

---

**Active Wetlands – the use of  
chemical amendments to  
intercept phosphate runoffs  
in agricultural catchments**

---

**Final report of the Active Wetlands Interreg IVA  
project**

**Risto Uusitalo, Aaro Närvänen, Kimmo Rasa, Tapio Salo,  
Jari Koskiaho, Markku Puustinen, Anne Brax, Elina Erkkilä,  
Sampsa Vilhunen, Päivi Joki-Heiskala, Antti Kaseva,  
Eemeli Huhta, Piia Leskinen, Martin Liira, Egle Saaremäe,  
Morten Poolakese, Toomas Tamm, Kuno Kasak,  
Indrek Talpsep, Ivar Tamm**



EUROPEAN UNION  
EUROPEAN REGIONAL DEVELOPMENT FUND  
**INVESTING IN YOUR FUTURE**



CENTRAL BALTIC  
INTERREG IV A  
PROGRAMME  
2007–2013



**ISBN** 978-952-487-447-2 (Printed version)  
**ISBN** 978-952-487-448-9 (Electronic version)  
**ISSN** 1798-6419  
[www.mtt.fi/mttraportti/pdf/mttraportti92.pdf](http://www.mtt.fi/mttraportti/pdf/mttraportti92.pdf)

**Copyright: MTT**

**Authors:** Risto Uusitalo, Aaro Närvänen, Kimmo Rasa, Tapio Salo, Jari Koskiaho, Markku Puustinen, Anne Brax, Elina Erkkilä, Sampsa Vilhunen, Päivi Joki-Heiskala, Antti Kaseva, Eemeli Huhta, Piia Leskinen, Martin Liira, Egle Saaremäe, Morten Poolakese, Toomas Tamm, Kuno Kasak, Indrek Talpsep, Ivar Tamm

**Distribution and sale:** MTT, 31600 Jokioinen

**Printing year: 2013**

**Cover picture:** Morten Poolakese

---

# Active Wetlands – maatalouden valumavesien fosforin sitominen kemikaalilisäyksen avulla

---

Risto Uusitalo<sup>1)</sup>, Aaro Närvänen<sup>1)</sup>, Kimmo Rasa<sup>1)</sup>, Tapio Salo<sup>1)</sup>, Jari Koskiahho<sup>2)</sup>, Markku Puustinen<sup>2)</sup>, Anne Brax<sup>3)</sup>, Elina Erkkilä<sup>3)</sup>, Sampsa Vilhunen<sup>3)</sup>, Päivi Joki-Heiskala<sup>4)</sup>, Antti Kaseva<sup>5)</sup>, Eemeli Huhta<sup>5)</sup>, Piia Leskinen<sup>5)</sup>, Egle Saaremäe<sup>6)</sup>, Morten Poolakese<sup>6)</sup>, Toomas Tamm<sup>6)</sup>, Martin Liira<sup>7)</sup>, Kuno Kasak<sup>8)</sup>, Indrek Talpsep<sup>8)</sup>, Ivar Tamm<sup>8)</sup>

<sup>1)</sup>MTT, FI-31600 Jokioinen, etunimi.sukunimi @mtt.fi

<sup>2)</sup>Suomen Ympäristökeskus, FI-00251 Helsinki, etunimi.sukunimi@ymparisto.fi

<sup>3)</sup>WWF-Finland, FI-00500 Helsinki, etunimi.sukunimi @wwf.fi

<sup>4)</sup>Paimionjoki-yhdistys ry, FI-31400 Somero, etunimi.sukunimi @somero.fi

<sup>5)</sup>Turun ammattikorkeakoulu, FI-20520 Turku, etunimi.sukunimi @turkuamk.fi

<sup>6)</sup>Estonian University of Life Sciences, EE-51014 Tartu, etunimi.sukunimi @emu.ee

<sup>7)</sup>University of Tartu, EE-50090 Tartu, etunimi.sukunimi @ut.ee

<sup>8)</sup>Estonian Fund for Nature, EE-50002 Tartu, etunimi.sukunimi @elf.ee

## Tiivistelmä

Suomessa ja Virossa tutkittiin mahdollisuuksia tehostaa liuenneen fosforin pidättymistä pieniin kosteikkoihin ja pelto-ojiin, jotka ovat yleensä huonoja pysäyttämään vesistöjä rehevöittävää liennutta fosforia.

Hankkeessa tehtiin kenttäkokeita 20 paikalla joko annostelemalla veteen liukenevaa rautasulfaattia ojaveteen tai ohjaamalla valumavesiä kiinteiden, fosforia pidättävien materiaalien läpi. Käytimme kokeissa kahdentyyppisiä kiinteitä aineita, rautahydroksideja sisältäviä Sachtofer PR -rakeita ja runsaasti kalsiumia sisältävää, palavakiven poltosta jätteenä jäävää murskettä.

Kun menetelmät toimivat moitteettomasti, vedestä saatiin sidottua liennutta fosforia hyvin tehokkaasti. Rautasulfaatti muodostaa veteen liuetessaan fosforin kanssa yhdisteitä, jotka eivät ole enää leville ja vesikasveille käyttökelpoisessa muodossa. Näin fosforin rehevöittävä vaikutus pienenee, vaikka yhdisteet jäisivätkin vesiympäristöön. Rautasulfaatin annostelulaitteet vaativat toiminnan seuraamista ja kemikaalin lisäämistä. Paras kustannus-hyötysuhde saavutetaan, kun valumaveden fosforipitoisuus on korkea, jolloin fosforikilon sitominen rauta-fosfori -yhdisteiksi tulee maksamaan vain muutamia kymmeniä euroja. Ojissa, joissa liuenneen fosforin pitoisuus oli matala, kustannukset kymmenkertaisuivat.

Tutkitut kiinteät fosforinpidättäjät ovat periaatteessa turvallisempia ja helpompia liukoisen fosforin poistajia kuin veteen liukenevat kemikaalit. Perustamisen jälkeen rakenteita ei tarvitse juurikaan huoltaa, minkä lisäksi fosforin pidättäminen kiinteään aineeseen mahdollistaa sen keräämisen pois vesiympäristöstä ja siten myös kierrätyksen takaisin pelloille. Tässä hankkeessa tutkitut rakenteet kuitenkin toimivat toivotulla teholla vain hetken aikaa. Kokeiden aikana muodostuneet oikovirtaukset ja mm. leväkasvu heikensivät lopputulosta. Molemmat prosessit estivät veden ja pidättäjäaineiden välisen kontaktin ja heikensivät fosforin pidättymistä.

Uudet, aktiiviset vesienkäsittelymenetelmät ovat parhaimmillaan hyviä apukeinoja fosforikuorman vähentämisessä. Ne kannattaa sijoittaa paikkoihin, joissa esiintyy todennetusti korkeita liuenneen fosforin pitoisuuksia. Kuitenkin näemme selviä kehitystarpeita, jotta nämä menetelmät saadaan toimimaan luotettavasti ja turvallisesti. Haastattelututkimuksiin osallistuneilla viljelijöillä oli pääsääntöisesti myönteinen asenne ravinnekulkeumien vähentämiseen, myös kemiallisilla menetelmillä.

## Avainsanat:

fosfori, kosteikot, kemiallinen käsittely, rautasulfaatti, rautaoksidit, palavakivi, saostuminen, pidättäminen, fosfaatin sitominen, maatalous, valumavedet, rehevöityminen

---

# Active Wetlands – the use of chemical amendments to intercept phosphate runoffs in agricultural catchments

---

Risto Uusitalo<sup>1)</sup>, Aaro Närvänen<sup>1)</sup>, Kimmo Rasa<sup>1)</sup>, Tapio Salo<sup>1)</sup>, Jari Koskiaho<sup>2)</sup>, Markku Puustinen<sup>2)</sup>, Anne Brax<sup>3)</sup>, Elina Erkkilä<sup>3)</sup>, Sampsa Vilhunen<sup>3)</sup>, Päivi Joki-Heiskala<sup>4)</sup>, Antti Kaseva<sup>5)</sup>, Eemeli Huhta<sup>5)</sup>, Piia Leskinen<sup>5)</sup>, Egle Saaremäe<sup>6)</sup>, Morten Poolakese<sup>6)</sup>, Toomas Tamm<sup>6)</sup>, Martin Liira<sup>7)</sup>, Kuno Kasak<sup>8)</sup>, Indrek Talpsep<sup>8)</sup>, Ivar Tamm<sup>8)</sup>

<sup>1)</sup>MTT Agrifood Research, FI-31600 Jokioinen, [firstname.lastname@mtt.fi](mailto:firstname.lastname@mtt.fi)

<sup>2)</sup>Finnish Environment Institute, FI-00251 Helsinki, [firstname.lastname@ymparisto.fi](mailto:firstname.lastname@ymparisto.fi)

<sup>3)</sup>WWF-Finland, FI-00500 Helsinki, [firstname.lastname@wwf.fi](mailto:firstname.lastname@wwf.fi)

<sup>4)</sup>Paimionjoki-yhdistys ry, FI-31400 Somero, [firstname.lastname@somero.fi](mailto:firstname.lastname@somero.fi)

<sup>5)</sup>Turku University of Applied Sciences, FI-20520 Turku, [firstname.lastname@turkuamk.fi](mailto:firstname.lastname@turkuamk.fi)

<sup>6)</sup>Estonian University of Life Sciences, EE-51014 Tartu, [firstname.lastname@emu.ee](mailto:firstname.lastname@emu.ee)

<sup>7)</sup>University of Tartu, EE-50090 Tartu, [firstname.lastname@ut.ee](mailto:firstname.lastname@ut.ee)

<sup>8)</sup>Estonian Fund for Nature, EE-50002 Tartu, [firstname.lastname@elfond.ee](mailto:firstname.lastname@elfond.ee)

## Abstract

In this project—conducted in Finland and Estonia—we studied different applications that can be used to boost the retention of dissolved phosphorus (P) in agricultural wetlands and field ditches. Wetlands are usually inefficient in retaining the dissolved P component that has a profound effect on eutrophication in surface waters, such as nuisance growth of algae and macrophyte plant species.

The work included field-scale studies at twenty test sites where precipitation of dissolved P was obtained by dosing ferric sulphate (a soluble metal salt) to water, or water was brought into contact with solid P sequester materials. We tested two different types of solid P retention materials: Sachtofer PR, a granulated product that contains iron hydroxides, and oil shale ash, which contains reactive calcium minerals.

Testing revealed that dissolved P concentrations can be effectively reduced by the methods used when they work as intended. Ferric sulphate binds dissolved P in a form (Fe-P associations) that is no longer available for biological utilization by algae or other water biota, and thus decreases the eutrophying effects of the P load. The dosers used in administering ferric sulphate to water, however, require maintenance and oversight, such as filling up the chemical storage and checking on the pH of the treated water. When applied at sites with a high dissolved P concentration, ferric sulphate proved to be very cost-efficient—the cost of treating a kilogram of dissolved P was only in the tens of euros. At sites with a low dissolved P concentration, however, the cost of binding a kilogram of dissolved P in a non-bioavailable form was in the hundreds of euros.

On the other hand, at their best, solid P sequester materials are maintenance-free after construction and allow for the collection of P out of the water system for possible recycling; however, they proved to work with poor efficiency when a long test period (up to several years) was concerned. Problems encountered with the solid P sequesters were associated with processes that inhibited contact between the water and the reactive surfaces of the materials. Consequently, the high P retention capacities of these materials were not realized in practice.

Farmers generally had positive attitudes towards methods that reduce nutrient transports from soil to water, including the use of chemicals. Treating field runoffs to bind dissolved P is a viable and new option in nutrient mitigation that could be successfully used at the so-called hot-spots of P loading, i.e., at sites that produce higher dissolved P concentrations than the surrounding areas. The tested solutions should be further developed to ensure safe and efficient operation before they are recommended for practical water protection work.

## Keywords:

phosphorus, wetlands, chemical amendments, ferric sulphate, iron oxides, oil shale, precipitation, adsorption, phosphate retention, agriculture, runoff, eutrophication

---

# Contents

---

<b>1 Introduction</b> .....	<b>6</b>
1.1 Phosphorus, wetlands and active measures .....	6
1.1.1 Phosphorus and agriculture .....	6
1.1.2 Phosphorus forms and eutrophication potential .....	6
1.1.3 Wetlands and nutrient retention .....	7
1.1.4 Chemical amendments to increase P retention in wetlands .....	7
1.2 Project description and objectives .....	8
1.3 Permissions and legislation .....	9
<b>2 Material and methods</b> .....	<b>11</b>
2.1 Selection of test sites .....	11
2.1.1 Site surveys in Finland .....	11
2.1.2 Site surveys in Estonia .....	12
2.1.3 Selection criteria for the test sites .....	13
2.2 Tested chemicals .....	16
2.2.1 Ferric sulphate and its dosing .....	16
2.2.2 Tests with solid P retention media .....	17
2.3 Sampling and methods of water analyses .....	19
2.4 Test set-ups at different sites .....	20
2.4.1 Hovi wetland without chemical amendments .....	20
2.4.2 Nautela tests with ferric sulphate .....	21
2.4.3 Lake Nuutajärvi area tests with ferric sulphate .....	22
2.4.4 River Paimiojoki area and Tammela tests with ferric sulphate .....	23
2.4.5 Rahinge tests with ferric sulphate .....	25
2.4.6 Ojainen tests with Sachtofer PR granules .....	26
2.4.7 Rahinge tests with Sachtofer PR granules .....	27
2.4.8 Rahinge tests with oilshale ash .....	29
2.5 Interviews with farmers .....	29
2.5.1 Interviews conducted in Finland .....	29
2.5.2 Interviews conducted in Estonia .....	30
<b>3 Results</b> .....	<b>31</b>
3.1 Wetlands without chemical amendments .....	31
3.1.1 Hovi constructed wetland .....	31
3.1.2 Snapshots of P concentrations in other wetlands .....	33
3.2 Precipitation of P with ferric sulphate .....	34
3.2.1 Nautela tests .....	34
3.2.2 Nuutajärvi tests .....	36
3.2.3 Paimionjoki and Tammela tests .....	38
3.2.4 Rahinge tests .....	39
3.3 Solid P retention materials .....	39
3.3.1 Ojainen tests with Sachtofer PR granules .....	39
3.3.2 Rahinge tests with Sachtofer PR granules .....	41
3.3.3 Rahinge tests with oilshale ash .....	42
3.4 Disturbances and risks associated with the use of chemicals .....	43
3.5 Poll of farmers .....	45
3.5.1 Interviews conducted in Finland .....	45
3.5.2 Interviews conducted in Estonia .....	46
<b>4 Discussion</b> .....	<b>47</b>
4.1 Phosphorus retention in wetlands without chemical treatments .....	47
4.2 Precipitation of dissolved P by ferric sulphate .....	48
4.3 Solid P retention media .....	49
4.4 Communication of the Active Wetlands project .....	50
<b>5 Conclusions</b> .....	<b>51</b>
<b>6 References</b> .....	<b>52</b>

---

# 1 Introduction

---

## 1.1 Phosphorus, wetlands and active measures

### 1.1.1 Phosphorus and agriculture

Phosphorus (P) is one of the major elements that plants need for growth and seed production. A century ago soils were largely deficient in this essential nutrient and P applications clearly increased yields of cultivated plants. Between the 1950s and the late 1990s, however, applications brought increasingly larger surpluses to an average field hectare in many industrialized countries. For example, P use in Finland peaked in the late 1980s and at that time P inputs to an average field hectare were about 30 kg larger than P removal by harvested crops. It was estimated by Saarela (2002) that P applications to Finnish agricultural soils have led to doubling the total P content of the plough layer of agricultural fields during the last one hundred years.

As a result of increasing the P content of agricultural soils, P transport from land to water has increased over time, as an increase in soil P status translates into higher P concentrations in runoff and drainage waters (e.g., Heckrath et al., 1995; Uusitalo and Jansson, 2002). To cope with the eutrophication of surface waters, the EU Water Framework Directive (Directive 2000/60/EC) targets the restoration or enhancement of the chemical and ecological status of water bodies, and for this purpose the main nutrient sources need mitigation. Because agriculture is currently considered as a major contributor to P loading of surface waters in all countries around the Baltic Sea (see HELCOM, 2009), agricultural sources need to be covered in mitigation plans.

When the soil P status is high, a reduction in P transport from the soil to water would require lowering the soil P content. In practice, P applications to these fields should be withheld, or at least greatly reduced so that the P balance (P inputs less P outputs) would be negative (i.e., more P is harvested from the field than added with fertilizers and animal manure). Turning the surplus P applications into balanced applications, or in high P soils into negative P balances, is especially problematic in areas where animal husbandry has increased in intensity. Because animal farms have concentrated in certain regions, and feed for domestic animals is increasingly imported from outside these regions, there is a continuous surplus of nutrient balances in animal farms and areas where they are concentrated. Even when P inputs to agricultural soils can be reduced, it takes considerable time to reduce the soil P stock and thus affect P losses to water.

### 1.1.2 Phosphorus forms and eutrophication potential

Phosphorus in runoff or drainage waters is operationally defined as particulate and dissolved forms. Particulate P is associated with sediment matter, whereas the pool of dissolved P includes orthophosphate and P of dissolved organic molecules. The dissolved fraction is commonly taken to be totally available for biological utilization (Ekholm and Krogerus, 2003), but the bioavailability of particulate P is lower. Earlier studies on runoff and drainage waters from Finnish clay soils have suggested that, depending on the soil P status, 20–50% of particulate P may in a short term turn into dissolved form (Uusitalo et al., 2003). Because particulate P often makes up a major proportion of the total P in agricultural runoff, both forms may, however, substantially contribute to the eutrophication of receiving waters.

The particulate and dissolved P pools continuously change as a result of changes in water chemistry and biological activity. The water chemistry-driven changes involve reactions such as a P release from a particulate pool (including bottom sediment) into dissolved pool, the retention of dissolved P to particle surfaces, and precipitation/dissolution reactions. The partitioning of P in particulate and dissolved pools is driven by changes in P concentration in water, pH, the reduction–oxidation state of sediment and water, and concentrations of dissolved ions in water (i.e., ionic strength of water). In general, the retention of P on particle surfaces is increased with an increase in P concentration in water, a decrease in pH, the presence of dissolved oxygen, and an increase in ionic strength. Conversely, P solubilisation from particles to dissolved pool is increased at a low P concentration in water, a high pH, a low supply in dissolved oxygen, and at a low concentration of dissolved ions.

The biological cycle, in turn, withdraws P from the solution phase and embeds it in living cells as storage compounds (e.g., inositol phosphates of plant seeds or polyphosphates of bacterial cells), as parts of cell

wall structures (phospholipids), as building blocks of nucleic acids (DNA, RNA), and as parts of cell energy storage systems (e.g., in mitochondria). Upon the death of plants and other organisms these phosphorus compounds are released into the surroundings and after decomposition may re-enter the biological and chemical cycles. Larger bursts of P from the biological compartment may occur as a result of frost and drought.

### **1.1.3 Wetlands and nutrient retention**

In pristine landscapes wetlands develop on sites where the water flow slows down before entering waterways. When the water flow calms down, particulate matter sedimentation occurs and algae, bacteria and higher plants may assimilate nutrients from water and sediment. Of the main water pollutants due to agricultural operations, that is, phosphorus and nitrogen (N), P may be retained in a wetland by deposition and assimilation. For N, the main sink is, however, the atmosphere where N ends up after the conversion of nitrate (NO<sub>3</sub>) to nitrogen gas (N<sub>2</sub>) by denitrifying bacteria. Nitrogen removal in wetlands is well established (e.g., Tanner et al., 2010), but studies on P removal from runoff and drainage water by wetlands show variable efficiencies (cf. Koskiaho et al., 2003; Tanner and Sukias, 2011).

Biological accumulation of P in wetlands directly involves dissolved P only. Due to biological activity that is regulated by temperature, P assimilation in wetlands takes place during the warm season, whereas a variable part of the accumulated nutrients are re-released into water from decaying biomass during the cold season. As a result, in the warm season and low-flow periods wetlands act as nutrient sinks, but commonly turn into nutrient sources in the cold season and high-flow periods. During an annual cycle the net accumulation of phosphorus may take place if there is net sediment accumulation and/or if the roots of wetland plants are permanently buried in the sediment and only undergo partial and slow decomposition. However, studies on established wetlands suggest that the net P accumulation over several years may in most cases be of minor importance (see Tanner and Sukias, 2011).

Particulate P accumulation in wetlands takes place as a result of sediment deposition which thus requires that the water flow calms down. It is the small soil particles that contain clearly higher P concentrations than larger ones (e.g., Sharpley, 1985; Uusitalo et al., 2001), but in a small wetland fine-grained particles may not settle at all or flow peaks may cause resuspension of settled particles and transport them further downstream. Especially in landscapes with fine soil texture wetlands should have a sufficient size in relation to the size of its catchment area in order to provide calm conditions for the settling of particulate matter.

In Finland, the recommended size for a constructed wetland for the treatment of agricultural runoff is 1–2% of the catchment area (Koskiaho and Puustinen 2005, Puustinen et al. 2007). Wetlands and ponds falling below the lower limit have shown poor P retention performance, while wetlands exceeding this relative size have been found to retain P over many years (Puustinen et al. 2007, Koskiaho et al. 2009). However, due to the high price of land, the lack of suitable places for construction, and the eligibility limit for agri-environmental subsidy (0.5% wetland-to-catchment area ratio), wetlands that are currently established typically have a smaller area ratio than would be ideal for efficient P retention. Moreover, because the number of agri-environmental wetlands established in Finland so far is not very high (Aakkula et al. 2010), their overall effect on P loading of the surface waters of our country is presumably low.

### **1.1.4 Chemical amendments to increase P retention in wetlands**

Phosphorus retention in wetlands may be accentuated by adding chemicals or a medium that reacts with dissolved P. There are two main options for doing this, namely adding chemicals that dissolve in water and strip P from the water column as a precipitate, or adding in the path of water a solid medium that binds P on its reactive surfaces. The first approach includes metal salts such as ferric or aluminium sulphates and chlorides. Metal salts are widely used in water and wastewater purification and they can be regarded as a proven option that, when combined with wetlands, is applied in a new context. The second approach, solid P sequesters, may involve materials originating from, for example, side flows of industrial or mining operations. The use of retention media is an approach that was presented already in the 1960s (Yee, 1966; Neufeld and Thodos, 1969), and since then has been widely tested in laboratory and short-term field experiments, but only a few long-term field-scale tests have been reported to date (see Klimeski et al., 2012).

The use of a solid retention medium has several potential advantages over the use of soluble chemicals. First, after the construction of a structure that holds the solid material the need for maintenance is less than for soluble chemicals that require continuous oversight. Another advantage of a solid medium is that P is retained in the structure and P removed from the aquatic system when the used medium is changed. This may also allow the recovery of the P collected in the medium in a form that can be recycled in fertilizers. Further, depending on the medium, possible hazards associated with overdose are likely to be less than when soluble chemicals are used. There are, however, prerequisites for using solid P retention media. The material should have a high affinity for P, it should be permeable and maintain sufficient hydraulic conductivity in variable flow conditions, and it should be non-toxic for water organisms (preferably only modest effects on, for example, the pH of water, low in soluble heavy metals, etc.). Ideally, the material would also have a good availability and price making the use feasible in selected applications and sites.

A number of different types of materials have been tested as potential P retention media. The most interesting are those that contain abundant Ca or Mg in a form that is entirely or partly soluble, and those that contain metal (Al or Fe) hydroxides that are known to have a high affinity for soluble P. There are also materials that contain both metals and soluble Ca or Mg (or both), such as steel slag which typically contains iron in relatively high concentrations, but also soluble Ca oxides as a result of heating the ore and additives (e.g. charcoal) to high temperatures. The total concentrations of the listed elements cannot, however, be used as the sole selection criterion as they should be in a form that is reactive, thus having an affinity for P. For example, iron oxides with a highly ordered crystalline structure are much less reactive than poorly crystalline iron hydroxides, why the latter are a better candidate as a P sequester material.

As stated above, most of the testing reported in academic articles originates from studies conducted in laboratory. The large scale studies reported include studies of wastewater in England (Heal et al., 2004; Dobbie et al. 2009) and New Zealand (Shilton et al., 2006). The P retention material in the studies of Heal et al. (2004) and Dobbie et al. (2009) was mine drainage residual, or ochre, which is an iron hydroxide precipitate; whereas steel smelter slag was tested by Shilton et al. (2006). Similar materials have been also tested to treat agricultural runoff in the US (Penn et al., 2007, 2012) and New Zealand (McDowell et al., 2007). Materials that contain only Ca have been studied on larger scales by, for example, Kirkkala et al. (2012).

The longest field study is probably that of Shilton et al. (2006) who followed for 11 years a large (>1000 m<sup>3</sup>) steel works slag filter installed in a wastewater treatment plant. Phosphorus concentration of the feed liquor was at about 8 mg l<sup>-1</sup>, and the filter lowered it by 75–80%, to about 2 mg l<sup>-1</sup>, during the first five years of operation. After that P retention started to gradually decrease with time. High initial P removal efficiencies were also reported by Dobbie et al. (2009) and Penn et al. (2007) for mine drainage residuals, and by McDowell et al. (2007) for steel works by-product. Kirkkala et al. (2012) in turn measured 46–62% P removal efficiencies during 1.5–6 years for three different lime (CaO/Ca(OH)<sub>2</sub>/CaCO<sub>3</sub>) filters that were buried in soil and took variable flows of ditch or runoff water. Lime caused the precipitation of soluble P and, as shown by the high pH in outflow of their filters (up to pH value of 12 in one of the filters), the filters had reactive lime present throughout their study period. There are thus examples of solutions that have worked well, at least for some periods.

## 1.2 Project description and objectives

The core idea of the Active Wetlands project was to find out how the efficiency of small wetlands in nutrient retention could be improved. The project was a joint effort of the following Finnish and Estonian partners:

- MTT Agrifood Research Finland, Plant Production section (MTT)
- Finnish Environment Institute, Research Department/Research Programme for Integrated River Basin Management (SYKE)
- Turku University of Applied Sciences (TUAS)
- WWF-Finland (WWF)
- Estonian Fund for Nature (ELF)
- Estonian University of Life Sciences, Institute of Forestry and Rural Engineering, Department of Water Management (EULS)

The main objectives of our project were:

1. To generate knowledge and explore the applicability of different active measures to increase the efficiency of small wetlands in P retention (i.e., to develop active wetlands).
2. To test practical designs for constructing active wetlands on a field scale.
3. To raise public awareness of the use of active treatment of agricultural runoff and to discover the attitudes of farmers to such methods.
4. To test the potential of active wetlands in nutrient retention of agricultural runoff at the watershed level through mathematical and economic models.
5. To assess the possibilities of including the active measures in nutrient sequestration to agricultural policy.
6. To develop trans-boundary co-operation of the concept “active wetlands” by sharing ideas from local/regional/national wetland design, construction and management, and by improving together public awareness of wetlands and their potential in nutrient retention from agricultural runoff.

The project’s findings are published in two separate reports. This report focuses on constructing and testing new methods that would enhance P retention in watersheds, including basic calculations on the site-specific costs and benefits of the methods tested. We also include in this part aspects of public opinion and farmers’ views on the use of chemicals for P sequestering from agricultural runoff. As a result, this report focuses on objectives 1–3, whereas objectives 4 and 5 are discussed in a separate report that takes an in-depth look at the modelling work. Objective 6 has been worked on since the beginning of the project and a lot has been learned within the project from the experiences in different areas.

The entire project was funded by the European Regional Development Fund, Central Baltic Interreg IVA programme during 2009–2013.

### 1.3 Permissions and legislation

When planning chemical treatments as a part of nutrient mitigation projects, different kind of permissions are needed. For all activities the permission of the land and/or water owners is naturally required. Additional permissions and documentation may vary widely, depending on where the planned activities take place. Here we describe the process of applying for permissions for chemical use at two sites, one in Finland and the other in Estonia.

#### *Experiences in Finland*

In Finland, small treatment units placed in minor ditches need to be notified to the local Centre for Economic Development, Transport and the Environment (ELY Centre). Any constructions or actions in larger streams, or other actions that may be regulated by the Water Act (587/2011) or the Environmental Protection Act (86/2000) require permissions from the Regional State Administrative Agencies (AVI, Aluehallintovirasto).

The Finnish study sites built in this project were located in minor ditches and thus gained approval from the ELY Centres of the regions in question. Each application letter stated the following points:

- the aim of the activity and its duration
- specified sites, marked in maps
- landowners and their statements of approval
- chemicals to be used (with product data sheets as appendices)
- detailed plans on how the constructions are to be done and how they might affect the surrounding land and recipient water
- how the activities and their effects are followed during the tests

In their response, ELY Centres stated that it is not likely that the described activities would cause any harm to the environment or the surroundings, and hence testing could be conducted once the landowners agree. In addition, responsibility for any possible damage to the surroundings, the neighbourhood, land owners, etc., is governed by the Water Act and falls on the party that conducts the actions.

In Finland, there are no specific guidelines for the chemical or physical properties of (soluble or solid) materials used for the treatment of runoff waters in small ditches, but their suitability is judged by ELY Centre personnel. Obviously, the application of directly toxic elements is not permitted, but, for example, changes in the pH of water due to the treatment or content and solubility of heavy metals (or other potentially harmful elements) in the materials have no stated guideline values. When applying for the permits we referred to guideline concentrations for soil amendments, which apparently satisfied the ELY Centres. At present, the sites where chemicals or solid P sequesters are used are very few, and it is likely that there will be limits on the chemical properties of these types of materials in the future, especially if small scale testing is a success and interest in the wider use of these methods increases.

### *Experiences in Estonia*

In Estonia, any treatment of agricultural drainage waters is regulated by the Water Act (RT I 1994, 40, 655) and the Ministry of the Environment Regulation No. 18 entitled “Proceedings for issue, amendment and revocation of permits for the special use of water and temporary permit for special use of water, a detailed list of the information necessary for applying for a permit and the format of an application for a permit” (RTL 2002, 48, 664). The Water Act specifies the main legal obligations and regulation of activities, whereas a permit for the special use of water is necessary if a water body is dammed, resulting in the alteration of the water table by 0.3 m or more, or chemicals are applied to water.

The Environmental Board, operating under the Ministry of the Environment, can issue permits for the special use of water after considering an application. The application should contain the following:

- name or business name, registry code, if one exists, and the domicile of the applicant
- location of the activities for which the permit for special use of water is applied
- a short description of the activities for which the permit is applied (the duration of the activities, chemicals to be used, description of the treatment unit construction)
- measures reducing the effect of special use of water on water bodies and recipients, and the terms for application of the measures
- damming effects on the surrounding land
- permission of the landowner(s)
- permission of the municipality.

The issuer of the permits for special use of water announces the permit in the official publication “Ametlikud Teadaanded” within seven days after issuing it. A prerequisite for a successful application is that the quality of the water body in question shall not deteriorate as a result of the actions.

The assessment of the status of water bodies is based on Ministry of the Environment Regulation No. 44: “Procedures for establishing surface water bodies, list of surface water bodies whose status class is to be determined, status classes for surface water bodies and procedures for determining quality indicator values corresponding to the status classes” (RTL 2009, 64, 941). This regulation establishes the quality indicators and the procedures for classifying water bodies. Estonian legislation recognizes five classes of water bodies, depending on the purity of the water, with the designations and guideline concentrations for total nitrogen (N) and phosphorus (P) presented in Table 1.

Table 1. Estonian classification of water quality by the guideline concentrations of total nitrogen and phosphorus.

Quality indicator	High	Good	Moderate	Somewhat poor	Poor
N <sub>tot</sub> , mg l <sup>-1</sup>	< 1.5	1.5–3.0	> 3.0–6.0	> 6.0–8.0	> 8.0
P <sub>tot</sub> , mg l <sup>-1</sup>	< 0.05	0.05–0.08	> 0.08–0.1	> 0.1–0.12	> 0.12

The classes “High” and “Good” correspond to the status of unpolluted natural water, or a status close to that. “Moderate” water quality relates to water bodies on which human activity has had a moderate impact. The classes “Somewhat poor” and “Poor” include water bodies that are considered to be polluted, or highly polluted, by human activity.

## 2 Material and methods

### 2.1 Selection of test sites

#### 2.1.1 Site surveys in Finland

A preliminary search for suitable test sites (selection criteria discussed later under subheading 2.1.3) in Finland was conducted among the wetlands that were known to exist in the south of the country; for example, the WWF has built tens of wetlands in agricultural areas in Finland. During this search 12 wetlands were visited and samples were taken. However, after laboratory analyses of the water samples taken from these sites it became clear that almost none of them had P concentrations high enough that the use of chemical methods would be justified. Following discussions with the project steering group, it was agreed that in order to study the core topic of the project, i.e., to discover the potential of the methods of active P removal, the tests should not be exclusively carried out at sites with an existing wetland or a sedimentation pond, but the methods could be also tested at other sites that had elevated concentrations of dissolved P in ditch water. The following second survey was extended to an additional 23 sites, a number of which were known from the earlier work of the institutions to deliver high-P waters.

At the beginning of 2010, TUAS conducted a separate site survey in order to find a suitable ditch and wetland for the pilot studies. The survey was carried out in Turku and its neighbouring municipalities. Potential sites were selected in a map survey and an enquiry was directed to wetlands planners. For the final site selection, water samples were taken from three potential sites. From the information collected, a small agricultural ditch located in Lieto was selected for the pilot studies.

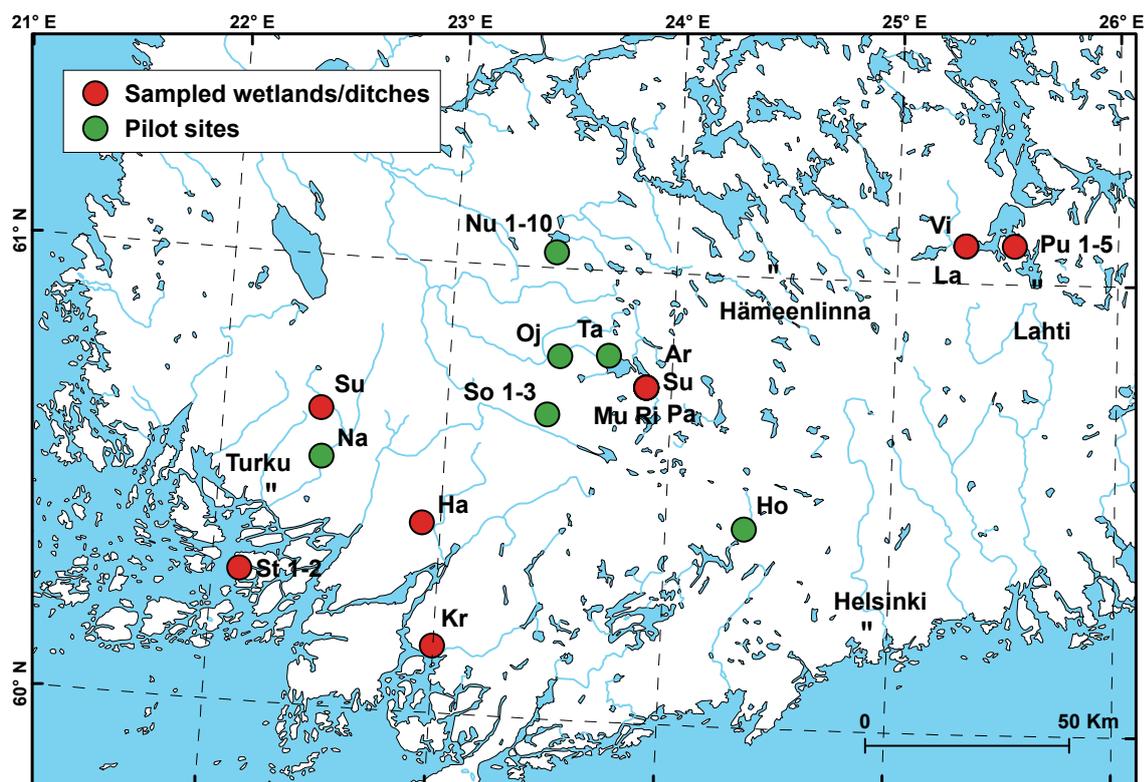


Figure 1. The locations surveyed in Finland. The final test sites are marked with green markers. The sites are identified on this map using the two first letters of their names (see Figure 2).

The pilot tests were finally run in 17 locations in Finland, three of which were associated with a wetland. Of the wetland sites, one (Hovi) did not receive any chemical amendment, whereas P precipitation by soluble metal salt (ferric sulphate) was tested on one site (Nautela) and a solid P requestor material

(Sachtofer PR Ca-Fe oxide granules) at the other site (Ojainen). The rest of the tests were run in ditches that drained variable types of watersheds. The surveyed locations and the selected test sites are shown in Figure 1, and the P concentrations at all sites in Figure 2.

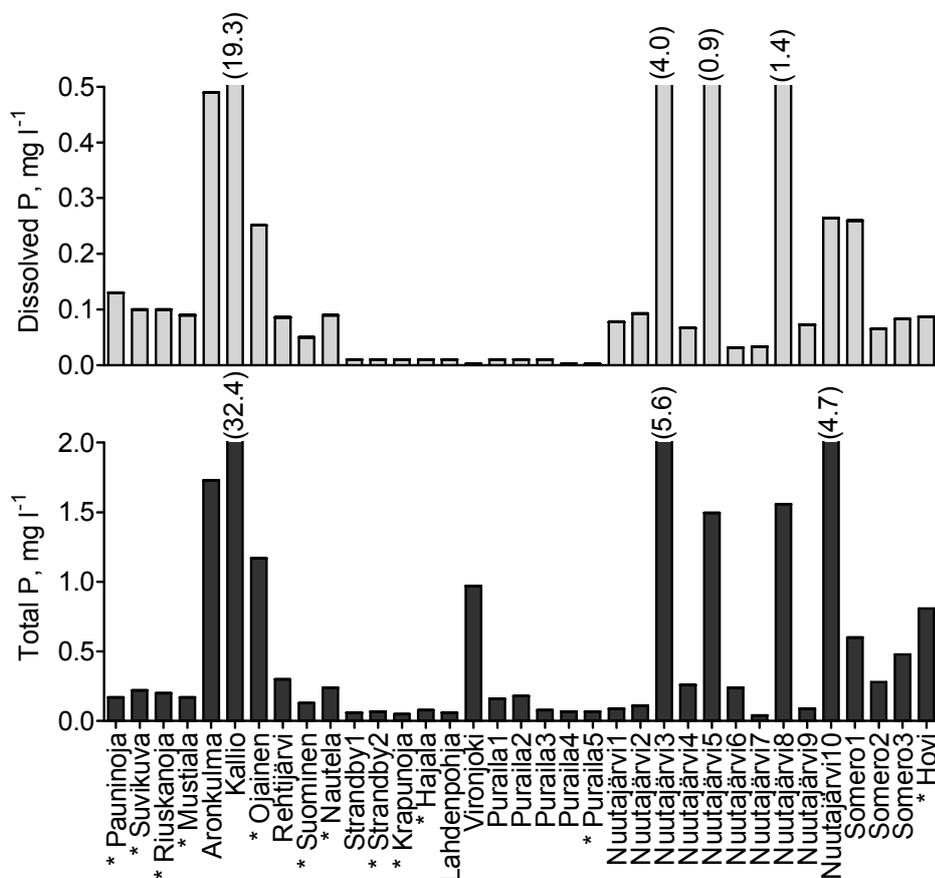


Figure 2. Concentrations of dissolved P (upper graph) and total P (lower graph) in water samples collected during site surveys in Finland. The numbers in parentheses show the concentrations that exceed the y-axis scales. Wetland sites are marked with asterisks.

### 2.1.2 Site surveys in Estonia

From May 2010 to November 2011 EULS and ELF made an extensive, country-wide survey of possible test sites in Estonia (Figure 3). For the survey, data from the State Environmental Monitoring Programme were searched for elevated P concentrations in river water across the priority counties of the INTERREG programme (i.e., those bordering the Baltic Sea). In the second stage, satellite photos and map databases of the catchments of selected rivers were searched for farmland and drainage ditches, so that potential pilot sites could be located. After that, the locations were visited, and, if the site seemed appropriate, a water sample was taken for nutrient analyses.

During this survey 79 water samples were collected to map the quality of agricultural drainage waters (Figure 4 and 5). According to the results, the water quality parameters of 10 ditches indicated “Poor” quality associated with severe pollution by human activities. The sites were located near large farms, in areas with intensive agricultural activity, or downstream of less well functioning wastewater treatment facilities.

Alongside water quality, the final site selection was made by taking into account land ownership, the willingness of land owners to co-operate, and accessibility to the site. During this process some sites had to be discarded; for example, a good candidate site at Arkna in Northern Estonia was investigated further. Several additional water samples that were taken from the Arkna ditch indicated poor water quality, with total phosphorus and total nitrogen concentrations of 0.076–0.16 mg l<sup>-1</sup> and 7.6–10.2 mg l<sup>-1</sup>, respectively.

However, the site was far from any road and during the wet periods (when sampling would be most intensive) the site became practically inaccessible. Finally, a field area in Rahinge, Tartu, proved to be an ideal candidate, with high dissolved P concentrations and easy access, ensuring that the site could be visited daily.

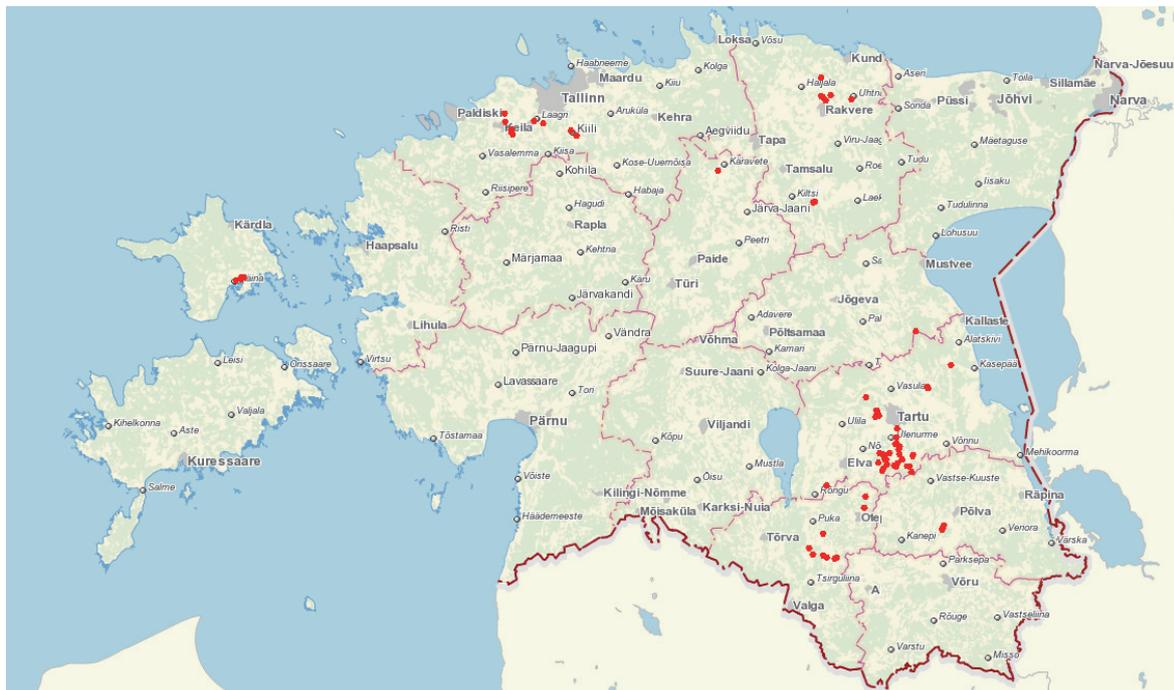


Figure 3. The locations surveyed in Estonia.

### 2.1.3 Selection criteria for the test sites

In the evaluation of potential test sites we initially applied the following criteria:

- a wetland exists or is easily constructed in a ditch that drains areas with agricultural activities, preferably animal farms within the proximity of the site;
- phosphate concentration in water exceeds the “normal” concentration level for agricultural runoff; phosphate concentrations were considered “normal” when at about the  $100 \mu\text{g l}^{-1}$  level or lower;
- the optimal size of the catchment would be 30 ha or less; the larger the size of the catchment, the higher the peak flow volume and thus bigger units should be built for testing;
- sampling of water before and after the test site should be possible, meaning that there would be some slope in the ditch;
- on sites with a higher flow, a Ferix doser was considered a more appropriate alternative than solid P retention buffers, because of the lower risk for ponding the site over field drain outlets;
- for solid P retention materials, a buffer size of about  $3 \text{ m}^3$  was considered optimal, as it could be fitted to relatively small ditches.

After visiting a number of existing wetland sites in both participating countries, it became impossible to find wetlands that met all of these criteria. At only a couple of the existing wetlands did the phosphate concentration exceed the above criterion. The low concentrations were either because most of the wetlands did not receive high-P waters at all, or, if there were some smaller areas in the catchment that had high P loading potential, water from these was diluted by pure water before entering the wetlands.

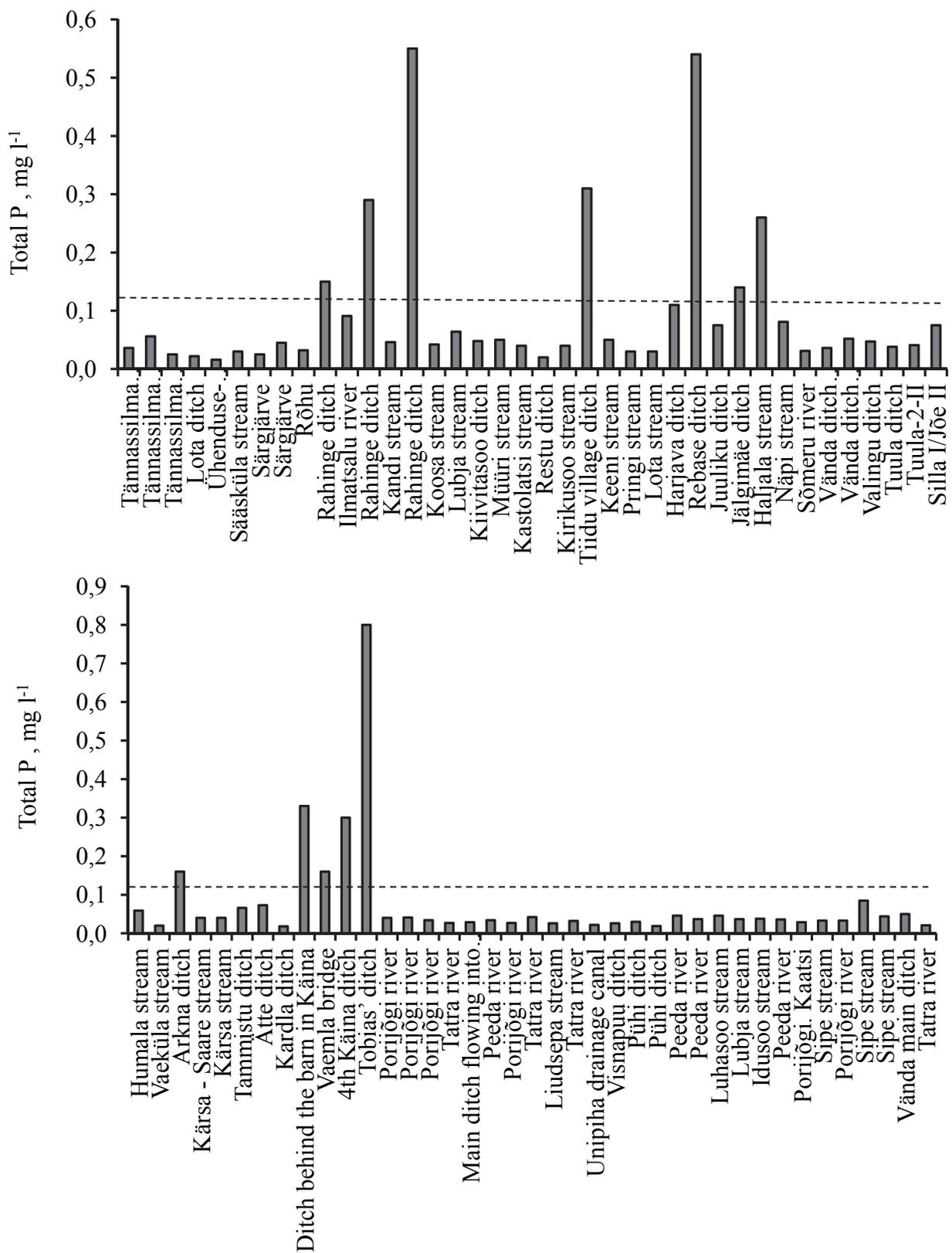


Figure 4. The concentrations of total phosphorus from sampled sites in Estonia. The dotted line indicates the limit value for "Poor" water quality.

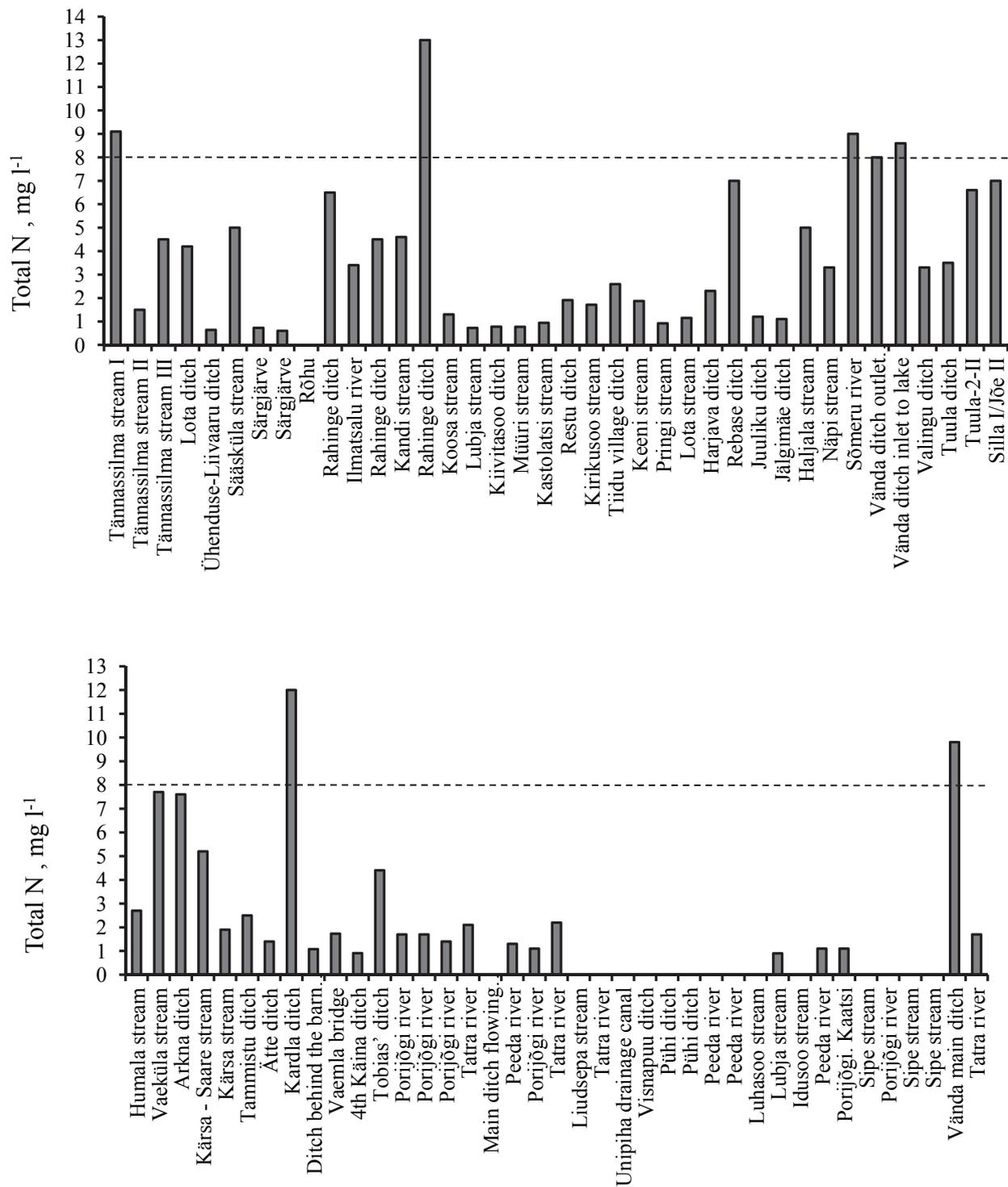


Figure 5. The concentrations of total nitrogen from sampled sites in Estonia . The dotted line indicates the limit value for "Poor" water quality.

## 2.2 Tested chemicals

### 2.2.1 Ferric sulphate and its dosing

For stripping P with soluble metal salt we tested ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3$  with the trade name Ferix-3 (Kemira Kemwater, Helsinki, Finland). Ferix-3 is used in municipal waste water treatment plants and in tap water production to precipitate solids, organic matter and dissolved P. It has an iron content of about 20%, with the iron entirely in an oxidation state +III. The chemical is soluble in water so that 50-50 (weight-%) solutions are stable to use. Ferric sulphate falls into the chemical hazard class “irritating”, but with a pH of water solutions less than 2. Consequently, care should be taken upon handling the chemical. Ferix-3 comes in granules with a typical mean diameter of 2 mm (96% between 0.2–5 mm) and it has a volume weight of  $1.2 \text{ kg l}^{-1}$ .

For dosing of Ferix-3, we used a doser previously developed at MMT by Aaro Närvänen (see Närvänen and Jansson, 2007; Närvänen et al., 2008). A schematic picture of the doser and two units in operation are shown in Figure 6. The unit consists of a chemical storage (150–600 litre sand box) that has one or two 200 mm polyethene pipes attached through the bottom, and a cone-shaped polyester netting(s) attached to the lower end of the hanging polyethene pipe. Ferix-3 is fed from the storage to the polyethene pipe by gravity and down to the netting cone where water dissolves the chemical. When the water level in the upstream part of the v-notch weir rises, more of the netting cone is submerged (more surface area of the chemical containing cone is exposed to water), and more Ferix-3 dissolves. As a result, an increase in water flow leads to a dissolution of higher amounts of the chemical in the water.

It is possible to adjust the dosing of the chemical by changing the angle of the v-notch weir; in this work the v-notch weirs were in some cases at  $90^\circ$ , but mostly  $120^\circ$  angles. The  $120^\circ$  angle is usually sufficient when the ratio of administered Ferix-3 to ditch water is one kilogram of Ferix-3 to about  $50 \text{ m}^3$  of water (1:50k). This has been found in earlier tests to cause precipitation of most of the dissolved P, but without precipitation of much of the suspended solids. The precipitation of solids would have resulted in the production of large volumes of sludge that would have certainly caused aesthetic issues. With the 1:50k dosing the amount of sludge was moderate. Some units were equipped with  $90^\circ$  v-notch weirs, but in those cases the ditches were a few meters distant from joining a larger channel, and a higher amount of Ferix-3 was dosed to supply also the larger channel with some of the chemical.

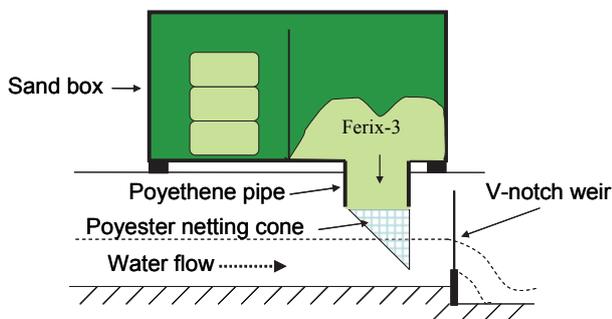


Figure 6. Upper graph: schematic figure of the Närvänen-type Ferix doser. The photographs show a smaller doser unit (left-hand) that is sized for relatively small ditches, and (right-hand) a larger unit that is equipped with two doser socks and a 600-litre storage compartment to ensure a high enough feed during peak flow. Photographs by Aaro Närvänen.

For the selection of the proper size of Ferix doser units for the pilot sites, an assessment of the amount of ferric sulphate needed to be fed for each ditch was based on an empirical equation (according to earlier laboratory work at MTT):

The amount of chemical needed (in kg yr<sup>-1</sup>) =  $19.113 \times C_p^{-0.5659} \times b \times m_p$  [Eq. 1]

In Eq. 1.,  $C_p$  is the typical concentration of dissolved P in water (mg l<sup>-1</sup>),  $b$  is calculated as: 100/Fe content of the chemical (in %; for Ferix-3 this ratio is 100/20 = 5), and  $m_p$  is the annual load of dissolved P (in kilograms) that is to be treated.

The cost of Ferix-3 was found to be highly variable, largely depending on the quantity bought at one time. The lowest cost was 0.35 eur kg<sup>-1</sup> (excl. VAT), purchased for the Nuutajärvi tests, and the highest 0.55 eur kg<sup>-1</sup> (excl. VAT) for the Nautela tests; the cost of Ferix-3 purchased for the Nautela tests increased (from 0.46 eur) by 18.5% over the two years of testing.

## 2.2.2 Tests with solid P retention media

Two types of solid retention media were tested in this project. The material tested in both participating countries was Sachtofer PR, which is a granular product manufactured by Sachtleben Pigments' plant in Pori, Western Finland. The other material tested, only in Estonia, was waste ash obtained from an Estonian electrical power plant fuelled with crushed oil shale.

Solid P sequesters are used as permeable barriers through which water flow is directed. Because the reactions linked with P retention are either sorption (attachment to, for example, Fe and Al oxides) to the surface of material, or precipitation of sparsely soluble phosphate species (e.g., Ca-P precipitates), water must come into good, long enough contact with the P retention material. For precipitation reactions the material must also be able to supply enough soluble cations (e.g., Ca<sup>2+</sup>) so that the solubility constant of a given precipitate is exceeded. For efficient precipitation, the pH of the solution has to be on the basic side of the pH scale. For a more thorough discussion on P retention mechanisms and materials, see, for example, Klimeski et al. (2012).

### *Sachtofer PR granules*

Sachtofer PR is a granular material that contains Ca and Fe, obtained as a co-product of titanium dioxide pigment and associated ferrous sulphate production at the plant of Sachtleben Pigments Oy in Pori, Western Finland. The material is made by mixing acidic ferrous sulphate (FeSO<sub>4</sub>) with calcium oxide (CaO) and water in a granulator. The end product's chemical composition is mostly gypsum (CaSO<sub>4</sub>·2 H<sub>2</sub>O) with about 10% Fe content (likely as a mixture of Fe hydroxides and oxides, FeOOH, Fe<sub>2</sub>O<sub>3</sub>). When stirred into water the pH rises to about 9–11, which indicates presence of Ca(OH)<sub>2</sub>. The volume weight of the granules is about 1.5 kg dm<sup>-3</sup>. The granule size of the product varies, but usually 90% of the mass consists of greater than 1 mm particles. The manufacturer's estimate of the price at the plant-gate is EUR 100–150 per tonne.

Due to the lack of official limits for harmful elements in materials that are used for the purpose of P retention in wetlands or ditches, the concentrations of metal elements in Sachtofer PR were compared to those for which there are guideline concentrations in the statute (Statute No. 9/09 of the Ministry of Agriculture and Forestry, Finland) associated with the Fertilizer Product Act (539/2006). The contents of potentially harmful elements were found to be less than the guideline concentrations for soil amendment materials, or, with the exception for total chromium (Cr), also below the permissible concentrations for fertilizer products. As of Cr, the concentration of the toxic, water-soluble form, Cr(VI), is below the guideline limit. In this work we analysed Cr and Ni concentrations in water samples (during the unfrozen period at about one-month intervals) from the start of the field test done in Jokioinen, Finland, (launched in 2010) to the end of 2012, but did not find that the Sachtofer PR granule buffer would have elevated the Cr or Ni concentrations in water; the Cr concentrations remained below 2 µg l<sup>-1</sup> and the Ni concentrations below 6 µg l<sup>-1</sup>, i.e., below or at the detection limit of the ICP analyser used.

According to an earlier laboratory study (Uusitalo et al., 2012), the granules have a P retention capacity that is an order of magnitude higher than what Finnish soils typically have, and they can be regarded as efficient P sequesters. According to the earlier study, more than 50% of the retention of dissolved P can be obtained in 30 minutes contact or longer with water, which means that a P barrier made of Sachtofer PR granules could be a suitable mitigation option for relatively small drainage areas. Because of the

relatively high cost (EUR 100–150 per Mg<sup>-1</sup>) Uusitalo et al. (2012) stated that cost-efficient use of this material will be restricted to sites with a high P concentration in the water.

In the current project, the Sachtofer PR granules were tested at one site in Finland and at one site in Estonia. The Estonian University of Life Sciences also conducted further studies on the granules on smaller scales.

### *Oil shale ash*

Oil shale ash is a Ca-rich residue derived from burning in electric power plants low-caloric value solid fuel oil shale (kukersite) in Estonia. The utilization of oil shale leaves after combustion 45–48% of the oil shale dry mass (Bauert and Kattai, 1997), and totally about 6–8 million tons of waste ash is produced annually at Estonian power plants. The ash removal at electric power plants is managed by hydraulic transportation of ash-water slurry mixed at a ratio of 1:20. The piled ash plateaus near power plants cover an area of about 20 km<sup>2</sup> and contain about 300 million tons of hydrated ash (Figure 7).



Figure 7. Ash plateaus in Estonia. Photographs by Egle Saaremäe.

Estonian oil shale is highly calcareous, with a calcite/dolomite content of 40–60%, and the ash remaining after combustion is due to thermal decomposition of carbonate minerals and subsequent reactions with sulfur-containing flue gases rich in highly reactive free lime (CaO) and anhydrite (CaSO<sub>4</sub>). In addition, the ash contains an amorphous aluminum-silicate glass like phase and a variety of Ca(Mg)-silicate minerals from decomposition and reactions between clay minerals, K-feldspar, quartz, and CaO. Lime and anhydrite begin to react with water in the ash removal system, and the hydration processes continue in the piles, forming a variety of secondary Ca minerals such as ettringite, Ca-aluminates, and calcite (Liira et al., 2009a). Kaasik et al. (2008) have shown that hydrated oil shale ash is composed of several Ca-phases including calcite and vaterite as Ca-carbonate phases (CaCO<sub>3</sub> and  $\gamma$ -CaCO<sub>3</sub>, respectively), ettringite [Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>×26H<sub>2</sub>O], hydrocalumite [Ca<sub>2</sub>Al(OH)<sub>7</sub>×6H<sub>2</sub>O], portlandite [Ca(OH)<sub>2</sub>], C2S belite [ $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>], merwinite [Ca<sub>3</sub>Mg(SiO<sub>4</sub>)<sub>2</sub>], melilite [(Ca,Na)<sub>2</sub>(Al,Mg,Fe)(Si,Al)<sub>2</sub>O<sub>7</sub>] and wollastonite [CaO×SiO<sub>2</sub>]. About 10–20% (maximum 40%) of the ash consists of amorphous glass-like aggregates of (alumino-) silicate composition (Mötlep et al., 2010).

Estonian oil shale is characterized by generally low micro- and heavy element concentrations. Similar to the shale, the content of trace/heavy elements in oil shale ash is low and does not exceed the average concentration in the Earth's crust, except for Mo and Pb (Table 2, after Ots, 2006 and Kaasik et al., 2008).

Table 2. Average concentrations of selected trace elements in hydrated plateau sediments and the Earth's crust (after Ots, 2006 and Kaasik et al., 2008). N/A = data not available.

Element	Ash-plateau sediment	Earth's crust
	mg kg <sup>-1</sup>	
Ni	27.0	60.0
Mo	3.7	1.5
Cu	8.6	47.0
Pb	42.1	16.0
Cd	<0.1	0.5
As	15.1	50.0
Sc	6.0	N/A
Zn	50.3	N/A

Veskimäe et al. (1997), Vohla et al. (2005), Kaasik et al. (2008), Liira et al. (2009b) and Kõiv et al. (2010) have shown in laboratory experiments the effectiveness of Ca-rich hydrated oil shale ash as a possible material for P removal in constructed wetland systems. In laboratory batch studies, P removal by fly ash and hydrated ash may be virtually complete, with maximum binding capacity as high as 65 mg P g<sup>-1</sup> (Vohla et al., 2005; Kaasik et al., 2008). Phosphorus retention by this Ca-rich material occurs through adsorption and precipitation into a solid phase. The remarkably high P-binding capacity of the oil shale ash is influenced by the complex physical-chemical properties of the material, especially its high content of different Ca- and Al-compounds, porosity, and high pH. However, there are still no long-term field studies to confirm the applicability of oil shale ash for P removal in practical applications.

## 2.3 Sampling and methods of water analyses

Samplings during the site surveys were done so that at least one sample was taken from each site to obtain an idea of the chemical water quality. In the Finnish survey on wetlands, two samples were taken from each site: one from the inlet and another from the outlet of the wetlands. When the surveys were extended to embrace ditch waters, one sample was taken from each site. Water sampling during the pilot tests was done mostly manually and always comprising a sample pair that was taken from the inlet and outlet of the site.

For phosphorus analyses in the laboratory, water samples were split into two, with one portion passed through a membrane filter and the other portion stored as unfiltered. Filtering was done using 0.2 µm pore size membranes, with the exception of the samples that were obtained from the Paimionjoki sites, which were analysed in a commercial lab that used 0.4 µm pore size membranes.

The filtered subsamples were analysed for dissolved P, either without digestion or for the Paimionjoki area and Nautela samples after digestion with peroxodisulphate in an autoclave. The digestion step would liberate any P attached to colloidal mineral and organic matter that has passed through the filter membrane used, and the results of dissolved P therefore describe slightly different P pools for the samples that were put through different pre-treatments in the laboratories. However, if the methods applied for retaining P from the runoff water are good at doing their job, the results would nevertheless point in the same direction.

The unfiltered subsamples were analysed for total P (and N) concentrations after digestion in an autoclave. Phosphorus analyses were conducted in all laboratories with flow-injection analysers, using modifications of the molybdate blue method of Murphy and Riley (1962).

Water pH was measured in the laboratories using electrodes, and (in Nautela) monitored with automatic sensors (YSI Inc., Yellow Springs, Ohio, USA).

Heavy metal Cr and Ni concentrations were measured from a set of filtered (0.2 µm) influent and effluent samples at the Ojainen site where Sachtofer PR granules were used. This was done to check earlier laboratory findings that these heavy metals do not leak from the material. Measurement was done using an inductively coupled plasma atomic emission spectrometer (ICP–AES) at MTT, Jokioinen. Other laboratory analyses were also conducted on water samples, but because of the focus on phosphorus in this report, they will be reported in scientific articles that are currently under preparation.

## 2.4 Test set-ups at different sites

### 2.4.1 Hovi wetland without chemical amendments

Hovi wetland (N 60.25.392, E 24.22.480) was constructed by MTT and SYKE in 1998 for research and demonstration purposes. The characteristics of the Hovi wetland are presented in Table 3.

Table 3. Characteristics of the Hovi wetland

Wetland area	Catchment area	Wetland-to-catchment ratio	Mean slope	Land use	Soil type
_____ ha	_____	_____ %	_____	100% field (row crops)	Heavy clay
0.6	12	5	2.8		

A schematic map of the Hovi wetland is presented in Figure 8. The most important features of the wetland are (i) distinct deep and shallow areas, (ii) the spits of land that create a tortuous, as-long-as-possible flow path and (iii) dense, uniform vegetation distributing the flow evenly through the shallow zone. All these features create diverse environments for different water purifying processes. Measured water concentrations and runoff as reported by Koskiahio et al. (2009) are presented in Table 4.

Table 4. Measured flow-weighted suspended solids and nutrient concentrations in inflow to the Hovi wetland, and runoff from the catchment area, during two earlier monitoring periods.

	Suspended solids	Total P	Dissolved P	NO <sub>3</sub> -N	Runoff from the Hovi catchment
	_____ mg l <sup>-1</sup>				_____ mm
1999–2000	530	0.57	0.065	9.2	340
2007–2008	520	0.81	0.087	2.4	420

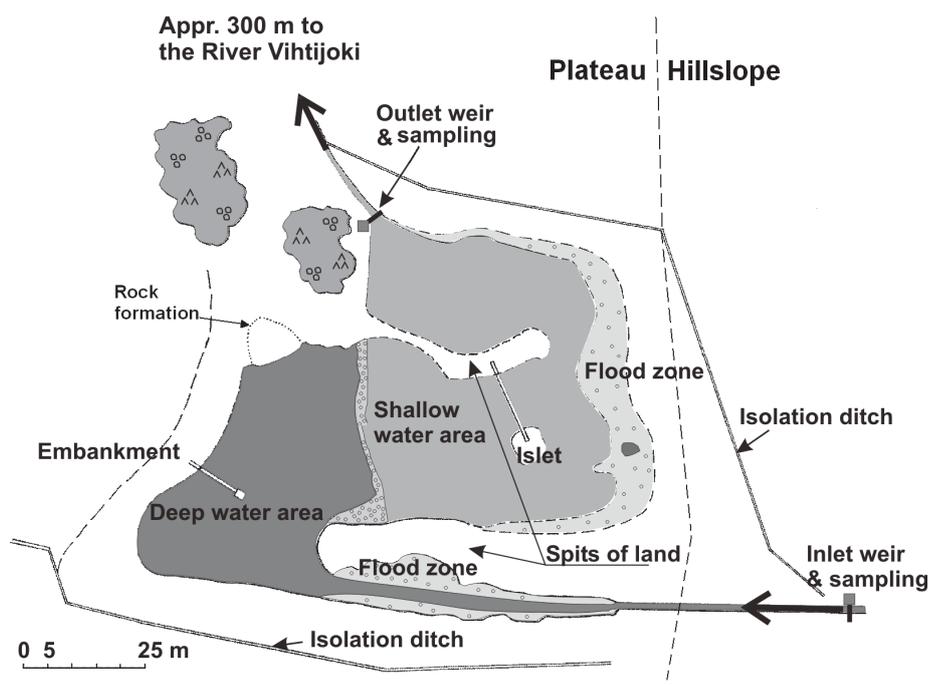


Figure 8. A schematic map of the Hovi wetland.

## 2.4.2 Nautela tests with ferric sulphate

The Nautela site was located in Lieto near the city of Turku, SW Finland. This site was constructed and monitored by TUAS, and equipped with sensors that continuously monitored water flow, the pH and turbidity of the water in two spots in a stream, before and after a ferric sulphate doser.

The pilot site is a small ditch surrounded by agricultural fields. There are two constructed sedimentation ponds in a chain, created by bottom dams, about 100 meters apart from each other (see Figure 9). The catchment area of the ditch is about 60 hectares and the share of fields in the catchment is 63%. The main soil type is clay and the fields have a typical slope of less than 3%. The fields were under cereal production during the test period.

A ferric sulphate doser equipped with a 350-liter chemical storage and a 120°-angle v-notch weir were installed at the site in the autumn 2010 upstream from the lower pond. A pressure sensor and water level sensor was installed in the vicinity of the weir to enable discharge calculations. Online measurement systems were installed for influent and effluent water quality monitoring (Figure 9), and manual sampling for additional water quality parameters was conducted at these same spots. Due to the ditch freezing over during the winter, the monitoring was by necessity periodic. As the first test period in 2010 was very short, we present the results from the 2011 and 2012 test periods only. These cover the ice-free season from spring floods to the onset of frost in winter.



Figure 9. Location of the ferric sulphate doser (marked with red flag) and water quality monitoring spots (marked with blue points).<sup>1</sup>

Altogether 58 paired water samples were taken manually from April 2011 to October 2012 for the analysis of dissolved P; two evidently corrupted sample pairs were ignored in the data analysis. Manual sampling was generally done once every one to two weeks, but the flow in the ditch was taken into consideration so that sampling concentrated on high-flow regimes. Continuous water quality monitoring was carried out by online systems every 30 minutes using a YSI 6920 series multiparameter sonde and a S::can nitro::lyser for pH, electrical conductivity, turbidity, oxygen and nitrate concentrations, and water temperature. The water level was continuously monitored by a Keller DCX-22 pressure sensor. The multiparameter sondes were regularly calibrated, and the measured water level was confirmed by comparing with manual water level checks.

<sup>1</sup> Orthophoto aerial photograph (3/2013) obtained from the National Land Survey of Finland, Topographic database 06/2012. Licence: [http://www.maanmittauslaitos.fi/avoindata\\_lisenssi\\_versio1\\_20120501](http://www.maanmittauslaitos.fi/avoindata_lisenssi_versio1_20120501).

### 2.4.3 Lake Nuutajärvi area tests with ferric sulphate

In spring 2012 P precipitation by ferric sulphate was tested in 10 ditches draining into Lake Nuutajärvi in Urjala. Lake Nuutajärvi has a history of algal blooms in several summers during the last decade, and the input of dissolved P per area unit of Lake Nuutajärvi is substantial, about tenfold as compared to the next lake (Lake Rutajärvi) in the lake chain. The P sources were earlier studied by MTT (Närvänen et al., 2003) and these data provided us with background data for the initial selection of appropriate sites for testing.

The site survey and selection of ditches was done during 6–22 September 2011 in co-operation with the lake protection associations of lakes Nuutajärvi, Rutajärvi and Kortejärvi. The survey included 17 ditches, 10 of which were found suitable for the installation of ferric sulphate dosers. The selected ditches had variable catchment sizes and nutrient sources, some areas were associated with animal husbandry and some with fields only. Four of the sites were small ditches that drained areas of five hectares or less, but also three ditches draining at least 50-hectare areas were included (see Table 5). The site characteristics of all the selected ditches are shown in Table 5 and the location of the doser sites is in Figure 10. All of the ditches selected were located along the main channels that enter the lake.

Agreements on the tests with the land and water owners were negotiated by the lake protection associations. All sites were planned and the dosers prefabricated by MTT at the end of 2011. The costs of the dosers plus chemicals to be used during spring 2012 were covered by funding from the Pirkanmaa Centre for Economic Development, Transport and the Environment (ELY Centre). The installation of the dosers was carried out by the lake associations under MTT's guidance.

Table 5. Characteristic of the selected sites in the lake Nuutajärvi area.

Site	Catchment area, ha	Source of the loading	Estimated chemical need/ recommended dosing period
1	< 5ha fields + forest	Cowshed, exercise yards	200 kg/spring
2	50 ha fields + forest	Cowshed, exercise yards	>1000kg/spring
3	appr. 1 ha	Cowshed and surroundings	300 kg/whole year
4	< 10 ha	Pasture and cowshed area	600 kg/whole year
5	< 5 ha	Cowshed, exercise yards	400 kg/whole year
6	appr. 50 ha	Fields	1000 kg/spring
7	20 ha	Fields	500 kg/spring
8	appr. 5 ha	Horse stable area	300 kg/spring
9	> 100 ha	Fields and forest (equal shares)	1000 kg/spring
10	0.2 ha	Horse stable area	100 kg/whole year

The test periods were agreed for spring 2012 and spring 2013. Concentrating the tests on springtime was motivated by the fact that most of the dissolved P entering the lake is carried by the spring flood. Also, due to the residence time of about seven months in Nuutajärvi, the spring flow has a substantial impact on the summertime water quality of the lake. Hence, by stripping bioavailable P during the spring flow it would be possible to moderate algal growth in the lake with modest efforts.

There were three sizes for the dosers built, depending on the expected water flow and P load. The ditch draining from the smallest horse stable area (site 10) was equipped with 150-litre storage box, six dosers (sites 1, 3, 4, 5, 7 and 8) with 350-litre storage capacity, whereas the ditches with the largest catchments or expected P load (sites 2, 6 and 9) were equipped with boxes with a 600-litre storage capacity. Sites 2 and 8 were equipped with double doser socks, where one doser sock operated continuously during all flow conditions and the additional dosing sock operated under a high flow regime to ensure a high enough chemical feed to the peak flow.

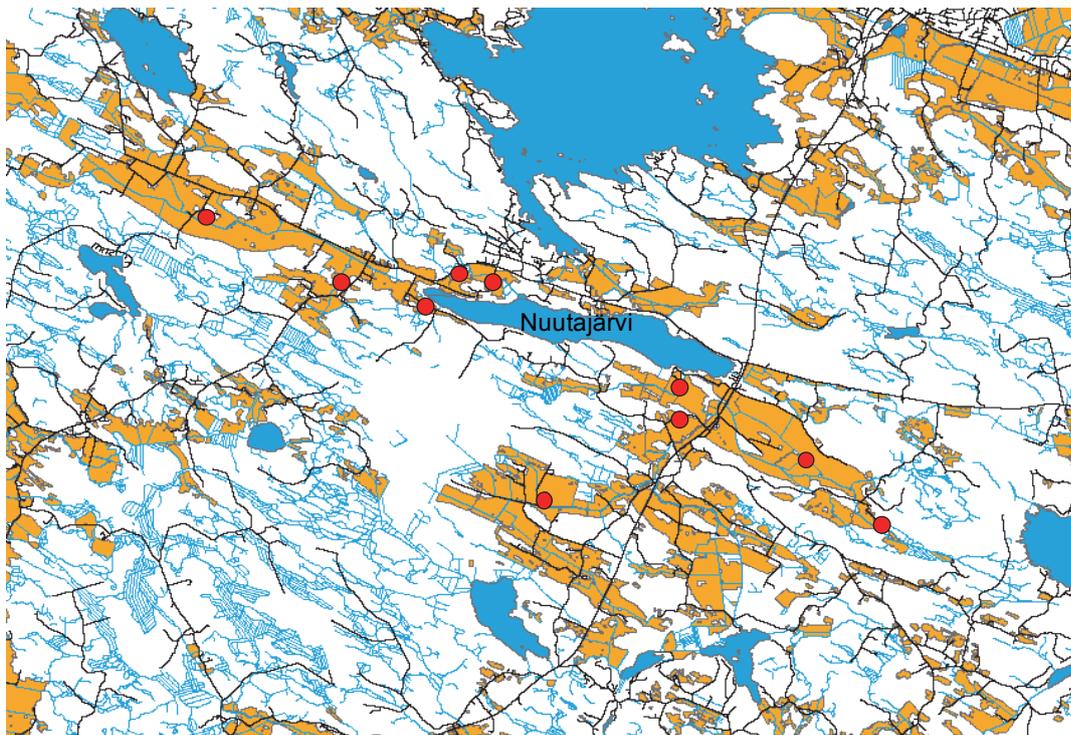


Figure 10. Location of the ditches that were selected for the Ferix dosing tests in the lake Nuutajärvi area.

On 3 March 2012 the dosers were ready for use in the selected locations and dosing was started at the beginning of snowmelt on 22 March. Chemicals were distributed and the chemical storage of the dosers was re-filled by volunteers from the lake protection associations. Water sampling was carried out by the Active Wetlands project personnel. At the same time, the Pirkanmaa ELY Centre ran an intensified sampling of water quality of Lake Nuutajärvi, accompanied by additional summertime Secchi depth measurements by the lake protection association.

#### 2.4.4 River Paimiojoki area and Tammela tests with ferric sulphate

The River Paimionjoki has a drainage basin of about 1000 km<sup>2</sup> in SW Finland and it delivers a substantial nutrient load, 60 Mg yr<sup>-1</sup> of total P and 530 Mg yr<sup>-1</sup> of total N, to the Archipelago Sea. There are a number of animal farms in the area, and agriculture is estimated to contribute by 80% to the P load and by 68% to the N load that discharges to the Baltic Sea via the River Paimionjoki. The Association of River Paimionjoki has been working since 2010 in order to decrease the nutrient load in the river, and together with MTT and WWF conducted a site survey for the selection test sites in this area.

Three sites in the community of Somero were found suitable for the installation of ferric sulphate dose (Table 6). Site P1 was installed below a small sedimentation pond, whilst the two other sites were a ditch draining from a field area where pig slurry is applied in most years (P2) and a ditch that passes a piggery/cowshed yard. There was no opportunity to construct wetlands on any of these sites. The P1 site drained directly to the River Paimionjoki and the two other ditches drained to the River Jaatilanjoki, which is a sub-basin of the River Paimionjoki drainage area. The site characteristics of all the selected ditches are shown in Table 6 and the location of the sites in Figure 11.

There were two sizes of dosers built, depending on the expected water flow. The ditch draining from the sites P2 and P3 were equipped with 350-litre storage boxes, whereas the ditch with the larger catchment (P1) was equipped with a box with a 600-litre storage capacity. All of these devices were equipped with one doser sock. Installation on the sites was carried out in September and October 2012, and the tests were launched in October. The doser P3 was in use from 8 October and the two others (P1 and P2) from 15 October until 5 November 2012. The re-fill of the chemical storage and sampling of water was carried out by personnel from the Association of River Paimionjoki. Frost at the beginning of November ended the tests so that the total time for testing was only about one month.

The Tammela site, operated by MTT, was selected as a test site due to the very high (up to 19 mg l<sup>-1</sup>) concentrations of dissolved P in the ditch water. The ditch, which was small in size and often dried during summers, obviously received liquors from a manure storage and a silo used as ensilage storage, plus wastewater from a house with an insufficient and outdated sewage system. The Tammela site was equipped with a 150-litre doser unit.

Table 6. Characteristic of the selected sites at the river Paimionjoki area and in Tammela.

Site	Catchment area, ha	Source of the loading	Estimated chemical need/ recommended dosing period
P1	50 ha fields + 110 ha forest	Fields and forest	1500kg/spring
P2	20 ha fields	Piggery, fields receiving pig slurry	400 kg/spring
P3	15 ha fields + 5 ha forest	Pasture, cowshed, piggery	800 kg/whole year
Tammela	> 1 ha cowshed area, residential	Manure storage-affected ditch, household wastewater	200 kg/whole year



Figure 11. Location of test sites in Paimionjoki.

For those sites (the Paimionjoki and Tammela, Nuutajärvi, and Ojainen sites) for where the flow was only recorded during visits to the sites, the P fluxes to be presented are estimates based on an assumption that the flow increases or decreases linearly between the recorded values. This, of course, is an incorrect assumption as peak flows (especially in small catchments) change rapidly, and these rapidly evolving peaks are not included in the flow and loading estimates, resulting in the underestimation of actual water and nutrient flows. As a result, in the results sections dealing with the sites mentioned, we focus on the concentration changes due to the chemical applications rather than the changes in loadings. However, estimates of P loading also presented as P fluxes are needed for the calculation of the economy of the chemical usage. The changes in P fluxes obtained by chemicals were calculated using an average percent change due to chemical treatment and the estimated total P flux through a given site. For the Ferix tests, dosing of the ferric sulphate was found to work better for the high-flow events than at low flow (as demonstrated at the Nautela site), and the estimated effects on the P mass loading (based on incomplete flow data) are probably therefore rather underestimated than overestimated.

## 2.4.5 Rahinge tests with ferric sulphate

The Estonian tests with the ferric sulphate doser were conducted near Tartu, southern Estonia, at the Rahinge ditch. The catchment of the Rahinge ditch is approximately 7 km<sup>2</sup> and the recipient is the Ilmatsalu reservoir. The land use of the watershed consists of approximately 64% fields, 24% forest and 12% residential areas. In the Rahinge catchment there are two farms, but water from a small wastewater treatment facility contributes to the nutrient input.

The water quality of the Rahinge ditch was monitored at different spots from autumn 2010 to winter 2012. During that period, 31 water samples were taken and the concentrations of total P, dissolved P (phosphate-P), total N and nitrate-N were analysed. There was a substantial variation in the water quality during the monitoring period, with ranges of 0.08–0.73 mg l<sup>-1</sup> for total P and 0.08–0.68 mg l<sup>-1</sup> for dissolved P. For N, the concentrations varied between 0.58–16 mg l<sup>-1</sup> for total N and 0.01–15 mg l<sup>-1</sup> for NO<sub>3</sub>-N. The high-end concentrations indicate significant pollution by human activities.

Tests at Rahinge were conducted in three locations along the Rahinge ditch (Figure 12). With the selection of these three locations there was access for variable P concentrations and flow rates. In general, site 1 had the lowest concentrations and highest flow, whereas site 3 had the highest nutrient concentrations and lowest flow.

A flow-through column experiment with Sachtofer PR granules was conducted at site 1. The tests with a ferric sulphate doser were conducted at site 2, whereas further column experiments with Sachtofer PR granules, and overflow flume tests with Sachtofer PR and oil shale ash were conducted at site 3.

At site 2 (coordinates x: 6475010.9; y: 652971.6) where testing of the ferric sulphate doser took place, a sedimentation pool with the following dimensions was dug: width 5.5 m, length 15 m and depth 1.5 m. Flow measurement at this site was performed using a v-notch weir and a pressure sensor (OTT Orpheus) that continuously recorded the water level above the v-notch.

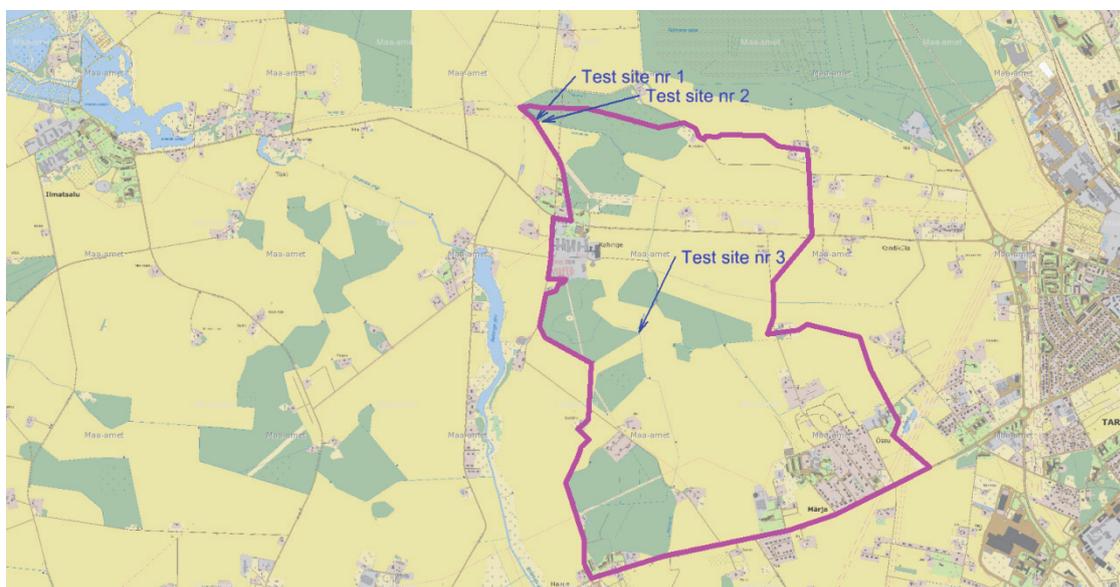


Figure 12. Rahinge sites.

Doser installation took place in December 2011 when a 150-liter storage box and a doser sock with a diameter of 160 mm were put in place, and field tests were carried out from December 2011 to December 2012. The Rahinge ditch had highly variable flow conditions, (Figure 13), from 3 l s<sup>-1</sup> up to 1011 l s<sup>-1</sup>, and due to the flow regimes it was possible to only run short-term (1–12 hours, depending on flow rates) dosing experiments. During the tests, stream water was sampled above the v-notch weir (inflow samples) and approximately 25 m after the doser, i.e. after the sedimentation pool.



Figure 13. Different seasonal situations on Rahinge site no 2. 1) water flood in March 2011, 2) frozen site in January 2012, 3) minimum flow rate in summer 2012. Photographs by Morten Poolakese and Toomas Tamm.

#### 2.4.6 Ojainen tests with Sachtofer PR granules

The Finnish site where a solid P sequester was tested was located in Jokioinen/Ojainen, SW Finland. A reactive permeable barrier made of Sachtofer PR granules was built at the outlet side of a constructed wetland. It was thought that the wetland would to some degree even out flow peaks whereby the flow through the barrier could be maintained relatively constant for the major part of the year. In the construction of the site, an old dam construction and a pre-existing flow regulation structure was utilized, and a new dam was added about 6 m below the existing one to pond water; the space between the two dams was filled with Sachtofer PR granules (Figure 14 and 15). The inflow into this buffer was from below via a perforated drainage pipe laid at the bottom and further into a 30 cm layer of gravel that distributed water, through the granule mass, and finally out of the buffer via a v-notch weir over the lower dam. The 6-m area between the dam structures contained about 6 m<sup>3</sup> (about 9 Mg<sup>-1</sup>) of Sachtofer PR granules, and the theoretical P retention capacity of this granule mass would be more than 60 kg of P. Concentrations of dissolved P at this site were in spring 2010 up to 300 µg l<sup>-1</sup> which was considered high enough for testing purposes.

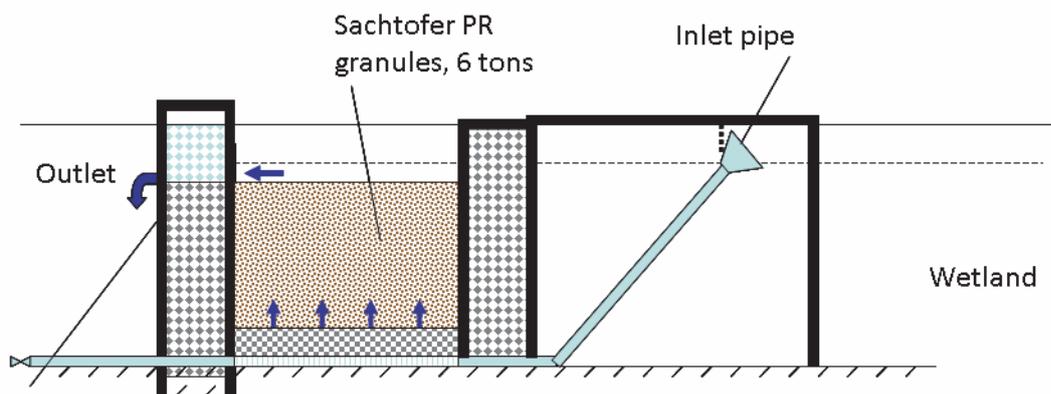


Figure 14. Schematic figure of the Ojainen P buffer with Sachtofer PR granules as P retention medium. The buffer is constructed at the mouth of a outlet ditch of a small constructed wetland.



Figure 15. Ojainen P buffer site photographed in summer 2011. The constructed wetland is not shown in the picture, but is located to the right-hand side of the photograph. Photo: Aaro Närvänen.

The Ojainen buffer was visited at least once a week during the unfrozen period and samples were taken manually during the fall 2010 and spring 2011 flow periods when flow over the v-notch occurred. In the summer 2011, the site was equipped with automatic sample collectors that took a small portion of the inflow and outflow every second hour to separate canisters that were sampled weekly during the flow periods. Flow was assessed during the visits by measuring the height of the water level at the v-notch weir and this reading recalculated to discharge. Because the flow volumes are high during the snowmelt in spring, the site is equipped with a 40 cm diameter by-pass pipe that leads water past the barrier structure so that the surrounding field area would not be flooded in spring. It was estimated that about 20% of the annual flow passed through the granule mass, the rest escaping through the by-pass pipe, mostly during the spring flow.

#### 2.4.7 Rahinge tests with Sachtofer PR granules

##### *Stacked element test*

Due to the relatively large watershed area, and therefore high flow during the wet periods, it was decided not to implement the method where the water passes filter material either horizontally or vertically. This

type of structure would have inevitably needed damming to overcome the hydraulic friction loss in the filter. Instead, after a preliminary test with a small scale flume with its bottom covered with Sachtofer granules, it was found that letting the water flow over a surface covered with the granules also showed a considerable purification effect. Thus, at Rahinge it was tested whether a structure that would not cause any alterations in the water table would be a working solution.

This full-scale field experiment with Sachtofer PR granules in the Rahinge ditch was constructed at site 1 (GPS coordinates x: 6475024.2; y: 652917.6). For these tests a stacked elements structure (horizontal 'shelves' covered with granules and densely stacked over each other on a frame) containing Sachtofer PR granules was built and tested in different flow rates and variable contact surface areas. Unlike the Ojainen test where the water flow was directed through a granule mass, this structure, similar to a bookshelf with shelf elements of 0.25 m width, 1.2 m length and 0.6 m height, was immersed into the ditch. The size of a single element was selected so that one person could alone maintain the structure, i.e. change the elements after saturation with phosphorus (Figure 16).

In the first stage, there were seven filter elements installed, with a contact surface area of 5 m<sup>2</sup>. The number of the frames was then increased so that in the second test another frame with eight more filter elements was installed, for a total of 15 elements and a contact surface of 13 m<sup>2</sup>. In the third test seven more filter elements were installed, for a total of 22 elements with a contact surface of 18.75 m<sup>2</sup>. In the fourth test 11 more filter elements were installed, for a total of 33 elements and a contact surface of 26.9 m<sup>2</sup>.



Figure 16. Stacked filter elements at Rahinge site no 1. Photographs by Egle Saaremäe and Indrek Talpsep.

The field experiment was conducted from July to September 2011. The flow rate was measured from 2011 by flow gauging (OTT ADC), and the water was sampled upstream and downstream of the stacked filter elements. Between the dates when the number of the stacked filter elements was increased, two pairs of water samples were taken for laboratory analyses.

#### *Overflow flume tests*

A flume experiment (Figure 17) with Sachtofer PR granules was carried out at site 3 (GPS coordinates x: 647338; y: 653716). The aim of this test was to find out the P removal efficiency while water flowed along the granules' surface. A 7.5 m long and 0.3 m wide flume channel was constructed of waterproof plywood and its bottom was covered with a 3 cm layer of Sachtofer PR granules. The inflow to the flume was adjusted to have six different flow rates from 0.01 to 0.44 l s<sup>-1</sup>. The inlet phosphate concentration was during this test constant at 0.52 mg l<sup>-1</sup>.

A second, continuous flume experiment was carried out in June–July 2012. In this test, the inlet phosphate concentration ranged naturally from 0.2 to 1.48 mg l<sup>-1</sup>. During the four weeks of the test, water

samples were taken seven times from the inlet and outlet of the flume. The flow rates were measured by recording the time during which outlet water filled up a vessel with a known volume.



Figure 17. Flume experiment on the left and column experiment on the right. Photograph by Morten Poolakese.

### *Column tests*

The aim of this column test (Figure 17), conducted at site 3, was to explore the effect of retention time on P sorption by the granules while applying a flow-through column filter system. For the test, a flow-through column was constructed from a PVC tube with an inside diameter of 10.4 cm. A granule mass of 10 kg was placed inside the column and ditch water was pumped up to the top of the column and allowed to drain under gravity. Variable retention times were achieved by regulating the effluent flow rates with a valve attached to the lower end of the column. Flow rates were measured by recording the time it took to fill up a vessel with a known volume from the drain valve. During the tests, inlet water phosphate concentrations varied from 0.078 to 1.0 mg l<sup>-1</sup>, but they were measured during the testing to allow calculation of P retention.

#### **2.4.8 Rahinge tests with oilshale ash**

Besides the Sachtofer granules, oil shale ash was also tested in overflow flumes at the site 3 in a six-week experiment. For this test, the oil shale ash was crushed to 5–25 mm pieces that were placed on the test flume. The flume test parameters were the same as given above for the test with Sachtofer PR. During these tests, flow rates varied between 0.02–0.09 l s<sup>-1</sup>, and the inlet concentrations of dissolved P between 0.2–0.72 mg l<sup>-1</sup>.

## **2.5 Interviews with farmers**

### **2.5.1 Interviews conducted in Finland**

In addition to running the ferric sulphate dosers, farmers in the Paimionjoki area were interviewed on how they found the construction and use of the equipment. All land owners of the pilot sites (five of them, two of the sites were bordering two farms), and also three other animal farmers with no tests conducted on

their land, took part in these interviews. The interviews were conducted three times during the autumn of 2012, and included questions concerning possible construction-related problems and ideas, any opinions that farmers might have on the use and development of applications of this type, and about other possible solutions to reduce nutrient loading from their farms (e.g., buffer zones, wetlands, etc.). The first interviews were conducted immediately after the construction of the pilot sites. The second round was in November, with the third in mid-December, after the pilot site runs had been stopped for the winter.

To find out attitudes of a larger number of farmers, WWF Finland commissioned a farmer poll from Suomen Gallup Elintarviketieto Oy. The poll inquired the attitudes of Finnish farmers towards wetlands and the use of chemicals in capturing nutrients from field runoffs. An invitation to the poll was sent out to a group of 1253 randomly selected farmers in the South-West Finland and Uusimaa regions. Of the invited, 372 farmers answered the questions, that is, about 10% of all of the farmers in the region. Of the participants 283 were running crop production farms and 89 livestock farms.

The farmers were asked the following questions:

1. Was the concept of 'agricultural wetlands' already familiar to you?
2. Have agricultural wetlands (one or more) already been established on your farmland?
3. According to your evaluation, would there be appropriate places on your farmlands for establishing agricultural wetlands?
4. Do you feel that farmers receive sufficient information about wetlands and their establishment?
5. Does the fact that the removal of nutrients in runoff water can be improved through chemical methods increase the appeal of establishing wetlands?
6. Would you be prepared to implement chemical treatment for the elimination of nutrients from runoff water?
7. Would you be prepared to participate in a half-day training session on the use of active methods?
8. According to your evaluation, does your farm produce soluble phosphorus effluent/runoff?
9. Would you like to receive more information about the occurrence of soluble phosphorus and prevention of runoff?
10. Should the use of active methods receive support in the form of environmental investments?
11. In addition to funding from environmental support, would you also be prepared to contribute to the costs of implementing active methods that retain soluble phosphorus?
12. Would you be prepared to spend your own working time on the practical work involved with implementing the active method?
13. Do you feel that the remaining naturally-occurring wetlands should still be drained, or should attempts be made to return them to their natural state?
14. Can you be contacted in the future in matters related to environmental conservation and agriculture?

## **2.5.2 Interviews conducted in Estonia**

ELF made an inquiry among innovative organic producers about their attitudes towards constructed wetlands. Two in-depth interviews were made and 30 innovative farmers (participants of Demo Farm project, participants of agricultural exhibition) answered the questionnaires. In case of limited resources and before conducting large studies, even a small-scale study like this gives an overview into the topic. The selection criteria of active and innovative farmers based on an idea that these qualities would be essential in adoption of a relatively new method like active wetlands. These farmers could also act as positive examples and group stakeholders capable of mentoring others. In introducing constructed wetlands it is possible to use both mediated experiences (success stories) and direct practical counselling. Advice from practitioners would be most likely the most efficient.

The previous experience of ELF is based on Demo Farm project ("Development of Latvian-Estonian network for demonstration of environmentally friendly farming practices"); farmers participated in the project were one of the target groups of the current survey.

An earlier survey "A farmer's view on the Baltic Sea" was used to compare the information. This survey was conducted in the framework of Baltic Deal project to find out the attitude of agricultural producers towards water protection. Five Hiiumaa and five Saaremaa island's farmers were questioned to get an overview of situation.

---

## 3 Results

---

### 3.1 Wetlands without chemical amendments

#### 3.1.1 Hovi constructed wetland

In this study, Hovi wetland represents a constructed wetland that has a very high wetland-to-catchment ratio, and hence presumably falls into the category of the most efficient where nutrient retention is concerned. Chemical treatments were not carried out at the Hovi wetland or its catchment area, but this wetland served as a benchmark site for this project.

According to the monitoring carried out during 1999–2002, suspended solids and total P retention in the Hovi wetland were high from the very beginning (Koskiaho et al. 2003). After construction, annual total P retention in the Hovi wetland was reported to be 62% of the input, whereas dissolved P retention remained clearly lower, but nevertheless substantial, at 27%. Soil matter that makes up the bottom and banks of the wetland is thought to be the major P sink in this wetland. Because the P retention capacity of the soil and sediment matter is limited, it was expected that with time dissolved P retention in Hovi might decrease, and, in the worst case, turn into an annual net release of previously retained dissolved P. Hence, after the first sampling campaign, additional intensive samplings have been conducted at intervals of some years.

The second intensive sampling of the Hovi wetland was carried out in 2007–2008, when the retention of dissolved P was calculated to equal 60%, i.e. twice the relative rate as during the first sampling (Koskiaho et al. 2009). In absolute terms, the dissolved P retention was 0.72 and 2.58 kg yr<sup>-1</sup> during the periods 1999–2000 and 2007–2008, respectively. In October 2007, instrumentation of the Hovi site was complemented with sensors that automatically detect and record hourly values of turbidity in water. Unlike dissolved P that does not correlate with any sensor-readable property in water and therefore needs to be determined by laboratory analyses of discrete water samples, a strong mutual correlation exists between turbidity and particulate P. When the bulk of total P is in particulate P form, as is the case at Hovi, turbidity readings also correlate with total P. Based on such conversion from turbidity sensor readings, Hovi wetland was estimated to have during the full one-year period in 2007–2008 retained total P at a somewhat higher annual rate than it did eight years earlier, at 67% or 27 kg.

In the Active Wetlands project, another sampling campaign was performed in 2011 to find out whether the unexpectedly high dissolved P retention in the Hovi wetland still takes place more than 10 years after the construction date. Dissolved P concentrations of the water samples, taken at the inlet and at the outlet of the wetland in 2011, are presented together with the flow in Figure 18. The fluxes of dissolved P calculated from these data suggested that during the calendar year 2011 about 65% (or 1.4 kg) of the dissolved P input was retained in the wetland.

The short January flow peak and the flows of December, shown in Figure 18, were not sampled for analysis of dissolved P and, hence, we cannot rule out that a flush of dissolved P out of the wetland would have occurred during these flow events. It is known that frost injured plants may leak dissolved P in runoff (e.g., Uusi-Kämpä et al., 2012) and the first events of the spring flow may contain high concentrations of dissolved P that most likely originates from plant and algae cells that have burst and perhaps partially decomposed during the winter. In most of the samples taken during 2011 the outlet concentrations of dissolved P were much lower than in the samples taken from the inlet side of the wetland, but the highest dissolved P concentration (108 µg l<sup>-1</sup>) of all observations was detected at the outlet for a spring flow sample (5 April).

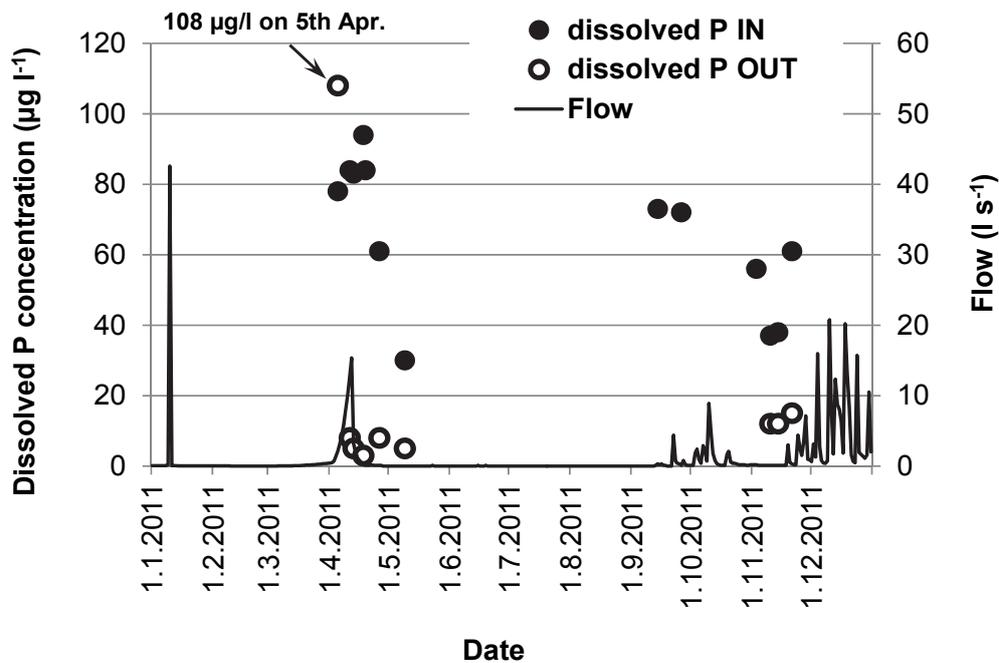


Figure 18. Inflow volume ( $l s^{-1}$ ) and dissolved phosphorus concentration ( $\mu g l^{-1}$ ) at the inlet and outlet of the Hovi wetland in 2011.

The total P flux variations shown in Figure 19, obtained from the sensor-detected turbidity data at Hovi, shows a typical P mobilization and transport pattern in agricultural catchments. High total P concentrations in water are detected during spring flow peaks that first arise from snow melting and later in the spring after rain showers on water-saturated soil of the catchment area that does not have any growing plant cover to protect it from the energy of raindrop splash. In the summer, precipitation may be as high as during the other seasons but high evapotranspiration and soil protection by the plant canopy result in only small transports of water and P in the runoff or drainage waters. After the harvest, transpiration of water by plants ceases and soils start to gain moisture, and finally, in most years, become nearly saturated by the early winter. At the same time, autumn tillage exposes soil to rain drop impact that silts up soil matter to flowing water, resulting in higher P concentrations in water draining from agricultural fields.

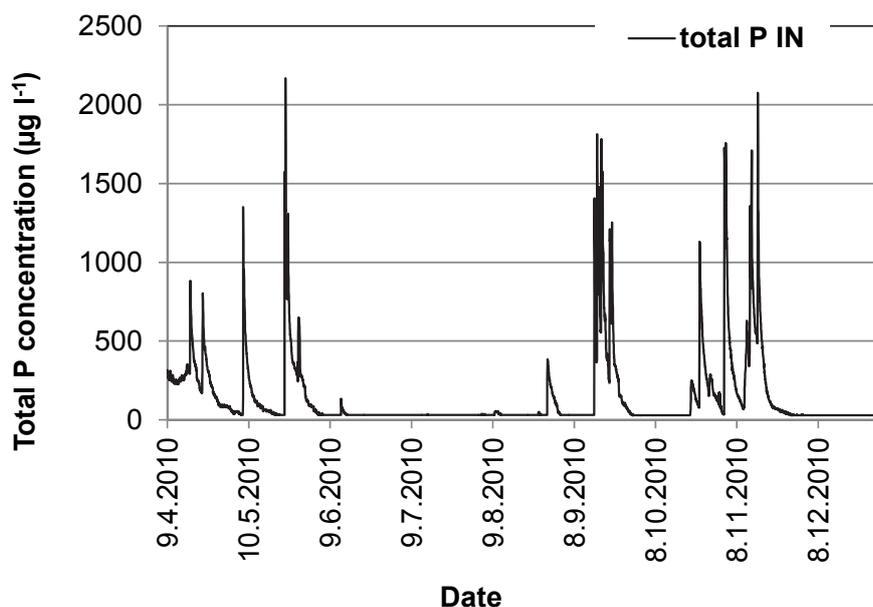


Figure 19. Hourly time series of total phosphorus concentration ( $\mu g l^{-1}$ ) in the inflow to the Hovi wetlands as estimated by the measurements of a turbidity sensor during 9 April to 31 December 2010.

### 3.1.2 Snapshots of P concentrations in other wetlands

To obtain a snapshot of P concentrations in eight wetlands built by WWF in southern Finland, water samples were taken from the inflow and outflow on two occasions in 2012. Sampling was conducted by external personnel hired by WWF. In the water analyses, the levels of dissolved P were under special interest since these relatively small wetlands are usually not good at tackling this component.

The combined results from the eight wetlands (Figure 20) showed that in spring time both total and dissolved P concentrations were moderately higher in the outflow than in the incoming water. This is a rather typical phenomenon and likely results from the release of phosphorus from decomposing wetland plant biomass that has accumulated in the wetland during the previous growing season. During the second sampling event in the autumn, phosphorus levels in the outflow were, in turn, lower than in the incoming water. In September and October, samplings were performed at temperatures that were still high enough to sustain plant and algae biomass production and P uptake, thus lower levels of dissolved P in the wetland outflow water.

The actual P levels of the autumn sampling, however, were higher than during the spring. This may indicate that our spring sampling missed the snowmelt peak from the field areas. Runoff from field areas is typically higher in dissolved P than runoff from forested areas that grow plants that are more frost-tolerant and liberate less P to snowmelt water. When field openings are already free of snow, forested areas may still have snow cover that supplies relatively clean water to ditches and further to wetlands. These wetlands had forest in their catchments (20–80% of the total catchment area) which may explain the lower P concentrations of springtime samplings.

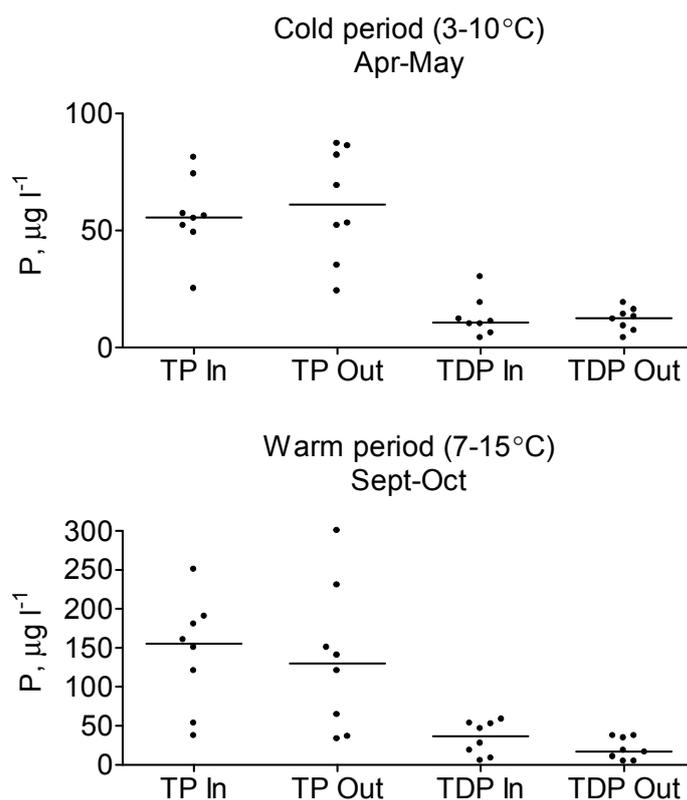


Figure 20. Concentrations of total P (TP) and total dissolved P (TDP) in inlet (In) and outlet (Out) points of eight wetlands in south Finland that were sampled in spring and autumn of 2012 by WWF. The horizontal lines indicate median concentrations.

## 3.2 Precipitation of P with ferric sulphate

In these pilot sites ferric sulphate was dosed so that we could obtain a decrease in dissolved P concentration. After adding the chemical dissolved P is converted to an Fe associated, biologically non-available form, but remains in the system. Flock formation of the solid matter (and the associated particulate P) that runoff waters contain does not effectively take place with these relatively small ferric sulphate additions. Furthermore, removal of solids would require calm water in which flock formation can take place and that allows sedimentation of the flocks formed. The pilot sites were not designed in a way that would have made these processes work. Because a reduction in total P concentration in the water was therefore not expected, the following results and discussion are entirely focused on dissolved P. The reduction of total P concentration can be assumed to have been minimal, and usually no changes were recorded in the paired samples taken from inlet and outlet waters.

### 3.2.1 Nautela tests

Efficiency for precipitation of dissolved P was studied at the Nautela pilot site with continuous measurements of water quality throughout the unfrozen seasons of the years 2011 and 2012. During the study, flow fluctuations in the ditch were considerable, varying from less than 0.1 l s<sup>-1</sup> in drier seasons to several hundreds of liters per second under heavy rain falls. Dissolved P concentrations in inflow varied from 0.027 to 0.160 mg l<sup>-1</sup>, and total P concentrations from 0.075 to 0.560 mg l<sup>-1</sup>. Most of the total P was in particulate form, dissolved P making up just 24% of the total P in the inflow water samples.

The estimated P removal by ferric sulphate dosing was 5.5 and 18.6 kg in 2011 and 2012, respectively (Table 7). Precipitation efficiency was during the two years in the range 49–84% (depending on the year, and whether simple average or flow-weighted concentrations were used in the calculation). In both years, consumption of ferric sulphate was about 2500 kg yr<sup>-1</sup>. The chemical dose applied varied according to the flow, and ranged from zero dosing to tens of kilograms per hour at the peak flow. The yearly averaged Ferix-3 doses were 23 and 16 g m<sup>-3</sup> (or 1:43k and 1:63k chemical-to-water ratio) in 2011 and 2012, respectively.

Table 7. Measured flow range, mean flow-weighted dissolved P inflow, ferric sulphate use, and achieved precipitation efficiency at the Nautela pilot site during the two test years.

Year	Flow (min–max)	Diss. P inflow	Ferix-3 used	P retention efficiency		Dissolved P precipitated <sup>2</sup>	Average dosing <sup>3</sup>
				Unweigh. mean <sup>1</sup>	Flow- weighted		
	l s <sup>-1</sup>	mg l <sup>-1</sup>	kg	%		kg	g m <sup>-3</sup>
2011	0.09–299	0.054	2560	49	69	5.5	23
2012	0.05–552	0.133	2520	60	84	18.6	16

<sup>1)</sup> Average dissolved P reduction between influent and effluent water samples.

<sup>2)</sup> Estimation of precipitation efficiency based on flow-weighted dissolved P concentrations.

<sup>3)</sup> Ferix-3 applied (in grams) to one m<sup>3</sup> of water volume, calculated for dosing periods only; chemical run-out situations not included.

During 2011, with the chemical price of 0.47 eur kg<sup>-1</sup> (0% VAT, cargo not included), the estimated cost for precipitating one kilogram of dissolved P was EUR 216. In 2012, despite the price of Ferix-3 raised to 0.55 eur kg<sup>-1</sup>, the cost for one kilogram of precipitated dissolved P fell to EUR 74 (the differences in these estimates are, however, partly influenced by sampling strategy and associated calculations of precipitation efficiency as discussed below).

Dissolved P precipitation efficiency varied widely, particularly during low flow situations, (Figure 21), and we observed a general tendency to better efficiencies in high-flow regimes. Thus the flow-weighted precipitation efficiencies presented in Table 7 are substantially higher than those that were calculated from unweighted mean values. In the latter part of 2012, an extra effort was made to obtain more water samples from high flow situations, which is the reason for the increase of the apparent precipitation efficiencies reported in Table 7 and the better cost-efficiency during the year 2012.

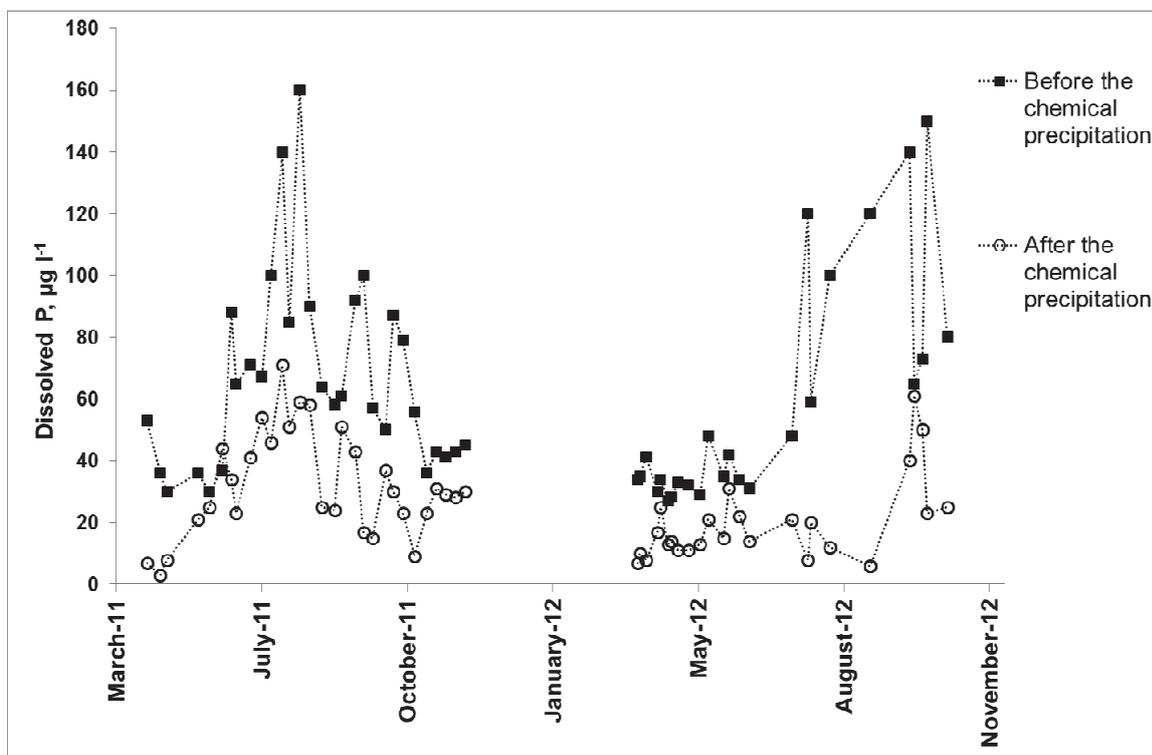


Figure 21. Dissolved P concentration in water samples.

Dissolution of ferric sulphate leads to pH decrease in water, because its reaction with water leads to the formation of ferric hydroxides and the liberation of protons from water molecules (simplified reaction may be written as:  $\text{Fe}_2(\text{SO}_4) + 4\text{H}_2\text{O} \rightarrow 2\text{FeOOH} + 6\text{H}^+ + 3\text{SO}_4^{2-}$ ), thus a drop in pH. In Nautela, we observed that pH was lowered especially as the flow peaked, as shown in Figure 22. Whereas pH decrease at lower flow volumes remained at about 0.5 units or less, high flows were associated with up to 2.5 unit decrease in pH. This is a clear indication of relatively higher doses of ferric sulphate to high flow. By looking at the pH curves it becomes clear why P precipitation was more efficient at higher flow regimes – simply because relatively more chemical was fed to high flows than to low flows (Figure 23). The dosing discrepancy was traced back to spring 2011 when ferric sulphate feed first exceeded the target value, and a considerable drop in pH (to pH 4) was observed. To rectify this, the doser head piece was adjusted 2 cm higher than before in order to avoid such pH declines.

Because sudden or severe changes in pH may affect water biota, highly soluble chemicals may be problematic if widely used in larger ditches. A potentially serious incident was experienced in Nautela in December 2011 when the doser platform collapsed into the ditch. This resulted in a sudden dramatic pH drop by 4.5 units, shown in Figure 22. The low pH readings of ditch water (momentarily down to pH 2.7) recovered to a normal level within four hours.

With soluble chemicals it is advisable to rather downsize than have a very large capacity of chemical storage so that upon incidents like this chemical feed does not continue for a long period. Of course, the downside of small-sized storage is the burden of refilling the doser more frequently. In Nautela, the doser equipped with a 350-liter chemical storage proved to be small in relation to flow peaks as heavy rains occasionally emptied the doser. These short-term chemical run-out events are detectable in the parameters followed by the water quality sensors.

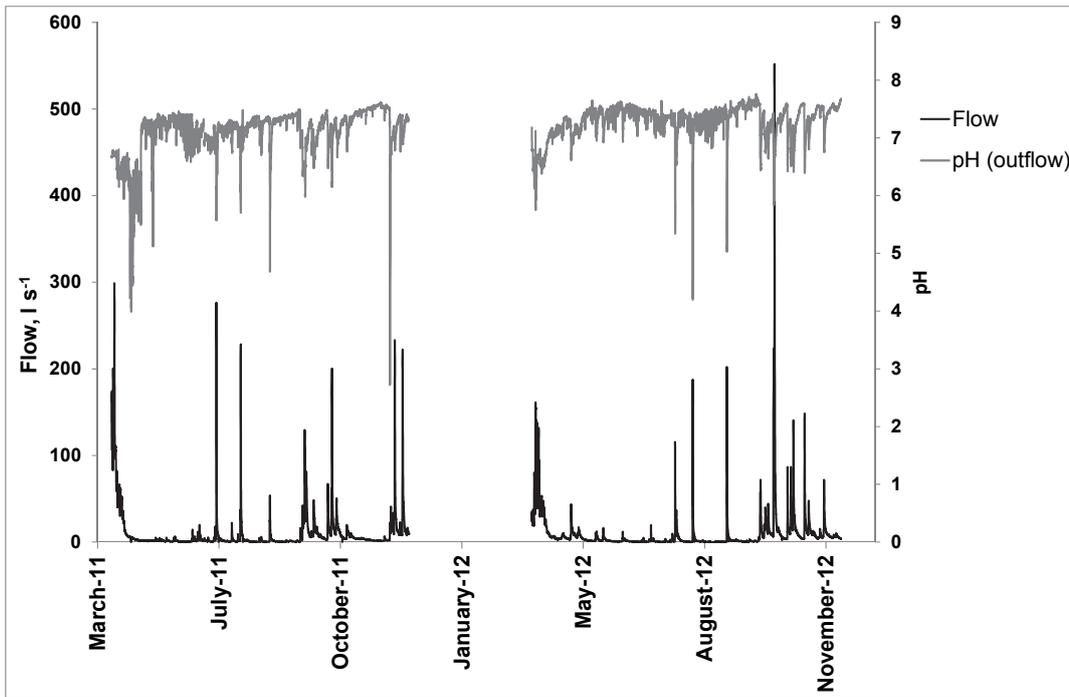


Figure 22. Flow and effluent water pH variations over the years 2011 and 2012.

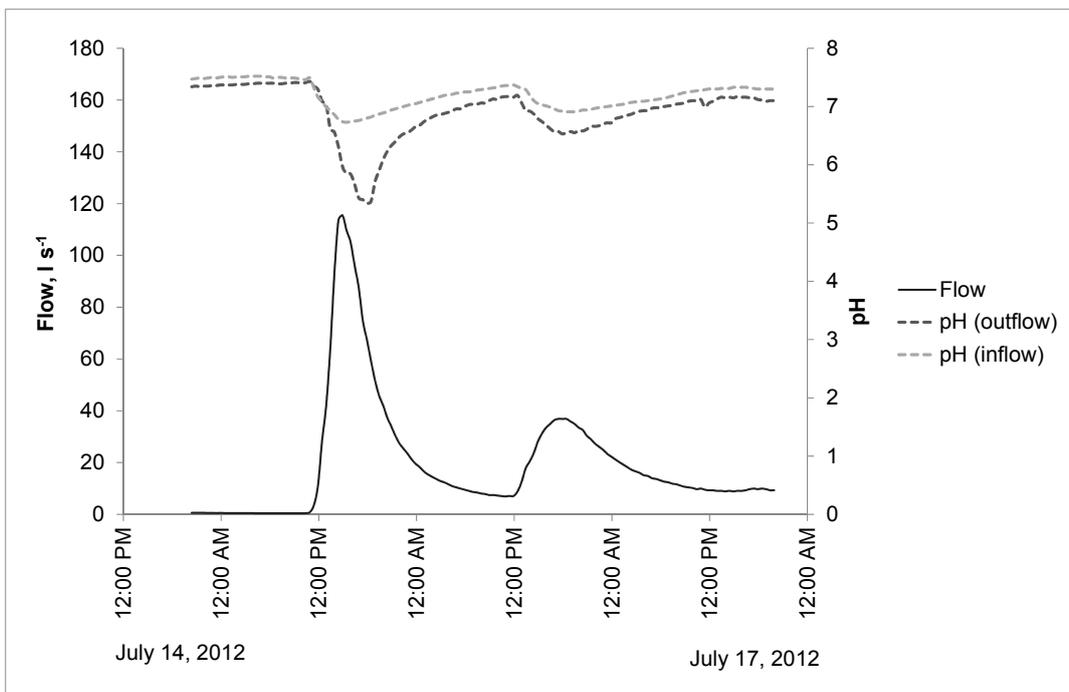


Figure 23. Changes in water pH during two rain events.

### 3.2.2 Nuutajärvi tests

In spring 2012 we tested P precipitation by ferric sulphate in 10 ditches draining to Lake Nuutajärvi in Urjala. There was no opportunity to construct wetlands on these sites, but the study allowed us to evaluate the potential and the costs of the method in several field-scale applications from sites with variable types of inflow water (even if the results were not obtained from wetlands, they are also applicable to such sites that have wetlands). In Nuutajärvi we focused on the spring flow period that carries most of the dissolved P from the catchment.

Altogether 61 water samples were retrieved from the Nuutajärvi sites during the period from 22 March to 26 April. Of the samples taken, 52 were of paired samplings of water before and after the Ferix doser

units. Sites 1–5, selected because there were cowsheds in the area that drained to these ditches, had moderate to very high average concentrations of dissolved P, ranging from 0.040 to 1.38 mg l<sup>-1</sup> (Table 8). In turn, water sampled from those ditches that received water from fields (and forested areas), i.e., sites 6, 7 and 9 were low in dissolved P, at 0.012–0.024 mg l<sup>-1</sup>. Site 8 was influenced by runoff from a horse stable area and also had high concentration of dissolved P, 0.942 mg l<sup>-1</sup> on average. At two of the sites, numbers 4 and 10, sampling or flow measurement was not possible because water flow took a route under the snow and ice cover, and water flow practically ended before these ditches were free of ice. Hence, results from sites 4 and 10 are incomplete. Also, only one sampling was possible at site 6 (this result is shown in Table 8 but not discussed further).

For the paired samples taken upstream and downstream of the doser units, we achieved a mean 65% reduction in dissolved P concentration, with 3% to higher than 95% range for the individual sampling events. The total estimated amount of precipitated P in all of the studied sites was about 9.3 kg, corresponding to about 58% of the estimated total mass (of 16 kg) of dissolved P transported to the lake via the studied ditches. The total amount of ferric sulphate used during the study was 4850 kg, which means that on average 522 kg ferric sulphate was used to precipitate a kilogram of dissolved P. With the price of 0.35 eur kg<sup>-1</sup> (0% VAT) paid for the chemical for these sites, the average cost of precipitating one kilogram of dissolved P was EUR 183.

The best chemical use efficiencies, and the highest overall scoring in Table 8, were obtained at sites 8 and 3. At these sites 125 and 166 kg of ferric sulphate (for sites 8 and 3, respectively) was required to precipitate one kilogram of dissolved P. Both sites had high average dissolved P concentrations (Table 8). Site 8 was already at the planning stage equipped with a double sock unit due to the high dissolved P concentrations in the water, so it was ensured that the peak flow events also received adequate amount of the chemical. It is known from previous experiments with precipitation chemicals that their efficiency is as a rule best at high concentrations and relatively modest water flow, and both of these prerequisites were fulfilled at site number 8. At site 3, dissolved P concentrations fluctuated widely from the very high 4.0 mg l<sup>-1</sup> during the first sampling to 0.02 mg l<sup>-1</sup> during the last sampling three weeks later. The flow at site 3 was low (about 0.2 l s<sup>-1</sup>) during all samplings. The costs of precipitating one kilogram of dissolved P at these sites were as low as EUR 45 and EUR 58.

Table 8. Flow, P concentrations and use of ferric sulphate at the Nuutajärvi area sites. N/A = not applicable (no data).

Site ID (overall scoring) <sup>1</sup>	Max measured flow	Dissolved P (inflow)	Ferix-3 used (spring 2012)	Precipitation efficiency	Dissolved P precipitated	Average dosing
	l s <sup>-1</sup>	mg l <sup>-1</sup>	kg	%	kg	g m <sup>-3</sup>
1 (+)	25	0.054	550	70	0.5	46
2 (-)	250	0.04	940	37	2.6	6
3 (++)	0.5	1.38	120	76	0.7	171
4 (0)	20	N/A	80	N/A	N/A	N/A
5 (++)	0.6	0.786	320	75	0.7	267
6 (0)	90	0.012	620	>95 <sup>2</sup>	1.0 <sup>2</sup>	19
7 (-)	100	0.019	680	71	1	11
8 (++)	15	0.942	260	84	2	68
9 (+)	100	0.024	1200	30	0.9	25
10 (0)	N/A	0.264	80	N/A	N/A	N/A

<sup>1)</sup> Overall scoring shows if dosing site was appropriately selected and if the doser worked well throughout the testing; all good (++), with minor issues (+), with major issues (-), or performed poorly (--). Score 0 indicates that samples or flow measurements could not be done at this site.

<sup>2)</sup> Estimates based on one paired sampling only.

Of all of the sites in the Lake Nuutajärvi catchment the largest amount of P was precipitated at site 2 where P removal was estimated to be 2.7 kg, and a kilogram of precipitated P required 344 kg of ferric sulphate. This site was also equipped with a double sock unit, but for this ditch concentrations were not abnormally high for field ditches (0.03–0.07 mg l<sup>-1</sup>). Instead, the double sock unit was used at this site

because of the relatively high flow volumes, with the maximum measured flow being 250 l s<sup>-1</sup>. Due to the high water volumes, ditch 2 was estimated to have carried as much as 6.5 kg of dissolved P load to the lake. Because the chemical feed at this site did not function without interruptions (the doser unit was partly submerged twice, resulting in a hard clump of ferric sulphate inside the dosing sock and hence blocking the chemical feed) some of the P load that could have been stripped from the water escaped being precipitated. It is noted that the load estimates at this site are uncertain, because it was impossible to install a v-notch weir in the ditch due to the level topography. However, we made an estimate of the cost for removing a kilogram of dissolved P that came to EUR 120.

Site 5 with a high (0.786 mg l<sup>-1</sup>) average of dissolved P concentration due to cowshed influence had a narrower v-notch weir (90° angle) that fed a higher amount of ferric sulphate to the ditch. The high chemical feed was motivated by the fact that the ditch after some meters downstream from the doser joined a larger drainage channel. The amount of ferric sulphate fed to the ditch was 1 kg to 4 m<sup>3</sup> of water, which was the highest ratio of all of the dosers used and about tenfold the recommended ratio of about 1:50 m<sup>3</sup>. The idea with this high dose was to feed the main channel with the chemical that would react with P flowing in the main channel, as well. As a result, much more ferric sulphate, 454 kg, was added for a kilogram of precipitated P at this site than at the other high-P sites. The abundant chemical feed precipitated 75% of the dissolved P mass passing through this site, but increased the cost of a kilogram of P precipitated to EUR 159. This calculation does not include the P precipitation possibly occurring in the main channel below the sampling point after the doser.

The field sites (sites 6, 7 and 9) had relatively low average dissolved P concentrations (0.012–0.024 mg l<sup>-1</sup>) and a relatively high dose of chemical (659–1316 kg) was required to strip a kilogram of dissolved P. The estimated cost was accordingly relatively high, EUR 231–461 for a kilogram of precipitated P. For the present study, we cannot give any reasonable relationships between P retention efficiency and P concentrations in water because the chemical feed was highly variable at the different sites (Table 8). The estimates of P precipitation efficiency are also based on a few samplings from each site. It is, however, clear that chemical treatment is most efficient at sites with elevated P concentrations, and units should be in the first place built at such sites.

### 3.2.3 Paimionjoki and Tammela tests

Altogether seven water samples were retrieved from the Paimionjoki sites during the period 3.9.–5.11.2012. Of the samples taken, five were of paired samplings of water before and after the Ferix doser units. Sites P2 and P3 had relatively high average concentrations of flow-weighted dissolved P, ranging from 0.14–0.17 mg l<sup>-1</sup> (Table 9). In turn, water sampled from a ditch that received water from fields and forested areas (P1) was lower in dissolved P.

Table 9. Flow, dissolved P concentration, chemical use and P-binding efficiency in the River Paimionjoki and Tammela sites.

Site ID (overall scoring) <sup>1</sup>	Max. measure d flow	Dissolved P (inflow) <sup>2</sup>	Ferix-3 used <sup>3</sup>	Precipitation efficiency	Dissolved P precipitated <sup>2</sup>	Aver. dosing <sup>3</sup>
	l s <sup>-1</sup>	mg l <sup>-1</sup>	kg	%	kg	g m <sup>-3</sup>
P1 (+)	35	0.08	160	42	1.47	10
P2 (+)	4	0.17	120	77	0.29	20
P3 (+)	10	0.14	160	29	0.50	30
Tammela (-)	0.3	5.15	165	53	3.70	118

<sup>1</sup>) Overall scoring shows if dosing site was appropriately selected and if the doser worked well throughout the testing; all good (++), with minor issues (+), with major issues (-), or performed poorly (- -). Score 0 indicates that samples could not be taken at this site.

<sup>2</sup>) For the sites P1–P3 estimates are based on five paired sampling in October–November 2012, and for the Tammela site for samplings conducted in 2010–2012.

<sup>3</sup>) For P1–P3 amounts of Ferix-3 used during autumn 2012, but the dosers were not in use continuously. For Tammela, the sum of Ferix-3 used in 2010–2012.

For the paired samples taken upstream and downstream of the Paimionjoki area doser units, we achieved a mean 49% reduction in dissolved P concentration. The total estimated amount of precipitated P in all of

the Paimionjoki sites during October 2012 was 2.3 kg and the largest amount was obtained at site P1 where removal was estimated to be 1.5 kg. With the Ferix-3 price of 0.35 eur kg<sup>-1</sup>, the costs for a kilogram of precipitated P varied between EUR 38 and EUR 145.

The dosers at the Paimionjoki sites were not operated continuously, but ferric sulphate was only added after rain events, hence the overall scoring that indicates minor issues. Non-continuous dosing is motivated by the dissolved P concentrations that were not very high, albeit mostly higher than 100 µg l<sup>-1</sup>.

In Tammela, concentrations of dissolved P were an order of magnitude higher than at any other sites in this project, and with a wide variation from sampling to another. Occasionally extreme dissolved P concentrations of up to 19 mg l<sup>-1</sup>, associated with a dark brown water colour, and foaming, indicate flooding of the manure storage and ensilage silo that the ditch passes by. There were several pauses in the dosing of ferric sulphate and the doser's functioning was generally unreliable due to low flow (usually about 0.1 l s<sup>-1</sup>) in the ditch. However, the need for mitigation measures at this site was clear, and the site is an obvious representative of those ditches that are the priority targets for active purification.

The amount of P precipitated in Tammela was assessed to amount to 3.7 kg from a water volume totalling only 1400 m<sup>3</sup>. Consumption of ferric sulphate was 165 kg for the whole study period extending from autumn 2010 to the end of the year 2012. For a kilogram of precipitated P, we used about 45 kg of ferric sulphate, and with the 0.35 eur kg<sup>-1</sup> chemical price the cost of a kilogram of precipitated P would be as low as EUR 16.

### 3.2.4 Rahinge tests

During the test period 40 water samples were taken from the Rahinge site upstream and downstream of the Ferix doser between April and December in 2012. Dissolved P concentrations varied in the range of 0.45 to 0.07 mg l<sup>-1</sup>. The water flow rate ranged between 4 to 127 l s<sup>-1</sup>, and the higher discharges from the watershed had a diluting effect on dissolved P. During the winter time no sampling was performed due to ice covering the ditch and blocking the cone of the doser.

By applying ferric sulphate we achieved an average reduction in dissolved P concentration by 64%. Altogether 143 kg of ferric sulphate was used during the experiment and the total estimated amount of precipitated P was 0.57 kg. To precipitate a kilogram of dissolved P 237 kg of ferric sulphate was required. With the price of 0.52 eur/kg (0% VAT) paid for the chemical for the Rahinge site, the average cost of precipitating one kilogram of dissolved P was EUR 123 euro.

## 3.3 Solid P retention materials

### 3.3.1 Ojainen tests with Sachtofer PR granules

The Sachtofer PR buffer at Ojainen takes water from the outlet of a constructed wetland through a PVC pipe that leads the water to a perforated feed pipe laid at the bottom of a 6 m<sup>3</sup> granule layer. Water from the feed pipe is first distributed through a layer of coarse gravel and then rises through the granule bed and to its surface. Once on the surface, water flows out of the buffer construction through a v-notch cut on the upper edge of a dam construction.

A first version of the buffer was built in spring 2010, but already during the summer it became clear that the openings of the feed pipe that leads water to the bottom of the granule layer were too big, and water forced its way straight to the surface of the granule bed through a few preferential flow channels inside the granule bed. This appeared on the surface of the granule bed as a few small "springs" that spouted water from beneath. Hence, the contact between the water and the granule bed was minimal and dissolved P did not have time to react with the material. The granule mass used in this first construction was relatively fine-grained, which also contributed to the inception of flow along a few channels through the granule bed.

In August 2010 the buffer was dug open to rectify the uneven flow. To do that, the feed pipe was changed to a polyethene subsurface drainage pipe that has small, cut perforations, the gravel layer was thickened to 0.3 m, and a new batch of granules that were sieved to a larger than 3 mm size fraction was applied. After these changes no apparent by-pass flow channels were observed, and sampling was commenced.

During the first autumn of operation (in 2010) the Ojainen buffer decreased the averaged dissolved P concentration by 45% of the average inlet concentration of  $65 \mu\text{g l}^{-1}$ . The estimated mass of dissolved P fed through the buffer during the first autumn was about 70 g and of that the buffer retained 37 g, or 53% (Figure 24). In 2010, after seven days of frost in November, we drained the feed pipe to let the granule mass freeze in as non-saturated state as possible so that we would not have to wait for the melting of ice inside the buffer construction in the following spring.

In spring 2011, daily temperatures kept below zero until the beginning of April. The first samples were taken on 4 April, and until 15 April the concentrations of dissolved P in incoming water remained above  $100 \mu\text{g l}^{-1}$  (up to  $171 \mu\text{g l}^{-1}$ ). The outflow from the buffer during the spring flow had about 60% lower concentrations than the inlet water. Thereafter retention efficiency of dissolved P decreased to 25% and only in five samplings out of 29, conducted from mid-April to the end of December, retention exceeded 50%. Retention efficiency seemed not to have been influenced by flow, nor did it become gradually lower with time, but varied in a seemingly random manner. The total mass of dissolved P in inflow during the year 2011 was estimated to be about 860 g, 35% of which was retained in the buffer (Figure 24). The buffer construction was again let to drain in mid-December.

In 2012, sampling started on 19 March, a week after daily temperatures had risen above zero. Concentrations of dissolved P during the spring 2012 were lower than in the previous year, on average  $70 \mu\text{g l}^{-1}$  (up to  $90 \mu\text{g l}^{-1}$ ), and the buffer lowered the dissolved P concentration by only 8%. The concentrations rose during some intense summer storms, and after the harvest in September, to a mean  $154 \mu\text{g l}^{-1}$  (up to  $200 \mu\text{g l}^{-1}$ ), and the retention efficiency rose during that period to close to 20% on average. For the whole year 2012, we calculated an average retention of 16% of the 675 g mass of dissolved P that entered the buffer (Figure 24).

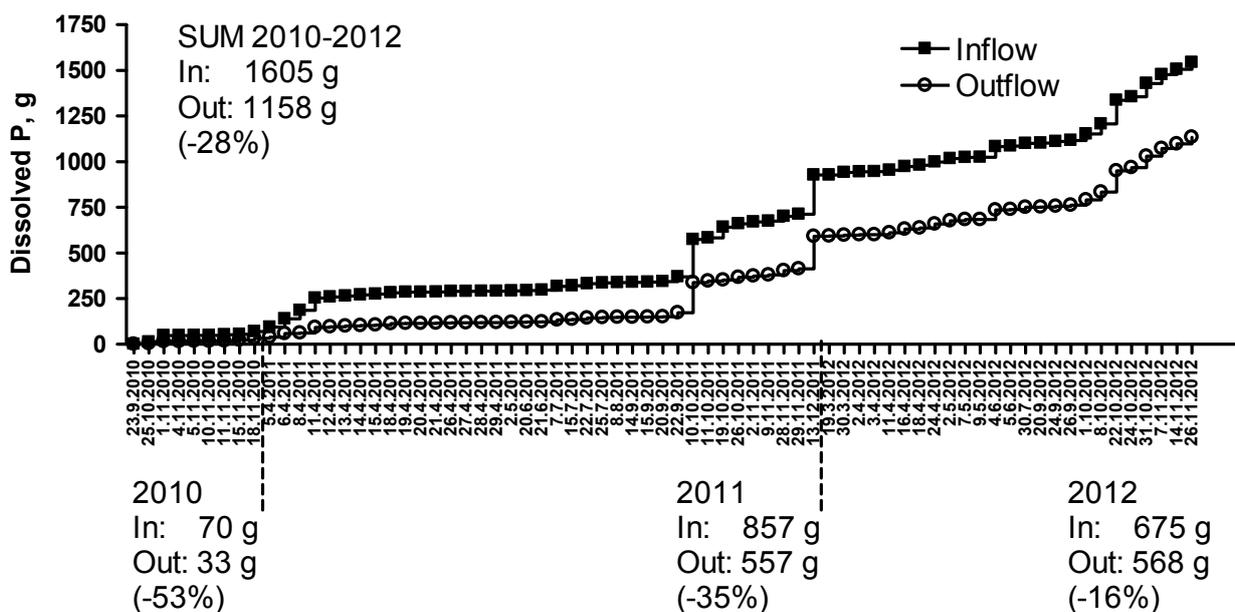


Figure 24. Estimated inflow and outflow dissolved P masses through the Ojainen Sachtofer PR buffer in 2010–2012. The numbers in parentheses indicate reduction in dissolved P mass.

In spring 2012 there had again been signs of preferential flow channels on the surface of the buffer. Hence, in June 2012 a pulse of blue dye was poured into the inlet pipe of the filter and its appearing on the surface of the granule bed was observed. As shown by a blue stream of water appearing within a minute of its being fed into the inlet pipe in a few spots on the surface of the granule bed, preferential flow paths inside the granule bed had been activated once again. As the dye pulse passed through the buffer in minutes, it became obvious that during high flows there would not be enough long contact between water and the granules to obtain any significant retention of dissolved P. At low flows at the end of the year 2012 we still recorded on average somewhat (less than 10%) lower P concentration in outflow than in inflow, but it is expected that the retention efficiency after that would be negligible.

Retention of particulate P as determined from water samples was negligible throughout the study (results not shown). Some solid matter, however, remained in the granule bed during the test and probably contributed to the development of preferential flow channels by partly filling the voids in which flow velocity was slow. We also observed that clay particles had attached to the granules and thereby blocked some of the reactive surface. At the beginning of the test particle deposition in the granule bed may have been due to the elevated ionic strength of the water, caused by the dissolution of gypsum from the granule mass. At the later phases, when the gypsum dissolution phase had passed, a gradual decrease in flow velocity in some parts of the granule bed most likely allowed the formation of clay linings on the granule surfaces.

### 3.3.2 Rahinge tests with Sachtofer PR granules

#### *Stacked filter element tests*

Another type of Sachtofer PR filter was tested in Estonia in full-scale field experiments. Sachtofer PR was applied on stacked filter elements placed in the Rahinge ditch. Contact with the water was established with a layer of the granules placed on the horizontal elements, so that the water did not pass through the granule mass, but flowed between the filter element shelves. This structure showed dissolved phosphorus removal efficiencies of 4–25%, depending on contact surface, contact time and biological processes in the ditch. The removal efficiency was 7–9% when the elements' total surface area was 5 m<sup>2</sup>, and rose to 25% as the surface area was increased to 13 m<sup>2</sup>. It is noted here that the achieved purification effect was considerable, taking into account the flow rate and the amount of granules used in the filter. However, as more filter elements were put into the ditch in August, increasing the surface area to about 19 m<sup>2</sup>, P removal efficiency fell to 6%. Finally, in September, when the surface area was increased to about 27 m<sup>2</sup>, we measured 0–11% P removal.

The seemingly illogical results have an explanation in algae growth on granule surfaces (Figure 25). The first algae on the filter elements were observed in July when temperatures rose and nutrient concentrations in the ditch increased, and the further the summer proceeded the more densely the algae covered the elements. As a result, the initial P removal efficiencies measured on a clean contact surface of granules increased, whereas later in the summer, when more filter elements were introduced, algae that covered the surface of the filter elements blocked the granule surfaces and inhibited contact with the water.

#### *Column and flume tests*

In a short column test, the Sachtofer PR granules showed rapid P removal from ditch water with naturally varying concentrations from 0.2 to 1.0 mg l<sup>-1</sup>. Contact time of less than 1 min was sufficient for removal of over 50% of the inflow phosphate, which was a surprisingly high P removal rate for such a short contact. The test was terminated after 2 hours, so the results apply for granules in a fresh, unleached state.

Because the granules appeared somewhat brittle after being used in columns, we made a separate column test on how hydraulic conductivity developed over time when continuously fed with inflow water. Initially flow through the 24 cm thick granule bed was rapid, with 1.87 m d<sup>-1</sup>, but as the test proceeded hydraulic conductivity decreased in 24 hours to only 0.23 m d<sup>-1</sup>. The test was continued for additional 500 hours and at that point conductivity value of 0.003 m d<sup>-1</sup> was recorded. The initial flow velocities correspond to flow through coarse gravel whereas the low value is similar as flow in homogenous clay.

In the next stage, testing was continued on a 7.5 m long flume where water was flowing over a shallow (3 cm) layer of Sachtofer PR granules. The aim of this test was to find out whether this kind of set-up where water is partly moving inside a granule layer and partly on it, would have P removal comparable with the flow in columns. That type of a construction would at least partly rectify the problems associated with the drop in hydraulic conductivity that was observed during the column tests.

Flow rates were during the test regulated between 0.01 and 0.44 l s<sup>-1</sup>. From the initial 0.52 mg l<sup>-1</sup> inflow concentration of dissolved P removal rates of 25% to 71% were recorded, depending on the flow rate and thus contact time between granules and water. The longer was the contact time, the higher the P removal rate. The high flow rates clearly reduced P retention, and it could be concluded that contact cannot be maintained similarly as in flow-through columns where substantial P retention took place rapidly. It is

likely that the water on the surface of the granule layer is more mobile than the water inside the granule bed, and these water do not effectively mix.

Even though the fast flow rates were associated with lower P retention, there was substantial retention from low flows. To explore whether high P retention at lower flows sustains over longer periods of time, an additional test was conducted at flow rates of 0.02–0.09 l s<sup>-1</sup>. During this test, the concentrations of dissolved P in inflow water varied considerably, between 0.6–1.48 mg l<sup>-1</sup>. Nevertheless, the range represents the typical quality of Rahinge ditch water. During the observation period, June 8. to July 10. 2012, 7 water sample pairs were retrieved. The retention rates of dissolved P were 60% in the beginning of the test and decreased to 4–20% to the end of the test period. According to a rough calculation of P mass removal, the granules would have during the monitoring period retained up to 3 grams dissolved P per kilogram of the granule mass.

The weakness of the broad overflow flume was that the granules were well exposed to the sunlight, making algae to grow on their surface. In addition, algae growth was also favored by warm water and plentiful nutrient supply (Figure 25).

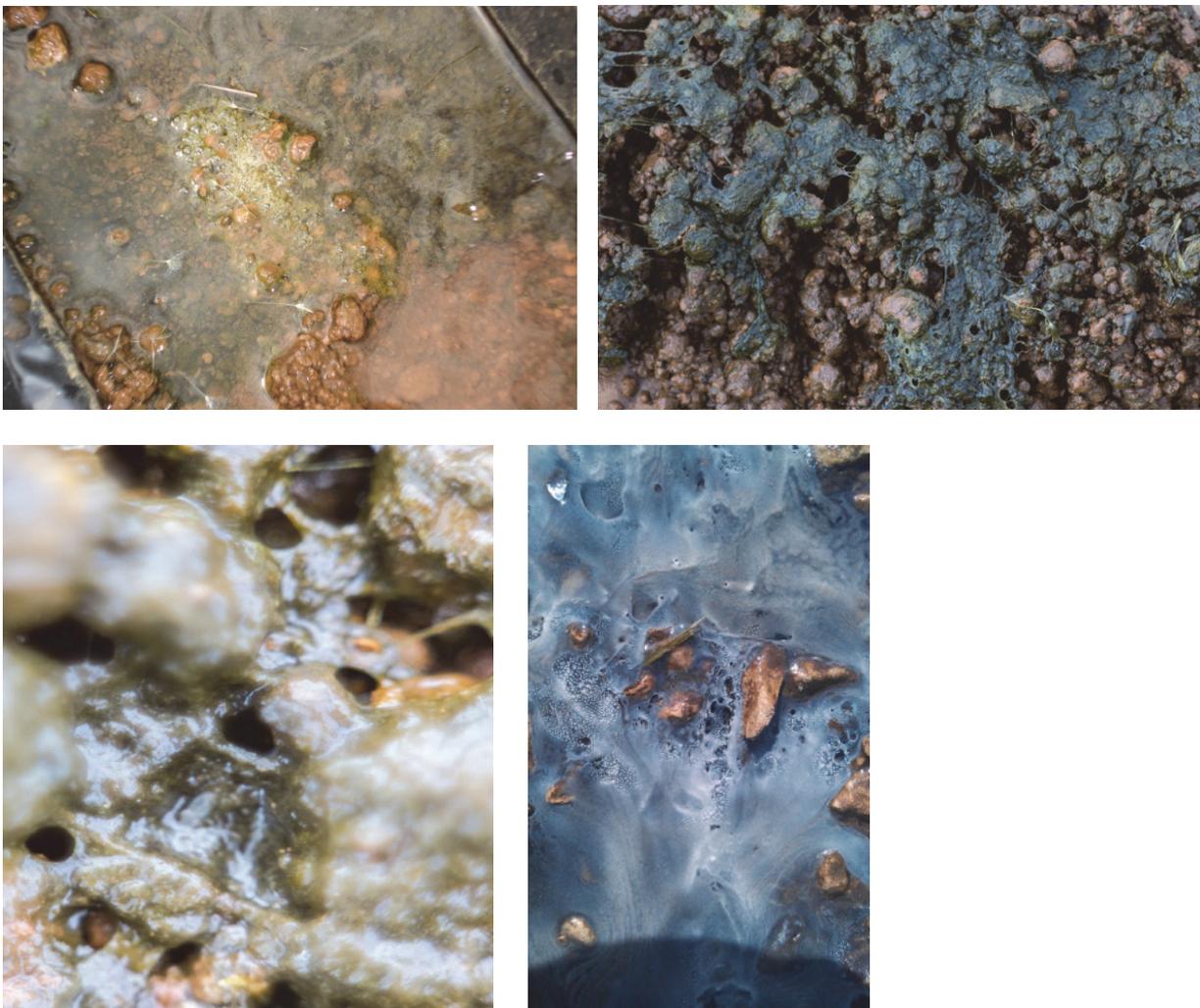


Figure 25. Algae covering the P retention materials. Photographs by Morten Poolakese

### 3.3.3 Rahinge tests with oilshale ash

A similar flume experiment as the one described above was also done with oil shale ash. The test started on June 8. and ended on July 25. 2012. During the experiment 7 water samples were taken from inlet and

outlet of the flume. Inlet phosphate concentration ranged from 0.2 to 0.72 mg l<sup>-1</sup>, and flow rates were in the range 0.02–0.09 l s<sup>-1</sup>.

Dissolved P removal rates up to 76% were measured in the beginning of the test, but they fell to 2% already in the third sampling conducted one week later. Similarly as for the Sachtofer PR tests, the purification was hampered due to vigorous algae growth on the material in warm water rich in plant nutrients. Inflow water was characterized by pH slightly above neutral (pH 7.4), and at outflow end it had increased to 7.6–7.8. Thus, no great increase of pH took place. As example in the earlier tests by Liira et al. (2009b), who used higher amount of oil shale ash relative to the flow, the filters produced effluent with pH 9 or higher for the whole 5-month test period.

### 3.4 Disturbances and risks associated with the use of chemicals

#### *Ferric sulphate*

Issues with ferric sulphate dosing were apparent at some pilot sites in this project. The effects of overdosing are best shown in the Nautela site results (section 3.2.1) because of continuous pH monitoring in this pilot. The target pH change with ferric sulphate doser-equipped sites was 0.5 to 1.0 pH unit, and this (or a lesser change in pH) was generally achieved most of the time. However, apart from the collapse of the doser in Nautela, at some other sites snow and ice caused ponding of water in early spring and hindered the flow over the v-notch weirs. If there was ferric sulphate left in the dosers, dissolution of the chemical took place in a small volume of ponded water during the rise in water level above the weir, and a distinct drop in pH was recorded. Hence, there is a real risk of acidification of ditch water, with possible consequences for water organisms. Our recommendation is that when planning to set up ferric sulphate dosing, small ditches should be preferred over larger streams. This means that any possible overdosing will only have a local impact on the small ditch, and the water would be diluted when it joins a larger stream.

There is obviously a trade-off between the size of the chemical storage of the doser (the larger the storage compartment, the less often it needs to be re-filled) and the consequences of misfortunate incidents (e.g., risks of potential damage to water organisms). Preferably the target period for dosing should be the spring flow period, with dosers that are sized so that they would need refilling at least every two or three days. This means the chemical would be added at a time when the bulk of P runs off to waterways, and the dosers would be under constant surveillance. In addition to the potential risk for ecological impacts, from the cost-efficiency point of view also ferric sulphate dosers should in the first place be operated in small ditches close to the sources of P leakage.

Not only has the lowering of the pH been a concern, but also questions about possible effects of sulphate input on water have been addressed to the project personnel. It is thought that ferric sulphate additions might disturb the formation of natural iron hydroxides at the sediment-water interface. The iron hydroxides are important in keeping up the ability of P retention by lake sediments, and it is known that in high-sulphate environments (as in sea water) ferrous sulphide (FeS) type minerals form after iron has reduced to an oxidation state +II and dissolved in water. In contrast to iron hydroxides, iron sulphides are not capable of reacting with phosphate anions and hence their formation may reduce the capacity of sediments to bind P. When discussing the context of this project it should be kept in mind that the input of sulphate is small when ferric sulphate is dosed at a ratio of 1:50k, i.e., 1 kg Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> to 50 m<sup>3</sup> of water, and it increases sulphate concentration by 14 mg l<sup>-1</sup> in the treated water volume<sup>2</sup>. For example, Wilander (1993) reported the present median sulphate concentration of 132 µeq l<sup>-1</sup> (up to 250 µeq l<sup>-1</sup>) in a material of about 4,000 Swedish lakes, and this equivalent mass translates to a sulphate concentration of 6.3 (up to 12) mg l<sup>-1</sup>. Thus, at the median concentration level in lake water an increase due to ferric sulphate dosing could be detected, but only if the whole lake's water volume would be treated with the chemical (at the 1:50k dosing ratio). In dosing to a minor volume of runoff that annually replaces a part of the water column in a lake, concerns about sulphate-induced eutrophication appear theoretical. A substantial consumption of the native sediment Fe is unlikely also because iron, too, is at the same time fed into the system with ferric sulphate.

---

<sup>2</sup> With 1:50k dosing, 20 mg of ferric sulphate is added to one liter of water. As the share of sulphate in the mass of the chemical is 72%, this gives an increase in sulphate concentration of about 14 mg l<sup>-1</sup>.

Other difficulties in the operation of ferric sulphate dosers arose from the hygroscopic nature of granulated product during periods with high air moisture, typically in autumn. A combination of low flow and damp air caused ferric sulphate clumping that in some cases blocked the doser head piece. This property was discussed with the manufacturer, who has tested different types of coating materials to overcome problems associated with hygroscopicity, but currently there seems to be no appropriate coating materials available. Coating of the chemical grains would also increase the price, which is an important factor in chemical selection by the main users (water and wastewater treatment plants).

#### *Solid P retention materials*

The solid P sequesters tested in this project, Sachtofer PR (Ca-Fe oxide) granules and oil shale ash, have a pH-elevating effect when first coming into contact with ditch water. Even though natural waters may periodically have relatively high pH values, such as during vigorous growth of algae, sustaining a high pH may mobilize organic matter from wetland sediments and thus degrade water quality by increasing chemical and/or biological oxygen demand (COD, BOD).

Water suspension of Sachtofer PR granules has a pH of about 9, but the soluble Ca hydroxides present in the material are rapidly dissolved. At the Ojainen site we only found a slight, less than 0.5 unit increase in the pH as water passed the newly added granule mass. After the initial effect that passed in a few weeks, the pH of influent and effluent were practically the same.

According to a recent laboratory study (Uusitalo et al., 2012), the retention of dissolved P by the Sachtofer PR granules partly takes place as Ca phosphate precipitation in a fresh granule mass, but shifts to P retention by the Fe hydroxide component as soluble Ca hydroxide is dissolved from the material. There is no need to keep up the elevated pH and, if the basic conditions are thought to harm water organisms, the granules may be pre-leached before placing them in a ditch. Pre-leaching has no distinct effect on the P retention capacity of the granules (Uusitalo et al., 2012).

Instead of the chemical properties, the main issue with Sachtofer PR granules rather seems to be associated with the physical strength of the granules that affects particle-size distribution and the flow of water inside a granule bed. The short, column-scale experiments performed in Estonia showed that saturated hydraulic conductivity of a granule bed decreased rapidly when water was allowed to drain through a column filled with the granules. This was thought to be because the granules disintegrated to a variable degree and the granule bed packed by its own weight when in contact with water.

Disintegration of the granules may have occurred also during field testing at the Ojainen site. There, preferential flow through a very limited portion of the granule bed became obvious when we fed the buffer with a blue dye in summer 2012. In a granule bed where particle size distribution (either originally, or as a result of granule break-down) is heterogeneous, the voids between larger spheres are filled with smaller particles and, as a result, water flow through the voids is restricted. Initially, water through the Ojainen buffer seemed to pass slowly through the entire granule bed, but gradually the water started to find routes with lower resistance and carried along the smaller particles on the surface of the buffer construction. Once the flow had cleared these voids, the hydraulic resistance difference between the open voids and the surrounding granule bed became larger, and finally most of the flow used the preferential flow channels only. When the active flow routed through a small portion of the granule bed, the contact time with the granules became shorter and there was no time for dissolved P to react with Fe oxides on the granule surfaces. Finally, a major part of the total volume of the buffer was composed of dead zones with no active flow, and virtually no P retention took place.

Previous studies with oil shale ash have shown that pH elevation is substantial as water is fed through a bed of the ash. As example, Liira et al. (2009b) measured pH readings initially at about pH 12 and after 5 months of running the test still at about pH 9. During the tests made in the present project, pH was elevated to 7.8 at maximum which is not a level that can be assumed to harm water organisms. The lower pH readings of our tests were due to the relatively small amount of oil shale ash used. As P retention by oil shale ash is based on precipitation of Ca phosphates, highly efficient P precipitation would require elevated pH. Hence, open systems with periodically high flows, such as large ditches and wetlands, are not optimal for the use of materials that operate by Ca-phosphate precipitation. Instead, they would certainly work well in more closed systems where flow can be adjusted and effluents brought easily back to neutral pH readings.

## 3.5 Poll of farmers

### 3.5.1 Interviews conducted in Finland

WWF Finland commissioned from Suomen Gallup Elintarviketiето Oy a poll of farmers. The poll inquired about the attitudes of Finnish farmers towards wetlands and the use of chemicals in capturing nutrients from field runoffs. An invitation to the poll was sent out to a group of 1,253 randomly selected farmers in the South-West Finland region. Of the invited farmers, 372 answered the questions, that is, about 10% of all of the farmers in the region. Representation from farms with animal and plant production was ensured.

The main findings of the poll show that farmers would want to have more information on how wetlands can be used in mitigating eutrophication from agriculture. Secondly, farmers do not feel that they receive enough information about the prevention of phosphorus runoff in general. Over 60% of the questionnaire participants would also like more information about soluble phosphorus and how to prevent runoff. Interestingly, over half of farmers estimate that their farms do not produce any soluble nutrient runoff.

More than one third of the respondents judged that if active measures, such as the use ferric sulfate, work well, this would increase the attractiveness of establishing wetlands. One in four of the respondents was prepared to use chemical methods on their own lands. The respondents with the most positive views on chemicals were those who had already established a wetland. Farmers would also be willing to contribute with some of their own time and money to put chemicals into use. However, more than 90% of the respondents felt that the use of active methods should receive support from the Environmental Support Scheme of the Agri-Environmental Programmes.

Two thirds of the respondents felt that they did not receive enough information about establishing wetlands. Therefore, if we want to get more wetlands built in agricultural areas, one of the main conclusions that can be drawn from the survey is that more effort has to be put into guidance, training and communication on this topic. Farmers also appear to be very open-minded about new innovations in agriculture in order to protect waterways. An interesting detail of the study was that nearly all of the respondents felt that the draining of natural wetlands should be stopped.

Along the River Paimionjoki, three farmers were interviewed in depth. These farmers had been testing the application of chemicals to runoff water in practice. The farmers considered the devices for chemical application to be easily constructed. Yet the devices required maintenance, and especially during the spring, this was thought to be rather laborious. Farmers also came up with ideas on how to develop the chemical applying device; for instance, using a bigger storage box for chemicals, an extra sack of chemicals hanging above the device, or having the funnel part placed inside the box.

Farmers understood that these applications were still in a piloting phase, and thought that testing them in the field was necessary and gave valuable information. The farmers found it surprising that phosphorus did not precipitate right below the chemical applying device, but only downstream from it. Farmers raised their concerns over what happens to the sludge formed, and suggested that there should be a sedimentation pool downstream from the device where the P could then be collected and returned to the fields.

The farmers were intrigued by the cost-efficiency of the tested method. They would be ready to apply the method in everyday life if the cost-efficiency would be evident and if public money would be used in their support. The farmers thought that the tested activity could be part of the Environmental Support Scheme, yet the cost for time spent in running the devices should be fully compensated for without an increase in the bureaucracy associated with compensations.

The participating farmers found it interesting to receive information on the substances of runoff water. They were also partly troubled by the information. They were positively surprised at how much phosphorus in total could be captured by the method, although it was applied in rather small ditches.

The main motivation for these farmers to use the active measures would be tackling nutrient runoffs. However, the use of active measures should always be voluntary according to their view. Taking part in the research got the farmers, in their own words, thinking about the environment and related matters. A

disappointment was that taking part in this research did not mean building a wetland in their neighbourhood.

### **3.5.2 Interviews conducted in Estonia**

The pilot study in the framework of AW conducted to find out farmers' attitudes towards constructed wetlands shows that the water protection issues and questions concerning the use and storage of fertilizers are important among the Estonian farmers. Most of the agricultural producers interviewed considered the improper use of fertilizers, pesticides and manure handling (haystacks, storages) the biggest environmental issue in the agriculture. In this field, as well as looking for solutions to the question, the opinions were similar between organic and conventional producers.

The results differ from those of the earlier survey "A farmer's view on the Baltic Sea", conducted in the framework of Baltic Deal project, among some Hiiumaa and Saaremaa island's farmers. In that survey the interviewed farmers did not see the connection between agriculture and situation of the Baltic Sea. This also refers to the prevailing importance of awareness raising campaigns.

What comes to the pollution already exposed to the environment, three-quarter of respondents of the AW survey were not aware of the opportunity to establish constructed wetlands. The awareness among the organic producers was a bit higher, showing how essential it is to raise awareness on this topic.

It is seen that establishment of constructed wetlands brings a number of benefits, and it was interesting to find out precisely what is considered important. Again, there was not much difference between the organic and conventional producers. The farmers were most interested in obtaining clean water and less interested in using reed and bulrush as construction materials. Most likely this would need separate popularization campaign. The list of benefits according to the interest starting from the most attractive one to least attractive was following: clean water, more diverse landscape and richer flora and fauna, possibility of fish farming (crustacean farming), introducing the wetland to people interested in it, sediment usage as fertilizer, using constructed wetland for swimming, and using reed and bulrush as construction materials. The organic producers considered using sediment as fertilizer more important than conventional producers.

If Estonia would support the establishment and maintenance of wetlands based on the Finnish model, the support would be definitely additional reason to adopt the measure. Only two respondents of thirty claimed that they would not establish a constructed wetland for some reasons. Views diverged on the amount of the annual subsidies (in euro) for the agricultural producers to lay down 1 ha of arable land for constructed wetland. One respondent claimed the price for 1 ha of arable land for that purpose to be 3000–4000 euro, while on the other edge some would not ask money for establishment of smaller wetland, or would ask only symbolic amount, like 1 euro. Other opinions were 2000, 500, 250, 100 or 50 euro.

---

## 4 Discussion

---

### 4.1 Phosphorus retention in wetlands without chemical treatments

According to our understanding, wetlands usually retain P in the warm season due to assimilation in vegetation and bacteria, and by sedimentation in low-flow periods, but may release at least a part of the retained P when plants, algae and bacteria die during the cold season, or as a result of the resuspension of sediment in high-flow situations. It is the dissolved P component that has the most distinct annual pattern of retention and release (see Tanner and Sukias, 2011), and is least efficiently retained in wetlands.

The snapshot pictures of P concentrations that we obtained from the eight wetlands that were sampled on two occasions (section 3.1.2) do not conflict with this view, but these data are not sufficient to prove any claims of P retention efficiencies or variations within the annual cycle. Also, at the Hovi wetland, which was followed more closely, there are obvious uncertainties in the calculated dissolved P fluxes, largely due to the non-sampled periods with unexpectedly high flows in January and December 2011. The data that was available from the Hovi wetland, however, showed no net dissolved P outflow during the sampled period in 2011. But, as stated, with this conclusion we cannot exclude the possibility that wintertime runoff might have shown some P release from the wetland sediments.

Probably the most important feature enabling high sediment and nutrient retention of the Hovi wetland is its high wetland-to-catchment area ratio, resulting in the long residence time of water. This enables efficient nutrient use by biological activity and sedimentation of soil matter during low-flow periods. Not only emergent and submerged macrophyte vegetation, but also bacteria and algae have strongly increased in the wetland during its existence. On the other hand, the capacity of soil matter embedded on the sediment and banks cannot have greatly improved during the 12 years that have elapsed from the construction. In highly productive wetlands degrading organic matter becomes attached to the surfaces of metal oxides (the primary P-adsorbing sediment constituents) and thus consumes some of the P retention capacity of the mineral component. Hence, assimilation of P by wetland biota, and subsequent burial into the wetland sediment as root biomass and accumulated organic sediment matter are probably important, previously a less well recognized mechanism behind the high P retention of the Hovi wetland.

In a separate, ongoing study on wetland sediments, Laakso et al. (2013) have found that the sediment retrieved from the Hovi wetland contained several times higher concentrations of bioavailable P (anion exchange resin-extractable P) than the soil matter of the surrounding fields (i.e., the source of the sediment's mineral component). Among the sediments of the six wetlands studied by Laakso et al. (2013), the bioavailable P concentrations were the highest in the Hovi and the Ojainen wetland sediment. These two wetlands both have water entering them exclusively (or almost so in Ojainen) that originates from agricultural fields, and dissolved P concentrations in inflow water are always higher than in the forest runoff. We may speculate that the base level concentration at Hovi (and at Ojainen) may never drop to so low that the sediment would release substantial amounts of P in the water column, unless a severe oxygen deficiency occurs. In the Hovi wetland, there is a small (about 6 m<sup>2</sup>), 1.5 m deep pothole area (right before the water enters the outlet ditch) that is a spot that may become anoxic during the winter. The high concentration observed on 5 April 2011 in the outlet side might show an instance of anoxia-related P release from this area.

Among the Finnish constructed wetlands, the Hovi wetland is most likely one of the most efficient ones. Usually the efficiency in P retention is associated with the size of the wetland in relation to the size of its catchment so that the bigger the surface area of the wetland in relation to the catchment size, the higher the P retention (e.g., Uusi-Kämpä et al., 2000). However, in their summary of P retention in constructed wetlands in the Nordic countries, Uusi-Kämpä et al. (2000) found a relatively low slope value for this relationship; for example, when the surface area of the wetland was increased from 0.1 to 0.2% of the catchment, P retention was increased by less than five percentage points (e.g., from 30% to 35%), and (as it was stated that P removal occurs as sedimentation of eroded soil matter) this increase largely referred to particulate P. Dissolved P is known to be problematic to tackle, and only a few authors have addressed

this P form in the wetland context<sup>3</sup>. Dissolved P, however, is the P form that is 100% bioavailable for growing algae, bacteria and macrophytes, and it thus has the highest potential to fuel the eutrophication of receiving waters.

## 4.2 Precipitation of dissolved P by ferric sulphate

The purpose of ferric sulphate dosing was to bind dissolved P in a form that is only sparsely available for aquatic organisms. This would suppress the growth of algae and other biomass in the receiving waters, and enhance the settling of P bound as Fe-P associations to ditches or wetland sediments. A doser device that was earlier developed for this kind of application (Närvänen and Jansson, 2007; Närvänen et al., 2008) provided us with a ready concept to work with.

Overall, the results suggested that in most of the pilot sites, a notable reduction in dissolved P could be achieved, from about 30% and up to 75–80%. This is an impressive reduction as compared to any other measure that is used in agricultural water protection, and one of the few methods that decreases the bioavailable, eutrophication-fuelling component of the P load. In addition, there is no lag period after implementation but P precipitation in treated water takes place at once.

Despite the high effectiveness, we emphasize that the dosers should be selectively used, in the first place at sites with high dissolved P concentrations, but not in every ditch within a catchment. This is because (when all other factors are equal) the higher the concentration of dissolved P, the better the precipitation efficiency. Treating only high-P ditches usually shows an effect in the recipient waters, because a large part of dissolved P loads in a catchment often originate either from a minor part of the field area, or via single ditch(es) that may receive leakage from manure storage, as exemplified at the Tammela site.

Logically the P concentrations have a direct effect on the economy of chemical use. In Tammela, cost-efficiency in precipitation of a kilogram of dissolved P was very low (EUR 15–20, with a chemical price of 0.35 eur kg<sup>-1</sup>). At some of the other sites, however, the price for precipitating a kilogram of P was higher, up to about EUR 230–460, but at these ditches only field runoffs were treated. For most sites in this project the price of precipitating a kilogram of dissolved P fell within the range of EUR 100–200. Naturally, the unit price of the chemical, in our project sites ranging from 0.35 to 0.55 eur kg<sup>-1</sup>, also makes a difference. In relation to the results obtained in precipitation of dissolved P, the price is certainly lower than for any measure that is included in the Finnish Agri-Environmental Programme.

The dosers did not work flawlessly, but most breaks in chemical feed were associated with delayed fill-up of the chemical storage. A small storage box can be seen as a shortcoming, but, as discussed earlier, it is advisable to rather downsize than construct dosers with very large capacity, as these may pose a threat to water organisms if they fail and empty a large amount of the chemical into a ditch. It should also otherwise be kept in mind that the use of chemicals such as ferric sulphate needs consideration, including proper personal protection.

With the dosing that we targeted here, ferric sulphate strips dissolved P from the water, but does not yet effectively flocculate particles (soil matter). If removal of soil particles is desired, the dosing should be higher, and the system needs to be optimized for that (i.e., mixing and settling adjusted, pH should possibly also be controlled, etc.). Such high doses of ferric sulphate that also flock solid matter would, however, bring large volumes of sludge that needs calm water to settle. Once settled, sludge should be removed from the ditch or wetland. All this is relatively easily arranged and adjusted in waterworks and wastewater treatment plants, but it would be a challenge to bring about such arrangement in field margins. Some flock formation may take place with the recommended dosing, too, but this was not experienced as disturbing or unaesthetic at the test sites.

---

<sup>3</sup> There is a possibility that dissolved P is disregarded because of the so-called publication bias, which means that positive results are preferably published, whereas data from studies that show no effect remain at the bottom of the researcher's draw. However, see the informative paper of Tanner and Sukias (2011).

### 4.3 Solid P retention media

In principle, a construction with a solid P retention media that has a high retention capacity would be an ideal solution for P mitigation in field ditches. Such a solution would not need much maintenance other than changing the retention media at intervals, P collected from water would be preserved inside the structure for possible recycling, and potential risks associated with handling and use would be much smaller as compared to the use of soluble chemicals. The idea of the use of solid adsorbents in removing P from water was presented at least half a century ago (see Yee, 1966; Shiao and Akashi, 1977), a vast number of laboratory studies performed to find good candidates for P adsorbents, and tests in different scales have been conducted (e.g., see the review of Klimeski et al., 2012). However, there are not many examples of applications that are proven to do the job for longer periods of time.

The decades of laboratory work have shown that there are in practice two types of materials that possess high the P retention required for P sorbents. The one contains metal (hydr)oxides that are also known to be the principal components responsible for P retention in non-calcareous soils and sediments, and possess maximum P retention on the acidic side of the pH scale. The other type of material that sequester P from the solution phase contains soluble earth metals Ca or Mg, which in basic pH form sparsely soluble precipitates with P. In this project, we tested both types of materials, Sachtofer PR being rich in Fe oxides, whereas oil shale ash contains Ca oxides/hydroxides and thus supply  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions to the ambient solution.

Both materials have been tested in laboratory flow-through column studies. Sachtofer PR could in the laboratory retain totally 6–7 mg P  $\text{g}^{-1}$  of fresh material until it reached P saturation (Uusitalo et al., 2012). Retention efficiencies varied from more than 60% during the initial phase to 10–15% at the end of the test. During a five-month test of P retention by oil shale ash, the amount of P retained exceeded 1.6 mg  $\text{g}^{-1}$ , of the about 2.5 mg  $\text{g}^{-1}$  P mass fed in the system (Liira et al., 2009a). After the five months of running the experiment, oil shale ash was not P-saturated, but retention efficiency had decreased from the high 80% to 55% of the P input. Hence, both materials have retention capacities that widely exceed the level that is typically measured for soils, and merited field testing.

In our field tests the materials' P retention was a fraction of that measured in the lab. Initially, in the autumn 2010 and spring 2011, the Sachtofer PR buffer at the Ojainen site showed almost as high sampling-wise retention efficiencies as the earlier laboratory work, at about 50% of the P inflow. However, from the early summer 2011 onwards retention dropped and finally in the autumn of 2012 virtually no P retention could be observed. During the project, the annually averaged P removal efficiency seemed to have always halved from the previous year, and only a fraction of the P retention capacity of the granule mass was utilized. As shown by the tracer test with blue dye that was introduced to the Ojainen buffer, the reason for the poor performance was that water passed through only a fraction of the granule bed and the contact time between the granules and water was very short.

Also at the Rahinge site column tests with Sachtofer PR showed similar or higher P removal efficiencies than was measured at Ojainen, 22–77% and 34–95% removal rates for dissolved P in two different columns, and a clear dependence between P removal and contact time. In addition, a strong reduction in hydraulic conductivity was observed in column tests at the Rahinge site. The stacked filter elements immersed in the ditch showed surprisingly high initial P removal, up to 25%, even though the flow was not directed through the granules. Finally, as soon as algae growth on the surface of the granules took place, the contact between the granules and ditch water was blocked and P retention ceased. In the flume experiments at Rahinge, about 70% maximum P removal rates were recorded. Similar initial P removal rates were also measured for the oil shale ash placed in the flume structure.

With these test set-ups solid P retention materials did not produce high alkalinity in water, nor was there any other harmful element leakage from the materials. The challenges arose more in alterations in the material, such as the break-up of Sachtofer's granular structure that caused flow restriction and most likely affected the onset of preferential flow through the granule bed, or biological growth on the material surfaces. In both cases the result was insufficient contact between the materials and the water, and thus the termination of P retention. Our conclusion is that solid P sequesters remain a promising option to collect P from runoff waters, but the structure design is truly challenging due to the processes in nature favour the formation of short-cuts through the system, or utilize the surfaces for other purposes than those we intend them to be used.

## 4.4 Communication of the Active Wetlands project

### *Finland*

Web pages ([www.wwf.fi/activewetlands](http://www.wwf.fi/activewetlands)) created for communication in the beginning of the project included pilot site introductions with text, photos and videos. A project brochure and a poster were made to be delivered in relevant occasions.

Three media trips were arranged to the pilot sites. The first pilot site in operation of MTT in Jokioinen was presented to media 9.9.2010. A video was made during that media trip presenting the concept of Active Wetlands (AW). The TUAS pilot site in Lieto was presented to the media 13.5.2011, and a third media trip was arranged 15.10.2012 to Paimionjoki pilot site in Somero.

In addition to the technical arrangements and environmental aspects also the motivation and experiences of the farmers were discussed in Somero. The farmer poll, which was made in autumn/winter 2012, was communicated with a press release in January 2013. A general brochure describing different kind of wetlands, the people behind the projects, and also the active measures will be published in April 2013. The brochure will be available in the Internet and is directed to farmers, decision makers and wetland-interested audience.

### *Estonia*

In the beginning of the project web page in Estonian Fund for Nature's (ELF) homepage was created (<http://www.elfond.ee/et/teemad/raba/aktiivmaergalad>). The pages included information about the project, presentations made during the project, information about water samples, pilot investigations made from Estonian University of Life Sciences, and actions in Finland. Furthermore, ELF experts compiled a book (Tehismärgalad: põllumees puhastab vett) describing water protection methods, which is available at: <http://www.elfond.ee/et/teemad/raba/aktiivmaergalad/raamat-tehismaergaladest>.

During the project several seminars and presentations have been made by ELF experts. The concept of AW, novel water protection methods and pilot site in Rahinge was presented in 13.09.2011. ELF experts also introduced AW Project in "Wetlands workshop", which took place in Helsinki (20.09.2011). Several other presentations were made in different events (PhD students seminar, farmers seminar, Estonian wetlands seminar, etc.). In addition, 4 presentations were made, describing a new book (Tehismärgalad: põllumees puhastab vett). During the project, total of 11 presentations were made (including AW final seminar in Estonia (26.03.2013).

---

## 5 Conclusions

---

Most use of a given amount of chemicals or P retention materials can be obtained at sites that are characterized by high concentrations of dissolved P. Such sites are usually limited in size, and/or drain from animal yards or other places where there is manure production, handling and storage. It is these sources of P loading that methods studied in this project should be implemented. Seeking these first-priority (hot-spot) P sources requires sampling along the waterways, but when the measures can be targeted to treat water with high P concentrations, treatment facilities or structures don't need to be sized to also treat other waters that mix with the high-P streams. Hence, when deciding where to install chemical dosers or P sequesters, we suggest that dissolved P concentrations are used as a guideline, rather than plain mass flows. The higher is the dissolved P concentration, the more of the administered chemical is utilized on strictly stripping P, meaning that we get the most use of the money spent on the chemicals.

Ferric sulphate is a particularly good product for P precipitation. It forms ferric hydroxides (Fe compounds that are found in all soils and sediments) when reacting with water and binds dissolved P in a form that is practically non-available nutrient source for algae and plants. In recycling point of view, this may be regarded as a downside, because the material cannot be directly used as a fertilizer product; there is always the trade-off between efficient, reliable P retention and the ease of recycling. However, if the primary target is to quickly decrease fluxes of algal-available P to a lake or a stream from a hot-spot P source, and nutrient recycling only comes in other hand, the used ferric sulphate doser provides a ready concept to work with.

When ferric sulphate is administered to water, a pH decline is observed. In ditch water, an about 0.5 unit drop in pH has been found to be associated with precipitation of most of the dissolved P, but formation of large volume of sludge does not usually take place at this stage. Because a failure in chemical dosing is possible, ferric sulphate dosers need oversight when applied in open systems such as field ditches and wetlands.

Solid P sequester materials also worked well in P retention for some time, but their potential was not demonstrated in field-scale testing. In the field ditches and wetlands, solid surfaces soon become covered with biofilms. Once the surfaces of the solid P retention media become covered, there is no direct contact between the reactive sites and water, and P retention ceases. Even in structures where water passes through a bed of a P retention medium and growth of biofilms is slower, material alterations with time, accumulation of organic molecules, possible clogging of pore volume (due to suspended solids, as example) and formation of preferential flow paths, are other factors that gradually (or abruptly) decrease P retention efficiency. According to our view, the tested solid materials are efficient P sequesters, but the practical application should be further developed.

According to the farmer interviews wetlands are considered as positive landscape elements. They are also taken to decrease some nutrient losses from field areas to surface waters. The idea of enhancing the effectiveness of wetlands in nutrient retention was taken as a positive thought, also when this would be obtained with chemicals. Farmers were also willing to spend some time in maintenance work, but with compensation from the Environmental Support Scheme.

Active Wetlands is an Estonian-Finnish project funded by the Central Baltic Interreg IVA Programme 2007–2013. Co-financing was obtained from all the participating organizations, the Lake Vesijärvi-foundation and national co-financing from the Finnish Ministry of Environment. Authors wish to thank the farmers of the River Paimionjoki and the stakeholders of The Lake Nuutajärvi for co-operation, Ms. Outi Mäkilä (MTT) for her help in editing the report and prof. Eila Turtola (MTT) for valuable comments.

---

## 6 References

---

- Aakkula, J., Manninen, T. and Nurro, M. (eds.) 2010. Maatalouden ympäristötuen vaikuttavuuden seurantatutkimus (MYTVAS 3) – väliraportti. (*Follow-up study of the impacts of agri-environment measures (MYTVAS 3) – interim report*). Publications of the Ministry of Agriculture and Forestry 1/2010. In Finnish.
- Bauert, H., Kattai, V. 1997. *Kukersite oil shale*. pp. 313–327. In: Raukas, A., Teedumäe, A. (Eds.), *Geology and Mineral Resources of Estonia*. Estonian Academy Publishers, Tallinn, Estonia.
- Dobbie, K.E., K.V. Heal, J. Aumônier, K.A. Smith, A. Johnston and P.L. Younger. 2009. Evaluation of iron ochre from mine drainage treatment for removal of phosphorus from wastewater. *Chemosphere* 75: 795–800.
- Ekholm, P. and Krogerus, K. 2003. Determining algal-available phosphorus of differing origin: routine phosphorus analyses versus algal assays. *Hydrobiologia* 492 (1-3), 29-42.
- Heal, K.V., K.A. Smith, P.L. Younger, H. McHaffie and L.C. Batty. 2004. *Removing phosphorus from sewage effluent and agricultural runoff using recovered ochre*. pp. 321-335. In: E. Valsami-Jones. *Phosphorus in Environmental Technologies: Principles and Applications*. IWA Publishing. London, UK. 656 p.
- Heckrath, G., Brookes, P.C, Poulton, P.R. and Goulding, K.W.T. 1995. Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. *Journal of Environmental Quality* 24: 904–910.
- HELCOM. 2009. Eutrophication in the Baltic Sea – An integrated thematic assessment of the effects of nutrient enrichment and eutrophication in the Baltic Sea region: Executive Summary. *Baltic Sea Environment Proceedings* No. 115A.
- Kaasik, A., Vohla, C., Mõtsep, R., Mander, Ü. and Kirsimäe, K. 2008. Hydrated calcareous oil-shale ash as potential filter media for phosphorus removal in constructed wetlands. *Water Research* 42 (4-5): 1315–1323.
- Kõiv, M., Liira, M., Mander, Ü., Mõtsep, R., Vohla, C., Kirsimäe, K. 2010. Phosphorus removal using Ca-rich hydrated oil shale ash as filter material – the effect of different phosphorus loadings and wastewater compositions. *Water Research* 44(18): 5232–5239.
- Kirkkala, T, A.-M. Ventelä and M. Tarvainen. 2012. Long-term field-scale experiment on using lime filters in an agricultural catchment. *Journal of Environmental Quality* 41: 410–419.
- Klimeski, A., Chardon, W.J., Turtola, E. and Uusitalo, R. 2012. Potential and limitations of phosphate retention media in water protection: A process-based review of laboratory and field-scale tests. *Agricultural and Food Science* 21: 206–223.
- Koskiaho, J., Ekholm, P., Rätty, M., Riihimäki, J. and Puustinen, M. 2003. Retaining agricultural nutrients in constructed wetlands - experiences under boreal conditions. *Ecological Engineering* 20(1): 89–103.
- Koskiaho, J. and Puustinen, M. 2005. Function and potential of constructed wetlands for the control of water pollution by diffuse loading. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances & Environmental Engineering* 40(6-7): 1265–1279.
- Koskiaho, J., Puustinen, M. and Kotamäki, N. 2009. Retention performance of a constructed wetland as measured automatically with sensors. Proceedings of the International Symposium on Environmental Science and Technology, June 02-05, 2009 Shanghai, China. *Progress in Environmental Science and Technology*, Vol. II, Part A, 21–30.
- Laakso, J., Uusitalo, R. and Yli-Halla, M. 2013. *Constructed wetland sediment as a source of plant-available phosphorus*. pp. 88–89. In: Maankäytön kestävyys – VII Maaperätieteiden päivien abstraktit (*Sustainability of land use – abstracts of the VII National Congress of Soil Sciences*). Pro Terra 61. In Finnish.

- Liira, M., Kirsimäe, K., Kuusik, R., Mötlep, R. 2009a. Transformation of calcareous oil-shale circulating fluidized-bed combustion boiler ashes under wet conditions. *Fuel* 88(4): 712–718.
- Liira, M., Kõiv, M., Mander, Ü., Mötlep, R., Vohla, C., Kirsimäe, K. 2009b. Active filtration of phosphorus on Ca-rich hydrated oil shale ash: does longer retention time improve the process? *Environmental Science and Technology* 43 (10): 3809–3814.
- McDowell, R.W., Hawke, M. and McIntosh, J.J. 2007. Assessment of a technique to remove phosphorus from streamflow. *New Zealand Journal of Agricultural Research* 50: 503–510.
- Mötlep, R., Sild, T., Puura, E. and Kirsimäe, K. 2010. Composition, diagenetic transformation and alkalinity potential of oil shale ash sediments. *Journal of Hazardous Materials* 184 (1-3): 567–573.
- Neufeld, R.D. and Thodos, G. 1969. Removal of orthophosphates from aqueous solutions with activated alumina. *Environmental Science and Technology* 3: 661–667.
- Närvänen, A., Jansson, H. 2007. Ferrisulfaatti saostaa ojavesisistä liuenneet fosforit. (*Ferric sulphate strips dissolved P from ditch water*). Maaseudun Tiede 64 (2), p. 13. In Finnish.
- Närvänen, A., Puronummi, N. and Jansson, H. 2003. Vesistökuormituskartoitus Etelä-Pirkanmaan alueella. (*Sources of nutrient loading to surface waters in the south Pirkanmaa region*). MTT:n selvityksiä 41. 28 p. In Finnish.
- Närvänen, A., Jansson, H., Uusi-Kämpä, J., Jansson, H. and Perälä, P. 2008. Phosphorus load from equine critical source areas and its reduction using ferric sulphate. *Boreal Environment Research* 13: 265–274.
- Ots A. 2006. Oil Shale Fuel Combustion. Tallinna Raamatutrükikoda, Tallinn, Estonia. p. 833
- Penn, C.J., Bryant, R.B., Kleinman, P.J.A. and Allen, A.L. 2007. Removing dissolved phosphorus from drainage ditch water with phosphorus sorbing materials. *Journal of Soil and Water Conservation* 62: 269–276.
- Penn, C.J., McGrath, J. M., Rounds, E., Fox, G. and Heeren, D. 2012. Trapping phosphorus in runoff with a phosphorus removal structure. *Journal of Environmental Quality* 41:672–679.
- Puustinen, M., Koskiaho, J., Jormola, J., Järvenpää, L., Karhunen, A., Mikkola-Roos, M., Pitkänen, J., Riihimäki, J., Svensberg, M. and Vikberg, P. 2007. Maatalouden monivaikutteisten kosteikkojen suunnittelu ja mitoitus (Multipurpose wetlands for agricultural water protection – guidelines of wetland planning and dimensioning). *The Finnish Environment* 21/2007. Finnish Environment Institute (SYKE). Helsinki. 77 p. In Finnish with English abstract.
- Saarela, I. 2002. Phosphorus in Finnish soils in the 1900s with particular reference to the ammonium acetate soil test. *Agricultural and Food Science in Finland* 11: 257–271.
- Sharpley, A.N. 1985. The selective erosion of plant nutrients. *Soil Science Society of America Journal* 49: 1527–1534.
- Shiao, S.J. and Akashi, K. 1977. Phosphate removal from aqueous solution from activated red mud. *Journal of Water Pollution Control Federation* 49, 2: 280–285.
- Shilton, A. N., I. Elmetri, A. Drizo, S. Pratt, R.G. Haverkamp and S.C. Bilby. 2006. Phosphorus removal by an ‘active’ slag filter—a decade of full scale experience. *Water Research* 40: 113–118.
- Tanner, C.C., Sukias, J.P.S. and Yates, C.R. 2010 New Zealand guidelines: Constructed wetland treatment of tile drainage. *NIWA Information Series No. 75*. National Institute of Water & Atmospheric Research. Ltd. Hamilton, New Zealand.
- Tanner, C.C. and Sukias, J.P.S. 2011. Multiyear nutrient removal performance of three constructed wetlands intercepting tile drain flows from grazed pastures. *Journal of Environmental Quality* 40: 620–633.
- Uusi-Kämpä, J., Braskerud, B., Jansson, H., Syversen, N. and Uusitalo, R. 2000. Buffer zones and constructed wetlands as filters for agricultural phosphorus. *Journal of Environmental Quality* 29:151–158.

- Uusi-Kämpmä, J., Turtola, E., Närvänen, A., Jauhiainen, L. and Uusitalo, R. 2012. Phosphorus mitigation during springtime runoff by amendments applied to grassed soil. *Journal of Environmental Quality* 41:420–426.
- Uusitalo, R. and Jansson, H. 2002. Dissolved reactive phosphorus in runoff assessed by soil extraction with an acetate buffer. *Agricultural and Food Science in Finland* 11: 343–353.
- Uusitalo, R., Turtola, E., Kauppila, T. and Lilja, T. 2001. Particulate phosphorus and sediment in surface runoff and drainflow from clayey soils. *Journal of Environmental Quality* 30: 589–595.
- Uusitalo, R., Turtola, E., Puustinen, M., Paasonen-Kivekäs, M. and Uusi-Kämpmä, J. 2003. Contribution of particulate phosphorus to runoff phosphorus bioavailability. *Journal of Environmental Quality* 32: 2007–2016.
- Uusitalo, R., Ekholm, P., Lehtoranta, J., Klimeski, A., Konstari, O., Lehtonen, R. and Turtola, E. 2012. Ca–Fe oxide granules as potential phosphate barrier material for critical source areas: a laboratory study of P retention and release. *Agricultural and Food Science* 21: 224–236.
- Veskimäe, H., Kuusik, R., Veiderma, M. 1997. Phosphorus removal from solutions by carbonaceous wastes. *Proceedings of the Estonian Academy of Sciences. Chemistry* 46 (1/2): 21–30.
- Vohla, C., Pöldvere, E., Noorvee, A., Kuusemets, V., Mander, Ü. 2005. Alternative filter media for phosphorus removal in a horizontal subsurface flow constructed wetland. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering* 40 (6-7): 1251–1264.
- Wilander, A. 1994. Estimation of background sulphate concentrations in natural surface waters in Sweden. *Water, Air and Soil Pollution* 75: 371–387.
- Yee, W.C. 1966. Selective removal of mixed phosphates by activated alumina. *Journal of the American Water Works Association* 58: 239–247.