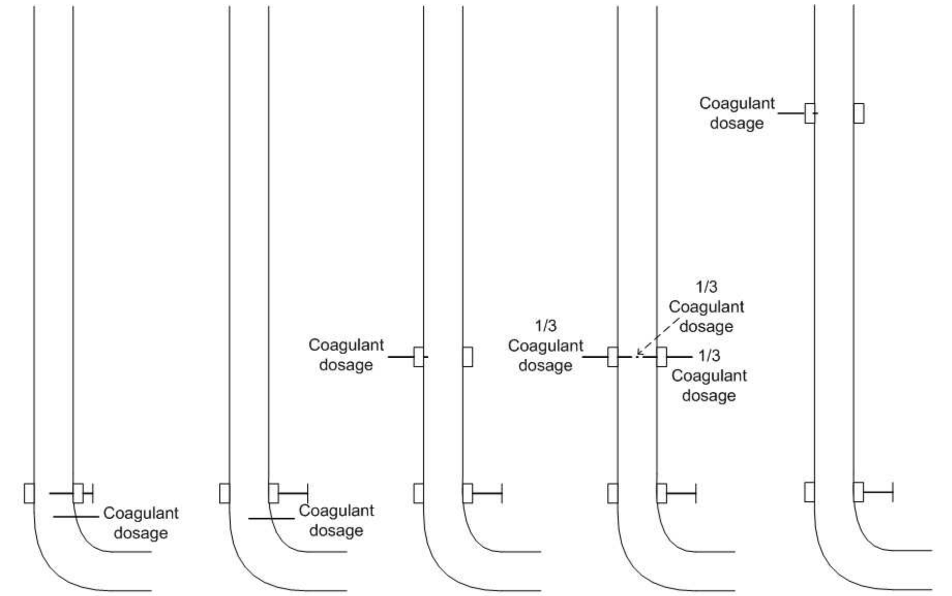
5.2.2 Minimum initial mixing energy

Research to determine the minimum required mixing energy which is needed to bind all orthophosphorus was conducted at the Horstermeer WWTP and at the Leiden Zuidwest WWTP. Although the results led to the same conclusion, both experiments are described since the experimental situation differed greatly. It should be kept in mind that samples taken from the upper water layer were taken in the top layer of the water body which is near the inlet of the filter and, therefore, the samples represent the phosphorus distribution after coagulation.

The Horstermeer WWTP

In 2008 phosphorus distributions were made in the upper water layer of the dual media filter to define the influence of the initial mixing energy on orthophosphorus binding. The pH of the water varied between pH 6.03 and pH 7.15 and the temperature varied between 10° C and 22° C. The filtration rate used was 10 m/h. The metal/orthophosphorus ratio varied between 1 and 5. Samples were taken in the upper water layer of the filter. In total 35 measurements were conducted with 5 different settings (Figure 5-7):

- Gate valve 70% closed, G-value of 1000 s^{-1}
- Gate valve fully open, G-value of 120 s^{-1}
- Injection ring 0.5 m from the corner, 1 injection point along the wall side
- Injection ring 0.5 m from the corner, 3 injection points in the centre of the pipe
- Injection ring 1.0 m from the corner, 1 injection point along the wall side



Gate valve 70% closed

Gate valve fully open

Injection ring 0.5 m from the corner, 1 injection point along the wall side

Injection ring 0.5 m from the corner, 3 injection points in the centre of the pipe

Injection ring 1.0 m from the corner, 1 injection point along the wall side

Figure 5-7 – Different experimental settings to define the influence of the initial mixing energy

By choosing 1 injection point along the wall side and 3 injection points in the centre of the pipe, two opposite situations were examined. The measurements for the injection points 0.5 metres and 1.0 metres after the corner are conducted to determine the effect of the corner on the mixing.

Figure 5-8 shows the concentration Al^{3+}, which is dosed, on the horizontal axis, and shown on the vertical axis the concentration orthophosphorus in the upper water layer which is bound and converted to metal-bound phosphorus. The concentration Al^{3+} is used instead of the orthophosphorus concentration in the feed water because the metal/orthophosphorus ratio varied between 1 and 5 mol/mol. The figure shows for coagulant dosage with the injection ring a larger spread in the measurements compared to dosage just before the gate valve. The orthophosphorus concentration converted to metal-bound phosphorus is mostly lower for dosage with the injection ring compared to dosage before the gate valve. The difference between the initial mixing energy of 120 s^{-1} and 1000 s^{-1} is minimal for the gate valve. The results for the measurements for the injection ring 1.0 m from the corner do not show a decrease in converted orthophosphorus. The cause might be that the effect of the corner is noticeable for several meters.

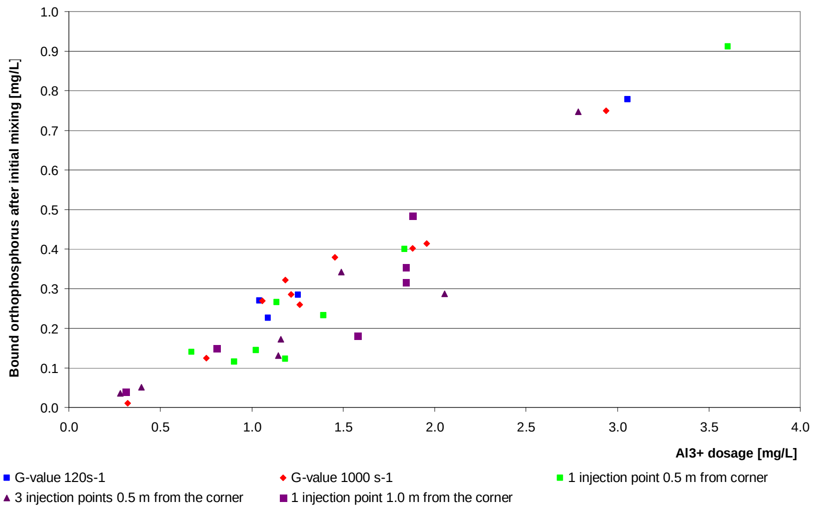


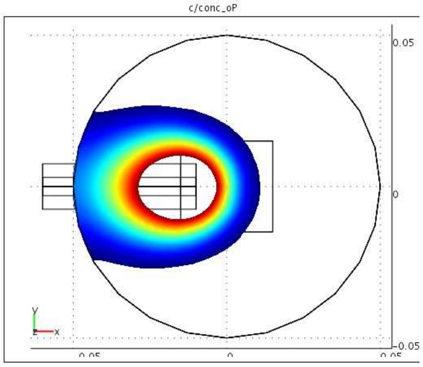
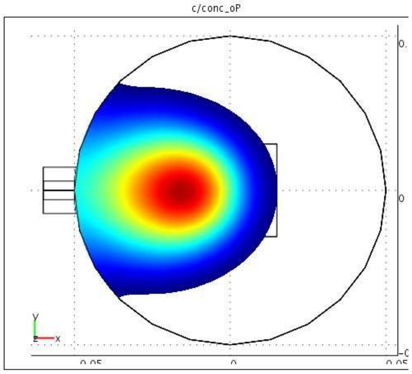
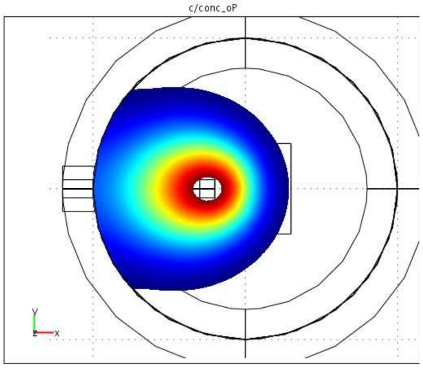
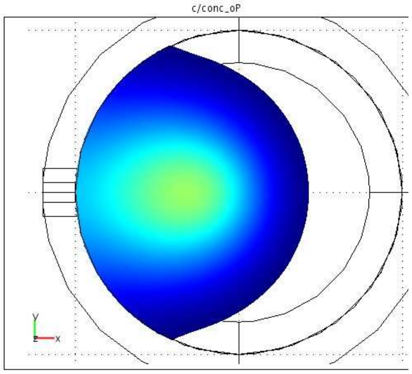
Figure 5-8 - Influence of the initial mixing energy on the orthophosphorus binding

To estimate the effect of the corner on the initial mixing, three cases were simulated with computational fluid dynamics (CFD) modelling (De Niet, 2008). The first case (c1) was a simulation of the situation without a gate valve and a long pipe without a corner. The second case (c2) was a simulation of a long straight pipe with a gate valve and the third simulation (c3) was made for the situation with a gate valve and a corner. The model made simulates the orthophosphorus which is bound to aluminium (Al^{3+}) after a certain distance after dosage. The Al^{3+}/orthophosphorus ratio which was used for the simulation was approximately 4 mol/mol. The flow was calculated with the k-epsilon turbulence model of Comsol Multiphysics 3.5. The calculations dealing with the aluminium concentrations were based on a convection-diffusion equation. In this equation the diffusion is caused by turbulence.

In Table 5-5 the percentage of orthophosphorus which was converted to metal-bound phosphorus (bound to Al^{3+}) is shown. These percentages were calculated by the cross-sections where the Al^{3+} concentration was higher compared to the orthophosphorus concentration. This is the part where orthophosphorus was completely bound. For the areas where Al^{3+}/orthophosphorus ratios were < 1 mol/mol, the ratio was used to calculate the percentage which was converted to metal-bound phosphorus. The sum of the percentages for a complete binding of orthophosphorus and where orthophosphorus was partly bound is displayed in Table 5-5. Results show that the influence of the corner is significant. The percentage of bound orthophosphorus for c3 after dosage is, for all distances, higher compared to the other cases. In c3 almost all the orthophosphorus is bound to Al^{3+} after 0.5 m.

Table 5-5 - Percentage orthophosphorus converted to metal-bound phosphorus (De Niet, 2008)

Cases	**c1**	**c2**	**c3**
0.05m (0.18 s) from the injection point	16	17	24
0.28m (0.99 s) from the injection point	41	55	81
0.50m (1.77 s) from the injection point	54	74	98

	After 0.28 m (0.99 s)	**After 0.50 m (1.77 s)**
c1		
c2		

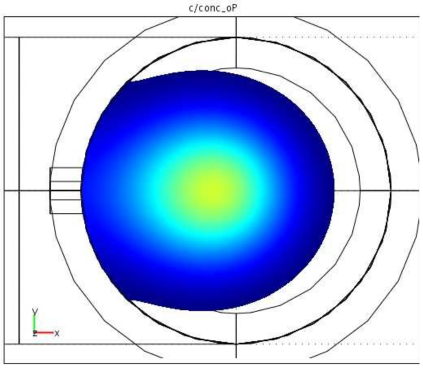
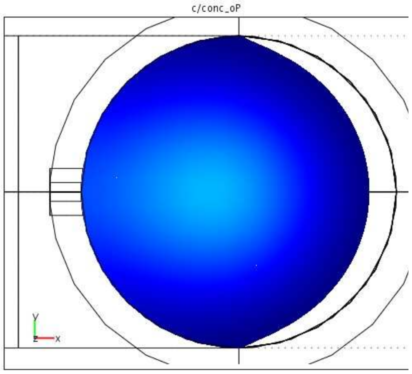
	After 0.28 m (0.99 s)	**After 0.50 m (1.77 s)**
c3		

Figure 5-9 - Ratio of the Al^{3+} concentration and the orthophosphorus concentration at 0.28and 0.5 meters after injection (De Niet, 2008)

Figure 5-9 shows the ratios of the Al^{3+} concentration and the orthophosphorus concentration at 0.28 and 0.5 meters after injection. The figures show the injection point on the left side of the cross-section. The non-colored areas represent an Al^{3+}/orthophosphorus ratio <1 mol/mol. In this area, most certainly no orthophosphorus will be bound to aluminium. The colored areas represent an Al^{3+}/orthophosphorus ratio >1 mol/mol. In the colored areas, orthophosphorus will be bound to Al^{3+}. The red color represents the highest ratio which is 4 mol/mol. The Al^{3+}/orthophosphorus ratio decreases with an increasing distance from the injection point since Al^{3+} reacts with orthophosphorus. The dark blue color represents the areas where the Al^{3+}/orthophosphorus is 1 mol/mol.

The Leiden Zuidwest WWTP

In January and February 2008 phosphorus size fractionations and distributions with an initial mixing of 300 s^{-1} and 2,000 s^{-1} were made. The pH of the effluent was ±7.0, the temperature varied between 12°C and 13°C. The filtration rate used was 10 m/h and the metal/orthophosphorus ratio used was 4 mol/mol. The results show how the phosphorus size fractionations and phosphorus distributions are independent of the initial mixing energy and show the effect of increasing orthophosphorus concentrations in the filtrate of the CFB (feed water). Samples were taken of the filtrate of the continuous sand filter B, of the upper water layer in the dual media filter and of the filtrate of the dual media filter. Street A was not researched.

Figure 5-10 shows the phosphorus size fractionations which were made for an initial mixing of 300 s^{-1} and 2,000 s^{-1}. For both tested initial mixing energies, the phosphorus percentage for each fraction is set out against the orthophosphorus concentration in the filtrate of the CFB (feed water). The graphs with a marker belong to 300 s^{-1} and the graphs without a marker belong to 2,000 s^{-1}. The results show that the distribution of the phosphorus over the forms is independent on the initial mixing. This is concluded because the graphs of 300 s^{-1} and 2,000 s^{-1} are quite similar. The figure shows that the orthophosphorus concentration in the filtrate of the CFB (feed water) had a major influence on the deviation of the phosphorus over the different forms. With an increasing orthophosphorus concentration in the filtrate of the CFB, the percentages of orthophosphorus between 2 – 0.45 µm decreased (red graphs) and the percentages of orthophosphorus between 10 – 2 µm increased (green graphs). The fractions >10 µm and <0.45 µm are nearly constant. It needs to be taken into account that the coagulant dosage ratio is constant, which implies that the Fe^{3+}concentration (mg/L) increases with an increasing orthophosphate concentration.

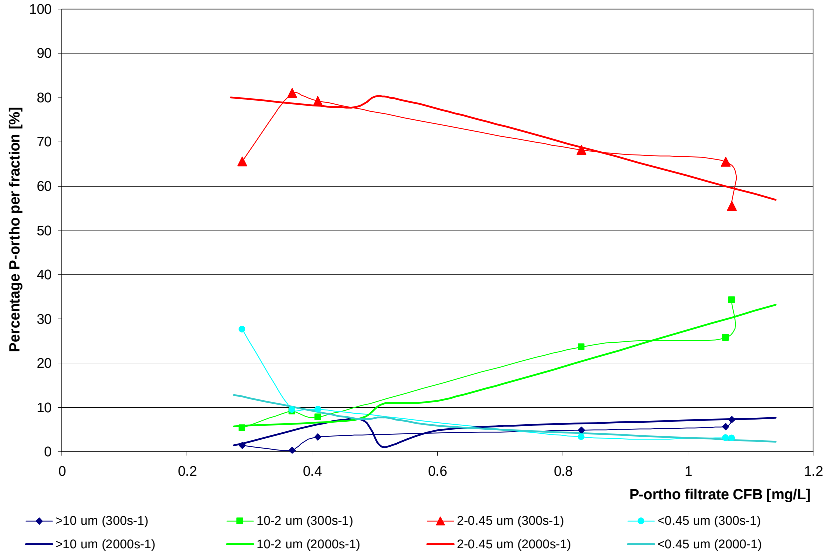


Figure 5-10 - Results of the phosphorus forms made for an initial mixing of 300 s^{-1} and 2000 s^{-1} measured with different orthophosphorus concentrations in the filtrate of the CFB (Van den Berg van Saparoea, 2008)

Figure 5-11 shows the results of the phosphorus distribution for an initial mixing of 300 s^{-1} and 2,000 s^{-1}. The graph shows the phosphorus concentration of each phosphorus form relative to the orthophosphorus concentration in the filtrate of the CFB (feed water). The graphs without a marker belong to an initial mixing energy of 300 s^{-1} and the graphs with a marker to 2,000 s^{-1}.

The results show that the phosphorus distribution is independent of the initial mixing. This can be concluded because the graphs for an initial mixing of 300 s^{-1} and 2,000s^{-1} are nearly the same. The orthophosphorus concentration in the filtrate of the CFB (feed water) is an influence on the phosphorus distribution. The metal-bound phosphorus concentration (red graphs) in the upper water layer of the dual media filter increased with increasing orthophosphate concentrations in the filtrate of the CFB (feed water). Dissolved “organic” phosphorus, particulate “organic” phosphorus and orthophosphate remained constant with an increasing orthophosphate concentration (green, dark blue and light blue graphs).

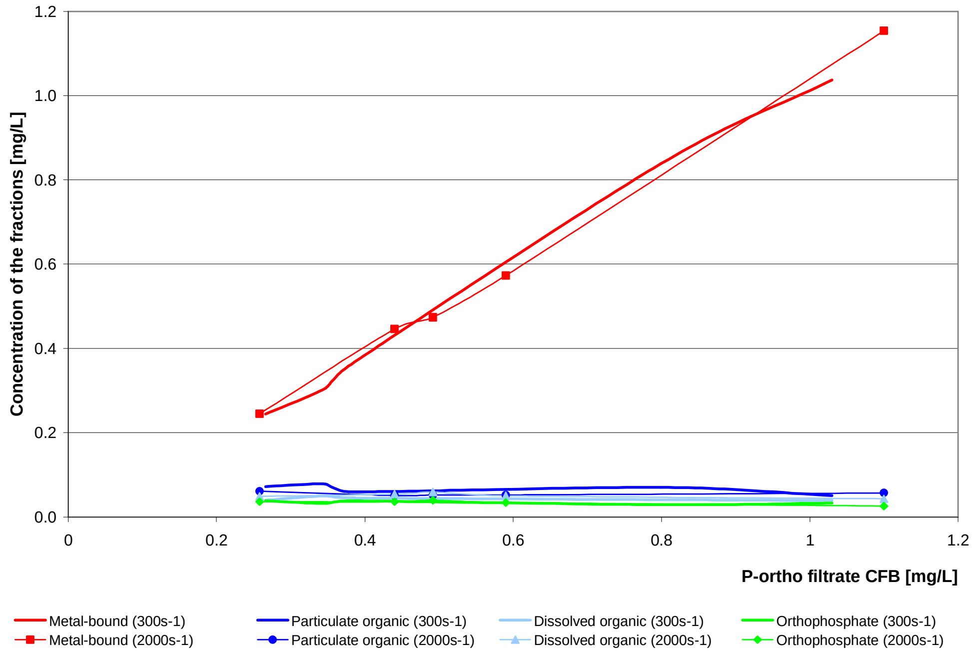


Figure 5-11 - Results of the phosphorus distributions made for an initial mixing of 300 s^{-1} and 2,000 s^{-1} with different orthophosphate concentrations in the filtrate of the CFB (Van den Berg van Saparoea, 2008).

5.2.3 Changes of the phosphorus distribution after coagulation

In the period from March to November 2008 a total of 13 phosphorus distributions were made for the 1-STEP® filter. The average results are shown in Figure 5-12. All phosphorus distributions were made with an Al^{3+}/P-ortho ratio of 4 mol/mol and a filtration rate of 10 m/h. The figure shows the phosphorus distribution for the WWTP effluent and the upper water layer of the filter. The results are shown in concentrations and in percentages.

The top graph in Figure 5-12 shows a small increase of 0.09 mg/L for the total phosphorus concentration in the upper water layer compared to the WWTP effluent. More information about the cause of this increase is described in Subsection 4.4.2. Apart from the higher total phosphorus concentration, the top graph shows that nearly all the orthophosphorus (green bar left column) is bound to metal ions after coagulation. This is seen by the remaining green bar for the upper water layer and the increase in the red bar. The dissolved “organic” phosphorus decreased after coagulation and the particulate organic phosphorus increased, which suggests that a part of the dissolved “organic” phosphorus is colloidal or associated with colloidal material (Stevens and Stewart, 1982).

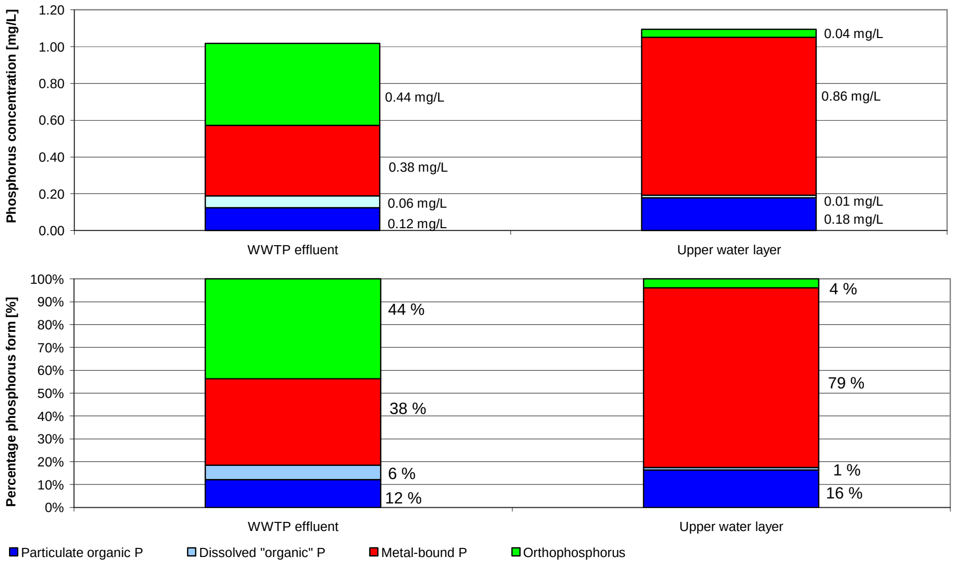


Figure 5-12 – Average (13 measurements) phosphorus distribution for WWTP effluent and the upper water layer of the 1-STEP®

The bottom graph in Figure 5-12 shows that the total phosphorus in the WWTP effluent consists of 44% orthophosphorus, of 38% metal-bound phosphorus, of 6% dissolved “organic” phosphorus and of 12% particulate organic phosphorus. In the upper water layer, the distribution shows that the total phosphorus in upper water layer consists of 4% orthophosphorus, of 79% metal-bound phosphorus, of 1% dissolved “organic” phosphorus and of 16% particulate organic phosphorus.

5.2.4 Changes of the phosphorus size fractionation by coagulation

At the Horstermeer WWTP as well as at the Leiden Zuidwest WWTP, phosphorus size fractionations are frequently made. Samples were taken in the upper water layers of the fixed-bed filters at both locations. Figure 5-13 shows results which are representative for the dataset. The phosphorus size fractionation of the 1-STEP® at the Horstermeer WWTP (left graph) was made the 23rd of March 2008 with a metal/orthophosphorus ratio of 4 mol/mol and a filtration rate of 10 m/h. The phosphorus size fractionation of the dual media filter at the Leiden Zuidwest WWTP (right graph) was made on the 29th of January 2008 with a metal/orthophosphorus ratio of 4 mol/mol and a filtration rate of 10 m/h.

The red bars in the graphs of Figure 5-13 show the phosphorus size fractionation of the WWTP effluent, the blue bars show the phosphorus size fractionation in the upper water layer after coagulant dosage. The fractionation of the effluent of the Horstermeer WWTP (left graph, red bars) illustrate that the phosphorus is distributed over all the fractions. The largest fraction is <0.45 μm which means that most of the present phosphorus is orthophosphorus. The second largest fraction is >10 μm; from this it can be concluded that the secondary sedimentation tank does not efficiently remove the metal-bound phosphorus flocs formed in the main process of the treatment plant. After coagulant dosage the distribution over the fractions changes (left graph, blue bars). Almost all the present orthophosphorus is bound to the metal ions; this can be seen by the large decrease in the phosphorus in the fraction <0.45 µm. In the upper water layer approximately 20% of the phosphorus is within the fraction 0.45 – 2 µm, 20% is within the fraction 2 – 10 µm and by far the most, approximately 40%, is in the fraction >10 µm.

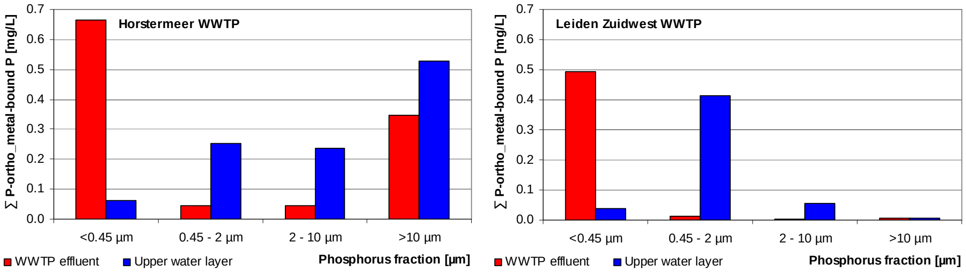


Figure 5-13 – Phosphorus size fractionations for the WWTP effluent and the upper water layer of the Horstermeer WWTP (1-STEP® filter) and the Leiden Zuidwest WWTP (dual media filter). The used metal/orthophosphorus ratio used was 4 mol/mol and had a filtration rate of 10 m/h.

The results of the Leiden Zuidwest WWTP show the same effect, specifically a large decrease in the phosphorus <0.45 µm in the upper water layer after coagulant dosage. A difference in the results of the Horstermeer WWTP is that nearly all the phosphorus in the WWTP effluent is orthophosphorus, seen in the fraction <0.45 µm. This corresponds to the results of the phosphorus distributions described in Section 5.1. Another difference is the distribution over the fractions in the upper water layer. At the Leiden Zuidwest WWTP, flocs do not become larger than 10 µm.

Figure 5-14 illustrates the relationship between the ferric(III)chloride dosage and the average size of the formed flocs in the upper water layer of the dual media filter at the Leiden Zuidwest WWTP (January and February 2008). In the graph the estimated floc size is set out against the ferric(III)chloride dosage. The metal/orthophosphorus was 2, 4 and 8 mol/mol. The graph clearly shows that the estimated floc size increased with an increasing dosage. As already stated in Subsection 5.2.2, the initial mixing energy had no influence on the phosphorus size fractionation.

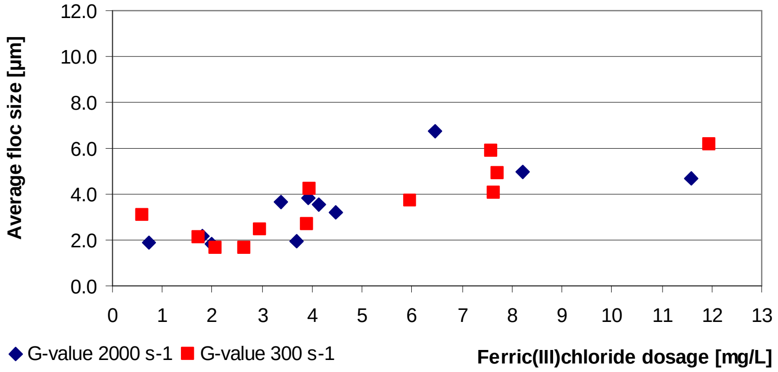


Figure 5-14 – Relationship between ferric(III)chloride dosage and the estimated floc size of the formed metal-bound phosphorus for the dual media filter at the Leiden Zuidwest WWTP. The metal/orthophosphorus ratios used were 2, 4 and 8 mol/mol (Scherrenberg et al., 2008)

5.2.5 Floc growth with a minimum and maximum flocculation time

The influence of the flocculation time on the estimated floc size was investigated at the Leiden Zuidwest WWTP because flocculation tanks with a total flocculation time of 14 minutes were available, in addition to the 10-minute flocculation time in the upper water layer of the dual media filter. This is the maximum available flocculation time for a filtration rate of 10 m/h. The applied shear force in the flocculation tanks under these circumstances is 50 s^{-1}. Phosphorus size fractionations were made for samples taken from the upper water layer. Since the samples were taken from the upper water layer, they represent the phosphorus size fractionation after the flocculation tanks, including the flocculation time of 10 minutes in the upper water layer. When samples are taken with a tap just above the anthracite layer (including the 10 minutes of flocculation time in the upper water layer), flocs will break due to the high G-values in the tap and will therefore give an incorrect phosphorus size distribution. The estimated floc sizes for the situation of 10-minute and 24-minute flocculation time are set out against the ferric(III)chloride dosage. The concentration Fe^{3+} was used instead of the orthophosphorus concentration in the feed water because the metal/orthophosphorus ratio varied during the experiments. This is shown in Figure 5-15. The average temperature of the water was 12.5°C in combination with pH 7.0.

Figure 5-15 shows that the estimated floc size with a flocculation time of 24 minutes is approximately 7 – 12 µm, which is larger compared to the size of flocs formed with a flocculation time of 10 minutes. These flocs are approximately 2 – 5 µm.

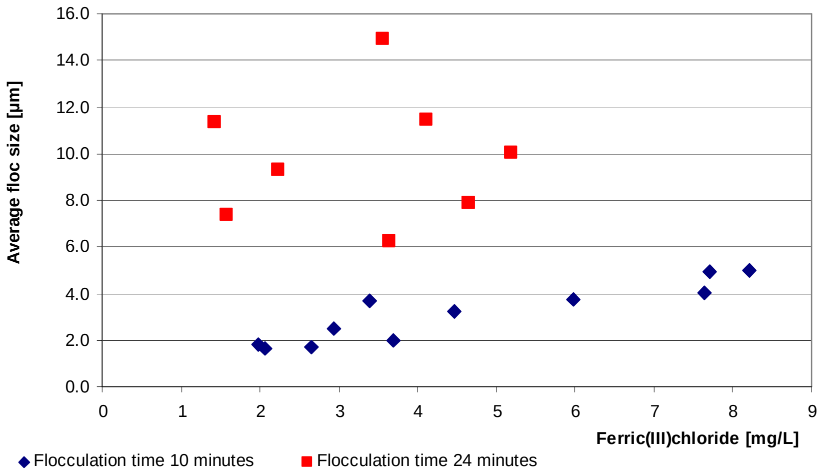


Figure 5-15 – The estimated floc size set out against the ferric(III)chloride dosage for a minimum flocculation time of 10 minutes and a maximum flocculation time of 24 minutes at the Leiden Zuidwest WWTP (Scherrenberg et al., 2008)

5.3 Summary

The results for the characterisation of the WWTP effluent show that the phosphorus distribution is site specific. Temperature, seasonal and pH influences on the phosphorus distribution were not found. A linear relationship between the total phosphorus concentration and the unfiltered orthophosphorus (sum of orthophosphorus and metal-bound phosphorus) or the filtered orthophosphorus might be found.

The initial mixing energy had no influence on the phosphorus size fractionation and phosphorus distribution in the upper water layer of a fixed bed filter. This means that the initial mixing energy of 300 s^{-1} is satisfactory. Coagulant dosage in combination with a 90° bent may already be satisfactory to have a good mixture of coagulant with the water.

After coagulation orthophosphorus is bound to metal ions and forms metal-bound phosphorus. The dissolved “organic” phosphorus decreased after coagulation and the particulate organic phosphorus increased, which suggests that part of the dissolved “organic” phosphorus may be colloidal or associated with colloidal material.

The size of the formed flocs can be influenced by the coagulant dosage and the flocculation time. The results show that the estimated floc size with a flocculation time of 24 minutes is approximately 7 – 12 µm, which is larger compared to the size of flocs formed with a flocculation time of 10 minutes, these flocs are 2 – 5 µm.

5.4 References

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6 Filtration

Granular media filtration, such as continuous sand filtration or fixed bed filtration, is commonly used for the removal of phosphorus precipitates formed during the coagulation and flocculation process. A sand filter (partly) retains suspended solids and ferric and aluminium precipitates, but can also contain biomass for the removal of dissolved substances like nitrate. More information about filtration is presented in Section 2.4. During this research, experiments with regard to the phosphorus removal were conducted with single media filtration (1-STEP® filtration), dual media filtration and continuous sand filtration.

Chapter 6 deals with phosphorus removal in a filter bed with and without biomass. Section 6.1 describes the results of filtration without biomass in the filter bed. Section 6.2 describes the results of filtration with biomass. A comparison of the results for filtration with and without biomass is given in Section 6.3. The results of 1-STEP® filtration are described in a separate paragraph; this is Section 6.4. An overview of phosphorus removal with different techniques and process circumstances is given in Section 6.5.

6.1 Filtration without biomass in the filter bed

Filtration without biomass was mainly tested in Street B at the Leiden Zuidwest WWTP where continuous sand filtration is used as a first step for denitrification and dual media filtration as a second step for phosphorus removal. The results for filtration without biomass contain phosphorus distributions, phosphorus size fractionations, profile measurements and on-line data.

This section is divided into six subsections. Subsection 6.1.1 describes the influence of filtration on the phosphorus distribution. Subsection 6.1.2 describes how the phosphorus size fractionation changes as a result of the filtration process. The results for the optimal filtration rate are described in Subsection 6.1.3. The influence of the floc size on the phosphorus removal by the filter bed is described in Subsection 6.1.4. This paragraph ends with Subsection 6.1.5 which is about the influence of the filter runtime on phosphorus removal.

6.1.1 Changes in the phosphorus distribution after filtration

From October 2007 to January 2008, 11 phosphorus distributions were made for the dual media filter (fine filter bed) at the Leiden Zuidwest WWTP. The average results are shown in Figure 6-1. All phosphorus distributions were made with Fe^{3+}/orthophosphorus ratios of 4 mol/mol and a filtration rate of 10 m/h. The graph shows the phosphorus distribution into particulate organic phosphorus (dark blue bars), dissolved “organic” phosphorus (light blue bars), metal-bound phosphorus (red bars) and orthophosphorus (green bars) for the filtrate of the Continuous Sand Filter B, after coagulation in the top layer of the upper water layer and the filtrate of the dual media filter.

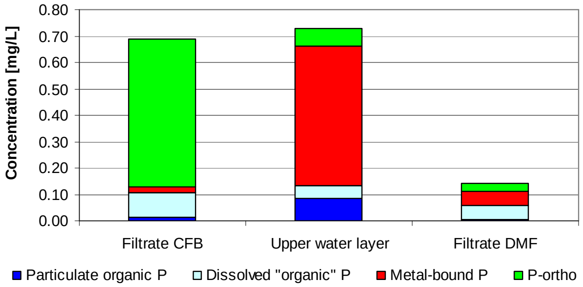

Figure 6-1 – Average (11 samples) phosphorus distribution for the filtrate of CFB, after coagulation in the upper water layer and the filtrate of the dual media filter (Filtrate DMF) for the Leiden Zuidwest WWTP (fine filter bed)

Figure 6-1 shows a small increase of 0.013 mg/L for the total phosphorus concentration after coagulation compared to the filtrate of CFA (see Subsection 5.2.3). The graph clearly shows that the majority of the orthophosphorus (green bar left column) is bound to metal ions after coagulation (see the remaining green bar in the middle column). A large part of the metal-bound phosphorus, approximately 90%, was removed in the filter bed (see the remaining red bar right column). Approximately 60% of the remaining orthophosphorus concentration in the upper water layer was also removed in the filter bed. This 60% was probably colloidal metal bound phosphorus and therefore measured as orthophosphorus. The dissolved “organic” phosphorus decreased after coagulation and the particulate organic phosphorus increased after coagulation, which suggests that it may be colloidal or associated with colloidal material (Stevens and Stewart, 1982). Most of the particulate organic phosphorus, approximately 87%, was removed in the filter bed. Dissolved “organic” phosphorus will pass through the filter bed.

6.1.2 Changes in the phosphorus size fractionation after filtration

At the Horstermeer WWTP phosphorus size fractionations were made for the dual media filter without methanol dosage. Two situations are compared, namely no coagulant dosage and a constant coagulant dosage, which was 2 mg/L. The filtration rate used was 10 m/h in both situations.

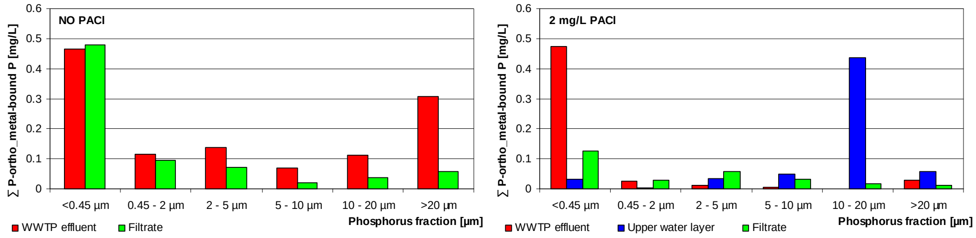

Figure 6-2 – Phosphorus size fractionation of WWTP effluent, upper water layer and dual media filtrate of the Horstermeer WWTP. No coagulant and no methanol dosage, 11 May 2007 (left graph) and 2 mg/L PACl dosage 1 June 2007 (right graph).

The results are illustrated in Figure 6-2, with the phosphorus size fractionation without coagulant dosage on the left side and the phosphorus size fractionation with a dosage of 2 mg/L on the right. The red bars indicate the results for the WWTP effluent, the blue bars for the upper water layer and the green bars for the filtrate. The results show for the situation without coagulant dosage that orthophosphorus (< 0.45 μm) was not removed in the filter bed. A small removal was found for phosphorus in the fraction of 0.45 – 2 μm. The other fractions show at least a removal rate of 50%. With a constant PACl dosage of 2 mg/L, approximately 75% of the orthophosphorus in the WWTP effluent was removed in the filter bed. An increase in the phosphorus concentration can be seen in the fractions 0.45 – 2 μm, 2 – 5 μm and 5 – 10 μm. Phosphorus in the fractions 10 -20 μm and >20 μm were nearly completely removed. On the 1st of June 2007, the estimated floc size in the WWTP effluent was 26.0 μm, in the upper water layer 18.0 μm, and in the dual media filtrate 9 μm.

6.1.3 Optimal filtration rate

The optimal filtration rate was investigated with the dual media filter (fine filter bed) at the Leiden Zuidwest WWTP. Three different filtration rates were tested, namely 10 m/h, 15 m/h and 20 m/h. The metal/orthophosphorus ratio was 7.5 mol/mol for an orthophosphorus concentration in the WWTP effluent of <0.15 mg/L and 4 mol/mol for orthophosphorus concentrations of >0.15 mg/L. The results are shown in Figure 6-3: the red bars represent the total phosphorus concentration in the WWTP effluent, the green bars represent the total phosphorus concentration in the filtrate water for a filtration rate of 10 m/h, the dark blue bars represent 15 m/h and the light blue bars represent 20 m/h. On-line data were used to construct Figure 6-3; the number of data points per average value varied between 300 and 7000. Figure 6-4 shows the removal efficiency for total phosphorus for the different concentration areas. In this figure the green dots represent the removal efficiency for a filtration rate of 10 m/h, the dark blue dots for a filtration rate 15 m/h and the light blue dots for 20 m/h.

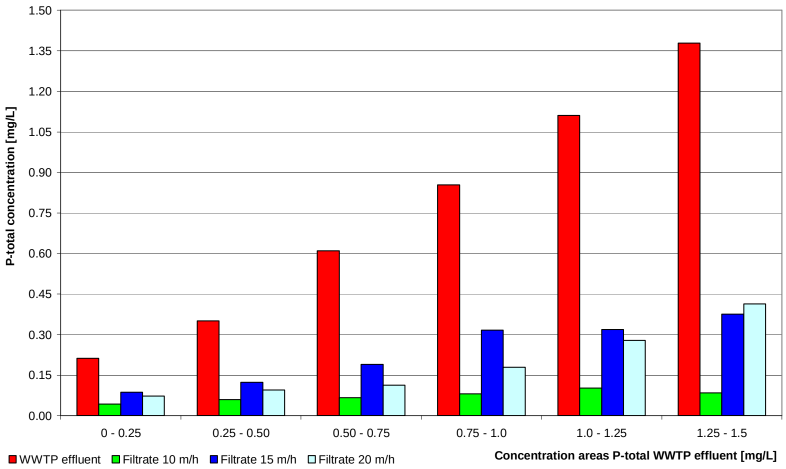

Figure 6-3 – Average phosphorus removal for the dual media filter at the Leiden Zuidwest WWTP (fine filter bed) for 10, 15 and 20 m/h (STOWA, 2009a)

Figure 6-3 shows that a filtration rate of 10 m/h (green bars) results in a very small increase in the total phosphorus concentration in the filtrate, from 0.04 mg/L to 0.1 mg/L for increasing total phosphorus concentrations in the feed water. The removal efficiency (Figure 6-4) for filtration with 10 m/h was between 80% and 94%. For a filtration rate of 15 m/h (dark blue bars), the total phosphorus concentration in the filtrate increases from 0.09 mg/L to 0.38 mg/L. Between 0.50 – 0.75 mg/L and 0.75 – 1.0 mg/L a sudden increase in the total phosphorus in the filtrate can be seen (increase of 0.13 mg P-total/L). For total phosphorus concentrations in the feed water above 0.75 mg/L, the total phosphorus concentration in the filtrate remains quite steady. The removal efficiency for filtration with 15 m/h was between 59% and 73%. For a filtration rate of 20 m/h (light blue bars), the relative increase in the total phosphorus concentration in the filtrate is more consistent compared to a filtration rate of 15 m/h. The increase in the total phosphorus concentration is from 0.07 mg/L to 0.41 mg/L for increasing total phosphorus concentrations in the feed water. This more consistent increase results in lower total phosphorus concentrations in the filtrate for a filtration rate of 20 m/h compared to 15 m/h for total phosphorus concentrations in the feed water up to 1.25 mg/L, but the filter runtime decreased with 3 to 4 hours. The removal efficiency for filtration with 20 m/h was between 66% and 81%.

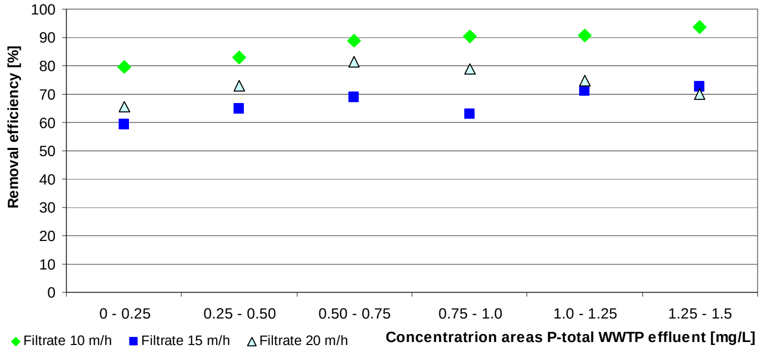

Figure 6-4 – Removal efficiency for the dual media filter at the Leiden Zuidwest WWTP (fine filter bed) for 10, 15 and 20 m/h

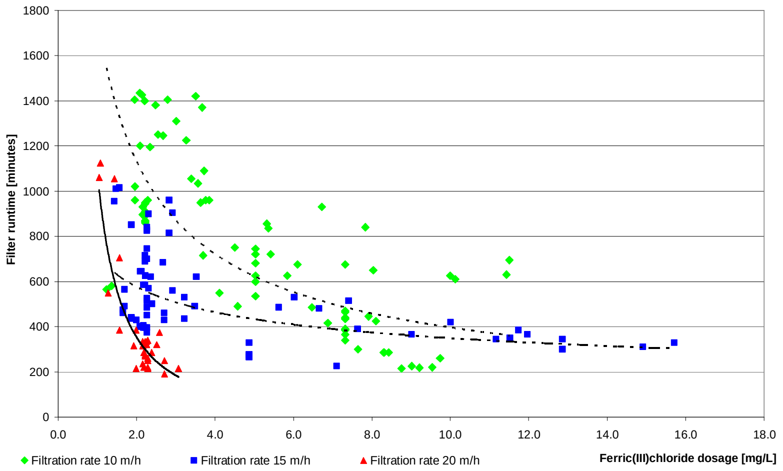

Figure 6-5 – The influence of the coagulant dosage (ferric(III)chloride) on the length of the filter runtime for the dual media filter at the Leiden Zuidwest WWTP (fine filter bed) illustrated for a filtration rate of 10 m/h, 15 m/h and 20 m/h (STOWA, 2009a)

With increasing filtration rates the filter runtime can decrease because the maximum removal capacity is reached. For a filtration rate of 10 to 15 m/h in combination with a metal/orthophosphorus ratio of 4 mol/mol and total phosphorus concentrations in the feed water of < 1.0 mg/L, the average filter runtime is 8 to 10 hours (STOWA, 2009a). The filter runtime depends on the total phosphorus concentration in the feed water. The influence of the coagulant dosage on the length of the filter runtime for a filtration rate of 10 m/h (green dots), 15 m/h (blue dots) and 20 m/h (red dots) is shown in Figure 6-5. The graph shows, for all the tested filtration rates, a decreasing filter runtime with an increasing ferric(III)chloride dosage. The maximum filter runtime was 24 hours (1440 minutes). After this period a backwash started automatically. For a filtration rate of 10 m/h in combination with a maximum ferric(III)chloride dosage of 3.5 mg/L, the maximum filter runtime of

1440 (24 hours) can be reached. A sharp decrease with increasing ferric(III)chloride dosage is seen for a filtration rate of 20 m/h.

6.1.4 Influence of the floc size on the phosphorus removal

The influence of the flocculation time on the estimated floc size was investigated at the Leiden Zuidwest WWTP, where flocculation tanks with a total flocculation time of 14 minutes were available in addition to the 10 minutes of flocculation time in the upper water layer of the dual media filter. The effect of the flocculation time on the phosphorus size fractionation is described in Subsection 5.2.5. The results showed that the estimated floc size with a flocculation time of approximately 24 minutes was 7 – 12 μm which was approximately twice the size of the flocs which were formed with a flocculation time of 10 minutes.

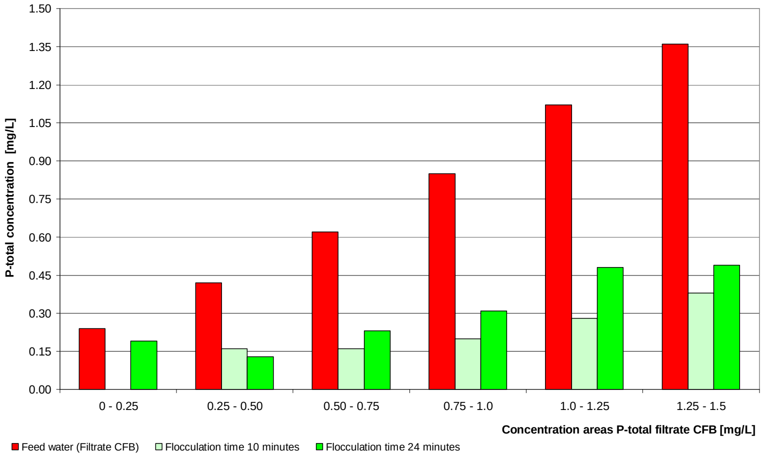

Figure 6-6 – Results for phosphorus removal of the DMF at the Leiden Zuidwest WWTP with a flocculation time of 10 minutes (light green bars) and a flocculation time of 24 minutes (dark green bars) (Scherrenberg et al., 2008)

Figure 6-6 shows the average total phosphorus concentration in the filtrate of the CFB (red bars), in the filtrate water of the dual media filter for a flocculation time of 10 minutes (light green bars), indicating that only the upper water layer is used, and in the filtrate water of the dual media filter for a flocculation time of 24 minutes (dark green bars), which is the maximum flocculation time of the flocculation tanks and the upper water layer together. The figure was constructed with data from the on-line analysers during a two-week period (last week of January and first week of February 2008) with an average metal/orthophosphorus ratio of 4 mol/mol and the fine filter bed in the dual media filter. The figure shows that, for total phosphorus concentration of >0.50 mg/L in the feed water, the larger flocs formed with a flocculation time of 24 minutes do not result in higher removal efficiencies in the filter bed. It even appears that the average total phosphorus concentration after filtration with a maximum flocculation time was higher compared to the situation with a minimum flocculation time.

As described in Subsection 5.2.5, the floc size increases with higher dosage ratios and/or with an increase in flocculation time. According to Yukselen and Gregory (2004) and Gregory (2006), flocs which are formed with higher dosage ratios have a more open structure; because of this structure, flocs can easily fall apart. Flocs which fall apart can partly recover but will not recover to their original size (Yukselen and Gregory, 2004). During filtration high G-values occur in the filter bed, which only increase within the runtime due to a decreasing porosity. Because of these high G-values, flocs with a more open structure can fall apart and breakthrough of the filter bed can occur. This might be the explanation for the decrease in removal efficiency for flocs formed with a maximum flocculation time.

6.1.5 Change of phosphorus removal in the filter bed during the filter runtime

In Figure 6-7 the phosphorus removal of the dual media filter with the fine filter bed at the Leiden Zuidwest WWTP is shown for a three-day period. The figure shows the flow rate (blue graph, secondary y-axis), which is 30 m^3/h during this period. The sharp decreases seen for the flow rate represent the backwashes of the filter bed. A backwash was initiated when the upper water layer exceeded the maximum level, or when the turbidity in the filtrate water was higher than 2 NTU, or when the maximum runtime of 24 hours was exceeded. In total, six backwashes are shown in the graph. The dotted line represents one backwash. The red graph represents the total phosphorus concentration in the WWTP effluent (primary y-axis); the green graph represents the total phosphorus concentration in the filtrate water of the dual media filter (primary y-axis).

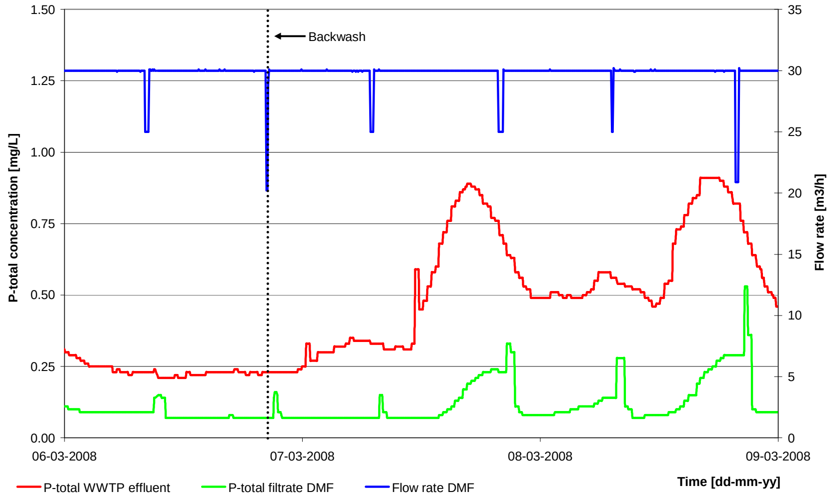

Figure 6-7 - Change of phosphorus removal for the filter bed during the filter runtime for the dual media filter (fine filter bed, without biomass) at the Leiden Zuidwest WWTP

Figure 6-7 illustrates the changes in the phosphorus removal in the filter bed during the filter runtime. The graph shows a short increase in total phosphorus in the filtrate water of the dual media filter after a backwash. The total phosphorus concentration rises approximately 0.1 mg/L during 30 minutes. The graph also shows that, for a steady total phosphorus concentration in the WWTP effluent, the total phosphorus concentration in the filtrate water of the dual media filter should not increase during the filter runtime. For a total phosphorus concentration in the WWTP effluent above 0.5 mg/L, the total phosphorus concentration in the filtrate water of the dual media filter increases.

6.2 Biomass in the filter bed

Filtration with biomass was tested in Street A and B at the Leiden Zuidwest WWTP. In Street A continuous sand filtration was used for simultaneous denitrification and phosphorus removal. In a later stage of the research Continuous Sand Filter B was bypassed and the dual media filter of Street B was used for simultaneous denitrification and phosphorus removal. This was tested for the fine and the coarse filter bed. At the WWTP Horstermeer results are available for the dual media filter. The results for filtration with biomass contain phosphorus distributions, phosphorus size fractionations, profile measurements and on-line data.

The section is divided into six subsections. Subsection 6.2.1 describes the influence of filtration with biomass on the phosphorus distribution. Subsection 6.2.2 describes how the phosphorus size fractionation changes as a result of the filtration process. The results on the optimal filtration rate are described in Subsection 6.2.3, and the phosphorus removal in the filter bed in Subsection 6.2.4. Subsection 6.2.5 is about the influence of the filter runtime on the phosphorus removal. Subsection 6.2.6 describes the results of the phosphorus uptake by denitrifying biomass.

6.2.1 Changes of the phosphorus distribution after filtration

From March to November 2008, 14 phosphorus distributions were determined for the dual media filter at Horstermeer WWTP. From October 2007 to January 2008 in total 22 phosphorus distributions were made for Continuous Sand Filter A at the Leiden Zuidwest WWTP. In August 2008 only two phosphorus distributions were made for the dual media filter (fine filter bed) with biomass. All phosphorus distributions were made with a metal/orthophosphorus ratio of 4 mol/mol. The filtration rate for the dual media filters was 10 m/h and for the continuous sand filter A 15 - 20 m/h. The average results are shown in Figure 6-8 and 6-9.

The left graph in Figure 6-8 shows the phosphorus distribution into particulate organic phosphorus (dark blue bars), dissolved “organic” phosphorus (light blue bars), metal-bound phosphorus (red bars), and orthophosphorus (green bars) for the WWTP effluent and for the filtrate of the dual media filter at the Leiden Zuidwest WWTP. The right graph in Figure 6-8 shows the phosphorus distribution for the WWTP effluent, after coagulation, and in the filtrate of continuous sand filter A. For the dual media filter, no data are available after coagulation. The filter runtime at the time of sampling was approximately 2 hours for the dual media filter. Figure 6-9 shows the phosphorus distribution for the WWTP effluent, after coagulation (the upper water layer of the filter), and for the filtrate of the filter. The filter runtime at the time of sampling was between 4 and 11 hours for the dual media filter at the Horstermeer WWTP.

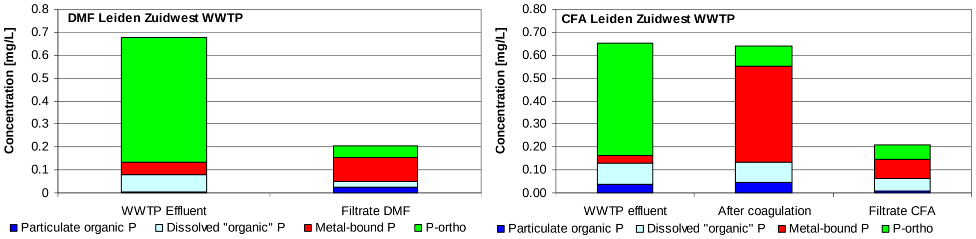

Figure 6-8 – **Left side:** average (2 samples) phosphorus distribution for the WWTP effluent and the filtrate of the dual media filter (Filtrate DMF) for the Leiden Zuidwest WWTP (fine filter bed). **Right side:** average (22 samples) phosphorus distribution for the WWTP effluent, after flocculation and the filtrate of continuous filter A (CFA) for the Leiden Zuidwest WWTP.

The phosphorus distribution for the dual media filter at the Leiden Zuidwest WWTP shows a decrease in the orthophosphorus concentration in the filtrate (see green bar in the WWTP effluent and the remaining green bar in the filtrate). Approximately 75% of the remaining orthophosphorus concentration in the upper water layer for the dual media filter at the Horstermeer WWTP was removed in the filter bed. The concentrations for metal-bound phosphorus and particulate organic phosphorus increased in the filtrate (see the red and dark blue bars for the WWTP effluent and the increased bars for the filtrate). The concentration dissolved “organic” phosphorus concentration decreased (see light blue bars in the WWTP effluent and the remaining bar in the filtrate). The results for the filtrate of the continuous sand filter A are comparable to the filtrate of the dual media filter of the Leiden Zuidwest WWTP and with the filtrate of the dual media filter at Horstermeer.

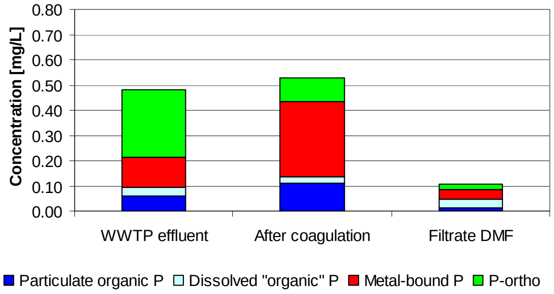

Figure 6-9 –average (14 samples) phosphorus distribution for the WWTP effluent, after flocculation and the filtrate of the dual media filter (Filtrate DMF) for Horstermeer WWTP.

When comparing the phosphorus distributions of the continuous sand filter A and the dual media filter at the Horstermeer WWTP, it is seen that a large part of the orthophosphorus (green bar, left column) is bound to metal ions after coagulation (see the remaining green bar in the middle column). A large part of the metal-bound phosphorus, 80% for the continuous sand filter and 86% for the dual media filter at the Horstermeer WWTP, was removed in the filter bed (see the remaining red bar right column). The dissolved “organic” phosphorus decreased after coagulation, and the particulate “organic” phosphorus increased after flocculation, which suggests that it may be colloidal or associated with colloidal material (Stevens and Stewart, 1982). From 80%-90% particulate organic phosphorus was removed in the filter bed. Dissolved “organic” phosphorus will pass the filter bed. Figure 6-9 shows an increase in the total phosphorus concentration in the upper water layer compared to the WWTP effluent. This is seen frequently and was previously described in Subsection 4.4.2.

6.2.2 Changes of the phosphorus size fractionation after filtration

At the Horstermeer WWTP phosphorus size fractionations were made for the dual media filter with biomass. The metal/orthophosphorus ratio used was 4 mol/mol and the filtration rate was 10 m/h. The results are illustrated in Figure 6-10. The red bars in this figure indicate the results for the WWTP effluent and the green bars for the filtrate. The results show a decrease in all the size fractions with the exception of the fraction 2 – 5 μm where a small increase in phosphorus is measured. The estimated floc size was 18.0 μm in the WWTP effluent and in the dual media filtrate 14.0 μm.

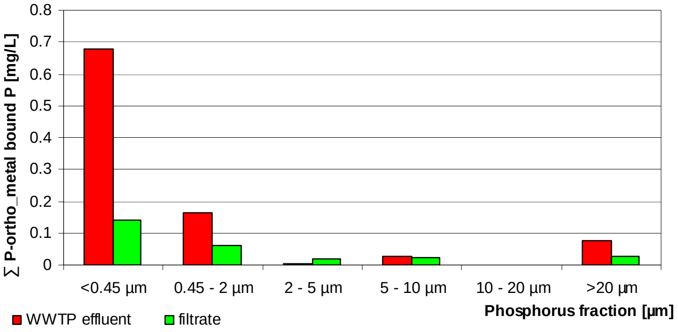

Figure 6-10 – Phosphorus size fractionation of WWTP effluent and dual media filtrate at Horstermeer WWTP. PACl dosage 5 mol/mol (1.02 mg/L) and methanol dosage MeOH/NO_x-N 3 g/g, 26 July 2007

6.2.3 Optimal filtration rate

The optimal filtration rate was investigated in the period April to October 2008 for continuous sand filter A and for the dual media filter (fine filter bed) at the Leiden Zuidwest WWTP. For the continuous sand filter, filtration rates of 15 m/h and 20 m/h were tested, for the dual media filter four different filtrate rates were tested: 5, 10, 15 and 20 m/h. With both filter types, the metal/orthophosphorus ratio was 7.5 mol/mol for orthophosphorus concentrations in the WWTP effluent of <0.15 mg/L and the ratio was 4 mol/mol for orthophosphorus concentrations >0.15 mg/L.

The results for the continuous sand filter Are shown in Figure 6-11: the red bars represent the total phosphorus concentration in the WWTP effluent, the light blue bars represent the total phosphorus concentration in the filtrate water for a filtration rate of 5 m/h, the green bars represent 10 m/h, the dark blue bars represent 15 m/h, and the dark purple bars represent 20 m/h. On-line data were used to construct Figure 6-11. The number of data points per average value varies between approximately 200 and 3500 for the concentration ranges 0 – 0.25, 0.25 – 0.50 and 0.50 – 0.75 mg P-total/L. For the concentration ranges 0.75 – 1.0, 1.0 – 1.25 and 1.25 – 1.50 mg P-total/L, between 30 – 200 data points are available. The results presented in Figure 6-11 show very steady and hardly increasing total phosphorus concentrations in the filtrate in the WWTP effluent for all the tested filtration rates. The removal efficiencies of the different filtration rates do not differ much and are approximately 55% for total phosphorus concentrations of 0 – 0.25 mg/L in the WWTP effluent, increasing up to 90% for total phosphorus concentrations in the WWTP effluent of 1.25 – 1.50 mg/L.

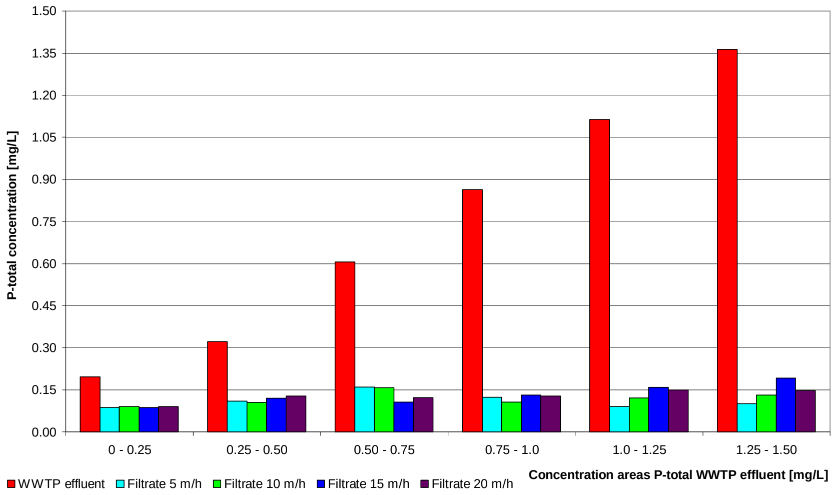

Figure 6-11 – Average total phosphorus removal for the continuous sand filter A of the Leiden Zuidwest WWTP for filtration rates of 5 m/h, 10 m/h, 15 m/h and 20 m/h

The results for the dual media filter are shown in Figure 6-12. The red bars represent the total phosphorus concentration in the WWTP effluent, the light blue bars represent the total phosphorus concentration in the filtrate water for a filtration rate of 5 m/h, the green bars represent 10 m/h, and the dark blue bars represent 15 m/h. On-line data were used to construct Figure 6-12. The number of data points per average value varied between approximately 100 and 7500. Only for the dataset of 5 m/h, in the concentration ranges 0.75 – 1.0, 1.0 – 1.25 and 1.25 – 1.50 mg P-total/L, are fewer than 50 data points available.

The results illustrated in Figure 6-12 show increasing total phosphorus concentrations in the filtrate water with increasing total phosphorus concentration in the WWTP effluent. The total phosphorus concentrations in the filtrate do not differ much when comparing the different tested filtration rates for the concentration ranges 0 – 0.25, 0.25 – 0.50 and 0.50 – 0.75 mg/L. Since the dataset of 5 m/h contains fewer than 50 data points in the concentration ranges 0.75 – 1.0, 1.0 – 1.25 and 1.25 – 1.50 mg P-total/L, these data have a high uncertainty. When comparing the results in the concentration ranges 1.0 – 1.25 and 1.25 – 1.50 mg P-total/L for a filtration rate of 10 m/h and 15 m/h, similar total phosphorus concentrations are found. The removal efficiencies of the filtration rates of 10 m/h and 15 m/h do not differ much and are approximately 60% for total phosphorus concentrations of 0 – 0.25 mg/L in the WWTP effluent, increasing up to 70% for total phosphorus concentrations in the WWTP effluent of 1.25 – 1.50 mg/L.

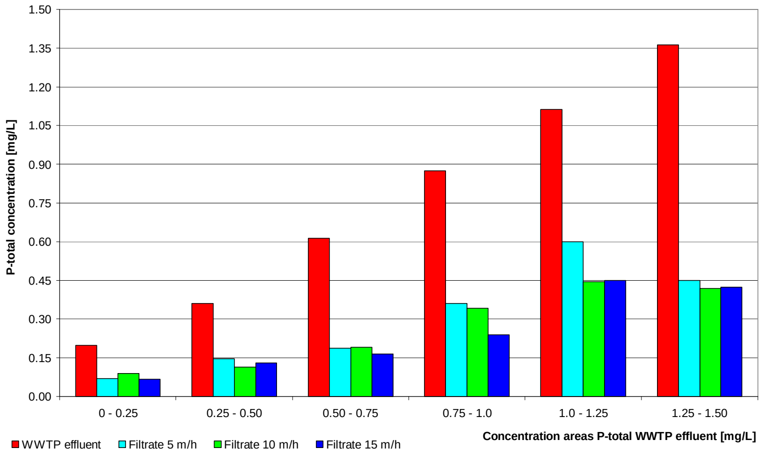

Figure 6-12 – Average total phosphorus removal for the dual media filter of the Leiden Zuidwest WWTP (fine filter bed with biomass) for filtration rates of 5 m/h, 10 m/h and 15 m/h

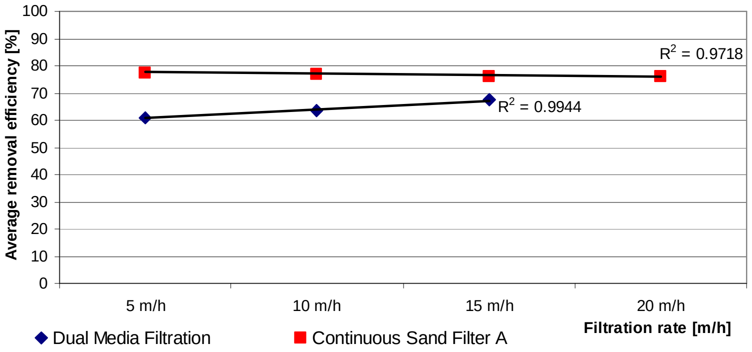

Figure 6-13 – Average removal efficiency for continuous sand filter A and the dual media filter of the Leiden Zuidwest WWTP (fine filter bed with biomass) for filtration rates of 5 m/h, 10 m/h, 15 m/h and 20 m/h.

In Figure 6-13 an overview of the average removal efficiency for the different filtration rates which were tested for continuous sand filter A and the dual media filter are presented. This figure shows that the removal efficiency for continuous sand filtration slightly decreased from 77.5% to 75% with increasing filtration rates. For the dual media, the removal efficiency increased from 60% to 67% with increasing filtration rates.

6.2.4 Phosphorus removal in the filter bed

Figure 6-14 shows the profile measurements made for the dual media filter at the Horstermeer WWTP. This profile measurement was made on the 19th of November 2008. The metal/orthophosphorus ratio used was 4 mol/mol and the filtration rate was 10 m/h. The profile measurement shows the phosphorus distribution through the filter bed. The information provided from these results show which phosphorus form was removed in the filter bed. The graphs show the orthophosphorus (green line), the metal-bound phosphorus (red line), the particulate organic phosphorus (dark blue line), and the dissolved "organic" phosphorus (light blue line) concentrations through the filter bed.

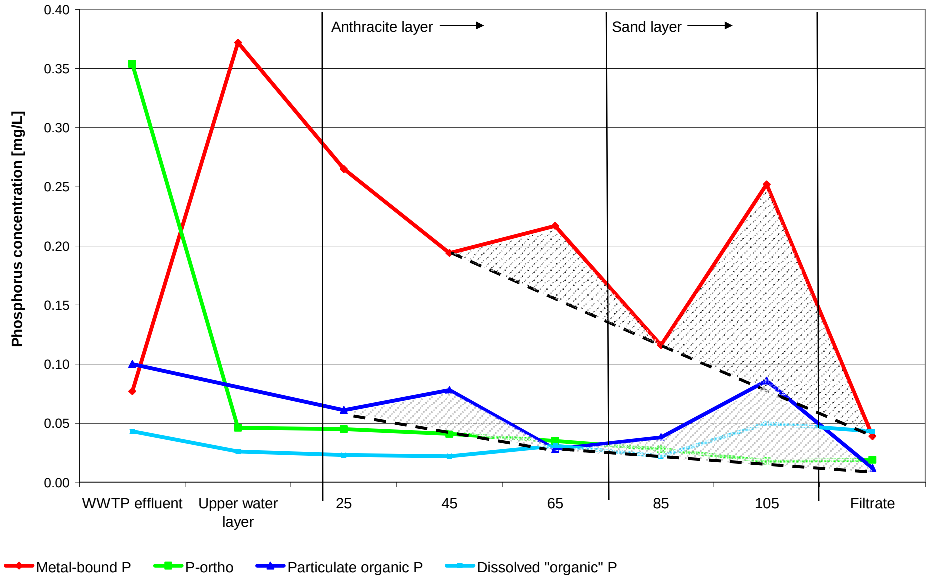

Figure 6-14 – Profile measurement combined with the TU Delft phosphorus distribution method for the dual media filter 19 November 2008 at the Horstermeer WWTP (Scherrenberg et al., 2009)

Figure 6-14 shows that nearly all the orthophosphorus (decreasing green line) which was available in the WWTP effluent binds to metal ions after coagulation and flocculation (see the increasing red line in the upper water layer) and becomes metal-bound phosphorus. Metal-bound phosphorus and particulate organic phosphorus are removed in the filter bed. A part of the orthophosphorus which was not transferred to metal-bound phosphorus will still be removed in the filter bed; this is probably due to uptake by biomass and the flocculation of colloidal metal-bound phosphorus. Dissolved "organic" phosphorus will pass the filter bed. The removal of phosphorus in the filter bed is strictly caused by filtration. The figure shows an increase in metal-bound phosphorus before the sand layer is entered and before the bottom plate of the filter bed is reached (see the cross-hatched areas in the graph). The cause of this increase was discussed in Section 4.6.

6.2.5 Change of phosphorus removal in the filter bed during the filter runtime

In Figure 6-15 the phosphorus removal of the dual media filter with the fine filter bed and biomass at the Leiden Zuidwest WWTP is shown during two-and-a-half days. The figure shows the flow rate (blue graph, secondary y-axis), which was 30 m^3/h (filtration rate of 10 m/h) during this period. The sharp decreases in the flow rate represent backwashes of the filter bed. A backwash was initiated when the upper water layer exceeded the maximum level, or when the turbidity in the filtrate water was higher than 2 NTU, or when the maximum runtime of 24 hours was exceeded. In total, six complete backwashes are shown in the graph. The filter runtime varied in the shown period between 8.5 and 10.5 hours. The dotted line represents one backwash. The red graph represents the total phosphorus concentration in the WWTP effluent (primary y-axis), the green graph represents the total phosphorus concentration in the filtrate water of the dual media filter (primary y-axis).

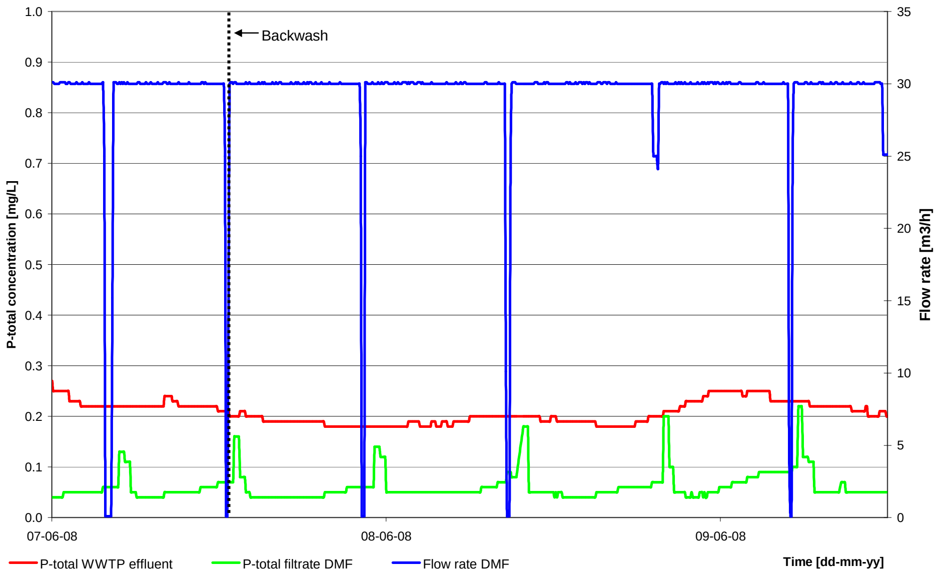

Figure 6-15 – Change in the phosphorus removal for the filter bed during the filter runtime for the dual media filter (fine filter bed, with biomass) at the Leiden Zuidwest WWTP

Figure 6-15 illustrates the changes in phosphorus removal in the filter bed during the filter runtime. The graph shows a short increase of total phosphorus in the filtrate water of the dual media filter after a backwash. The total phosphorus concentration rose by approximately 0.1 mg/L in 55 minutes. Another aspect of the graph is that the total phosphorus concentration in the filtrate water of the dual media filter increased at the end of the filter runtime. This is called a breakthrough of the filter bed. The backwash was initiated by the upper water layer which exceeded the maximum level.

6.2.6 Phosphorus uptake by denitrifying bacteria

At the WWTP Leiden Zuidwest WWTP research was conducted to determine the phosphorus uptake by denitrifying bacteria. The coagulant dosage for continuous sand filter A was paused for a week in March 2008, but the methanol dosage continued with 5 kg methanol/kg NO_x-N. The filtration rate was 15 m/h. Figure 6-16 shows the results for the orthophosphorus removal in the filter bed (blue dots) for removed NO_x-N concentrations of 0 mg/L to 8 mg/L and shows the theoretical orthophosphorus removal for the methanol dosage (red line). To construct Figure 6-16, only the results which contained between 100 to 500 data points were used.

Figure 6-16 shows that the orthophosphorus removal is initially higher. This is seen in the graph for a removal of 0.0 mg/L where the orthophosphorus theoretically is 0.0 mg/L, but the trend line of the measured data shows an orthophosphorus removal of 0.033 mg/L. The slope of the trend line made for the practical data is 0.018 mg P-ortho/mg NO_x-N removed. The slope of the theoretical orthophosphorus removal is 0.010 mg P-ortho/mg NO_x-N removed. The effect of this higher orthophosphorus removal might have been caused by the biological conversion of (ortho)phosphorus, removal of colloidal and bound (particulate) phosphorus by the biofilm and the filter bed, or by adsorption (STOWA, 2009a).

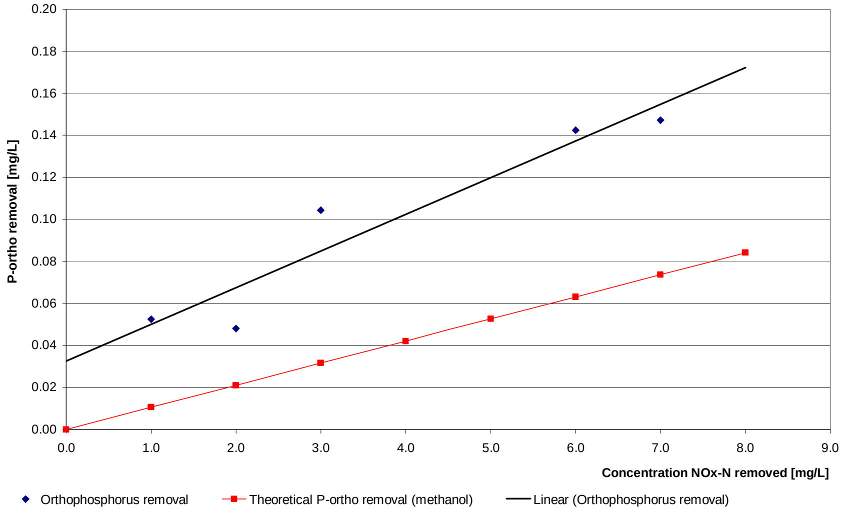

Figure 6-16 – A comparison of the theoretical orthophosphorus removal by biomass (methanol dosage, STOWA, 2009a) and the measured results of Continuous Sand Filter A without coagulant dosage.

6.3 Comparing with or without biomass

The previous sections presented the results of filtration without biomass (Section 6.1) and filtration with biomass (Section 6.2). Results of the combination of adsorption and filtration with biomass are described in Section 6.4. The results shown in this section are the results of the dual media filter of the Leiden Zuidwest WWTP. The average phosphorus distribution of the filtrate (Subsection 6.3.1), the differences in the phosphorus removal in the filter bed (Subsection 6.3.2), the decrease in storage capacity of the filter bed due to biomass and the decrease in filter runtime are described (Subsection 6.3.3).

6.3.1 Comparison of the phosphorus distribution after filtration

The average phosphorus distributions for the dual media filter at the Leiden Zuidwest WWTP (fine filter bed) were used to compare the phosphorus removal with or without biomass. The average phosphorus distribution without biomass was previously described in Subsection 6.1.1 and with biomass in Subsection 6.2.1.

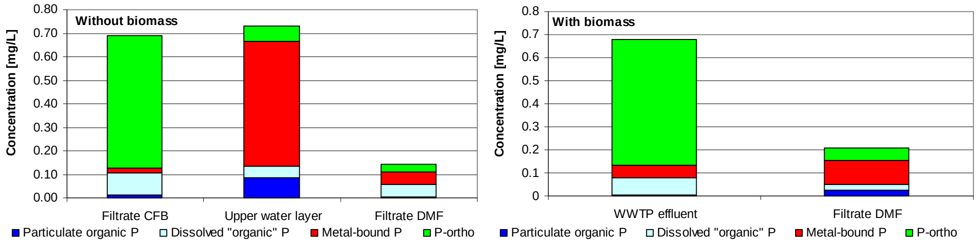

Figure 6-17 – Left: Average (11 samples) phosphorus distribution for the filtrate of CFB, after coagulation in the upper water layer and the filtrate of the dual media filter (Filtrate DMF) for the Leiden Zuidwest WWTP (fine filter bed, **without biomass**). **Right**: Average (2 samples) phosphorus distribution for the WWTP effluent and the filtrate of the dual media filter (Filtrate DMF) for the Leiden Zuidwest WWTP (fine filter bed, **with biomass**).

For both situations the initial total phosphorus concentration in the feed water was approximately 0.7 mg/L. The fine filter bed without biomass reached the average removal efficiency for total phosphorus of approximately 80%, for filtration with biomass the average removal efficiency was approximately 70%. This was largely caused by the metal-bound phosphorus concentration which was 0.10 mg/L in the filtrate of the dual media filter with biomass and was 0.05 mg/L for filtration without biomass. Another difference which is seen when comparing the two situations is the removal of the organic phosphorus forms. The feed water for filtration without biomass contained, 0.09 mg/L dissolved “organic” phosphorus and 0.01 mg/L particulate organic phosphorus, for filtration with biomass the feed water contained 0.08 mg/L dissolved ‘organic” phosphorus and no particulate organic phosphorus was present. In the case of filtration without biomass, the concentration of dissolved “organic” phosphorus was 2.5 times the concentration of filtration with biomass. This might have been caused by the composition of the dissolved “organic” phosphorus which may contain varying concentrations of colloidal organic phosphorus.

6.3.2 Changes in the removal in the filter bed

The pressure along the filter bed is read by manometers which are attached on the taps which can be used for sample tanking, by doing this a Lindquist diagram can be made (see also Section 3.4). Lindquist diagrams were constructed for the dual media filter at the Leiden Zuidwest WWTP for the situations with and without biomass. The Lindquist diagrams which are shown in Figure 6-18 were made for a filtration rate of 10 m/h and a constant ferric(III)chloride dosage of 5.0 mg/L. The left graph represents the Lindquist diagram without biomass and the right diagram represents the results with biomass. Pressure readings were conducted during the filter runtime (different lines, legend shows the minutes of the filter runtime), which was approximately 11 hours for the situation without biomass and approximately 6 hours for the situation with biomass. The horizontal axis represents the pressure in the meter water column and the vertical axis represents the filter bed height.

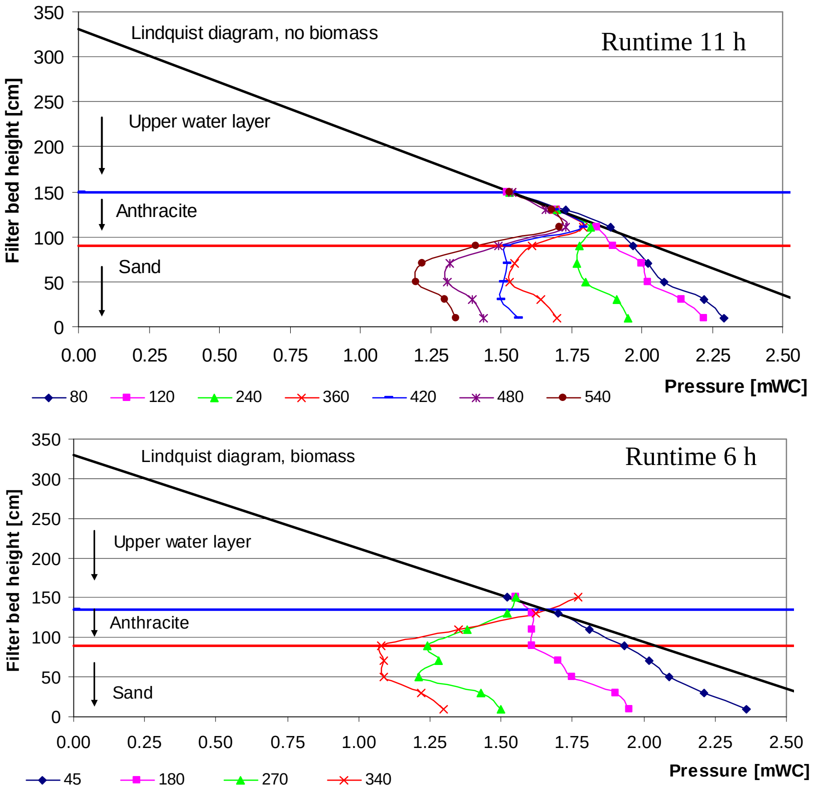

Figure 6-18 – Lindquist diagram for the dual media filter of the Leiden Zuidwest WWTP (fine filter bed). Top graph shows the Lindquist diagram during the filter runtime without biomass, the bottom graph shows the Lindquist diagrams with biomass. In both situations a filtration rate of 10 m/h and a constant coagulant dosage of 5 mg Fe^{3+}/L was used (Van den Berg van Saparoea, 2008).

The top graph of Figure 6-18 shows that, for the situation without biomass, the pressure is increasing in the anthracite layer, just above the sand layer. The maximum filter bed resistance was found in the middle of the sand layer, around a filter bed height of 50 cm and at approximately 1.2 mWC. The Lindquist diagram with biomass (bottom graph) shows a maximum filter bed resistance at the transition point between the anthracite layer and the sand layer. The maximum filter bed resistance is approximately 1.1 mWC. From this it can be concluded that the removal in the anthracite layer is higher when biomass is present in the filter bed compared to the situation without biomass.

6.3.3 Decrease of storage in the filter bed; decrease of the runtime

A decrease in the storage capacity for phosphorus is expected for filtration with biomass when compared with filtration without biomass. To investigate this, the ferric(III)chloride concentration was measured in the filtrate of the dual media filter at the Leiden Zuidwest WWTP for the fine filter bed. The ferric(III)chloride concentration is comparable to the phosphorus concentration, but the advantage is that ferric(III)chloride can be dosed in a constant amount which makes it easier to compare different settings. Table 6-1 shows the results for a filter bed with and without biomass, for a filtration rate of 10 m/h and 15 m/h combined with ferric(III)chloride dosages between 2.5 mg/L and 7.5 mg/L. The ferric(III)chloride storage in the filter bed was calculated by making a mass balance over the filter bed.

Table 6-1 – Average phosphorus removal of the dual media filter during the filter runtime (Van den Berg van Saparoea, 2008)

Situation	Filtration rate	$FeCl_3$ dosage		Runtime	Fe^{3+} in filtrate	Fe^{3+} storage
	[m/h]	[mg/L]	[l/h]	[min]	[mg/L]	[kg/run]
Without biomass	10	5.0	0.77	745	0.85	1.70
	10	7.5	1.12	435	0.62	1.57
Without biomass	15	3.2	0.74	435	1.50	0.76
	15	5.0	1.15	265	1.12	0.86
	15	7.5	1.72	195	0.94	1.02
With biomass	10	2.5	0.38	550	1.20	0.41
	10	5.0	0.77	370	0.90	0.80
	10	7.5	1.12	365	0.73	1.27
With biomass	15	2.5	0.57	320	0.52	0.54
	15	5.0	1.14	200	0.69	0.71

As described in Subsection 6.1.3, the coagulant dosage has a major influence on the filter runtime. This was confirmed by the results shown in Table 6-1, indicating a decreasing filter runtime for an increasing ferric(III)chloride dosage. It should be taken into account that the filter runtime presented in the table for a filtration rate of 10 m/h without biomass in combination with 5 mg Fe^{3+}/L is extremely long when compared with the (average) on-line data. Therefore, it can be assumed that the filter runtime for filtration with biomass is approximately 70 – 150 minutes shorter compared to filtration without biomass. The Fe^{3+} storage shows increasing values for increasing ferric(III)chloride dosages except for a filtration rate of 10 m/h without biomass in combination with 5 mg Fe^{3+}/L. The available storage in the filter bed was approximately 0.76 – 1.7 kg Fe^{3+}/run for filtration without biomass and 0.41 – 1.27 kg Fe^{3+}/run for filtration with biomass. The difference in storage gives an estimation of the biomass present in the filter bed. The measured difference in Fe^{3+} storage between filtration with and without biomass is approximately 0.39 kg Fe^{3+}/run.

6.4 Filtration with the 1-STEP® filter

This section describes the results of the 1-STEP® filter which was used at the pilot installation at the Horstermeer WWTP. The results for the 1-STEP® filter contain phosphorus distributions, phosphorus size fractionations, profile measurements and on-line data. This section is divided into six subsections. Subsection 6.4.1 describes the results of the influence of 1-STEP® filtration on the phosphorus distribution. Subsection 6.4.2 describes the results of 1-STEP® filtration on the phosphorus size fractionation. The optimal filtration rate and the consequences of flow fluctuations with regard to the phosphorus removal are described in Subsection 6.4.3. Phosphorus removal through the filter bed is described in Subsection 6.4.4. Subsection 6.4.5 describes the adsorption of phosphorus onto the activated carbon and Subsection 6.4.6 describes the changes in the phosphorus removal during the filter runtime.

6.4.1 Influence of 1-STEP® filtration on the phosphorus distribution

In the period from March to December 2008, a total of 14 phosphorus distributions were made; the averaged results are shown in Figure 6-19. All phosphorus distributions were made with a metal/orthophosphorus ratio of 4 mol/mol and a filtration rate of 10 m/h. The graph shows the phosphorus distribution into particulate organic phosphorus (dark blue bars), dissolved “organic” phosphorus (light blue bars), metal-bound phosphorus (red bars) and orthophosphorus (green bars) for the WWTP effluent, the upper water layer of the filter and the filtrate. The results are shown in concentrations.

Figure 6-19 shows an increase in the total phosphorus concentration in the upper water layer compared to the WWTP effluent. The cause of this increase was discussed in Subsection 4.4.2. Apart from this, the graph shows that nearly all orthophosphorus (green bar, left column) is bound to metal ions after coagulation and flocculation (see the remaining green bar in the middle column). Nearly all the orthophosphate which is not bound will pass the filter bed. Almost all the metal-bound phosphorus, approximately 93%, was removed in the filter bed (see the remaining red bar in the right column). The dissolved “organic” phosphorus decreased after flocculation and the particulate organic phosphorus increased after flocculation, suggesting that it may be colloidal or associated with colloidal material (Stevens and Stewart, 1982). The particulate organic phosphorus was almost completely removed in the filter bed (removal efficiency of 95%). Dissolved “organic” phosphorus will pass through the filter bed.

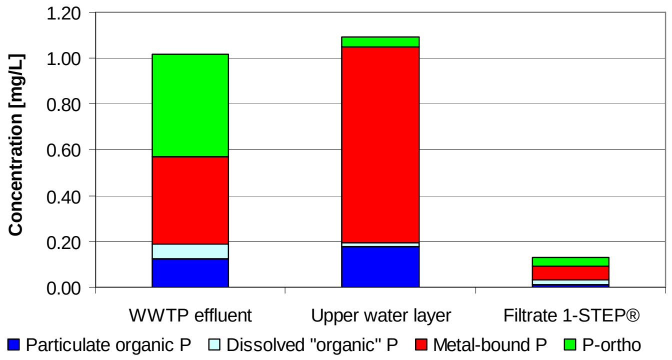

Figure 6-19 - Average phosphorus distribution (14 measurements) for the 1-STEP® filter at the Horstermeer WWTP (STOWA, 2009b)

6.4.2 The influence of 1-STEP® filtration on the phosphorus size fractionation

At the Horstermeer WWTP, phosphorus size fractionations were made for the 1-STEP® filter. The metal/orthophosphorus ratio was 4 mol/mol and the filtration rate was 10 m/h. The results are illustrated in Figure 6-20. The red bars in this figure indicate the results for the WWTP effluent and the green bars for the filtrate. The results show a decrease for all the size fractions with the exception of the fraction 0.45 – 2 µm where a small increase in phosphorus was found. The estimated floc size in the WWTP effluent was 10.1 µm and in the filtrate 4.3 µm

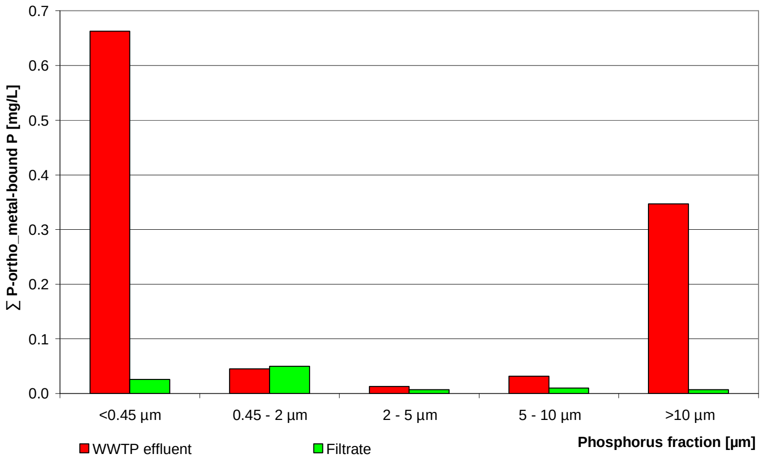

Figure 6-20 – Phosphorus size distribution of WWTP effluent and of the 1-STEP® filtrate of 23 March 2008

6.4.3 Optimal filtration rate: flow fluctuations compared with a constant filtration rate

To investigate whether a constant filtration rate or a varying filtration rate has an influence on the phosphorus removal, experiments were conducted. For the constant flow situation a filtration rate of 10 m/h was used. On-line data for the period January – August 2008 were analysed. For the flow fluctuations, a simulation with a filtration rate of 10 m/h (16 hours) and a filtration rate of 15 m/h (6 hours) was run in September and October 2008. When changing the filtration rates, a period of 1 hour was used to slowly increase or decrease the filtration rate to the new setting. The results for both situations are illustrated in Figure 6-21. The top graph shows the results for a constant filtration rate of 10 m/h. The bottom graph shows the results of flow fluctuations. The red bars represent the total phosphorus concentration in the WWTP effluent, these concentrations are calculated with Figure 5-4, because only the orthophosphorus concentration is measured in the WWTP effluent. The blue bars represent the sum of the orthophosphorus and the metal-bound phosphorus in the filtrate, and the green bars represent the total phosphorus concentration in the filtrate. The number of data points used for the constant filtration rate varied between 50 and 4300. For the total phosphorus concentrations in the WWTP effluent ≤ 1.0 mg/L, more than 200 data points were available. For the dry weather and rainy weather simulations, between 10 and 4200 data points were available. For total phosphorus concentrations in the WWTP effluent ≤ 0.7 mg/L, more than 150 data points were available.

The results for the flow fluctuations show an increased phosphorus removal for total phosphorus concentrations in the WWTP effluent of >1.3 mg/L compared to a constant filtration rate, but this was probably caused by the small number of data points which were available in this concentration range. Both situations show, for total phosphorus concentrations in the WWTP effluent between 0.1 – 1.3 mg/L, a very steady phosphorus removal with total phosphorus concentrations in the filtrate around 0.1 mg/L. The filter runtimes decreased from 12 hours to approximately 6 hours during the simulation test period.

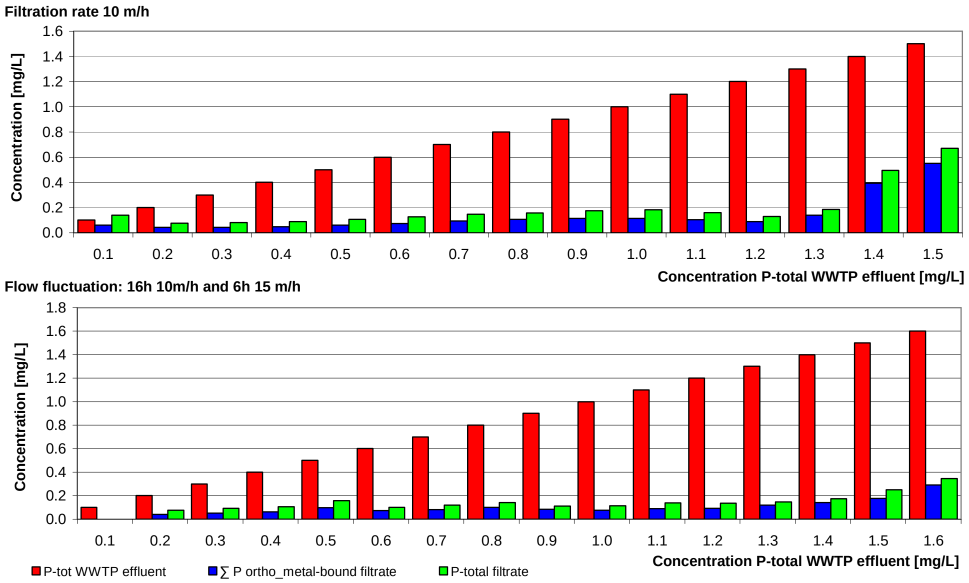

Figure 6-21 – A constant filtration rate of 10 m/h compared to flow fluctuations

During the test period, the influence of the filtration rate on the phosphorus removal was investigated. Normally, increased filtration rates at the wastewater treatment plant are caused by storm water; in that case the increase of the filtration rate will be combined with a dilution of the wastewater. This effect was not tested and therefore the presented results will overestimate the concentrations of the WWTP effluent.

6.4.4 Removal of phosphorus through the filter bed

Figure 6-22 shows a profile measurement which was made in combination with phosphorus distributions. This profile measurement was made on the 19th of November 2008. The metal/orthophosphorus ratio used was 4 mol/mol and the filtration rate was 10 m/h. The profile measurement shows the phosphorus distribution through the filter bed. The information provided from these results show which phosphorus form was removed in the filter bed. The graph shows the orthophosphorus (green line), the metal-bound phosphorus (red line), the particulate organic phosphorus (dark blue line) and the dissolved “organic” phosphorus (light blue line) concentrations through the filter bed.

Figure 6-22 shows that nearly all the orthophosphorus (decreasing green line) which was available in the WWTP effluent is bound to metal ions after coagulation and flocculation (see the increasing red line in the upper water layer) and becomes metal-bound phosphorus. Metal-bound phosphorus and particulate organic phosphorus were removed in the filter bed. Dissolved “organic” phosphorus will pass the filter bed, despite the filter media of activated carbon. Adsorption of “organic” phosphorus did not occur. The removal of phosphorus in the filter bed was strictly caused by filtration. The profile measurement shows an increase in metal-bound phosphorus just before the bottom plate of the filter bed is reached (see the cross-hatched area in the graph). The cause of this increase was discussed in Section 4.6.

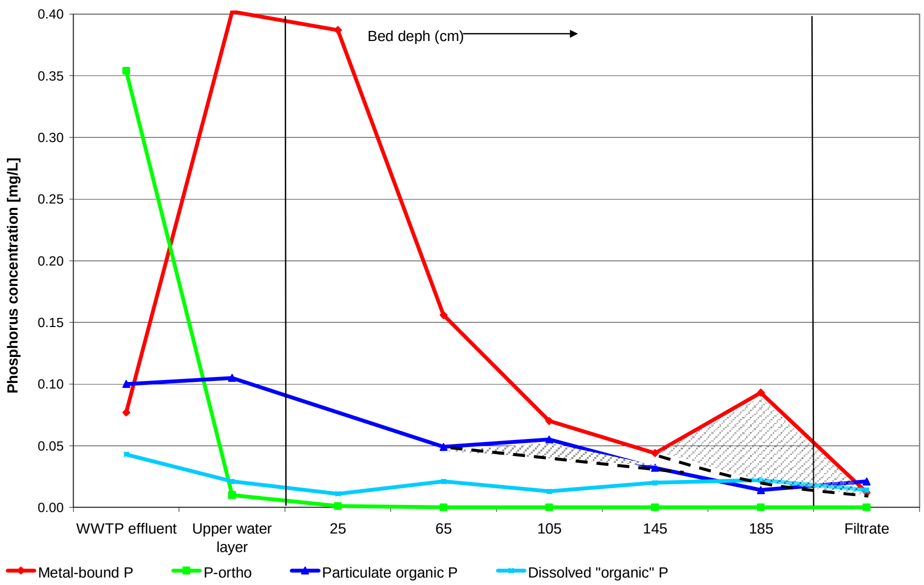

Figure 6-22 – Profile measurement combined with the TU Delft phosphorus distribution method for the 1-STEP® filter, 19th November 2008 at the Horstermeer WWTP

6.4.5 The adsorption of organic phosphorus

Activated carbon samples were taken at three different filter bed heights to investigate the adsorption of organic phosphorus forms on the activated carbon. The sample points are

- new activated carbon;
- upper layer of the filter bed (0 - 40 cm depth);
- middle layer of the filter bed (80 - 120 cm depth);
- bottom layer of the filter bed (147 - 187 cm depth).

The determination of the phosphorus was conducted by Norit. The results are shown inTable 6-2.

To determine the phosphorus concentrations in activated carbon samples, first the mass percentage of total phosphorus was analysed for all the different samples. This was converted to the theoretical orthophosphorus concentration by multiplying the mass percentage of total phosphorus with the molar weight of orthophosphorus divided by the molar weight of the phosphorus element. Acid extraction of the orthophosphorus (extractive P-ortho) made it possible to measure the orthophosphorus concentration which was attached to the activated carbon. It should be noted that metal-bound phosphorus will dissolve and form orthophosphorus due to the acid environment and, therefore, will be measured as orthophosphorus.

Table 6-2 – Phosphorus measurements activated carbon (STOWA, 2009b)

Sample point	P-total [M%]	Extractive P-ortho [M%]	Theoretical P-ortho [M%]	Difference P-ortho [M%]
Unused activated carbon	1.21	4.70	3.71	1.03
Upper layer	1.09	3.40	3.34	0.06
Middle layer	1.06	3.60	3.25	0.35
Bottom layer	1.01	3.45	3.10	0.35

Comparison of the mass percentages for the maximal theoretical orthophosphorus with the measured orthophosphorus shows that the measured orthophosphorus concentrations are higher for all samples. These results indicate that all the phosphorus which is present in the activated carbon samples is orthophosphorus. It is likely that organic phosphorus is not adsorbed or that very little is adsorbed to the activated carbon. The removal mechanism for organic phosphorus is filtration.

6.4.6 Change of phosphorus removal of the filter bed during the filter runtime

Figure 6-23 shows the changes in the phosphorus removal in the filter bed during the filter runtime. To determine the changes in the phosphorus removal on-line data were used for the period June to November 2008. From June to September, a constant filtration rate of 10 m/h was used, and in October and November a dry weather and rainy weather (see Subsection 6.4.3) simulation program was used. The maximum filter runtime was 12 hours, with bump cleanings every 3 hours. The metal/orthophosphorus ratio used was 4 or 5 mol/mol.

The results shown in Figure 6-23 are average values of approximately 300 data points for orthophosphorus and for total phosphorus in the filtrate during the filter runtime. The shaded areas represent the bump cleanings. The average total phosphorus concentration in the filtrate varies between 0.0075 mg/L and 0.11 mg/L. Although this difference is very small, a clear pattern is visible. Just after a backwash, at the beginning of a filter run, the orthophosphorus and the total phosphorus concentration in the filtrate rose for about 50 minutes. The concentrations will decrease until a bump cleaning starts; after a bump cleaning the orthophosphorus and the total phosphorus concentrations rose again. This is especially true after the third bump cleaning. From a filter runtime of 7 hours, the orthophosphorus and the total phosphorus concentration in the filtrate increased. This increase is partly recovered after the third bump cleaning, but after a filter runtime of 10 hours the concentrations increased again.

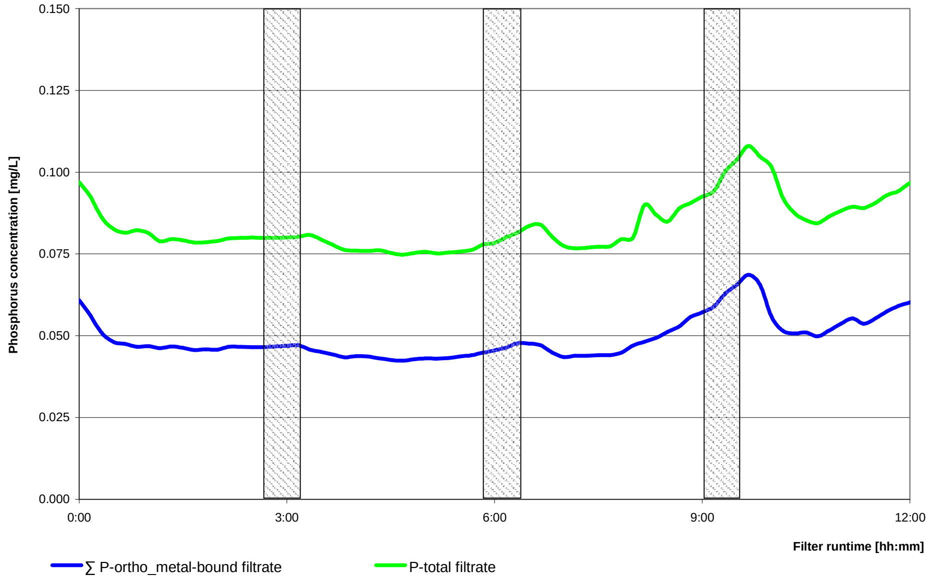

Figure 6-23 – Orthophosphorus and total phosphorus concentrations in the filtrate of the 1-STEP® filtrate (Horstermeer WWTP) during the filter runtime. The runtime is 12 hours, every three hours a bump cleaning takes place. The results show average values of approximately 300 measurements

6.5 Phosphorus removal from WWTP effluent

This section presents the phosphorus removal for all the different filtration techniques and process conditions which were tested during this research. Subsection 6.5.1 describes the results of the dual media filtration at the Leiden Zuidwest WWTP without biomass for a fine and a coarse filter bed. Subsection 6.5.2 describes the results of filtration with biomass. Dual media filtration at the Horstermeer WWTP, continuous sand filtration and dual media filtration at the Leiden Zuidwest WWTP (coarse and fine filter bed) are described in this subsection. 1-STEP® filtration is described in Subsection 6.5.3. Finally, a comparison of the removal efficiencies of the different techniques is given in Subsection 6.5.4.

6.5.1 Filtration without biomass

To investigate the total phosphorus removal from WWTP effluent for a fine and a coarse filter bed without biomass, on-line data for the dual media filter of the Leiden Zuidwest WWTP was used. Data used for the coarse filter bed were from January 2007 to mid- June 2007 and for the fine filter bed from mid-June 2007 until mid-April 2008. In Figure 6-24, the results are illustrated for the coarse filter bed and the fine filter bed. Data used for the construction of the graph all had a filtration rate of 10 m/h and a metal/orthophosphorus concentration of 4 mol/mol. The red bars in Figure 6-24 represent the average total phosphorus concentration in the WWTP effluent; the green bars represent the average total phosphorus concentration in the filtrate of the dual media filter with the coarse filter bed. The blue bars represent the average total phosphorus concentration in the filtrate of the dual media filter with the fine filter bed. The number of data points used to calculate the average concentrations were between 100 and 4300.

The results provided in Figure 6-24 show increasing total phosphorus concentrations in the filtrates of both filter beds for an increasing total phosphorus concentration in the feed water. The difference between the total phosphorus concentration in the filtrate for the fine and the coarse filter bed is quite constant and is on average 0.13 mg P-total/L. The difference between the coarse filter bed and the fine filter bed is clearly seen for all total phosphorus concentrations in the WWTP effluent. For a fine filter bed, the total phosphorus concentration in the filtrate increased in stages. An increase in the total phosphorus concentration can be seen for total phosphorus concentrations in the feed water of 0.2 – 0.6 mg/L. For total phosphorus concentrations in the feed water of 0.7 – 1.1 mg/L a total phosphorus concentration of approximately 0.30 mg/L can be found in the filtrate. For total phosphorus concentrations in the feed water of 1.1 – 1.5 mg/L, a total phosphorus concentration of approximately 0.4 mg/L can be found in the filtrate.

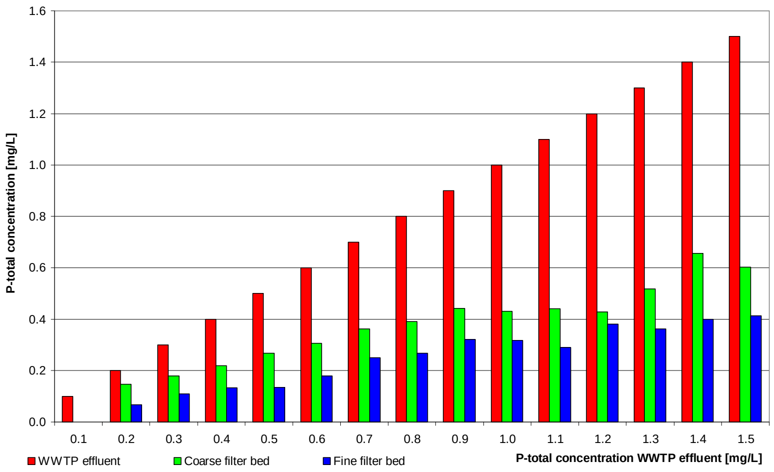

Figure 6-24 – Average total phosphorus removal for a coarse and a fine filter bed without biomass. Made with on-line data available for the Leiden Zuidwest WWTP

The removal efficiency for total phosphorus for the coarse filter bed is approximately 26% for a total phosphorus concentration in the WWTP effluent of 0.2 mg/L, and is approximately 50 - 60% for total phosphorus concentrations in the WWTP effluent of 0.6 mg/L to 1.5 mg/L. The removal efficiency for total phosphorus is for the fine filter bed approximately 65 - 75% for total phosphorus concentrations in the WWTP effluent of 0.2 mg/L to 1.5 mg/L.

6.5.2 Filtration with biomass

Phosphorus removal in combination with denitrification was tested with the Continuous Sand Filter A and the dual media filter at the Leiden Zuidwest WWTP and with the dual media filter at the Horstermeer WWTP. The results of these three installations are presented in this section. For the dual media filter at the Leiden Zuidwest WWTP, results are shown for the fine and the coarse filter beds.

Dual media filter at the Horstermeer WWTP

Figure 6-25 was made with the on-line data from 2007 and 2008. The reason for the use of two years of on-line data is the frequent malfunction of on-line analysers. Data with metal/orthophosphorus ratios between 3 and 5 mol/mol were selected. The figure shows the total phosphorus concentration in the WWTP effluent (red bars). These concentrations are calculated with Figure 5-4, because only the orthophosphorus concentration is measured in the WWTP effluent. The blue bars represent the sum of the orthophosphorus and metal-bound phosphorus in the filtrate, and the green bars represent the total phosphorus in the filtrate. The concentrations shown are average values. The number of data points used to calculate the average concentrations are between 20 and 2500 data points. For the total phosphorus concentrations in the WWTP effluent of 0.8 mg/L and higher, fewer than 50 data points were available. Because of this, the graph only shows an orthophosphorus range in the WWTP effluent of 0.1 mg/L to 1.0 mg/L.

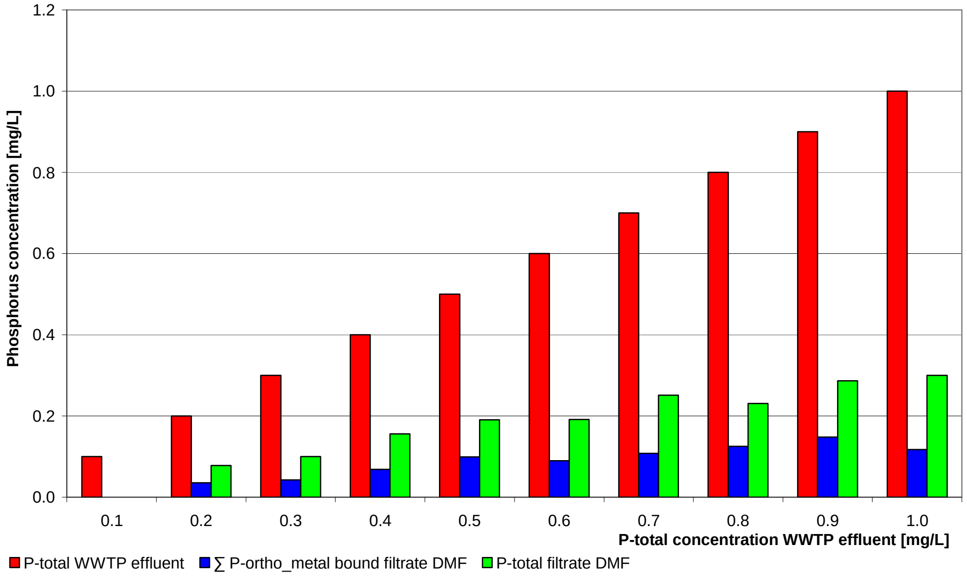

Figure 6-25 – Removal of phosphorus with coagulant and methanol dosage for the dual media filter at the Horstermeer WWTP

Figure 6-25 shows for increasing total phosphorus concentrations in the WWTP effluent also increasing orthophosphorus (+metal-bound phosphorus) and total phosphorus concentrations in the filtrate. The removal efficiency for total phosphorus was approximately 60% for total phosphorus concentrations in the WWTP effluent of 0.2 - 0.5 mg/L and was approximately 70% for total phosphorus concentrations in the WWTP effluent of 0.6 mg/L to 1.0 mg/L.

Continuous sand filtration at the Leiden Zuidwest WWTP

For the construction of Figure 6-26, on-line data from January 2008 to July 2008 were used. These are the data which were available for a filtration rate of 20 m/h in combination with a metal/orthophosphorus ratio of 7.5 for orthophosphorus concentrations in the WWTP effluent < 0.15 mg/L and a ratio of 4 mol/mol for orthophosphorus concentrations in the WWTP effluent > 0.15 mg/L. The figure shows the total phosphorus concentration in the WWTP effluent (red bars), the sum of the orthophosphorus and metal-bound phosphorus in the filtrate (blue bars), and the total phosphorus in the filtrate (green bars). The concentrations shown are average values. The number of data points used to calculate the average concentrations are between approximately 100 and 1500 data points for the concentration area of 0.1 – 0.7 mg/L and between 20 and 50 data points for the concentration area of 0.8 – 1.5 mg/L.

Figure 6-26 shows, for increasing orthophosphorus concentrations in the WWTP effluent, very steady orthophosphorus (+metal-bound phosphorus) and total phosphorus concentrations in the filtrate. The total phosphorus concentration in the filtrate varies around 0.15 mg/L for the whole range. The removal efficiency for total phosphorus is approximately 30% for a total phosphorus concentration in the WWTP effluent of 0.1 mg/L and is 90% and higher for total phosphorus concentrations in the WWTP effluent of 0.8 mg/L to 1.5 mg/L.

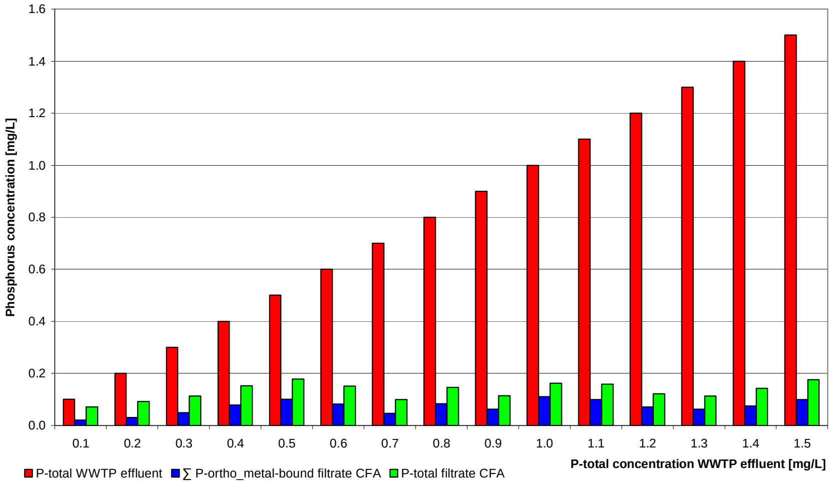

Figure 6-26 – Removal of phosphorus with coagulant and methanol dosage for continuous sand filter at the Leiden Zuidwest WWTP

Dual media filtration at the Leiden Zuidwest WWTP

To investigate the total phosphorus removal from WWTP effluent for a fine and a coarse filter bed with biomass, on-line data were used. The data used for the coarse filter bed were from mid-April 2008 to mid-October 2008 and for the fine filter bed from mid-October 2008 until mid-January 2009. In Figure 6-27 the results are illustrated for the coarse filter bed and the fine filter bed with biomass. Data used for the construction of the graph all had a filtration rate of 10 m/h and a metal/orthophosphorus concentration of 4 mol/mol. The red bars in Figure 6-27 represent the average total phosphorus concentration in the WWTP effluent; the green bars represent the average total phosphorus concentration in the filtrate of the dual media filter with the coarse filter bed. The blue bars represent the average total phosphorus concentration in the filtrate of the dual media filter with the fine filter bed. The number of data points used to calculate the average concentrations were between 20 and 1100 data points for the coarse filter bed and between 50 and 3700 data points for the fine filter bed.

The results displayed in Figure 6-27 show increasing total phosphorus concentrations in the filtrates of both filter beds for an increasing total phosphorus concentration in the feed water. The total phosphorus concentration in the filtrate of the coarse filter bed increased more rapidly compared to the fine filter bed. For total phosphorus concentrations in the WWTP effluent of 0.8 – 1.3 mg/L, the total phosphorus concentrations in the filtrate of the coarse filter bed are approximately double the concentration of the fine filter bed. The removal efficiency for total phosphorus is approximately 50% for a total phosphorus concentration in the WWTP effluent of 0.2 mg/L in the coarse filter bed, and is approximately 25 - 35% for total phosphorus concentrations in the WWTP effluent of 0.8 mg/L to 1.3 mg/L. The removal efficiency for total phosphorus is approximately 20% for a total phosphorus concentration in the WWTP effluent of 0.1 mg/L for the fine filter bed, and is approximately 60 - 70% for total phosphorus concentrations in the WWTP effluent of 0.3 mg/L to 1.5 mg/L.

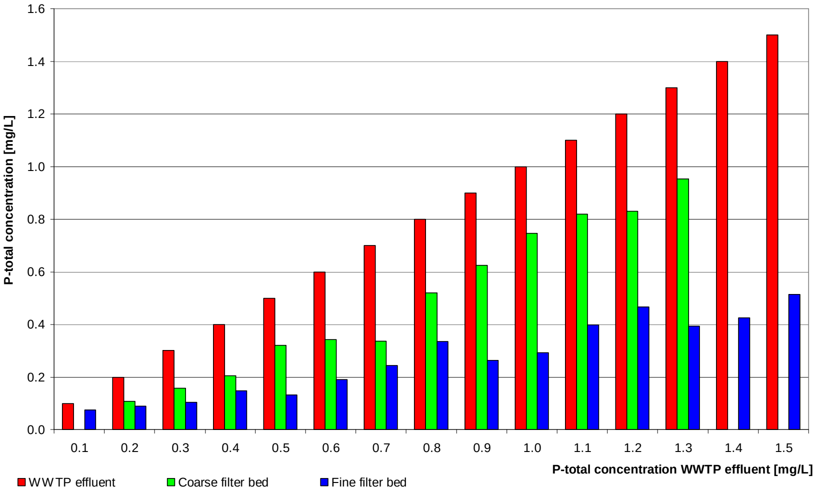

Figure 6-27 – Average total phosphorus removal for the coarse and the fine filter bed with biomass and a filtration rate of 10 m/h. Made with on line data available for the Leiden Zuidwest WWTP

6.5.3 1-STEP$^{®}$ filtration

Figure 6-28 was made using the on-line data of 2008. Data with metal/orthophosphorus ratios between 3 and 5 mol/mol were selected. The figure shows the total phosphorus concentration in the WWTP effluent (red bars). These concentrations are calculated with

Figure 5-4, because only orthophosphorus of the WWTP effluent were measured. The blue bars represent the sum of the orthophosphorus and metal-bound phosphorus in the filtrate, and the green bars represent the total phosphorus in the filtrate. The concentrations shown are average values. The number of data points used to calculate the average concentrations were between 75 and 8300 data points. For the total phosphorus concentrations in the WWTP effluent of 1.2 mg/L and higher, less than 200 data points were available.

The results show a consistent response. The total phosphorus concentration in the filtrate slightly increased with an increasing total phosphorus concentration in the WWTP effluent up to 1.3 mg/L. When the total phosphorus concentration in the WWTP effluent exceeded 1.3 mg/L, the total phosphorus concentration increased rapidly. The removal efficiency for orthophosphorus was between 80% and 90% for total phosphorus concentrations in the WWTP effluent of 0.2 mg/L to 1.3 mg/L.

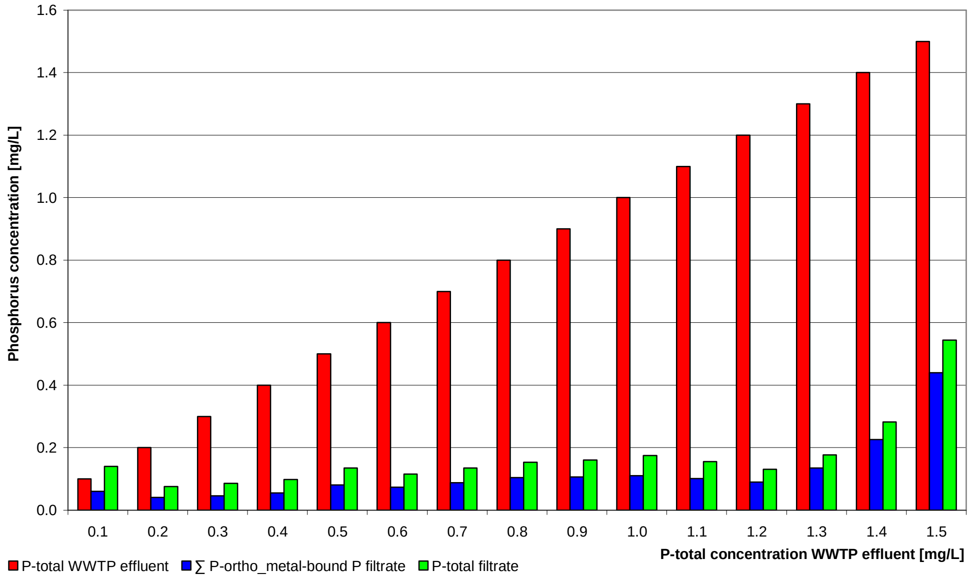

Figure 6-28 - Removal of phosphorus with coagulant and methanol dosage for the 1-STEP® filter at the Horstermeer WWTP

6.5.4 Comparing the removal efficiencies

In Figure 6-29 the total phosphorus removal efficiencies for dual media filtration at the Leiden Zuidwest WWTP (coarse filter bed, without biomass), dual media filtration at the Leiden Zuidwest WWTP (fine filter bed, without biomass), dual media filtration at the Horstermeer WWTP (with biomass), continuous sand filtration at the Leiden Zuidwest WWTP (with biomass), dual media filtration at the Leiden Zuidwest WWTP (coarse filter bed, with biomass), dual media filtration at the Leiden Zuidwest WWTP (fine filter bed, with biomass) and 1-STEP® filtration are presented.

The two lowest removal efficiencies (black and orange lines) shown in Figure 6-29 were reached by the dual media filter in combination with the coarse filter bed (with and without biomass) at the Leiden Zuidwest WWTP. The removal efficiencies remained mainly below 60%. For the same dual media filter but with the fine filter bed (pink and green lines) the removal efficiencies are comparable for the situation with or without biomass, namely between 60% and 70%. The dual media filter at the Horstermeer WWTP (with biomass) shows removal efficiencies in the range of 60% to 85% (red line). The 1-STEP® filter at the Horstermeer WWTP (blue line) shows higher removal efficiencies compared to dual media filtration, namely a removal efficiency in the range of 60% up to 90% for total phosphorus concentrations of 0.2 – 1.2 mg/L. The highest removal efficiencies were reached with Continuous Sand Filter A (turquoise line) at the Leiden Zuidwest WWTP, removal efficiencies of 90% up to 95% were reached for total phosphorus concentrations in the WWTP effluent of 0.7 – 1.5 mg/L.

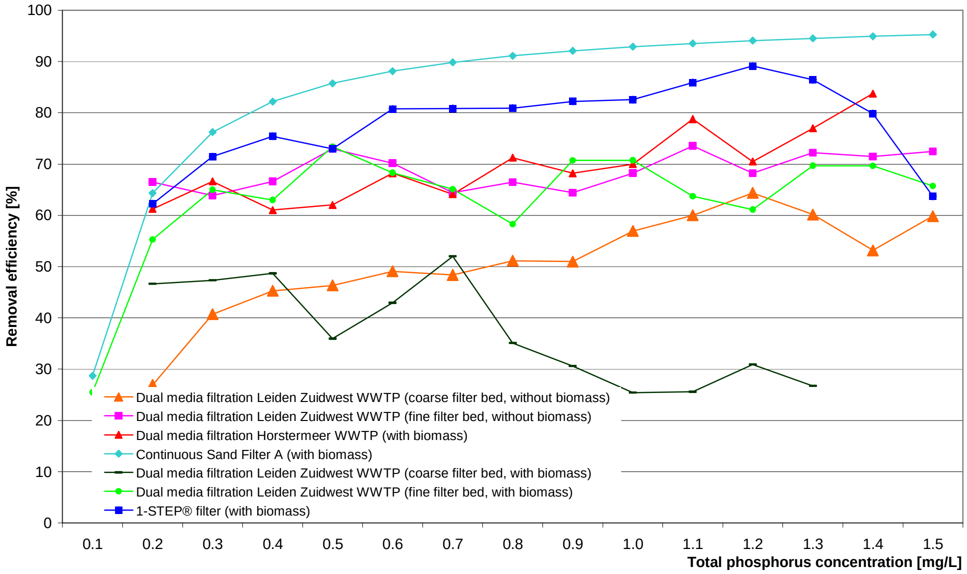

Figure 6-29 – Removal efficiencies for the different filtration techniques with or without biomass at the Horstermeer WWTP and the Leiden Zuidwest WWTP

6.6 Summary

This chapter describes the phosphorus removal with single media filtration (1-STEP® filtration), dual media filtration and continuous sand filtration. Phosphorus distributions, phosphorus size fractionations and profile measurements are presented for filtrate water using different filtration techniques. The results describe the optimal filtration rate, the influence of the floc size on the phosphorus removal, the removal of phosphorus through the filter bed, the changes in the phosphorus removal during the filter runtime and the phosphorus uptake by denitrifying bacteria. The main findings in this chapter are described in this summary.

- Increasing total phosphorus concentrations in the feed water result in increasing total phosphorus concentrations in the filtrate water. The coagulant dosage is of major influence on the filter runtime. With increasing coagulant dosage, the filter runtime decreases.

- Larger flocs formed with a flocculation time of 24 minutes do not result in higher removal efficiencies in the filter bed. It appears that the average total phosphorus concentration after filtration with a maximum flocculation time is higher compared to the situation with a minimum flocculation time. Not only is the floc size important but the floc strength is also of high importance.

- For dual media filtration, increasing total phosphorus concentrations in the feed water result in increasing total phosphorus concentrations in the filtrate water, but for continuous sand filtration this increase did not lead to higher total phosphorus concentrations in the filtrate.

- The removal mechanism of particulate organic phosphorus and dissolved “organic” phosphorus is filtration. This can be concluded from the profile measurements and the phosphorus determination on the activated carbon.

- 1-STEP® filtration reaches higher removal efficiencies compared to dual media filtration. Continuous sand filtration reached the highest removal efficiencies for total phosphorus concentrations of 0.1 – 1.5 mg/L.

6.7 References

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7 Temperature influences

The influence of temperature on the coagulation and flocculation processes is a known phenomenon and many literature references can be found (Subsections 2.2.2 and 2.3.2). However, information about temperature influences on phosphorus removal by filtration is hard to find. Research was conducted at the Horstermeer WWTP and at the Leiden Zuidwest WWTP to investigate the temperature influence on the coagulation, flocculation and filtration processes.

This chapter describes the temperature influence on the phosphorus distribution in the WWTP effluent and after coagulation/flocculation (Section 7.1). Experiments to investigate how the floc size is influenced by the temperature were conducted with jar tests. Water samples from the effluent of the Horstermeer WWTP and the Leiden Zuidwest WWTP were used. The results of these jar tests are described in Section 7.2. The results of the temperature influence on the filtration are described in Section 7.3.

7.1 Temperature influence on the phosphorus distribution

To determine the effect of the temperature on the phosphorus distribution of WWTP effluent data from the Horstermeer WWTP are used. The dataset is divided into water temperatures of <13°C, ≤13 - <18°C and ≥ 18°C. The results are shown on Figure 7-1. In the graph the green bars represent orthophosphorus, the red bars represent metal-bound phosphorus, the light blue bars represent dissolved “organic” phosphorus and the dark blue bars represent particulate organic phosphorus. The figure shows the highest total phosphorus concentrations for water temperatures of <13°C. This is mainly caused by increased metal-bound phosphorus (red bars) and the particulate organic phosphorus (dark blue bars) concentrations when compared to higher temperatures. The orthophosphorus concentration (green bars) is constant for all temperatures and is approximately 0.3 mg/L. The dissolved “organic” phosphorus concentration (light blue bars) is also constant and is approximately 0.04 mg/L for all temperature ranges. The lowest total phosphorus concentration in the WWTP effluent is found for water temperatures of ≤13 - <18°C. Temperatures higher than 18°C mainly show an increase of metal-bound phosphorus compared to ≤13 - <18°C.

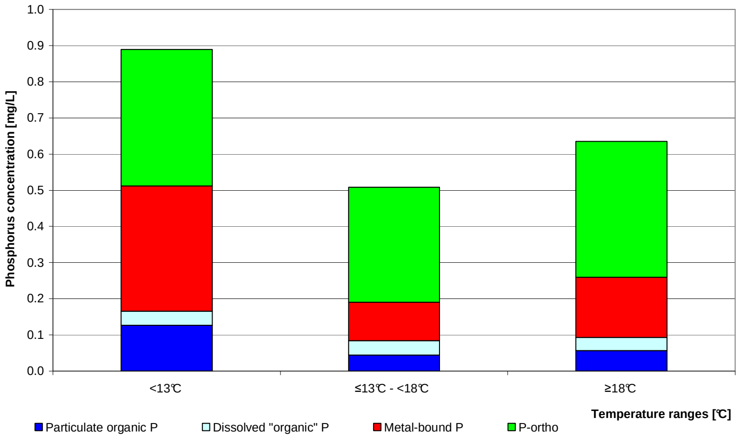

Figure 7-1 - Comparison of the phosphorus distribution of WWTP effluent for water temperatures of <13°C (6 data points), ≤13 - <18°C (16 data points) and ≥ 18°C (46 data points)

It can be concluded that the water temperature influences the concentrations of the particulate phosphorus forms in this WWTP effluent. The optimal temperature range is ≤13 - <18°C.

7.2 Temperature influence on coagulation

To determine the effect of temperature on coagulation, data from the Leiden Zuidwest WWTP were used. Figure 7-2 shows the results of the phosphorus distributions in concentrations and proportionally for a water temperature higher than 15°C (4 measurements) and lower than 15°C (13 measurements). In the graphs, the green bars represent orthophosphorus, the red bars represent metal-bound phosphorus, the light blue bars represent dissolved “organic” phosphorus and the dark blue bars represent particulate organic phosphorus. Samples were taken of the WWTP effluent and after coagulation/flocculation, which was from the upper water layer of the dual media filter.

When comparing the phosphorus distributions for <15°C and >15°C, it becomes clear that no obvious differences can be found for the WWTP effluent as well as after coagulation. In both situations the orthophosphorus concentration in the WWTP effluent was about 75% of the total phosphorus concentration. Approximately 80% of the orthophosphorus was transferred to metal-bound phosphorus after coagulant dosage. This was independent of the temperature.

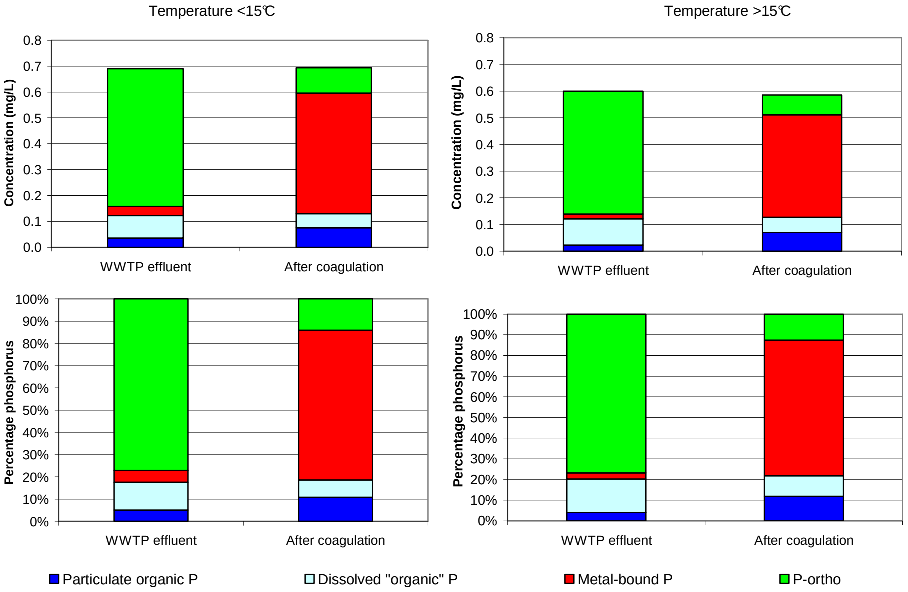

Figure 7-2 - Comparison of the phosphorus distribution of WWTP effluent and after coagulation (upper water layer of the dual media filter) for water temperatures of >15°C (left) and <15°C (right)

7.3 Temperature influence on the floc size

The effect of temperature on floc formation and floc size was tested with jar tests at three different temperatures. The results are divided into two subsections: the first, Subsection 7.3.1, deals with the data available for the Horstermeer WWTP where PAX-11 (poly aluminium chloride) was used as a coagulant. The second, Subsection 7.3.2, deals with the results of the Leiden Zuidwest WWTP where ferric(III)chloride and Q-pus (poly aluminium chloride) were used as the coagulants.

7.3.1 Flocculation with poly aluminium chloride at the Horstermeer WWTP

The jar tests at the Horstermeer WWTP were conducted with PAX-11 (poly aluminium chloride) at temperatures of 10°C, 15°C and 20°C. The metal/orthophosphorus ratio used was 16 mol/mol and the pH of the WWTP effluent was pH 6.1. The metal/orthophosphorus ratio is relatively high; this is due to a constant dosing of 7 mg Al^{3+}/L to be able to compare the results with the experiments conducted at the Leiden Zuidwest WWTP. Table 7-1 and Figure 7-3 show the results of the phosphorus size fractionations for WWTP effluent (red bars), after coagulation and flocculation at 10°C (blue bars), at 15°C (green bars) and at 20°C (purple bars).

Table 7-1 and Figure 7-3 show that the WWTP effluent consists mainly of orthophosphorus (red bar <0.45 µm). After coagulant dosage, orthophosphorus is transformed to metal-bound phosphorus (see fraction <0.45 µm for the blue, green and purple bars). Results show that the temperature had no effect on the transformation of orthophosphorus to metal-bound phosphorus. This can be concluded because the orthophosphorus concentration (<0.45 µm) after coagulation and flocculation was 0.005 mg P-ortho/L for the three tested temperatures. This confirms the results presented in Section 7.2. A clear temperature influence cannot even be found in the fraction of 2 – 0.45 µm. With an increasing temperature, the estimated floc size increased from 12.1 µm to 13.9 µm. The concentration of metal-bound phosphorus between 5 – 2 µm decreased with increasing temperatures. The concentration of metal-bound phosphorus in the fractions 10 – 5 µm and >10 µm shows an increasing trend, which means that flocs become larger with higher temperatures.

Table 7-1 - Results of jar tests with PAX-11 at 10°C, 15°C and 20°C. Metal/orthophosphorus ratio of 16 mol/mol.

Dosage [mg/L]	Temperature [°C]	Average floc size [µm]	Concentration [mg/L]				
			Unfiltered	10 µm	5 µm	2 µm	0.45 µm
7	10	12.1	0.626	0.468	0.162	0.020	0.005
7	15	14.7	0.622	0.400	0.111	0.040	0.005
7	20	13.9	0.635	0.445	0.053	0.011	0.005
0	12	3.6	0.586	0.524	0.529	0.512	0.498

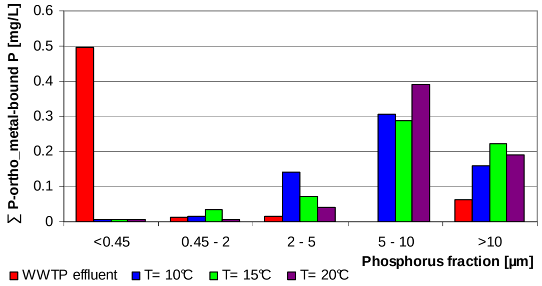

Figure 7-3 - Effects of temperature on phosphorus size distribution. Results of jar tests with PAX-11 at 10°C, 15°C and 20°C. Metal/orthophosphorus ratio of 16 mol/mol.

7.3.2 Flocculation with ferric(III)chloride and poly aluminium chloride at the Leiden Zuidwest WWTP

The jar tests at the Leiden Zuidwest WWTP were conducted with ferric(III)chloride and Q-pus (poly aluminium chloride) at temperatures of 10°C, 15°C and 20°C. The metal/orthophosphorus ratio used was 4 mol/mol and the pH in both situations was pH 7.0 before and after dosage. Photographs of the difference in floc formation at 10°C and 20°C with ferric(III)chloride are shown in Figure 7-3. The photographs show hardly any flocs at 10°C, but at 20°C many flocs can be seen.

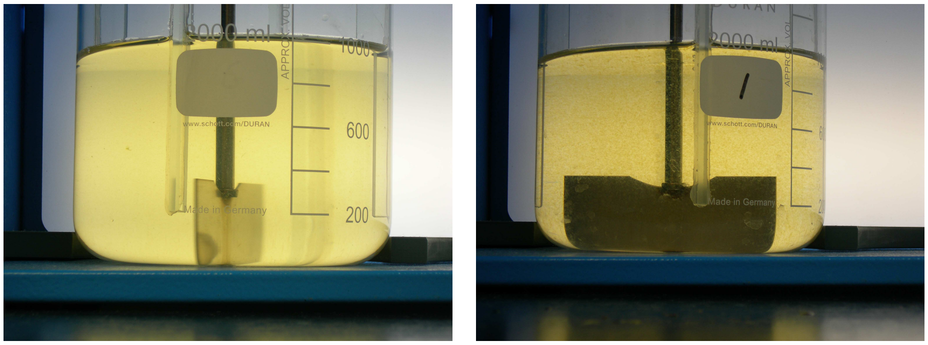

Figure 7-4 - Photograph of flocculation with ferric(III)chloride at a metal/orthophosphorus ratio of 4 mol/mol at temperatures of 10°C (left) and of 20°C (right)

The results of the jar tests conducted with ferric(III)chloride are shown in Table 7-2 and Figure 7-5, for Q-pus in Table 7-3 and Figure 7-6. Both figures show the phosphorus size fractionations of the WWTP effluent (red bars), after coagulation and flocculation at 10°C (blue bars), at 15°C (green bars) and at 20°C (purple bars).

Table 7-2 and Figure 7-5 show that the WWTP effluent mainly consisted of orthophosphorus (red bar <0.45 µm). After coagulant dosage, orthophosphorus is transferred to metal-bound phosphorus (see fraction <0.45 µm for the blue, green and purple bars). After coagulation and flocculation, the orthophosphorus concentration is smaller than 0.03 mg/L, which means that 97% of the orthophosphorus is transferred to metal-bound phosphorus. These results, which are comparable to the results of the Horstermeer WWTP conducted with PAX-11, show that the temperature has no effect on the transfer of orthophosphorus to metal-bound phosphorus. With increasing temperatures the estimated floc size increases. The concentration of metal-bound phosphorus between 2 – 0.45 µm decreases with increasing temperatures and orthophosphorus remains constant. The concentration of metal-bound phosphorus increased in the fractions 5 – 2 µm, 10 – 5 µm and >10 µm which means that flocs became larger with higher temperatures.

Table 7-2 - Results of jar tests with ferric(III)chloride at 10°C, 15°C and 20°C. Metal/orthophosphorus ratio of 4 mol/mol.

Dosage [mg/L]	Temperature [°C]	Average floc size [µm]	Concentration [mg/L]				
			Unfiltered	10 µm	5 µm	2 µm	0.45 µm
7	10	3.6	1.050	1.010	0.904	0.595	0.013
7	15	5.0	1.050	0.982	0.774	0.440	0.027
7	20	5.7	1.030	0.953	0.694	0.334	0.028
0	12	1.0	1.040	1.020	1.020	1.030	1.010

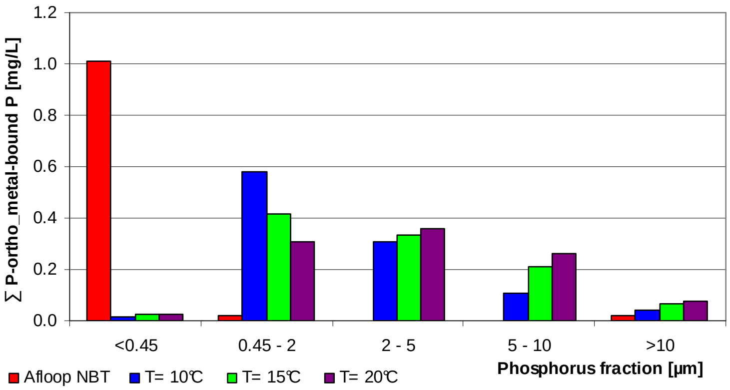

Figure 7-5 - Effects of temperature on the phosphorus size distribution. Results of jar tests with ferric(III)chloride at 10°C, 15°C and 20°C. Metal/orthophosphorus ratio of 4 mol/mol.

In Table 7-3 and Figure 7-6 results for Q-pus are presented for the same feed water as used for ferric(III)chloride. The metal/orthophosphorus ratio again is 4 mol/mol. After the coagulant dosage of 0.1 mg/L, orthophosphorus was not transferred to metal-bound phosphorus. This residual orthophosphorus concentration is higher compared to that of ferric(III)chloride. Comparable to ferric(III)chloride is that flocs become larger with increasing temperatures. See the decrease of the metal-bound phosphorus concentrations between 2 – 0.45µm and the increase between 2 – 5µm, in Figure 7-6. A difference which can be seen when comparing ferric(III)chloride with Q-pus is that flocs become larger with ferric(III)chloride at all temperatures. The estimated floc sizes for ferric(III)chloride are between 3.6 µm (10°C) and 5.7 µm (20°C) and for Q-pus approximately 3.0 µm. For Q-pus flocs hardly become larger than 5 µm, even with a temperature of 20°C.

Table 7-3 - Results of jar tests with Q-pus at 10°C, 15°C and 20°C. Metal/orthophosphorus ratio of 4 mol/mol.

Dosage [mg/L]	Temperature [°C]	Average floc size [µm]	Concentrations [mg/L]				
			Unfiltered	10 µm	5 µm	2 µm	0.45 µm
7	10	3.3	1.05	0.980	0.990	0.890	0.090
7	15	1.9	1.02	1.010	0.990	0.860	0.100
7	20	2.8	1.03	0.990	0.980	0.730	0.140
0	12	1.0	1.040	1.020	1.020	1.030	1.010

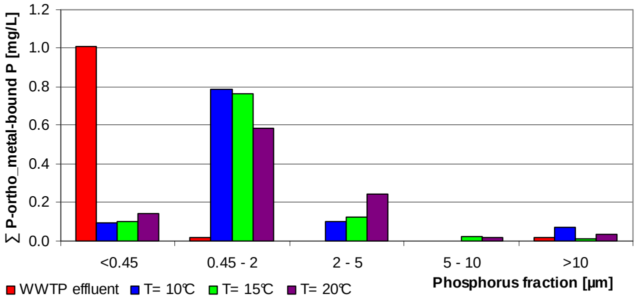

Figure 7-6 – The effect of temperature on the phosphorus size distribution. Results of jar tests with polyaluminiumchloride at 10°C, 15°C and 20°C. Metal/orthophosphorus ratio of 4 mol/mol.

7.4 Filtration

Temperature influences on the total phosphorus removal by filtration were investigated at the Horstermeer WWTP and at the Leiden Zuidwest WWTP. This section is divided into four subsections. Subsection 7.4.1 describes the temperature influence on filtration with a dual media filter with biomass. Subsection 7.4.2 describes the influence of temperature on filtration with a continuous sand filter. Dual media filtration with biomass is described in Subsection 7.4.3, and 1-STEP® filtration is described in Subsection 7.4.4.

7.4.1 Dual media filtration without biomass

To investigate the temperature influence on total phosphorus removal from the WWTP effluent for a fine filter bed without biomass, the on-line data for the dual media filter of the Leiden Zuidwest WWTP were used. The data were from mid-June 2007 until mid-April 2008. In Figure 7-7 the results are illustrated. Data used for the construction of the graph had a filtration rate of 10 m/h and a metal/orthophosphorus concentration of 4 mol/mol. The figure shows the orthophosphorus concentration in the WWTP effluent (red bars), the total phosphorus concentration in the filtrate for a temperature of < 13°C (dark blue bars), the total phosphorus in the filtrate for a temperature between 13°C and 18°C (green bars) and the total phosphorus in the filtrate for a temperature ≥ 18°C (light blue bars). The shown concentrations are averaged values. The number of data points used to calculate the average concentrations were between 20 and 2200. For temperatures <13°C at least 235 data points were available per concentration in the WWTP effluent, for temperatures ≥ 18°C few data were available.

Figure 7-7 shows increasing total phosphorus concentrations in the filtrate for increasing total phosphorus concentrations in the WWTP effluent. For total phosphorus concentrations in the WWTP effluent of 0.8 mg/L and higher, the total phosphorus concentrations in the filtrate for temperatures between 13°C and 18°C are compared to the total phosphorus concentration at temperatures <13°C. For total phosphorus concentrations in the WWTP effluent from 0.2 mg/L up to 0.8 mg/L, the lowest total phosphorus concentrations in the filtrate were reached at temperatures ≥ 18°C.

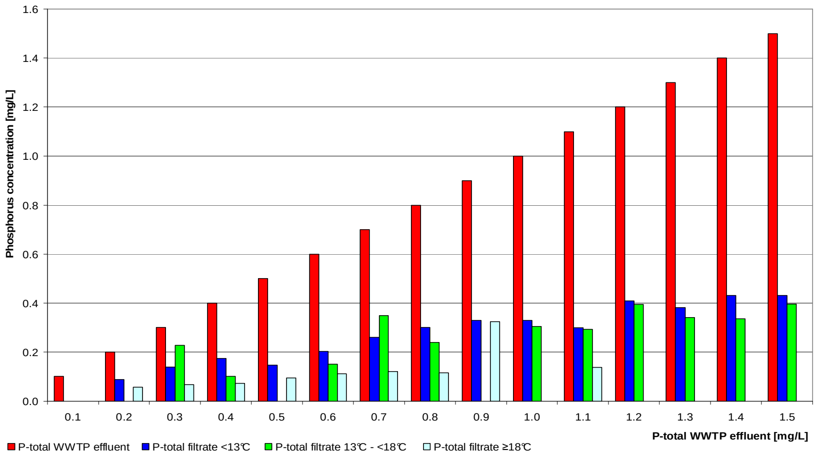

Figure 7-7 – Temperature influence on the total phosphorus concentration in the filtrate of the dual media filter (without biomass, fine filter bed) at the Leiden Zuidwest WWTP. Filtration rate of 10 m/h and a metal/orthophosphorus concentration of 4 mol/mol.

7.4.2 Continuous sand filtration

To investigate the temperature influence on total phosphorus removal from the WWTP effluent for continuous sand filtration, on-line data were available from the Leiden Zuidwest WWTP. For the construction of Figure 7-8, the on-line data were from January 2008 until July 2008. These data were available for a filtration rate of 15 - 17 m/h in combination with a metal/orthophosphorus ratio of 7.5 for orthophosphorus concentrations in the WWTP effluent < 0.15 mg/L and a ratio of 4 mol/mol for orthophosphorus concentrations in the WWTP effluent > 0.15 mg/L. The figure shows the orthophosphorus concentration in the WWTP effluent (red bars), the total phosphorus concentration in the filtrate for a temperature of < 13°C (dark blue bars), the total phosphorus in the filtrate for temperatures between 13°C and 18°C (green bars) and the total phosphorus in the filtrate for a temperature ≥ 18°C (light blue bars). The shown concentrations are averaged values. The number of data points used to calculate the average concentrations were between approximately 100 and 6300. For the concentration area of 0.9 – 1.5 mg/L for temperatures between 13°C and 18°C and for the concentration area of 1.2 – 1.5 mg/L for temperatures ≥ 18°C, fewer than 100 data points were available. In all the other cases, at least 100 data points were available.

For temperatures of <13°C and between 13°C and 18°C, Figure 7-8 shows gradually increasing total phosphorus concentrations in the filtrate for increasing total phosphorus concentrations in the WWTP effluent. For temperatures of ≥ 18°C the total phosphorus remains steady at a concentration of approximately 0.12 mg/L. For all the total phosphorus concentrations in the WWTP effluent, a decreasing trend is shown for total phosphorus concentrations in the filtrate with increasing temperatures.

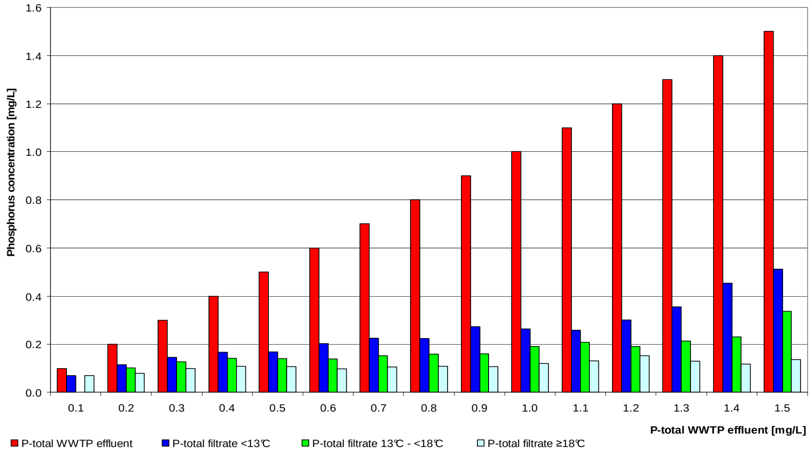

Figure 7-8 – Temperature influence on the total phosphorus concentration in the filtrate of the Continuous Sand Filter A at the Leiden Zuidwest WWTP. filtration rate of 15 -17 m/h and a metal/orthophosphorus concentration of 7.5 - 4 mol/mol.

7.4.3 Dual media filtration with biomass

For the construction of Figure 7-9, the on-line data of 2007 and 2008 for the dual media filter at the Horstermeer WWTP were used. For the Leiden Zuidwest WWTP insufficient data were available to investigate the influence of temperature on filtration. The reason for the use of two years of on-line data is the regular malfunction of the on-line analysers. Data with metal/orthophosphorus ratios between 3 and 5 mol/mol were selected and a filtration rate of 10 m/h. The figure shows the total phosphorus concentration in the WWTP effluent (red bars; calculated with Figure 5-4), the total phosphorus concentration in the filtrate for a temperature of < 13°C (dark blue bars), the total phosphorus in the filtrate for temperatures between 13°C and 18°C (green bars), and the total phosphorus in the filtrate for a temperature ≥ 18°C (light blue bars). The shown concentrations are averaged values. The number of data points used to calculate the average concentrations were between 100 and 1400. For the orthophosphorus concentrations in the WWTP effluent of 0.8 mg/L and higher, fewer than 100 data points were available. Because of a further decreasing number of data points for concentrations above 1.0 mg/L, the graph only shows an orthophosphorus range in the WWTP effluent of 0.2 mg/L to 1.0 mg/L.

Figure 7-9 shows for all temperatures, an increasing total phosphorus concentration in the WWTP effluent and an increasing total phosphorus in the filtrate. The total phosphorus concentrations in the filtrate for temperatures between 13°C and 18°C (green bars) are lower when compared with the results for temperatures <13 °C and ≥ 18°C. This is clearly seen in the range of orthophosphorus concentrations in the WWTP effluent of 0.6 mg/L up to 1.0 mg/L. The total phosphorus concentration in the filtrate remains more consistent and does not increase as fast as in other temperature ranges. The rapid increase in the total phosphorus concentration in the filtrate for temperatures >18°C was probably caused by the more open structure flocs get with higher temperatures. This issue was already described in Subsection 2.3.2.

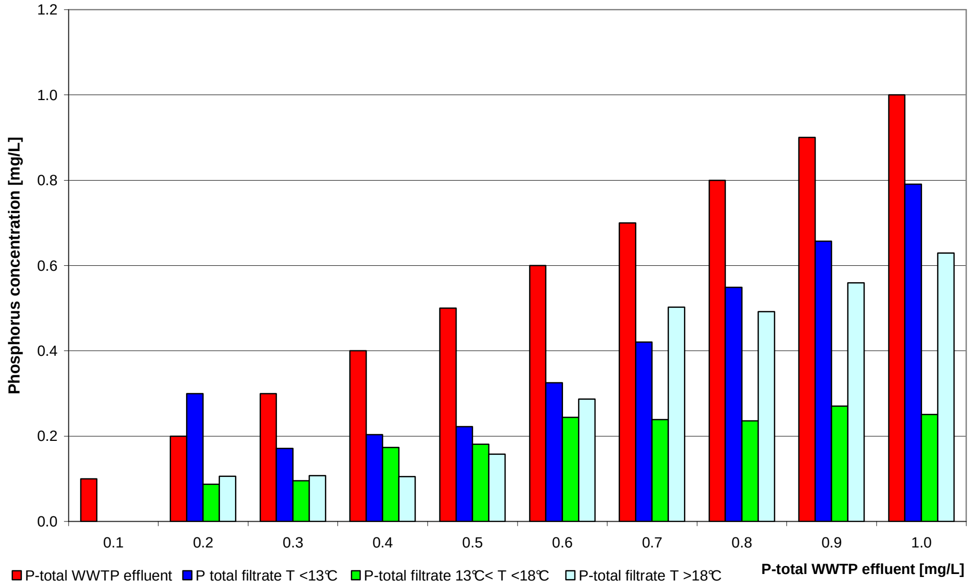

Figure 7-9 – Temperature influence on the total phosphorus concentration in the filtrate of the dual media filter at the Horstermeer WWTP. Filtration rate of 10 m/h and a metal/orthophosphorus concentration of 3 - 5 mol/mol.

7.4.4 1-STEP® filtration

For the construction of Figure 7-10 the on-line data of 2008 were used. Data with metal/orthophosphorus ratios between 3 and 5 mol/mol were selected and a filtration rate of 10 m/h. The figure shows the total phosphorus concentration in the WWTP effluent (red bars; calculated from Figure 5-4), the total phosphorus concentration in the filtrate for a temperature of < 13°C (dark blue bars), the total phosphorus in the filtrate for temperatures between 13°C and 18°C (green bars), and the total phosphorus in the filtrate for a temperatures ≥ 18°C (light blue bars). The concentrations shown are averaged values. The number of data points used to calculate the average concentrations were between 5 and 3200 data points. For temperatures < 13°C the available data points for the total phosphorus concentrations of 1.1 – 1.5 mg/L in the filtrate were fewer than 20. Therefore, these data can be considered highly inaccurate.

Figure 7-10 shows that the total phosphorus concentrations in the filtrate for a temperature of <13°C (blue bars) are always higher compared to concentrations at higher temperatures. For total phosphorus concentrations in the WWTP effluent of 0.3 – 0.8 mg/L, a decreasing trend is shown for total phosphorus concentrations in the filtrate with increasing temperatures. For total phosphorus concentrations in the WWTP effluent of 0.9 mg/L and higher, the total phosphorus concentration in the filtrate for temperatures <13°C and ≥18°C is higher compared to temperatures between 13°C and 18°C. The total phosphorus concentration in the filtrate increased for total phosphorus concentrations in the WWTP effluent of 0.9 mg/L and higher for temperatures <13°C and ≥18°C, but remained consistent for temperatures between 13°C and 18°C. The differences are probably due to the more open structure of the flocs formed at higher temperatures, which probably results in floc breakage in the filter bed.

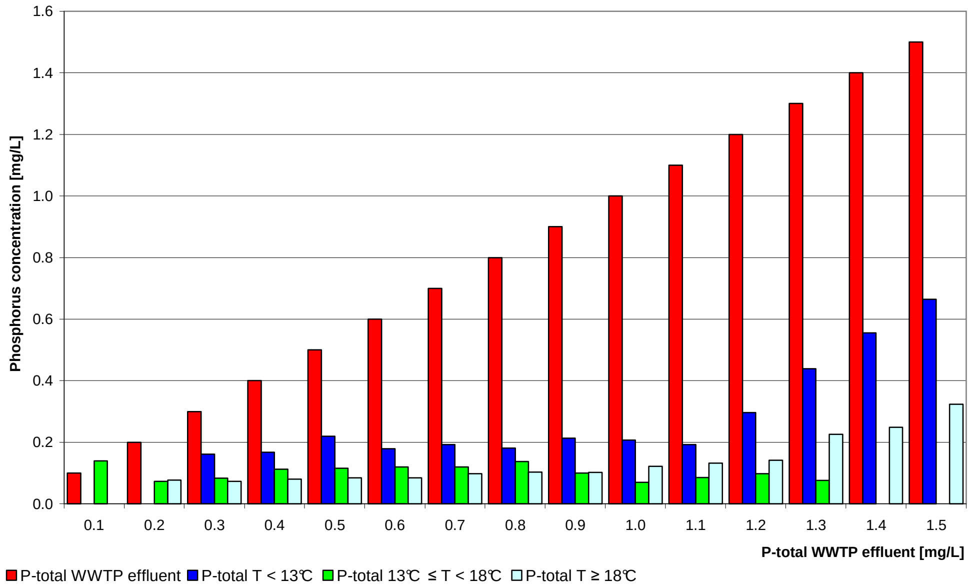

Figure 7-10 – Temperature influence on the total phosphorus concentration in the filtrate of the 1-STEP® at the Horstermeer WWTP. Filtration rate of 10 m/h and a metal/orthophosphorus concentration of 3 - 5 mol/mol.

7.5 Summary

The phosphorus distribution and the phosphorus size fractionation showed that the rate of metal-hydroxide precipitation (the transfer of orthophosphorus to metal-bound phosphorus) is not significantly inhibited by temperature. The jar tests conducted in combination with the phosphorus size fractionations showed that flocs become larger with increasing temperatures.

All tested filtration techniques contained the highest total phosphorus concentrations in the filtrate for water temperatures of < 13°C. However, differences exist between down flow depth filtration and continuous sand filtration. Low phosphorus concentrations in the WWTP effluent show decreasing total phosphorus concentrations for down flow depth filtration in the filtrate for increasing temperatures. For higher phosphorus concentrations, the optimal temperature range is between 13°C and 18°C and not ≥18°C. The turning point varied per installation and was probably influenced by the velocity (shear rate) in the filter bed and the floc strength. For continuous sand filtration, increasing temperatures result in decreasing total phosphorus concentrations in the filtrate.

8 Phosphorus limitation

When combining nitrogen and chemical phosphorus removal in a single filter, phosphorus limitation may occur (see also Subsection 2.5.4 for more information). Low orthophosphorus concentrations may affect the denitrification conversion rate by inhibiting the rapid growth of heterotrophic microorganisms in response to increasing nitrate (NO_3-N) loads (Husband and Becker, 2007). Inhibition of the denitrification can be caused by many factors besides a shortage of phosphorus. For example, the presence of oxygen, the pH, toxic substances and a shortage of carbon source may also cause inhibition of the denitrification.

To be able to exclude inhibition by oxygen, chemical oxygen demand (COD) and pH from the datasets used, profile measurements for the dual media filter and 1-STEP® filter at the Horstermeer WWTP were made for oxygen and COD. For the Continuous Sand Filter A at the Leiden Zuidwest, WWTP the oxygen and COD concentrations were regularly measured in the feed water and in the filtrate water of the filter. At both locations, the pH was regularly measured in the feed water and filtrate water of the filters. Profile measurements show that the oxygen concentrations in the second half of the filter bed and in the filtrate water of the filters were always below 0.5 mg/L and should therefore not inhibit the denitrification (Van der Graaf, 1996). COD concentrations in the feed water were 1 or 2 mg/L higher compared to the concentrations in the filtrate water which varied between 25 and 35 mg COD/L. Therefore, denitrification was not likely to be inhibited by the COD concentration. The average pH in the feed water and filtrate water of the filters at the Horstermeer WWTP was 6.4 and was 7.0 for the feed water at the Leiden Zuidwest WWTP. The optimal pH range for denitrification is 7 – 9 (Van der Graaf, 1996) and, therefore, the pH of the feed water of the filters at the Horstermeer WWTP might cause inhibition of the denitrification. However, the pH of the feed water was approximately 6.4 all year and inhibition of the denitrification in combination with nitrite accumulation of 2 – 4 mg/L was rarely found.

In Section 8.1 in this chapter, the minimum required PO_4-P/NO_x-N ratio for denitrification conversion rates of 70% and higher is determined as well as which denitrification reduction step is sensitive to low PO_4-P/NO_x-N ratios. In Section 8.2 profile measurements are described to locate phosphorus limitation. Section 8.3 gives a possibility for solving the phosphorus limitation and, finally, in Section 8.4 a new coagulant dosage system is introduced. This dosage system minimises the risk of phosphorus limitation and saves coagulant.

8.1 Minimum required PO_4-P/NO_x-N ratio

Theoretically, phosphorus becomes a limiting factor for the denitrification rate when concentrations are below 0.04 mg P/mg NO_x-N in the feed water, assuming 3 mg of methanol (MeOH) per mg NO_x-N (deBarbadillo et al., 2006; Husband and Becker, 2007). Research (e.g. deBarbadillo et al., 2006; Hanner et al., 2003) shows that a PO_4-P/NO_x-N ratio of approximately 0.02 mg/mg or higher does not appear to have any impact on the denitrification rate. Differences in the minimum PO_4-P/NO_x-N ratio might be due to the culture history (Nordedeit et al., 1994). See also section 6.2.6. This section describes the results for the Horstermeer WWTP (Subsection 8.1.1) and the Leiden Zuidwest WWTP (Subsection 8.1.2). The results presented for the Leiden Zuidwest WWTP are based on Scherrenberg et al. (2008). For both locations the minimum required PO_4-P/NO_x-N ratio is defined for denitrification conversion rates of 70% and higher. The orthophosphorus, nitrate and nitrite analyses made for grab samples taken of the WWTP effluent and the filtrate of the 1-STEP® filter at the Horstermeer WWTP were used to investigate which denitrification reduction step is sensitive to low PO_4-P/NO_x-N ratios.

8.1.1 The Horstermeer WWTP

As stated before, the literature values for the minimum required PO_4-P/NO_x-N ratio to prevent inhibition of the denitrification efficiency caused by phosphorus limitation differ. To determine the minimum PO_4-P/NO_x-N ratio required for denitrification conversion rates (i.e. removal efficiency) of 70% and higher, the on-line data from August – October 2009 were used for the 1-STEP® filter at the Horstermeer WWTP. In this period, the metal/orthophosphorus ratio for the 1-STEP® filter was between 0 and 5 mol/mol.

On the left side of Figure 8-1, the NO_x-N removal efficiency relates to the PO_4-P/NO_x-N ratio in the WWTP effluent is shown, and on the right side how the removal efficiency relates to the $\sum PO_4$-P_metal-bound phosphorus/NO_x-N ratio in the filtrate water. The cross-hatched areas in the graphs show that NO_x-N removal rates below 70% occur frequently for PO_4-P/NO_x-N ratios below 0.055 mg/mg in the WWTP effluent and for $\sum PO_4$-P_metal-bound phosphorus/NO_x-N ratios of 0.035 mg/mg in the filtrate water. In these cross-hatched areas, phosphorus limitation might be the cause of the decreasing denitrification efficiency.

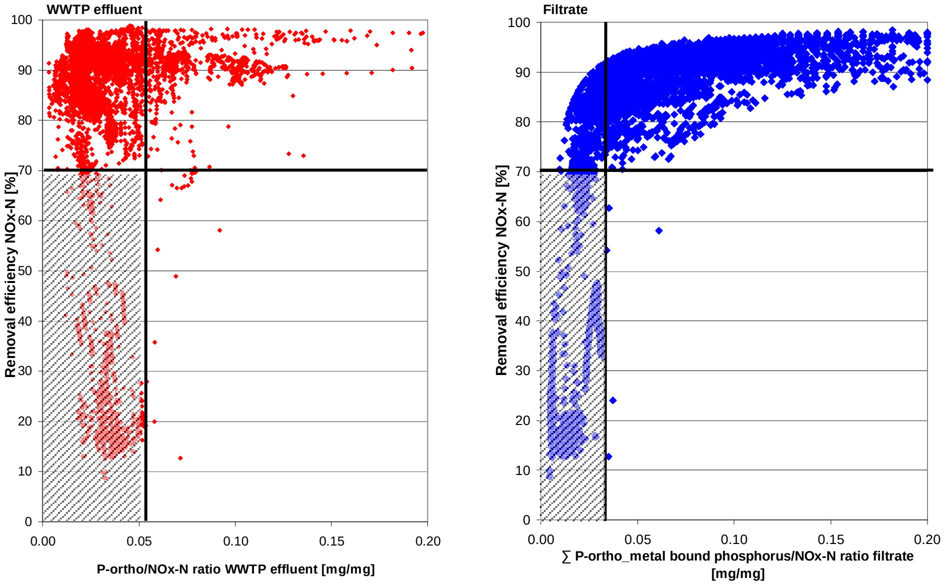

Figure 8-1 - Influence of the PO_4-N/NO_x-N ratio of the WWTP effluent (left graph) and the filtrate (right graph) on NO_x-N removal efficiency

The relative number of measurements with an NO_x-N removal efficiency of <70% was calculated per PO_4-P/NO_x-N ratio; this is shown in Figure 8-2. This figure shows no significant percentages for PO_4-P/NO_x-N ratios >0.055 mg/mg, meaning that nearly all the measured NO_x-N removal rates are above 70%. For PO_4-P/NO_x-N ratios <0.055 mg/mg, percentages up to 30% were found, meaning that the number of data points for NO_x-N removal rates of <70% are significant. Therefore, the set point for the 1-STEP® filter at Horstermeer WWTP is 0.055 mg/mg.

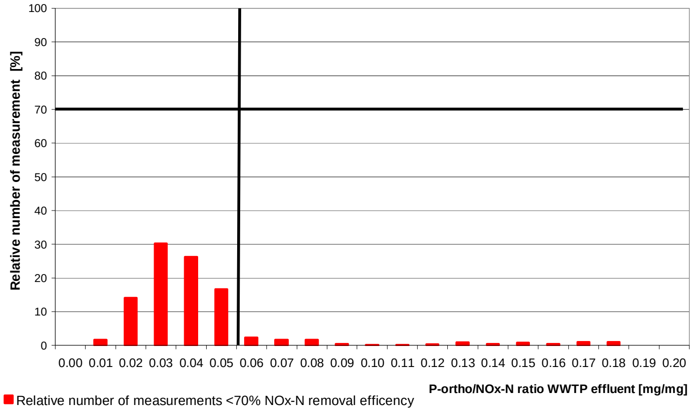

Figure 8-2 – Relative number of measurements with a NO_x-N removal efficiency of <70%. Derived from Figure 8-1 (left graph)

Decreasing removal efficiencies for NO_x-N as shown in Figure 8-1 are caused by a decreasing efficiency of the denitrifying reduction steps of either $NO_3^- \rightarrow NO_2^-$ or $NO_2^- \rightarrow NO$. Normally, nitrite is consumed at a rate twice the nitrate reduction rate; therefore, the rate-limiting step for denitrification is the reduction from nitrate to nitrite (Timmermans and Van Haute, 1983).

Figure 8-3 shows which reduction step causes the decrease in the NO_x-N removal efficiency and is therefore more sensitive to low PO_4-P/NO_x-N ratios in the feed water. Figure 8-3 shows how the NO_3-N concentrations in the WWTP effluent and in the filtrate (top graph) and the NO_2-N concentrations in the WWTP effluent and in the filtrate (bottom graph) vary with the PO_4-P/NO_x-N ratio in the WWTP effluent. All data presented in the graphs are the result of grab samples. In every grab sample the nitrate, nitrite and orthophosphorus concentrations were measured. Only data with a maximum NO_3-N concentration of 10 mg/L in the WWTP effluent are shown. The two grab samples with PO_4-P/NO_x-N ratios of 0.17 and 0.21 mg/mg indicate a malfunction at the WWTP: orthophosphorus concentrations in the WWTP effluent are 1.14 mg/L and 1.57 mg/L, yet the yearly average in 2008 was 0.4 mg PO_4-P/L (see also Section 3.1). The top graph in Figure 8-3 shows that the NO_3-N concentration in the WWTP effluent varied between approximately 4 mg/L and 10 mg/L. The NO_3-N concentrations in the filtrate water always vary between 0 mg/L and approximately 1.5 mg/L, even though the PO_4-P/NO_x-N ratios are below 0.05 mg/mg. It can therefore be stated that the $NO_3^- \rightarrow NO_2^-$ reduction step is not sensitive to low PO_4-P/NO_x-N ratios.

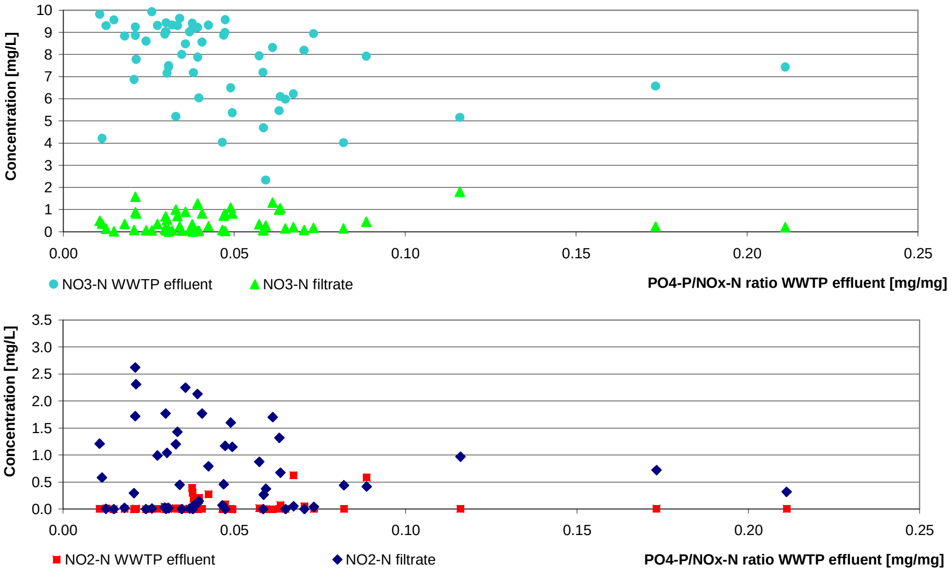

Figure 8-3 – Variation of NO_3-N concentrations in the WWTP effluent and in the filtrate (top graph) and of NO_2-N concentrations in the WWTP effluent and in the filtrate (bottom graph) with the PO_4-P/NO_x-N ratio in the WWTP effluent

The bottom graph of Figure 8-3 shows that the NO_2-N concentration in the WWTP effluent was close to 0 mg/L, though sometimes higher concentrations were found. The NO_2-N concentrations in the filtrate water varied between 0 mg/L and 2.6 mg/L. The results of the NO_2-N measurements in the filtrate water show that, for 75% of the measurements, an increase in the NO_2-N concentration of 0.5 mg/L or more, and 55% of the measurements show an increase in the NO_2-N concentration of 1.0 m/L or more. These results suggest that the $NO_2^- \rightarrow NO$ reduction step is sensitive to low PO_4-P/NO_x-N ratios in the WWTP effluent and, therefore, nitrite accumulation might occur in the filter bed during periods of low PO_4-P/NO_x-N ratios.

8.1.2 The Leiden Zuidwest WWTP

In March 2007 experiments are conducted to determine the minimum PO_4-P/NO_x-N ratio required for denitrification. During this period the nitrate concentrations in the WWTP effluent were extremely low. Therefore sodium nitrate was dosed at the feed water of continuous sand filter A to reach average nitrate concentrations of 8 mg/L. No coagulant dosage is used in this period. The filtration rate is 22.5 m/h. The orthophosphorus analyser measures the orthophosphorus concentration without filtration through 0.45 μm and therefore metal-bound phosphorus is included, as described in Section 3.2.8. But the results of the TU Delft phosphorus distribution method (subsection 5.1.1) show that on average 0.04 mg/L (7% of the total phosphorus concentration) is metal-bound phosphorus. The orthophosphorus concentration is on average 0.39 mg/L (71% of the total phosphorus concentration) and therefore the concentration metal-bound phosphorus can be neglected and the PO_4-P/NO_x-N ratio can determined with the analyser.

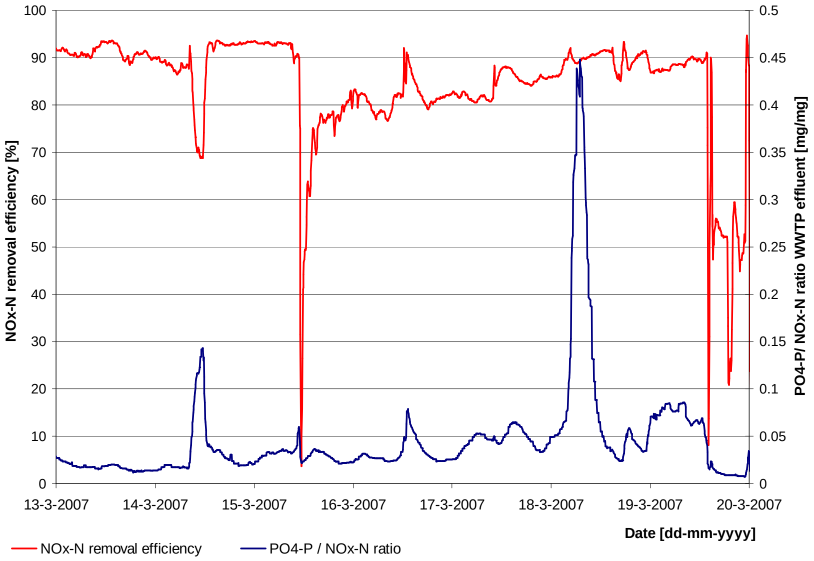

Figure 8-4 - Denitrification conversion rate (primary y-axis) and the PO_4-P/NO_x-N ratio (secondary y-axis) during a period with sodium nitrate dosage to average NO_x-N concentrations of 8 mg/L and no coagulant dosage (Malsh, 2008)

Figure 8-4 shows the removal efficiency (primary y-axis) for NO_x-N for continuous sand filter A and the PO_4-P/NO_x-N ratio (secondary y-axis) in the WWTP effluent during a week. Results show that no limitation of denitrification efficiency occurs even with PO_4-P/NO_x-N ratios of 0.025 mg/mg, denitrification conversion rates stay at 90%.

In February and March 2008, experiments with low PO_4-P/NO_x-N ratios in the WWTP effluent were repeated, this time with ferric(III)chloride dosage. To reach total phosphorus concentrations of approximately 0.20 mg/L, extra ferric(III)chloride was dosed in the activated sludge process of the WWTP. The experiments were conducted with continuous sand filter A with a filtration rate of 15 m/h. Ferric(III)chloride was dosed with a metal/orthophosphorus ratio of 4 mol/mol. During this period the nitrate concentrations in the WWTP effluent were again extremely low. Therefore, sodium nitrate was dosed at the feed water of continuous sand filter A. According to Malsch (2008), the orthophosphorus consumption for the growth of biomass in continuous sand filter A is 0.057 mg orthophosphorus per mg NO_x-N. Figure 8-5 shows the NO_x-N removal efficiency (primary y-axis) in continuous sand filter A, the orthophosphorus concentrations and the total phosphorus concentrations in the WWTP effluent (secondary y-axis). The average nitrate concentration in the feed water was 8 mg/L during this period; therefore, the variations in the PO_4-P/NO_x-N ratio are the result of fluctuations in the PO_4-P concentration in the effluent. This figure shows that the denitrification removal efficiency varied between 30% and 90%.

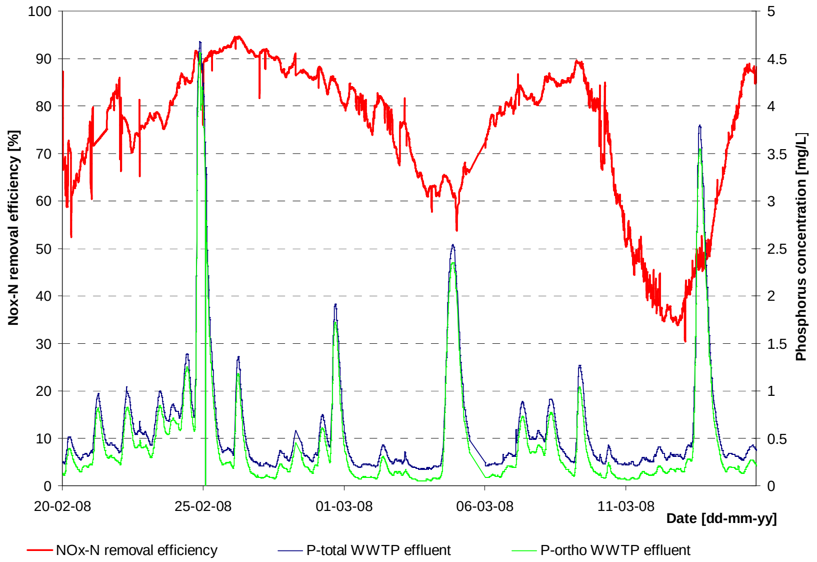

Figure 8-5 - Results of the NO_x-N removal efficiency (primary y-axis) in continuous sand filter A, the orthophosphorus concentration and the total phosphorus concentration (secondary y-axis) in the WWTP effluent (Malsh, 2008). Average nitrate concentration in this period was 8 mg/L.

Figure 8-6 is derived from Figure 8-5 and shows the NO_x-N removal efficiency (primary y-axis) and the average PO_4-P/NO_x-N ratio in the WWTP effluent (secondary y-axis). The figure shows in the first period, from the 22nd - 27th of February 2008, that adaptation of the biomass occurs in response to increased nitrate concentrations, due to the sodium nitrate dosage. In the second period, from the 27th of February to the 5th of March 2008, the average PO_4-P/NO_x-N ratio is 0.04 mg/mg. During this period the NO_x-N removal efficiency slowly decreased, which might be interpreted as a critical PO_4-P/NO_x-N ratio. In the third period, from the 5th – 9th March 2008, recovery of the NO_x-N removal efficiency took place at a PO_4-P/NO_x-N ratio of 0.05 mg/mg. The fourth period, from the 9th – 13th of March 2008, shows what was probably phosphorus limitation. During this period the average PO_4-P/NO_x-N ratio is 0.02 mg/mg. This period shows that the denitrification removal efficiency decreased rapidly from 90% to 35%. In the fifth period, from the 13th - 16th of March 2008, the PO_4-P/NO_x-N ratio increased to 0.09 mg/mg and the NO_x-N removal efficiency recovered rapidly to the initial value of the first period.

Figure 8-6 indicates that phosphorus might become a limiting factor for denitrification efficiency when PO_4-P/NO_x-N ratios are below 0.05 mg/mg. This ratio is higher compared to the ratio found without ferric(III)chloride dosage, which was 0.025 mg/mg. Therefore, it can be concluded that metal-bound phosphorus is hardly or not at all available for the heterotrophic microorganisms.

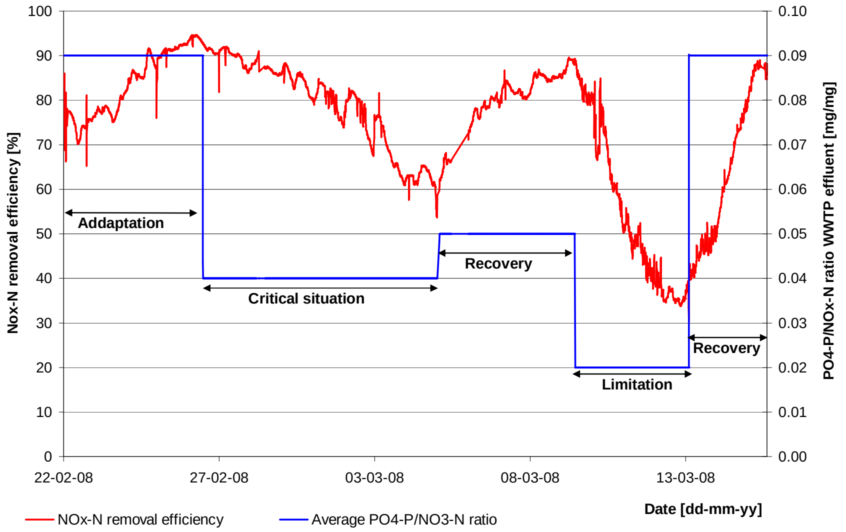

Figure 8-6 - Results of the denitrification conversion rate (primary y-axis) and the average PO_4-P/NO_x-N ratio (secondary y-axis) calculated with concentrations before coagulant dosage (Malsch, 2008)

To determine the minimum PO_4-P/NO_x-N ratio required for denitrification conversion rates (i.e. removal efficiency) of 70% and higher, on-line data were used for the continuous sand filter A. Figure 8-7 shows how the denitrification removal efficiency depends on the PO_4-P/NO_x-N ratio in the WWTP effluent. The cross-hatched area shows that NO_x-N removal rates below 70% occurred frequently for PO_4-P/NO_x-N ratios below 0.05 mg/mg in the WWTP effluent. In this cross-hatched area, phosphorus limitation might be the cause of the decreasing denitrification efficiency. This corresponds with the results shown in Figure 8-6.

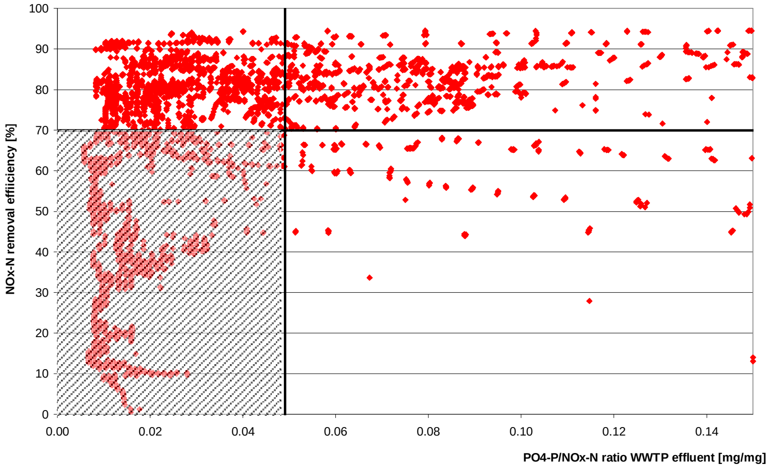

Figure 8-7 - The NO_x-N removal efficiency in relation to the PO_4-P/NO_x-N ratio in the WWTP effluent

Phosphorus distributions made for the WWTP effluent and after coagulant dosage for the different installations at the Leiden Zuidwest WWTP and the Horstermeer WWTP show that approximately 90% of the available orthophosphorus in the WWTP effluent was bound to metal salt after coagulant dosage. Therefore approximately 10% of the available orthophosphorus in the WWTP effluent remained dissolved after coagulation. The results of the Leiden Zuidwest WWTP show that metal-bound phosphorus was hardly or not at all available for the heterotrophic microorganisms. Therefore the actual PO_4-P/NO_x-N ratio in the feed water entering the filter bed, after coagulant dosage, is just 10% of the ratio found for the WWTP effluent before coagulant dosage. This results in a minimum required PO_4-P/NO_x-N ratio of 0.0055 mg/mg for the Horstermeer WWTP and a PO_4-P/NO_x-N ratio of 0.005 mg/mg for the Leiden Zuidwest WWTP. These values are much lower compared to the values found in the literature.

8.2 Locating phosphorus limitation in a filter bed

In order to investigate the decreasing denitrification efficiencies which are found for PO_4-P/NO_x-N ratios of 0.055 mg/mg in the WWTP effluent, profile measurements were made on a regular basis. For a profile measurement, samples are taken of the WWTP effluent (see also Section 4.6), the upper water layer of the fixed filter bed, every 10 or 20 cm in the filter bed, and in the filtrate water of the filter. The orthophosphorus, nitrate, nitrite, and COD are measured. The PO_4-P/NO_x-N ratio in mg/mg is calculated for every sample point. This section gives the results of the profile measurements for the dual media filter (Subsection 8.2.1) and the 1-STEP® filter (Subsection 8.2.2), both located at the Horstermeer WWTP.

8.2.1 Dual media filtration

In July 2008 nitrite formation was measured after increasing the filter bed height from 120 cm (80 cm anthracite and 40 cm sand) to 150 cm (80 cm anthracite and 70 cm sand). One of the profile measurements from this period is shown in Figure 8-8. The pH in the feed water was approximately 6.4 and the COD concentration in the filtrate water was 57.2 mg/L. In the upper graph of the figure, the nitrate (NO_3-N; brown line) and the nitrite (NO_2-N; green line) concentrations are presented on the primary y-axis and orthophosphorus (PO_4-P; blue line) concentration is presented on the secondary y-axis. In the bottom graph, the PO_4-P/NO_x-N ratio is given for every sample point. The graphs show that nitrate is mainly removed in the sand layer in the lower part of the filter bed. The orthophosphorus concentration decreases more rapidly compared to nitrate concentration, causing the PO_4-P/NO_x-N ratio to decrease. The ratio even goes below the critical value of 0.0055 mg/mg after coagulant dosage. The combination of this low PO_4-P/NO_x-N ratio in the filter bed and nitrite accumulation, almost 4 mg/L nitrite is measured in the filtrate, indicates that phosphorus limitation is likely to occur.

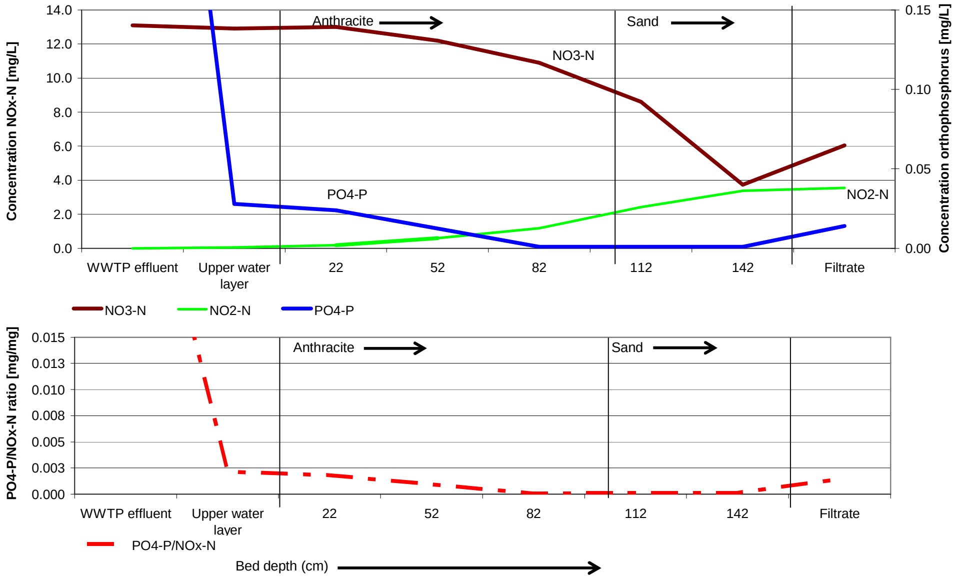

Figure 8-8 - Profile measurements for dual media filtration <u>with</u> nitrite accumulation, 24 July 2008 (Scherrenberg et al., 2009b)

From August to November 2008 the filter bed height was reduced stepwise to 120 cm (80 cm of anthracite and 40 cm of sand) to investigate whether the problem of nitrite accumulation could be solved. By changing the filter bed configuration, the pattern of nitrate and orthophosphorus removal in the filter bed can be influenced. When nitrate and orthophosphorus are removed in parallel through the filter bed, the PO_4-P/NO_x-N ratio remains constant and phosphorus limitation may be prevented as long as the PO_4-P/NO_x-N ratio in the WWTP effluent is higher than the critical ratio.

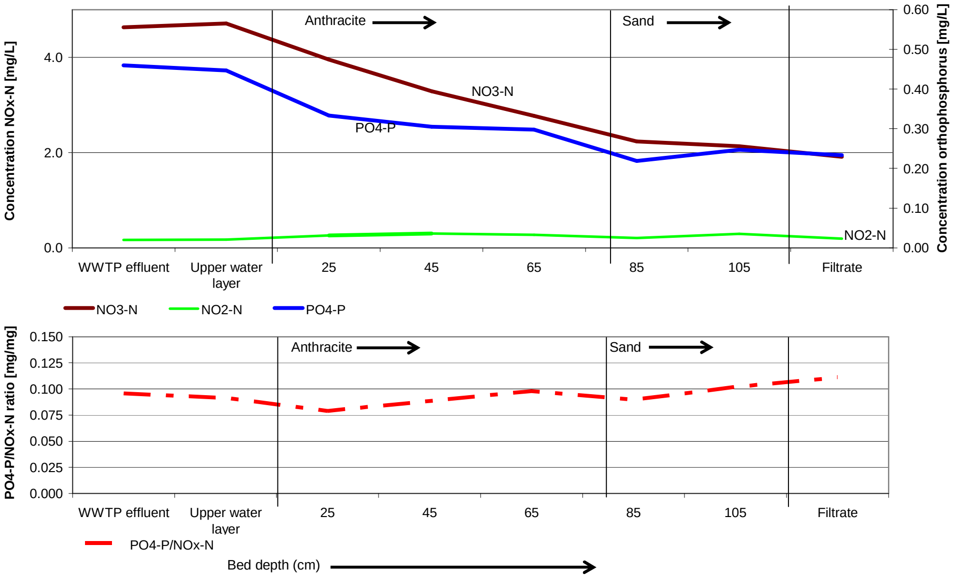

Figure 8-9 - Profile measurements for dual media filtration <u>without</u> nitrite accumulation, 15 January 2009 (Scherrenberg et al., 2009b)

Figure 8-9 shows a profile measurement made for the new filter bed configuration. In the upper graph of the figure, the nitrate (NO_3-N; brown line) and the nitrite (NO_2-N; green line) concentrations are presented on the primary y-axis and the orthophosphorus (PO_4-P; blue line) concentration is presented on the secondary y-axis. In the bottom graph, the PO_4-P/NO_x-N ratio is given for every sample point. This figure shows that nitrate is linearly removed in the anthracite layer. The nitrate removal efficiency is low, namely 44%. The PO_4-P/NO_x-N ratio in the WWTP effluent is 0.10 mg/mg and thus well above the critical value of 0.055 mg/mg which is required in the WWTP effluent before coagulant dosage. The ratio remained, after coagulant dosage and within the filter bed, above the critical value of 0.0055 mg/mg. However, phosphorus is not removed to the desired level. Nitrite accumulation was not found and therefore no indication of phosphorus limitation was found.

8.2.2 1-STEP® filtration

Figure 8-10 shows a profile measurement of the 25th of February 2009. The COD concentration in the filtrate water was 24.9 mg/L. In the upper graph of the figure, the nitrate (NO_3-N; brown line) and the nitrite (NO_2-N; green line) concentrations are presented on the primary y-axis and the orthophosphorus (PO_4-P; blue line) concentration is presented on the secondary y-axis. In the lower graph the PO_4-P/NO_x-N ratio is given for every sample point. The upper graph shows that the nitrate removal is almost complete and no nitrite formed. The bottom graph shows that the PO_4-P/NO_x-N ratio amply remains above the critical value of 0.0055 mg/mg. Because no nitrite accumulation was measured, the nitrate removal is almost complete and the PO_4-P/NO_x-N ratio is well above the critical value; no indication was found for phosphorus limitation.

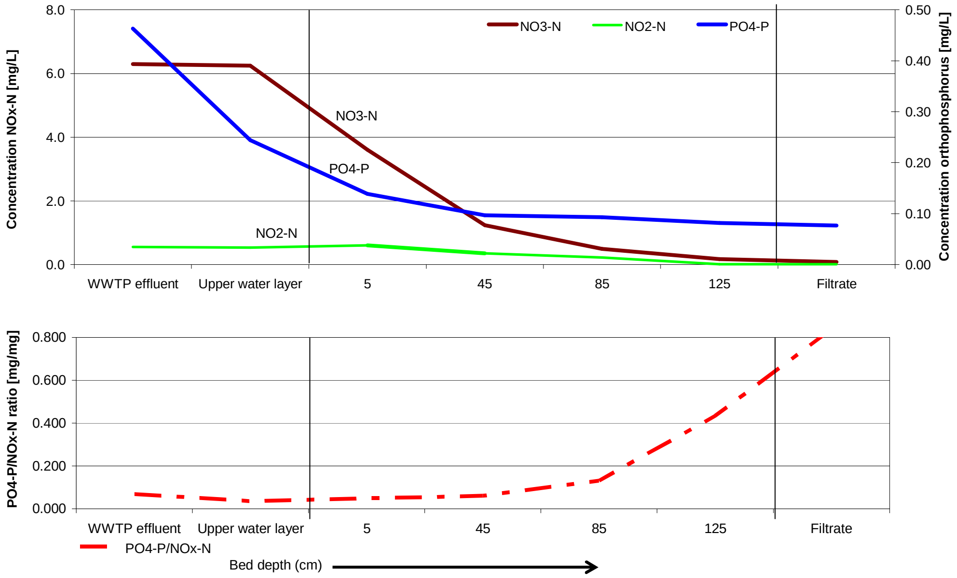

Figure 8-10 - Profile measurements for the 1-STEP® filter without nitrite accumulation, 25 February 2009 (Scherrenberg et al., 2009c)

When comparing Figure 8-9 and 8-10 it is noticed that even though the PO_4-P/NO_x-N ratio is within the same range and in both situations no nitrite is formed that the NO_x-N removal efficiency of the dual media filter is just 44% and for the 1-STEP® filter >95%. This might be explained by the research of Sison et al. (1996), see also section 2.6. This study shows that granular activated carbon can function as a temporary storage for the supplied external carbon source. The denitrifying bacteria consume the carbon source during periods of shortage.

In November 2008 nitrite formed in the 1-STEP® filter. The cause of this rapid nitrite formation is not clear. Profile measurements were made, see Figure 8-11. The COD concentration was 26 mg/L in the filtrate water. In the upper graph of the figure, the nitrate (NO_3-N; brown line) and the nitrite (NO_2-N; green line) concentrations are presented on the primary y-axis and the orthophosphorus (PO_4-P; blue line) concentration is presented on the secondary y-axis. In the lower graph the PO_4-P/NO_x-N ratio is given for every sample point. The upper graph in Figure 8-11 shows that nitrate is mainly removed in the first 65 cm of the filter bed. Orthophosphorus is almost completely removed in the first 25 cm of the filter bed. The PO_4-P/NO_x-N ratio in the WWTP effluent is above the critical value of 0.055 mg/mg, the ratio decreased in the filter bed below the critical value of 0.0055 mg/mg which is required after coagulant dosage. Nitrite formed in the filter bed up to almost 4 mg/L. All these results indicate that phosphorus limitation might occur. The filter bed configuration of this filter cannot be changed; therefore, the PACl dosage is decreased from a metal/orthophosphorus ratio of 4 mol/mol to 1 mol/mol to increase the available orthophosphorus concentration in the filter bed (see section 8.3).

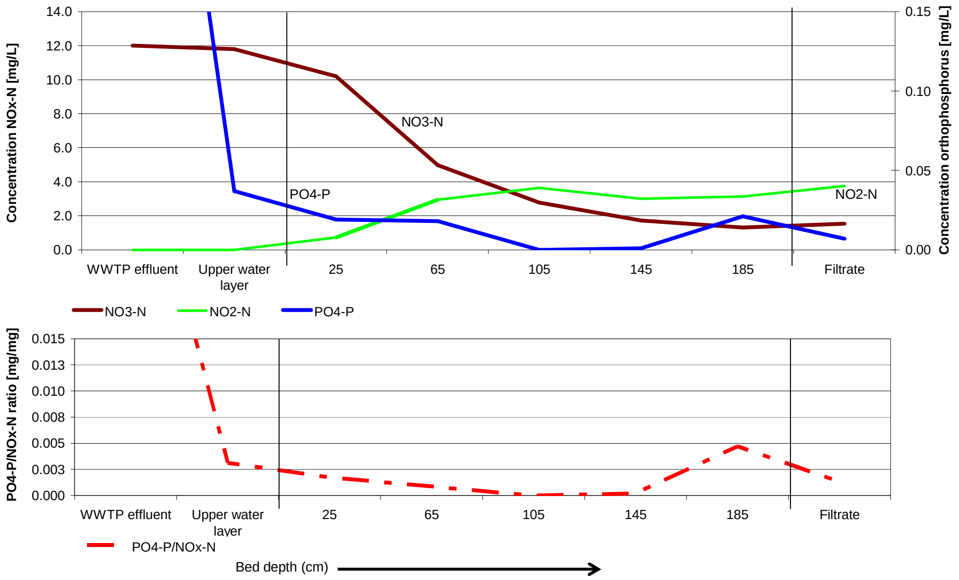

Figure 8-11 - Profile measurements for the 1-STEP® filter with nitrite accumulation, 7 November 2008 (Scherrenberg et al., 2009b)

8.3 Solving phosphorus limitation

In the beginning of February 2009, nitrite formation probably caused by phosphorus limitation again occurred in the 1-STEP® filter. This time the metal/orthophosphorus ratio was 5 mol/mol. Nitrite concentrations in the filtrate water measured around 4 mg/L. Figure 8-12 illustrates the NO_x-N concentrations in the WWTP effluent (blue line) and in the filtrate water (green line). From time to time the NO_x-N concentration in the WWTP effluent exceeded the measuring range of the on-line analyser (max. 15 mg NO_x-N/L) causing a flat line in the graph. The nitrate and nitrite concentrations which are represented by the dots in the graph were measured by grab samples. The metal/orthophosphorus ratio was decreased from 5 mol/mol to 1 mol/mol on 12 February. The decrease in PACl dosage resulted in an increase in the PO_4-P/NO_x-N ratio in the filter bed because less metal-bound phosphorus formed, therefore, more orthophosphorus was available for the heterotrophic bacteria. During this period the orthophosphorus concentration in the WWTP effluent was steady around 0.3 mg/L. The graph shows very clearly that the NO_x-N concentration in the filtrate water decreased. The grab samples show that the nitrite concentration decreased to close to 0 mg/L within 8 days, even though a brief period with an MeOH shortage occurred.

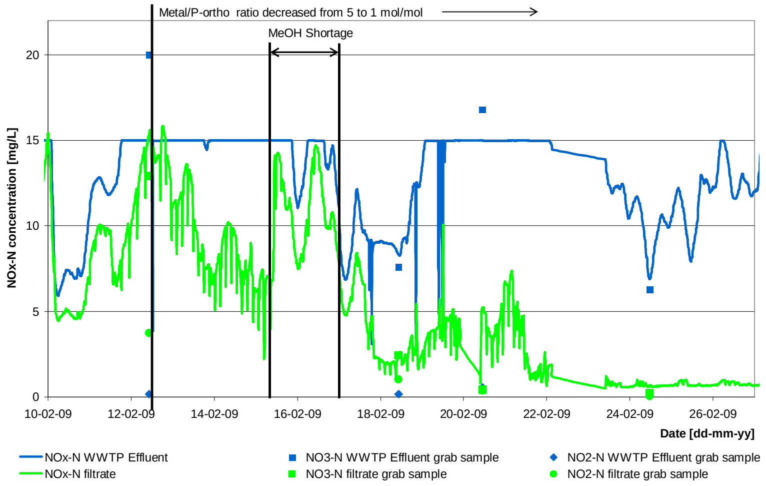

Figure 8-12 – Results for a decrease in the metal/orthophosphorus ratio (Scherrenberg et al., 2009c)

8.4 A new coagulant dosage system - Preventing phosphorus limitation

This section first explains the developed coagulant dosage system (Scherrenberg et al., 2009a) used to maintain high removal efficiencies for nitrate and orthophosphorus and to reduce the risk on phosphorus limitation. After describing the coagulant dosage system, the results and cost savings are described. Next, optimisations for the coagulant dosage system are provided. It should be remembered that phosphorus limitation cannot be prevented in all cases. When the PO_4-P/NO_x-N ratio in the WWTP effluent is already below the critical PO_4-P/NO_x-N ratio, the coagulant dosage has to stop, but phosphorus limitation might still occur.

8.4.1 The coagulant dosage system

The developed and tested coagulant dosage system is shown in Figure 8-13. For this dosage system, three on-line analysers are required, namely:

- an orthophosphorus analyser in the WWTP effluent;
- a total phosphorus analyser in the filtrate;
- an NO_x-N analyser in the WWTP effluent.

When a relationship between the orthophosphorus and total phosphorus concentration in the WWTP effluent or in the filtrate water is established, an orthophosphorus or a total phosphorus analyser can be used. The total phosphorus concentration in the filtrate was measured every 10 minutes; this value was compared with the set point “P-total set point” in Figure 8-13. When the measured total phosphorus concentration was higher than the set point (this is the maximum allowable total phosphorus concentration in the filtrate water, or the discharge limit), the coagulant dosage was increased with “+Delta MeP” (per 10 minutes), meaning that the metal/orthophosphorus (MeP) ratio increased with a certain step, for example 0.5 mol/mol per 10 minutes. The maximum “Actual MeP ratio” which can be applied is 5 mol/mol. When the total phosphorus concentration in the filtrate water was below or equal to the “P-total set point”, two things were checked:

1. The orthophosphorus concentration in the WWTP effluent was compared with the “minimum PO_4-P set point”. This minimum set point represents the orthophosphorus concentration which is removed in the filter bed by the denitrifying biomass without coagulant dosage.
2. The PO_4-P/NO_x-N ratio in the WWTP effluent was compared with the “P limitation set point” which represents the minimum PO_4-P/NO_x-N ratio required to prevent phosphorus limitation. This value is location specific.

The “actual MeP ratio” will decrease with “-Delta MeP” (per 10 minutes) if the orthophosphorus concentration in the WWTP effluent or the PO_4-P/NO_x-N ratio in the WWTP effluent is below the set points. The minimum “Actual MeP ratio” which can be applied is 0 mol/mol. The “actual MeP ratio” will be unchanged when the orthophosphorus concentration in the WWTP effluent and the PO_4-P/NO_x-N ratio in the WWTP effluent is higher than the given set point.

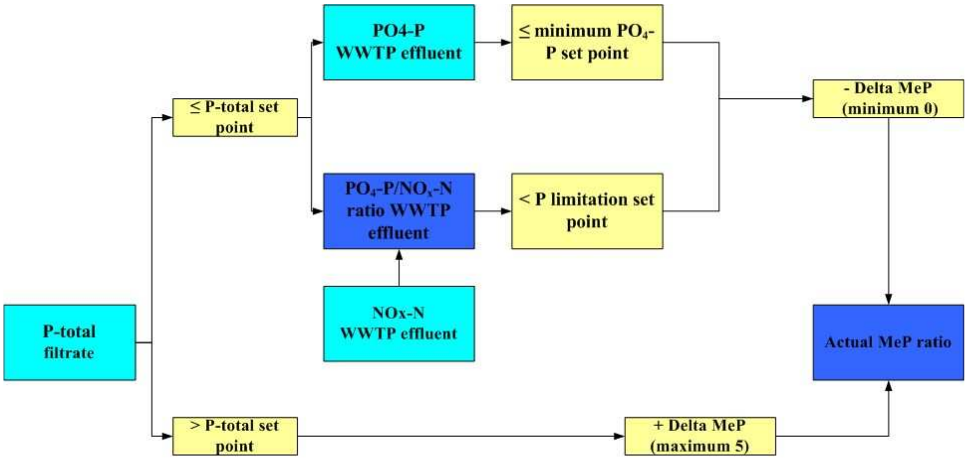

Figure 8-13 - Coagulant dosage system as tested at the Horstermeer WWTP (Scherrenberg et al., 2010)

8.4.2 Phosphorus and nitrogen removal

Phosphorus removal with a continuous MeP ratio (former situation)

Figure 8-14 shows the phosphorus removal for a continuous metal/orthophosphorus ratio of 4 mol/mol in combination with a filtration rate of 10 m/h. The period in question is 15 - 20 August 2008. The dark blue line represents the orthophosphorus concentration in the WWTP effluent, the green line represents the total phosphorus concentration in the filtrate water, and the light blue line represents the orthophosphorus concentration in the filtrate water. The red line represents the total phosphorus target concentration, which was set during this period at 0.15 mg P-total/L in the filtrate water. The figure shows that the total phosphorus concentration in the filtrate water is below the target concentration and even below 0.10 mg/L except when the orthophosphorus concentration in the WWTP effluent dramatically increases.

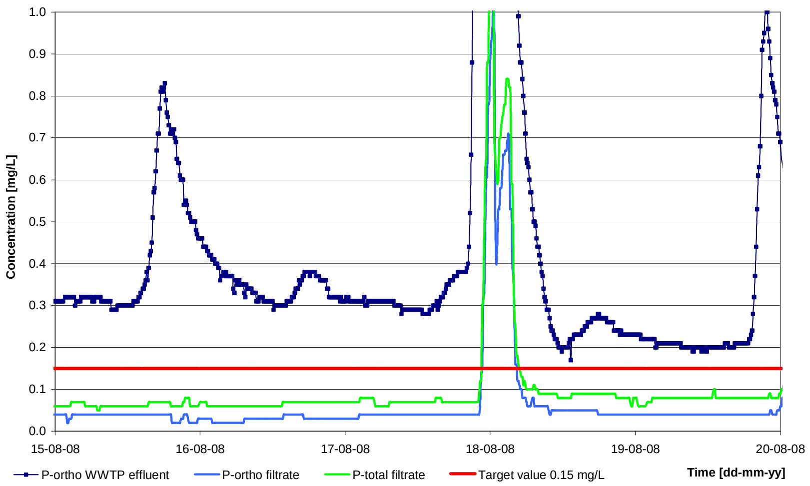

Figure 8-14 - Phosphorus removal for a continuous coagulant dosage of 4 mol/mol (Scherrenberg et al., 2010)

Phosphorus removal with the new coagulant dosage system

The set points used during the test period from August to October 2009 are described in Table 8-1. The filtration rate during this period was 10 m/h. Figure 8-15 shows the phosphorus removal from 15 to 20 August. The dark blue line represents the orthophosphorus concentration in the WWTP effluent, the green line represents the total phosphorus concentration in the filtrate water, and the light blue line represents the orthophosphorus concentration in the filtrate water. The red line represents the target concentration of 0.15 mg P-total/L. The figure shows that the total phosphorus concentration in the filtrate water varies between 0.08 mg/L and 0.17 mg/L but remains stable even when the orthophosphorus concentration in the WWTP effluent increases.

Table 8-1 - Set points used during the testing period

Parameter	Set point	Unit
P-total set point	0.15	mg/L
P-limitation set point	0.06	g PO4-P/g NOx-N
+ Delta MeP	2	mol/mol/10 min
- Delta MeP	0.5	mol/mol/10 min
Minimum PO_4-P set point	0.1	mg/L

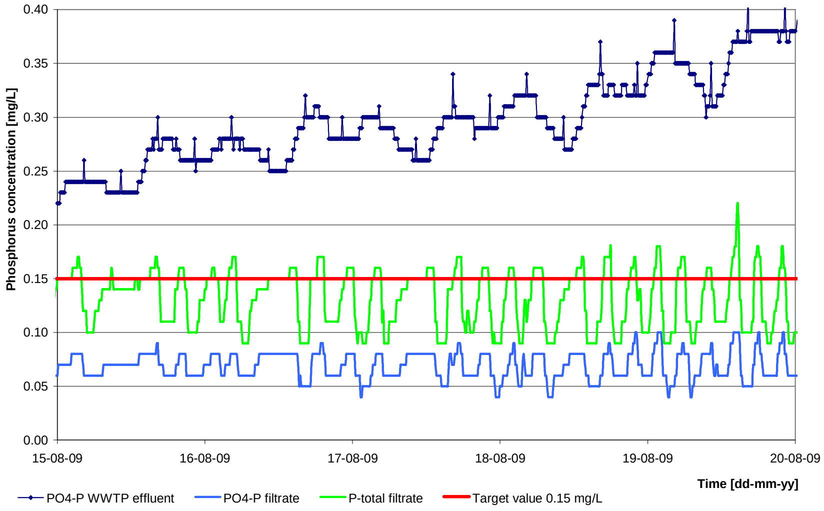

Figure 8-15 - Phosphorus removal during the test period (Scherrenberg et al., 2010)

The PO_4-P/NO_x-N ratio in the WWTP effluent was, on average, 0.042 mg/mg and in the filtrate water 0.127 mg/mg during the test period. For the same period in 2008 (August to October), a continuous coagulant dosage of metal/orthophosphorus was 4 mol/mol as the PO_4-P/NO_x-N ratio, in the WWTP effluent 0.036 mg/mg, and in the filtrate water 0.101 mg/mg. The higher PO_4-P/NO_x-N ratio in the filtrate water of 0.02 mg/mg during the test period reduced the risk of phosphorus limitation.

The results in Figure 8-16 show the average phosphorus removal during the test period and during 2008. The red bars represent the orthophosphorus concentrations in the WWTP effluent, the blue bars represent the average total phosphorus concentrations in the filtrate water during the test period and the green bars represent the average total phosphorus concentration in 2008. The error bars show the 95% confidence interval. The results during the test period show higher total phosphorus concentrations for orthophosphorus concentrations in the WWTP effluent of 0.1 – 0.6 mg/L compared to the results of 2008; this is due to the “P-total set point” for the filtrate which was 0.15 mg/L. For orthophosphorus concentrations in the WWTP effluent of 0.9-1.2 mg/L, the total phosphorus concentrations in the filtrate water was higher during the test period when compared with 2008. The cause might be a too small “+Delta MeP” or the time loop of 10 minutes is too long. With this set point, the coagulant dosage system reacts too slowly on peak loads. The target concentration of 0.15 mg P-total/L can be fulfilled for orthophosphorus concentrations in the WWTP effluent with a maximum of 0.7 mg/L. This is for the test period as well as for the results of 2008.

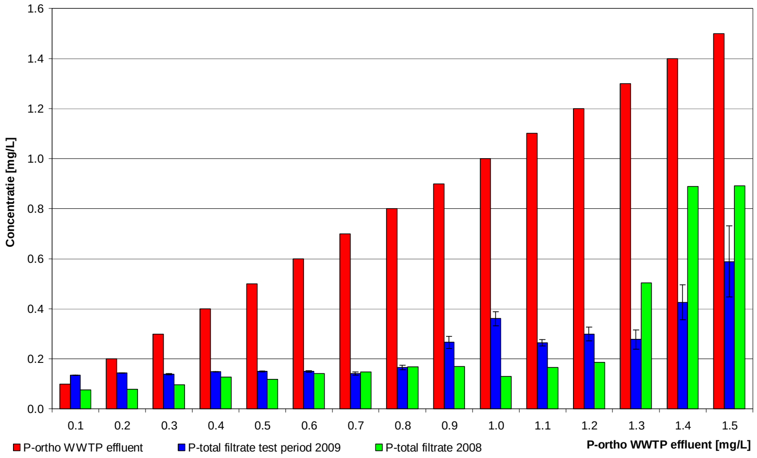

Figure 8-16 - Average phosphorus concentration during the test period compared to the 2008 yearly average

Nitrogen removal

The results displayed in Figure 8-17 show the average NO_x-N removal during the test period and during 2008. The red bars represent the NO_x-N concentrations in the WWTP effluent, the blue bars represent the average NO_x-N concentrations in the filtrate water during the test period, and the green bars represent the NO_x-N concentrations in the filtrate water for 2008. The error bars show the 95% confidence interval. During the test period the NO_x-N concentrations in the filtrate water are lower compared to the 2008 yearly average.

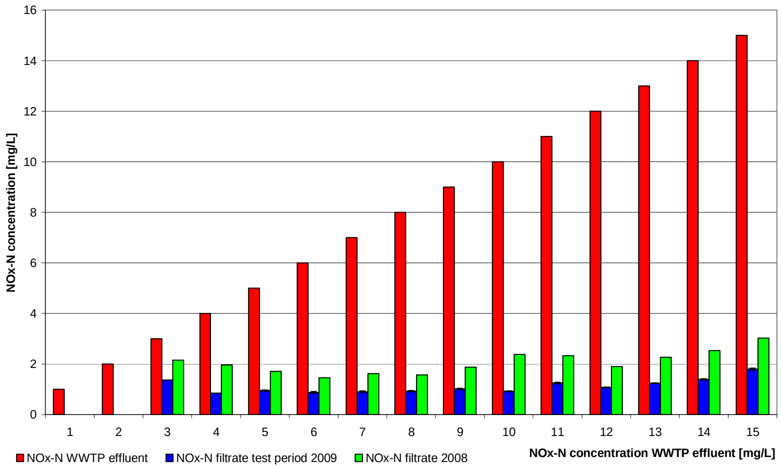

Figure 8-17 - Average NO_x-N concentration during the test period compared to the yearly average of 2008

8.4.3 Cost savings

The developed dosage system, which greatly reduces the chances of nitrite accumulation, reduces the total coagulant dosage. Table 8-2 shows the liters of coagulant which were dosed durig the test period. The coagulant dosage which would be dosed if a continuous coagulant dosage ratio of metal/orthophosphorus 4 mol/mol or metal/orthophosphorus 5 mol/mol would have been used was calculated for the test period and is presented in Table 3. The results show a reduction in the coagulant dosage for the coagulant dosage system of 11% when compared to a continuous dosage ratio of metal/orthophosphorus 4 mol/mol and a reduction of 29% when compared to a continuous dosage ratio of metal/orthophosphorus 5 mol/mol.

Table 8-2 - Total coagulant dosage during the test period with the dosage system and calculated coagulant dosage for a continuous dosage ratio of metal/orthophosphorus 4 mol/mol and metal/orthophosphorus 5 mol/mol

	Total Coagulant dosage [L]	Coagulant reduction [%]
Coagulant dosage system	183	-
Continuous MeP 4 mol/mol	207	11%
Continuous MeP 5 mol/mol	258	29%

For the WWTP Horstermeer a flow of 25,000 m^3/day (average 1040 m^3/h) with an average orthophosphorus concentration of 0.37 mg/L needs to be treated. This requires a coagulant dosage of 1640 m^3/y when the coagulant dosage system is used (see Table 8-3). Compared to a continuous coagulant dosage ratio of metal/orthophosphorus 4 mol/mol, the coagulant can be reduced by 211 m^3 or even 672 m^3 of coagulant when compared with a continuous coagulant dosage ratio of metal/orthophosphorus 5 mol/mol. The cost savings varies between €5,300 and €17,000 when making use of PAX-11.

Table 8-3 - Overview of the cost savings[1)] of coagulant by using the coagulant dosage system

	Dosage per year [m^3]	Costs per year [€]	Cost saving [€]
Coagulant dosage system	1640	41,525	-
Continuous MeP 4 mol/mol	1851	46,867	5,342
Continuous MeP 5 mol/mol	2312	58,540	17,015

[1)] Price for poly aluminium chloride (PAX-11): €211 per 1000 kg (July 2009).

8.4.4 Optimised coagulant dosage system

After the test period with the coagulant dosage system, a few changes were made. These changes are explained below. The same three on-line analysers are required, namely:

- an orthophosphorus analyser in the WWTP effluent;
- a total phosphorus analyser in the filtrate water;
- an NOx-N analyser in the filtrate water.

When a relationship between the orthophosphorus and total phosphorus concentration in the WWTP effluent or in the filtrate water is established, an orthophosphorus or a total phosphorus analyser can be used. The total phosphorus concentration in the filtrate water was measured every 10 minutes; this value is compared to the set point "P-total set point" in Figure 8-18. When the measured total phosphorus concentration was higher than the set point (this is the maximum allowable total phosphorus concentration in the filtrate water, or the discharge limit), the coagulant dosage was increased with "+Delta MeP" (per 10 minutes), meaning that the metal/orthophosphorus (MeP) ratio was increased with a certain step, for example 0.5 mol/mol per 10 minutes. The maximum "Actual MeP ratio" which can be applied is 5 mol/mol.

When the measured total phosphorus concentration in the filtrate water was lower or equal to the set point, the orthophosphorus concentration in the WWTP effluent was measured and compared to the minimum set point for orthophosphorus. This minimum set point represents the orthophosphorus concentration which was removed in the filter bed by the denitrifying biomass without coagulant dosage. When the orthophosphorus concentration in the WWTP effluent was equal to or below the minimum orthophosphorus concentration, the dosage of coagulant stopped, as shown in Figure 8-18 (i.e. MeP 0). When the orthophosphorus concentration in the WWTP effluent was higher than the minimum orthophosphorus concentration, the PO_4-P/NO_x-N ratio in the WWTP effluent is of importance. Therefore, the NO_x-N concentration in the WWTP effluent was measured. The PO_4-P/NO_x-N ratio in the WWTP effluent was compared to the "P limitation set point" which represents the minimum PO_4-P/NO_x-N ratio required to prevent phosphorus limitation. This value is location specific. When the PO_4-P/NO_x-N ratio in the WWTP effluent is higher or equal to the minimum P limitation set point, the metal/orthophosphorus ratio needs to be decreased to prevent phosphorus limitation in the filter bed. This is shown in Figure 8-18 as "–Delta MeP". When the PO_4-P/NO_x-N ratio in the WWTP effluent is higher than the minimum P limitation set point, the metal/orthophosphorus ratio remains unchanged, shown as "Delta MeP=0".

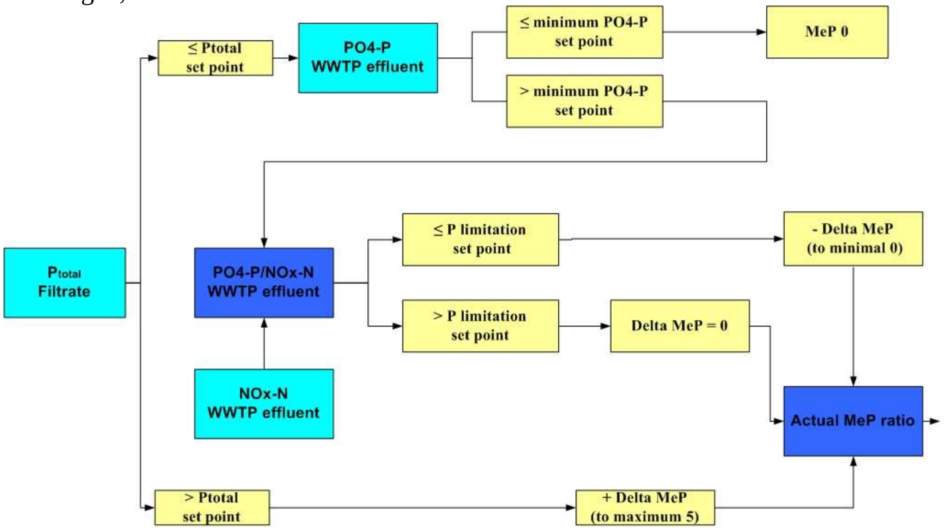

Figure 8-18 - Coagulant dosage system

8.5 Summary

When combining nitrogen and chemical phosphorus removal in a single filter, phosphorus limitation may occur. Inhibition of the denitrification can be caused by many factors besides a shortage of phosphorus. For example, the presence of oxygen, the pH, toxic substances and a shortage of carbon source may also cause inhibition of the denitrification. Therefore, the oxygen and COD concentrations and pH values were measured frequently during this research.

Data analyses made for the Horstermeer WWTP and the Leiden Zuidwest WWTP show that inhibition of the denitrification, probably due to phosphorus limitation, might occur for PO_4-P/NO_x-N ratios below 0.055 mg/mg in the WWTP effluent. Assuming that 90% of the orthophosphorus is transformed into metal-bound phosphorus after coagulant dosage and that metal-bound phosphorus is hardly or not at all available for heterotrophic bacteria, the minimal PO_4-P/NO_x-N ratio is 0.0055 mg/mg entering the filter bed after coagulation. This value is lower than the values in the literature.

Profile measurements were made for the dual media filter and the 1-STEP® filter at the Horstermeer WWTP. The profiles showed that for the situation that the PO_4-P/NO_x-N ratio goes below 0.0055 mg/mg after coagulation for a certain period of time, orthophosphorus limitation might occur.

Experiments with a decreasing coagulant dosage and therefore increased PO_4-P/NO_x-N ratios after coagulant dosage showed a rapid increase in the denitrification efficiency. The newly developed coagulant dosage system increased the PO_4-P/NO_x-N ratio after coagulation, in the filter bed, and in the filtrate compared to a continuous dosage ratio of 4 mol/mol. This decreased the risk of phosphorus limitation.

Besides a decreasing risk of phosphorus limitation and therefore a more stable process, also a reduction of the coagulant dosage was found for the new coagulant dosage system. The coagulant dosage was reduced by 11 % when compared to a continuous metal/orthophosphorus dosage ratio of 4 mol/mol and reduced by 29% when compared to a continuous metal/orthophosphorus dosage ratio of 5 mol/mol.

8.6 References

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9 Evaluation and discussion

In Chapter 9 the results presented in Chapters 5 through 8 are evaluated and discussed. This chapter is divided into four sections; each section evaluates the results of the chapters in this thesis. The results of the characterisation of phosphorus and the distribution of total phosphorus into orthophosphorus, metal-bound phosphorus, dissolved “organic” phosphorus and particulate organic phosphorus are discussed in Section 9.1. This section also deals with the results of coagulation and flocculation. In Section 9.2 the different aspects and results of the filtration processes are discussed. Section 9.3 evaluates and describes the influence of temperature on coagulation, flocculation and filtration processes. Section 9.4 describes the possibility of phosphorus limitation when combining biological denitrification with advanced phosphorus removal.

9.1 Characterisation, coagulation and flocculation

The phosphorus distribution method developed at TU Delft is used to characterise the total phosphorus concentration in the WWTP effluent (distribution of total phosphorus into four forms, namely metal-bound phosphorus, orthophosphorus, dissolved “organic” phosphorus and particulate organic phosphorus) and to determine the optimal conditions for coagulation and flocculation. This method is described in Chapter 4. An important issue that is described in this chapter is the measurement error that is introduced by the colloidal fraction due to filtration through 0.45 μm. The colloidal fraction causes an overestimation of the dissolved “organic” phosphorus concentration. More information about the uncertainties of the TU Delft phosphorus distribution method can be found in Subsection 4.4.2.

This section is divided into two subsections. The first, Subsection 9.1.1, describes the results of the characterisation of the WWTP effluent. The second, Subsection 9.1.2, describes the results of the coagulation and flocculation processes.

9.1.1 Characterisation of WWTP effluent

Characterisation of the total phosphorus concentration in the WWTP effluent shows a site-specific distribution. Variation in the distribution may be caused by the treatment plant itself. A treatment plant that removes phosphorus with metal salts is expected to have a higher concentration of metal-bound phosphorus in its effluent, compared to a treatment plant where phosphorus is removed biologically. Table 9-1 and Figure 9-1 present the average phosphorus distribution of the WWTP effluent for four WWTPs with chemical phosphorus removal and four WWTPs with biological phosphorus removal. All the WWTPs are within Waternet's district. The results show that the orthophosphorus concentration (green bars) and the particulate organic phosphorus concentration (dark blue bars) are higher for the treatment plants with biological phosphorus removal. The metal-bound phosphorus concentration (red bars) in the WWTP effluent of the treatment plants with chemical phosphorus removal is higher compared to the treatment plants with biological phosphorus removal.

Table 9-1 – Average phosphorus distributions for WWTP effluent in four WWTPs with chemical phosphorus removal and four WWTPs with biological phosphorus removal within the Waternet district

Location	Unit	Ortho-phosphorus	Dissolved "organic"	Particulate organic	Metal-bound
Chemical phosphorus removal	mg/L	0.32	0.07	0.12	0.19
Biological phosphorus removal	mg/L	0.42	0.07	0.18	0.12

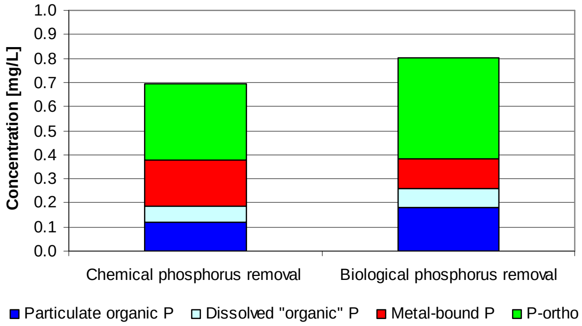

Figure 9-1 – Average phosphorus distributions for WWTP effluent of four WWTPs with chemical phosphorus removal and four WWTPs with biological phosphorus removal, within the district of Waternet

Highly loaded secondary sedimentation tanks may also contribute to higher metal-bound phosphorus and particulate organic phosphorus concentrations due to poor settling of particles and sludge. Discharges from industries on the sewage system may influence the phosphorus distribution. For example, in a forested area higher concentrations of humic and fulvic acids are expected in the WWTP effluent and, because phosphorus can be an integral part of humic and fulvic acids, higher dissolved “organic” phosphorus concentrations are expected. Seasonal, temperature and pH influences on the phosphorus distribution were not found.

A linear relationship in the WWTP effluent between the total phosphorus concentration and the unfiltered orthophosphorus (sum of orthophosphorus and metal-bound phosphorus) or the filtered orthophosphorus concentration was found. This is illustrated in Figure 9-2 for the Horstermeer WWTP (left graph) and the Leiden Zuidwest WWTP (right graph). Relationships between phosphorus forms might be site specific and should therefore be investigated per location.

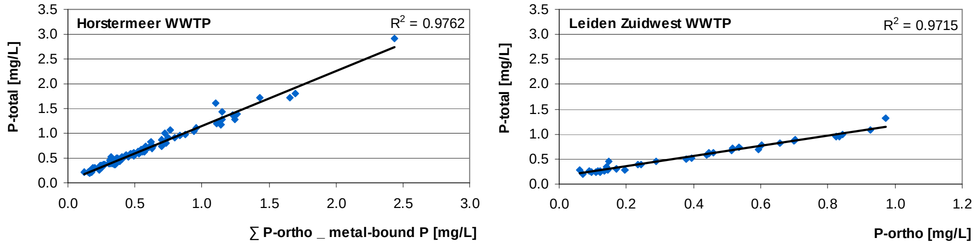

Figure 9-2 – Relationship between total phosphorus and the sum of orthophosphorus and metal-bound phosphorus for the Horstermeer WWTP (left graph) and the relationship between total phosphorus and orthophosphorus for the Leiden Zuidwest WWTP (right graph)

9.1.2 Coagulation and flocculation

For chemical phosphorus removal, the coagulant dosage, the initial mixing energy and the estimated floc size are expected to be important. The results of the investigations for these different aspects are evaluated in this subsection. Research was conducted with jar tests, phosphorus size fractionations and phosphorus distributions. Subsection 9.1.2.1 describes the results of the coagulant dosage; Subsection 9.1.2.2 describes the results of the experiments conducted to find the optimal initial mixing energy, and Subsection 9.1.2.3 describes the changes in the phosphorus distribution and the phosphorus size fractionation.

9.1.2.1 Coagulant dosage

The type of coagulant used was investigated by jar tests. For the Horstermeer WWTP, poly aluminium chloride was used with a metal/orthophosphorus ratio of 4 mol/mol. For the Leiden Zuidwest WWTP ferric(III)chloride was used with a metal/orthophosphorus ratio of 8 mol/mol for orthophosphorus concentrations in the feed water of <0.15 mg/L and a metal/orthophosphorus ratio of 4 mol/mol for orthophosphorus concentrations in the feed water of >0.15 mg/L. The strategy of applying a higher dosage ratio for low orthophosphorus concentrations was developed at the Leiden Zuidwest WWTP to make sure that enough metal hydroxide complexes were available to create a floc large enough to be removed in the filter bed.

9.1.2.2 Optimal initial mixing energy

In the literature, contradictory initial mixing energies, or so called G-values, are given for the optimal initial mixing energy required for an efficient coagulation. Nevertheless, an initial mixing energy of 1,000 s^{-1} is commonly used. Experiments to determine the optimal initial mixing energy were conducted at the Horstermeer WWTP and at the Leiden Zuidwest WWTP. These experiments were conducted with G-values varying between 300 s^{-1} and 2000 s^{-1}. The results show that the initial mixing energy has no influence on the phosphorus size fractionation and also no influence on the phosphorus distribution in the upper water layer of a fixed bed filter. This means that an initial mixing energy of 300 s^{-1} is satisfactory, which leads to energy savings because of less head loss. Coagulant dosage in combination with a 90° angle may already be sufficient to have a good mixture of coagulant with the feed water.

9.1.2.3 Changes in the phosphorus distribution and size fractionation

The phosphorus distribution and the phosphorus size fractionations after coagulation show that orthophosphorus is bound to metal ions and forms metal-bound phosphorus; this complies with the literature. The results of the experiments conducted show that the size of the formed flocs increases with an increasing coagulant dosage. The results presented in Figure 9-3 show an increasing estimated floc size for an increasing coagulant dosage.

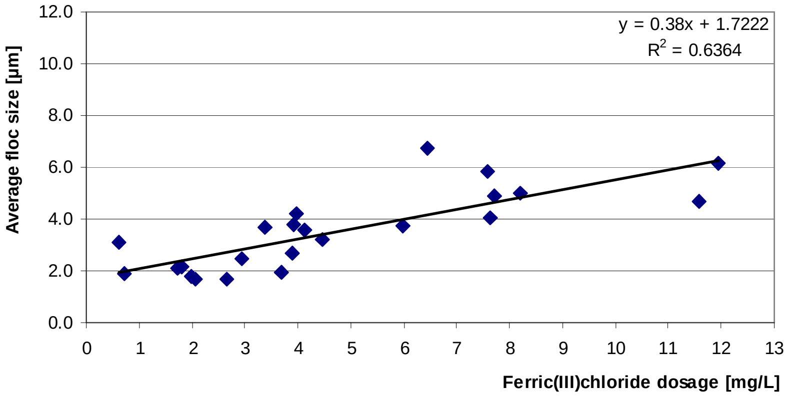

Figure 9-3 – Relationship between ferric(III)chloride dosage and the estimated floc size of the formed metal-bound phosphorus for the dual media filter at the Leiden Zuidwest WWTP. The metal/orthophosphorus ratios used were 2, 4 and 8 mol/mol (Scherrenberg et al., 2008).

The relationship between the coagulant dosage and the floc size was used to develop the coagulant dosage strategy at the Leiden Zuidwest WWTP. This strategy was developed to create flocs large enough to be removed in the filter bed even though orthophosphorus concentrations in the WWTP effluent were below 0.15 mg/L. By increasing the metal/orthophosphorus ratio from 4 mol/mol to 8 mol/mol, the metal salt concentration increased and therefore the floc size increased, which made it possible to remove the flocs in the filter bed. Besides the coagulant dosage, also the flocculation time can also influence the floc size. When extra flocculation tanks with a retention time of 24 minutes are compared to a flocculation time of 10 minutes, the results show that the estimated floc size almost doubled to 7 – 12 μm.

Phosphorus distributions show that the dissolved “organic” phosphorus concentration decreases after coagulation and the particulate organic phosphorus concentration increases. This suggests that a part of the dissolved “organic” phosphorus may be colloidal or associated with colloidal material. This is found in the literature and in the results of the error analysis conducted for the phosphorus distribution which shows an overestimation for the dissolved “organic” phosphorus concentration caused by colloidal material.

9.2 Filtration processes

For phosphorus removal by filtration, the optimal filtration rate, the filter bed configuration and the presence/absence of biomass are expected to be of importance. The results of the investigations for these different aspects are evaluated in this section. Research was conducted with phosphorus size fractionations and phosphorus distributions, but mainly data available from the on-line analysers were used.

9.2.1 Changes in the phosphorus distribution and size fractionation

The phosphorus distributions (in the upper water layer after coagulation/flocculation and in the filtrate water), which were made for the different filter concepts in combination with or without biomass, showed comparable results:

- orthophosphorus in the upper water layer was partly removed (40% - 75%) in the filter bed;
- metal-bound phosphorus was removed in the filter bed (80% - 93%);
- dissolved “organic” phosphorus will pass the filter bed;
- particulate organic phosphorus was removed in the filter bed (80% - 95%).

The 1-STEP® filter shows the highest removal efficiencies for all phosphorous forms. The removal of orthophosphorus in the filter bed was probably due to orthophosphorus uptake by biomass and the flocculation of colloidal metal-bound phosphorus. This colloidal metal-bound fraction in the upper water layer was partly measured as orthophosphorus due to the filtration step through 0.45 μm.

When comparing total phosphorus removal for filtration with and without biomass, it is expected that the phosphorus removal efficiency will be higher for filtration with biomass. Firstly, this is expected because of the decreasing pore size due to the biomass, which increases the capacity to maintain smaller particles in the filter bed, and, secondly, because the biomass requires orthophosphorus for growth. But a comparison of the phosphorus distributions made for filtration with and without biomass shows something different. Namely, the results show higher removal efficiencies for filtration without biomass, see Figure 9-4.

The higher removal efficiency for filtration without biomass was, for a large part, caused by the metal-bound phosphorus concentration, which was 0.10 mg/L in the filtrate water of the dual media filter with biomass and was 0.05 mg/L after filtration without biomass. An increase in the metal-bound phosphorus concentration in the filtrate water may have been caused by higher velocity gradients in the filter bed with biomass due to lower filter bed porosities. This might have caused a breakage of flocs and finally a breakthrough of metal-bound phosphorus. Another difference which is seen when comparing the two situations is the removal of the organic phosphorus forms. In the situation of filtration without biomass, the concentration of dissolved “organic” phosphorus is 2.5 times the concentration after filtration with biomass. This might have been caused by the composition of the dissolved “organic” phosphorus which may have contained varying concentrations of colloidal organic phosphorus. Since there are no phosphorus distributions available for the upper water layer for filtration with biomass, it is difficult to assert that the difference in the dissolved organic phosphorus concentration was caused by the biomass.

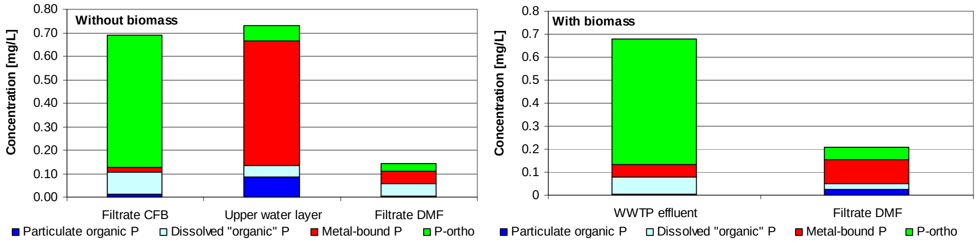

Figure 9-4 – Left: Average (11 samples) phosphorus distribution for the filtrate water of CFB, after coagulation in the upper water layer and the filtrate water of the Dual media filter (Filtrate DMF) for the Leiden Zuidwest WWTP (fine filter bed, **without biomass**). **Right**: averaged (2 samples) phosphorus distribution for the WWTP effluent and the filtrate water of the dual media filter (Filtrate DMF) for the Leiden Zuidwest WWTP (fine filter bed, **with biomass**).

The left graph of Figure 9-4 shows a phenomenon which is frequently seen, namely an increase in the total phosphorus concentration in the upper water layer compared to the total phosphorus concentration in the feed water of the filter. The cause of this increase is not clear. Hach Lange states in the product information (Hach Lange, 2009) that Fe^{3+} and Al^{3+} do not cause interference for concentrations up to 50 mg/L. The concentrations used for Fe^{3+} and Al^{3+} never exceeded 50 mg/L, therefore, the increase, which was measured after coagulation, was most likely not caused by the coagulant dosage. A cause, which is most likely responsible for the increase of the total phosphorus concentration in the upper water layer, may be a form of accumulation. The upper water layer of a fixed bed filter can be compared with a continuously stirred tank reactor, even though the motions are very low. A sample taken from the upper water layer will therefore represent the situation after coagulation and flocculation.

With a constant coagulant dosage without biomass, phosphorus concentrations in the fractions 0.45 – 2 μm, 2 – 5 μm and 5 – 10 μm increased and the phosphorus concentrations in the fractions 10 -20 μm and >20 μm are nearly completely removed. For the situation with biomass and coagulant dosage, phosphorus concentrations in the fractions 0.45 – 2 μm and 2 – 5 μm slightly increase and the phosphorus concentrations in the fractions 5 – 10 μm, 10 -20μm and >20 μm are nearly completely removed. Smaller particles can be removed by filtration with biomass, thus the biomass contributes to the filtration process, possibly by decreasing the pore size in the filter bed.

9.2.2 Need for flocculation

The estimated floc size can be influenced by the coagulant dosage and the flocculation time. Phosphorus size fractionations show that an extra flocculation time of 24 minutes almost doubles the estimated floc size (2 – 5 μm with 10 minutes flocculation time and 7 - 12 μm with 24 minutes) compared to a situation without extra flocculation time. The aim of this extra flocculation time is to reach higher removal efficiencies for total phosphorus, but a comparison of the phosphorus removal for both situations shows that this is not the case. It appears that the average total phosphorus concentration after filtration with an extra flocculation time of 24 minutes is actually higher compared to the situation without extra flocculation time.

As the literature shows (Subsection 2.3.1), the floc size increases with an increased flocculation time. These large flocs may have a more open structure and as a result of this structure the flocs can easily fall apart. During filtration, high velocity gradients occur in the filter bed. Due to the high velocity gradients, flocs with a more open structure can fall apart and a breakthrough of the filter bed can occur. This might be an explanation for the decrease in removal efficiency for flocs formed with a maximum flocculation time. It can be concluded that additional flocculation tanks are not necessary when using dual media filtration.

9.2.3 Phosphorus removal in the filter bed

Profile measurements make it possible to investigate phosphorus removal in the filter bed. The results described below are all based on down flow depth filtration (dual media filter with and without biomass and the 1-STEP® filter). When taking samples, it should be taken into account that deposed sludge will be drawn out together with the water when opening the tap for sampling, even though this effect is minimised by running the tap for 20 seconds before taking a sample. The result is an overestimation of the particulate phosphorus forms and therefore also an overestimation of the total phosphorus concentration.

Lindquist diagrams (see Figure 6-18) were used to investigate the differences between filtration with and without biomass. For the situation without biomass, the pressure increases in the anthracite layer, just above the sand layer. The maximum filter bed resistance is found in the middle of the sand layer, around a filter bed height of 50 cm. The Lindquist diagram with biomass shows a maximum filter bed resistance at the transition point of the anthracite layer to the sand layer. Because of this it can be concluded that the removal of suspended solids in the anthracite layer is higher when biomass is present in the filter bed compared to the situation without biomass. This is probably due to a decrease in the pore size in the filter bed caused by the biomass.

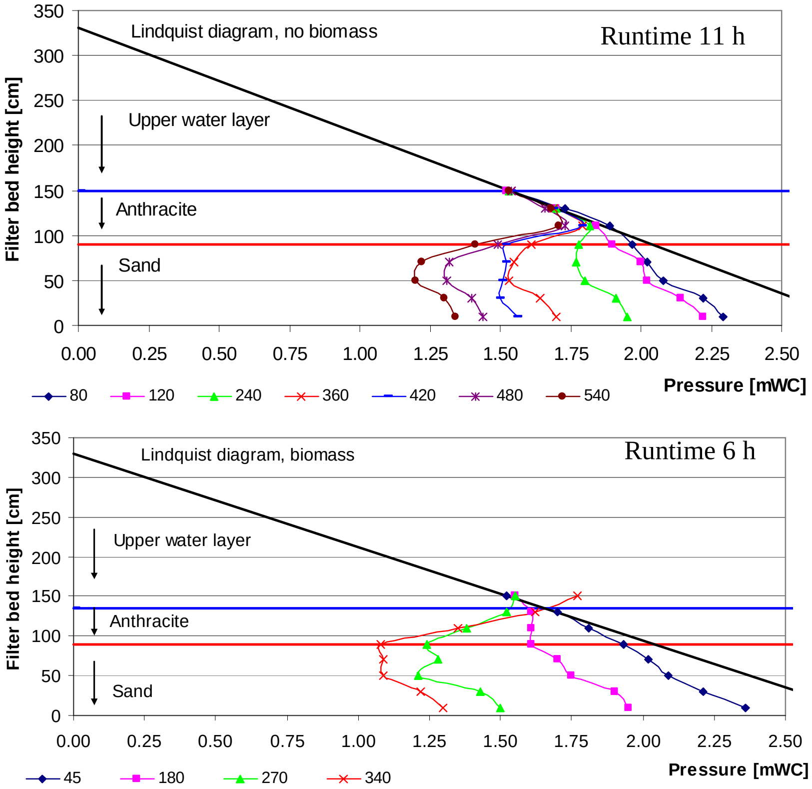

Figure 9-5 – Lindquist diagram for the dual media filter of the Leiden Zuidwest WWTP (fine filter bed). Left graph shows the Lindquist diagram during the filter runtime without biomass and the right graph shows the Lindquist diagrams with biomass. In both situations a filtration rate of 10 m/h and a constant coagulant dosage of 5 mg Fe^{3+}/L was used (Van den Berg van Saparoea, 2008).

Removal of the different phosphorus forms through the filter bed is defined with profile measurements. Phosphorus distributions were made for each sample point. The results show that orthophosphorus, metal-bound phosphorus and particulate organic phosphorus are removed in the filter bed. Dissolved “organic” phosphorus will pass the filter bed. The removal of phosphorus in the filter bed is mainly caused by filtration. These results comply with the results of the phosphorus distribution discussed in Subsection 9.2.1. An increase in metal-bound phosphorus can be found around the transition layer of the filter bed media or just above the bottom plate. This increase was probably caused by deposited metal-bound phosphorus or sludge.

The results of the activated carbon analyses for the 1-STEP® filter conducted by Norit (Subsection 6.4.5) indicate that all phosphorus which is present in the activated carbon, is orthophosphorus. Therefore, it is likely that organic phosphorus is not adsorbed to activated carbon. Because of this, it can be concluded that the removal mechanism for particulate and dissolved "organic" phosphorus is filtration. This complies with the results of the phosphorus distributions (Subsection 9.2.1) and the profile measurements.

9.2.4 Decrease of the filter runtime caused by biomass

The results presented in Subsection 6.3.3 show that the filter runtime for filtration with biomass was approximately 70 – 150 minutes shorter compared to filtration without biomass. The available storage in the filter bed was approximately 0.76 – 1.7 kg Fe^{3+}/run for filtration without biomass and 0.41 – 1.27 kg Fe^{3+}/run for filtration with biomass. The difference in storage gives an estimation of the biomass present in the filter bed. The measured difference in Fe^{3+} storage between filtration with and without biomass is approximately 0.39 kg Fe^{3+}/run.

The phosphorus removal efficiency for a dual media filter in combination with the coarse filter bed (with and without biomass) at the Leiden Zuidwest WWTP shows removal efficiencies mainly below 60%. For the same dual media filter but with the fine filter bed, the removal efficiencies are comparable for the situation with or without biomass, namely between 60% and 70%. Thus, filtration with dual media filtration with or without biomass gives comparable removal efficiencies. But the advantage is, as discussed in Subsection 9.2.1., that smaller particles can be removed by filtration with biomass.

9.2.5 Continuous or downflow depth filtration

During this research the differences between continuous and discontinuous filtration (down flow depth filtration) with regard to phosphorus removal were investigated. A comparison of the removal efficiencies between the two filtration techniques shows the highest removal efficiencies for continuous sand filtration.

The effect of increasing total phosphorus concentrations in the feed water of the different filtration techniques differs. Increasing total phosphorus concentrations in the feed water of down flow depth filters (dual media filter with and without biomass and the 1-STEP® filter), shows increasing total phosphorus concentrations in the filtrate water. This phenomenon is not seen for continuous sand filtration, where the total phosphorus concentration in the filtrate water remains stable. The difference might be due to the rapidly increasing velocity gradient in a down flow depth filter bed caused by a decreasing pore size. These high velocity gradients will result in floc breakage followed by a breakthrough of metal-bound phosphorus. This is emphasised by results which show a clear decrease in the filter runtime for an increasing coagulant dosage, which occurs for higher total phosphorus concentrations in the feed water. The velocity gradient in the filter bed of a continuous sand filter remains quite stable because the sand bed is continuously washed.

9.2.6 Single layer or double layer filter bed

The differences between a single layer filter bed and a double layer filter bed are described in Subsection 2.4.2. The main findings when comparing a single layer filter bed with a double layer filter bed are that the turbidity in the filtrate water is comparable between the two filter types, but the filter runtime for the dual media filter is 3 to 4 times higher. This phenomenon is explained by the removal of larger particles in the coarse anthracite layer, whereas the smaller particles are trapped in the finer sand layer. This maximises the filter loading and, therefore, the filter runtimes are longer compared to single media filtration runtimes.

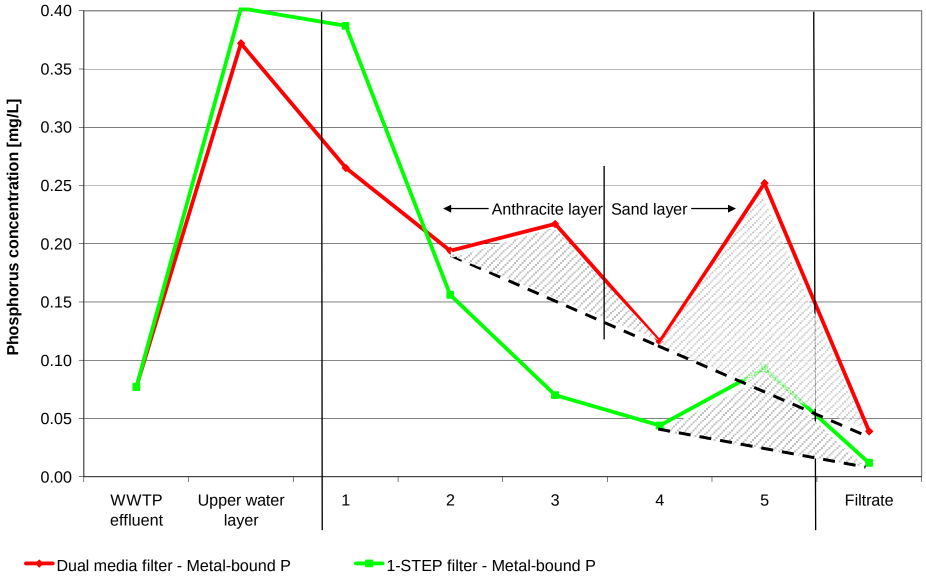

Figure 9-6 – Removal of metal-bound phosphorus through the filter bed for dual media filtration and 1-STEP® filtration (single media filtration)

The dual media filter and the 1-STEP® filter at the Horstermeer WWTP can be described as down flow depth filters with a single layer and a double layer. It is valid to describe the 1-STEP® filter as a single layer filter bed because the results show that the removal of phosphorus in the 1-STEP® filter is most likely only by filtration (see also Subsection 9.2.3). This means that the granular activated carbon can be compared with sand or anthracite with the same grain size. A comparison of the phosphorus removal in the filter bed shows for the 1-STEP® filter a more gradual decrease in metal-bound phosphorus and particulate organic phosphorus compared to dual media filtration. In Figure 9-6 the removal of metal-bound phosphorus is presented for the dual media filter (red line) and the 1-STEP® filter (green line). The irregular removal in the dual media filter is mainly caused by the transition between the anthracite layer and the sand layer (see also Figure 9-6, at a filter bed height of 125 cm). In this transition area the metal-bound phosphorus concentration increased and therefore the measured total phosphorus concentration increased; this might be caused by a form of cake layer filtration on top of the sand layer due to a decrease in the pore size. A more gradual decrease in the pore size might minimise this effect. The dual media filter shows removal efficiencies in the range of 70% to 85%. The 1-STEP® filter shows higher removal efficiencies, namely in the range of 80% up to 90% for orthophosphorus concentrations of 0.2 – 1.2 mg/L.

9.3 Temperature influences

Temperature influences were investigated with jar tests and with the on-line data available from the on-line analysers at the Horstermeer WWTP and the Leiden Zuidwest WWTP. There was no influence found for temperature on the coagulation. This complies with the results of the experiments conducted by Morris and Knocke (1984) which showed that a low temperature (1°C) does not significantly inhibit the rate of metal-hydroxide precipitation and that precipitation occurs within a minute. The results of the jar tests show that the temperature influences phosphorus size fractionation. For higher temperatures, larger flocs are found. The fact that higher temperatures produce larger flocs is a commonly found result in other research. However, these flocs break more easily and reform less well than flocs produced at lower temperatures (Fitzpatrick et al., 2004).

The results of the different filtration techniques all show the highest total phosphorus concentrations in the filtrate water for water temperatures <13°C. This might be due to the smaller floc sizes which are harder to retain in the filter bed. The results of the continuous sand filter show for increasing temperatures decreasing total phosphorus concentrations in the filtrate water. Thus, the removal efficiency of total phosphorus increases with increasing temperatures. The highest removal efficiency is found for temperatures ≥18°C. The results of the dual media filters and the 1-STEP® filter show for low phosphorus concentrations in the WWTP effluent decreasing total phosphorus concentrations in the filtrate water for increasing temperatures. Again, the highest removal efficiency is found for temperatures ≥ 18°C. For higher phosphorus concentrations, the optimal temperature range is between 13°C and 18°C. The turning point varies per installation and is probably influenced by the velocity (shear rate) in the filter bed in combination with floc strength. As stated before, higher temperatures produce larger flocs, but these flocs break more easily.

9.4 Phosphorus limitation

When combining nitrogen and chemical phosphorus removal in a single filter, phosphorus limitation may occur (see also Subsection 2.5.4 for more information). Low orthophosphorus concentrations may affect the denitrification conversion rate by inhibiting the rapid growth of heterotrophic microorganisms in response to increasing nitrate (NO_3-N) loads. Theoretically, phosphorus becomes a limiting factor when concentrations are below 0.04 mg P/mg NO_x-N in the feed water, assuming 3 mg of methanol (MeOH) per mg NO_x-N.

9.4.1 Minimum required PO_4-P/NO_x-N ratio

At the WWTP Horstermeer and the WWTP Leiden Zuidwest the minimum PO_4-P/NO_x-N ratio which was required for denitrification conversion rates (i.e. removal efficiency) was determined as 70% and higher. The results show that NO_x-N removal rates below 70% occur frequently for PO_4-P/NO_x-N ratios below 0.055 mg/mg in the WWTP effluent. An investigation to determine which denitrification reduction step was responsible for the decreasing denitrification efficiency showed that nitrite concentrations of 1 mg/L and higher were only found for PO_4-P/NO_x-N ratios of approximately 0.06 mg/mg and lower. Because of these results, it seems safe to say that the $NO_2^- \rightarrow N_2$ reduction step is sensitive to low PO_4-P/NO_x-N ratios in the WWTP effluent and, therefore, nitrite accumulation might occur in the filter bed during periods of low PO_4-P/NO_x-N ratios.

Phosphorus distributions made for the WWTP effluent and after coagulant dosage for the different installations at the WWTP Leiden Zuidwest and the WWTP Horstermeer show that approximately 90% of the available orthophosphorus in the WWTP effluent is bound to metal salt after coagulant dosage. Therefore, approximately 10% of the available orthophosphorus in the WWTP effluent remains dissolved after coagulation. The results of the WWTP Leiden Zuidwest show that metal-bound phosphorus is hardly or not at all available for the heterotrophic microorganisms. Therefore, the actual PO_4-P/NO_x-N ratio in the feed water, after coagulant dosage entering the filter bed, is just 10% of the ratio found for the WWTP effluent before coagulant dosage. This results in a minimum required PO_4-P/NO_x-N ratio of 0.0055 mg/mg for the WWTP Horstermeer and a PO_4-P/NO_x-N ratio of 0.005 mg/mg for the WWTP Leiden Zuidwest. These values are much lower compared to the values found in the literature.

Profile measurements made it possible to investigate where and when phosphorus limitation occurs in a filter bed. The results show that in the case where orthophosphorus is removed more rapidly compared to nitrate, the PO_4-P/NO_x-N ratio decreases in the filter bed. When the PO_4-P/NO_x-N ratio goes below 0.0055 mg/mg for a certain period of time, orthophosphorus limitation might occur. The heterotrophic bacteria use phosphorus for growth and, because of this, the effect of PO_4-P/NO_x-N ratios below the critical value will not be directly noticeable as it would be if phosphorus was needed for the process of NO_x-N removal.

9.4.2 Preventing phosphorus limitation – A new coagulant dosage system

Generally, phosphorus will be added to the feed water when phosphorus limitation occurs, see Subsection 2.5.4. Of course, this increases the chemical dosage needed for good operation of the denitrification and therefore the costs increase. Results during this research showed that a decrease in coagulant dosage resulted in an increase in the PO_4-P/NO_x-N ratio in the filter bed because less metal-bound phosphorus formed and therefore more orthophosphorus was available for the heterotrophic bacteria. During a period when nitrite concentrations of 4 mg/L occurred in the filtrate water, the coagulant dosage was decreased from a metal/orthophosphorus ratio of 5 mol/mol to 1 mol/mol. The results showed that the nitrite concentration decreased to close to 0 mg/L within 8 days, even though a brief period of an MeOH shortage occurred. This contributed to the development of a new coagulant dosage system.

The dosage system was developed to prevent phosphorus limitation, without increasing the risk of exceeding the discharge limit for total phosphorus. The coagulant dosage system increases the PO_4-P/NO_x-N ratio in the filtrate water compared to a continuous metal/orthophosphorus dosage ratio of 4 mol/mol. This decreases the risk of phosphorus limitation because a higher concentration of orthophosphorus was available through the filter bed. A reduction of the coagulant dosage of 11 % was found for the coagulant dosage system when compared to a continuous metal/orthophosphorus dosage ratio of 4 mol/mol and a reduction of 29% when compared to a continuous metal/orthophosphorus dosage ratio 5 mol/mol.

9.5 Applications

To summarise this chapter, cases have been made to illustrate how the knowledge collected during this research can be applied. Subsection 9.5.1 illustrates under which circumstances a particular technique can be applied. This subsection is based on Section 6.5. Subsection 9.5.2 illustrates how the TU Delft phosphorus distribution method can be applied to investigate causes of unacceptable phosphorus removal.

9.5.1 Choosing a filtration technique for extension of an existing WWTP

This subsection describes three different cases as a way to illustrate which of the tested techniques (dual media filtration (with or without biomass), continuous sand filtration or 1-STEP® filtration) should be applied in a certain case.

Case 1. A WWTP in the Netherlands which treats the wastewater of >100.000 p.e. has to fulfil the current discharge limit of 1 mg P-total/L (see also Table 1-2 on page 19). In the future, due to the European waterframework directive (WFD), this discharge limit will become 0.3 mg/L. The current yearly average concentration in the WWTP effluent of total phosphorus is 0.9 mg/L, with wide variations during the year (0.15 – 1.5 mg P-total/L).

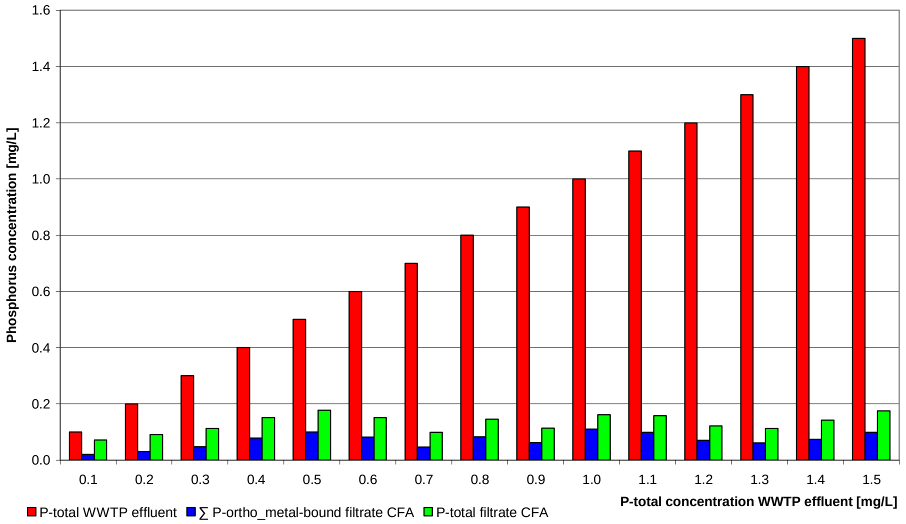

Figure 9-7– Removal of phosphorus with coagulant and methanol dosage for a continuous sand filter at the Leiden Zuidwest WWTP

The decision is made to extend the treatment plant with a filtration technique to remove total nitrogen and total phosphorus simultaneously, but the question is: which technique should be applied? The answer to this question is continuous sand filtration (see Figure 9-7). This technique has proven ability to remove total phosphorus below 0.3 mg/L for total phosphorus concentrations in the feed water between 0.1 – 1.5 mg/L. A 1-STEP® filter (see Figure 9-7) which also produces consistent results, with regard to phosphorus removal, is an alternative but the results show that 0.3 mg/L in the filtrate water can only be reached for orthophosphorus concentrations in the feed water of 1.2 mg/L (approximately 1.3 mg P-total/L).

Case 2. A WWTP in the Netherlands which treats the wastewater of >100.000 p.e. has to fulfil the current discharge limit of 1 mg P-total/L (see also Table 1-2 on page 19). In the future, due to the WFD, this discharge limit will become 0.15 mg/L. The current yearly average concentration in the WWTP effluent for total phosphorus is 0.5 mg/L. The WWTP produces effluent with rather steady concentrations of total nitrogen and total phosphorus all year. The decision is made to extend the treatment plant with a filtration technique, but the question is: which technique should be applied? The answer to this question is 1-STEP® filtration. This technique proved capable of treating the feed water to a total phosphorus concentration below 0.15 mg P-total/L for total phosphorus concentrations in the feed water of 0.8 mg P-total/L. An alternative would be continuous sand filtration. Dual media filtration would not fulfil the discharge limits.

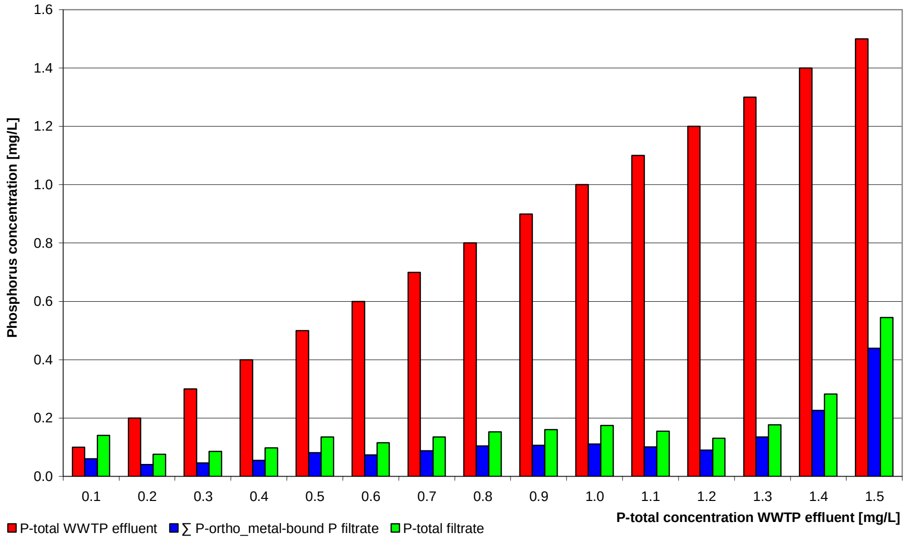

Figure 9-8 - Removal of phosphorus with coagulant and methanol dosage for the 1-STEP® filter at the Horstermeer WWTP

Case 3. A WWTP in the Netherlands which treats the wastewater of <100.000 p.e. has to fulfil the current discharge limit of 2 mg P-total/L (see also Table 1-2 on page 19). In the future, due to the WFD, this discharge limit will become 0.5 mg/L.

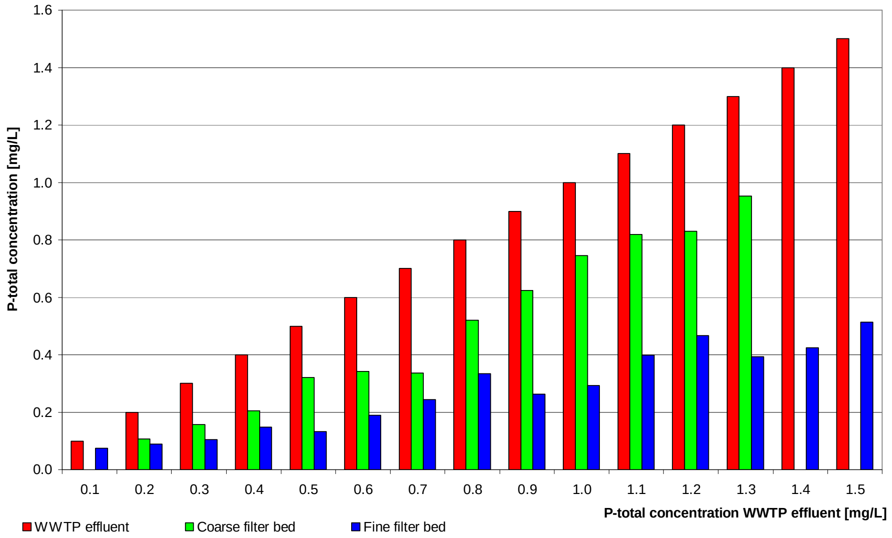

Figure 9-9 – Average total phosphorus removal for the coarse and the fine filter beds with biomass and a filtration rate of 10 m/h. Made with on-line data available at the Leiden Zuidwest WWTP

The current yearly average concentration in the WWTP effluent of total phosphorus is 1.0 mg/L, with wide variations during the year (0.5 – 1.5 mg P-total/L). The decision is made to extend the treatment plant with a filtration technique to remove total nitrogen and total phosphorus simultaneously, but the question is: which technique should be applied? This can be continuous sand filtration or dual media filtration. Dual media filtration with biomass and a fine filter bed is able to fulfil the discharge limit for total phosphorus concentrations in the feed water up to 1.5 mg/L (see also Figure 9-9). This is not reached for a dual media filter with a coarse filter bed. Improvement of the wastewater treatment plant is another option which should be considered before choosing and placing filtration techniques.

9.5.2 Finding the cause when phosphorus removal is not satisfying

A WWTP is extended with dual media filtration for denitrification and simultaneous chemical phosphorus removal. The phosphorus removal is not optimal and the discharge limit for total phosphorus, which is 0.15 mg/L, is not reached. Total phosphorus concentrations in the filtrate water are on average 0.4 mg/L. Knowledge of the phosphorus distribution is required to be able to solve this problem. The phosphorus distribution will show whether all the orthophosphorus in the feed water is transferred to metal-bound phosphorus in the upper water layer. The coagulant dosage should be checked whether the phosphorus distribution in the upper water layer shows an orthophosphorus concentration of nearly 0 mg/L. When the phosphorus distribution in the upper water layer mainly contains metal-bound phosphorus but the phosphorus distribution in the filtrate water also contains metal-bound phosphorus, a breakthrough of the filter bed occurs. The velocity gradients in the filter bed may be too high, causing floc breakage. Therefore, a backwash of the filter bed is required. The available storage in the filter bed is approximately 0.41 – 1.27 kg Fe^{3+}/run for filtration with biomass. Metal-bound phosphorus in the filter bed may also be caused by over-dosage of coagulant, for example, or by high water temperatures. Besides a problem with the transfer of orthophosphorus to metal-bound phosphorus and the retention of flocs in the filter bed, low removal rates can also be caused by high concentrations of dissolved “organic” phosphorus in the feed water. Only some of the colloidal organic phosphorus might be removed due to coagulation/flocculation, the part which is not within flocs will be transported through the filter bed. The phosphorus distribution will make this visible, too. If this is the problem, research should be conducted to find the source of the high concentrations of dissolved “organic” phosphorus. It may be caused by industrial discharges into the sewer.

9.5.3 Choosing the optimal filtration rate

The decision is made to treat WWTP effluent with dual media filtration for the removal phosphorus. The discharge limit for this location is 0.15 mg P-total/L. A fine filter bed is chosen to improve the phosphorus removal, because it is not a denitrifying filter. The question is which filtration rate is optimal? The optimal filtration rate is 10 m/h. When this filtration rate is applied, can the filter fulfill the discharge limit up to total phosphorus concentrations of 1.5 mg/L in the WWTP effluent. When higher filtration rates are applied will the discharged limit be exceeded for total phosphorus concentration in the WWTP effluent of 0.5 mg/L for 15 m/h and 0.75 mg/L for 20 m/h. With increasing filtration rates the filter runtime can decrease because the maximum removal capacity is reached. For a filtration rate of 10 to 15 m/h in combination with a metal/orthophosphorus ratio of 4 mol/mol and total phosphorus concentrations in the feed water of < 1.0 mg/L, the average filter runtime is 8 to 10 hours (STOWA, 2009).

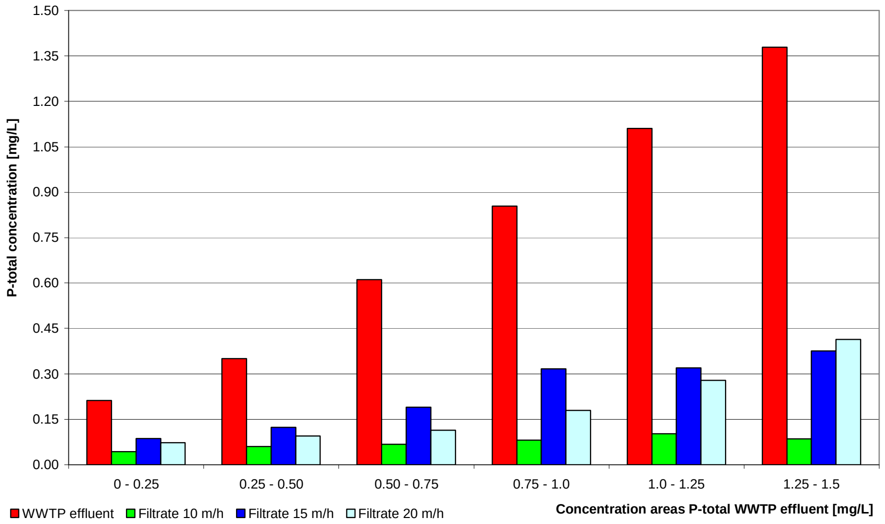

Figure 9-10 – Average phosphorus removal for the dual media filter at the Leiden Zuidwest WWTP (fine filter bed) for 10, 15 and 20 m/h (STOWA, 2009)

9.5.4 What's the limit?

Finalising this thesis with the title "Reaching ultra low phosphorus concentrations by filtration techniques" raises the question whether ultra low phosphorus concentrations are reached by the filtration techniques used. First of all it should be defined, what an ultra low phosphorus concentration is. Ultra low is defined within this thesis as total phosphorus concentrations below 0.15 mg/L (see Section 1.3). The filtration techniques used have proven to be able to produce filtrate water with ultra low phosphorus concentrations.

If ultra low is defined as total phosphorus concentrations which approach 0 mg/L, are other techniques like membrane filtration required. The filtrate water of the filtration techniques examined for this research all contain metal-bound phosphorus and a small fraction of particulate organic phosphorus. The concentration of metal-bound phosphorus in the filtrate water of the filtration techniques varied between 0.03 – 0.1 mg/L. This fraction of metal-bound phosphorus needs to be removed from the filtrate water when total phosphorus concentrations need to approach 0 mg/L. This can be done, for example, by ultrafiltration. When this fraction is removed from the filtrate water by membrane filtration, total phosphorus concentration below 0.05 mg/L can be reached (see also section 2.7).

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10 Conclusions

Main research goal:

- Ultra low phosphorus concentrations can be reached with effluent filtration but under stringent conditions and with specilised/adapted filtration systems.

- 1-STEP® filtration reaches higher removal efficiencies compared to dual media filtration. Continuous sand filtration reaches the highest removal efficiencies for total phosphorus concentrations of 0.1 – 1.5 mg/L.

Sub-questions:

- The TU Delft phosphorus distribution (Section 4.4) was developed to have an easy and quick method to determine orthophosphorus, metal-bound phosphorus, dissolved “organic” phosphorus and particulate organic phosphorus. The method makes it possible to compare different filter concepts and different process settings.

- Orthophosphorus, metal-bound phosphorus and particulate organic phosphorus are removed in the filter bed. Dissolved “organic” phosphorus will be transported through the filter bed. The removal of phosphorus in the filter bed is mainly caused by filtration (Subsections 6.2.4 and 6.4.4).

- An initial mixing energy of 300 s^{-1} is satisfactory (Section 5.2).

- The size of the formed flocs (Subsection 5.2.5) can be influenced by the coagulant dosage and flocculation time. The results show that the estimated floc size with a flocculation time of 24 minutes is approximately 7 – 12 µm, which is larger than the size of flocs formed with a flocculation time of 10 minutes, these flocs are approximately 2 – 5 µm. But these larger flocs formed with a flocculation time of 24 minutes do not result in higher removal efficiencies in the filter bed. Therefore additional flocculation is not necessary. This suggests that not only is the floc size important but the floc strength is also of high importance.

- Increasing total phosphorus concentrations in the feed water result in increasing total phosphorus concentrations in the filtrate water (Section 6.5). The coagulant dosage is of major influence on the filter runtime. With increasing coagulant dosage the filter runtime is decreasing. For continuous sand filtration, increasing total phosphorus concentrations in the feed water do not result in higher total phosphorus concentrations in the filtrate water.

- The rate of metal-hydroxide precipitation (the transfer of orthophosphorus to metal-bound phosphorus) is not significantly inhibited by temperature, but flocs become larger with increasing temperatures (Section 7.2). During filtration all tested filtration techniques contain the highest total phosphorus concentrations in the filtrate for water temperatures of < 13°C (Section 7.3). For continuous sand filtration results an increasing temperature in decreasing total phosphorus concentrations in the filtrate. This same trend is found for down flow depth filtration techniques but for higher phosphorus concentrations (>0.8 mg/L) the optimal temperature range is between 13°C and 18°C and no longer ≥18°C. The turning point varies per installation and is probably influenced by the velocity (shear rate) in the filter bed and the floc strength.

- Inhibition of the denitrification (Section 8.1), probably due to phosphorus limitation, might occur for PO_4-P/NO_x-N ratios below 0.055 mg/mg in the WWTP effluent. A newly developed coagulant dosage system decreases the risk of phosphorus limitation (Section 8.4) and, besides this, a reduction in the coagulant dosage is found.

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The past four years were absolutely fantastic. During my PhD I got the opportunity to conduct research at different Dutch wastewater treatment plants (WWTP). During two years I spent a lot of time at the Leiden Zuidwest WWTP and over three years at the Horstermeer WWTP. Working at the Horstermeer WWTP meant that I returned at Waternet (formerly DWR) for the 5th time, after an internship and several additional jobs during my bachelor and master study. I have to thank all the people working at the treatment plants for helping me out so many times and making me go to work with a smile every day! Especially the guys from the Horstermeer WWTP made me enjoy working there! Thank you for always making time to help me out, to explain certain disorders at the treatment plant and of course for all the fun during the lunch breaks! I sure laughed a lot because of you!

The moments of brainstorming and creative thinking within project groups, trying to solve problems or to explain certain results, are of course important to a PhD student but to me it always gave a lot of energy. Every time it was very exiting to figure out the solution, even if it was in the middle of the night. Manon Bechger, Jaqueline de Danschutter, Peter Postma, Wouter Zijlstra, Wilbert Menkveld, Remmie Neef, Jeffery den Elzen, Arjen van Nieuwenhuijzen and Anne-Marie te Kloeze, I have to thank you all for the many fruitful discussions and project meetings we had.

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List of publications

International refereed journals

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Curriculum Vitae

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Work Experience

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