Impacts of agricultural water protection measures on erosion, phosphorus and nitrogen loading based on high-frequency on-line water quality monitoring

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ACADEMIC DISSERTATION
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Abstract

There is an urgent need to decrease agriculture-contributed nutrient loading to surface waters. Excess amounts of phosphorus and nitrogen may lead to severe environmental problems, such as eutrophication and toxic algal blooms. Potential mitigation measures have been introduced to reduce loading, but their impacts on erosion, phosphorus and nitrogen loading are difficult to detect, due to challenging monitoring of diffuse (nonpoint) loading. New methods for defining nutrient loads are therefore needed. Accurate quantifying of diffuse loading also provides valuable information on developing adaptation strategies and efficient management practices to attain targets set by the European Union Water Framework Directive.

Here, high-frequency on-line water quality and quantity monitoring (HFM) was used to detect the impacts of various agricultural mitigation measures on erosion, phosphorus and nitrogen loading on the catchment scale. Gypsum, wetland and wintertime vegetation cover in a cold climate were examined. The benefits of HFM were assessed by comparing the impacts of varying sampling frequencies on nutrient load estimations in stream waters. The effectiveness of the mitigation measures was assessed in different sized catchments under varying hydrologic conditions. Here, we 1) determined how HFM can be used to obtain more precise estimations of nutrient loads on the catchment scale, 2) tested an approach to identifying the changes in nutrient loading due to management practices conducted in the catchment and 3) studied the impacts of various agricultural mitigation measures (gypsum, wetland and wintertime vegetation), using HFM.

Comparing the various sampling intervals in the load calculations clearly revealed the value of HFM. We found that with discrete water samples, phosphorus load was more likely underestimated compared to sensor-based reference load. Based on hysteresis analysis, fields were considered important source areas of phosphorus. Gypsum reduced erosion and phosphorus loading very effectively in clayey agricultural catchment. Dissolved reactive phosphorus concentrations also became lower after gypsum application. The wintertime vegetation cover decreased the total phosphorus loads under mild winter conditions, when phosphorus loading is usually major. No impact on the dissolved reactive phosphorus concentration was observed. Small constructed wetland retained phosphorus and nitrogen on a yearly basis. The wetland retained most of the incoming phosphorus and nitrogen loads during the growing season, but in spring and autumn the effectiveness was weak. The seasonal and short-term variation in nutrient removal efficiency would not have been detected without HFM.

In conclusion, we provide a guideline on how to develop future water quality monitoring and how to assess the effectiveness of the various mitigation measures on the catchment scale. HFM can be used not only for estimating the impacts of agricultural mitigation measures, but also for providing more information on the water quality

impacts of land-use changes or impacts of stormwater treatment practices, as well as for developing models to produce more reliable scenarios for nutrient loading in changing climates. The most effective way to reduce nutrient loading in arable clayey catchments may be mitigation measures such as gypsum and wintertime vegetation conducted in large field areas.

Tiivistelmä

Pintavesiä rehevöittävän maataloudesta peräisin olevan ravinnekuormituksen vähentämiseksi tarvitaan kiireellisesti lisää toimia. Vesistöihin päätyvä ylimääräinen fosfori ja typpi saattavat aiheuttaa vakavan riskin ympäristölle rehevöitymisen ja lisääntyvien myrkyllisten sinileväkukintojen myötä. Kuormituksen vähentämiseksi on käytetty erilaisia vesiensuojelumenetelmiä, mutta niiden todellisen tehokkuuden ja vaikutusten todentaminen valuma-aluetasolla on vaikeaa johtuen hajakuormituksen mittaamisen hankaluudesta. Hajakuormituksena vesistöihin päätyvän ravinnekuormituksen tarkka mittaaminen edistäisi kehitystä kohti tehokkaita vesiensuojelumenetelmiä hyödyntäviä strategioita, joilla Euroopan Unionin vesipuitedirektiivin (VPD) asettamat tavoitteet voitaisiin saavuttaa.

Tässä väitöskirjatyössä selvitettiin, miten automaattista tiheän mittausvälin veden laadun ja määrän seurantaa voidaan hyödyntää todentamaan maatalouden vesiensuojelumenetelmien vaikuttavuutta valuma-aluetasolla. Automaattisen veden laadun seurannan tuomaa hyötyä ravinnekuormituksen arvioinnissa selvitettiin vertailemalla eri näytteenottotiheyksien vaikutusta virtavesien ravinnekuormitusarvioihin. Vesiensuojelumenetelmien tehokkuutta arvioitiin erikokoisilla valuma-alueilla erilaisissa hydrologisissa olosuhteissa. Työn tavoitteena oli 1) tutkia, miten automaattista veden laadun seurantaa voidaan hyödyntää tarkentamaan ravinnekuormitusarvioita valuma-aluetasolla, 2) selvittää automaattista veden laadun seurantaa hyödyntäviä lähestymistapoja, joilla vesiensuojelumenetelmien vaikutukset ravinnekuormitukseen voidaan valuma-aluetasolla todentaa, ja 3) tutkia kolmen eri vesiensuojelumenetelmän (kipsi, kosteikko ja talviaikainen kasvipeitteisyys) vaikutuksia valuma-alueella.

Näytteenottotiheyksiä vertailemalla havaittiin automaattisen tiheän mittausvälin seurannan tärkeys kuormituslaskennassa. Yksittäisten vesinäytteiden perusteella fosforikuorma todennäköisimmin aliarvioidaan verrattuna tarkempaan, antureilla määritettyyn vertailukuormaan. Hysteresis-analyysin perusteella voitiin vahvistaa peltojen olevan merkittävä fosforikuorman alkulähde tutkimusalueilla. Kipsin havaittiin vähentävän hyvin tehokkaasti eroosiota ja fosforikuormaa savisella peltovaltaisella valuma-alueella. Myös liukoisen fosforin pitoisuudet laskivat kipsin levityksen jälkeen. Talviaikainen kasvipeitteisyys vähensi fosforikuormaa leudoissa talviolosuhteissa, jolloin kuormitus yleensä on voimakasta. Liukoisen fosforin pitoisuuksissa ei havaittu muutoksia. Pieni rakennettu kosteikko vähensi fosfori- ja typpikuormaa vuositasolla. Kosteikko pidätti fosforia ja typpeä tehokkaimmin kasvukaudella, mutta kasvukauden ulkopuolella sen teho oli heikko. Kosteikon tehokkuuden nopeaa ja vuodenaikojen välistä vaihtelua ei olisi havaittu ilman automaattista tiheän mittausvälin seurantaa.

Työn lopputuloksena laadittiin suositukset veden laadun seurannan kehittämiselle lähitulevaisuudessa sekä valuma-aluetasolla tapahtuvan vesiensuojelutoimenpiteiden vaikutusten seuraamiselle. Automaattista veden laadun seurantaa voidaan hyödyntää paitsi maatalouden vesiensuojelumenetelmien vaikutusten todentamisessa, myös maankäytön muutosten ja hulevesien käsittelyn vaikutusten seuraamisessa. Tarkempaa tietoa voidaan myös hyödyntää ravinnekuormitusmallien tarkentamisessa ja tuottamaan luotettavampaa tietoa ilmastonmuutoksen vaikutuksista ravinnekuormitukseen. Tehokkain lähestymistapa maatalouden kuormituksen vähentämiseksi savisilta peltoalueilta on hyödyntää laajalla pelto-

pinta-alalla toteutettavia vesiensuojelumenetelmiä, kuten kipsi ja talviaikainen kasvipeitteisyys.

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I'd like to acknowledge the Maa- ja vesitekniikan tuki ry, Yara Finland Oy, the Uusimaa Centre for Economic Development, Transport and the Environment, Pro Agria Southern Finland and Water Protection Association of the River Vantaa and Helsinki Region, which funded the monitoring programme in the Lepsämänjoki River and in Nummenpää ditch.

Thank you my family, my dear wife Hanna and our lovely children Saana, Aaro and Aamos.

Maybe you thought that Dad's going to work forever with his dissertation. I don't blame you.

In Helsinki March 14th 2018

Pasi Valkama

Contents

List of original publications

This thesis is based on the following publications:

I **Valkama, P**. & Ruth, O. (2017). Impact of calculation method, sampling frequency and hysteresis on suspended solids and total phosphorus load estimations in cold climate. *Hydrology Research,* 48:6, 1594–1610.

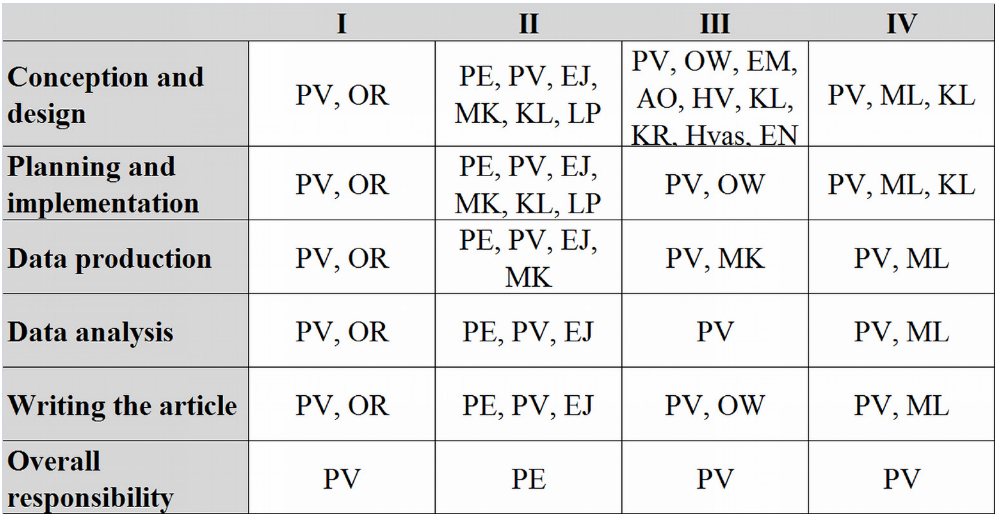
II Ekholm, P., **Valkama, P.**, Jaakkola, E., Kiirikki M., Lahti K. & Pietola L. (2012). Gypsum amendment of soils reduces phosphorus losses in an agricultural catchment. *Agricultural and Food Science* 21, 279–291.

III **Valkama, P**., Mäkinen, E., Ojala, A., Vahtera, H., Lahti, K., Rantakokko, K., Vasander, H., Nikinmaa, E & Wahlroos, O. (2017). Seasonal variation in nutrient removal efficiency of a boreal wetland detected by high-frequency on-line monitoring. *Ecological Engineering* 98, 307–317.

IV **Valkama, P.**, Luoto, M. & Lahti K. (2017) Phosphorus load can be reduced by wintertime vegetation cover in boreal agricultural catchment. Submitted to Environmental Monitoring and Assessment.

The publications are referred to in the text by their roman numerals.

Division of labour in coauthored articles



	I	II	III	IV
Conception and design	PV, OR	PE, PV, EJ, MK, KL, LP	PV, OW, EM, AO, HV, KL, KR, Hvas, EN	PV, ML, KL
Planning and implementation	PV, OR	PE, PV, EJ, MK, KL, LP	PV, OW	PV, ML, KL
Data production	PV, OR	PE, PV, EJ, MK	PV, MK	PV, ML
Data analysis	PV, OR	PE, PV, EJ	PV	PV, ML
Writing the article	PV, OR	PE, PV, EJ	PV, OW	PV, ML
Overall responsibility	PV	PE	PV	PV

PV = Pasi Valkama, OR = Olli Ruth, PE = Petri Ekholm, EJ = Elina Jaakkola (Röman), MK = Mikko Kiirikki, LP = Liisa Pietola, OW = Outi Wahlroos, EM = Emmi Mäkinen, AO = Anne Ojala, HV = Heli Vahtera, KL = Kirsti Lahti, KR = Kari Rantakokko, HVas = Harri Vasander, EN = Eero Nikinmaa, ML= Miska Luoto

Abbreviations

BMP	Best management practices
DO	Dissolved oxygen
DRP	Dissolved reactive phosphorus
GLM	Generalized linear model
HFM	High-frequency monitoring
NO_3-N	Nitrate nitrogen
PP	Particulate phosphorus
SS	Suspended solids
TN	Total nitrogen
TP	Total phosphorus
WFD	Water Framework Directive
WVC	Wintertime vegetation cover

List of tables and figures

1 Introduction

Hydrogeographic research, as a part of physical geography, has traditionally focused on the causal connection between humans and water systems. Anthropogenic alterations in the water environment have dramatically increased, due to industrialization and global population growth. Increasing demands for food production have been fulfilled not only through fertilizers, pesticides and irrigation, but also by developing more productive plants. The volume of nutrients lost in the global food-supply chain has altered the natural balance, and thus nutrients are concentrated in surface waters (Abel 1968; Biswas & Biswas 1975; Kaplan & Thode 1981; Pimentel *et al.* 1995; McConville *et al.* 2015).

Eutrophication and toxic algal blooms are some of the most visible examples of the impacts of human activities altering natural nutrient cycles (Zamparas & Zacharias 2014). Excessive amounts of the main nutrients phosphorus (P) and nitrogen (N) discharged into freshwater and marine systems have degraded the water environment throughout the globe (Bechmann *et al.* 2008; Kronvang *et al.* 2009; Elser 2012). Mitigation options for reducing P and N loading is a priority in many countries. For example, the EU Water Framework Directive (WFD) obligates member countries to improve the quality of surface waters to achieve good ecological status of all waters (European Parliament 2000). In the USA, the adverse effects of eutrophication have been estimated to cost $ 2.2 billion annually (Dodds *et al.* 2009). Point sources of nutrients have been effectively decreased, e.g. by the establishment of wastewater treatment plants, and thus managing nutrient loading from diffuse sources has become more important. Nutrient surpluses, especially from agricultural activities, have contributed to diffuse nutrient loading to re-

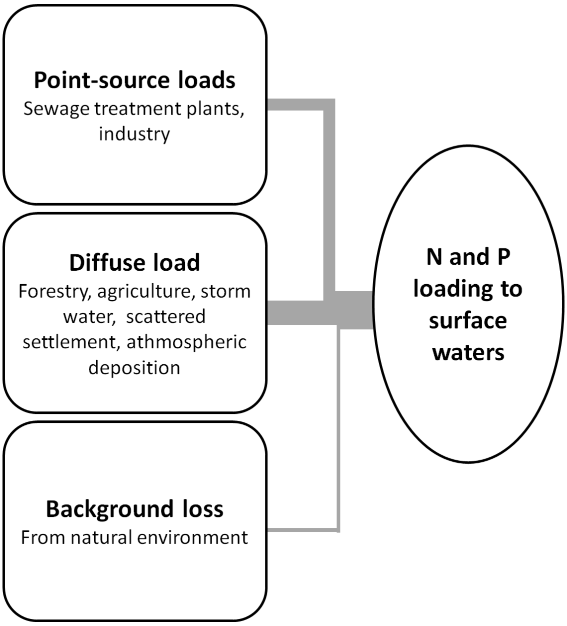


Figure 1. Source apportionment of nutrient loads discharging to surface waters. Point-source loading is usually easy to quantify. Diffuse loading and background loss are more challenging to quantify and qualify, due to their complex behaviours and dependency on hydrologic factors (precipitation, runoff).

ceiving waters (Grizzetti *et al.* 2012; Withers *et al.* 2014). Therefore, managing nutrient supplies from agriculture plays an important role in reducing eutrophication impacts on bodies of water.

Various management practices for reducing agricultural loading have been implemented in many countries (Syversen 2005; Deasy *et al.* 2009; Moore *et al.* 2010; Hughes & Quinn 2014; Land *et al.* 2016). The impacts of these mitigation measures on nutrient loads have been studied in controlled systems at field plot scales (Muukkonen *et al.* 2007; Withers *et al.* 2007; Deasy *et al.* 2009; Smith & Francesconi 2015), but it is not fully known whether this also applies to improved water quality at the catchment scale. Further studies concerning more complicated systems under varying hydrological conditions at the catchment scale are needed. Studies performed to detect agricultural diffuse loading and the impacts of mitigation measures at the catchment scale are still mostly based on discrete water samples (Hughes & Quinn 2014; Reza *et al.* 2016). Low sampling frequency may be biased towards low-flow conditions in catchments with flashy characteristics (Letcher *et al.* 1999), and thus load calculations based on discrete samples will more likely lead to too small estimations (Jones *et al.* 2012). Detecting the impacts of management practices at the catchment scale, based on discrete water samples, is challenging due to the complex behaviour of agricultural diffuse loading (Cherry *et al.* 2008). Unreliable load estimations make it impossible to detect changes in nutrient loading due to mitigation measures. More accurate methods in water quality monitoring are needed to determine the range of diffuse loading and to detect the impacts of mitigation measures at the catchment scale.

Here, a high-frequency monitoring (HFM)-based approach to detect the impacts of management practices (mitigation measures) in variously sized catchments was developed. HFM was then utilized to determine the efficiency and applicability of three different mitigation measures (gypsum, wetland and wintertime vegetation) to reduce nutrient loading in boreal environments. Finally a guideline for improving future water-quality monitoring was developed. The main

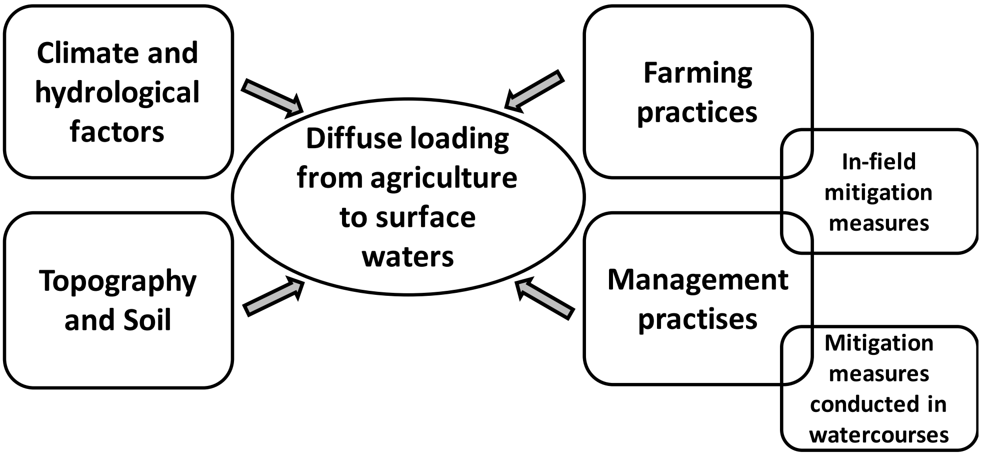


Figure 2. Main factors affecting agricultural diffuse loading. The climate and hydrological factors include temperature, precipitation and runoff, while topography and soil include slope length and steepness, soil type and compaction, and farming practices that comprise fertilizing, cultivation, vegetation cover and manure management. With sustainable farming practices and mitigation measures nutrient loading can be decreased.

sources and their contribution to N and P loading in catchments are presented in Figure 1.

1.1 Complexity of agricultural diffuse load monitoring

Nutrient losses from agriculture are dependent on a variety of factors (Figure 2), such as precipitation and temperature, soil moisture and compaction, fertilization, soil and vegetation characteristics, management practices and slope steepness and length (Haygarth & Jarvis 1999). Diffuse loading is highly flow-dependent. High levels of precipitation or snowmelt will lead to higher erosion rates and higher amounts of fertilizers to be flushed away to surface waters (Langlois *et al.* 2005; Gao *et al.* 2007; Drewry *et al.* 2009). Thus, diffuse loading occurs episodically in short-term peaks, and annual loads will vary according to precipitation and flow.

Point-source loading is usually easy not only to quantify and qualify, but also to control (Loague & Corwin 2005). In boreal climate regions, most of the diffuse (nonpoint) nutrient loading occurs outside the growing season (Puustinen *et al.* 2007). Most of the loading is contributed by the spring snowmelt period and autumn rains, while the nutrient loads are transported during relatively short periods in several individual flow events (Langlois *et al.* 2005; Gao *et al.* 2007; Drewry *et al.* 2009). Thus, mitigation measures that can reduce load under most loading conditions outside the growing season are needed.

Due to its relatively constant input, the concentration of a point load is diluted when river flow increases, whereas a diffuse (nonpoint) load usually increases with river flow (Bowes *et al.* 2008). The contribution of high-flow events has been noticed more likely to show trends in stream chemistry (Murdoch & Shanley 2006), and thus the change in diffuse loading is evident especially during a flood period. When the evidence for impacts of management practices is investigated, the study should focus on flood periods (Campbell *et al.* 2015). Due to the rapid changes in water quality and the highly fluctuating quality and quantity of stream water, the highest flow peaks are more likely to be missed with traditional discrete water sampling (Jones *et al.* 2012, Skarbovik *et al.* 2012). Therefore the impacts of management practices may be difficult to detect without HFM.

1.2 Mitigation measures for reducing agricultural nutrient loading

A wide variety of management practices for reducing nutrient loading from agriculture has been implemented. The best management practices (BMP) may include control of excess nutrient fluxes from agriculture to the surface waters and groundwater (Birgand et al. 2007). Diffuse sources of pollution are typically scattered around the catchment, a problem often encountered in targeting the mitigation measures to the most important source areas (Cherry *et al.* 2008). Buffer zones have been studied and implemented in North America and Europe (Dunn *et al.* 2011; Weissteiner *et al.* 2013). They reduce P and N concentrations, especially in surface runoff. To reduce agricultural loading efficiently buffer zones should cover most of the banks of ditches and rivers. However, the problem could still be encountered in cold regions where the vegetation is dormant outside the growing season, when most of the loading occurs (Uusi-Kämppä 2005). The effectiveness of buffer zones is also lowered in areas where large volumes of water and nutrients are bypassed via subsurface drainage (Osborne & Kovacic 1993).

The impact of wetlands on nutrient load reduction has been studied widely in various climate regions (Fisher & Acreman 2004; Braskerud *et al.* 2005; Hansson *et al.* 2005; Land *et al.*

Figure 3. Photograph of erosion in a ploughed field. Erosion in unprotected fields may be severe at the end of the snowmelt period. Water flowing from fields causes erosion and flushes suspended solids (SS) and phosphorus (P) into field ditches and onwards to watercourses. Erosion control in such areas is therefore vital (Nummenpää catchment, 9.4.2008).

2016). Usually, investigations concerning the efficiency of wetlands are based on discrete water sampling (Vohla *et al.* 2007; Lu *et al.* 2009; Dias & Baptista 2015), but sensors have also been used to detect the impacts of wetlands (Wahlroos *et al.* 2015). The efficiency of wetlands in retaining total phosphorus (TP) and total nitrogen (TN) is based on vegetation uptake and trapping, denitrification, hydraulic retention time and sedimentation (Braskerud 2002; Brix *et al.* 2003; Stottmeister *et al.* 2003 Silvan *et al.* 2004; Vymazal 2007). In Finland, farmers have received public subsidies for constructed wetlands since 1995 as part of the Finnish agroenvironmental programme (Valpasvuo-Jaatinen *et al.* 1997).

Reduced tillage and no-tillage decrease erosion and P loading (Muukkonen *et al.* 2007; Withers *et al.* 2007; Ulén *et al.* 2010; Soane *et al.* 2012; Smith & Francesconi 2015). Conventional tillage increases the risk not only of erosion and compaction of soils, but also the loss of organic matter (Tebrügge 2001). No-tillage may also reduce the risk of N leaching, due to decrease in N mineralization (Hansen *et al.* 2010; Morris *et al.* 2010). The disadvantage of no-tillage, reduced tillage and wintertime vegetation cover (WVC) may be the increasing dissolved reactive phosphorus (DRP) fluxes due to P stratification in the topsoil layer (Rankinen *et al.* 2015; Baker *et al.* 2017). Christianson *et al.* (2016) showed that no-tillage increased DRP loading in field-scale studies, but they also emphasized the need for further investigations concerning the impact of cropping management, fertilizer application, soil property and drainage design impacts on P runoff. Lemke *et al.* (2011) observed no changes in water quality, despite BMP (no-tillage, buffer zones) being conducted in the agricultural catchments.

1.3 Water quality sensors in nutrient load monitoring

Water quality sensors have been used increasingly in recent years to detect changes in important water quality parameters, such as dissolved oxygen (DO), temperature, conductivity and turbidity (Pellerin *et al.* 2012; Bende-Michl *et al.* 2013; Bowes *et al.* 2015; Campbell *et al.* 2015; Lloyd *et al.* 2014). Technical development of sensors has increased the number of parameters that may be measured in situ.

Turbidity has been used as a surrogate measure for SS- and sediment-associated contaminants, such as P, in many studies (Gippel 1995; Wass & Leeks 1999; Pavanelli & Pagliarani 2002; Stubblefield *et al.* 2007; Jones *et al.* 2011; Viviano *et al.* 2014). Clay particles are often associated with P, due to their large surface area, high exchange capacity and charged surfaces (Stone & English, 1993). High-frequency SS and TP data have been utilized to clarify the benefit of HFM in monitoring water quality and load estimations (Jones *et al.* 2012; Skarbovik *et al.* 2012). Bende-Michl *et al.* (2013) used HFM to study the nutrient concentration dynamics in mixed land-use catchments in Australia.

Continuous monitoring provides more precise information on the nutrient load, dynamics and potential sources and can aid in designing efficient catchment management practices. Lloyd *et al.* (2016a) examined the changing relationships between discharge and water quality to reveal likely source areas and flow pathways of nutrients in the catchment. Campbell *et al.* (2015) studied the impact of changes in soil P status and septic tank systems on water quality in the UK. A bankside analyser was used to measure TP at high frequency. Bowes *et al.* (2015) gathered high- frequency P and nitrate nitrogen (NO_3-N) data with an autosampler/analyser and a probe, based on ultraviolet (UV) absorption, to study P and N inputs from different sources to a rural river system.

High-resolution water quality data gathered with in-situ sensors have enabled the detection of the more complex behaviour of concentration/discharge patterns. Due to the wide variation in runoff, the concentrations of pollutants may be different in the rising and falling stages of the hydrograph (Bieroza & Heathwaite 2015). In hydrologic studies, this varying nonlinear relationship is usually termed hysteresis (Bowes *et al.* 2015). The varying relationship between discharge and concentration complicates load estimations based on discharge/concentration rating curves (Gentile *et al.* 2010). The size and shape of the hysteresis loops may be used as indicators of the location of the nutrient sources and the runoff processes in a catchment (Krueger *et al.* 2009; Bowes *et al.* 2015; Lloyd *et al.* 2016a)

1.4 Research aims and background

Insufficient knowledge of the efficiency of various mitigation methods for decreasing nutrient loading, as promoted in the Finnish agroenvironmental programme, obligates us to obtain scientifically reliable answers of nutrient loading from fields at the catchment scale (Uusitalo *et al.* 2014). Here, we describe in-situ monitoring methods, their applicability to quantifying diffuse nutrient loading from arable land and efficiency of various mitigation methods in reducing loading from fields to watercourses under different hydrological conditions.

In **Paper I** we verified the hypothesis of the benefit of HFM in diffuse load monitoring and nutrient load calculation (Figure 4), but also studied the contribution of fields in P loading and

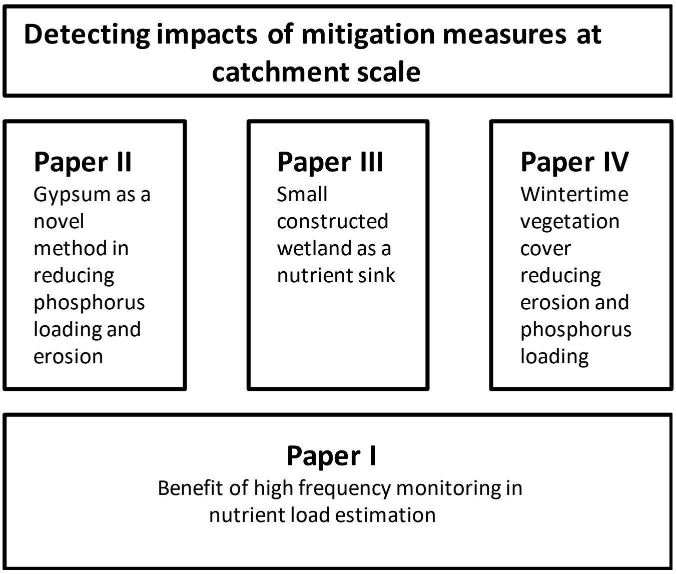


Figure 4. Schematic structure of the thesis. The groundwork was formed (**Paper I**) for the method used later in **Papers II–IV**. The overall aim was to determine how HFM can be utilized to detect the impacts of agricultural mitigation measures.

erosion. In **Papers II** and **IV** we investigated HFM in detecting the impacts of water-protection measures conducted in fields (gypsum and WVC), and in **Paper III** HFM was used to study the impacts of a measure conducted in a water environment (wetland) to mitigate SS and nutrient loading.

Here, we aimed at 1) determining how HFM can be used to obtain more precise estimations of nutrient loads, 2) developing an approach to identify the changes in nutrient loading due to management practices conducted at the catchment and 3) examining the impacts of various agricultural mitigation measures (gypsum, wetland and WVC) at the catchment scale. Finally, we created a guideline for developing future water-quality monitoring and for demonstrating how to assess the effectiveness of the various mitigation measures at the catchment scale.

2 Materials and methods

2.1 Study areas

All the study catchments were located in southern Finland in the boreal climate region. The area of the catchments varied from 2.45 km^2 to 23 km^2 and the agricultural field cover 15–41% of the catchment area (Table 1). The fields were typically located in relatively flat clay soil areas and thus particulate phosphorus (PP) is the main form of P in these catchments.

The annual mean precipitation in southern Finland is 660 mm and mean temperature 5 °C. During the cold winter seasons, the surface waters are typically covered with ice. Normally, this climate region has four distinct seasons with two flood periods: snowmelt-induced flooding in spring and flood peaks after the autumn rains. Most of the diffuse nutrient load is transported during these two flood periods (Puustinen et al.

Table 1. Study catchments area, proportion of clayey soils and main land use.

Study site	Area (km²)	Clay (%)	Forest (%)	Field (%)	Urban (%)
Lepsämänjoki River	23.00	52	47	37	12
Lukupuro River	7.60	33	43	18	36
Nummenpää ditch	2.45	50	44	41	11
Stream Kilsoi	5.50	27	43	15	42

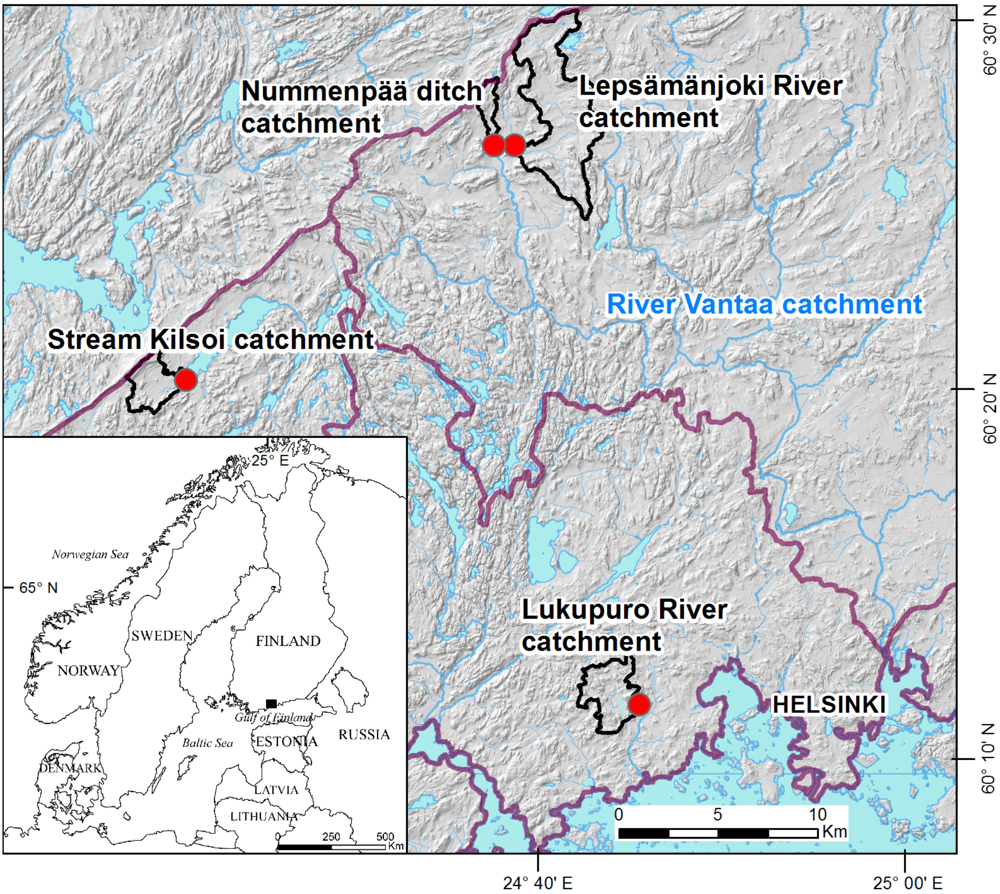


Figure 5. Location of the study catchments (black line). The Nummenpää ditch and the Lepsämänjoki River are located inside the Vantaa River catchment, which is one of the main catchments (purple line) on the coast of southern Finland. The red dots indicate the HFM stations.

2007).

2.2 On-line monitoring of water quality and quantity

Water quality and quantity were monitored at 10–60-min intervals, depending on the monitoring site. Sensors were installed in the water, attached to a metallic rack, and submerged at the bottom of the ditch, stream or river. The quality and quantity were measured concomitantly to create nearly continuous concentration/runoff

Figure 6. Photograph of the sensors used in the study. Sensors based on ultraviolet-visible (UV-VIS) spectroscopy (left) used to measure turbidity, nitrate-nitrogen (NO_3-N) and dissolved organic carbon (DOC) in the Lepsämänjoki River and the wetland studies. A YSI sensor (right) monitoring turbidity, conductivity and temperature in front of a V-notch weir in a small field ditch at the gypsum application study site (left: Lepsämänjoki River monitoring site, Nurmijärvi 21.3.2007, right: Nummenpää ditch, Nurmijärvi 14.11.2011)

pairs for load determination (Equation 1).

$$L=\sum^{n}_{i=0}Q(t)C(t) \qquad \text{(Eq. 1)}$$

where L is the hourly load, Q(t) the discharge at time t and C(t) the concentration at measuring time t.

Turbidity was measured in the Lepsämänjoki River (**I**, **II** and **IV**) and Lukupuro River (**I**) with a YSI 600 XLM (Yellow Springs Instruments (YSI) Inc., Yellow Springs, OH, USA) multiparametric sonde at 1-h intervals. In 2007, a Scan spectrolyser (Scan Messtechnik GmbH, Vienna, Austria) was added in the Lepsämänjoki River to measure NO_3-N, turbidity and dissolved organic carbon (DOC), also at 1-h intervals. YSI turbidity is based on nephelometric measuring and Scan on the absorbance of certain wavelengths of light. Scan and YSI turbidity was calibrated against the turbidity analysed in the laboratory. The flow velocity and water level in the Lepsämänjoki River were measured with an acoustic flow meter (StarFlow; Unidata Pty Ltd, O'Connor, ACT, Australia). Discharge was calculated as a function of flow velocity and cross-sectional area at certain water levels. A measuring weir was used in the Lukupuro River to record water level and determine the discharge. The data recorded were transmitted to a data server over a Global System for Mobile communication (GSM) network and visualized in an on-line data service. Weather data concerning the Lepsämänjoki River catchment were gathered from the closest Finnish Meteorological Institute's weather station (the Geophysics Observatory station in Nurmijärvi).

The sensors used to measure turbidity at 1-h intervals in the Nummenpää catchment (**II**) were YSI 600 OMS devices (YSI Inc.). Runoff was obtained by means of a V-notch weir that was constructed at the central monitoring site. Runoff at the lower site was calculated, based on the runoff measured at the central site and the catchment's relative size (lower-site catchment size/ central-site catchment size). Precipitation was recorded with a precipitation gauge at 1-h intervals.

Water quality in the wetland study (**III**) was collected by YSI (turbidity, DO) and Scan sensors (NO_3-N) at 10-min intervals. Data from the Scan sensors were calibrated based on manual water samples analysed in the laboratory. Flow velocity and water level were measured at the inflow of the wetland with an acoustic flow meter (StarFlow; Unidata). At the outflow, the water level was measured with a pressure gauge (STS Sensor Technik Sirnach AG, Sirnach, Austria).

Discharge was calculated as a function of the flow velocity and cross-sectional area of a certain water level. Outflow discharge was calculated, based on the inflow discharge and the wetland's own catchment size (540 ha / 550 ha). Precipitation was recorded with a Vaisala WXT weather transmitter at the inflow monitoring station at 10-min intervals.

2.3 Water quality and soil analyses

Water-quality analyses were used to obtain information on the parameters we could not detect with sensors, determine calibration data and verify sensor functioning. Manual water samples were mostly collected, using a 2-l Limnos sampler (Limnos Oyj, Turku, Finland). In the Nummenpää catchment, the water samples were collected with sample bottles, because the water depth was too low for the Limnos sampler. The samples from all monitoring stations corresponded to the depth and time of the sensor recordings.

The SS concentrations from the water samples were measured by filtration through 0.45 µm Nuclepore filters (SFS-EN 872). Turbidity was measured nephelometrically with a Hach 2100 AN IS turbidometer (Hach Company, Loveland, CO, USA), according to SFS-EN ISO 7027. The concentration of P was analysed with the ammonium molybdate spectrometric method (SFS ISO 6878), with ascorbic acid as a reducing agent. Before TP analysis the sample was digested by acid peroxodisulphate at 120 °C. DRP was determined in a filtered sample (Whatman Nuclepore polycarbonate, pore size 0.45 µm; Whatman plc, GE Healthcare Life Sciences, Little Chalfont, Buckinghamshire, UK) without digestion. NO_3-N in the wetland study was analysed according to SFS EN ISO 13395/DA in an accredited laboratory.

Soil analysis (**II**) was used to gather information on changes in soil chemistry before and after gypsum ($CaSO_4{\bullet}2H_2O$) application. Soil samples were taken from fields before sowing and fertilizing once before and five times after gypsum amendment ($4.1*10^3$ kg/ha). Ca, Mg, K and S were determined, using inductively coupled plasma (ICP) after the extraction of dry soil with a solution of 0.5 M ammonium acetate and 0.5 M acetic acid at pH 4.65. P was determined with the molybdenum blue method. Conductivity and pH were measured from a soil-water suspension.

2.4 Statistical analysis

Paper I: Differences between the turbidity in the manual samples and sensor data in the Lepsämänjoki and Lukupuro Rivers were compared, using the nonparametric Mann-Whitney U-test for two unrelated populations, due to the non-normal distribution of most of the datasets (Rock 1988; Ranta *et al.* 1991). Normality and log-normality were tested, using the Kolmogorov-Smirnov test and by visual evaluation of frequency distribution, as suggested by Reimann & Filzmoser (2000). Correlation coefficients were used in the analysis between turbidity and SS and turbidity and TP. The errors in the models created were studied, using RMSE (root-mean-square error), as suggested by Jones *et al.* (2011). The two-tailed paired T-test was used for comparison between the laboratory analyses and the sensor data measured at the sampling time to test the proper functioning of the sensors and to reveal possible systematic malfunctioning in the turbidity sensors. The differences and correlations were considered statistically significant at the risk level of 0.05. All statistical analyses were performed with IBM SPSS Statistics 22 (IBM SPSS, Armonk, NY, USA).

Paper II: Changes in soil chemistry over time were studied, using repeated measures analysis of variance (ANOVA) with SAS Proc Mixed (SAS for Windows; SAS Institute Inc., Cary, NC, USA). The effect of fluctuating hydrological conditions was taken into account by analysing the differences in the relationship between turbidity and the concentrations of PP and DRP and flow before and after the gypsum amendment, with the aid of analysis of covariance (with SAS Proc GLM). In the covariance model, gypsum application was set as a qualitative and runoff volume as a quantitative variable with interaction taken into account.

Paper III: The minimum, maximum and median values of the parameters were calculated as descriptive statistics. The normal distribution of the data was studied, using the Kolmogorov-Smirnov test. The varying transformation of the data was tested, but non-normal distribution was still found. The statistical significance of the differences in TP and NO_3-N concentrations at the inflow and outflow was therefore analysed, using the nonparametric Wilcoxon signed-rank test. The null hypothesis was that wetlands did not impact the nutrient concentrations. The differences were considered statistically significant when $p < 0.01$.

The impacts of temperature, DO, inflow concentrations and inflow discharge on nutrient removal were analysed, using Pearson Correlation analysis. A level of significance of $p < 0.01$ was considered statistically significant. All statistical analyses were performed with IBM SPSS Statistics 22 (IBM SPSS).

Paper IV: Generalized linear modelling (GLM) was used to analyse the effects of runoff and air temperature on TP loading outside the growing seasons in 2007–2008 (low WVC) and 2013–2014 (high WVC). The values for TP load were non-normally distributed, bounded to zero on the lower side of the data and showed relatively strong overdispersion (residual deviance > degrees of freedom) (Crawley 2012). We therefore applied a quasi-Poisson distribution of error assumption with a logarithmic link function in the GLM, using the statistical program R (v. 3.3.3; R Development Core Team, 2017). The statistical significance of the change in deviance after including (or excluding) an explanatory variable in the model was determined, using an F-ratio test with a 5% significance level as the criterion.

2.5 Geographic Information System (GIS)-based catchment analysis

The catchment borders were delineated, using lidar data provided by the National Land Survey of Finland. Sewer network maps (by the municipality of Vihti), which were available for the Stream Kilsoi (**III**) area were used to define the catchment borders in the urban areas. The fields' subsurface drainage networks were not considered in the delineation, because the overland flow pathways were considered to be important route of SS and TP in clayey catchments.

Corine Land Cover (CLC) 2006 and 2012 were used to determine the catchment land use. The proportion of clayey soils was investigated from the data provided by the Geological Survey of Finland. The locations of the field plots and the spatial distribution of the cultivation methods (ploughed or with WVC) were examined from the data provided by the Agency for Rural Affairs. Empirical observations and farmer interviews conducted in the area of the Nummenpää ditch and Lepsämänjoki River were used to define the farming procedures used in the fields. All analyses were conducted, using ArcMap 9.2 or 10.2.2.

3 Summary of the original publications

3.1 Paper I

The benefit of HFM in load estimations was investigated in a cold climate region. HFM of water quality and quantity was conducted in two differently sized catchments throughout the year to examine the functioning of the sensors under different hydrological circumstances. Turbidity measured with sensors was used as a surrogate for TP and SS. In clayey catchments, turbidity correlated with SS as well as with TP, which is mainly in PP form, and thus more turbid water contains more P. Various SS and TP load calculation methods were compared, and the impact of sampling frequency on TP load estimations was tested. In both study catchments, we observed that load calculations based on discrete water samples were more likely underestimated than in sensor-based reference loads (Figure 7). This was due to the fact that the changes in concentrations and runoff in this cold climate region were very rapid, and thus the highest loading peaks were mostly missed with discrete sampling.

Hysteresis analysis was used to study the origin of TP in different seasons under varying hydrological conditions. The field areas were important sources of TP in both catchments. Hysteresis also impacted TP load. If the maximum TP and discharge were to occur in parallel, load

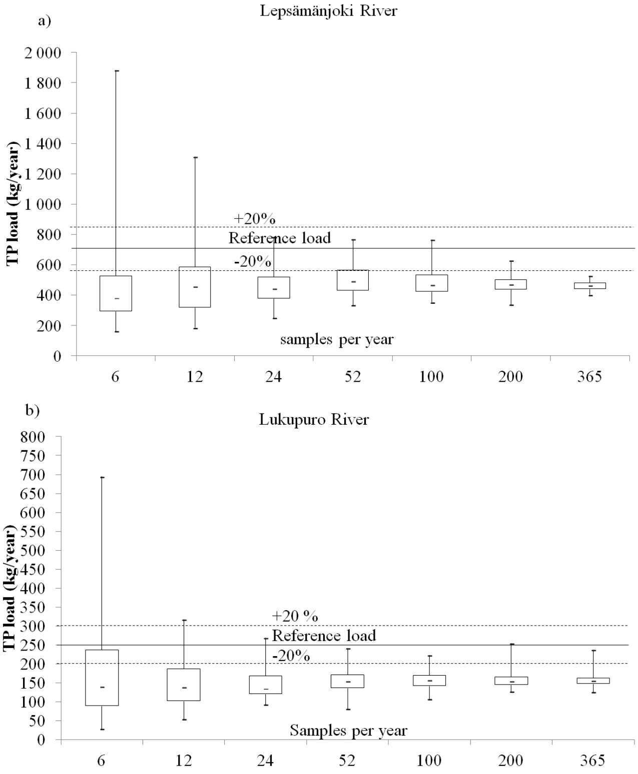


Figure 7. Impact of sampling frequency on yearly total phosphorus (TP) loads in the Lepsämänjoki River (a) and Lukupuro River (b). It was very difficult to achieve satisfactory results, based on discrete water samples. Clearly, the impact of mitigation measures would be masked by the inaccurate load monitoring resulting from the use of sparse sampling frequency.

Figure 8. Photograph of the profound impact of gypsum. Water in the field with no gypsum treatment (left) and in the field treated with gypsum (right). With the aid of gypsum, soil particles form larger aggregates and settle to the bottom of ponds (both pictures from the Nummenpää catchment, Nurmijärvi 10.11.2008).

would be very high.

In conclusion, HFM is a viable method for detecting wide ranges and more accurate amounts of SS and TP loading in small watercourses. We also concluded that it may be possible to detect the impact of certain water protection measures conducted in the upper catchment. Using discrete samples, changes in nutrient loading are very difficult to detect, due to highly biased estimations.

3.2 Paper II

The impact of gypsum amendment on P loading and erosion was examined, using HFM. Water quality and quantity were monitored before and after gypsum was applied in the catchment fields. We considered that change in the relationship between runoff and turbidity indicated lower erosion rates in the fields and thus lower PP loads.

Water quality and runoff were monitored with HFM at two sites in the lower and central parts of the catchment. Turbidity was used as a surrogate for PP and, together with runoff data, the hourly PP load was calculated. Soil samples were taken at depths of 0–20 cm in fields treated with gypsum. Samples were taken before and after gypsum application ($4.1*10^3$ kg/ha) to investigate the changes in soil chemistry.

Using a covariance model, we estimated that the gypsum reduced the loss of PP by 64%. Gypsum also reduced the DRP by one third, although the effectiveness was calculated, based on discrete water samples and was thus less precise. There were no similar changes in the water quality of the nearby reference catchment without any gypsum amendment. The ionic strength and SO_4 of the soils increased after gypsum application. No other changes were detected in the soil samples.

We concluded that gypsum was one of the most effective methods for reducing P loading to receiving waters, and thus is highly recommended. However, large-scale gypsum applications are not recommended for freshwater lake catchments, due to the elevated risk of P being released from sediments. High SO_4 concentrations can increase the magnitude of P released from sediments (Caraco *et al.* 1993).

3.3 Paper III

We examined the effectiveness of a small constructed wetland (0.5 ha) in reducing nutrient loading in different seasons throughout the year. Wetlands have been introduced as a measure for diminishing nutrient loading, e.g. from agriculture. However, studies of nutrient removal efficiency of wetlands are usually based on discrete water samples that may lead to largely biased load estimations. Thus, the accurate and short-term functioning of wetlands is impossible to detect.

HFM stations were installed at the inlet and outlet of the wetland receiving its waters from rural and urban subcatchments. Turbidity, NO_3-N and runoff were monitored at 10-min intervals. Sensor turbidity was converted to TP, using linear regression analysis, and sensor NO_3-N was calibrated with laboratory analysis. We estimated that the agricultural catchment contributed over 10 times higher P loads than the urban catchment. The impact of sampling frequency on TP and NO_3-N load calculation was estimated by subsampling the TP and NO_3-N concentrations and parallel discharge from HFM data at daily, weekly and monthly intervals.

The study wetland reduced P loading on a yearly basis by 13% and NO_3-N loading by 14%, thus enhancing the ecological state of Lake Enäjärvi. The wetland retained most of the incoming load during the growing season, and in June and July the reduction in TP was nearly 30% and the NO_3-N reduction in July was over 80%. The effectiveness was weakest under most loading conditions outside the growing season. In February, the wetland retained 5.5% of the incoming TP, while in November the NO_3-N reduction was only 3.5%.

The sampling frequency test showed that even though based on daily sampling, the TP and NO_3-N loads would have been underestimated, compared with the HFM reference data. With monthly sampling, the TP load estimations were 22–30% lower and NO_3-N load estimations 17–28% lower than the reference. We concluded that the HFM was essential for investigating the seasonal and annual efficiency of such small constructed wetlands. The actual impacts of wetlands on nutrient loading can only be detected with HFM.

3.4 Paper IV

The impact of the arable land's WVC on TP loading was estimated in an erosion-sensitive clayey catchment in the boreal region. Long-term HFM data of the Lepsämänjoki River were used to show the varying load on a yearly scale and in event scale under different hydrological conditions. The WVC is one of the mitigation measures that farmers use to obtain subsidies in Finland. No-tillage, reduced tillage, stubble fields and grasslands were considered as wintertime vegetation. The proportion of WVC in the fields of the Lepsämänjoki River increased from 38% to 71% in 2006–2014.

Turbidity and runoff were monitored at 1-h intervals in 2006–2014. Turbidity was converted to TP, based on the correlation between sensor turbidity and the TP analysed in the laboratory. Hourly, daily and annual TP loads were calculated and annual and short-term fluctuations examined. GLM was used to analyse the effect of runoff and air temperature on TP outside the growing seasons in 2007–2008 (low WVC) and 2013–2014 (high WVC).

The annual TP load varied between 0.23 and 0.78 kg ha^{-1} y^{-1}. The TP load in a mild winter season (December–March) in 2007–2008 was 30 times higher than in the cold winter of 2009–2010. Thus, the risk that TP loading will increase if mild winters become more frequent due to climate change will dramatically increase. Runoff was correlated significantly with the annual TP load, but in an hourly perspective there was usually positive hysteresis, suggesting that the maximum TP concentration occurred before the runoff maximum.

Comparison between the TP loads outside the growing seasons in 2007–2008 and 2013–2014 indicated that the increasing WVC in the catchment fields of the Lepsämänjoki River reduced erosion and the P fluxes during the mild winter conditions. The DRP concentrations did not increase.

The WVC reduced the TP load at our study site. Effective agricultural mitigation measures are needed in the boreal region under future climate conditions, because milder winters with increased precipitation have been predicted. This would increase erosion and nutrient loading in winter, and thus mitigation measures that function effectively, particularly outside the growing season, would be essential.

4 Discussion

4.1 Surrogate measures for obtaining high-frequency nutrient load data

Even though the number of water quality parameters that can be measured with in-situ sensors has increased in recent years, it is not possible to measure all parameters. However, it is still possible to use certain parameters, such as turbidity, as surrogates for other parameters. Turbidity is a relatively easy and robust parameter to measure in watercourses. It has been used as a surrogate for SS, PP and TP in many studies (Gippel 1995; Grayson & Finlayson 1996; Wass & Leeks 1999; Pavanelli & Pagliarani 2002; Jones et al. 2011; Viviano *et al.* 2014). Using turbidity to derive continuous SS, PP or TP data was one of the main methods used throughout this thesis. Turbidity increases when the SS concentration increases. In clayey catchments, such as the study sites of this thesis, most of the P is bound to clay particles, and thus turbidity also correlates significantly with TP (Stone & English, 1993).

When high-frequency SS or TP data are obtained using turbidity as a surrogate, a careful site-specific calibration should always be performed. As shown by Viviano *et al.* (2014), even the origin of the P may affect the relationship between turbidity and TP. They observed a slope factor (turbidity/TP) and a constant increased from the natural watershed to an urban point-source-polluted watershed. At our study site, the turbidity/TP slope factor varied between 1.02 and 1.39 and the constant between 16.5 and 50.8. The constants of the equations indicate the baseline concentration of dissolved P in the study catchments. When water samples are collected for calibration, a wide range of TP and SS concentrations should be captured to avoid extrap-

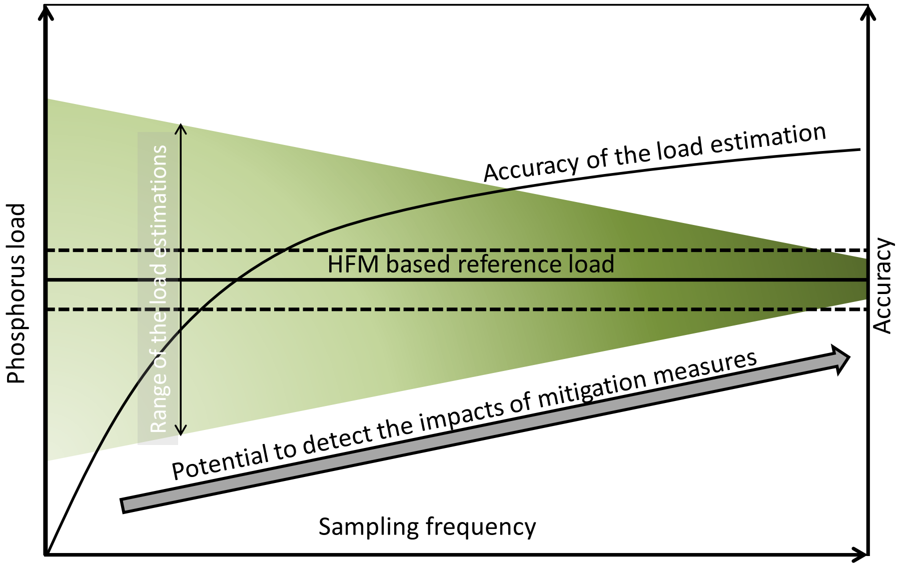


Figure 9. Increasing the sampling frequency results in improved accuracy of the load estimations. Consequently, the potential ability to detect the impacts of the mitigation measures also improves.

olation in conversion equations. If the size and shape of particles suspended in the water vary widely, a scattered relationship may appear not only between turbidity and SS but also between turbidity and TP (Zabaleta *et al.* 2007; Viviano *et al.* 2014).

4.2 Applicability of HFM in detecting changes in water quality and loading

The potential use of HFM in detecting changes in water quality and loading has been emphasized throughout this thesis. We studied the impact of sampling frequency to reveal the benefits of using HFM, especially in load calculations (**I**). Roughly, the more frequent the concentration/runoff data, the more accurate the load estimations (Jones et al. 2012; Skarbovik *et al.* 2012) (Figure 9). There are high levels of uncertainty in load calculations when infrequent and sparse datasets of concentrations are used (Cassidy & Jordan 2011).

Determining the proper measuring frequency is dependent on the site. A principle that may be followed in deciding on the frequency of measuring could be that no information should be lost if the sampling/measuring frequency is lowered (Kirchner *et al.* 2004; Halliday *et al.* 2012; Jones *et al.* 2012). This can be tested, e.g. by initiating the monitoring at very high frequency (5–10 min) and then deciding what should be the final frequency used to obtain sufficiently accurate range of concentration and runoff. Although some of the parameters may react more intensively to the catchment processes than others, the measuring frequency used should be decided, based on the most sensitive parameter.

As stated in **Paper I**, using HFM enables the detection of changes in water quality and loading. If the concentration or load data are very biased, it is impossible to evaluate the load and state of the surface waters correctly (Bende-Michl *et al.* 2013; Campbell *et al.* 2015). If the state in general is evaluated incorrectly, then it is also impossible to detect changes or the turning point at which the state becomes better or worse. The HFM can be used to evaluate the starting point or base level of loading and when the desired state (according to the WFD) is obtained. It is also possible to investigate more accurately the effectiveness of various mitigation measures that affect the diffuse agriculture-contributed nutrient loading. We evaluated the benefits of HFM in determining the efficiency of a small constructed wetland (**III**). Our study supplemented the gap in knowledge of wetlands as stated by Land *et al.* (2016): further research is needed on the effects of seasonality and hydrologic pulsing on wetlands used to treat agricultural and urban runoff. With discrete water sampling, the wetland's true functioning and seasonal variation in TP and NO_3-N reduction would not have been detected.

4.3 Detecting the impacts of mitigation measures conducted in fields (gypsum and wintertime vegetation)

Two different approaches to detect the impacts of agricultural mitigation measures conducted in the catchment fields were utilized. We studied the impact of gypsum by comparing the water quality before/after gypsum amendment (**II**). As additional evidence, another similar, although larger, catchment was used as a reference for impacts of gypsum. The impact of increased WVC of the catchment fields was investigated under circumstances of low and high vegetation cover (before/after comparison). Both mitigation measures reduced the erosion, and thus in clayey catchments the SS and TP loads are both decreased. With mitigation measures conducted in fields, it is possible to affect the concentration of water flowing from individual fields (Campbell *et al.* 2015). Even though the runoff processes (hydrology) cannot be altered, by lowering the concentration, the load is decreased. The impact is evident, especially in high-flow events, when the load is high (Murdoch & Shanley 2006). If mitigation measures lower concentrations during periods of high flow, a clear decrease in the load is actualized (Figure 10).

Many investigations of the effectiveness of mitigation measures have been conducted at the field plot scale under easily controlled circumstances (Muukkonen *et al.* 2007; Withers *et al.* 2007; Smith & Francesconi 2015), but other more recent studies have also investigat-

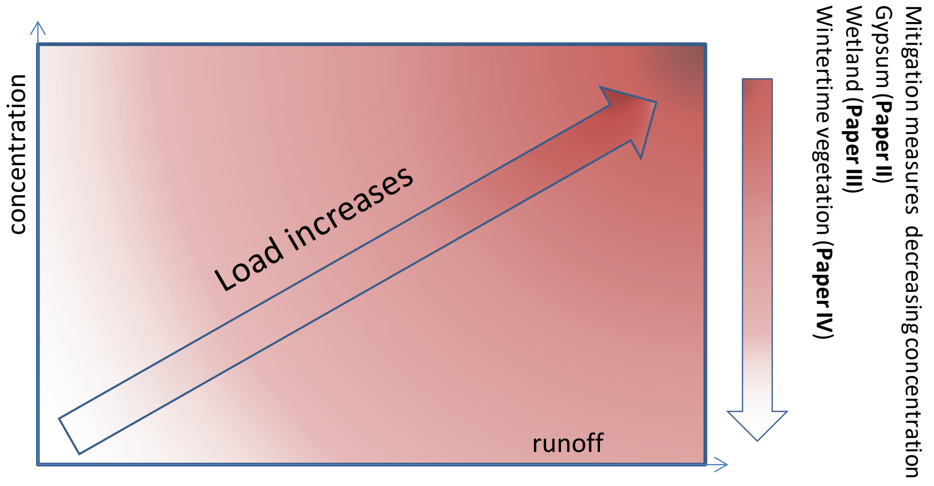


Figure 10. Parallel high nutrient concentration and high runoff mean major nutrient load. With the mitigation measures (gypsum, wetland, wintertime vegetation cover) investigated in this thesis, the concentration may be lowered, leading to reduced nutrient load.

ed measures at the catchment scale. Campbell *et al.* (2015) used bankside analysers to investigate changes in TP in high-resolution in two small agricultural catchments in the UK. They focused especially on high-flow events to detect the changes in TP loading from field areas. Despite the decrease in soil P status in the catchment fields and HFM, the impacts were not evident in water quality. When the impacts of mitigation measures are investigated at the catchment scale, the implementation of the mitigation measures should include most of the field areas. We suggest this procedure, because TP loading is more likely unevenly originated, thus entailing greater chances of also treating the highest risk fields.

Diffuse load sources are typically scattered within the catchment, thus targeting the mitigation measures to the areas of greatest loading is difficult (Cherry *et al.* 2008). In the study concerning the efficiency of gypsum (**II**) in reducing PP loading, the area treated with gypsum covered almost all the fields in the catchment. Even though the P load did not originate uniformly from every field, by treating as much of the potential area as possible the most loaded fields would probably also have been treated. Similarly, when WVC increased significantly, the treatment was also probably allocated to high-risk fields (**IV**).

4.4 Retaining the nutrients in a water environment (wetland)

Nutrient loading can also be decreased by removing nutrients from the water, usually in wetlands or settling ponds or even with chemicals (Fisher & Acreman 2004; Braskerud *et al.* 2005; Hansson *et al*. 2005; Vohla *et al.* 2005; Land *et al.* 2016). The impact of a small constructed wetland was studied by comparing water quality and load at the inflow and outflow (**III**). We carried out a study concerning the efficiency of a small constructed wetland in retaining TP and NO_3-N. On an annual basis, this small wetland did reduce TP and NO_3-N loading, but the seasonal variation in efficiency was high. The efficiency was lowest outside the growing season when nutrient loading was highest. We considered this to have been due mainly to a lack of vegetation that trapped sediment and P, as well as to insufficient retention time. Vegetation affects the settling rate of SS by slowing down flow velocity and by providing obstacles to disrupt their flow path; vegetation also decreases the resuspension of particles (Braskerud 2002; Brix *et al.* 2003; Vymazal 2007). Particles may also be trapped directly on plant leaves and stick to the biofilm of the macrophytes (Braskerud 2001). Thus, the challenge in using wetlands to reduce SS and TP loading in boreal clayey catchments is the inefficient functioning outside the growing season when wetland vegetation is dormant.

The fundamental problem in using wetlands in clayey boreal catchments as SS and TP sinks was identified by Hjulström (1935) and Maggi (2013). The flow velocity required for clay-sized particles to be suspended in flowing water is higher than that required for the particles to be deposited on the bottom. If the clay particle (containing P) is eroded and suspended in the water mass, it is very difficult for it to be deposited on the bottom of the wetland. The same phenomenon is encountered in reducing NO_3-N loading, but in this case is due to temperature and vegetation dependency. Low temperatures slow down denitrification outside the summer months (Song *et al.* 2011), and the dormant vegetation uptake of soluble NO_3-N is significantly reduced in N removal (Poe *et al.* 2003).

The efficiency of our study wetland in reducing nutrient loading was high in the summer months when recreational use of surface waters is common in Finland. Thus, nutrients are effectively kept away from the water environment when the risk of harmful algal blooms is high.

4.5 Reliability and validity

Sensor monitoring may be vulnerable to malfunctioning, even though careful installation and maintenance procedures are followed. In our studies, the maintenance interval was set appropriately to avoid unrealistic peaks, creeping of or missing data. There are always errors in sensor measuring, laboratory analyses and conversion of turbidity to SS and TP. Lloyd *et al.* (2016b) also highlighted the meaning of the uncertainty of discharge monitoring in load calculations. A more systematic review of observational uncertainties in load calculation should be executed.

As we concluded, when turbidity is used as a surrogate for TP and SS, one should always perform site-specific analyses (**I**). This requires manual sampling over a wide range of concentrations to avoid extrapolation that can increase uncertainty. The correlation may change at higher concentrations, and this should be taken into account when turbidity is converted to TP and SS.

In assessing the changes in nutrient loading based on concentration/discharge correlations there is always a risk of misinterpreting the data if all the factors are not taken into account. As stated by Haygarth & Jarvis (2002), there are a host of factors affecting diffuse loading. But during investigation, especially of erosion-induced SS and TP loading, the runoff induced by rainfall and snowmelt is the most determinant factor. All remarkable changes in land use of the catchment should be identified to avoid mistaken conclusions (Lloyd *et al.* 2014).

5 Future water quality monitoring: towards automation

Further studies utilizing HFM in detecting various management practice impacts and efficiency should be conducted in different environments (soil, land use, climate). There is still a lack of knowledge of the impacts of many mitigation measures on SS and nutrient loading at the catchment scale. We furnished here three examples of how HFM can be used to detect the impacts of mitigation measures in clayey catchments in boreal regions. The approach can be used as a guideline for future studies concerning the impacts of mitigation measures. Sensor monitoring will become more available, reliable and easier to conduct when sensor techniques, storage capacity and telemetry are developed further (Bowes *et al.* 2015).

The value of long-term HFM data will increase when effective catchment management strategies are developed to meet the targets of the WFD. The agroenvironmental policy has given direction to farming practices in Finland, and the reduction detected in TP loading in clayey areas is evidence that the policy has at least partly been a success. As we pointed out, the impacts of mitigation measures are very difficult to detect without HFM, and thus the improved state would certainly have been missed with sparse sampling.

That mitigation measures function efficiently, particularly outside the growing season, is vital under changing climate conditions. The increase in wintertime temperature and precipitation in cold climate areas (Graham 2004; Deelstra *et al.* 2011) will also increase future nutrient loads (Hägg *et al.* 2014). Mitigation measures, such as gypsum and wintertime vegetation, are promising methods for keeping nutrients away from surface waters under future climate conditions. We also encourage the use of gypsum as a subsidized mitigation measure.

The technical development of sensors and increased data-storage and data-transmitting capacity and reliability will make HFM more achievable in different water environments and more useful in detecting the impacts of various management practices. The number of parameters that are available in sensors will also increase; e.g. there is clearly a need for easy-to-use robust sensors for measuring DRP directly in surface waters. Sensors should secure reliable operation throughout the year in cold climate regions.

Traditional monitoring of streams and rivers is time-consuming and inefficient with regard to the amount of information it produces. Using water quality sensors in water monitoring will not automatically lead to lower labour costs. Careful maintenance of sensors to assure reliable data is labour-intensive and time-consuming. Water samples for calibrating sensors and for obtaining information on the parameters that are not available with sensors will still be needed.

HFM may be utilized to obtain more accurate data on the riverine loads discharging into surface waters, e.g. of the Baltic Sea. A future HFM network covering the largest coastal rivers in Finland should be established. On the other hand, a sensor network covering small catchments would also be crucial to deriving new and more precise information on the effects of varying land use on water quality. The factors affect-

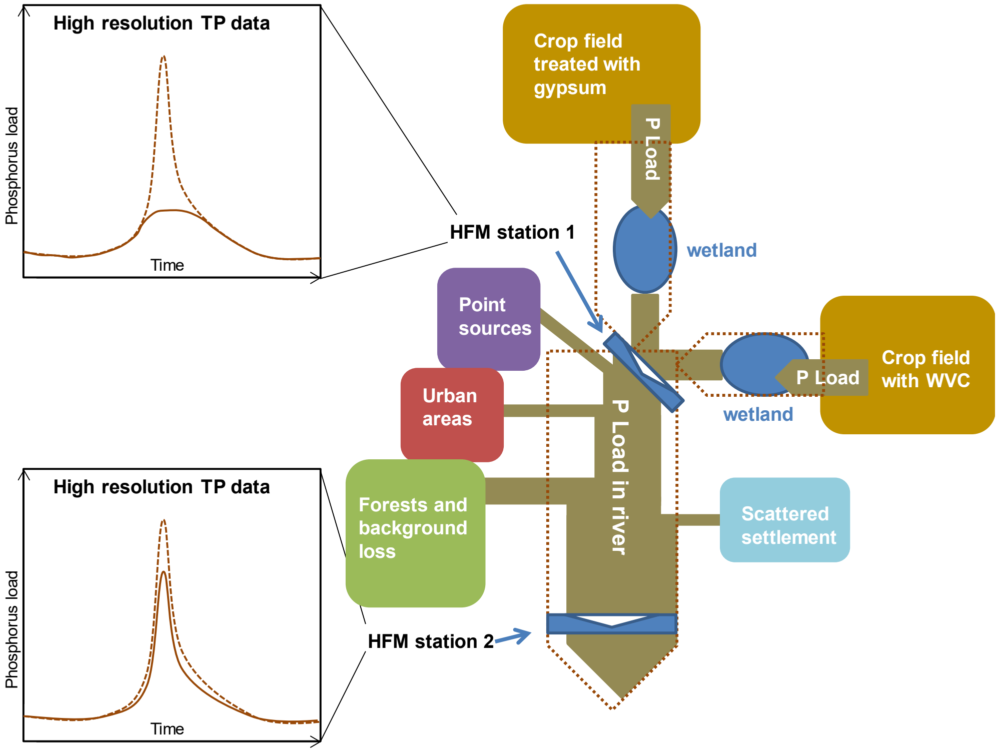


Figure 11. An effective system for reducing phosphorus (P) loading from clayey agricultural fields consists of mitigation measures conducted in the fields and in the water environment. Reduction is detected by high-frequency monitoring (HFM). The monitoring station was encouraged to remain close to the management areas (HFM station 1) if the relative proportion of the catchment total load was low in the field areas. Other remarkable source areas complicate detection of the impacts, as demonstrated by HFM station 2. The dashed arrows indicate P loading without implementation of mitigation measures.

ing water quality in small catchments are easier to manage than in larger catchments.

Determining nutrient loading and sources in the catchment with HFM supports implementation of the most efficient management practices. Precise information on the origin (spatial or land use) of the load enables cost-effective targeting of the mitigation measures, and thus the BMPs in each catchment could be implemented.

6 Guidelines for establishing HFM stations to detect impacts of mitigation measures

Three approaches for detecting the impacts of mitigation measures were introduced in this thesis: 1) monitoring water quality and quantity (load) at one station before and after mitigation practices were conducted (before/after comparison); 2) monitoring water quality and quantity upstream and downstream of the area in which the mitigation measure was conducted to reveal the changes occurring between stations and 3) monitoring water quality and quantity in the catchment where the mitigation measure was conducted and concomitant monitoring in the reference catchment with no mitigation measure. Nearby catchments should be as similar as possible.

Investigating the changes in the concentration/discharge relationship is a practical way of detecting the impact of efficient mitigation measures. If there is point-source loading of nutrients in the catchment, the discharge data can be ranked and discharge ranges extracted (Campbell *et al.* 2015). Concentration during base flow reveals the proportion of point-source loading, but diffuse loading and possible mitigation may be evident, especially in high-flow events (Murdoch & Shanley 2006). It is important to measure both the quality and quantity of the water in high frequency. All the changes occurring in the catchment during a study should be investigated to avoid erroneous conclusions.

When the proportion of the agricultural load is high, reduction in nutrient loading may be easier to detect. The lower the relative proportion of agricultural loading and the lower the efficiency of the mitigation measure, the more important HFM becomes. The impacts of the mitigation measures are also more difficult to observe if the monitoring point is far from the treated field areas and when the contribution of other source areas increases (Figure 11).

7 Conclusions

High-frequency on-line monitoring of water quality and quantity in stream waters was a viable method for obtaining more accurate and reliable estimations of nutrient loading than with discrete water samples. HFM can be used to observe the impacts of mitigation measures conducted in the catchment. Gypsum application and WVC were effective agricultural mitigation measures for reducing P loading and erosion in arable fields. A small constructed wetland retained nutrients effectively in the growing season, but under most loading conditions in winter and spring the relative reduction rates were significantly lower.

Mitigation methods such as gypsum and WVC, which are implemented in large field areas, are strongly recommended for reducing erosion and P loading in boreal agricultural clayey catchments. These mitigation measures are effective, particularly in mild winter seasons, and thus will also be beneficial under future climate conditions. Since some nutrient leaching from fields will still occur despite the use of mitigation measures, small constructed wetlands may be used to further enhance nutrient reduction. A problem concerning wetlands as a mitigation measure is that they do not function efficiently during the critical times of load generation. If wetlands are located close to the source area, where concentrations are high and the amount of water is small, they could function more efficiently.

We encourage the use of automated water-quality monitoring to obtain not only more accurate water quality and load information, but also more precise knowledge of the impacts of varying land use in small catchments.

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