MITIGATING AGRICULTURAL PHOSPHORUS LEACHING

The Effect of Timing in Grass Harvesting in Mitigating Wintertime Phosphorus Leaching

Katariina Yli-Heikkilä

Bachelor's thesis
June 2012
Environmental Engineering
Tampere University of Applied Sciences

TAMPEREEN AMMATTIKORKEAKOULU
Tampere University of Applied Sciences

ABSTRACT

Tampereen ammattikorkeakoulu
Tampere University of Applied Sciences
Degree Programme in Environmental Engineering

YLI-HEIKKILÄ, KATARIINA: Mitigating Agricultural Phosphorus Leaching

The Effect of Timing in Grass Harvesting in Mitigating Wintertime Phosphorus Leaching

Bachelor's thesis 61 pages, appendices 10 pages
June 2012

The purpose of this thesis was to study how much the above-ground grass biomass, harvested at different times during the growing season, contains phosphorus at the end of the growing season, and how much of it is leached after freezing and thawing. The study aims to give information about the ideal time for grass harvesting in order to mitigate the wintertime phosphorus leaching.

The grass biomass was harvested from managed uncultivated arable field at MTT Agrifood Research Centre experimental site in Jokioinen, Finland. The grass biomass was taken from an area of 0.25 m^2 on 26 September 2011. The first growth of each experiment was harvested as follows: June (22 June), July (5 July) and August (1 August). The grass biomass contained grass, legumes and weed. Four freeze−thaw cycles were conducted for a 10 grams sample (fresh weight) in laboratory conditions. In every cycle the thawed grass biomass was leached with deionised water (400 ml). The water samples were analyzed for dissolved reactive phosphorus and total phosphorus. The dried grass biomass was analyzed for the phosphorus concentration.

The grass biomass that had grown after the harvest in June had the highest phosphorus content at the end of the growing season (628−871 mg m^{-2}). The grass biomass harvested in July had the least phosphorus (380−538 mg m^{-2}). The grass biomass harvested in August had phosphorus content 436−601 mg m^{-2} at the end of the growing season. Also the dry matter yield was to a similar extent, being the highest in June harvested grass biomass (255−341 g m^{-2} dry matter). The highest dissolved reactive phosphorus and total phosphorus concentrations were in the water samples from the youngest grass biomass harvested in August. However, it did not effect on the total phosphorus leaching as the dry matter yield was rather low. Also the difference in the phosphorus concentration of the water samples of different harvesting times was negligible. The water sample results showed that 90% of the total phosphorus of the grass biomass was leached after the second freeze−thaw cycle.

According to the results it is recommended to harvest the grass biomass later during the growing season. Also it is recommended to collect the swath in order to mitigate the leaching of dissolved reactive phosphorus. The current harvesting time instructions for managed uncultivated fields are therefore suitable (latest 31 August and for buffer zones harvest after 1 August). It is though important not to damage the soil structure when harvesting later in autumn.

Key words: agriculture, eutrophication, freezing, leaching, phosphorus

TIIVISTELMÄ

Tampereen ammattikorkeakoulu
Environmental Engineering koulutusohjelma

YLI-HEIKKILÄ, KATARIINA: Fosforihuuhtouman vähentäminen maataloudessa
Talviaikaisen fosforihuuhtouman vähentäminen nurmen oikea-aikaisella niitolla

Opinnäytetyö 61 sivua, josta liitteitä 10 sivua
Kesäkuu 2012

Tämän opinnäytetyön tarkoituksena oli tutkia, kuinka paljon eri aikaan niitettyjen nurmien kasvustoissa oli kasvukauden päättyessä fosforia, ja paljonko kasvustoista huuhtoutui fosforia jäätymisen ja sulamisen seurauksena. Tavoitteena oli löytää optimaalinen niittoajankohta nurmikasvustoille talviaikaisen fosforihuuhtouman vähentämiseksi.

Nurminäytteet kerättiin Maa- ja elintarviketalouden tutkimuskeskuksen hoidetun viljelemättömän pellon koekentältä Jokioisilla. Näytteet otettiin 0,25 m^2:n alalta kasvukauden lopussa 26.9.2011. Koejäsenet oli niitetty kerran aikaisemmin kasvukaudella joko kesäkuussa (22.6.), heinäkuussa (5.7.) tai elokuussa (1.8.). Tutkittava nurmibiomassa koostui heinistä, palkokasveista ja rikkakasveista. Näytteistä otettiin 10 gramman (tuorepaino) otos jäätymis-sulamiskoetta varten. Laboratorio-olosuhteissa toteutettiin neljä viikonmittaista jäätymis-sulamissykliä. Joka syklissä sulatettua nurmibiomassaa huuhdeltiin deionisoidulla vedellä (400 ml). Vesinäytteistä analysoitiin kokonaisfosfori ja liukoinen fosfori. Kuivatusta kasviaineksesta määritettiin kuiva-aine- ja kokonaisfosforipitoisuudet.

Kesäkuussa niitetyssä biomassassa oli kasvukauden päätyttyä eniten fosforia (628−871 mg m^{-2}) ja heinäkuussa niitetyssä kasvustossa vähiten (380−538 mg m^{-2}). Elokuussa niitetyssä kasvustossa oli fosforia 436−601 mg m^{-2}. Myös kuiva-ainesato oli suurin kesäkuussa niitetyssä kasvustossa (255−341 g m^{-2} kuiva-ainetta). Vaikka suurimmat fosforipitoisuudet huljutteluvesissä oli nuoressa elokuussa niitetyssä kasvustossa, se ei ollut niin merkittävää kokonaisfosforihuuhtouman kannalta, koska biomassasato oli vielä vähäinen nuoressa kasvustossa. Erot vesinäytteiden fosforipitoisuuksissa olivat pienet. Huljutteluvesitulosten mukaan jo toisen jäätymis- ja sulamiskerran jälkeen kasvin kokonaisfosforimäärästä oli poistunut lähes 90 %.

Tulosten perusteella voidaan todeta, että myöhäinen niittoajankohta kesällä on suositeltava ja niittojätteen kerääminen pellolta vähentää talvella liukoisen fosforin huuhtoumaa. Nykyiset niittoajankohtasuositukset hoidetuille viljelemättömille pelloille ovat hyviä (luonnonhoitopelloilla viimeistään 31.8., suojakaistavyöhykkeillä aikaisintaan 1.8.). Syksyllä niitettäessä on huomioitava, ettei märkää maata tiivistetä raskailla niittokoneilla.

Asiasanat: fosfori, huuhtoutuminen, jäätyminen, maatalous, rehevöityminen

ACKNOWLEDGEMENT

This work has been conducted as thesis study for Bachelor of Engineering degree at Tampere University of Applied Sciences. The experimental part of this thesis has been carried out in the facilities of MTT Agrifood Research in Jokioinen. The work has been funded by Maa- ja vesitekniikan tuki ry, and Marjatta ja Eino Kollin säätiö.

I wish to thank all the colleagues at MTT for getting me interested in the secrets of soil science and guiding me through this thesis work. Furthermore I wish to thank the ever so helpful laboratory personnel at MTT who assisted me in the process of this work.

I wish to thank the thesis supervisors, lecturer in Environmental Engineering Eveliina Asikainen at TAMK and PhD, senior research scientist Jaana Uusi-Kämppä at MTT for the constructive criticism and encouragement to successfully carry out this thesis in a short period of time.

Loimaa, June 2012

Katariina Yli-Heikkilä

TABLE OF CONTENTS

1 INTRODUCTION

1.1 Theoretical background

Eutrophication of water courses is a serious ecological problem and dissolved reactive phosphorus (DRP) has been proven to be the main trigger of eutrophication. In Finland almost 70% of the phosphorus (P) load entering the water course, as generated by human activity, is estimated to originate from agriculture. More than 90% of P load occur outside the growing season, that is, winter time. Vegetation cover is one way of mitigating wintertime P leaching in agriculture, and it is effective especially in reducing P attached to soil particles. However, earlier studies have proven that wintertime vegetation may even increase the leaching of DRP. Therefore it is recommendable to study and develop methods to mitigate the leaching of P in agriculture. (Puustinen et al. 2007a; Uusi-Kämppä & Jauhiainen 2010; SYKE 2012)

Earlier studies have proven that leaching of DRP increases if the above-ground biomass freezes or dries (e.g. Timmons, Holt & Latterell 1970; Miller, Beauchamp & Lauzon 1994; Uusi-Kämppä & Jauhiainen 2010). Significant part of arable land area in Finland has winter time vegetation cover (e.g. grasslands, nature management fields, green fallows and grassed buffer zones). Hence there is a significant amount of biomass containing P frozen over the winter which is leached in spring by snow melt and rain. Concern over diffuse P losses from agricultural lands to surface waters in frigid climates has focused attention on the role of freezing and thawing on P loss from crops (Liu, Khalaf & Ulén 2011). Therefore it is important to study different methods of mitigating wintertime P losses.

Also the depletion of P raw material calls for better nutrient management in agriculture. The production of food depends on a constant supply of P. Securing sufficient P for agricultural production is one of the biggest global challenges for the future to provide food for growing population. (Cordell, Drangert & White 2009)

1.2 Objective

The aim of this work is to study how much the grass biomass, harvested at different times during the growing season, contains P at the end of the growing season, and how much of it is leached by demonstrating the wintertime freeze−thaw cycle in laboratory conditions. Earlier study has proven that the amount of P differs during the growing season. Usually the amount of P is highest at the early stages of the growth (Uusi-Kämppä & Kilpinen 2000). The purpose is to find an optimal harvesting time for the grass biomass to mitigate the wintertime P losses on vegetation covered fields. The other important nutrient, nitrogen, was left out of the study because of technical reasons.

1.3 Material and methods

This study focuses on the effect of harvesting time of grass biomass in mitigating wintertime P leaching. The grass biomass samples for the study are collected from perennial managed uncultivated field. Fertilizer has not been applied to the field. The grass biomass used in the study consists of grass, legumes and weed (Niemeläinen 2012) and is here after referred to as grass biomass. The grassland is located at MTT Agrifood Research Finland’s experimental field in Jokioinen in southwest Finland. The wintertime P leaching is studied in laboratory conditions by demonstrating wintertime freeze−thaw event in freezer and cold room. The initial P content of the grass biomass is measured, and the amount of leached P after each freeze−thaw cycle.

1.4 MTT Agrifood Research Finland

MTT Agrifood Research Finland (later MTT) is the leading research institute developing sustainability and competitiveness of the food system. MTT is operating under the Ministry of Agriculture and Forestry in Finland. This study is part of a research project at MTT in which plant residues from managed uncultivated fields are studied as a resource for biogas production. The results of this study can be used in other research projects at MTT related to mitigating P leaching. Also the results can be used in instructions and directives that aim at mitigating the P load from agriculture, preventing eutrophication and improving the quality of water courses.

In this thesis chapter 2 explains the theory behind eutrophication: the causes of eutrophication and the measures taken to restore the water courses in Finland. Chapter 3 concentrates on the importance of P as a depleting natural resource, and as a raw material in plant production and in food chain. This chapter also summarizes some of the previous studies on the effects of freezing and thawing in P leaching. Chapter 4 explains the impact of agriculture to water quality and review water protection measures on political level in agriculture. Chapter 5 describes few common measures in mitigating P leaching in agriculture. In chapter 6 and 7 concentrate on the empirical study describing the material and methods (chapter 6) and presenting the results (chapter 7). Finally results are discussed in chapter 8 and conclusions based on them are given in chapter 9.

2 EUTROPHICATION AND RESTORATION OF WATER COURSES

2.1 Eutrophication

Eutrophication is a serious ecological problem facing fresh waters and coastal waters in Finland. In aquatic ecosystems increased availability of main plant nutrients (phosphorus (P) and nitrogen (N)) results in eutrophication. P is usually the cause of eutrophication in fresh waters, while N is causing eutrophication in coastal waters. Though eutrophication is a natural phenomenon the anthropogenic influence such as excess nutrient pollution in wastewater, runoff from agriculture, and atmospheric deposition can trigger eutrophication processes. (Shortle, Abler & Ribaudo 2001, 4; SYKE 2012)

Increasing P level in slow-moving, shallow waters stimulates algae growth causing eutrophication and severely affecting the aquatic ecology. Eutrophication in lakes can be easily observed by turbidity, rising in plant productivity, and algae blooms. Algae blooms take up dissolved oxygen, depleting the oxygen available for fish and other aquatic life. Algae blooms can also block the sunlight needed by aquatic vegetation, causing the vegetation to die off. (Shortle et al. 2001, 4)

According to the Finnish Environment Institute SYKE (later SYKE) most the fresh water courses in Finland have good ecological status (FIGURE 1). 52% of rivers, 73% of the lakes, and 15% of the coastal waters (by numbers of water courses in each category) had high or good ecological status in Finland in 2008 (SYKE 2009). Though lakes and rivers in Finland tend to be in good condition approximately fifth of the Finnish surface waters is affected by eutrophication, that is, have moderate to bad ecological status. Most of Finnish river basins belong to the catchment area of the Baltic Sea thus causing the deterioration of the Baltic Sea as well. (SYKE 2012)

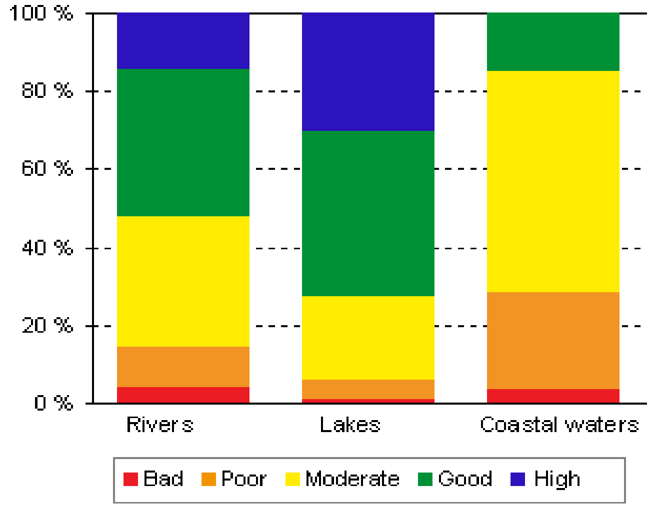


FIGURE 1. The ecological status of rivers, lakes and coastal waters (by numbers of water courses in each category) in Finland in 2008. 52% of rivers, 73% of the lakes, and 15% of the coastal waters have high or good ecological status. (SYKE 2009)

In the Finnish conditions especially the shallowness of the lakes triggers the nutrient enhancement. The Finnish lakes and coastal waters are naturally shallow because the rocks have been gradually evened out by erosion over millions of years, and during successive recent ice ages. Also the morphological features of the Finnish water courses have been altered in the course of time. Problems related to the shallowness of lakes derive largely from the period between the end of the 19th century and the 1960s, when the water level of several lakes was lowered to increase the arable land area. The natural morphology of streams has been severely altered by widening, deepening and straightening of the streams. Also natural obstacles such as large rocks have been removed and several rocky rapids have been destroyed to enhance forest industry. (SYKE 2012)

Eutrophication is also a societal challenge. Apart from reducing biodiversity, the loss of aquatic life because of eutrophication can cause significant aesthetic and economic damage. The growth and subsequent decomposition of algae can be unpleasant and generate malodorous, inconvenience environment for those living or working near polluted waters. Recreational fishing, boating and swimming can be adversely affected, to the harm of those who engage in these activities and those who earn their living from them. (Shortle et al. 2001, 5)

2.2 Point and diffuse sources of nutrient loading

Accelerated or anthropogenic eutrophication is caused by P entering streams from both point sources and diffuse sources. Point sources (e.g. centralized sewerage treatment plant outflows and industries) are relatively easy to identify, regulate, and clean up. Different regulations have ensured achievements in reducing the P loading from point sources. (Brady & Weil 2002, 596) Urban waste water treatment in Finland changed significantly in the 1950s−1960s when great deal of houses was installed with water pipes and the amount of grey water from kitchens and bathrooms, and waste from the flush toilets increased. In the 1970s 20−50% of P was removed from urban waste waters. Since that the nutrient removal methods have become more efficient. 96% of the P was removed from urban waste waters in Finland in 2007 covering about 83% of the Finnish population. (SYKE 2009)

Diffuse sources, on the other hand, are difficult to identify and control. Diffuse sources of P are principally runoff water and eroded sediments from soils, and atmospheric deposition (dust and rain) scattered throughout the affected catchment area. (Brady & Weil 2002, 596) Agriculture is reportedly the largest contributor to diffuse nutrient loading as generated by human activity. The impact of agriculture to water quality is more closely explained in chapter 4, and chapter 5 describes methods in mitigating P leaching in agriculture. In addition to agriculture, rural waste waters are causing diffuse loading. 17% of the Finnish population lives in sparsely populated areas not connected with centralized sewerage system. Their waste waters accounts for about 10% of the total P load. The new waste water treatment requirements came into force in 2011 and by 2018 all onsite wastewater systems should be equipped with best available treatment techniques. (SYKE 2012)

2.3 Restoration of water courses

The changes in the quality of water courses were recognized after the Second World War when, for example, in the 1960s some of the lakes in Finland did not meet the health regulations set for public beaches because of pollution. At first, restoration work was mainly designed to benefit fish stocks, but as the increased recreational use of the waters was affected by the deterioration of the rivers and lakes also the aims of restoration changed. Since then several Finnish lakes have been restored to achieve natural status. Traditionally restoration has been carried out by raising the water level and by using aeration or macrophyte (aquatic plants) control. Also the lake ecosystem can be altered by biomanipulation where certain selective fish are removed and the stock of piscivorous fish is increased. (SYKE 2012) New methods have been also studied and developed, for example methods to capture P in sediments (Turtola, Ekholm & Chardon 2010).

Sustainable restoration results are however impossible to achieve if the external nutrient loading from the entire catchment is not decreased. And even if the external loads of nutrient pollution entering aquatic ecosystems would be cut, a self-perpetuating process can continue as the internal loads of stored nutrients (accumulated in soil and water) are repeatedly reabsorbed into the water, where they feed the regrowth of plants. To decrease the internal loading, nutrients in the lake sediment have been removed by dredging or completely draining the lake (temporary). (SYKE 2012)

The Water Framework Directive of the EU supports the approach of taking the whole catchment area into account in water protection. The water protection in Finland aims at restoring water courses and shorelines to a natural state. Regional environment centers provide advice in planning and carrying out restoration projects together with municipalities, regional fisheries authorities and restoration consultants. Such restoration projects have been for example PUREVA1 (2005−2008) and PUREVA2 (2008−2012) projects for restoring brook and catchment areas in Central Finland, and VELHO (2011−2013) which aims at regional and local implementation of river basin and nature management in water courses in Southwestern Finland. SYKE participates in developing restoration methods and environmental education. (SYKE 2012)

3 PHOSPHORUS

3.1 Phosphorus as a natural resource

By far the largest use of P is in fertilizers, accounting for around 90% of total P consumption (Saavalainen 2012b). P containing fertilizers are manufactured from phosphate minerals. Apatite, which is found also in Finland, is one group of phosphate minerals. P containing fertilizers are manufactured from apatite by digesting with sulfuric acid to produce phosphoric acid and further processing that to fertilizers. Efficient use and management of P is necessary as phosphate is a non-renewable resource. Currently there is no known substitute for P in agriculture and no alternatives to phosphate rock either. (Cordell et al. 2009; Saavalainen 2012a)

Phosphate is a dwindling natural resource and there are several different estimations when the phosphate ore reserves will be depleted. U.S. Geological Survey (2012) has estimated that the US phosphate reserves would last for 25 years and the current global reserves may be depleted in 50−100 years. Other sources estimate the global reserves to last for 370 years but the reduction of good quality raw material will make the extraction more expensive. Nevertheless, according to scientific studies the world is facing peak phosphorus which will affect largely on food production and human nutrition. (Cordell et al. 2009; Saavalainen 2012a)

Depletion of P might cause geopolitical tension as the phosphate ore reserves are not evenly distributed in the crust of earth. For example 60% of the reserves are located in Western Sahara (controlled by Morocco) and it is estimated that by 2100 the reserves in Western Sahara will cover almost 90% of the total global reserves. Other major reserves are located in China, the United States, Jordan, and South Africa. The only phosphate ore mine in Western Europe is in Finland in Siilinjärvi and since 2007 it is owned by Norwegian chemical company Yara. The apatite reserve was found in 1950 by a worker during the construction of a railway. Another potential strategic phosphate ore reserves in Finland was found in 1967 in Sokli but the mining has not started yet. These both mines in Finland are significant as they offer good quality raw material for phosphorus, containing only small traces of hazardous heavy metals. The easily accessible apatite reserves in Siilinjärvi will last for at least 20 years and in Sokli for 20−30 years once a mine becomes operational. (Saavalainen 2012a; Saavalainen 2012b; U.S. Geological Survey 2012; Yara 2012)

To tackle the looming food crisis, the use of P needs to be controlled globally to provide adequate supply for all, especially in the areas of P deficient soils and famine (such as sub-Saharan Africa). (U.S. Geological Survey 2012) The gaps in the P cycle are also a significant economical challenge and in other words money is being wasted in P losses. The price of P has become highly variable. Before 2007 the price had been constant for several years, and in 14 months alone it rose from approximately 50 €/t to 350 €/t (700%). The price fell off almost as rapidly and has been around 150 €/t since. The sudden P price crisis is already an indicator of the looming P resource crisis. (Cordell et al. 2009; InfoMine 2012)

3.2 Phosphorus use in agriculture

The need for P is increasing as the need for fertilizers in food production is increasing. The global increase in meat and dairy production increases the amount of P needed in fertilizers. (Cordell et al. 2009; Saavalainen 2012b) Though the raw material for P is non-renewable resource, but unlike oil P can be recycled. To achieve efficient use of P more methods are needed to trap and recycle P. Also alternative sources of P for fertilizing has been studied and implemented such as recirculation of human excreta. Also fishing could be one way to recover and recycling P from the sea, as about 1% of the fresh weight of fish comprises of P. (Saavalainen 2012b; U.S. Geological Survey 2012) Waste water has a significant amount of P which is mostly removed in the waste water treatment process. Already 80% of the treated waste water treatment sludge is used in landscaping as fertilizer or soil enrichment. 12% of the sludge is used in agriculture and the rest is disposed on landfills. Because of possible traces of heavy metals and pathogens there are regulations that prevent to some extent the use of waste water sludge in agriculture. (SYKE 2012)

Manure is widely used as fertilizer in Finland especially in regions where animal husbandry is common (such as Ostrobothnia). Manure is high in P and the use and safety of manure as fertilizer has been studied to prevent any harmful impacts. The efficient use of animal manure would be a huge benefit, as large amounts of P ends up in the manure.

At the moment manure is not, however, used efficiently as fertilizer because industrial animal production is no longer linked closely with crop production. For larger scale use manure should be in an easily transportable form (e.g. briquette). In Finland this would allow transporting manure from Ostrobothnia to Southwest Finland. (Saavalainen 2012c)

As the world is facing peak phosphorus more methods are needed to return the P back to the nutrient cycle instead of releasing it to the water courses. The swath collected from nature management field could be used as cattle feed and the P could be returned to the field as manure. The swath could be also used in biogas production, for example, and the digest could be returned to the field as fertilizer.

3.3 Phosphorus cycle in plant production

Phosphorus (P), nitrogen (N) and potassium (K) together are the most limiting nutrients in plant production. P is an essential component for all organisms since it is part of fundamental processes such as storage and transfer of genetic information (DNA and RNA), cell metabolism, and in the energy systems of the cells (adenosine triphosphate, ATP). ATP drives most energy-requiring biochemical processes. For example, the uptake of nutrients and their transport within the plant are energy-using plant processes that require ATP. Plants contain only small amount of P (0.2−0.4% of dry matter). Too little P commonly limits the productivity of natural and cultivated plants and is the cause of widespread soil and environmental degradation. P-deficient plants, containing P 0.1% of dry matter (DM), are often severely stunted. (Jaakkola 1992, 223−224, 226; Ashman & Puri 2002, 63; Brady & Weil 2002, 592−593)

Plants take up P through their roots from soil water surrounding the roots. Plants retrieve P in the beginning of the growth and in the early stages of growing season. P is very mobile within the plant. P in older parts of the plant is mobilized and transferred to newer parts in case of P supply shortage. Approximately 10% of the P added to the soil in fertilizers is used by the plants. The rest of the needed P is retrieved from the soil P which is slowly diluted. Most of the soil P is in an unavailable form for the plant to use, that is, attached to soil particles. The concentration of P in soil water is typically low and plants can take up P only as orthophosphate ions $H_2PO_4^-$ or as $HPO^2{}_4^-$. The ionic form that is predominantly absorbed depends on soil pH. $H_2PO_4^-$ is more readily absorbed in low pH soils whereas HPO_4^{2-} is preferentially absorbed in high pH soils. The maximum amount of plant-available P occurs in the pH range of 6−7. Phosphate anions form insoluble compounds at low and high pH ranges. For example in lower than pH 6.0 conditions aluminum and iron are more soluble and absorb P. Supplying lime to the soil increases pH and increases the solubility of P in the soil. (Jaakkola 1992, 225−226; Ashman & Puri 2002, 66; Brady & Weil 2002, 593)

In Finland approximately 11,000 t/a P is added to the fields in fertilizers and 17,000 tons in manure. Some of the P added to the field is attached to the soil particles or leached to the rivers and lakes and 21,800 t/a P is removed in the harvest. Out of the harvested yield about 70−80% is used in cattle feed (and returned in the cycle as manure) and the rest in human nutrition and is ended up in the waste water. (Saavalainen 2012b)

In natural ecosystems the P removed by the plants from soil is mostly returned in plant residues and is available for future plant uptake. In agricultural ecosystems P constraints are much more critical because P in the harvested crops is removed from the system, with only limited quantities being returned in crop residues (FIGURE 2). As a result, extreme P deficiencies in soils are common (such as in sub-Saharan Africa) or excessive amounts of P is added to the soil to meet plant needs. (Brady & Weil 2002, 592)

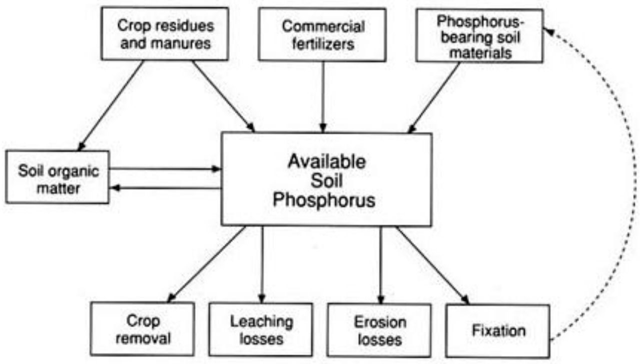


FIGURE 2. The cycle of phosphorus available to plant uptake. (Buchmann & Brady 1969)

During the past few decades in most areas of industrialized agriculture much more P was applied (fertilizers or manure) than was removed in harvested crops. FIGURE 3 shows the increase in phosphorus added in manure and fertilizers after the 1940s and the decrease after 1980s. As a result of increased fertilization, soils have accumulated rather high level of TP and DRP. (Hartikainen 1992, 316)

Different measures have been applied since to decrease the accumulation of P used in fertilizers. However, according to a recent study, there still was excessive P fertilizing applied to Finnish soils during 2005−2009 (Saavalainen 2012b). Runoff, leaching, and erosion from these soils have moved some of this P into streams, lakes, ponds, and reservoirs, triggering the process of eutrophication (Brady & Weil 2002, 592−593).

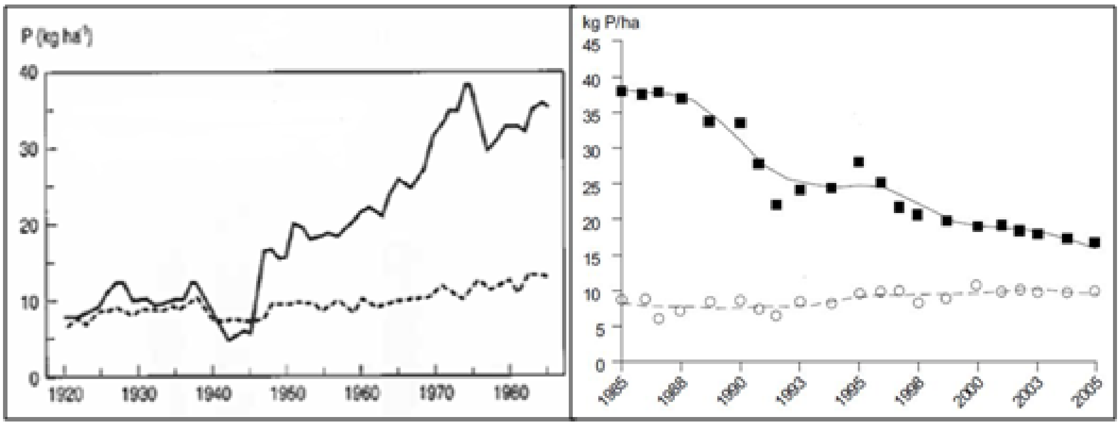


FIGURE 3. On the left side phosphorus added in manure and fertilizers in kg ha^{-1} (upper line) and phosphorus retrieved in the yield kg ha^{-1} (lower line) in Finland during 1920−1985. (Sillanpää 1986, cited in Hartikainen 1992, 316) On the right side the same after 1985 until 2005 (Turtola & Lemola 2008, 12)

3.4 The effect of freezing and thawing in phosphorus leaching

Manure and fertilizer leaching into water from arable land has been long regarded as a pollution hazard. Harley, Moon and Regeimbal (1951) studied the effect of plant material in nutrient leaching and discovered that plant cover may also be a source of nutrient losses. Later for example Timmons et al. (1970) and White (1973) studied the effects of freezing and drying on nutrient loss from above-ground biomass and discovered that the P leaching increases if the above-ground biomass freezes or dries. White (1973) also concluded that release of nutrients (including P) to runoff water after freezing was probably important if the vegetation is still growing when frozen. These effects may not be as great if the plant material has lost much of its moisture before freezing. At lower moisture contents the cell membranes will not be disrupted as much by freezing (White

1973). Several other studies on field and in laboratory conditions have been conducted on the effect of freezing and drying of biomass (for example Uhlen 1979; Ulén 1984; Miller et al. 1994; Bechmann, Kleinmann, Sharpley & Saporito 2005; Uusi-Kämppä & Jauhiainen 2010).

Permanent plant cover on field (e.g. buffer zones, cover crops) is one way of decreasing soil erosion and particulate P runoff (Bechmann et al. 2005; Uusi-Kämppä & Jauhiainen 2010). However, permanently vegetated field areas appear to be ineffective in reducing losses of DRP according to a study conducted on boreal clayey soils. On the contrary, DRP losses often increase when fields or field margins are left uncultivated. (Uusi-Kämppä & Jauhiainen 2010)

According to Uusi-Kämppä et al. (2011) the highest amount of P was on buffer zone plants that were not harvested at all during the growing season. Also it has been observed that the P content of buffer zone plants differ during the growing season (Uusi-Kämppä & Kilpinen 2000). The low frost tolerance of agricultural plants might lead to cell damage during the freeze−thaw events at winter time and may cause leakage of soluble components (Bechmann et al. 2005). Harvesting the grass biomass at the time of the highest P content and collecting the swath may decrease DRP runoff (Uusi-Kämppä & Kilpinen 2000).

4 WATER PROTECTION IN AGRICULTURE

4.1 The impact of agriculture to water quality

Agriculture has pervasive impacts on water quality. Conversion of areas in natural condition (e.g. forests, wetlands) to crop and grazing lands has reshaped landscapes and the hydrology and ecology of agriculturally developed regions. Dams and diversions (for irrigation and flood prevention) hinder fish migration, alter stream flow regimes and water temperatures, and trap sediments. Surface runoff from cropland carries salt, fertilizers, pesticides, pathogens and other pollutants into surface waters, damaging aquatic ecosystems and wildlife, degrading drinking water supplies and damaging water for commercial and recreational uses. Pesticides and other chemicals applied to cropland might also enter aquifers used for drinking water, posing risks to human and animal health. (Shortle et al. 2001, 1)

There are several reasons for the leaching of nutrients such as excessive fertilization, and the soil structure. Most of the arable land area in Finland is located in the western and southwestern parts of Finland where the landscape is flat and the soil structure is clayey. In these conditions the fields and also forests for timber and peat production has to be well drained. According to Finnish Field Drainage Association (2012) only 15% of land area in Finland would be arable without drainage. 75% of arable land in Finland is already sub-drained and 22% of the total forest area is drained. Such drainage schemes facilitate crop cultivation but well maintained ditches and streams carry eroded soil material, humus and nutrients to the larger water courses. Several studies suggest that eroded material can be transported also via subsurface drains (Uusitalo et al. 2001; Turtola et al. 2007; Vakkilainen et al. 2010) (Warsta 2011).

One of the leading water quality issue associated with agriculture is nutrient loading by P and N. The leaching of these nutrients agriculture is the principal cause of eutrophication of water courses. TABLE 1 demonstrates that in Finland, agriculture accounts for 68% of TP and 56% of TN load to water courses as generated by human activity (SYKE 2012).

TABLE 1. Phosphorus (P) and nitrogen (N) loading in Finland 2010. (SYKE 2012)

	P t/a	P %	N t/a	N %
Total loading	**4015**	**100.0**	**69566**	**100.0**
Point sources	**479**	**12**	**15513**	**22**
Pulp and paper industry	150	4	2434	4
Other industry	25	0.5	894	1
Municipalities	163	4	10650	15
Fish farming	76	2	620	1
Fur farming	45	1	430	0.5
Peat production	20	0.5	485	0.5
Diffuse sources	**3336**	**83**	**45253**	**65**
Agriculture	2750	68	39500	56
Forestry	231	6	3253	4
Dispersed settlement	355	9	2500	5
Deposition	**200**	**5**	**8800**	**13**

Nutrients can enter water courses in four ways. Runoff transports nutrients over the soil surface by rainwater, snow melt or irrigation water, and does not penetrate to soil. Nutrients are either dissolved in runoff water or adsorbed to eroded soil particles. Run-in transports chemical and nutrients directly to groundwater for instance through sink-holes, porous or fracture bedrock. Leaching is the movement of nutrients through the soil by percolating rain, thawing snow or irrigation water. N can also enter water courses through atmospheric deposition (rain or dust). N in the form of nitrate is easily soluble and is transported in runoff, in sub-surface drainage and with leachate. P is only fairly soluble and, the soil water concentration of phosphorus is very low. P is also not very mobile in soils, it is estimated that during the growing season it moves only few millimeters. However, erosion can transport considerable amounts of sediment-adsorbed P to surface waters. (Jaakkola 1992, 226; Shortle et al. 2001, 3−4)

In Finland the nutrient loading from agriculture is not evenly distributed in the country. Ostrobothnia and Southwest Finland are the largest areas of land use for agriculture. These areas are also the largest areas for animal husbandry (milk production, meat production, and fur farming). The combined centralization of crop cultivation and animal husbandry increases the amount of nutrient losses and makes the water courses heavily affected by the leaching nutrients. (TIKE 2010)

4.2 Political measures

The Second World War was a turning point in agricultural practices. After the war the political and cultural changes lead to intensive farming to meet the needs of the growing population. In Finland an agricultural support scheme was created to ensure the local food production and livelihood for farmers. Increased income led to changes in the agricultural technology as the farmers were able to invest in new machinery. Conventionally farmed fields cultivated by horse and man power for centuries were not used to heavy machinery. This led into changes in soil structure and biodiversity. Various pesticides, herbicides, fertilizers were invented, and also the breeding of cultivated crops and animals lead to changes in the mind-set of farmers. Agriculture became a livelihood instead of a way of life. Overproduction of food became reality, the yield needed to be increased and almost unnoticed the fields were filled with fertilizers. (Granberg 2004, 139−140; Roiko-Jokela 2004, 84−86)

The relation between agriculture and eutrophication of water courses was understood already in the 1960s. It was commonly acknowledged that P and N used in fertilizers were the major cause of anthropogenic eutrophication and changes in the biodiversity of lakes and streams. However, it took some time before actual measures were taken to decrease the nutrient loading. Also the studies in the 1980s proved that the cultivated soils were accumulated with excessive amounts of P. Water protection was introduced in the Finnish agricultural policy in the 1980s. Several measures to decrease nutrient loading from agriculture were applied: for example fertilizer taxation, reduction of P in fertilizers, incentives for buffer zones and fallows. By joining the EU in 1995, Finland was obliged by the EU’s Agri-Environmental Support Scheme. (Laurila 2004, 356, 369−371; Niemelä 2004, 219−222)

Finnish farmers receive support for agriculture. This support is divided into direct subsidies for farmers entirely paid from EU funds (CAP support), and agri-environmental support and natural handicap payments (LFA) partly funded by EU and partly nationally. The nationally funded supports are part of the Rural Development Programme for Mainland Finland 2007–2013. The reformed CAP is due to come into force after 2013. Finland is divided into seven main support regions for the purposes of agricultural support payments from south to north. (Finnish Ministry of Agriculture and Forestry 2011)

The farmers joining the Agri-Environmental Support Scheme are paid incentives to encourage them to take measures promoting biodiversity and reducing harmful impacts of nutrients in runoff from agriculture on inland waters and the sea. The Finnish agri-environmental programme consists of basic measures, additional measures and special measures. The basic measures are obligatory for all farmers who participate in the agri-environmental programme. Additional measures (such as reduced fertilizing, winter time vegetation cover) are optional and depend on the assisted region in question. For the period 2007–2013 about 90% of Finnish farmers have committed themselves to the scheme. Their farms account for approximately 95% of all farmland in Finland. (Finnish Ministry of Agriculture and Forestry 2011)

To improve the environmental protection actions of agriculture, EU countries have adopted common legislation, such as the Nitrate Directive and the Water Framework Directive. The latter sets the limits to the use of manure and aims at good ecological state of waters by 2015, respectively, and to prevent any deterioration in their state. (Turtola et al. 2010) The key objective in the Finnish Government decision-in-principle on Water Protection Policy Outlines to 2015 is that nutrient loads entering water courses from agriculture should be reduced by a third by 2015 compared to their levels over the period 2001–2005, and halved over a longer timescale (Ministry of the Environment 2007).

P scarcity and reduced accessibility to farmers is not yet considered a significant problem by decision makers even though the sufficiency of P is one of the biggest future challenges. Main motivation for the efficient use and management of P has been so far the environmental concerns, such as eutrophication. However the looming food crisis has made the EU drew up a plan, published in February 2012, to promote the sustainable use of P. The plan, known as Green Paper, is to secure sustainable food production by increasing the recycling of P through improved agricultural technology, increasing the utilisation of P in household waste, working for the more efficient processing of manure, and reducing food wastage. (Saavalainen 2012b)

4.3 The impact of climate change to agriculture

Global environmental change has several potentially beneficial and harmful impacts on agriculture in Finland. According to IPCC scenarios Finland belongs to global region where the climate warming is twice as fast as in average and in the future the winter precipitation is significantly increasing. Also torrential rain falls in summer are predicted. Changes in the precipitation and temperature lead to changes in runoff. Runoff is projected to increase by 10−20% by mid-century in Southern Finland. Winter precipitation potentially leads to a higher winter time erosion rates intensifying eutrophication of water courses. (IPCC Fourth Assessment Report 2007)

These predicted changes require sustainable means for adaptation of agricultural practices. Winter time crop cover in fields protects the soil surface reducing the risk of erosion and nutrient leaching, and improves soil quality by increasing soil organic matter content. The temperature changes might lead to several freeze−thaw cycles releasing more leaching nutrients. Also other consequences of climate change might have an effect to the increase in the nutrient discharge (longer growing seasons, increase in rainfall, warmer winters, less snow cover during winter and shorter period of soil frost). (Puustinen, Tattari, Koskiaho & Linjama 2007b)

5 MEASURES OF MITIGATING PHOSPHORUS LEACHING

5.1 Winter time vegetation cover and grasslands

Common measure taken on field in mitigating nutrient leaching is permanent vegetation cover such as crop or fallow plant, catch crops or stubble. Vegetation cover protects the topsoil of the fields against the erosive forces of rain, snow melt and runoff waters during winter and spring. Furthermore, it helps to improve the soil structure by increasing the amount of organic matter in the topsoil of the fields which decreases vulnerability of topsoil to silting. Especially on sloping soils it is an effective option to protect field from erosion, N and particulate P runoff. However, permanently vegetated field areas appear to be ineffective in reducing losses of DRP caused by freezing of plant material. (Uusi-Kämppä & Jauhiainen 2010; Uusi-Kämppä et al. 2011; Helcom 2012)

Approximately 30% of arable land area is used for grass cultivation (680,000 ha). Fallow lands cover 12% (275,000 ha) of the arable land of which 150,000 ha is nature management fields. During winter 2009−2010 53% of the used agricultural area had crop or fallow plant as soil cover over winter. Therefore significant amount of plant material freezes over the winter and thus some P is lost. The total biomass of this vegetation is difficult to estimate. On the other hand 21% of the area had bare soil winter cover. (TIKE 2011, Matilda 2012)

In the regulations of EU’s Agri-Environmental Support Scheme the harvesting needs to be done for green fallow latest 31 August and for buffer zones earliest 1 August, and to avoid harvesting during the nesting time of birds and mammals. It is a voluntary measure to remove the swath and use it. The regrowth after the first harvesting is not in some cases harvested at the end of the growing season and is left on the field over the winter (for example nature management fields). (MAVI 2012)

In buffer zones it is only recommended to harvest the growth once during the growing season and collect the swath. The biodiversity needs to be taken into consideration and therefore the harvesting is not allowed before 1 August. It is also possible to pasture the buffer zone. For nature management fields the harvesting is recommended only once in three years. Area of green fallow, buffer zones, and nature management fields is increasing and therefore more attention needs to be taken on the environmental impact of leached P from plants after freezing and thawing.

Winter time vegetation cover is an additional measure in the agri-environmental programme. In 2012 the support is 30 €/ha/a if the winter time vegetation cover is at least 30% of the total arable land area of the farm eligible for agri-environmental payments, and 45 €/ha/a for intensive winter time vegetation cover (50%). The measure is applicable only in support regions A and B. (MAVI 2012)

5.2 Reduced tillage

Agricultural management that involves disturbing the soil surface with tillage generally increases the amount of particle P carried away on eroded sediment. Studies have shown that reduced tillage reduces the amount of runoff P. No-tilling method does not disturb the soil between the harvests and seeding (for example not ploughed) and the soil is not prepared for seeding (for example harrowed). Reduced tilling or no-tilling benefits the biodiversity protection and has less production costs. There are however disadvantages for farmers such as later drilling of spring-sown crops because of lower soil temperature and higher moisture content. Also fertilizer or manure that is left unincorporated on the surface of cropland or pastures usually leads to increased losses of DRP in the runoff water. The total area ploughed in autumn has decreased as it has been replaced by reduced tillage and no-till method. However 60% of tilled arable land is cultivated conventionally by ploughing, and 40% of the arable land is cultivated by reduced tilling or no-till method (2010). (Brady & Weil 2002, 598; TIKE 2011)

Reduced tillage is an additional measure in the agri-environmental programme. In 2012 the support for combined winter time vegetation cover and reduced tillage is 11 €/ha/a (A, B and C support regions). (MAVI 2012)

5.3 Riparian buffer zones

The Finnish Water Act stipulates 60 cm wide buffer strips everywhere beside water courses and main ditches. As an additional measure grassed riparian buffer zones are widely used beside the field between annually tilled croplands and water courses to decrease off-site transport of soil matter and nutrients. Since 1995 when Finland joined the EU and was thus obliged by the EU’s Agri-Environmental Support Scheme the area of buffer zones has been expanding. 3-m buffer strips are obligatory and 15-m buffer zones are voluntary measures along Finnish streams and rivers, and around lakes. The permanent vegetation on the buffer area protects banks and littoral zones from erosion and from the leaching of nutrients, microbes and pesticides to the water. In addition, buffer zones also bring life to cultural landscapes and increase biodiversity in the area. From the viewpoint of water protection, buffer zones are particularly useful on fields that slope steeply towards water courses or main ditches. (SYKE 2012) Currently, narrow buffer strips and wider buffer zones are estimated to cover, in total, about 7,500 ha (2010) (Uusi-Kämppä 2012). The Finnish government has set a target to increase the area of buffer zones by 12,000 ha by 2015 (Government Secretariat for EU Affairs 2011).

The buffer zones are part of basic measures in agri-environmental programme. The support for the establishment and management of buffer strips and zones is max 450 €/ha (support regions A and B) and max 350 €/ha (support region C) (MAVI 2012).

5.4 Constructed wetlands

Wetlands are natural areas but several wetlands have been destroyed by draining to increase arable land area. The purpose of constructed wetlands is to reduce the concentration of nutrients and sediment from water flowing to the river or lake. Wetland can be versatile in depth, shape and vegetation depending of the purpose of the wetland. In addition to nutrient and sediment catchment, wetlands improve biodiversity and bring variation to agricultural landscape. Principal removal mechanisms for P are through a process of sedimentation (chemical precipitation), bound by suspended solids (adsorption), and plant uptake in aerobic conditions (biological process). (EC 2007; Puustinen et al. 2007a; Baltic Deal 2012)

DRP in input water adsorbs to sediment soil particles in the wetland. This is based on the P equilibrium in soil and water. If the DRP concentration of the input water is more than of the surrounding soil particles, P is adsorbed to the soil particles. DRP can be also released from the sediment to the water so it is recommendable to construct wetland in an area with high DRP content and low soil P content. Also other properties have an effect to this chemical process such as iron and aluminum in the suspended solids, oxygen content, and water residence time. (Puustinen et al. 2007a)

A wetland area is usually constructed by damming a small channel in a place where the water rising outside the channel does not cause significant damage to the surrounding area. The top soil is recommended to be removed. A suitable place has often been previously a wetland area. The efficiency of wetlands depends on how much field area is included in the upstream catchment area and what is the area of the wetland in relation to the catchment area. In Finland it is recommended that the area of the wetland should be at least 1–2% of the size of its catchment area. The wetland should also be situated near the nutrient loading source. (Puustinen et al. 2007a)

Management measures of constructed wetlands include checking and repairing the dam structures, and mowing or having animal grazing in the surroundings. Also, plants can be cut or removed from the wetland if they start to grow too tightly or widely. In addition, it might be necessary to dig up the bottom sediment if the basin gets too shallow or if the there is a risk that the sediment would flush away with the flood. Nesting of birds and mammals needs to be taken into consideration in timing of the management measures. (Puustinen et al. 2007a; Baltic Deal 2012)

Construction or re-establishment of wetlands in certain areas in Finland is part of the agri-environmental support for non-productive investments. If the constructed wetland meets the areal requirements farmers are compensated for any approved costs and loss of income incurred in connection with the establishment of wetlands (up to a maximum of 11,500 €/ha). Requirement is that 20% of the catchment area is arable land, and that the wetland is at least 0.5% of the size of its catchment area. The support for the management of multipurpose wetlands is max 450 €/ha. (MAVI 2012)

6 MATERIAL AND METHODS

6.1 Biomass sampling and sample preparation

In this study grass biomass samples were taken from nature management uncultivated arable field for a leaching study when samples were frozen and thawed in laboratory conditions. The grass biomass used in the study was harvested from grassland at MTT experimental site in Jokioinen in southwest Finland. There was no fertilizing for a considerable period that would affect the results. The freezing and thawing of samples in laboratory conditions demonstrated the spring time natural conditions on the field. The aim was to study if the timing of the grass cutting during the growing season could have an effect on the losses of wintertime P leaching from grass biomass.

FIGURE 4 presents the structure of the whole experimental site. Each experimental plot was 1.5 m wide and 10 m long, and the whole experimental site was 37.5 m wide. The experimental site was between small forest and forested road. There were five treatments, four replicates and control plot between the replicates. Plots 2, 3 and 4 were used in this study. The first growth of each experiment was harvested as follows: 22 June (treatment A), 5 July (treatment B) and 1 August (treatment C). Plots 1 and 5 were not used in this study as those samples were not needed because they were also harvested on 22 June. PICTURE 1 represents the replicate 1 of the experiment site.

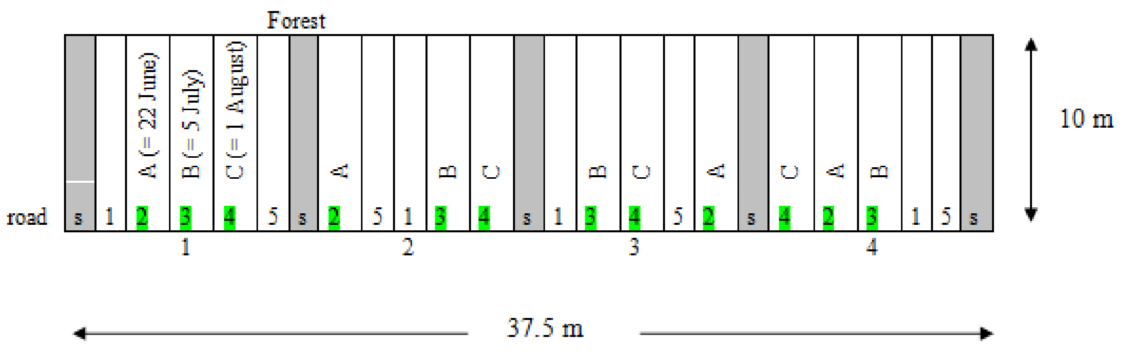
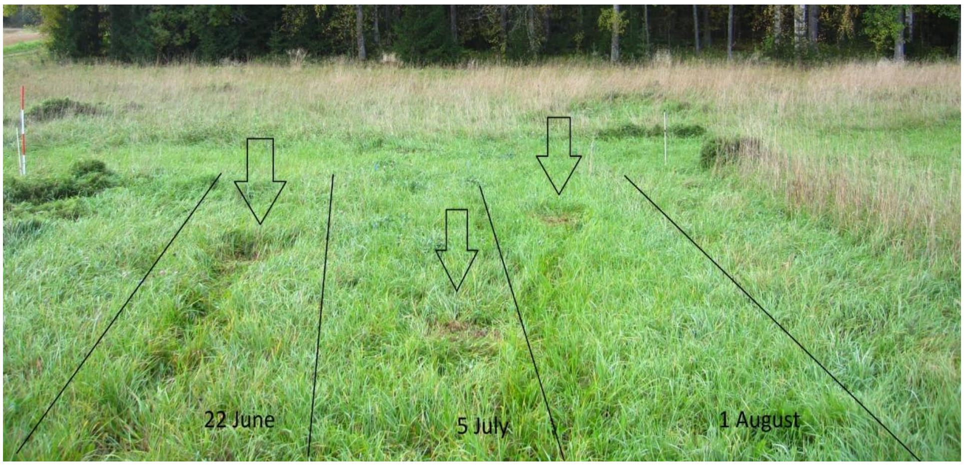


FIGURE 4. The experimental field was 37.5 m wide and 10 m long, and was divided into five different treatments and their four replicates. There was a control plot (s) between each replicate. Experimental plots 2, 3 and 4 were used in the study and their harvesting times are in the figure.



PICTURE 1. Replicate 1 of the experiment site, the different experimental plots and their harvesting times. The arrows indicate where the samples were taken. It can be seen that the different harvesting times were not that visual at the time of sampling.

The experimental plots had different harvesting treatments during the growing season (22 June, 5 July and 1 August) and the swath had been collected after the harvest. The grass biomass that had grown (for 96, 83 and 56 days, respectively) after the first harvest was collected for this study on 26 September 2011.

When the grass biomass was harvested for the first time, the grass biomass was separated to grass, legume and weed. Treatment A contained 82%, 5% and 13% of grass, legume and weed, respectively. The corresponding shares were for treatment B 86%, 9% and 5%, and for treatment C 76%, 11% and 13% (Niemeläinen 2012). The different plant species were not studied from the plant material.

The regrowth after the first harvesting was collected for the study at the end of the growing season. The harvesting was done for all the samples on 26 September 2011. The aim was to collect the samples just before the night temperatures reached zero, that is, just before the plant material froze for the first time. During the sampling the weather was dry and warm (around 10°C), and the ground and grass biomass was humid from previous rain.

By actual sight the experimental field mainly consisted of timothy (grass), clover (legumes) and dandelion (weed). The sampling points were selected so that the sample would contain the same portion of these plants. The grass biomass sample was cut to a stubble length of 2 cm from randomly selected plots of 0.25 m^2 by using a frame and scissors (PICTURE 2). The samples were placed in a paper bag and taken to the laboratory.

PICTURE 2. Sampling of grass biomass by using a frame of 50x50 cm and scissors.

In the laboratory a separate, homogenous portion of 10 g per plot (fresh weight) was taken of the total harvested grass biomass for freezing. Also another 10 grams portion was taken for back-up. The samples to be frozen were placed in 1 liter plastic boxes and stored in freezer at −24°C.

The fresh weight (and later dry weight) of the rest of the harvested sample was measured with scale (Sartorius LP 6200). The sample was dried in a circulating air drying oven at 60°C for 24 hours and then let to settle at 20°C. The dried grass biomass sample was mechanically ground in a cyclonic mill to pass 1 mm sieve (PICTURE 3) and analyzed for the initial P concentration (mg g^{-1}).

PICTURE 3. Cyclonic mill and the dried, ground grass biomass ready for analyzes.

6.2 Freeze−thaw cycles

The leaching experiment was conducted in laboratory conditions on grass biomass samples thus the effect of soil properties was neglected. The frozen grass biomass samples were placed to cold room to thaw over night. Temperature of the cold room was monitored and it was always around 5°C. Deionised water in a plastic container was also placed in the cold room to equal the room temperature. The next day 400 ml of the deionised water was added to the box with the grass biomass. The box was placed to a reciprocating shaker run at 200 rpm (revolutions per minute) for an hour (PICTURE 4).

PICTURE 4. After adding deionised water (400 ml) to the thawed grass biomass, the boxes were placed in a reciprocating shaker (run at 200 rpm for an hour).

After the shaking, the water and grass biomass were separated by cellulose paper (Tervakoski Tesorb 0%, 130 g m^{-2}). The filtration time of the each sample in each freeze−thaw cycle varied between 2−6 hours. The water sample was collected to 500 ml plastic bottles. After the filtration the biomass was collected back to the freezing box and placed in the freezer for five days. Freeze−thaw cycles were repeated four times until the leaching of P was negligible. The leaching was done once a week to have a constant cycle. At the end of the freeze−thaw cycle the grass biomass of each replicate was combined. The samples were dried, ground and analyzed for the remaining P concentration (mg g^{-1}) (PICTURE 5, PICTURE 6).

PICTURE 5. The water samples were filtrated through a cellulose paper.

PICTURE 6. The water and grass biomass material was separated through filtration paper and the biomass was collected back to freezing box and frozen.

6.3 Laboratory analysis

The following day after the filtration the water samples were analysed for DRP and TP (mg l^{-1}). The water samples were filtrated with Nuclepore® Polycarbonate filter (pore size 0.2 µm). The P was analysed at MTT laboratory with FIAstar auto analyzer according to Finnish standards SFS 3025 (1986) for DRP and SFS 3026 (1986) for TP.

The dried and ground grass biomass samples were measured for the initial P concentration and the residual P after the leaching experiment. The material was wet digested using nitric acid on a heating block (Huang & Schulte 1985).

6.4 Weather conditions during the growing season

The weather conditions during the growing season effect greatly on the uptake of nutrients and energy production. The weather conditions (daily rainfall (mm) and average daily temperature (°C)) during growing season 2011 are presented in a figure in appendix 1. Also the harvesting dates are indicated in the figure. After the harvesting on 22 June the weather was rather warm and dry. Between the harvest of 22 June and 5 July (13 days) the daily average maximum temperature was 24°C and the rainfall was 20 mm. Closer to the other harvest treatment 5 July the weather was relatively hot (even 30°C) and there was torrential rain on 3 July (33 mm). After 5 July harvest the temperature conditions were the same for the period of 13 days, the daily average maximum temperature was 23°C but there was more rainfall (63 mm). After 1 August harvest the temperature conditions were still quite similar of the first 13 days, the daily average maximum temperature was 20°C, the rainfall being 24 mm. According to the Finnish Meteorological Institute (2011), the thermal growing season in the sampling area begun on 16 April and lasted until 8 November. The harvesting treatments had growing degree days (GDD) at the time of the sampling 1025, 828, and 480 GDD, respectively.

Autumn 2011 was in general warm and rainy and the growing season lasted longer than usual. The length of the growing season was 207 days which is 27 days more than average in Southern Finland. The grass biomass samples were harvested on 26 September and the growing season ended 8 November according to the Finnish Meteorological Institute. Therefore presumably the growing season was not entirely over at the time of the sampling. According to the Finnish Meteorological Institute the night temperature reached zero on October 2 (−1.0°C) but still the daily average temperatures were relatively high in October (6°C).

7 RESULTS

7.1 Biomass analyses

The dried and ground grass biomass was analyzed for the P concentration (g kg $^{-1}$). For the calculation the unit was converted to mg g^{-1}. The laboratory results are presented in the appendices 2 and 3. The P content in the above-ground biomass (mg m^{-2}) was calculated by multiplying the P concentration (mg g^{-1}) with the DM yield (g m^{-2}) (TABLE 2).

TABLE 2. DM yield and initial P content for grass biomass of different harvesting times and their averages. After the leaching treatment the residual P concentration was measured from compound samples, and P content for the grass biomass was estimated.

Treatment	1st harvest	Replicate	DM yield g m^{-2}	Average DM yield g m^{-2}	P content mg m^{-2}	Average P content before leaching mg m^{-2}	P content after 4 freeze−thaw cycles mg m^{-2}
A	22 June	1	255.3	292	628.0	734	7.0
		2	283.0		696.1		
		3	341.8		871.6		
		4	286.0		740.6		
B	5 July	1	193.7	171	538.4	450	6.3
		2	182.7		458.6		
		3	167.7		422.6		
		4	138.7		380.0		
C	1 Aug	1	212.4	181	601.2	502	5.2
		2	192.3		519.3		
		3	145.5		451.2		
		4	175.2		436.3		

TABLE 2 shows that the highest average P content (734 mg m^{-2}) was on the grass biomass that had grown after the harvest on 22 June (treatment A). The results for the four replicates were between 628−871 mg P m^{-2}. The lowest average P (450 mg m^{-2}) was on grass biomass that had been harvested on 5 July (treatment B). The results for the replicates were between 380−538 mg P m^{-2}. The average P for grass biomass that had grown after the harvest on 1 August (treatment C) was 502 mg m^{-2} and the results varied between 436 and 601 mg P m^{-2}.

Also the average DM yield was to similar extent. The highest average DM yield (292 g m^{-2}) was observed in the treatment A and the lowest DM yield (171 g m^{-2}) was in the treatment B. In treatment C the average DM yield was 181 g m^{-2}.

After the freeze−thaw cycles the grass biomass samples of same harvest treatment were combined, dried and analyzed for the residual P concentration. From TABLE 1 can be seen the P content that was left after four freeze−thaw cycles. The above-ground grass biomass that had grown after harvest on 22 June (treatment A) had the highest P content (7.0 mg m^{-2}). The corresponding P contents were 6.3 and 5.2 mg m^{-2} for harvests on 5 July (treatment B) and 1 August (treatment C), respectively.

7.2 Water analyses

The filtrates of each four freeze−thaw cycles were sent to laboratory for analysis of DRP and TP (mg l^{-1}). The laboratory analyses are presented in appendices 5−7. From the laboratory analysis it can be seen that the highest concentration of DRP and TP (mg l^{-1}) were from the water samples for treatment C, and the lowest values were from the water samples for treatment A. The differences were not very significant. When the results from water samples were compared with the DM yield (g m^{-2}) the amount of leached TP content was the highest for treatment A. The leached DRP and TP content during the freeze−thaw events were calculated. All the results are presented in appendices 8−10.

The leaching results after each freeze–thaw cycle for the grass biomass harvested on 22 June are presented in TABLE 3. The average cumulative leached TP from four replicates of the grass biomass harvested on 22 June was 741 mg m^{-2} and 91% of TP was in dissolved form (DRP 675 mg m^{-2}). The leaching event was also efficient. After every leaching event, more than half of the P in the biomass was removed until the leaching was negligible.

In TABLE 2, it can be seen that the initial average TP in grass biomass was 734 mg m^{-2} which is 1% less than the leached amount of TP (741 mg m^{-2}). There may be some minor errors in these types of experiments. For example the DM percent in dried grass biomass sent for further analysis might not have been exactly the same as the DM percent of the grass biomass samples in leaching experiment.

TABLE 3. The leached DRP and TP during the four freeze−thaw cycles for treatment A (harvested on 22 June 2011).

	Freeze−thaw cycle	Replicate	DRP, mg m^{-2}	Average DRP, mg m^{-2}	TP, mg m^{-2}	Average TP, mg m^{-2}
Cumulative total				675		741
	1	1	281.9	403	301.5	434
		2	441.7		479.1	
		3	514.5		550.7	
		4	375.2		403.8	
	2	1	197.3	169	208.0	193
		2	157.3		168.6	
		3	209.2		227.6	
		4	112.6		168.0	
	3	1	72.6	66	83.3	74
		2	53.2		60.6	
		3	73.0		81.1	
		4	66.5		72.5	
	4	1	36.0	36	40.1	41
		2	27.1		31.1	
		3	44.9		48.9	
		4	37.4		42.0	

TABLE 4 presents the leaching results for the grass biomass for treatment B (harvested on 5 July). The average cumulative leached TP from the samples was 442 mg m^{-2} for the treatment and 92% of TP was in dissolved form (DRP 405 mg m^{-2}).

TABLE 5 presents the leaching results for the grass biomass for treatment C (harvested on 1 August). The average cumulative leached TP from the samples was 513 mg m^{-2} of which 87% of TP was in dissolved form (DRP 445 mg m^{-2}). In TABLE 1 the initial average TP was 502 mg m^{-2} which is 2% less than the leached amount of TP because of same error reasons as for the treatment A. Also in TABLE 5 it can be seen an irregularity in the fourth replicate of second freeze−thaw cycle in TP value (170.1 mg m^{-2}) and DRP value (57.3 mg m^{-2}). The values are not lined up with other values and can be assumed that there might have been some natural variation or an error has occurred during the leaching experiment or in the laboratory measurement of that specific water sample.

TABLE 4. The leached DRP and TP during the four freeze−thaw cycles for treatment B (harvested on 5 July 2011).

	Freeze−thaw cycle	Replicate	DRP, mg m^{-2}	Average DRP, mg m^{-2}	TP, mg m^{-2}	Average TP, mg m^{-2}
Cumulative total				405		442
	1	1	269.4	249	297.8	273
		2	274.9		301.5	
		3	269.6		296.0	
		4	182.2		197.1	
	2	1	109.8	100	119.1	108
		2	101.4		107.7	
		3	93.1		99.9	
		4	98.8		104.8	
	3	1	36.0	35	41.7	38
		2	37.0		40.7	
		3	29.2		32.0	
		4	36.7		39.6	
	4	1	20.2	21	22.9	23
		2	23.5		24.9	
		3	17.1		18.4	
		4	22.7		23.9	

TABLE 5. The leached DRP and TP during the four freeze−thaw cycles for treatment C (harvested on 1 August 2011).

	Freeze−thaw cycle	Replicate	DRP, mg m^{-2}	Average DRP, mg m^{-2}	TP, mg m^{-2}	Average TP, mg m^{-2}
Cumulative total				445		513
	1	1	361.2	310	398.7	337
		2	343.2		359.0	
		3	275.9		313.5	
		4	260.8		276.7	
	2	1	116.6	84	125.3	122
		2	75.3		101.7	
		3	85.7		91.3	
		4	57.3		170.1	
	3	1	38.5	32	41.9	34
		2	36.8		38.2	
		3	29.3		30.9	
		4	22.9		24.0	
	4	1	25.0	19	27.0	20
		2	20.9		21.6	
		3	16.7		17.7	
		4	13.6		14.0	

TABLE 6 collects all the average results of DM yield, P content of grass biomass and leached DRP and TP of the three treatments are presented.

TABLE 6. The DM biomass, P content of biomass after freeze−thaw cycles and leached DRP and TP loads during the four freeze−thaw cycles.

Treatment	1st harvest	DM biomass g m^{-2}	P content mg m^{-2}	Leached DRP, mg m^{-2}	Total leached TP, mg m^{-2}
A	22 June	292	734	675	741
B	5 July	171	450	405	442
C	1 August	181	502	445	513

Leached TP after each freeze−thaw cycle and residual TP are presented in FIGURE 5. Figure shows that the leached TP was the smallest (441 mg m^{-2}) when grass biomass was harvested on 5 July and that was because of small initial P in biomass (450 mg m^{-2}). The corresponding values for leached TP amounts were 513 and 741 (mg m^{-2}) for biomass harvested on 1 August and 22 June, respectively. The results for initial average TP reflect the results of leached TP. After four freeze−thaw cycles the biomass did not contain a significant amount of residual P.

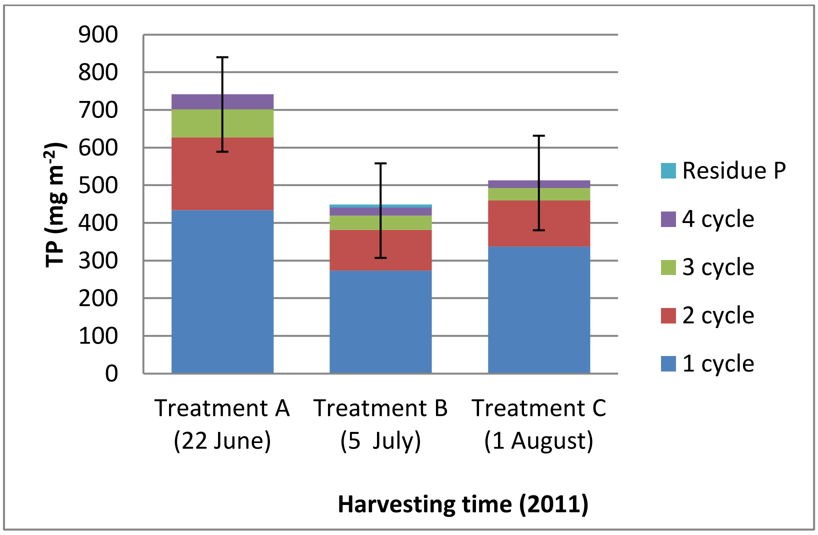


FIGURE 5. Average TP load after each freeze−thaw cycle and the residual amount that was left in the grass biomass samples after four cycles. The error bar shows min and max of the P content in the beginning of the study.

The leached DRP after each freeze−thaw cycles and residual TP are presented in FIGURE 6. As also seen in the FIGURE 5 the grass biomass harvested on 5 July had the least initial P content (450 mg m^{-2}) and therefore the least leaching of DRP (405 mg m^{-2}) was observed from this treatment. The corresponding amounts were 455 and 675 (mg m^{-2}) for biomass harvested on 1 August and 22 June. The figure shows the same as FIGURE 5 that almost 90% of the DRP was leached after the two first freeze−thaw events. Almost 90% of the TP in the biomass was in soluble form (DRP).

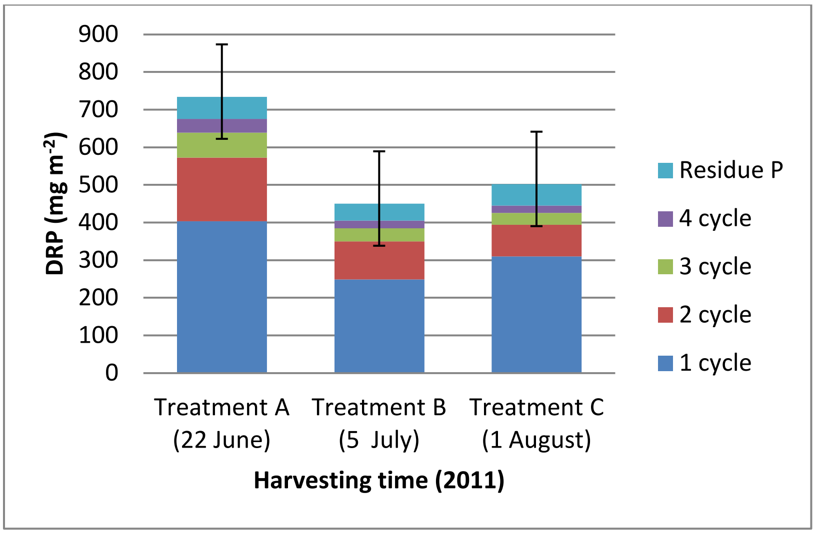


FIGURE 6. Average leached DRP after each freeze−thaw cycle and the residual TP that was left in the grass biomass samples after four freeze−thaw cycles. The error bar shows min and max of the P content in the beginning of the study.

FIGURE 7 shows that 59−67% of the TP was leached after the first freeze−thaw event, and after the second freeze−thaw event altogether 85−91% of the TP in the biomass was leached. After the four freeze−thaw cycles the leaching of P was negligible.

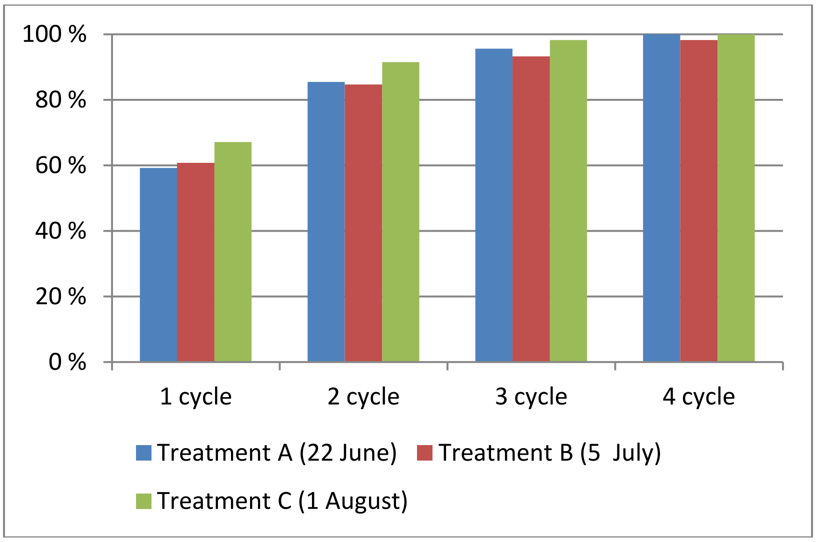


FIGURE 7. The cumulative percentage of TP leached after freeze–thaw cycles.

Also the P leaching of different harvesting treatment was compared in mg g^{-1} DM. And as can be seen in the FIGURE 8 and FIGURE 9 there are no significant differences between treatments.

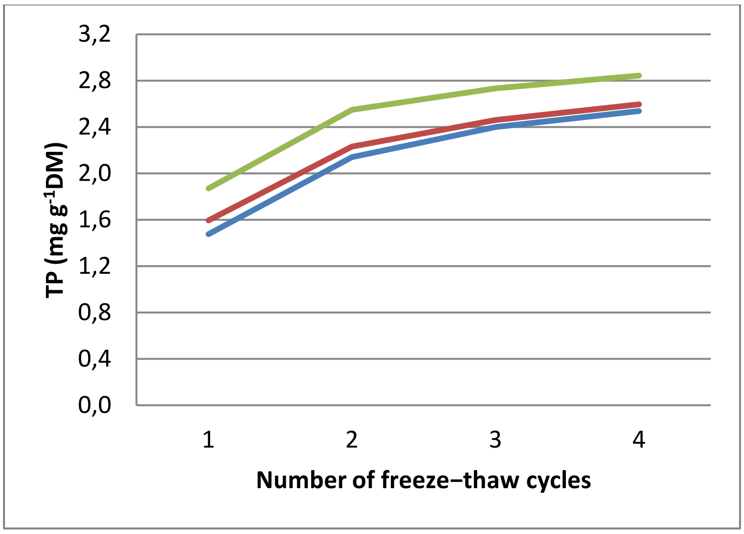


FIGURE 8. Cumulative leached TP (mg g^{-1} DM) for different treatments. The upper line is treatment A (22 June), the middle line treatment B (5 July) and the lowest line is treatment C (1 August).

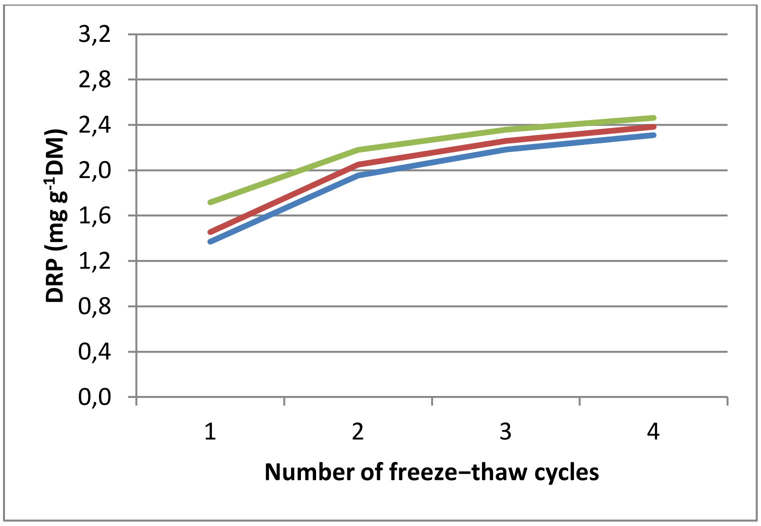


FIGURE 9. Cumulative leached DRP (mg g^{-1} DM). The upper line is treatment A (22 June), the middle line treatment B (5 July) and the lowest line is treatment C (1 August).

8 ANALYSIS AND DISCUSSION

8.1 Analysing the results

The aim of this work was to study how much the above-ground grass biomass, harvested at different times during the growing season, contains P at the end of the growing season, and how much of it is leached because of freezing and thawing. The study aims to give information about the ideal time for grass harvesting to mitigate the wintertime P leaching. The results can be compared with the current instructions, and the results can be applied to large quantity of arable land area in Finland. The results can be used, for instance, in instructions for unfertilized grass lands (such as buffer zones, managed uncultivated fields) in EU's Agri-Environmental Support Scheme.

Initial and residual TP content in the grass biomass (mg m^{-2}) and leached losses of DRP and TP (mg m^{-2}) after each of the four freeze−thaw cycles for different harvesting times (treatments A−C) were studied. The aim was to find which harvesting time had the least P content in above-ground biomass at the end of the growing season and how much of it is leached after freezing and thawing.

The lowest P content (mg m^{-2}) at the end of the growing season was found on above-ground grass biomass harvested on 5 July. The highest P content was on the grass biomass harvested on June 22. This P content was almost 70% higher than the P content of 5 July harvested grass biomass. Also the difference between the P content of 1 August harvest and 22 June was significant (almost 50% difference).

There was a strong relation between the DM yield and the TP content in the grass biomass. The highest DM yield was also on the grass biomass with the highest TP content (harvested on June 22).

More than half of the TP in the grass biomass was leached after each freeze−thaw treatment. There may be several freeze−thaw cycles in natural condition but the biomass cannot release more P than it contains. It is important to see in this study that almost 60% of the TP leached after the first freeze−thaw cycle and after the second cycle almost 90% of the TP was leached from the grass biomass. After four cycles the P content in the biomass was negligible.

8.2 Methodological considerations

The aim of the leaching experiment was to demonstrate the natural spring time conditions but the laboratory conditions are not equivalent with the nature. As the material used in this study was not grown in a greenhouse, the environmental factors in natural conditions during the growing season affected the results. The grass biomass was harvested at three different times during the growing season and the climatic circumstances (such as rainfall, temperature and light) affect the plant nutrient uptake and regrowth after the harvest. White (1973) for instance presented that at lower moisture contents the cell membranes would not be disrupted as much by freezing. In autumn the moisture content is relatively high due to weather conditions. The grass biomass used in this study had moisture content 75%. The ideal situation would have been to harvest the samples just before the first frost. Possibly the growing season was not entirely over and the plants were still storing some of its P to the roots. White (1973) explained that the leaching of P is more significant if the plant is still growing when frozen.

The biomass was not analyzed for different plant species for this study which made it difficult to compare the results with some other studies. For example Timmons et al. (1970) studied alfalfa, Kentucky bluegrass, barley straw stubble, and oats straw stubble; White (1973) also used several different plants as the samples were taken from natural prairie; Bechmann et al. (2005) studied ryegrass. Therefore it is recommendable that the same experimental field is used for further studies for comparative results. Also for further studies the plant material should be analyzed more closely.

According to the laboratory results there was a possible error in one of the water sample analysis. This result was not neglected, and it was included in the data for analysis. Also the results could have been statistically analyzed to outline small errors. Also in some earlier studies the leaching was done for the fresh biomass sample before freezing (for example Timmons 1970; Roberson et al. 2007). Thus to continue this study different treatment cycles and methods could be used. The laboratory conditions tried to simulate natural spring time conditions as much as possible. The amount of deionised water, 400 ml (simulating snow melt) added to the grass biomass in leaching was used in previous similar studies at MTT. In other similar type of studies different amount of water was used for 10 grams (fresh weight) plant sample, such as, 200 ml (Ulén 1984).

8.3 Discussion

Significant amount of plant biomass is frozen over the winter and leaches P. Harvesting the biomass and collecting the swath may decrease DRP losses. If the biomass is harvested at the end of the growing season the soil surface might be vulnerable for erosion by rain, depending on the stubble length and strength. P is mostly accumulated to the surface of soils and therefore the surface of the fields needs to be protected from the effect of heavy rains.

It is important to consider the harmful effects of harvesting to the biodiversity. Such harmful effects might be disturbing the nesting of birds and mammals, damaging the soil structure by heavy machines, disturbing the habitat of animals by removing shelters or food. Also it is not always possible to mechanically harvest certain grassed areas such as buffer zones which are usually narrow, slope, riparian areas. One way of decreasing the vegetation is, for example, to pasture the buffer zone but the dung might cause additional P losses.

Diffuse nutrient loading from agricultural areas is the biggest anthropological cause of eutrophication in lakes. Mitigating nutrient leaching from agriculture eventually leads to less diffuse loading and better quality of lakes. The need for remediation of water courses decreases. However, the change will take some time as the self-perpetuating process in the lakes will continue.

The availability of natural resources such as oil and raw materials for fertilizers is increasing the production costs of agriculture. The work needed for the additional harvest might increase the costs and the benefit of the work does not focus directly to the farm. The production of food depends on a constant supply of P, and clean nature. One of the biggest global challenges for the future is to secure the natural state of the nature and sufficient supply of P for agricultural production.

9 CONCLUSIONS

This study showed that out of the three selected harvesting times harvesting on 5 July had the least TP concentration and also the smallest leached P. The TP leaching from grass biomass harvested on 22 June and 1 August was 68% and 16% more, respectively, than from grass biomass harvested on 5 July. The difference in initial TP concentration between treatments was to a similar extent.

This study also showed that the effect of freezing and thawing affects efficiently to P leaching from above-ground biomass. Almost 60% of the TP was leached after the first freeze–thaw cycle and after the second cycle almost 90% of the TP was leached from the grass biomass. It has been already studied that collecting the swath from vegetation covered fields may decrease the amount of nutrient leaching. This was a small scale study to gain some estimation how the harvesting time affects the winter time P leaching. The study gave valuable results for further studies. By further studies on the interaction of harvesting time and nutrient leaching it is possible to conclude a regulation for suitable harvesting time for wintertime grass covered fields.

There are several factors regulating the agricultural practices. There are guidelines and restrictions on management of the vegetation covered fields. According to the results of this study the current instruction on the harvesting time are suitable (latest 31 August, and for buffer zones harvest after 1 August). As it is important to consider the effects of harvesting on the biodiversity of the area, the nesting of mammals and birds will not be disrupted when the harvesting is done later during the growing season. Also it is good to consider the use of heavy machinery at the end of the growing season when the soil is wet, and may cause damage to the soil structure.

Change in the agricultural practices is also a challenge as it requires a change in the mindset of farmers. It is significant that the removed swath has a value after the harvest, for example as a source for biogas production or as cattle feed. Also the harvesting should be economically profitable for the farmers. If the swath is used for instance for biogas production, the requirements for biogas raw materials needs to be taken into consideration. Eventually, decreased diffuse nutrient loading together with well-controlled point source loading will decrease the total anthropological nutrient loading to water courses. Consequently need for restoration measures in the water courses decreases.

Significant amount of effort used in studying the effects of freezing and thawing in plant residues also proves that the wintertime leaching is of great concern and plenty of research still needs to be done. Wintertime vegetation cover is widely used in Finland and significant amount of plant material freezes over the winter releasing P in leachate. The total biomass of this vegetation is difficult to estimate but a significant amount of DRP could be removed from the water course by removing biomass with high P concentration from the wintertime vegetation cover.

To have more specific results the study should be conducted in more natural conditions. As in this type of study the effect of soil needs to be neglected, a simulator could be used. For example, Virkajärvi and Saarijärvi (2010) studied the use of surface runoff simulator in enhancing the study on wintertime P losses from grassland.

A part of the P retrieved by the plant is stored in the roots at the end of the growing season. A recent study in Sweden (Liu et al. 2011) showed that also the roots of the plant may act as a source of P leaching when the plant cells are burst by frost. The study showed that the roots generally seemed to be more sensitive to frost damage than the above-ground biomass. Part of the P released from the roots will attach to the soil particles thus the leaching of P is not as significant as of the above-ground biomass but this particle P might slowly dilute to the soil water and thus be leachable. It would be interesting to compare the P concentration in the roots after different harvesting times.

For continuity a larger study should be conducted for the same experimental field with more data series (several replicates) and different treatments, for example, different freeze−thaw cycles, and leaching from fresh and dried samples. The changing climate will bring challenge to developing efficient methods for mitigating nutrient leaching. Climatic factors, particularly precipitation and temperature, affect the extent and seasonal variation of nutrient loading. Several freeze−thaw cycles combined with more precipitation and less soil frost will probably increase the amount of leaching nutrients in future.

REFERENCES

Ashman, M.R. & Puri, G. (eds.) 2002. The essential soil science: a clear and concise introduction to soil science. Cornwall: Blackwell Science Ltd.

Baltic Deal. 2012. Read 8.4.2012. http://www.balticdeal.eu/

Bechmann, M.E., Kleinmann, P.J.A., Sharpley, A.N. & Saporito, L.S. 2005. Freeze−thaw effects on P loss in runoff from manured and catch-cropped soils. Journal of Environmental Quality 34, 2301−2309.

Brady, N.C. & Weil, R.R. (eds.) 2002. The nature and properties of soils. 13th edition. New Jersey: Pearson Education, 592−620.

Buchman, H.O. & Brady, N.C. 1969. The nature and properties of soils. 7th edition. London: Macmillan. (cited in National Academy of Sciences, 2012)

Cordell, D., Drangert, J-O. & White, S. 2009. The story of P: Global food security and food for thought. Global Environmental Change 19, 292−305.

EC (European Communities). 2007. LIFE and Europe's wetlands: Restoring a vital ecosystem, 2007. Read 12.4.2012. http://ec.europa.eu/environment/life/publications/lifepublications/lifefocus/documents/wetlands.pdf

Finnish Field Drainage Association. 2012. Read 9.5.2012 http://www.salaojayhdistys.fi (In Finnish)

Finnish Meteorological Institute. 2011. Read 5.3.2012. http://ilmatieteenlaitos.fi/kasvukausi-2011 (In Finnish)

Finnish Ministry of Agriculture and Forestry. 2011. Read 21.5 2012. Agri-environmental payments. http://www.mmm.fi (In Finnish)

Government Secretariat for EU Affairs. 2011. Read 21.5.2012. http://valtioneuvosto.fi/tiedostot/julkinen/vn/pdf-tiedostot/Itaemeri-selonteon_seurantaraportti/Itameri-selonteon_seurantaraportti.pdf (In Finnish)

Granberg, L. 2004. Maatalouden tulojärjestelmän synty. In: Markkola, P. (ed.) 2004. Suomen maatalouden historia. Suurten muutosten aika, jälleenrakennuskaudesta EU-Suomeen. Osa 3. Suomalaisen kirjallisuuden seura. Jyväskylä: Gummerus, 90−140. (In Finnish)

Harley, C.P., Moon, H.H. & Regeimbal, L.O. 1951. The release of certain nutrient elements from simulated orchard grass mulch. Proceedings of the American Society for Horticultural Science 57, 7−23.

Hartikainen, H. 1992. Maatalous ja ympäristönsuojelu. In: Heinonen, R. (ed.) 1992. Maa, viljely ja ympäristö. Porvoo: WSOY, chapter 7. (In Finnish)

HELCOM (The Helsinki Commission). 2012. Read 3.5.2012. http://www.helcom.fi/

Huang, C.L. & Schulte, E.E. 1985. Digestion of plant tissue for analysis by ICP emission spectroscopy. Communications in Soil Science and Plant Analysis 16, 943−958.

IPCC Fourth Assessment Report. 2007. Read 5.3.2012. http://www.ipcc.ch

InfoMine. 2012. Read 23.5.2012. http://www.infomine.com/investment/metal-prices/phosphate-rock/5-years/

Jaakkola, A. 1992. Kasvinravitsemus. In: Heinonen, R. (ed.) 1992. Maa, viljely ja ympäristö. Porvoo: WSOY, chapter 4. (In Finnish)

Laurila, I.P. 2004. Maatalouden EU-aika. In: Markkola, P. (ed.) 2004. Suomen maatalouden historia. Suurten muutosten aika, jälleenrakennuskaudesta EU-Suomeen. Osa 3. Suomalaisen kirjallisuuden seura. Jyväskylä: Gummerus, 349−401. (In Finnish)

Liu, J., Khalaf R. & Ulén, B. 2011. Potential of P (P) release from eight catch crops. In: Realistic expectations for improving European waters. Final conference of COST Action 869. Mitigation options for nutrient reduction in surface water and ground waters. Keszthely, Hungary, 12–14 October 2011. Abstracts, 43.

MAVI (Finnish Agency for Rural Affairs). 2012. Read 4.6.2012. www.mavi.fi

Matilda. 2012. Read 28.5.2012 http://www.maataloustilastot.fi/kaytossa-oleva-maatalousmaa (In Finnish)

Miller, H.E., Beauchamp, E.G. & Lauzon, J.D. 1994. Leaching of nitrogen and P from the biomass of three cover crop species. Journal of Environmental Quality 23, 267−272.

Niemelä, J. 2004. Hevosista traktoreihin – lannasta väkilannoitteisiin. In: Markkola, P. (ed.) 2004. Suomen maatalouden historia. Suurten muutosten aika, jälleenrakennuskaudesta EU-Suomeen. Osa 3. Suomalaisen kirjallisuuden seura. Jyväskylä: Gummerus, 187−232. (In Finnish)

Niemeläinen, O. Principal Research Scientist. 2012. Botanical study for managed uncultivated field at MTT. Email message to author. oiva.niemelainen@mtt.fi. Printed 5.6.2012.

Puustinen, M. et al. 2007a. Multipurpose wetlands for agricultural water protection – guidelines of wetland planning and dimensioning. SYKE 21/2007. Vammala: SYKE. (In Finnish)

Puustinen, M., Tattari, S., Koskiaho, J. & Linjama, J. 2007b. Influence of seasonal and annual hydrological variations on erosion and P transport from arable areas in Finland. Soil & Tillage Research 93, 44−55.

Roberson, T., Bundy, L.G. & Andraski, T.W. 2007. Freezing and drying effects on potential plant contributions to phosphorus in runoff. Journal of Environmental Quality 36, 532−539.

Roiko-Jokela, H. 2004. Asutustoiminnalla sodasta arkeen. In: Markkola, P. (ed.) 2004. Suomen maatalouden historia. Suurten muutosten aika, jälleenrakennuskaudesta EU-

Suomeen. Osa 3. Suomalaisen kirjallisuuden seura. Jyväskylä: Gummerus, 27−90. (In Finnish)

Saarijärvi, K. & Virkajärvi, P. 2010. Surface runoff simulator (SIMU) hastens the research on P losses from grassland. In: Turtola, E., Ekholm, P. & Chardon, W. (eds.). 2010. Novel methods for reducing agricultural nutrient loading and eutrophication. MTT Tiede 10, 51.

Saavalainen, H. 2012a. Ehtyvän fosforin arvo kasvaa. Helsingin Sanomat, 1 May, B4. (In Finnish)

Saavalainen, H. 2012b. Fosforin kierrätys ontuu. Helsingin Sanomat, 7 May, B3. (In Finnish)

Saavalainen, H. 2012c. Pellot pärjäisivät pitkään lannalla. Helsingin Sanomat, 7 May, B3. (In Finnish)

SFS 3025. 1986. Finnish standard for determination of phosphate in water. Helsinki: Finnish Standards Association. (In Finnish)

SFS 3026. 1986. Finnish Standard for determination of total P in water: Digestion with peroxosulfate. Helsinki: Finnish Standards Association. (In Finnish)

Shortle, J.S., Abler, D.G. & Ribaudo, M. 2001. Agriculture and water quality: the issues. In: Shortle, J.S. & Abler, D.G. (eds.) 2001. Environmental policies for agricultural pollution control. Cambridge: CABI Publisher, chapter 1.

SYKE (Finnish Environment Institute). 2009. Ecological and chemical state of surface waters. Published 20.8.2009. Read 24.5.2012. http://www.ymparisto.fi/default.asp?node=24419&lan=en

SYKE (Finnish Environment Institute). 2012. Read 28.5.2012. http://www.ymparisto.fi (In Finnish)

TIKE (Information Centre of the Ministry of Agriculture and Forestry). 2010. Yearbook of Farm Statistics. Helsinki: TIKE. (In Finnish)

TIKE (Information Centre of the Ministry of Agriculture and Forestry). 2012. Read 4.5.2012. http://www.mmmtike.fi/www/fi/ (In Finnish)

Timmons, D.R., Holt R.F & Latterell J.J. 1970. Leaching of crop residue as a source of nutrients in surface runoff water. Water Resources Restoration 6, 1367−1375.

Turtola, E., Ekholm, P. & Chardon, W. (eds.). 2010. Novel methods for reducing agricultural nutrient loading and eutrophication. MTT Science 10.

Turtola, E. & Lemola, R. (eds.) 2008. Maatalouden ympäristötuen vaikutukset vesistökuormitukseen, satoon ja viljelyn talouteen v. 2000−2006. (MYTVAS 2) Maa- ja elintarviketalous 120. Jokioinen: MTT (In Finnish)

Uhlen, G. 1979. Virkning av planterester på smeltevannets kjemiske sammensetning. Vann 2, 140−143. (In Swedish)

Ulén, B. 1984. Nitrogen and P to surface water from crop residues. Ekohydrologi 18, 39−44.

Uusi-Kämppä, J. & Jauhiainen, L. 2010. Long-term monitoring of buffer zone efficiency under different cultivation techniques in boreal conditions. Agriculture, Ecosystems and Environment 137, 75−85.

Uusi-Kämppä, J. & Kilpinen, M. 2000. Suojakaistat ravinnekuormituksen vähentäjänä. Maatalouden tutkimuskeskuksen julkaisuja. Sarja A 83. (In Finnish)

Uusi-Kämppä, J., Turtola, E., Närvänen, A., Jauhiainen, L. & Uusitalo, R. 2011. Phosphorous mitigation during springtime runoff by amendments applied to grassed soil. Journal of Environmental Quality 41, 2, 420−426.

Uusi-Kämppä, J. Senior Research Scientist. 2012. Nutrient leaching from nature management fields. Email message to author. jaana.uusi-kamppa@mtt.fi. Printed 15.5.2012.

U.S. Geological Survey. 2012. Mineral Commodity Summaries, January 2012. Read 5.3.2012. http://minerals.usgs.gov/minerals/pubs/mcs/2012/mcs2012.pdf

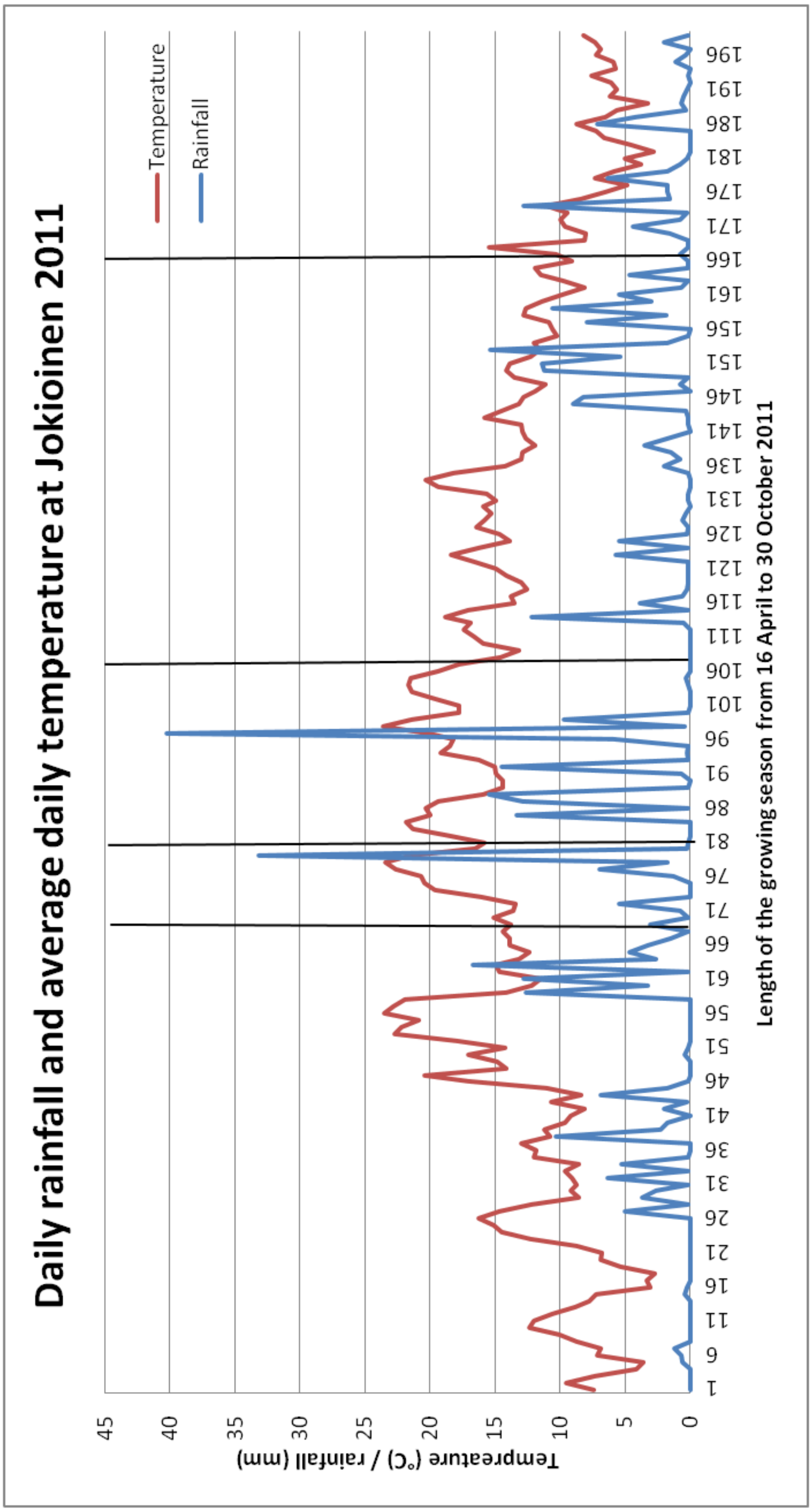
Warsta, L. 2011. Modelling water flow and soil erosion in clayey, subsurface drained agricultural fields. Ph.D. Aalto University.

White, E.M. 1973. Water-leachable nutrients from frozen or dried prairie vegetation. Journal of Environmental Quality 2, 1, 104−107.

YARA. 2012. Yaran historia. Read 5.3.2012. http://www.yara.fi/about/history/index.aspx (In Finnish)

APPENDICES

Appendix 1. Daily rainfall (lower line (blue)) and average daily temperatures upper line (red)) at Jokioinen during 16.4.−30.10.2011. The black vertical lines are the harvesting times 22 June, 5 July, 1 August, and the sampling date 26 September, respectively.



Appendix 2. Analysis report of TP (g kg^{-1}) for the dried grass biomass.

MTT
L-talo
31600 Jokioinen
\\midas\ohjelmat\Prosof\Dokum\nayte\2012\03\KIV\00000107_Suomi.rtf

ANALYYSITODISTUS 2012-107

1(1)
26.03.2012

KTL
Maa
Katariina Yli-Heikkilä
E-talo
31600 Jokioinen

FINAS
Finnish Accreditation Service
T024 (EN ISO/IEC 17025)
ilac-MRA

Näytetiedot

Näyte otettu	26.09.2011	Näytteen ottaja	
Saapunut	05.03.2012	Näytteenoton syy	Yhteistutkimukset
Tutkimus alkoi	12.03.2012		
Tutkimus valmis	26.03.2012		

Näyte: Heinä
Kokeen nimi: HVP biokaasuksi, Koepaikka: Jokioinen.

Analyysi / Yksikkö / Menetelmä Näyte	Fosfori g/kg ka. 1.2 ja 1.15 *
107-1, 1.1., Heinä	2,46
107-2, 2.1., Heinä	2,78
107-3, 3.1., Heinä	2,83
107-4, 4.1., Heinä	2,46
107-5, 5.1., Heinä	2,51
107-6, 6.1., Heinä	2,70
107-7, 7.1., Heinä	2,55
107-8, 8.1., Heinä	2,52
107-9, 9.1., Heinä	3,10
107-10, 10.1., Heinä	2,59
107-11, 11.1., Heinä	2,74
107-12, 12.1., Heinä	2,49

* = menetelmä on akkreditoitu.

Menetelmä Fosfori: Sisäiset menetelmät; 1.2 Kivennäisainemääritykset, märkäpoltto ja 1.15 Kivennäis- ja hivenaineiden sekä raskasmetallien määrittäminen ICP- ja ICP-MS:lla

Laadun-varmistus Referenssimateriaalina oli Hay -referenssi, jonka fosforipitoisuudet olivat hyväksyttäviä.

Merja Eurola
Tutkija

Riitta Sarkkinen
Laboratoriomestari

Analyysitulokset pätevät ainoastaan analysoiduille näytteille. Mikäli menetelmän mittausepävarmuutta ei ole ilmoitettu, sen saa pyydettäessä. Lausunto ei kuulu akkreditoinnin piiriin. Analyysitodistuksen saa kopioida vain kokonaan.

MTT, 31600 JOKIOINEN, puh. (03) 41 881, fax (03) 4188 3266

Appendix 3. Analysis report of residual TP (g kg^{-1}).

MTT
L-talo
31600 Jokioinen
\\midas\ohjelmat\Prosof\Dokum\nayte\2012\05\KIV\00000134_Suomi.rtf

ANALYYSITODISTUS 2012-134

1(1)
14.05.2012

KTL
Maa
Katariina Yli-Heikkilä
E-talo
31600 Jokioinen

FINAS
Finnish Accreditation Service
T024 (EN ISO/IEC 17025)

Näytetiedot

Näyte otettu	19.04.2012	Näytteen ottaja	
Saapunut	26.04.2012	Näytteenoton syy	Yhteistutkimukset
Tutkimus alkoi	08.05.2012		
Tutkimus valmis	14.05.2012		

Näyte: Heinä
Kokeen nimi: HVP biokaasuksi, Koepaikka: Jokioinen.

Analyysi Yksikkö Menetelmä Näyte	Fosfori g/kg ka. 1.2 ja 1.15 *
134-1, 1	0,85
134-2, 2	0,87
134-3, 3	0,78

* = menetelmä on akkreditoitu.

Menetelmä Fosfori: Sisäiset menetelmät; 1.2 Kivennäisainemääritykset, märkäpoltto ja 1.15 Kivennäis- ja hivenaineiden sekä raskasmetallien määrittäminen ICP- ja ICP-MS:lla

Laadun-varmistus Referenssimateriaaleina olivat IAG09 Alfalfa meal pellets ja Mixed feed sekä ARC/CL Wheat flour, joiden tulokset olivat hyväksyttäviä.

Merja Eurola
Tutkija

Riitta Sarkkinen
Laboratoriomestari

Analyysitulokset pätevät ainoastaan analysoiduille näytteille. Mikäli menetelmän mittausepävarmuutta ei ole ilmoitettu, sen saa pyydettäessä. Lausunto ei kuulu akkreditoinnin piiriin. Analyysitodistuksen saa kopioida vain kokonaan.
MTT, 31600 JOKIOINEN, puh. (03) 41 881, fax (03) 4188 3266

Appendix 4. The fresh and dry weight of the samples, and DM yield for treatments A (22 June), B (5 July) and C (1 August).

Experi-mental plot	Treat-ment	DM yield (g m^{-2})	Biomass fresh weigh (g)	Biomass dry weight (g)	Sample for freeze–thaw cycle fresh weigh (g)	Sample for freeze–thaw cycle dry weigh (g)
1	A	255,28	177,29	57,35	10	3,23
2	A	282,97	288,09	66,15	10	2,30
3	A	341,79	339,28	80,69	10	2,38
4	A	285,95	268,45	66,53	10	2,48
1	B	193,67	150,27	42,73	10	2,84
2	B	182,70	158,94	40,57	10	2,55
3	B	167,70	137,19	36,59	10	2,67
4	B	138,69	120,6	29,74	10	2,47
1	C	212,44	191,16	48,08	10	2,52
2	C	192,34	191,11	43,53	10	2,28
3	C	145,54	147,89	32,05	10	2,17
4	C	175,22	186,87	39,57	10	2,12

Appendix 5. Water analysis results of DRP (mg l^{-1}) and TP (mg l^{-1}) for treatment A (22 June).

Freeze–thaw cycle	Date of leaching	Experimental plot	DRP mg l^{-1} (SFS 3025)	TP mg l^{-1} (SFS 3026)
1	19.3.2012	1	8,93	9,55
1	19.3.2012	2	8,96	9,72
1	19.3.2012	3	8,95	9,58
1	19.3.2012	4	8,13	8,75
2	26.3.2012	1	6,25	6,59
2	26.3.2012	2	3,19	3,42
2	26.3.2012	3	3,64	3,96
2	26.3.2012	4	2,44	3,64
3	2.4.2012	1	2,30	2,64
3	2.4.2012	2	1,08	1,23
3	2.4.2012	3	1,27	1,41
3	2.4.2012	4	1,44	1,57
4	11.4.2012	1	1,14	1,27
4	11.4.2012	2	0,55	0,63
4	11.4.2012	3	0,78	0,85
4	11.4.2012	4	0,81	0,91

Appendix 6. Water analysis results of DRP (mg l^{-1}) and TP (mg l^{-1}) for treatment B (5 July).

Freeze–thaw cycle	Date of leaching	Experimental plot	DRP mg l^{-1} (SFS 3025)	TP mg l^{-1} (SFS 3026)
1	19.3.2012	1	9,89	10,93
1	19.3.2012	2	9,60	10,53
1	19.3.2012	3	10,72	11,77
1	19.3.2012	4	8,10	8,76
2	26.3.2012	1	4,03	4,37
2	26.3.2012	2	3,54	3,76
2	26.3.2012	3	3,70	3,97
2	26.3.2012	4	4,39	4,66
3	2.4.2012	1	1,32	1,53
3	2.4.2012	2	1,29	1,42
3	2.4.2012	3	1,16	1,27
3	2.4.2012	4	1,63	1,76
4	11.4.2012	1	0,74	0,84
4	11.4.2012	2	0,82	0,87
4	11.4.2012	3	0,68	0,73
4	11.4.2012	4	1,01	1,06

Appendix 7. Water analysis results of DRP (mg l^{-1}) and TP (mg l^{-1}) for treatment C (1 August).

Freeze–thaw cycle	Date of leaching	Experimental plot	DRP mg l^{-1} (SFS 3025)	TP mg l^{-1} (SFS 3026)
1	19.3.2012	1	10,69	11,80
1	19.3.2012	2	10,16	10,63
1	19.3.2012	3	10,27	11,67
1	19.3.2012	4	7,88	8,36
2	26.3.2012	1	3,45	3,71
2	26.3.2012	2	2,23	3,01
2	26.3.2012	3	3,19	3,40
2	26.3.2012	4	1,73	5,14
3	2.4.2012	1	1,14	1,24
3	2.4.2012	2	1,09	1,13
3	2.4.2012	3	1,09	1,15
3	2.4.2012	4	0,69	0,71
4	11.4.2012	1	0,74	0,80
4	11.4.2012	2	0,62	0,64
4	11.4.2012	3	0,62	0,66
4	11.4.2012	4	0,41	0,42

Appendix 8. Result table for treatment A (22 June).

Freeze-thaw cycle	Leaching date	Replicate	Treatment	DRP, mg/l	TP, mg/l	Sample's (10g) dry weight, g	Plant sample's P-content, mg/g of dry matter	P-content of the total sample, mg/m2	P-content of the leached sample, mg	DRP of the water sample (400ml), mg	TP of the water sample (400ml), mg	The share of DRP of the total P leached from the sample	The share of TP of the total P leached from the sample	Bio-mass (dry) g/m2	Leached DRP mg / g dry matter	Leached TP mg / g dry matter	Leached DRP, mg/m2	Leached TP, mg/m2	Leached DRP, kg/ha
1	19.3.12	1	A	8,93	9,55	3,23	2,46	627,99	7,96	3,57	3,82	0,45	0,48	255,28	1,104	1,181	281,89	301,46	2,82
1	19.3.12	2	A	8,96	9,72	2,30	2,46	696,10	5,65	3,58	3,89	0,63	0,69	282,97	1,561	1,693	441,68	479,14	4,42
1	19.3.12	3	A	8,95	9,58	2,38	2,55	871,55	6,06	3,58	3,83	0,59	0,63	341,79	1,505	1,611	514,49	550,70	5,14
1	19.3.12	4	A	8,13	8,75	2,48	2,59	740,60	6,42	3,25	3,50	0,51	0,55	285,95	1,312	1,412	375,22	403,83	3,75
2	26.3.12	1	A	6,25	6,59	3,23	2,46	627,99	7,96	2,50	2,64	0,31	0,33	255,28	0,773	0,815	197,29	208,02	1,97
2	26.3.12	2	A	3,19	3,42	2,30	2,46	696,10	5,65	1,28	1,37	0,23	0,24	282,97	0,556	0,596	157,25	168,59	1,57
2	26.3.12	3	A	3,64	3,96	2,38	2,55	871,55	6,06	1,46	1,58	0,24	0,26	341,79	0,612	0,666	209,24	227,64	2,09
2	26.3.12	4	A	2,44	3,64	2,48	2,59	740,60	6,42	0,98	1,46	0,15	0,23	285,95	0,394	0,587	112,61	167,99	1,13
3	2.4.12	1	A	2,30	2,64	3,23	2,46	627,99	7,96	0,92	1,06	0,12	0,13	255,28	0,284	0,326	72,60	83,34	0,73
3	2.4.12	2	A	1,08	1,23	2,30	2,46	696,10	5,65	0,43	0,49	0,08	0,09	282,97	0,188	0,214	53,24	60,63	0,53
3	2.4.12	3	A	1,27	1,41	2,38	2,55	871,55	6,06	0,51	0,56	0,08	0,09	341,79	0,214	0,237	73,01	81,05	0,73
3	2.4.12	4	A	1,44	1,57	2,48	2,59	740,60	6,42	0,58	0,63	0,09	0,10	285,95	0,232	0,253	66,46	72,46	0,66
4	11.4.12	1	A	1,14	1,27	3,23	2,46	627,99	7,96	0,46	0,51	0,06	0,06	255,28	0,141	0,157	35,99	40,09	0,36
4	11.4.12	2	A	0,55	0,63	2,30	2,46	696,10	5,65	0,22	0,25	0,04	0,04	282,97	0,096	0,110	27,11	31,06	0,27
4	11.4.12	3	A	0,78	0,85	2,38	2,55	871,55	6,06	0,31	0,34	0,05	0,06	341,79	0,131	0,143	44,84	48,86	0,45
4	11.4.12	4	A	0,81	0,91	2,48	2,59	740,60	6,42	0,32	0,36	0,05	0,06	285,95	0,131	0,147	37,38	42,00	0,37

Appendix 9. Result table for treatment B (5 July).

Freeze-thaw cycle	Leaching date	Replicate	Treatment	DRP, mg/l	TP, mg/l	Sample's (10g) dry weight, g	Plant sample's P-content, mg/g of dry matter	P-content of the total sample, mg/m2	P-content of the leached sample, mg	DRP of the water sample (400ml), mg	TP of the water sample (400ml), mg	The share of DRP of the total P leached from the sample	The share of TP of the total P leached from the sample	Bio-mass (dry) g/m2	Leached DRP mg / g dry matter	Leached TP mg / g dry matter	Leached DRP, mg/m2	Leached TP, mg/m2	Leached DRP, kg/ha
1	19.3.12	1	B	9,89	10,93	2,84	2,78	538,40	7,91	3,96	4,37	0,50	0,55	193,67	1,391	1,538	269,44	297,77	2,69
1	19.3.12	2	B	9,60	10,53	2,55	2,51	458,58	6,41	3,84	4,21	0,60	0,66	182,70	1,504	1,650	274,85	301,48	2,75
1	19.3.12	3	B	10,72	11,77	2,67	2,52	422,60	6,72	4,29	4,71	0,64	0,70	167,70	1,608	1,765	269,61	296,02	2,70
1	19.3.12	4	B	8,10	8,76	2,47	2,74	380,01	6,76	3,24	3,50	0,48	0,52	138,69	1,314	1,421	182,22	197,06	1,82
2	26.3.12	1	B	4,03	4,37	2,84	2,78	538,40	7,91	1,61	1,75	0,20	0,22	193,67	0,567	0,615	109,79	119,05	1,10
2	26.3.12	2	B	3,54	3,76	2,55	2,51	458,58	6,41	1,42	1,50	0,22	0,23	182,70	0,555	0,589	101,35	107,65	1,01
2	26.3.12	3	B	3,70	3,97	2,67	2,52	422,60	6,72	1,48	1,59	0,22	0,24	167,70	0,555	0,595	93,06	99,85	0,93
2	26.3.12	4	B	4,39	4,66	2,47	2,74	380,01	6,76	1,76	1,86	0,26	0,28	138,69	0,712	0,756	98,76	104,83	0,99
3	2.4.12	1	B	1,32	1,53	2,84	2,78	538,40	7,91	0,53	0,61	0,07	0,08	193,67	0,186	0,215	35,96	41,68	0,36
3	2.4.12	2	B	1,29	1,42	2,55	2,51	458,58	6,41	0,52	0,57	0,08	0,09	182,70	0,202	0,223	36,93	40,66	0,37
3	2.4.12	3	B	1,16	1,27	2,67	2,52	422,60	6,72	0,46	0,51	0,07	0,08	167,70	0,174	0,190	29,17	31,94	0,29
3	2.4.12	4	B	1,63	1,76	2,47	2,74	380,01	6,76	0,65	0,70	0,10	0,10	138,69	0,264	0,285	36,67	39,59	0,37
4	11.4.12	1	B	0,74	0,84	2,84	2,78	538,40	7,91	0,30	0,34	0,04	0,04	193,67	0,104	0,118	20,16	22,88	0,20
4	11.4.12	2	B	0,82	0,87	2,55	2,51	458,58	6,41	0,33	0,35	0,05	0,05	182,70	0,128	0,136	23,48	24,91	0,23
4	11.4.12	3	B	0,68	0,73	2,67	2,52	422,60	6,72	0,27	0,29	0,04	0,04	167,70	0,102	0,109	17,10	18,36	0,17
4	11.4.12	4	B	1,01	1,06	2,47	2,74	380,01	6,76	0,40	0,42	0,06	0,06	138,69	0,164	0,172	22,72	23,85	0,23

Appendix 10. Result table for treatment C (1 August).

Freeze-thaw cycle	Leaching date	Replicate	Treatment	DRP, mg/l	TP, mg/l	Sample's (10g) dry weight, g	Plant sample's P-content, mg/g of dry matter	P-content of the total sample, mg/m2	P-content of the leached sample, mg	DRP of the water sample (400ml), mg	TP of the water sample (400ml), mg	The share of DRP of the total P leached from the sample	The share of TP of the total P leached from the sample	Bio-mass (dry) g/m2	Leached DRP mg / g dry matter	Leached TP mg / g dry matter	Leached DRP, mg/m2	Leached TP, mg/m2	Leached DRP, kg/ha
1	19.3.12	1	C	10,69	11,8	2,52	2,83	601,21	7,12	4,28	4,72	0,60	0,66	212,44	1,700	1,877	361,17	398,67	3,61
1	19.3.12	2	C	10,16	10,63	2,28	2,70	519,32	6,15	4,06	4,25	0,66	0,69	192,34	1,784	1,867	343,18	359,06	3,43
1	19.3.12	3	C	10,27	11,67	2,17	3,10	451,17	6,72	4,11	4,67	0,61	0,69	145,54	1,896	2,154	275,88	313,48	2,76
1	19.3.12	4	C	7,88	8,36	2,12	2,49	436,30	5,27	3,15	3,34	0,60	0,63	175,22	1,489	1,579	260,82	276,71	2,61
2	26.3.12	1	C	3,45	3,71	2,52	2,83	601,21	7,12	1,38	1,48	0,19	0,21	212,44	0,549	0,590	116,56	125,34	1,17
2	26.3.12	2	C	2,23	3,01	2,28	2,70	519,32	6,15	0,89	1,20	0,15	0,20	192,34	0,392	0,529	75,32	101,67	0,75
2	26.3.12	3	C	3,19	3,4	2,17	3,10	451,17	6,72	1,28	1,36	0,19	0,20	145,54	0,589	0,628	85,69	91,33	0,86
2	26.3.12	4	C	1,73	5,14	2,12	2,49	436,30	5,27	0,69	2,06	0,13	0,39	175,22	0,327	0,971	57,26	170,13	0,57
3	2.4.12	1	C	1,14	1,24	2,52	2,83	601,21	7,12	0,46	0,50	0,06	0,07	212,44	0,181	0,197	38,52	41,89	0,39
3	2.4.12	2	C	1,09	1,13	2,28	2,70	519,32	6,15	0,44	0,45	0,07	0,07	192,34	0,191	0,198	36,82	38,17	0,37
3	2.4.12	3	C	1,09	1,15	2,17	3,10	451,17	6,72	0,44	0,46	0,06	0,07	145,54	0,201	0,212	29,28	30,89	0,29
3	2.4.12	4	C	0,69	0,71	2,12	2,49	436,30	5,27	0,28	0,28	0,05	0,05	175,22	0,130	0,134	22,84	23,50	0,23
4	11.4.12	1	C	0,74	0,80	2,52	2,83	601,21	7,12	0,30	0,32	0,04	0,04	212,44	0,118	0,127	25,00	27,03	0,25
4	11.4.12	2	C	0,62	0,64	2,28	2,70	519,32	6,15	0,25	0,26	0,04	0,04	192,34	0,109	0,112	20,94	21,62	0,21
4	11.4.12	3	C	0,62	0,66	2,17	3,10	451,17	6,72	0,25	0,26	0,04	0,04	145,54	0,114	0,122	16,65	17,73	0,17
4	11.4.12	4	C	0,41	0,42	2,12	2,49	436,30	5,27	0,16	0,17	0,03	0,03	175,22	0,077	0,079	13,57	13,90	0,14