Thesis for Master's degree in chemistry

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Monitoring Runoff Chemistry into the Vansjø Basin with Focus on the Role of Particles and DNOM in the Transport of Nutrients

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Abstract

This thesis work was conducted in Vansjø-Hobøl catchment (Morsa), which is one of the most studied watercourse, situated south east Norway, for its poor water quality status. The poor water quality status is due to the high diffuse phosphorus (P) loss from the agricultural watershed; and this causes major eutrophication problems in surface waters. The thesis work was part of a big EUTROPIA project funded by Research Council of Norway (RCN) (190028/S30). The main aim of the project was broadly to better understand the hydro-biogeo-chemical processes governing mobility of P into lake Vansjø. The specific objective of this thesis is to better understand the effect of land use on the transport and mobility of nutrients P in particular.

As part of the Morsa monitoring programme, water samples from selected inlet streams draining into western Vansjø were collected over an extended period. The samples were collected from three streams: Dalen, which is a generic of an aluminium (Al) rich first order stream draining forested sub-catchment with shallow acid sensitive soil; Støabbakken1, which represents P rich and neutral agricultural stream; and Huggenes, draining mixed land use. In addition to these stream water, soil water samples were also collected at one of the sampling streams (Dalen) to capture spatial difference of nutrients which contribute to the stream water chemistry. The collected stream water samples were analyzed for pH, total suspended solids (TSS), dissolved organic carbon (DOC), conductivity, major cations and anions and for tot-P along with the operationally defined P fractions. The operationally defined P fractions are particulate P (PP), organically bound P (DOM-P) and orthophosphate (PO_4-P). Statistical analysis was performed on measured parameters to show correlation among explanatory variables. Temporal variations in the data have been related to hydrological conditions and spatial variation to differences in land use in the catchments.

The water chemistry for the three streams is presented on median values. The pH for Støabbakken1, Huggenes and Dalen was 7.3, 7.1 and 4.6; conductivity (µS/cm) 397, 259 and 46.6, respectively. Sum of cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were 2650, 1950 and 242µeq/l and sum of anions (SO_4^{2-}, NO_3^- and Cl^-) were 2560, 1970 and 182µeq/l, respectively. Alkalinity values for Støabbakken1and Huggenes were 1597 and 687µeq/l, respectively. The results of tot-P content and contribution of P fractions were found to be greatly influenced with land-use distribution. It was found that the stream draining agricultural has elevated levels of tot-P (median 113µg/l) of which PP is the dominant fraction (55%) and significant amounts of PO_4-P (37%), whereas the lowest tot-P (median 8.3µg/l) content was found in the stream draining forest with 60% DOM-P. Tot-P content in the stream draining mixed land-use was 45.3µg/l with 63% in PP fraction. The stream draining forest showed considerable amounts of DOC (32mg/l) and DOC concentrations of Støabbakken1and Huggenes were 10.7mg/l and 15mg/l respectively. Moreover, the results of P contents from lysimeter soil water in Dalen showed DOM-P (40 to 90%) as a major fraction of tot-P in all soil plots of the soil horizons.

In the stream draining mixed land use (Huggenes), the results of tot-P content showed intermediate in rank between the two streams. Moreover, when runoff water from Dalen with low pH, aluminium rich and low ionic strength were conservatively mixed with runoff water from Støabbakken1 having high P content, in a ratio similar to agriculture to forest land-use in Huggenes, it was observed that measured tot-P to be 45% lower than what was calculated as a conservative mixture. Calculated concentrations of P fractions in the conservative mixture was higher than the measured concentration of P fractions at Huggenes and that confirms increased precipitation of P with aluminium. Calculated DOC concentration of the mixed water was observed to increase by 13% from the measured DOC content at Huggenes which implies increased leaching of DNOM which is due to the effect of reduction in acid rain.

The results also showed that tot-P content is positively correlated (r=0.881 at Støa1 and r=0.783 at Hug) with runoff rate in the streams draining agriculture indicating the P transport is more favoured with hydrology. Tot-P transport by month showed clear seasonal variation with generally large portion transported during periods of high flow events-spring and autumn (78 to 82% for Støabbakken1and Huggenes), suggesting the impact of runoff in the transport of P. TSS was best correlated to tot-P in the streams draining agriculture which indicates the case that sediment derived P transport is an important factor. It was further observed that the ratio of tot-P/TSS for Støabekken1 (12‰), Huggenes (6.74‰) and Dalen (1.6‰) on average which shows for a mass soil particle loss an amount of P is lost.

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Symbols, names and abbreviations

Al	Aluminum
Alk	Alkalinity
Ca	Calcium
CNP-autoanalyzer	Carbon, Nitrogen and Phosphorus autoanalyzer
DOM-P	Dissolved organically bound phosphorus
DOC	Dissolved organic carbon
DNOM	Dissolved Natural Organic Matter
EUTROPIA	Watershed Eutrophication management through system oriented process modeling of Pressures, Impacts and Abatement actions
Fe	Iron
GF/F	Grade for glass microfiber filter with pore size of 0.7µm
HNO_3	Nitric acid
HCl	Hydrochloric acid
H_2SO_4	Sulpheric acid
IC	Ion chromatography
ICP-OES	Inductively coupled plasma optical emission spectra
JOVA	National Agricultural Environmental Monitoring program
K	Potassium
LOD	Limit of detection
Mg	Magnesium
Mn	Manganese
NIVA	Norwegian institute for water research
Na	Sodium
OECD	Organization for Economic Cooperation and Development
OM	Organic mater
P	Phosphorus
pH	Negative logarithm of hydrogen activities
PP	Particulate bound Phosphorus
PO_4-P	Orthophosphates determined as phosphorus
RCN	The Research Council of Norway
RSD	Relative standard deviation
SOM	Soil organic matter
Tot-P	Total phosphorus
TSS	Total suspended solid
Type I	Ultra pure water
Type II	Pure water
UiO	University of Oslo
UV	Ultraviolet
UN	United Nations
WFD	Water Frame directive
XRF	X-ray refractive fluorescence

1 INTRODUCTION

The deterioration of the quality of surface water resources is a common concern throughout the world (Carpenter et al., 1998; Sharpley et al., 2003). Natural processes such as weathering and dissolution of local geological minerals and pollution arising from anthropogenic activities are some of the factors that influence the quality of water. A large number of anthropogenic pollution sources lead to degradation of surface water, such as excess nutrient influx from agricultural sites, acidification by atmospheric acid deposition or acid mine drainage, and contamination by influx of other long-range transported pollutants or industrial effluents (Carpenter et al., 1998; Rouco et al., 2011). The remedial strategies for polluted watersheds are difficult and expensive to implement and usually it takes a long time to achieve significant improvement in water quality. Therefore, damage prevention remains the most cost-effective means of ensuring sustainable management of water resources (Carpenter, 2005; Carpenter et al., 1998; Cordell et al., 2011; Sharpley et al., 2003).

Many studies on effect of nutrients have shown that phosphorus (P) is the key growth-limiting element that determines the primary productivity in fresh surface waters. This is mainly due to the low mobility and transport of bioavailable forms of P from the terrestrial to the aquatic environment (Carpenter, 2005; Reddy and DeLaune, 2008; Smith, 2003; Smith et al., 1999; Withers and Haygarth, 2007). In surface fresh water systems, P concentration exceeding 0.05mg/l usually leads to eutrophication (Hinesly and Jones, 1990). Enhanced fluxes of P to surface waters leads therefore to accelerated biological primary productivity. This accelerated biological primary productivity causes deterioration in quality of surface water. Nutrient enrichment of surface waters is either naturally or from anthropogenic inputs of nutrients. Natural eutrophication refers to the slow natural aging of a lake into a peat land, while anthropogenic eutrophication pertains to the set of feedback processes responding to large anthropogenic input of P and leading to a rapid negative decline in water quality in surface water. It is a process of nutrient enrichment in surface waters, which lead to accelerated biological primary productivity. This accelerated biological primary productivity cause deterioration in quality of surface water (Carpenter et al., 1998; Correll, 1998; Reddy and DeLaune, 2008; Withers and Haygarth, 2007).

Excessive supply orthophosphates primarily stimulates and enhances the growth of aquatic organisms (Carpenter, 2005; Smith et al., 1999), leading to algal blooms with eventually blue-green algae which release cyto-toxin. These organisms increase the biomass in the water environment with subsequent drizzle of dead aquatic organisms below the photic zone. This can have so many effects like decrease light penetration into the water, offensive odor and taste and can decrease the dissolved oxygen available for heterotrophic/aerobic organisms such as fish and invertebrates, and hence reduce aquatic biodiversity (Smith, 2003). The main problem with blue-green algae is that they produce toxins that make people and livestock sick whereas algal bloom or eutrophication is generally a term coined to the excessive growth of aquatic autotrophic organisms.

Long-term exposure to excessive algal production and with subsequent decomposition will therefore stress ecosystems and lead to undesirable problems associated with eutrophication. As P limits most fresh water eutrophication, decrease of P losses in agricultural runoff has become a major target to minimize water quality degradations (Carpenter, 2005; Carpenter et al., 1998; Smayd, 2008; Smith et al., 1999). This is due to that the successful reduction of point source of P in the past thirty recent years has left agricultural as a major source of P to surface waters. To this end there are so many proposed mechanisms to reduce P losses from agricultural fields which are discussed in next section 2.14.

1.1 Morsa catchment and the lake Vansjø (Motivation)

Vansjø-Hobøl (Morsa) is one of the most studied watercourses in Norway due to its poor water quality status. The poor water quality status is due to the high flux of nutrients, mainly phosphorus, leached out from the over fertilized agricultural soils and sediment release. This leads to undesirable water quality deterioration called eutrophication. Water quality problems in the lakes have been a major concern for decades in the western part of the catchment in particular (Skarbøvik and Bechmann, 2010). The lake's water quality problem draws attention of different stakeholders because of its multiple uses and due to its ecological and scientific importance. The lake is a recipient of waste runoff from the agricultural activities which holds an economically important location in the Norwegian agricultural context (Skarbøvik et al., 2011). In the years 1950-1980 there was a 30 to 80% shift of land usage from forestry to agriculture due to increasing demand of land for agricultural purposes. This shift in land use has led to observable deterioration of water quality and exacerbate of eutrophication in lakes (Lundekvam et al., 2003). Massive application of P fertilizers to the agricultural fields in order to increase crop yield is proved to be the main source of P to lakes in many parts of the world (Dokulil and Teubner, 2011; Sharpley et al., 2003; Skarbøvik and Bechmann, 2010).

Studies have been ongoing in lake Vansjø since 1980s on mapping of P fluxes from diffuse and point sources. Diffuse and point sources of P (section 2.5) are two important sources that increase P levels in the environment. P from point sources have been significantly reduced since the 1990s, whereas diffuse sources still remain a challenge (Ulen et al., 2007). Starting in the 1990ies efforts have been and are being made to improve water quality in lake Vansjø by implementing various long and short-term measures (Thuen and Buer, 2003). Mitigation measures, such as decreased application of P fertilizer to farm lands, shift in tillage practices and setting vegetative buffer zones have been implemented (Lundekvam et al., 2003). The mitigation measures focusing on reduction of the flux of P to the lakes are mainly aimed at minimizing transport of particle bound P by reducing soil erosion and decreased application of P-fertilizer (Ulen et al., 2007). Reduction up to 89% in erosion from sloped agricultural sites and thereby reducing particle transport of P has been achieved by discouraging the practice of autumn ploughing (Ulén et al., 2010).

The Morsa project has been established in 1999 and farmers have joined to enforce mitigation possibilities (Thuen and Buer, 2003). Farmers are given incentives to fully implement the intended mitigation actions. In 2008, 73% of the farmers in western Vansjø have officially registered and signed to follow the mitigation policies (Skarbøvik and Bechmann, 2010). In 2007, P-fertilizer application at the agricultural farms has reduced on average by 47% when compared to 2004 which was 75% (Øgaard and Bechmann, 2010). Although efforts have been made to reduce P transfer, the quality of lake water in the catchment remains eutrophic. Water quality problems have been more observed in the western part of the lake Vansjø. This is mainly due to the high P loading from the agricultural sub-catchment (Bechmann and Stålnacke, 2005).

Morsa catchment was selected as a pilot area for the practical implementation of European Union Water Framework Directive (EU-WFD) by the Norwegian Ministry of Environment as a campaign to reduce eutrophication (Skarbøvik and Bechmann, 2010). The EU-WFD water legislation was adopted in 2000 by 25 EU-member countries including Norway. Its ultimate objective is to have 'good ecological and chemical composition' of all lakes, rivers and coastal waters in the EU-region (OECD, 2008). An interdisciplinary research project, the EUTROPIA[1] project was launched in 2009. The project is funded by the Research Council of Norway (190028/S30) with main aim to investigate environmental processes governing the fluxes of phosphorus mobilization in the environment. In this research project several PhD and MSc. students are studying on how the environmental pressures influence the P loading to the lake system.

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[1] See: http://www.mn.uio.no/kjemi/english/research/projects/eutropia/index.html

1.2 Objectives of the master thesis

This thesis mainly focuses on the major mechanisms and processes governing mobilization, transport of P fractions from agricultural lands and forests into surface waters. Spatial and temporal fluctuations in the concentration of P-fractions, major cations and anions in streams are related to changes in environmental pressures influencing the flux of P. The objectives of this study have therefore been to:

- ✓ To assess the land use effect on transport of nutrients into the lake
- ✓ To assess the effect of runoff rate on nutrient mobility and transport that govern the variation and differences in fluxes of P in runoff in both time and space
- ✓ To assess seasonal fluctuation with main focus on the more frequent, intensive rain episodes which enhance eutrophication of lake water through increased erosion and leaching of nutrients

2 THEORY

2.1 Climate as a factors influencing the flux of P to recipient water

Major changes of land-use and global climatic changes during the past few decades have had profound impacts in the environmental water quality both at global and regional scales. There has been an increase in amount of precipitation and an increase in the average winter temperature during the past decades especially in 1989-2009 (Øygarden, 2000). Warmer atmospheric temperatures observed over the past three decades have led to more vigorous hydrological cycles with more extreme rainfall events. Increased amount and intensity of precipitation as a result of the warmer atmospheric temperature has enhanced the risk of flooding, frequency of soil erosion rates and thereby increased flux of nutrients like P (Øygarden, 2000; Skarbøvik et al., 2011). For example as a result of increased precipitation there was a major flood in 2000 in south eastern Norway which had great impact on deterioration of water quality. The hypothesis that flooded areas are more prone to provide reduced conditions in which P release is more enhanced due to the reduction of Fe^{3+} discussed in section 2.10. It is postulated that changes in climatic conditions affect the transport and mobility of nutrients like P (Skarbøvik et al., 2011; Ulén et al., 2010). Model simulation of future climatic changes predicted byRummukainen et al. (2003) suggests that there will be larger increases in temperature in Nordic countries than in the global mean temperature. As a result these countries are expected to experience shorter snow seasons and longer growing seasons. Complicated environmental interactions which have direct consequences in water deterioration are then due to the longer growing seasons.

Milder winters with higher intensity of precipitation due to warmer temperature are expected in the future. Rising in winter temperature has led to an earlier melting of snowpack, and more frequent freeze-thaw cycles. Transfer of bioavailable P during the dormant winter period is more widely possible due to the absence of plant uptake. Larger P releases from the soil as result of flooding of agricultural areas will continue as long as heavy snowmelt events and milder winter continue as the soil is either frozen or saturated with water (Aquarius, 2000; Bechmann et al., 2005). Large temporal variation in precipitation amount and timing are of great importance in transporting P. The two main seasons, the snowmelt and the rainy autumn, are termed as high flow seasons. These seasons are the main P transfer periods especially on tilled soils. In the snowmelt season, overland flow on frozen soils can result due to thawing of upper soils layers and frozen beneath soil layer. This creates low hydraulic conductivity which surface flow dominates and particle transport may be higher. Thus, Norwegian law prohibits P applications on snow covered soils and during rainy season (Øygarden, 2000).

During cold climates, freezing and thawing can play an additional important role in transport of dissolved P. Each freezing event can damage the plant cells. Damaged plant release dissolved P (Uhlen, 1989). Plot experiments and field observations conducted by Børresen and Uhlen (1991) in Norway, showed an increase in concentration of dissolved reactive P in runoff from ryegrass plots from 0.15mg/l before freezing to 0.68mg/l after freezing with most of this loss occurring in late winter due to plants physiological changes. Winter conditions like number of freeze-thaw events and soil moisture content at freezing have significant impacts on risk of P transfer. Øygarden (2000) noted that during snowmelt periods on frozen soils the erosion was observed all over large fields, whereas on non-frozen soils erosion occurred only in minor parts of the soil.

2.2 Runoff intensity and P mobility to water bodies

Hydrology is most important factor as it is mainly considered as an energy factor in the transport of nutrients including P associated with soil particles. The term 'runoff' is used to describe water movement in large scales in the absence of permeable subsoil parts. It is a hydrological term which describes the lateral movement of water on or under soil surfaces on slopes (Haygarth et al., 2005). P-saturated soils show little P leaching unless there is effective precipitation which induces the interaction between soil materials and precipitation which then favoured P transfer after detachment from soil materials. This is due to the reactive nature of P on soil surfaces. Surface P runoff describes transport of P that occurs exclusively over the surface soils during periods of heavy rainfall and is an important pathway for P transfer (Sharpley et al., 2003). A study by Sharpley (1985) described in a simulated field experiment that P is effectively transferred when there is effective interaction between soil surface and precipitation. The study showed that the P residing on the surface of the soil is most vulnerable to export in runoff and that the transfer was higher in less permeable pastoral lands.

Changes in precipitation has observed to affect the magnitude and time of runoff and thereby frequency and intensity of floods (Shigaki et al., 2007). Forms of P transport are also influenced by the different flow path regimes discussed in section 2.3. In surface runoff, P is mainly associated with soil particles and transported by the kinetic energy of the high intensity storm runoff (Sharpley et al., 1993). The energy of the flowing stream water or surface runoff mainly controls the amounts of specific size fractions of particulate materials which remain in suspension during water flows (Sporre-Moeny et al., 2004). More specifically, a study by Haygarth et al. (2005) concluded that P transported in surface runoff is associated with relatively larger soil particles whereas P in sub-surface runoff through macro pores and drains is transported with colloid-sized soil particles.

Although many reports showed that P transport from agricultural areas is predominantly surface runoff (Lundekvam et al., 2003; Sharpley et al., 1993), there are other transport mechanisms in which P can move in the environment. Surface runoff from grass, forest and uncultivated land for instance carries little sediment and is generally dominated by dissolved P (Sharpley et al., 2003). Furthermore, water flowing from different land-use systems play additional role to the flux of different P fractions. Release of P from these soil and plant materials occurs when rainfall water interacts with the layer of surface soil and plant material before leaving the field as surface runoff. Presence of dissolved P in soils increases as the contact time with soil surface increases (Sharpley, 1985; Sharpley et al., 1981; Sharpley et al., 2003).

2.3 Water flow paths and P transfer mechanisms from soils

P is generally immobile in soils unless it gets favourable hydrological conditions. Transport of P depends on factors related to hydrological conditions and soil management practices (O'Reilly et al., 2005). Total P loss is highest in areas which receive high amount of P-fertilizer or manure and where the areas are subjected to high risk of erosion. Hydrology is then among the many factors that play a decisive role in the transport of P to water bodies in the environment (Bechmann, 2005; McDowell et al., 2001; Sporre-Moeny et al., 2004). Although P is lost from soil to adjacent surface waters via different mechanism, the conceptual environmental transport of P can be categorized into the following major transport pathways indicated in (O'Reilly et al., 2005). Firstly, overland flow or surface runoff which occurs at high precipitation in sloppy regions with saturated soils and it is the most important P transfer mechanism as large P is resided in the upper part of soils. Secondly, subsurface flow including matrix and macropore flow at the soil profile scale, and artificial tile drainage at the hill slope scale which mainly occurs when water infiltrates laterally further until it reaches water table or a layer that impedes its flow down. This is the second most important mechanism in the transport of P. The third is groundwater flow, which is usually of less importance as transport pathway for P, but due to the residence time of the water, fates of some nutrients is largely determined by ground water flow paths.

The extent to which these pathways occurs is primarily dependent upon precipitation, soil physico-chemical properties, soil moisture status, soil P status and land-use management (O'Reilly et al., 2005). An increase in subsurface runoff is directly connected to mobilization of soluble soil P through ground water. As P is transported through soil matrix there is a long contact time with soil particles giving opportunities for adsorption/desorption reactions. Therefore, there is a direct influence on the concentration of nutrient availability in runoff as P concentration change in the water while moving through the soil. Sorption of P in soil generally minimizes P movement through the soil matrix, whereas P transported by macropore flow may bypass the soil particles and result in a direct transfer through fissures, macropores, wormholes and cracks (Ryan, 1998). If the incoming water has high concentrations of solutes and the water flow is high, preferential flow result in deeper movement of solutes especially in clay soils, which are vulnerable to cracking in dry periods (Elliott and Coleman, 1988). Withers and Jarvie (2008) pointed out that different areas have different P fluxes from different sources depending on anthropogenic pressures and discharge events. A report by Djodjic and Bergström (2005) documented that matrix flow mainly represents P leaching in dissolved forms while macropore flow showed the transfer of both PP and dissolved P forms.

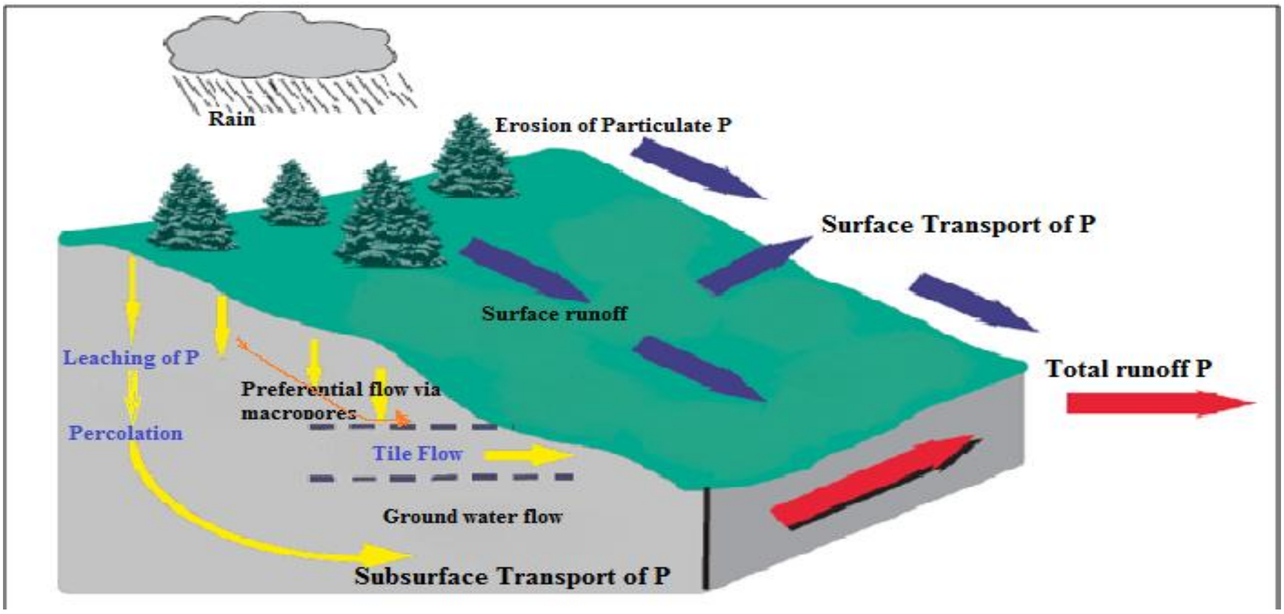

Figure 1: Hydrological P loss and transport mechanisms through different pathways from agricultural lands with surface and subsurface transport mechanisms distinguished by blue and red lines respectively taken Sharpley et al. (2003).

2.4 Relationship between tot-P concentrations and runoff intensity

Studies on the relationship between soil P and runoff P are typically derived by combining continuous water flowing from streams and P sources. Intensive field observations and some basic theoretical assumptions related to P transport by different studies have led to the conclusion that hydrological events of very short duration are typically responsible for the major P transport via surface runoff and showed dependency on adsorption/desorption kinetics (McDowell and Srinivasan, 2009; Pionke et al., 1999). The loss of P from agricultural fields is primarily attributed to erosion of P-rich particles that drain to receiving water bodies. An increase in soil erosion inherently increases particle transport. Eroded particles tend to be of small particle size and have a high content of total P adsorbed (Daniel T et al., 1994; Øygarden, 2000). One basic feature about P is that it remains in upper soils because of the sorption ability of P on amorphous oxides of Fe and Al. Besides, P is assimilated with plant roots and as a consequence groundwater dissolved P availability remain typically very low (Johnson et al., 1986).

Diffuse P sources primarily originate from P application on agricultural fields initiated after interaction between soil and precipitation which later carried out through surface water runoff. Studies in Norway have documented that more than 50% of the tot-P loss comes as surface runoff associated with particles (Lundekvam et al., 2003). Moreover, P transport through sub-surface runoff from agricultural drainage has been identified as an environmentally significant source under most frequent soil and growth conditions in Nordic climates (Christensen et al., 2001). These mechanisms that dissolved P most probably enter to water is as surface and subsurface flow paths and through agricultural tile drain (Akhtar et al., 2003). Generally dissolved reactive P in water bodies can constitute 20-70% of the tot-P (Ulen et al., 2007). In Norway for instance, agriculture is the prime source of all the anthropogenic inputs of P to the lake Vansjø, constituting more than 57% of the total load (Solheim et al., 2001).

2.5 Phosphorus sources and P-fractions in aquatic ecosystems

P plays an essential role in agricultural soils and is crucial element for all forms of life. In agricultural cropping system, adequate supply of P are essential for seed and root formation and is the largest pathway of P removal from agricultural soils. P is in scarce amount in natural systems and is efficiently recycled. There are two types of P sources which contribute to the tot-P flux. These are natural and anthropogenic sources (Brady and Weil, 2009; Withers and Jarvie, 2008). Natural sources can be weathering of soil parent materials with subsequent transport combined with dissolved natural organic matter, and by migratory fishes returning to their spawning grounds (Holtan et al., 1988; Nislow et al., 2004; Walling et al., 2008). Anthropogenic sources of P on the other hand, can originate from excessive application of P containing fertilizers to soils (Dokulil and Teubner, 2011; Withers and Jarvie, 2008).

Anthropogenic P inputs are commonly distinguished as point and non-point or diffuse sources. The levels and dynamics of P release both from point and diffuse sources influence the enrichment of the P in the downstream sections of the receiving open water bodies and has a profound effect on water quality issues (Carpenter et al., 1998; Foy and Bailey-Watts, 1998; Meyer-Reil and Köster, 2000; Withers and Jarvie, 2008). Point sources contain high concentration of soluble mostly bioavailable P. Seepage from landfills with industrial wastes and municipal sewage represent point sources. Point sources of nutrient loads to water bodies are inherently more localized and can be easily monitored and dealt with (Carpenter, 2005; Smith et al., 1999; Withers and Jarvie, 2008). Diffuse sources primarily originate from agricultural runoff, urban lands runoff, and runoff from pastures. These sources are difficult to control and are highly linked to agricultural runoff which contributes the largest P flux. Ulén et al. (2010) pointed out that agriculture remains the major contributor of P to inland and coastal water bodies in different areas of the world. Eutrophication originated from diffuse source is a major problem in many lakes in Norway, despite that there is only a relatively limited area (3%) of the total land of Norway that is being used for agriculture.

P exists in the environment both as organic and inorganic forms. The relative proportion and actual amount of P necessarily depends on factors such as land use characteristics, soil, geology, typography and vegetation of the catchments. Dissolved P and particulate bound P are the fractions that constitute tot-P. Particulate P constitutes particulate inorganic P (PIP) and particulate organic P (POP) whereas the dissolved P constitute dissolved organic P (DOP) and dissolved inorganic P. Among these P fractions, DIP is mainly the sum of all the orthophosphates species described as H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} and is the form of P that is conceived to be most readily available for biological uptakes (Boström et al., 1988; Holtan et al., 1988; Reddy and DeLaune, 2008; Sharpley et al., 1993).

In essence, biological availability of P is the sum of immediate available P and any P-fraction that can be transformed to bioavailable form by naturally occurring process such as physical process (desorption), chemical process (dissolution) and biological process like enzymatic degradations (Boström et al., 1988). Both biological and non-biotic processes regulate the transformation and translocation of P in the environment for plant availability. Biological include assimilation by plant, microorganisms and plankton and non-biotic process include sedimentation, precipitation, adsorption by soil particles and exchange of P between soil and overlying water column. Hence, bioavailable P uptake by plants in neutral and acidic conditions is restricted to $H_2PO_4^-$ while HPO_4^{2-}. However, due to precipitation reaction with metallic cations of Al^{3+}, Fe^{3+} and Ca^{2+}, or adsorption to oxides of these cations, clay and organic material in the soil or suspended solids, orthophosphate may be removed from water. This depends on different factors such as ionic strength, pH and temperature that affect desorption/adsorption process (Spivakov et al., 1999).

The relative concentrations of inorganic orthophosphate species are distributed as a function of pH (Figure 2). Orthophosphates exist in a pH range of 4.5-7. Phosphate ions readily precipitate with the metal cations Al^{3+}, Fe^{3+} and Ca^{2+} which depends on pH as pH governs the abundance of these metal cations in soil solution. Precipitation reaction typically follows at high concentrations of either phosphates or metallic cations (Rhue and Harris, 1999). In other words, the availability of P in mineral soils and in water is controlled by the solubility of Al, Fe and Ca compounds. At alkaline conditions solubility of Ca compounds controls P availability likewise, in acidic conditions solubility of Al and Fe minerals controls the availability of P. In acidic and near neutral conditions, release of Fe and Al ions, can precipitate $H_2PO_4^-$ ions to form amorphous solid compounds of Al and Fe.

Phosphate sorption process occurs at the edges of clay minerals with $FeOH_3$ and $Al(OH)_3$ forming amorphous oxy-hydroxy compounds of the form of $FeOOHPO_4$ and $AlOOHPO_4$ respectively. Thus, amorphous oxy-hydroxy compounds of Fe and Al eventually age to more crystalline minerals, such as Stregite ($FePO_4$), Vivianite ($Fe_3(PO_4)_2$) and Valiscite ($AlPO_4$) whereas, in alkaline conditions due to inherent high concentrations of Ca^{2+}, the HPO_4^{2-} precipitates to form complexes of less soluble hydroxyapatite minerals such as tricalcium ($Ca_3(PO_4)_2$, $Ksp=1.2x10^{-29}$), pentacalcium phosphate ($Ca_5(PO_4)_3OH$, $Ksp=6.8x10^{-37}$) and eventually age to least soluble apatite minerals. This process results in a significant decrease of available P in water column (Hinsinger, 2001; vanLoon and Duffy, 2007).

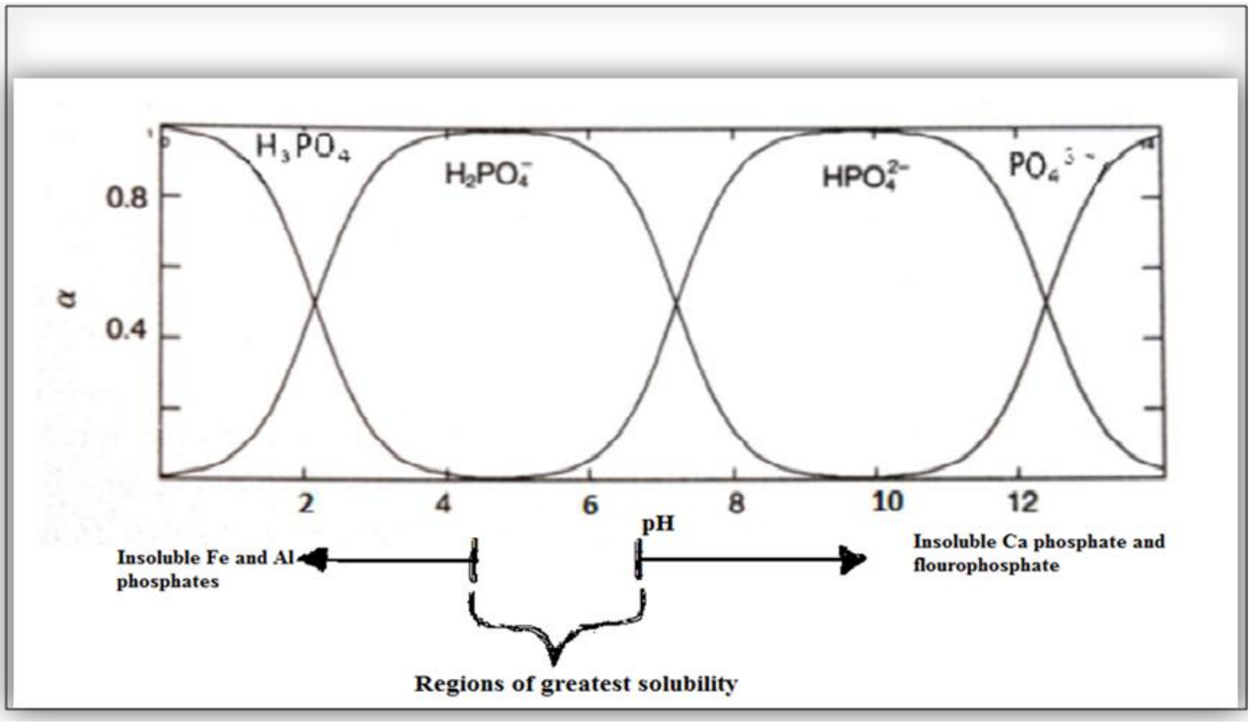

Figure 2: Distribution of phosphate species with pH. The graph dipicts at low pH solubility of Al and Fe phosphates determines the P content and at higher pH Ca phosphate solubility matters. Graph from vanLoon and Duffy (2007).

2.6 Soil types and P sorption on soils and sediments

Soils are generally sinks for P, though soils cannot indefinitely fix applied P. P sorption refers to retention of inorganic P in soils. Sorption of P is an important process that determines the transport of P in soil and water as well (Reddy and DeLaune, 2008). Sorption of P in soils includes specific physical and chemical adsorption, anion exchange, fixation and precipitation reactions. Continued application of P on soils beyond crop requirements is major cause of soil P saturation (Sharpley et al., 2003). It is mostly common case in agricultural areas where organic wastes (mainly manure) is heavily used. P can become adsorbed or desorbed to/from solid soil particles. Sorption is regulated by physiochemical properties such as soil type; soil P, amount of Ca, Fe, Al, organic matter, pH and redox potentials. Clay minerals act as excellent P adsorbents in soils mainly due to the chemically reactive nature of their surfaces. Adsorption on edges or on iron oxide coatings of clay minerals such as kaolinite $Al_2Si_2O_5(OH)_4$ is also a common phenomenon. Adsorbed P to oxides of Fe can also slowly age to minerals by the process known as aging (Appelo and Postma, 2007; Reddy and DeLaune, 2008; vanLoon and Duffy, 2007).

Anion exchange in soils is the process that takes place between soil solution and diffuse double layer on the surface of organic matter and in clay soil minerals in particular. Clay minerals have mostly permanent surface charges but oxides of Fe and Al in soil sediments have variable charges which depend on pH. A point at which the charge of a given mineral is changing is the point of zero charge (PZC). In this case soil mineral surfaces will have positive charge when the solution pH is less than PZC, it is the case where anions species like phosphates may be adsorbed, whereas mineral surface will attain negative charge when solution pH value is higher than PZC (vanLoon and Duffy, 2007). For extra information on PZC values of some minerals are given in Table 1 below.

Table 1: The point of zero charges, pH_{PZC} for clays and common soil oxides and hydroxides (Appelo and Postma, 2007)

Colloid	pH_{ZPC}	Surface charge, example at pH = 7
Kaolinite	4.6	_
Smectite	2.5	_
Gibbsite, ($Al(OH)_3$)	5.0	_
Corundum, ($Al2O_3$)	9.1	+
AlOOH	8.2	+
Geotitt, (FeOOH)	7.8	+
Hematite, (Fe_2O_3)	8.5	+
Calcite	9.5	+
Feldspar	2.2	_
Quarts	2.9	_
Hydroxyapatite, ($Ca_5OH(PO_4)_3$)	7.6	+
Birnessite, (MnO_2)	2.2	_

Sediment P losses include P associated with soil particles and organic material eroded during high flow events (Leone et al., 2008; Sharpley et al., 2003). In most soils, P contents of surface horizons are higher than P content in subsoil because of sorption ability of P, greater biological activity and more organic material on the surface layers (Sharpley et al., 2003). In mineral soil dominated areas, the proportion of organic P accounts 25 to 50% of total P, while on organic soil dominated areas, the pool of soil organic P constitute in the range of 60 to 90%. Norwegian agricultural soils generally constitute 50 to 80% of inorganic mineral soils. In the organic soil dominated areas the adsorbed P undergoes a mineralization process where organic P is converted to inorganic P. In the process of mineralization, organic P is broken down to soluble P and then assimilated in biomass. It is generally considered that P is retained strongly in soil particles within upper soil surfaces. However, subsoil parts of agricultural lands may contain significant concentration of dissolved inorganic P that moved due to leaching (Brady and Weil, 2009; Reddy and DeLaune, 2008). As 90% of the Morsa watershed catchment is situated below the marine limit, marine deposits are inherently rich in P as the marine sediment is the main sink of the P cycle.

2.7 Processes governing P mobilization in different soil compartments.

Despite all the recent advances in soil research, modeling soil P mobilization remains a difficult process. However, the conceptually defined forms of P-fractions constitute a basis for understanding P transfer processes from the lithosphere to the biosphere. This is normally related to the hydrological pathways by which P moves from the soil to water (Haygarth and Jarvis, 1999; Holtan et al., 1988). Soluble P in soils occurs in a very small quantities due to its naturally rapid cycling and immediate availability for plant uptake, whereas about 90% of total P is usually found as PP and transported in association with soil particles (Gburek and Sharpley, 1998; Reddy and DeLaune, 2008). In order to accurately define mechanisms of P mobilization across different soil compartments, it is important to understand the retention capacity of P in soils and this is discussed in section 2.9. P loss from soils to water in runoff is controlled by two major influencing factors, these are source and transport. Source factors typically contribute P to runoff and include soil P status, rate and timing, type of P form (mineral fertilizer, manure P input) and tillage in agricultural soils. Related to source factors there are organic (manures, processed sewage sludge) and inorganic (reactive rock phosphates, thermophosphates and acidulated triple phosphate). Transport factor on the other hand is mechanisms which provide energy for potential P transport from source to receiving water bodies by erosion and runoff (Gburek et al., 2000; Haygarth and Jarvis, 1999; McDowell and Sharpley, 2001).

P has been added to most agricultural soil surfaces as fertilizer or manure due to its solubility. This helps that immediate availability of P for plant uptake. Applied P is reactive and adsorbed to soil particles. In many areas of the world, soil P application is exceeding crop requirement levels and the surplus accumulates in plough soil layers (Sims et al., 2000). This leads to a global concern that continued P applications may cause soils to become P 'saturated'. As P saturated soils loses their capacity to retain applied P, soil solution P levels increase and resulting in deterioration of surface water quality. Due to the dynamic natural conditions and dissolution processes, P becomes readily mobile and can easily get into hydrographical network (Haygarth and Jarvis, 1999; Heckrath et al., 1995; Sims et al., 2000). Top soil layer of thickness 2-5cm, (part of the plough soil layer that range 30-50cm), is sensitive to soil erosion and contains particularly high amounts of P due to adsorption of P from applied fertilizers and manure. Therefore, P is easily transported by erosion adsorbed to soil particles, though erosion highly depends on topography of the catchments, soil structure and runoff conditions. It is stated that the concentration of P percolating through the soil profile is low because of P fixation by P deficit subsoil. P retention capacities are also observed to be higher in clay soils than sandy, acid organic and peaty soils (Sharpley et al., 2003).

2.8 The effect of land use - mainly agriculture and forest on P

Globally transport of P to surface waters from point sources has been greatly decreased to less than half from 1985 to 2001. The reduction in point sources leaves diffuse pollution sources from agricultural land as the main P source in the recent years (Ulén et al., 2010). It has been pointed out that land use is a factor that governs nutrient levels of streams. Agricultural runoff is all water draining from an agricultural area including surface runoff, subsurface flow, leaching and tile drainage process. There are several factors affecting the loads of P in surface runoff from agricultural lands. These include duration, amount and intensity of rainfall, rates of infiltration and percolation, slope, soil texture, nature and distribution of native soil, P-fertilization history, cropping practice, crop type, and crop cover density. Each factor plays an important role in the dynamics and transport of P loads. The reactive nature of P is heavily affected from every factor in the course of transport with respect to space and time. Moreover, the land use effects on distribution of P are highly related to soil property and topographic gradient.

Agricultural runoff is usually highly influenced by the presence of patterned drainage systems. Many agricultural fields require adequate artificial drainage (tiles, surface and open ditches) to attain maximum crops productivity and in some case as erosion protective (Øygarden, 2000). Snowmelt and prolonged rainfall can cause agricultural soils to be waterlogged where the deeper soil's infiltration capacity is low. For example, to achieve optimal work efficiency on the fields and proper plant growth, artificial field drainage systems are installed in most Norwegian agricultural areas (Bechmann et al., 2010) as these artificial drainage systems increase the rate of infiltration and percolation of soil solution. This can reduce contact times between soil solution and soil components which have capacity of sorbing inorganic P from solution and hence flushed into streams. Tile drains removes water from the surface horizons of the soil profile diminishing the possibility for contact between percolating water and more P-deficient subsoil material.

Field-tile drainage systems have been identified as potential conduits for transport of nutrients and contaminants (e.g. pesticides) from agricultural catchments to ditches or to lakes. This is because of the direct link between field tile drainage sources and streams. Water quality in recipient lakes may adversely be affected by the accelerated rate of P transport (Bechmann et al., 2010; Øygarden, 2000). These field drainage systems appear to be important sources of non-point pollution for streams in the watershed as agricultural chemicals and fertilizers are directly transported to tile drainage (Dils and Heathwaite, 1999).

Although P is mainly accumulated in top soil layers, studies on tile drainage effluents from cultivated agricultural soils proved that critically high concentrations of P are transported through tile drainage. This contention was proved on tile drained soils in a field study in Norway, Sweden, Ireland and UK (McDowell and Sharpley, 2001; Sharpley et al., 2003; Sharpley et al., 1994). In Norway for example it was found that 12 to 60% of total P transfer came from subsurface tile drainage (Øygarden, 2000; Ulen et al., 2007). Dissolved P loss was in the range from 9 to 93% (Uhlen, 1989; Ulen et al., 2007). Peak P concentrations were recorded during rainy seasons associated with increased flow. In Norway until 1990, 60% of the agricultural soils are well tile drained with field subsurface drainage systems (Bechmann, 2005; Øygarden, 2000). Tile drained fields include much of the cropland area and loss of P transported from the topsoil through soil macropores to the tile drainage system.

The amount of P in forest watersheds is low due to the relatively rapid assimilation by forest floor vegetation. Thus, the background P export in forest streams is a direct reflection of the different physical and chemical factors that affect P concentration in surface runoff and groundwater. The evidence to support this contention is the fact that most runoff from forested watershed arise from groundwater or subsurface runoff, present P is relatively small and is in dissolved form. Minor fluctuations in P concentrations are reported for forested streams suggest that P export is minimally affected by surface runoff.

2.9 Erosion – large effect on particulate bound phosphorus

Soil erosion at agricultural fields can be sheet and rill erosion, deeper riling due to surface runoff erosion, gully erosion and erosion with tile drains. All these forms of soil erosion from agricultural fields have been posing a problem in the environment as it carries nutrients which have an impact in pollution and eutrophication of fresh waters. Heavy precipitation in autumn on nearly saturated soil/sub-soil and heavy snowmelt in spring on frozen sub-soils can cause soil erosion and nutrient loss through surface runoff (Lundekvam and Skoien, 1998; Øygarden, 2000). P can be transported as a result of soil erosion on field slopes, channel banks and remobilization of stream sediments (Bechmann, 2005; Øygarden, 2000). The amount of P leaving the soil with runoff depends on the intensity of rainfall, amount and energy of the waters runoff, physical and chemical factors and some internal influences of the soil-water column (Sporre-Moeny et al., 2004). Understanding the transfer of P with soil particles mainly requires the knowledge of hydrological flow paths which is discussed in section 2.3

Erosion is often associated with P transfer by overland flow from arable agricultural lands, where loss of particulate bound P is high and constitutes most of the transferred total P. Soil erosion is a selective process with respect to particle size due to the energy limitations of runoff. P is transferred to surface water bodies due to the fact that a large percentage of total soil P is frequently associated with aggregates of clay sized materials on top soil layers (Haygarth and Jarvis, 1999; Sharpley et al., 2003; Sharpley et al., 2001; Sharpley and Syers, 1979). Transport of eroded soil particles by surface and subsurface soils is the dominant mechanism where P is delivered to surface water. Particulate bound P transport is mainly explained by the soil texture and erodability tolerance of soils. Eroded sediment particles play a decisive role in the transport of particulate P to low laying environments as much of the P is sorbed to these soil particles (Lundekvam and Skoien, 1998; Sporre-Moeny et al., 2004; Zhang et al., 2011). High runoffs from agricultural fields occur during storm events and bring high concentrations of P in to stream waters. During storm events, the delivery of different P forms to streams originates from varying source regions and is by different pathways. This may be particle erosion and re-suspension of stream sediments, surface runoff and flushing of soil water reservoirs

(House and Warwick, 1998).

2.10 Iron content – role of redox conditions on P

P is not readily bioavailable in the environment rather it is bound in the biomass, as organically bound or inorganically adsorbed to clay and silt soil particles. Mobilization of P from soils and sediments depends on several environmental factors. The amount and forms of Fe/Al oxides and hydroxides, clay, dissolved organic matter; redox potential and pH are some of the main factors (Reddy and DeLaune, 2008). The fate of P is highly influenced by redox conditions. Fe is known to exist in the forms of Fe^{3+} or in its reduced form Fe^{2+} in aquatic environments. In aerobic conditions, iron is in the stable Fe^{3+} form which may react with phosphates and precipitates out as the insoluble ($FePO_4$, $pK=4x10^{-27}$) and is common phosphate compound in aerobic conditions (Roden and Edmonds, 1997). However, in the pH ranges of 4-8, amounts of Fe^{3+} is not significant in the open water environment rather it is readily precipitated as ferric hydroxide ($Fe(OH)_3$, $Ksp= 2x10^{-29}$). Phosphate ions are adsorbed to the $Fe(OH)_3$ and form amorphous oxy-hydoxy FeOOHPO4 (Kalff, 2002). Therefore, FeOOH in the environment plays an important role in controlling the mobility and availability of P both in forests and agricultural stream waters.

P itself is not redox sensitive element. It exists in the +5 oxidation state in aquatic environments. However, due to the chemistry of Fe, solubility of P compounds is influenced by redox potential. Under anaerobic condition, oxidized forms of Fe function as electron acceptor and are reduced to ferrous iron which is most commonly occurring in lake sediments.

$$\mathbf{FePO_4 + H^+ + e^- \leftrightarrow Fe^{2+} + PO_4^{3-}}\text{.................}\textbf{Equation 1.}$$

In this case, availability of phosphates increases as iron bound phosphates is released and escapes by diffusing in to the aqueous environment (Hutchison and Hesterberg, 2004; Moore and Reddy, 1994; Patrick and Khalid, 1974). Fe^{2+}-phosphate ($Fe_3(PO4)_2.8H_2O$, $Ksp=1x10^{-36}$) compounds are in fact less soluble.

Studies indicate that sediment bacteria have significant role in uptake and storage of P including release of Fe bound phosphorus. When soils for instance become water logged, oxygen is depleted during microbial oxidation of organic matter and anaerobic environment is produced. Consequently O_2 as electron acceptor is replaced by species such as nitrates, sulphate, Mn(IV) and Fe^{3+} (Gächter and Meyer, 1993; Gachter et al., 1988). Iron reducing bacteria are necessary in order to decompose organic matter. The release of phosphate with the help of sulphate reducing bacteria from Fe^{3+} phosphate reduction ensures availability and transport of phosphates (Roden and Edmonds, 1997). Similarly, at lower redox potential (Eh) values, sulphate is reduced to sulphide. Reduced Fe^{2+}

sulphide can precipitate in various reactions which results in greater availability of phosphates. In anaerobic sediments where inputs of Fe minerals and sulphate are in interaction (Reddy and DeLaune, 2008), give the following biotic and abiotic interaction and reaction.

$$\mathbf{Fe^{3+} + e^{-} \leftrightarrow Fe^{2+}} \text{..............................}\textbf{Equation 2}$$

$$\mathbf{SO_4^{2-} \rightarrow H_2S \rightarrow FeS} \text{............................}\textbf{Equation 3}$$

This continuous bacterial action can use sulphide as an electron donor and can reduce $FePO_4$ resulting in a release of Fe^{2+}-hydroxides-phosphate minerals ($Fe_3(PO_4)_2.(H_2O)$). Subsequent removal of Fe^{2+} by reaction with sulphide leaves the system with greater availability of phosphates (Gächter and Meyer, 1993; Loeb et al., 2008; Roden and Edmonds, 1997). In systems where iron and calcium are dominant, Moore and Reddy (1994) observed two opposite phenomena. The first observation was that under aerobic conditions, iron oxides are likely to control the fate of inorganic P and secondly, calcium phosphate mineral precipitation governs the solubility of P under anaerobic conditions. This difference was reflected in the decrease in pH under aerobic conditions as a result of oxidation of ferrous iron compounds, whereas an increase in pH occurs under anaerobic conditions as a result of reduction of Fe^{3+} compounds.

Fertilized agricultural lands can be flooded resulting in solublisation of residual fertilizer nutrients with subsequent release of P. This increase in phosphate amount is attributed to the anaerobic reducing conditions occurring in the flooded soil (D'Angelo and Reddy, 1994; Loeb et al., 2008). Thus, the dissolution of iron minerals results in two important phenomena: increase in concentration of water soluble P and adsorbed P. The cycles of Fe^{3+} reduction, Fe^{2+} oxidation and sulphate reduction in soils can have significant effect on P mobilization from soil to water. Due to the low solubility of FeS at low redox potentials, as compared to the solubility of ferrous oxide minerals, precipitation of FeS comes from the dissolution of ferrous oxide minerals. Sorbed P is released to pore water resulting in phosphate availability in water (Loeb et al., 2008).

2.11 Reduction in acid rain and its role in P chemistry

Acid rain primarily affects acid sensitive catchments which are located in upper parts of catchments whose soils have limited ability to neutralize acidic compounds. The immediate effect of acidification is then a reduction in pH of soils which result an increase in labile Al concentrations. Acidification situation in south east Norway during the peak acid rain periods of 1970s and 1980s has led to increased mobilization of labile inorganic aluminum (Al_i) from forest catchment soils (Skjelkvåle et al., 1998; Wright et al., 1993). Primarily this labile Al_i is maintained in upstream forests by sulphate ions (SO_4^{2-}) functioned as a counter-ion for Al(III) in acidic stream waters.

$$\mathbf{2Al(OH)_{3(s)}+3H^{+}+3SO_4^{2-}\leftrightarrow 2Al^{3+}+3SO_4^{2-}+3H_2O}\text{.....}\textbf{Equation 4.}$$

During episodes of high flow events, most of this labile Al_i was transported into agricultural areas where there is usually high concentration of phosphates. In areas where geology is dominated by granitic rock types and thin soil cover, river water from forest is usually of low ionic strength and low acid neutralizing capacity with low pH due to organic acids. On the other hand agricultural waters have higher pH and ionic strength. When water with low pH from forest runoff is mixed with water high pH agricultural runoff downstream, a pH gradient appears which will influence Al chemistry, which these ions precipitate as amorphous oxy-hydroxides.

$$\mathbf{Al^{3+}+H_2O\leftrightarrow}\textbf{Al-oxy-hydroxides (e.g. }\mathbf{Al(OH)_{3(s)}}\textbf{)...........Equation 5.}$$

The precipitation of Al as ($Al(OH)_{3(s)}$) results in the sorption of $H_2PO_4^-$ which may age slowly into insoluble hydrous-$AlPO_4$ and finally augmented as $AlPO_4$ minerals (Moore and Reddy, 1994). The result is that the concentration of phosphate in streams and lakes is reduced where during growing seasons this gets less P and eutrophication problems in lakes is reduced.

However, the substantial reduction of acid rain since the 1980s in Europe due to reduction in sulphur deposition (UN-ECE, 1999), has reduced leaching of acid cations like Al (Skjelkvåle et al., 1998) from upstream forests and has led to a loss of a large amount of phosphate from agricultural fields which results to increase eutrophication. This is because P is carried down with runoff directly to the lake without any counteracting ions in precipitating the incoming P. It has been postulated that cycling of PO_4^{3-} and DNOM may become altered in acidic surface waters through interaction with Al as it plays significant role through adsorption and coagulation reactions which ultimately alters the cycling and presence of P (Driscoll and Schecher, 1990). Studies in Norway showed that there is a reduction of about 90% in sulphate deposition in recent years (Hyne and Wilson, 1997; Klif, 2011). As a result the mobilization of phosphorus to aqueous environments has increased four times since the 1980ies and eutrophication has registered to increase since the 1980s in south-eastern

Norway (Lundekvam et al., 2003). Forest stream waters today are containing lesser amounts of Al, passes agricultural fields receiving runoff which contain high amounts of P, results precipitation of P with aluminium oxy-hydroxides occurs to reduced extent. This results in high residual P concentrations entering to surface waters via streams. Lake Vansjø is one of the catchments in south-eastern Norway that experienced increased eutrophication with harmful blooming of toxic algae especially during the flood year in 2000 which lead to a ban of bathing and some other activities (Skarbøvik et al., 2011). This was due to the increased loading of especially bioavailable P partly due to the waterlogged soils which reduced iron losses its P holding capacity which is discussed in section 2.10.

2.12 Dissolved natural organic matter and background fluxes of P

Soil organic matter (SOM) has significant importance for soil quality as it influences many soil properties (Gregorich et al., 1994). Soil organic matter is formed through incomplete biotic or abiotic decomposition and transformation processes with some secondary synthesis mechanisms (MacCarthy, 2001). SOM generally fall into two categories which have distinct chemical characteristics, known as humic and non-humic matter. Humic matter includes mainly large molecular weight compounds with complex structures and is the dominating fraction of the soil organic matter (Anderson, 1979), whereas non-humic matter includes molecules of known biological forms such as fats, carbohydrates and amino acids-proteins. Part of the humic matter which is known as dissolved natural organic matter (DNOM) has important feature in that it is capable of complexing with some metal compounds such as Fe and Al in the transporting of crucial nutrients like P (Schnitzer, 1978).

DNOM sources in agricultural streams could be SOM transformation or plant litter (Kalbitz et al., 2000) and make its way down to streams through hydrological transport pathways. DNOM is not able to retain P by itself because of its negative charge sites, but with the help of bridges across Al and Fe, P can be bound to humic substances in soils (Gerke, 2010). Orthophosphates are not readily mobile in the environment as these are effectively held or adsorbed in the soil sediments and/or assimilated in biomass. P in natural watersheds is then typically associated and brought with dissolved natural organic matter. The natural background P fluxes from the forested catchments are therefore mainly related to the transport bound to DNOM. Furthermore, the background amount of DNOM has increased almost to double with decreasing acid deposition. This has inherently also to lead to increase the background loading of P. The concentration of labile aluminum in soil solution has decreased in the same regions due to the reduction of sulphur deposition in the recent years. This reduction of labile Al_i has led to increased solubility and transport of orthophosphates.

Flux of DNOM is governed by climatic factors such as intensity of precipitation, temperature and mainly acid rain. When acidification was in its peaks in 1970ies and 1980ies there was reduced DNOM concentration in region affected by acid rain. Leaching of substantial labile Al has led to decreased DNOM (Parekh, 2012). This was likely due to the increased ionic strength of waters coupled with the interaction between Al and DNOM in the environment. For instance, the application of $Al_2(SO_4)_3$ in water treatment works as coagulant traps high levels of DNOM which results in the reduced amounts of DNOM in waters (Hongve et al., 2004). In southern Norway, there has been a doubling in the concentration of DNOM after the acid period, and it is believed to increase in the future with increase in precipitation, precipitation being expected to increase in Nordic countries in particular. This will lead to the postulation that future increased leaching of DNOM will have great impact in the transport of P from forest catchments (Haaland et al., 2010; Hongve et al., 2004). Runoff intensity is a decisive factor for increased amount of humus in runoff that has been observed in the last decades. It is rather a case than an increase in temperature that increases in amounts of humus (Evans et al., 2001).

2.13 Previous findings from EUTROPIA studies at Morsa

Studies previously conducted in western Vansjø indicated that more phosphorus was leaving the lake than was received from eastern Vansjø. To achieve a more precise measure of the local influx of P from the sub-catchment of western Vansjø, research projects were carried out to get a better measure of the loading from local streams. The results from these studies (Bechmann et al., 2010) proved that the loading of P from the agricultural area was greater than anticipated. A possible important cause for this is that vegetable cultivation (fertilization of hot-spots) is more common in this sub-catchment than in other parts of the catchment (Bechmann et al., 2010). Furthermore, a complementing study showed that 60% of the total P loading to western Vansjø originates from the catchment around western Vansjø, while only 40% comes as inflow from eastern Vansjø (Bechmann et al., 2010). Benefits of local abatement actions are therefore of great importance for the western Vansjø area

The difficulty in data comparison of previous findings from Morsa is also the lack of uniformity in the operationally defined fractions of P and the methods used. In many of the studies, particularly those relating to surface runoff from agricultural land and forest areas, the measurement of P fractions has been considered. Loads of P in runoff and stream reveals significant differences in space and time. Relatively low levels of P were found in the runoff from forested sites, where large fractions of total P is organically bound due to the high concentration of DNOM.

Gebreslasse (2012) found that of the total load of P from the agriculturally drained stream sediments was higher which is about 90% of the tot-P is inorganic form. Inorganic P is usually associated with Al, Fe, Ca compounds with low solubility and thus unavailability to plants. The fraction of soluble P is found to be high in forest dominated draining streams though contribution of tot-P from forest is very small as compared to agriculturally drained streams. However, considering that the land use of the catchment is forest (85%), P contribution to the total load is of immense importance.

Opland (2011) conducted a study in agricultural soil-P content and stream water P content at Huggenes in western Vansjø and found that soil-P content is high especially in the Ap soil layer on which drainage pipes are buried. Opland (2011) added that drainage pipes located in the marine clay soil layer, which is rich in P, is an important pathway for dissolved P into the streams. A complementing study on nine streams water by Parekh (2012) showed that elevated free phosphates form from the agriculturally drained streams, while 30 to 60% of tot-P was found organically bound at the streams drained from forest dominated. A recent study by Shekobe (2012) found that most of this DOM-P is lost from solution by precipitation or sorption to particles when the runoff from the upstream forest passes through agricultural land. Shekobe (2012) concluded that much percent (75 to 85%) of the P fractions were precipitated when the pH gradient created by the low forest streams mixed with a stream which has higher pH from agricultural field.

2.14 Management practice and abatement actions in Morsa catchment

Reducing the flux of P from major anthropogenic sources is essential. Advanced sewage treatment plants are as such excellent management strategies for reducing nutrient fluxes from point sources (Carpenter et al., 1998). Agricultural sources of P are diverse and controlling P fluxes poses great difficulties. Application of nutrient management plans on all agricultural farms is essential in order to reduce potential P losses (Sharpley et al., 2003). Today a widely used strategy for reducing P losses from agricultural land is to target hot-spot source areas prone to erosion (Sharpley et al., 1994). Likewise, in Norway, one of the growing management strategies to reduce P transfer has been focusing on the reducing of soil erosion (Øygarden, 2000).

Reducing P loss in agricultural runoff may be achieved through source and transport control strategies (Sharpley et al., 2003). This includes targeting soil conservation practices such as reduced tillage or/and tillage shift, maintaining buffer strips of 5-10m wide belt along stream sides, constructing wetlands, reduced ploughing and planting catch crops. Conceptually, these practices reduce the impact of rainfall on soil surface; reduce runoff volumes and velocity which thereby reduce sediment transport and increase soil resistant to erosion. However, it is strongly suggested that none of these measures should be relied on as a sole practice to reduce P losses in agricultural runoff (Øgaard and Bechmann, 2010; Sharpley et al., 2003; Sharpley and Kleinman, 2003). The studies argue that some of the measures are only immediate solutions while others give long-term results. Sharpley et al. (2003) noted that erosion control will stop P losses in runoff but erosion control is not the sole answer. Those authors strongly suggest that long-term reduction of P fluxes to surface waters requires a combination of strategies and implementation at the source and along the course of transport. One-sided abatement aimed at reducing soil erosion may on the contrary lead to increased eutrophication by possible decreased scavenging of bioavailable P in the streams and lake waters as well decreased burial of P bound to particles into the sediments.

In Norway, ploughing of agricultural fields in spring instead of autumn has shown reduction of particle transport by up to 89% in slope fields prone to erosion. Direct drilling in spring as compared to autumn ploughing is estimated to reduce loss from clay soils by up to 79% (Ulén et al., 2010). A variety of studies have shown that no-tile practices decrease both erosion and sediment bound P losses relative to conventional tillage practices (Kleinman et al., 2008; Sharpley and Smith, 1994). A series of plot studies in buffered vegetated zones showed that the total P retention over the zone was from 55-95% though the efficiency varied with width of vegetative zone, type of vegetation used and seasonal variation in runoff. Total P retention capacities of 21 to 44% were observed in artificial constructed wetlands in Norway (Braskerud, 2001; Syversen, 2002). On the other hand, if these wetlands are not managed properly that have the potential to convert particle bound P into bioavailable P.

Catch crops, such as oil reddish and deep rooting crops, have been widely used as management practices to reduce nutrients loss from agricultural soils. However, successful control of one nutrient may worsen loss of another because plants themselves can release nutrients. Studies with catch crops have shown that there is increased transport of dissolved P reducing the benefit of using as controlling mechanism (Børresen and Uhlen, 1991; Uhlen, 1989). Despite negative side effects the catch crops are commonly used in Scandinavian countries to promote water quality protection methods (Ulén, 1997). In Norway farmers have been subsidized to grow catch crops since 1999 with the primary objective to minimize nitrogen leaching after summer crops have been harvested and to decrease soil erosion associated with particulate P losses from autumn ploughed soils (Lundekvam et al., 2003).

There has been a reduction in loads of total P and suspended particles in western Vansjø, Norway, since 1990 (Skarbøvik and Bechmann, 2010; Skarbøvik et al., 2011). However, Bechmann et al. (2010) and Ulén et al. (2010) documented that the total P losses from agricultural fields, especially from fields with vegetable crops, are still high. This is because vegetables in these fields require high levels of P and autumn ploughing. Hence, high losses of particulate bound P have been recorded from poorly protected clay rich soils. Agricultural practices for potatoes and vegetables crops pose additional challenges when it comes to management. This is because these areas need high application of P and frequent ploughing especially in spring period.

3 MATERIALS AND METHODS

3.1 Site description: Morsa- catchment and Lake Vansjø

Vansjø-Hobøl or Morsa (Figure 3) is a catchment located near the city of Moss, in the southeast Norway (59˚26’N, 10˚41’E), between the coastal areas of the Oslofjord and the Glomma River. The catchment covers an area of about 690km^2 with almost 90% of it lies below the marine limit of 214 meters above sea level (m.a.s.l). About 10% of the catchment lies above marine limit with thin end moraine soil layers on top of hard bedrock. Soil in the lower parts of the catchment is rich in nutrients due to the marine clays that mainly contain apatite (Skarbøvik et al., 2011). Metrological and hydrological measurements recorded that the catchment's mean annual air temperature is 5.6ºC and receives mean annual precipitation of 829mm, the precipitation is characterized by peak runoff events during autumn, winter and spring snowmelt periods (Skarbøvik and Bechmann, 2010; Skarbøvik et al., 2011). The catchment's detail explanation is also given in the introduction part in section 1.1

3.1.1 Relief, geology, and soil type of Morsa catchment

The catchment's relief varies considerably. Elevation ranges from about 346m.a.s.l in the upper part of the catchment to 25m.a.s.l in the lower parts of catchment. Poorly weatherable pre-cambrian (gneiss) and granitic bedrock with relatively thin bottom moraine layers dominate the Northern forested part of the catchment. Going southwards and mainly downstream in the catchment the soil gets richer in clay and silt (Skarbøvik et al., 2011). This is because the area was submerged under the sea during the quaternary period (10000 years ago). When the great inland glacier melted, the land rose up from the sea, leaving marine clay deposits that are suitable for farming. As the beach zone passed through the landscape wave actions have washed the ridges free of deposits, leaving mainly rock outcrop. Typically today south-western of the catchment, marine sediments are accumulated leaving large piles of deposits of glacio-marine end moraine what is known as the Ra. The damming of the mineral-rich clay and silt soil are suitable for agriculture (Skarbøvik and Bechmann, 2010).

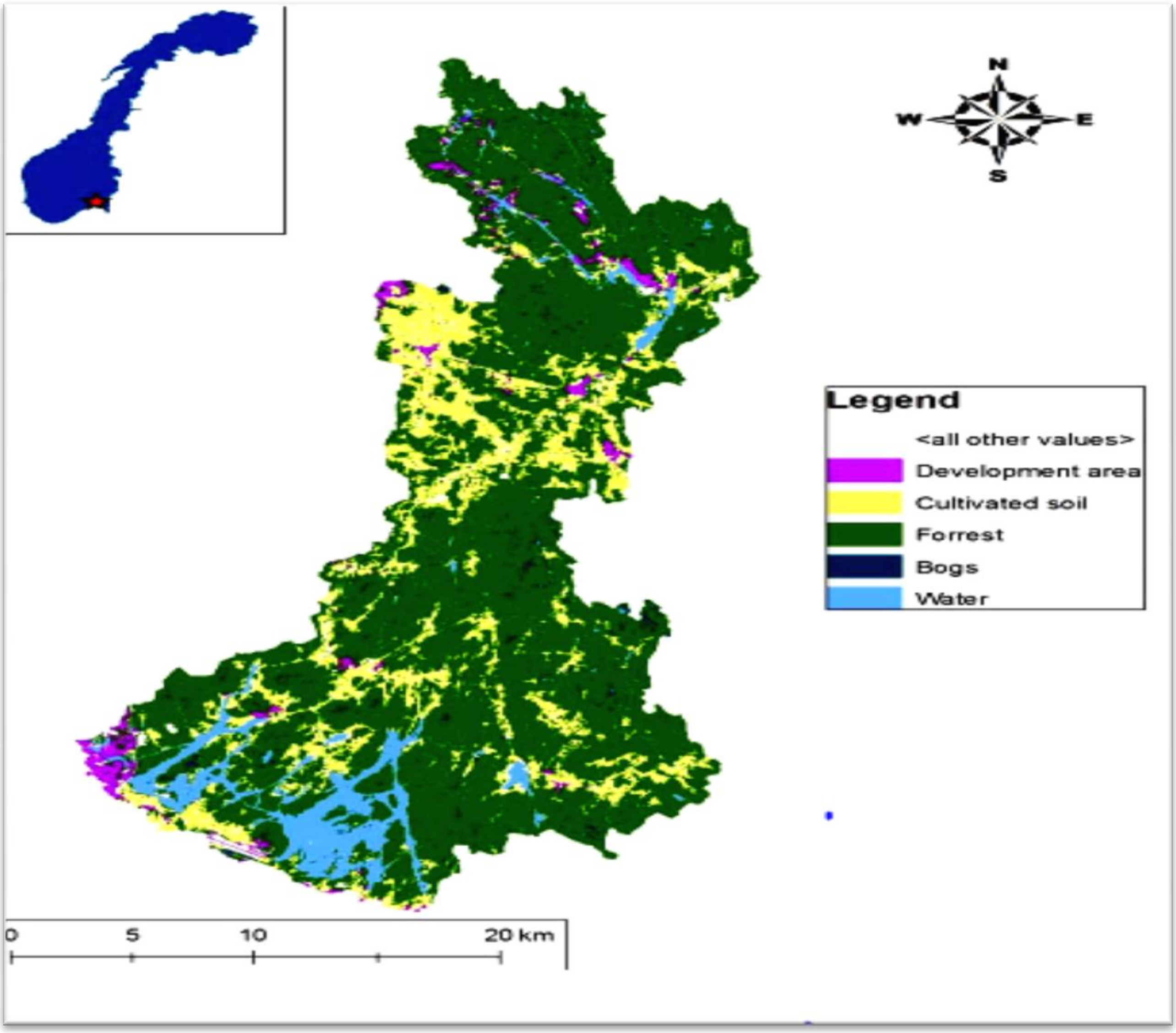

Figure 3: Map of the Vansjø-Hobøl watercourse (Bjørndalen et al., 2007)

3.1.2 Soil type and erosion risk in the Morsa catchment

The type of soil in the Morsa catchment is closely related to the quaternary geological history of the deposits. In the northern part of the catchment, the soils are predominantly coarse bottom moraine and in the lower southern part the soils are dominated by marine deposits rich in clay and silt. Clay content in agricultural soils in the bottom areas of the catchment can reach up to 80% clay (Skarbøvik and Bechmann, 2010). Soil texture is important in that it is the characteristics used in determining erosion risk and potential nutrient leaching. Morsa catchment is also characterized with different soil texture types and erosion risks. The predominant texture classes of the plow layers of the catchment range from fine sand to silt and sandy silt. The part of the catchment with most agriculture has more fine sand, while the part with more forest has more silt and sandy silt soils.

This is the characteristics of soil that determines the eroding tolerance in the tillage layers. Fine particles like clay and silt are vulnerable and washed away by erosion.

Table 2 shows different texture groups and erosion risks of plough layers of the western Vansjø. Erosion risk maps are produced based on soil and slope characteristics for Norwegian soils. Four erosion risk classes are distinguished on the erosion risk maps for Norway. These are low, medium, high and very high erosion risk classes. Thus, erosion code 1-4 indicates low, medium, high and very high erosion risks, respectively. The erosion risk of the tillage soil layer in the catchments of the studied streams is dominantly low to medium high showing that erosion risk for Støabekken1 for example lays between 1 and 2 which is approximately 90.2% and 9.8% respectively (Norwegian Forest and Landscape Institute, 2011). Erosion risk map can be found in Appendix-H.

Table 2: Texture groups and erosion risks of the plow soil layers in catchments of the studied streams (Norwegian Forest and Landscape Institute, 2011)

Sites	Texture code						Erosion risk (%)			
	1	2	3	4	5	6	1	2	3	4
Støa1	0.0	88.9	0.0	11.1	0.0	0.00	90.2	9.8	0.0	0.0
Hug	8.1	77.7	0.0	3.9	8.0	2.3	71.0	28.5	0.5	0.0

1-6 indicates soil texture code whereas % erosion risk code is given 1-4

Table 3 shows that the different quaternary deposit soil types of the three selected sites. Forested areas like Dalen are predominated by bare hills with thin humic cover; while an agricultural land (Støabakken1 and Huggenes) are characterized by sea beach deposits and is because these sites are situated on the Raet.

Table 3: The different quaternary deposit types of the three sampling sites in western Vansjø (Norwegian Forest and Landscape Institute, 2011)

	Quaternary deposits type (%)					
Sample site	BR	THC	SBD	BOGS	MBDCC	OTHERS
Støa1	5.50	0.00	80.2	0.00	14.3	0.00
Hug	13.4	4.20	32.6	0.00	49.8	0.00
Dalen	50.1	22.4	12.9	14.6	0.00	0.00

BM= Bare Rocks, THC= Thin Humic Cover, SBD= Sea and Beach Deposits, Bogs and MBDCC= Marine Beach Deposits Continuous Cover

3.1.3 Land use distribution in the catchment

It is known that the lower parts of the Morsa catchment have been experiencing human activities for the last 4000 years. As inhabitants increase over time, land use started to change from forestry to agricultural practices. This continues for centuries and today an average of 15% of the catchment is purely used for agriculture and 80% of it is forest (Skarbøvik and Bechmann, 2010).

Land use in the catchment greatly differs from a complete forest covered area to areas which are highly practiced for agriculture. Table 4 describes percentage distribution of land use in western Vansjø, part of the catchment used in the thesis. The breakdown of land use as a percentage of the total area for the selected sites is presented in Figure 4.

Table 4: Land-use distribution (%) of the three sampled streams in the catchments from (Norwegian Forest and Landscape Institute, 2011) and area data from (Skarbøvik et al., 2011)

Sample site		Land use type (%)		
	Area (daa)	Agriculture	Forest	Others
Støabekken 1	157	85	1	14
Huggenesbekken	810	59	32	9
Dalen	882	0	100	0

Daa= in hectares

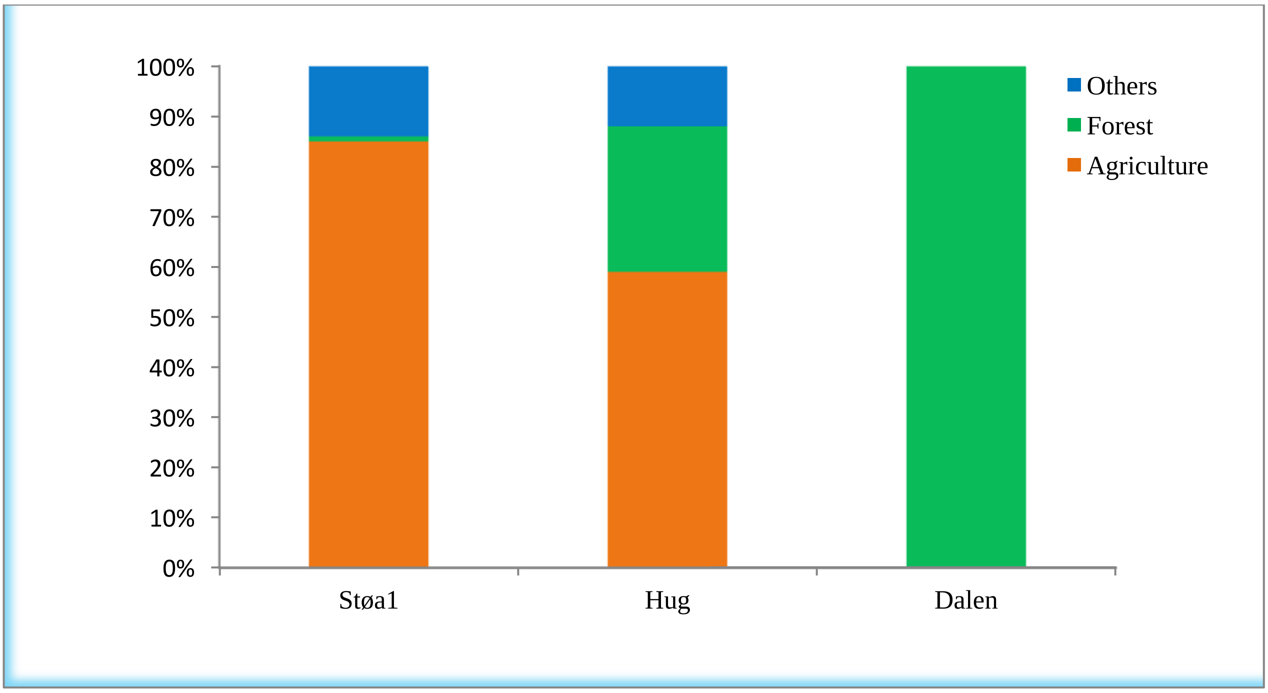

Figure 4: Percentage of land-use distribution of the three sampling stream sites in western part of the Vansjø-Hobøl catchment.

3.2 Lake Vansjø

As part of the Morsa watershed, lake Vansjø is a naturally low-land nutrient rich eutrophic lake (Figure 5). This is due to the substantial natural flux of P from those marine deposits. The surface of the lakes is situated at 25m.a.s.l. The lake is commonly known as lake Vansjø and is divided into two parts; namely the eastern part or Storefjorden and the western part commonly known as Vanemfjorden. Western Vansjø is shallower than eastern part (Bjørndalen et al., 2006). Within the two parts, there are many small first order streams, which drain into the western Vansjø basin. Both parts of the lakes receive considerable attention due to eutrophication problem.

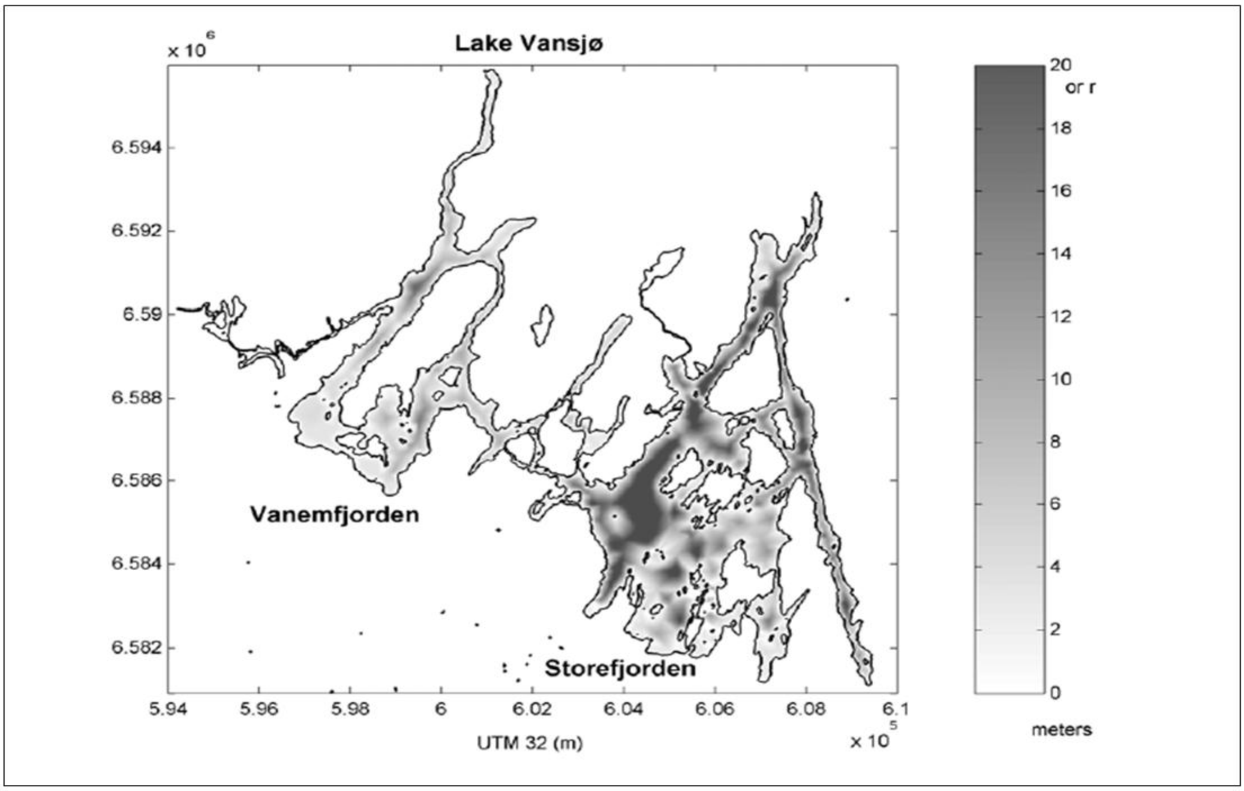

Figure 5: Map of eastern and western parts of the lake Vansjø; (Bjørdalen et al., 2007).

3.2.1 Western lake Vansjø and the selected sampling site

Western lake Vansjø (Figure 6), an area where the three sampling sites for this thesis are located, is part of the lake system that is most affected by eutrophication. Eutrophication has been a problem to the lake for decades. Diffuse P from agricultural fields have been the major sources in eutrophying the lake (Skarbøvik et al., 2011). Despite several mitigation measures taken to reduce P inputs, the lake does not show to fulfill the WFD environmental goal of good quality of water stated to be 50µg/l of P.

Three sampling streams sites Støabekken1, Huggenesbekken, and Dalen were selected to assess the effect of land use. The selection of sampling sites is purely based on land use differences in order to compare the P flux from two agricultural dominated sites and one forested catchment. Støabekken1 and Huggenesbekken are two agricultural draining stream sites flowing to western lake Vansjø from the southern part of the western basin with Huggenesbekken is less agriculture dominated. The forested sub-catchment has a single first order stream flowing out into western Lake Vansjø. Soil water of different generic soil horizons were also sampled from Dalen site along with stream water samples and are included in the thesis. The loadings of P to the lake from these two agricultural sites and one forest site are characterized with data obtained from detailed P analysis and discussion in section 4.

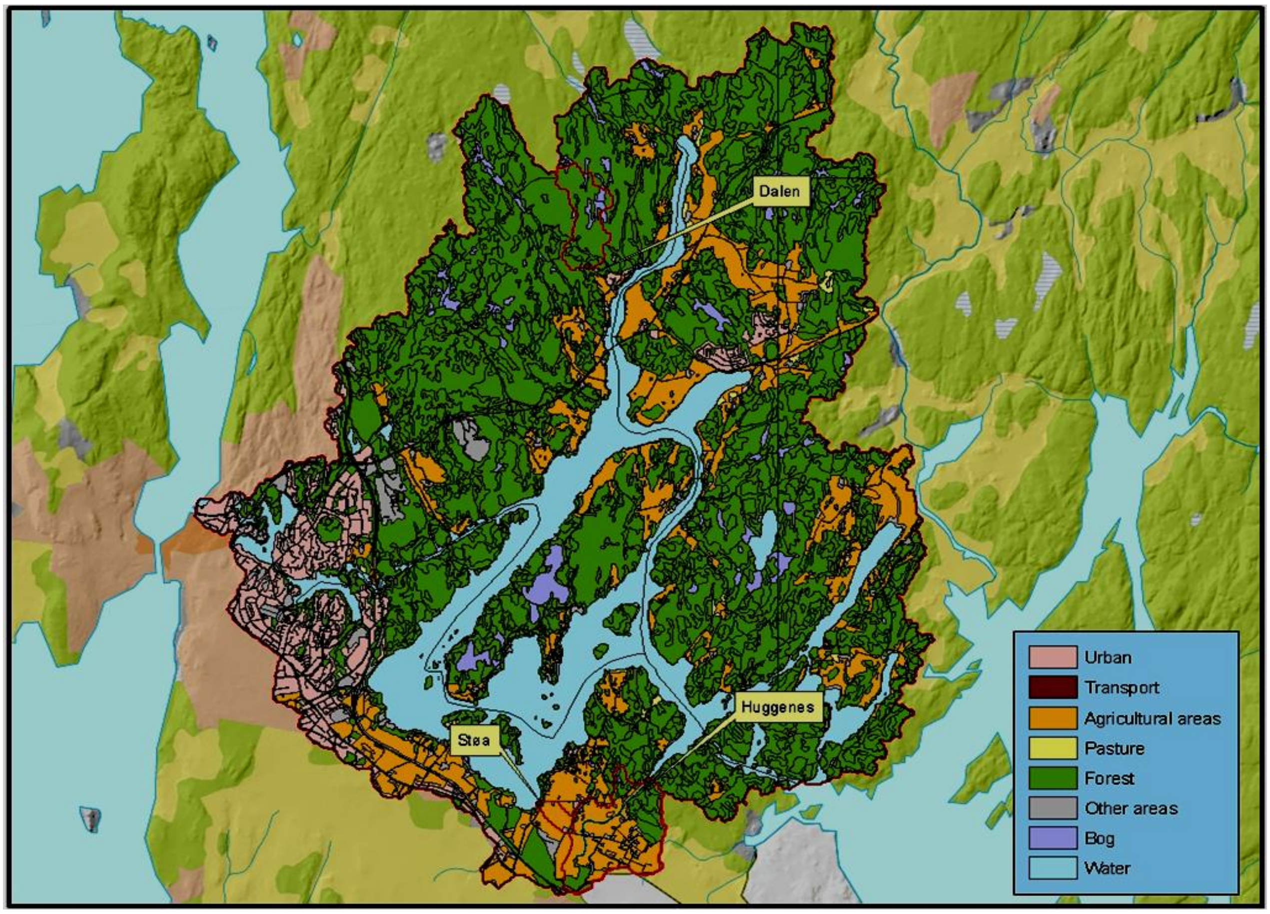

Figure 6: Land-use distribution of western Vansjø sub-catchments with names of sampling site indicated and boundaries of each site is indicated with red round lines. GIS map produced by Alexander M. Engebretsen.

3.3 Sampling

3.3.1 Stream water sampling and sample pretreatment

Stream water samples were collected from Støabekken1, Huggenesbekken and Dalen using field autosamplers (Figure 7). Automated pump samplers of type ISCO 6700 at Støabekken1 and Huggenesbekken sites, Manning automatic pump water sampler at the Dalen, all fitted with 12 polyethylene 0.5l bottles inside were used to collect stream water samples. These autosamplers are positioned near the bank of the sampling stream with tubing placed in the flowing stream water where homogeneity of water is considered appropriate for all hydrological conditions. Samples were transferred to prewashed polypropylene bottles manually.

Stream water samples were routinely collected every 14 days in the snow free seasons as a part of the Morsa monitoring programme with frequent sampling during episode flow events. Intense (2–6hour intervals) water sampling campaigns were performed over targeted hydrological storm episodes during spring and snowmelt events. The autosampling method provides opportunity for high sampling frequency during episodes (heavy rainfall or high snowmelt flow events) up to a maximum of 12 samples per day from each autosampler. All water samples were taken to Department of Chemistry, University of Oslo (UiO) and kept in a dark cold room, usually at 4°C for preservation until further analysis. Basic physicochemical properties of the water samples were determined at the chemistry laboratory in accordance with their respective ISO standards as described in respective sub chapters below.

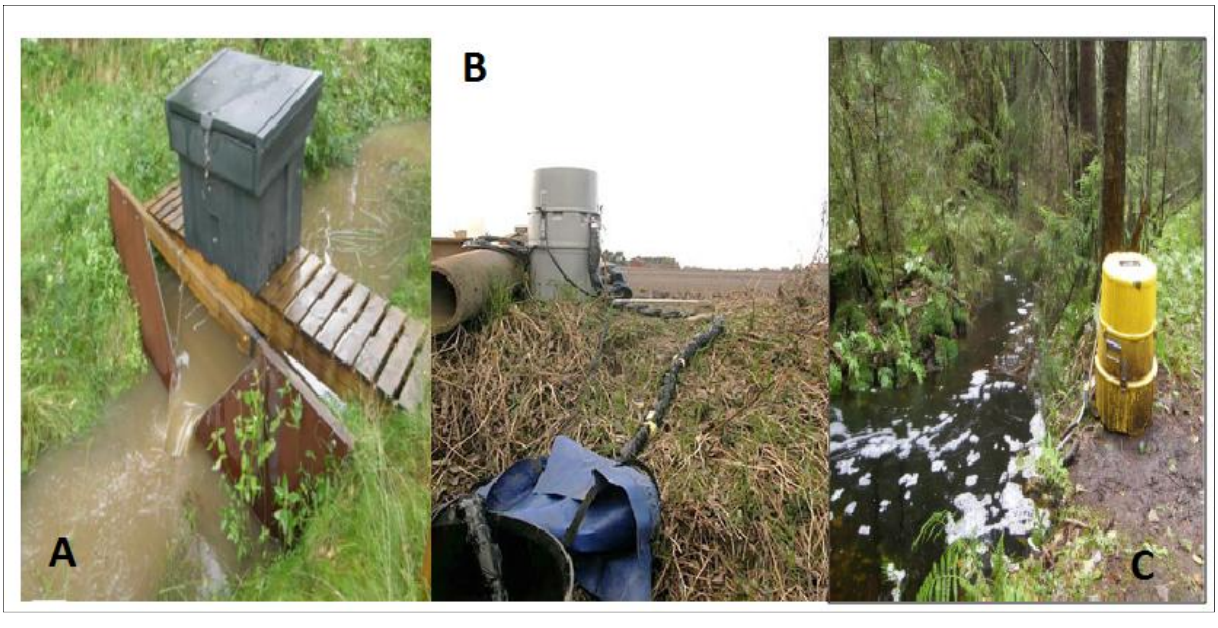

Figure 7: Autosamplers installed in 2009 at sampling streams. Pictures ‘A and B’ shows the ISCO 6700 autosamplers at Støa1 and Hug respectively while picture ’C' shows the Manning autosampler at Dalen. Photo by Prof. Rolf D. Vogt.

3.3.2 Soil-water sampling at Dalen sub-catchment

Soil-water was sampled along with stream water samples at Dalen site only. Three plots for sampling soil water had been instrumented within the Dalen area since 2009. Figure 8 indicates sampling plots on the ridge, slope and at the valley bottom. These plots were primarily selected in order to capture the main spatial variation in soil water chemistry within the Dalen watershed. This was done to better define and characterized the hydro-bio-geochemical processes governing the release, discharge, flux, and assimilation of P through the catchment. The soil water samples from O-horizons and lysimetric soil- waters have been collected in the following way.

Water passing through the forest canopy was collected in three throughfall collectors at each soil plot. The collector consists of an open funnel, having a diameter of 11.5cm, fitted to a sample collector bottle. The funnel was mounted 10cm above the ground while the sample bottle was kept below the soil surface to make sure that direct sun light interactions was prohibited, as this may change the soil-water chemistry. Soil water samples from the O, AE, B and C horizons were collected using porous ceramic suction cups installed in each soil horizon. The cups were connected with tubes to vacuum bottles. These permeable porous ceramic cups were capable of capturing the water percolating through the unsaturated soil zone. Detailed plot pictures and descriptive information on the sampling plots is well presented and can be found in master thesis by Mohr (2010), where he studied geochemical and hydrological processes governing the mobilization of P.

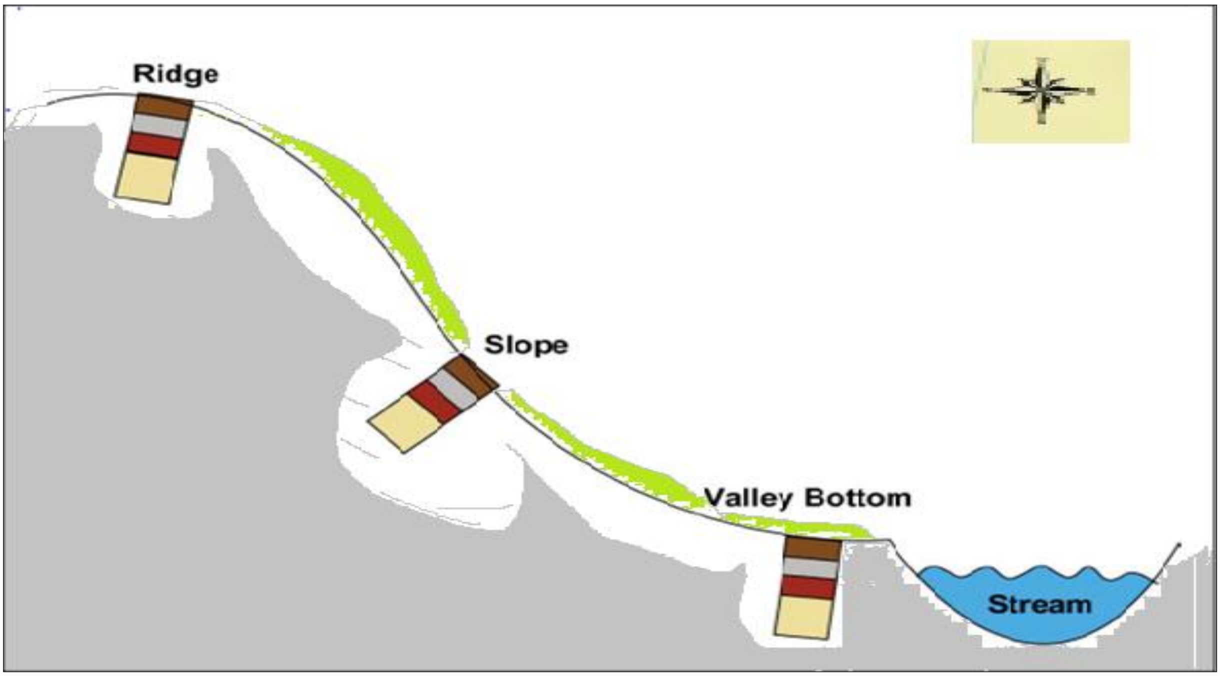

Figure 8: Dalen soil water sampling plots from (Mohr, 2010). Dalen stream site is presented in figure 6 along with other streams. This figure is only to show how sampling was done.

3.4 Analysis of water samples

The following physico-chemical parameters were determined in the water samples according to their specific ISO standards prior to filtration as described below. The measurements were done at the Department of Chemistry, UiO laboratory unless otherwise stated. Analysis was performed by Environmental chemistry group members. Information of the equipments used is given in appendix-B.

3.4.1 Determination of aluminum and fractionation

Determination of aluminium fractionation was performed on water samples whose pH was less than 5.5. Measurement of aluminium fractionations were based on work of Barnes (1975) and Driscoll and Schafran (1984) using extraction method with 8-hydroxyquinoline (MIBK). Fractionation of monomeric aluminium is extracted from the polymeric form by complexing with 8-hydroxyquinoline at higher pH of 8.3 and immediately extracted using MIBK into an organic phase. Amberlite IR-120 cation exchanger resin column was used in order to trap inorganic aluminium (Al_i) and thereby separate organic bound monomeric aluminium (Al_o). Aluminium complex with 8-hydroxyquinoline present in the organic extract was determined photometrically at λ=395 and 600nm. The concentration of Al_i retained in the ion exchange column was calculated as the difference between Al_a and Al_o.

3.4.2 Electrical conductivity and pH measurement

Prior to any measurement, water samples were kept at room temperature to attain stability. Electrical conductivity (EC) measurement was performed before pH measurement to prevent ion contribution from pH electrode solutions. This was done by taking an aliquot of approximately 20ml into a polyethylene cup and measured for EC reading. Measurements were performed in accordance with the international standards, ISO 7888 (1985) for EC and ISO 10523 (1994) for pH.

3.4.3 Determination of alkalinity

Alkalinity was determined in unfiltered water samples having pH greater than 5.5. Alkalinity determinations were made by titrating known volume of water sample against 0.0213M HCl to bring pH to 4.5. Measurements were done in accordance with international standard (ISO 9963-1, 1994). The acid solution was standardized with analytical-grade Na_2CO_3.

3.4.4 UV-Vis measurement

Absorbencies of water samples at selected UV (254nm) and visible (400nm) wavelengths were determined for all samples. Cuvattes were used as sample holders and these measurements were performed in accordance with the instructions given in the manufacturer's manual of the spectrophotometer.

3.4.5 Filtration of water samples and determination of total suspended solids (TSS)

Water samples (100–250ml) were filtered with the exception of soil water samples due to the fact that soil water samples were considered already filtered through suction lysimeter. Only a portion of filtrates were collected into clean 20-30ml size polyethylene bottles and stored in cold room at 4 ºC until further analysis. The suspended solids retained on the filter paper were dried at 105±10ºC to determine total suspended solids (TSS). This was calculated by filtering water sample onto a tarred filter (M_o), drying the filter at 105±10ºC to constant mass and weighing the dried filter (M_1).

Filtration was in accordance with standard method of NS-EN 872 (2005) with specific glass fibber filter. Filtration was carried out using 0.7µm GF/F Whatman filter and the choice of this over the standard 0.45µm filter paper was due to the fact that these filters are made up of glass fibres which have the advantage of withstanding high temperature of up to 440^{o}C for organic content determination and TSS at 105^{o}C. Measurements of TSS expressed as mg/l is in accordance with ISO 11923 (1997) modified to NS-EN 872 (2005).

3.4.6 Determination of major cations and major anions

Filtered water samples were analyzed for concentration of major cations; calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}) and potassium (K^{+}) using Inductively coupled plasma optical emission spectra (ICP-OES) according to ISO 22036 (2008). Cesium solution was added as an ionization buffer to all samples analyzed for major cations. Samples were acidified with 0.3% v/v HNO_3 (pH~1) prior to analysis. Detection limit for Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} were 0.08, 0.08, 0.05, and 0.05 mg/l respectively. Concentrations of major anions; sulphates (SO_4^{2-}), nitrate (NO_3^{-}), chlorides (Cl^{-}) and fluorides (F^{-}) were determined using ion chromatography (IC) in accordance with ISO 10204-1 (1992). Non-marine sulphates was calculated by subtracting the marine sulphate, calculated based on the sea-water sulphate to chloride ratio, from total sulphate, an equation developed by Appelo and Postma (2007). This is important so as to distinguish changes in anthropogenic sulphate deposition from sea-salt sulphate deposition originated from climate variation.

$$\textbf{Corrected } SO_4^{2-} = \text{tot-}SO_4^{\,2-} - (0.05*Cl) \textbf{.......Equation 6.}$$

In determining the electrical neutrality of water samples charges of anions and cations is never the same. It is because all charges are not determined using the analytical methods available. Hence, organic anions represented as (A^-) in the stream waters were determined by difference from the ionic charge balance. Organic charge density (in µeq/mg of carbon) is defined as A^- divided by TOC using the model developed by Oliver et al. (1983).

When water samples were analyzed for major cations and anions quality controls samples with known concentration were used alongside each batch of analysis. Information regarding IC and ICP-OES is found in Appendix-E and Appendix-F

3.4.7 Determination of dissolved organic carbon

Dissolved organic carbon, was determined on filtered samples that were acidified with HCl. The analyses were carried out with a UV enhanced-persulphate TOC analyzer (Shimadzu TO-5000A) by using the standards of high temperature (680^{o}C) catalytic oxidation and IR detection. Quality control standards were used alongside every batch of samples in every 10 samples and analysis was in agreement with ISO 8245 (1985). Further instrument information is found in Appendix-D.

3.4.8 P-fractionation methods and determination of tot-P and P-fractions

Figure 9 shows schematic fractionation method proposed by Vogt (2008) to obtain concentrations of different P fractions. Portion of the collected raw water and portion filtered water samples were analyzed for total phosphorus (tot-P) and orthophosphates (PO_4-P) respectively.

Table 5 shows the simple arithmetic calculations of the P fractions used in this master thesis. P measurements were performed using photometrical phosphomolybdic acid based methodology and modified according to Norwegian Water Research Institute (NIVA) standard procedures of the instruments (San^{++}analyzer skalar CNP autoanalyzer). Hence, for P analysis, three operationally defined fraction pre-treatment and measurements methods were followed.

[1]. Tot-P determinations were carried out on unfiltered water samples according to NS-EN-ISO 15691-1 (2004) after digestion by potassium peroxodisulphate ($K_2S_2O_8$) as described in Norwegian standard NS 4725 (1984). Digestion of samples with $K_2S_2O_8$ was necessary in order to decompose complex organic and inorganic compounds so that determination of samples for tot-P would be possible.

[2]. Determination of PO4-P was performed on filtered samples (0.7µm GF/F). Phosphate determination were based on molybdate blue method (MBM) developed by Murphy and Riley

(1962) and is according to ISO 6878 (2004). When ammonium heptamolybdate and potassium antimony (III) oxide tartrate in the presence of H_2SO_4, are left to react with dilute phosphate solutions, a yellow coloured complex compound of antimony molybdophosphate is formed. The phosphate complex is then reduced to phosphomolybdenum blue coloured complex in the presence of ascorbic acid catalyzed by potassium antimony tartrate. The blue colour complex is determined photometrically at λ=880nm which is proportional to the concentration of orthophosphate ions present in the complex.

[3]. Determinations of total dissolved phosphorus (TDP=PO_4-P+DOM-P) was also performed on filtered water samples. Thus, the operationally defined P fractionation methods of measurements were used to calculate P fractions of DOM-P, being the difference between TDP and PO_4-P, and PP being the difference between tot-P and TDP. Acidification of samples and standards were necessary and were done approximately one week before analysis with concentrated H_2SO_4 to obtain final SO_4^{2-} concentration of 0.04M. All P analysis was conducted by Neha Amit Parekh at NIVA.

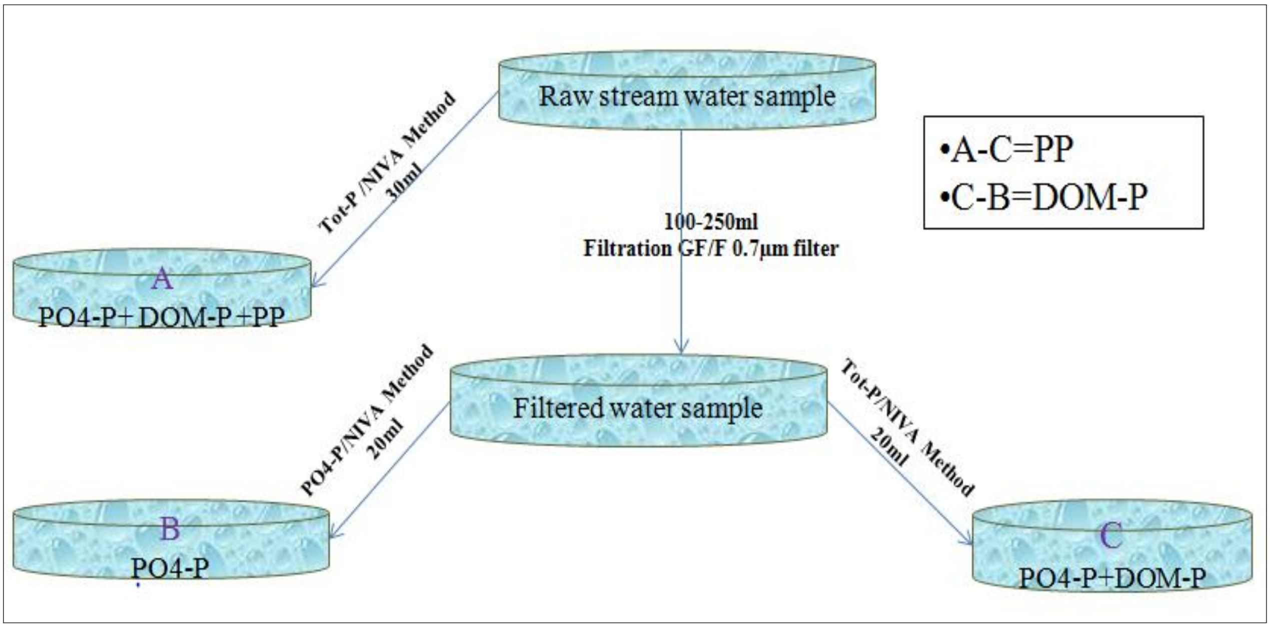

Figure 9: Schematic P-fractionation and determination method for water analysis. The operationally defined methods of P analysis are represented with letters 'A to C'. Modified from Mohr (2010).

Table 5: Schematic P-fractions determination of stream water samples.

P- Fractions	Groups/boxes
Total-P (Tot-P)..	Group-A
Dissolved organic-P (DOM-P)...	Group C-Group B
Inorganic particulate P (PP)..	Group A-Group C
PO_4-P...	Group B

3.5 Data for runoff, precipitation and temperature

Instantaneous and mean daily discharges at the three sub-catchments were calculated using a basic head-discharge calibration height formula. Runoff/discharge data for respective streams were obtained by measuring a height (m) of a flowing stream from which velocity is determined using a formula:

$$V^2 = 2gh \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{Equation 7}$$

V=Velocity (m/s)
g=acceleration due to gravity (m/s^2)
h=height (m)

Then the velocity is multiplied for selected stream area (m^2). It is a method called Area Velocity Method. Hence, the equation for runoff is:

$$\textbf{Runoff}(\textbf{Discharge}) = (\textbf{Velocity}\ (\textbf{m/s})\ \textbf{X Area}\ (\textbf{m2}\ )\ldots\ldots\ldots\ldots\ldots\ldots\textbf{Equation 8}$$

Thus, unit in this measurement, that is m^3/s, is then converted to l/s simply by equating 1m^3 is equal to 1000L. When calculating runoff there were some basic assumptions considered. Rate of runoff is a function of the average rainfall duration to the drainage area and rainfall intensity is constant throughout the storm events. The estimation of tot-P (µg/l) was determined from samples collected on episodic sampling campaigns, weekly and every 14th days to runoff. Results from this estimation help to assess seasonal variation of tot-P in the agricultural fields. Metrological measurements of precipitation and temperature were collected from Rygge station near the catchment which is supposed it share similar climatic conditions.

3.6 Statistical analysis

Statistical analysis has been performed using Minitab statistical program version 16. Pearson correlation analysis and principal component analysis (PCA) was performed. The relationship between TSS, PP, DOC, PO_4-P, DOM-P and hydro-climatological variables has been analyzed in order to show the factors controlling TSS, PP, DOC, and P transport during flood events. Pearson correlation matrix and fractional analysis that include specific variables like precipitation, discharge or runoff.

3.6.1 Principal component analysis (PCA)

Principal component analysis is a way of identifying patterns among large data set variables where the data set variables can reveal some differences or similarities between scores and variables (Jolliffe, 2005). Principal component analysis is a technique of reduced in dimensionality of variables while retaining originality. Variability of the scores in the data set can be explained by the PCA1, PCA2...so on.

4 RESULT AND DISCUSSION

4.1 Major cations and anions in the stream waters

Figure 10 presents the overall charge distribution of major ions in the stream water at the three sites (Støabekken1, Huggenes and Dalen). The solute concentration of major base cations, anions and pH in the streams showed variations across the three streams. The major difference in concentration of these solutes across the sampling sites is due to differences in land-use such as forest and agricultural practice. Within agriculture there are large spatial differences depending on different management practices such as amount of application of manure and other fertilizers. Temporal variations in the concentration of solutes have also been widely observed. These fluctuations are mainly governed by different flow regimes given by discharge/runoff levels. The concentrations of all solutes in the snowmelt season (March and April), which is characterized by prolonged period with high runoff intensity, exhibit relatively lower ion concentrations- except for Na^+ and Cl^- ions, in all the streams. This is explained by the dilution effect of soil derived ions during snowmelt with high runoff which at the beginning of snowmelt all the salts are washed out of the snowpack so that in the end there it is practically only diluted water. At Dalen the water drainage from the poorly weatherable soils on the ridges, slope and valley bottom controls the stream ion chemistry and keeps the concentration of ions much lower than ions in Støabekken1 and Huggenes.

In contrast to the stream draining forest catchment (Dalen), the water chemistry of streams draining agricultural land (Støabekken1) and mixed land use (Huggenes) were mainly characterized by comparatively high sum (2650µeq/l, 1950µeq/l) of cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+), and high sum (2560 and 1970µeq/l) of anions (SO_4^{2-}, NO_3^- and Cl^-), respectively. This is inherent in the farmers use of land as rich and carbonate containing soils are exploited for agricultural purpose, while the land with poorly weatherable soils are left for timber production. Moreover, the applications of lime and fertilizer to the agricultural fields keep the streams at relatively comparable higher pH, with elevated concentrations of major cations as well as carbonate. The dominant effect of land-use on the stream water concentrations of base cations and bicarbonate was apparent. Solute concentrations were much higher in Støabekken1 stream site followed by Huggenes and lower values in Dalen stream. Concentrations of Ca^{2+} and Mg^{2+} in Støabekken1 were found to be slightly higher than Huggenes and Dalen, with median values 1602µeq/l and 482µeq/l respectively, whereas at Huggenes concentrations of Ca^{2+} and Mg^{2+} were found to be 1093µeq/l and 444µeq/l, respectively. Ca^{2+} and Mg^{2+} ions are of lowest in Dalen with median concentration values of 62 and 37µeq/l respectively. Higher amount of Ca^{2+} and Mg^{2+} ions are found during baseflow periods (May through July). This is due to the predominance of groundwater contribution to baseflow which is due to lack of dilution. Ground water has longer residence time allowing for enhanced weathering. Ca^{2+} and Mg^{2+} were furthermore found to be strongly correlated with each other in the streams draining agricultural land (r=0.975 and 0.875 for Støabekken1 and Huggenes, respectively). This implies that these two cations have common sources from weathering of soil material in addition to the dissolution of lime added to the agricultural fields. In the streams draining agriculture, HCO_3^- was also among the dominant ions. This is mainly due to the liming of the agricultural fields in order to keep near neutral pH by buffering through dissolution of carbonate minerals.

Roughly comparable median SO_4^{2-} concentrations of 755µeq/l and 814µeq/l for Støabekken1 and Huggenes, respectively, were found which are much higher than the concentration found in the runoff from the forested Dalen catchment, with median SO_4^{2-} concentration of only 31µeq/l. There is strong evidence that measured SO_4^{2-} concentrations in Dalen are much lower than concentrations measured during the acid period. During the acid rain period in the 1970s and 1980s the southeastern Norway received high sulphate depositin from antropogenic inputs, which SO_4^{2-} concentrations were 122µeq/l (Wright et al., 1993). A study by Christophersen and Wright (1981) for instance, found a volume weighted average SO_4^{2-} concentration of 152µeq/l for stream (Birkenes) that drained forest in 1981. This high SO_4^{2-} concentration was explained by the increase deposition of mineral acid during that acid rain period (Klif, 2011). Today, sea-salt corrected SO_4^{2-} concentration at Dalen is found to be 24.5µeq/l. This indicates that input of anthropogenic SO_4^{2-} deposition contribute today less than 21% in Dalen. This is relatively small contribution as compared to the sulphate deposition during the acid peak period. This is due to the 80% reduction of sulphur deposition since the 1980s.

Significant amounts of NO_3^- (109µeq/l) at Støabekken1 and Huggenes (90µeq/l) streams was being leached out which may be attributed to the contribution of nitrates and nitrification of ammonium from the applied fertilizers, mineralization in the soil as well as nitrogen (N) fixation by legume plants. Comparable K^+ concentrations were found at both Støabekken1 (173µeq/l) and Huggenes (144µeq/l), while low values were observed in Dalen stream water (13.4µeq/l). Both NO_3^- and K^+ ions are rather immobile in the natural environment as there is low contribution of N fixation weathering along with a high demand by plants. Amounts of NO_3^- and K^+ was found to be positively correlated in the samples from both streams draining agricultural land, Støabekken1 and Huggenes, with r=0.827 and r=0.718, respectively. This suggests a common source of NO_3^- and K^+ from agricultural land, which is likely due to the excess addition of KNP[2] fertilizers. Relatively low median NO_3^- value in the Dalen stream (2.6µeq/l) is due to that the low natural fixation of reactive

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(KNP[2]), Potassium, Nitrogen and Phosphorus containing fertilizer

N and the deposition of reactive N is accumulated in the biomass of the forest, implying that the forest is not N saturated. Highest nitrate concentrations in the streams occurred during the relatively summer months of June, July and August. This is likely due to stagnant water with organic matter decomposition.

Concentrations of Na^+ (390µeq/l) and Cl^- (284µeq/l) ions were found to be comparable in all the streams and values are quite high. This may be due to the irrigation of water going on in western Vansjø which water is lost due to evapotranspiration, leaving ions less diluted. At Huggenes median values for Na^+ and Cl^- were 268µeq/l and 361µeq/l, respectively. Na^+ and Cl^- ions were the dominant ions in the stream draining the forested Dalen catchment with approximately comparable median values of 150µeq/l and 141µeq/l, respectively. This due to that the stream is influenced by the sea-salt aerosols loading as the sampling site is near the sea. In Dalen for instance, the ratio of Na/Cl of 1.1 is higher than in seawater (0.86) implying that there is a significant contribution of Na^+ from weathering of bedrock. It can also imply that the area is more influenced by sea salt. The concentration of Na^+ and Cl^- ions remains almost constant in each of the streams throughout the monitoring period. Generally, it was found that ionic strength of stream waters is much higher in the streams draining agricultural land than is in the forest draining stream, Dalen. This is due to the high contribution from some base cations like Ca^{2+}, Mg^{2+} and anions like HCO_3^-.

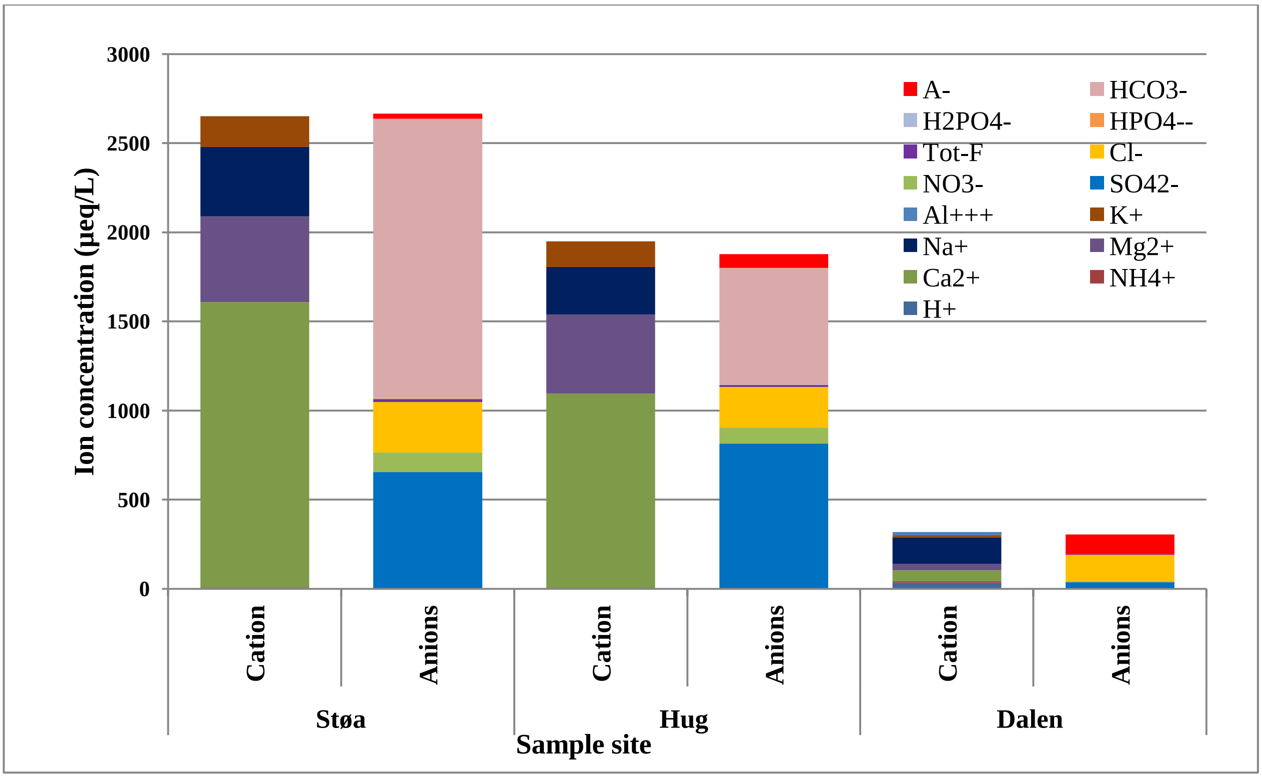

Figure 10: Median concentration of major cations and anions in the three investigated streams. For each stream, the concentration of cations and concentration of anions is shown next to each other. Number of samples for each calculated ion concentration varies from 45-157

4.2 pH and alkalinity of stream water

pH has a central role on the weathering of soil-minerals and determines the extent of hydrolysis reactions. The average pH value is the calculated average hydrogen-ion concentrations re-expressed as a pH values. Figure 11 presents overview of pH in three streams and display elevated acidity in the stream water draining forest. The pH values of stream water for Støabekken1, Huggenes and Dalen range from 6.3 to 8.1, 6.1 to 8.0 and 3.2 to 5.7 respectively. High pH values for all streams water were recorded during the months May, June, July and September. This is attributable to the predominance of groundwater contribution to baseflow during summer as groundwater has longer residence time allowing for enhanced weathering consuming acidity. There was a clear relation between land-use and pH, with higher pH values in the two streams draining watersheds containing agricultural land. In the agriculturally influenced streams, lime application in the agricultural fields may have substantial influence on the pH of the stream water which increases the pH of the water as it is carried out from the field in surface runoff to the streams. Furthermore, the water draining agricultural land during baseflow has longer residence time as the agricultural regions are generically located in areas with deeper soils. It is also described that the soils developed in marine deposits, which is commonly used for agricultural purpose, have naturally high base saturation which have greater influence on the pH of the water.

Soils in Dalen are rich in organic matter generating high concentrations of dissolved natural organic matter (average 32mgC/l,) which is leached into the stream as discussed by Mohr (2010). The high organic content, which contains organic matter with weak carboxylic acid and phenolic functional group, has strong influence on the pH by protolyzing H^+ ions. Thus, comparatively low pH values were observed in the stream water draining forest (Dalen). This low pH is thus mainly explained due to the higher acidity generated by these natural organic acids rather than the surface water acidity due to the reduction of acid rain in the recent yeas. Moreover, in Dalen higher acidity is not neutralized due to only a thin cover of poorly weatherable gneiss soil material which lack buffering capacity rendering waters with a low pH. It is important to note that significant concentrations of labile Al may exist in solution at pH values below 5.5. This trivalent acid cation is important precipitator of phosphates. At pH values above 7.5, Ca^{2+} ions are in abundance and the concentration of phosphates in solution is typically controlled by the solubility of calcium phosphate minerals.

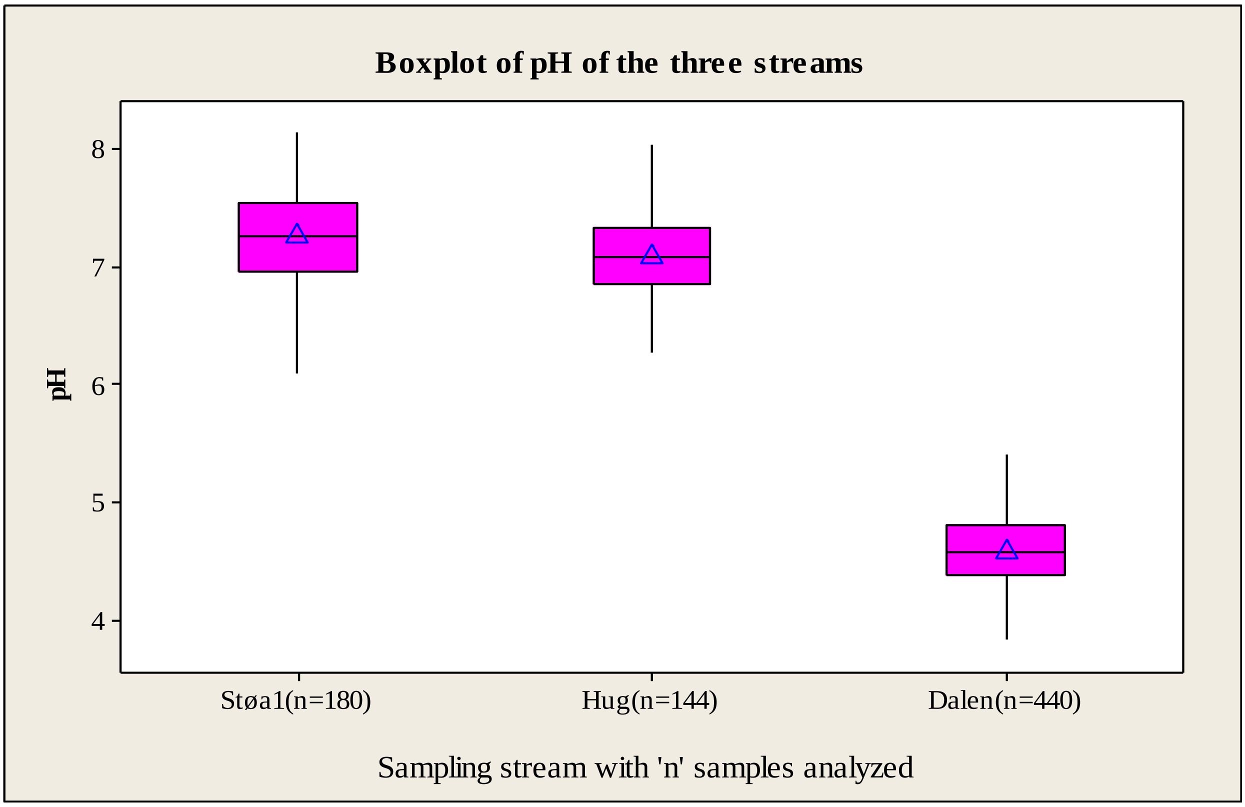

Figure 11: Boxplot of pH of the three studied streams. The boxes indicate median values with horizontal black line, minimum and maximum values indicated with a vertical line, box inside showing 25th and 75th percentiles of data series. 'n' in each site represent number of samples considered.

Alkalinity values for the two agriculture influenced streams are presented in Figure 12. pH in Støabekken1 and Huggenes is near neutral with slightly alkaline. Forest stream has basically no alkalinity due pH below 5.5 by natural organic acids and poor base saturation developed in the poorly weatherable unconsolidated soil material of gneiss rocks. Alkalinity in the two streams draining agricultural land, Støabekken1 and Huggenes, range between 541 to 3105, 417 to 1590µeq/l, with median values 1597 and 613µeq/l, respectively. Higher alkalinity values (Figure 11) also justify the higher pH found in Støabekken1 (median~7.3) and Huggenes (median ~7.1). Higher alkalinity implies that bicarbonate is a strong buffering component against the pH change in the streams. Higher alkalinity in the streams draining agricultural land may also be related to the weathering of carbonate minerals. This indicates that higher contribution of weathered minerals from the agricultural soils and lime that enters into the stream water through sub/surface runoff. Parekh, (2012) found that alkalinity is positively correlated to amount of agricultural land use and strongly negatively correlated to the extent of forest in watersheds of the same streams.

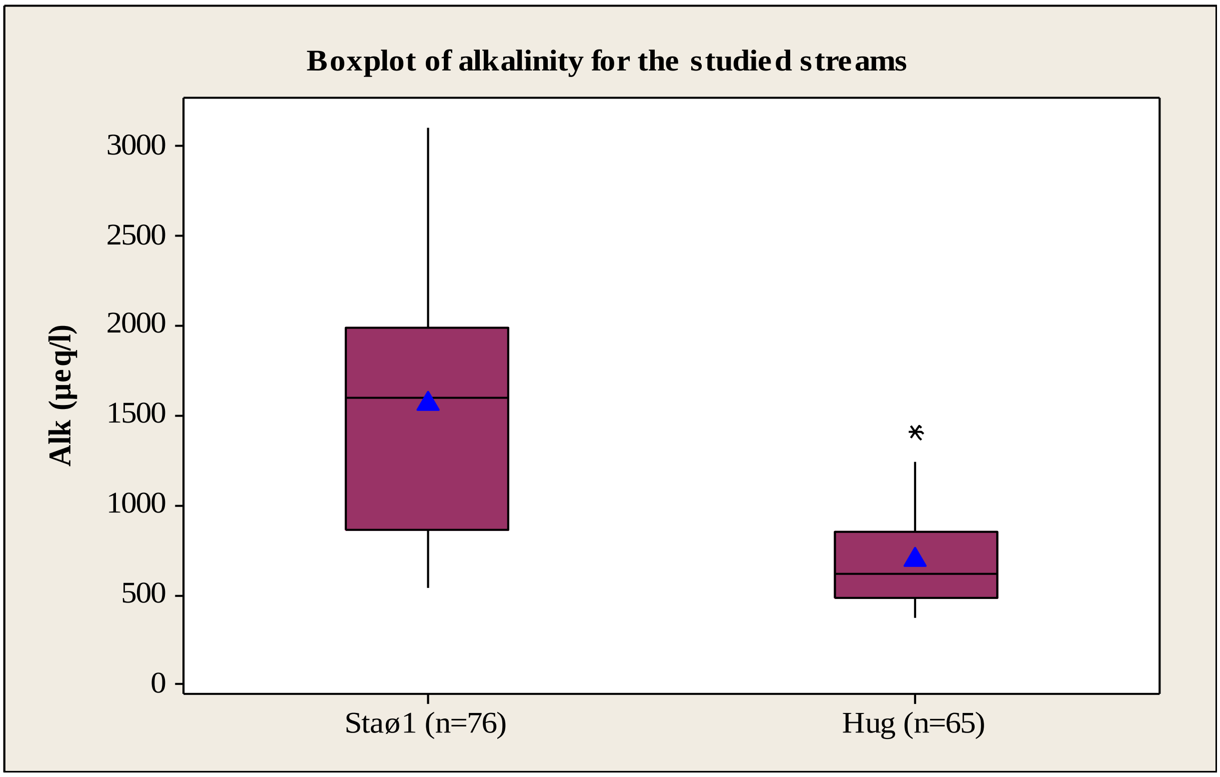

Figure 12: Boxplot for alkalinity of two streams with vertical line showing minimum and maximum. Horizontal line inside the box is showing median values with mean blue triangles. 75th percentiles above the median with 25th percentiles below the black horizontal line.

4.3 Dissolved natural organic carbon in the three stream waters

The level and range of concentrations of total dissolved organic carbon (DOC) of the three streams is given in Figure 13. DOC constitutes ~50% w/w of DNOM and is used as proxy for the amount of DNOM. The studied streams hold markedly different concentration of dissolved organic carbon. This difference in contribution of DNOM from each stream is governed by the land use in their respective watershed. Concentrations of DOC in streams draining an agriculture and mixed land-use ranged from 4 to 27mg/l C, while concentrations in the stream drained forest (Dalen) ranged from 12 to 45mg/l C, with one extreme value of 94 mg/l. Stream water from Dalen had median DOC concentration of 32mg/l C, while median values of DOC concentration of stream water samples from Støabekken1 and Huggenes were, 10 and 15mg/l of C, respectively.

The relatively high DOC concentrations in the Dalen stream water is due to the relatively higher mobility of DNOM along the flow path in the acid soils rendering soil water with low concentrations of base cations (less base saturation). DNOM has a key role in governing the chemistry of waters in poorly buffered forested watersheds of the boreal zone such as transporting important nutrients like P, C and N incorporated into the organic matter. Inherent in the DNOM is organically bound phosphorous (DOM-P) as organic phosphorous compounds are an integrate part of organic material. It is further documented that DNOM significantly lowers the concentration of orthophosphates through binding to complexed with Fe and Al. Positive correlation (r=0.815) between amount of DOC and H^+ ions was found in the stream draining forested Dalen catchment reflecting the importance of weak organic acid functional groups in the DNOM which provide H^+ to stream water.

A recent study by Shekobe (2012) was that most of DOM-P is lost from solution by precipitation or sorption to particles when the runoff from the upstream forest passes through agricultural land. Less concentration of DOC in the streams draining agricultural land as compared to the streams draining forest is also due to the fact that DNOM is less mobile in soils having high base saturation. This gives rise to a negative correlation (r=-0.549) of the amount of DOC and agricultural land use (Parekh, 2012). This leads to very limited leaching of DNOM from agricultural soils to the streams. The slight difference in DOC concentrations between the two agriculturally dominated streams Støabekken1 and Huggenes is possibly due to there is considerable forest cover (32%) at Huggenes. The mixed land use of Huggenes is also potentially characterized with having significant DNOM in the streams. More extreme hydrological regimes, as predicted for changing climate due to global warming, may impact transfer of DNOM between systems (Eimers et al., 2008; Harrison et al., 2008).

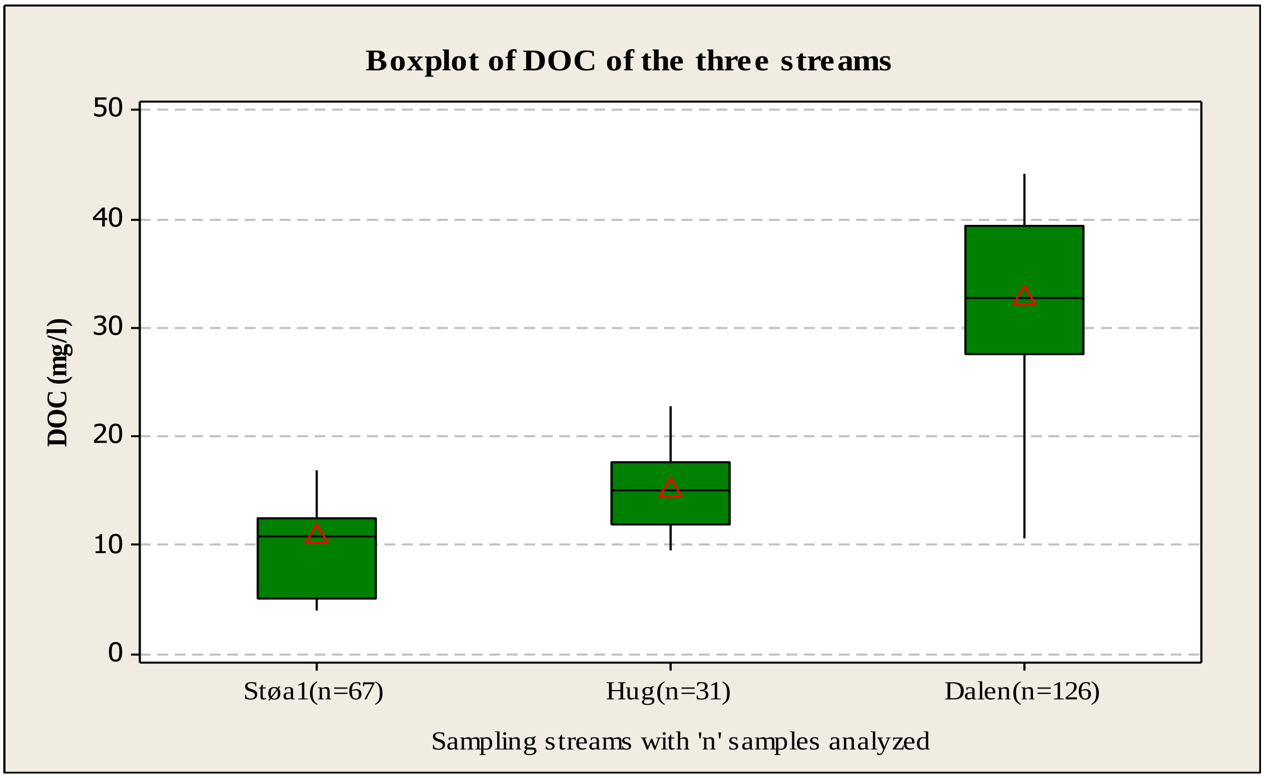

Figure 13: Boxplot showing concentration of dissolved organic carbon of the stream water samples in the investigated streams with mean concentration values on orange triangles. The boxplot also shows 25th percentiles below and 75th percentiles above the median of the data. Numbers of data samples are shown at each of the graphs.

4.4 Dalen soil water and stream water

As described in previous chapters Dalen stream water chemistry is characterized with less base saturation, low ionic strength, low pH and intrinsically higher DOC. In this sub-section it is tried to discuss soil water chemistry of the Dalen catchment and better understand the spatial variability observed. Water samples are taken from three plots arranged according to flow path (section 3.3.1).

4.4.1 Dissolved organic carbon at Dalen soil water

Dissolved organic carbon (DOC) concentrations of different generic soil horizons at Dalen are presented in Figure 14. Generally, there were large differences in DOC concentrations along the topographic gradient, from the ridge, slope and down to the valley bottom, and within the soil profiles. DOC in soil water samples is characterized by decreasing (with no clear trend) concentrations in the deeper soil horizons, from high concentrations in the organic-rich forest floor O horizon (average 106mg/l) to low concentrations (average 5mg/l) in the mineral soil below the Eluvial (E) horizon. Average DOC concentrations in the throughfall, in all soil plots ranged from 6mg/l in the valley bottom to 23mg/l in the slope. After passing through the organic forest floor the median concentration rises to as high as 109mg/l on the ridge. Then the median concentration of DOC sharply decreases to as low as 4mg/l in the deeper soil horizons at valley bottom soil plots. Decreasing DOC concentration down the soil profiles is generally found in the environment (Thurman, 1985), due to the biodegradability, adsorption and decreasing in soil organic matter (SOM) with depth. Biodegradability is the process experienced by higher microbial activities in the upper A-horizon, whereas adsorption is a process encountered in the organic poor B horizons (Piccolo, 1996). High levels of DNOM in the surface horizons may result in the overall higher concentrations of DOC in the surface runoff during periods of high flow due to a predominant sub-lateral flow path as the soils are water logged and flow is more favoured laterally.

There was a topographic gradient variation with higher DOC concentrations on the ridge and lower concentrations in the valley bottom (Figure 14). The relatively lower DOC content in the slope and valley bottom is due to adsorption of DNOM along the flow paths in the mineral soils. The high concentration in the forest floor on the ridge is partly due to up-concentration due to evapotranspiration in the vadoze zone. Furthermore, during periods of heavy rain the ground water is replenished by water passing through the forest floor through macropores picking up very little DNOM on its way. The level of DNOM in the stream is high compared with the levels of DNOM in the mineral soils. This implies that substantial DNOM contribution to the stream must come from the bogs (most upper soil horizon rich in DNOM) as surface runoff and contribution from soil horizons below the bogs leached through sub-lateral flow. Less base saturation of the Dalen sub catchment allow DNOM leaching and transport along the flow paths during flow events. Large temporal variation of DOC concentration was observed in waters of the upper soil horizon, with relatively small variation below the B-horizon and the stream water.

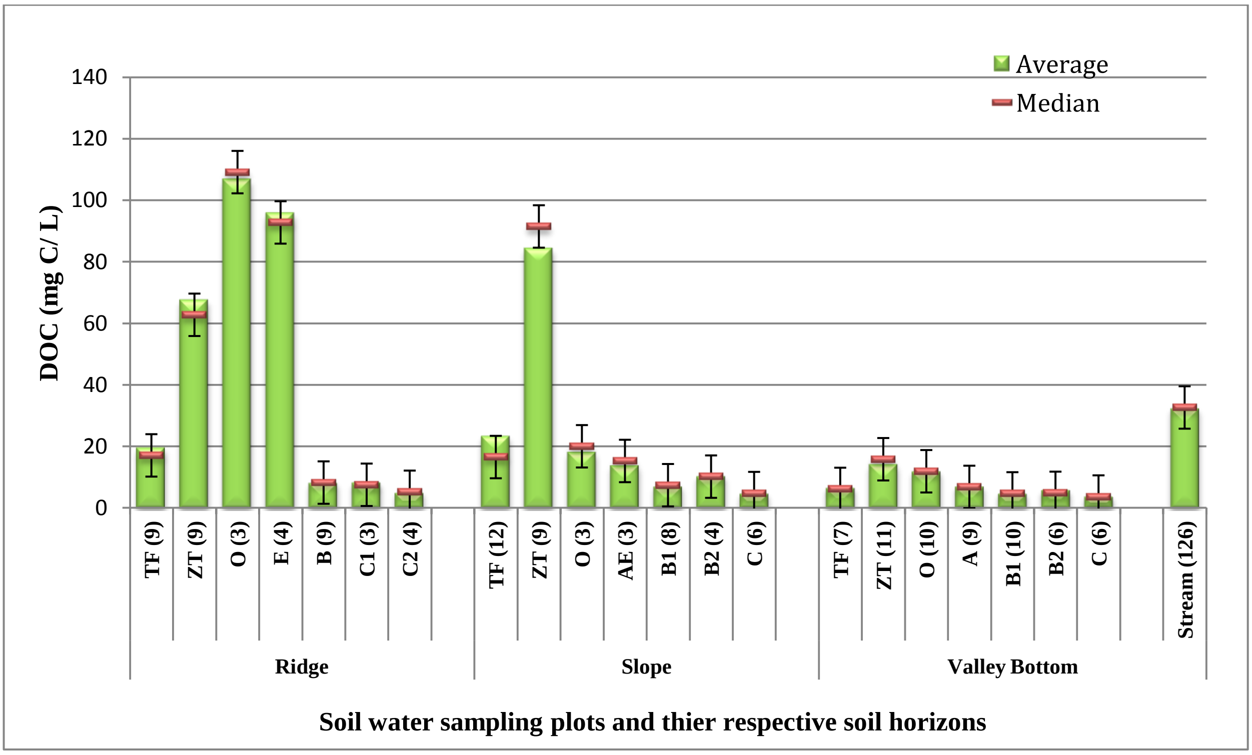

Figure 14: DOC concentration of different generic soil horizons at the three plots in Dalen. Number of samples considered is presented in each soil profile indicated by braces.

4.4.2 pH and aluminium in Dalen soil water and stream water

pH of soil water in different generic soil horizons and stream water of Dalen is summarized in the Figure 15. The soil water in all generic soil horizons on the ridge is more acidic ranging 3.8-5.2 with increasing pH down through the mineral soil profiles. Natural organic acids in the DNOM, derived from partly decomposed organic matter, decreases the pH to surprisingly low pH values of 3.2 in the zero tension lysimeter (ZT), water draining from the upper organic soil. This may be attributed to the acidic nature of the organic forest floor layer. Increase in pH was also observed down the topographic gradient of plots, from ridge to slope and to valley bottom. In the valley bottom pH is higher than at the other soil plots with values ranging on average 4.9 to 6.9. The increase in pH down the soil profiles, in all soil plots, is due to longer residence time of soil water allowing for enhanced neutralization by ion exchange with acid cations (especially aluminium) and some weathering of feldspars in the soil.

A higher pH value in the valley bottom as compared to the ridge and slope suggests that pH is more strongly influenced with weathering. It may also indicate poor drainage, as the area is more flooded. As a result ions are free to diffuse in all direction resulting in a more even chemical distribution between all horizons. The stream draining forest is a mixture of drainage from these soils and exhibits low pH values due to the high concentration of organic acid functional groups contributed from the high levels of DNOM. Low pH values (<5) in the soil water may have strong influence in the composition of DNOM by protonation of the acidic carboxylic and phenolic functional groups thereby decrease charge and molecular weight. This in turn reduces solubility and mobility of DNOM in the environment.

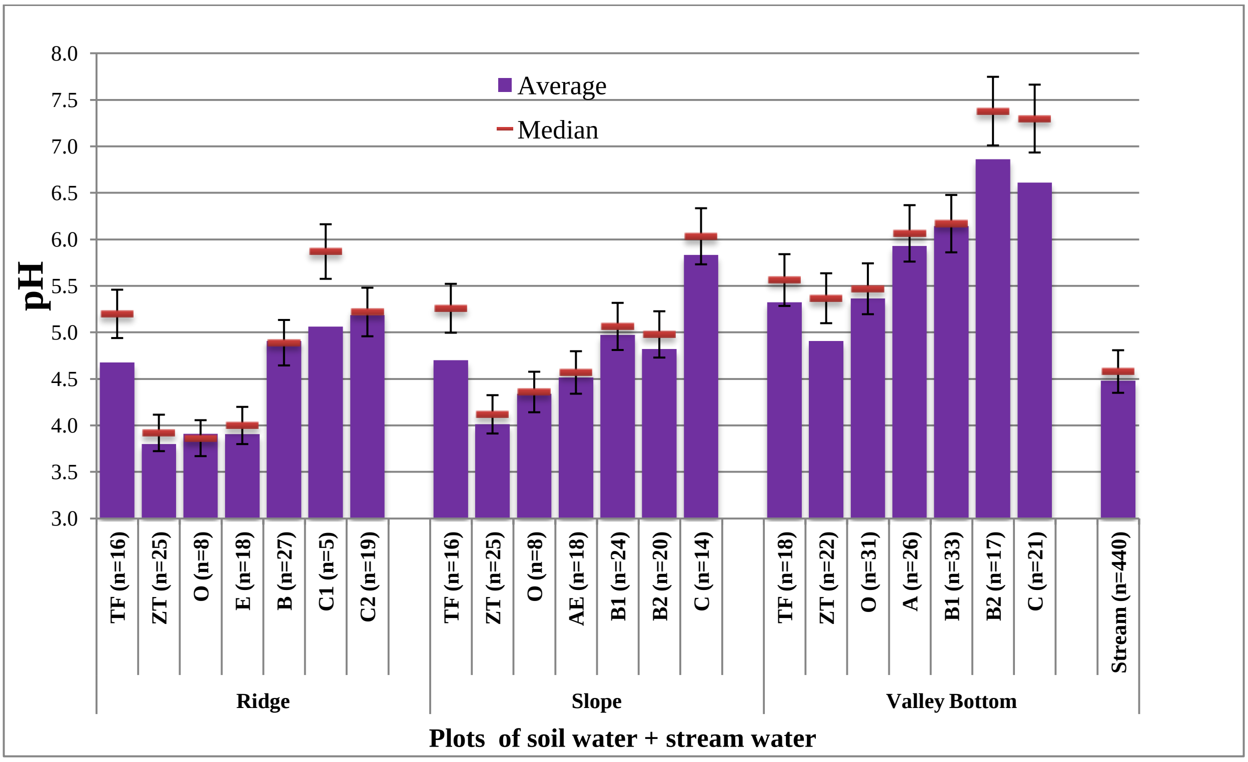

Figure 15: pH of the different soil horizons and stream water in Dalen. Bars indicate the mean of the pH and red boxes with line crossed are median values. Numbers indicated alongside with generic soil horizons in brackets are number of samples analyzed.

Figure 16 indicates inorganic aluminium (Al_i) and organicaly bound monomeric and mainly labile aluminium (Al_o) average concentrations found in the soil water and in stream water at Dalen. Levels of Al_i showed almost miror image of the pH in Figure 15. This is attributable to the buffering of soil waters for pHs less than 5.5. The amounts (average) of Al_i found in the slope soil plot water ranges from 7.4 to 28.5µM and from 2.7 to 30µM on the ridge. This may indicate that buffering of soil water comes from the ion exchange with Al^{3+} and dissolution of Al containing minerals. In the stream water it was found significant levels of both Al_i (average 4.8µM) and Al_o (average 16µM). This suggests that Al-species mobilized from the slope and ridge may leach down to the stream water. Interestingly, it was found that Al_o is strongly correlated (r=0.897) with DOC in the stream water as low pH in the soil and high organic content in the streams allow for high concentration of Al_o. Through adsorption, direct precipitation and coagulation interactions, Al may influence the availabality and thereby alter the cycling of important nutrients like DOC and P (Dickson, 1978). Coagulation and precipitation limit the release of P from the decomposition of DNOM and subsquently reduce transport of P to waterways.

It is specualted that the 80% reduction of acid deposition since the 1980s (Evans et al., 2001; Klif, 2011; UN-ECE, 1999), may have counteracted the meaures to reduce P leaching to the surface waters causing the effects of abatement actions to appear less efficient. This is because reduction of acid deposition (sulphate concentrations) has led to a huge decrease of inorganic labile aluminium (Al_i) concentrations in the streams draining out of upstream forested head catchments (Klif, 2011). Al_i precipitates as aluminium oxy-hydroxides at pH above 5.5 and efficiently co-precipitates PO_4 which in time may cristalizes to $AlPO_4$. The decline in Al_i concentrations from upstream forests causes therefore a loss of process that previously led to precipitation and removal of bioavailable PO_4. During the acid rain period (1970s and 1980s), there was elevated amount of Al_i in runoff from acid sensitive catchments and this had crucial avantage in precipitating phosphates where the forest runoff mixed downstream with neutral or alkaline runoff rich in PO_4 from agriculture.

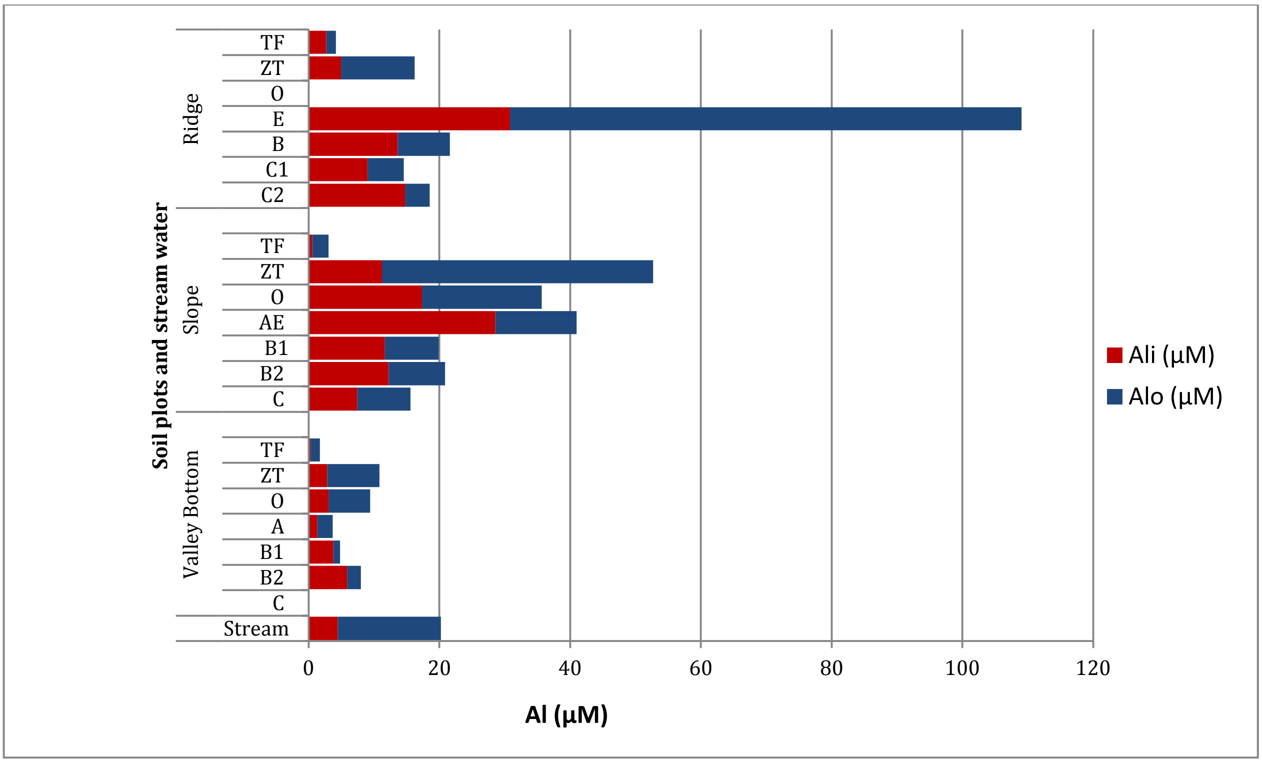

Figure 16: Average concentration of monomeric inorganic aluminium (Al_i) and organic aluminium (Al_o) in the soil plot together with respective soil horizons. There was no data for O horizon in the ridge and C in the valley bottom, so is not considered. Number of samples ranges from 5 to 27.

4.4.3 Major cations and anions in Dalen soil water

Average concentration of major anions and cations in throughfall, in the generic soil water horizons and in the stream are presented in Figure 17. Concentrations shown are unweighted values. Notable changes in the water chemistry occurs when the water from throughfall flows through the soil profiles; sulphate and base cations generally showed an increase in concentration both down into soil profiles and down the topographic gradients from the ridge to the valley bottom. This is due to up-concentration due to evapo-transpiration, dissolution of the acid DNOM and solute input from weathering. Na^+ and Cl^- ions showed increasing values in all the gradient plots with slight variation reflecting that these ions have the same main source from sea salts. In going down the soil profiles in all soil plots, there is a slight increase for sodium that values are higher in the deeper soils horizons. The ratio of Na^+/Cl^- of 0.97 in the upper soil horizons which increases in concentrations of these ions along the flow path in all the soil plots is greater than the seawater (0.86) suggests there is addition of Na^+ due to weathering.

The up-concentration of Cl^- along the flow-path of water through the watershed is mainly therefore due evapotranspiration processes. This is a strong factor in the forest system as the forests water holding capacity is high due to high vegetation cover. Increase in base cation concentrations, such as Ca^{2+}, down the soil profiles and across the plots is due to ion exchange reactions with ions in the diffuse double layer liberating base cations into solution in exchange for H^+. The concentrations of nitrates and sulphates were very low in Dalen stream water, with median values 2.6µeq/l and 31µeq/l, respectively, as compared to Støabekken1 and Huggenes, which have order of magnitude higher concentrations (section 4.1).

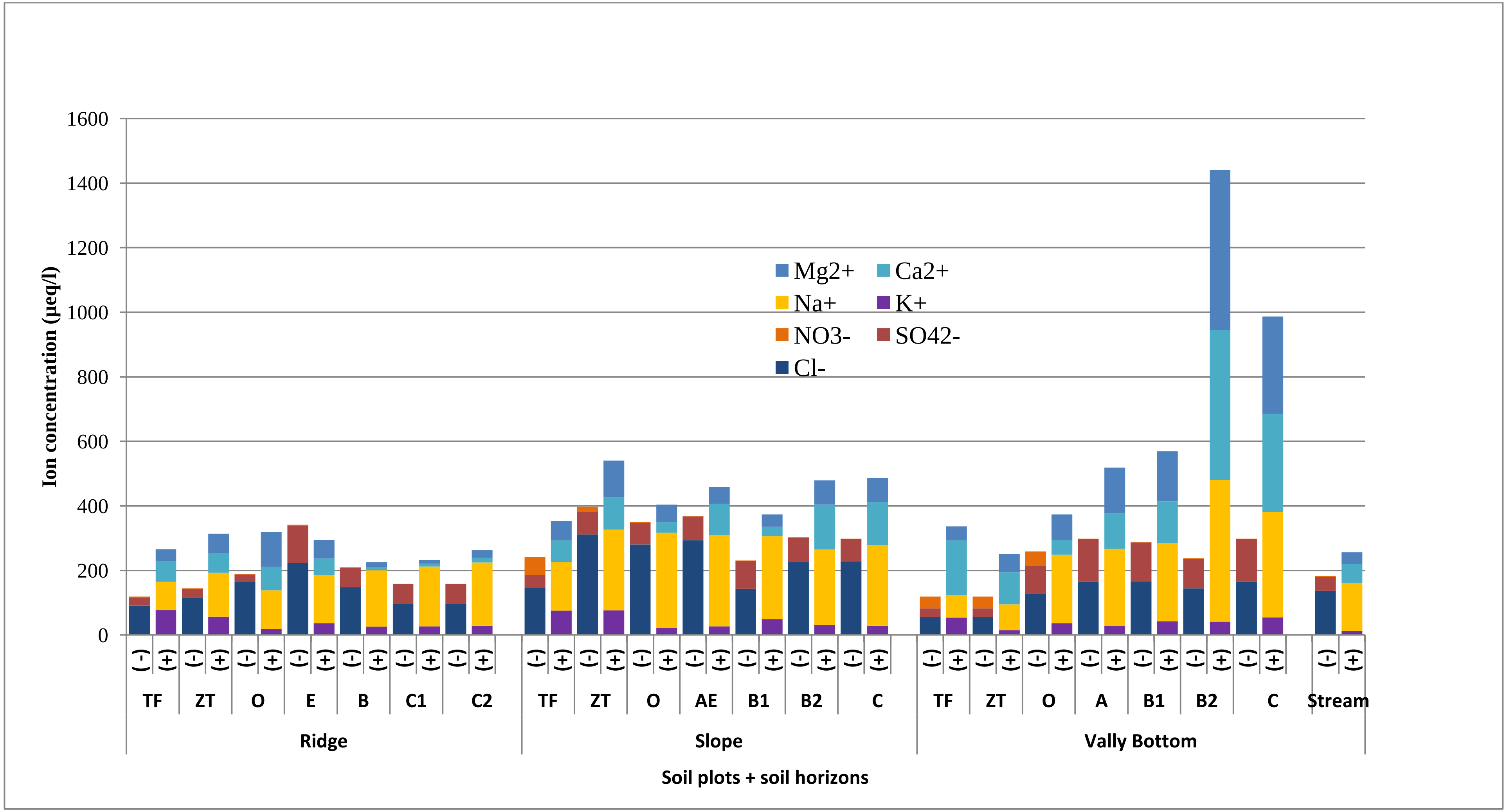

Figure 17: Major cations and anion concentration (µeq/l) across the soil water plots with respective generic soil horizons at Dalen. Number of data points ranges from least being 7-29 in the soil horizons to 137 in the stream. Cations represented as (+) and anions are represented as (-).

4.4.4 P-fractions in soil water in Dalen

Concentrations of dissolved ortophosphate (PO_4-P) and dissolved organically bound phosphate (DOM-P) in throughfall (TF), soil water, and stream water samples are shown in Figure 18. Results show that concentrations of tot-P are low except for TF and 'ZT'. The amount of PO_4-P ranged from 0.45µg/l in the C-horizon to 2µg/l in the E horizon of the ridge with exceptionally high values in the throughfall of all the soil plots (Figure 18A). Dissolved P concentrations (both PO_4-P and DOM-P) were high in the throughfall and soil horizons above the root zone (B) in all the soil water plots with PO_4-P as the dominant P-fraction in the throughfall. This is due to the rapid internal P circulation with the vegetation. PO_4-P is released from the canopy and litter decomposition and assimilated again by the roots of plants. The 'O' and 'E' soil horizons in the ridge have relatively high P concentrations consisting mainly of DOM-P. Tot-P levels in the stream are low compared to the streams in the area but still significant relative to the levels of dissolved phospohrous in the lake.

Figure 18B shows the same as Figure 18A after TF and ZT horizons of P-fraction concentrations are excluded for graphing porpuses. The slope soil plot has approximately comparable total P-fraction, while the ridge and the valleybottom showed a decreasing trend that P is lowest down the soil horizons. Lower values may be due to the fact that P is adsorbed on top soil surfaces (Sharpley et al., 1985), and due to the evidences that as water flows vertically through the soil (e.g. matrix flow), the P concentration deacreases due to adsorption on soil particles and assimilation by plant roots (Haygarth et al., 1998). It is also emperically explained that increased mobility of DOM-P from soils is due to the increasing ratio of hydrophobic to the hydrophilic acids. More hydrophilic condition in the bottom layers may lead to less dissolution (less solubility of DNOM) of DOC that limits DOM-P transport/mobility vertically. Decreased levels of acidity increases solubility (hydrophobicity), of specially the high molecular wieght and more coloured fraction of the organic matter. The ratios of DOM-P/DOC in the ridge are 1.10‰, 0.52‰, 0.11‰, 0.10‰ and in the slope is, 2.0‰, 0.60‰, 0.17‰, 0.19‰ while in the valley bottom is also 2.8‰, 0.71‰, 0.45‰, 0.50‰ respectively. This decreasing trends in the ratio of DOM-P/DOC along the flow path in all soil plots, keeping that DOC constant down the soil horizons, indicate that P is held at the top soil surfaces. Transport of DOM-P down the horizons is decreased due to the deacrease in the ratio of hydrophobic to hydrophilic acids. This suggests that the decrease in acid rain is the main reason for that the amount and transport of DOM-P has increased in areas that previously received high sulphate deposition during the acid period.

DOM-P concentration in all the soil plots accounts for between 66 to 90% (Appendix G-2) of the total dissolved P forms except in the TF and ZT. This illustrates that P is mainly transported as DOM-P in natural systems. In the TF and ZT, PO_4-P is the dominant fraction which accounts for about 85 to 90%. The high DOM-P values all way down the soil horizons indicates that macropore flow of DNOM through the B and C-horizon from the O layer contributes to the significant levels. Low PO_4 is due to the availability to plant assimilation in the root zone. Concentrations of P in the stream water was 7µg/l with more than 75% (Figure 18) of dissolved organic P form. Dalen stream water tot-P concentration is discussed in section 4.5.1 and percent contribution of DOM-P to the tot-P is 60% discussed in section 4.5.2; Figure 20.

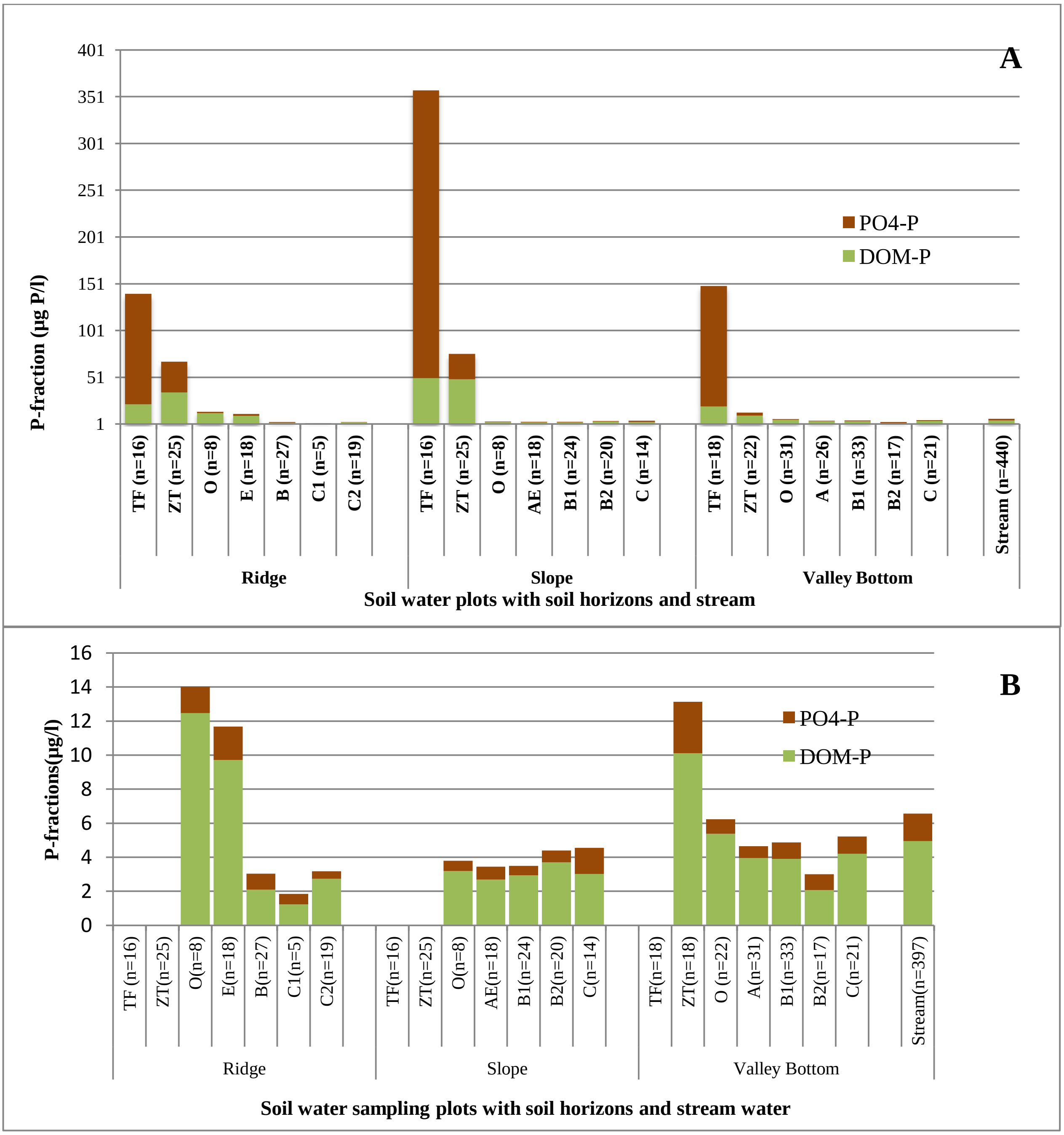

Figure 18: PO_4-P and DOM-P in different generic soil horizons in three soil plots at Dalen

4.5 Distribution of tot-P and its fractions in the stream waters

This sub-section covers the discussions of tot-P content and distribution in the stream waters, P-fractions in the sampled three streams, effect of mixing of water of different land use, effect of runoff intensity in the transport of P in the streams and temporal variation in the transport of P.

4.5.1 Total phosphorus in the streams

Tot-P concentrations in the water samples from the three studied streams are presented with a boxplot in Figure 19. Tot-P concentration showed a vast concentration range from lowest values of approximately 3µg/l in Dalen to high values of 356µg/l in the Støabekken1with an outlier of 1.561mg/l in Huggenes stream and 752µg/l in Støabekken1stream. High values were observed mainly during autumn rainy seasons and spring snowmelt seasons, which were termed as high flow events and outliers are treated and discussed in the next section 4.5.4. The highest tot-P concentration (median 113µg/l) was found in the stream draining agriculture dominated (89%) watershed, Støabekken1. An intermediate median value of 45.5µg/l was found for the Huggenes stream draining mixed land use with 60% agriculture. The lowest concentration (8.3µg/l, median) was found in the stream draining purely forest. Therefore, tot-P concentrations in respective streams may reflect application of P and share of agricultural land use. This is explained with empirical relationships of variables with land use.

The levels of tot-P is positively correlated (r=0.751) to the fraction of agricultural land in the watershed (Parekh, 2012). This implies that agricultural soils are prone to accumulate applied P. The high tot-P accumulation in the streams draining agricultural land is therefore achieved through following reasons. Primarily, P fertilizer application on the Ap layer of the agricultural land by farmers is high (though reduction in P-fertilizer recorded in recent years). For instance, Opland, (2012) found that 0.7 to 0.8g/kg of tot-P in Huggenes agricultural soils down in 1m depth, which is relevant to the C-horizon where the field drainage pipes are buried. This suggests long time over-fertilization with P-fertilizer leads to an accumulation of a large pool of P in the soils. It is widely reported that excessive application of P-bearing fertilizers in agricultural districts pose great problem to surface waters (Sharpley et al., 2003). Solheim et al. (2001) for instance, reported that agriculture as the main anthropogenic P source to lake Vansjø, south-eastern Norway, which accounts for about 76% of the anthropogenic tot-P load to the lake. Furthermore, 90 % of the Vansjø-Hobøl catchment is situated below the marine limit. The marine clay soils are therefore naturally rich in P containing apatite. During heavy rainfall or snowmelt episodes the P is prone to leach out of the Ap soil layer and can be transported down through surface runoff and through the soil profile in macropores and be flushed to the streams through sub-surface runoff in the drainage pipes. The streams of Støabakken1 and Huggenes are made up of entirely from drainage pipes.

The tot-P content in stream water draining a mixed land use (Huggenes in this case) was found to be comparatively smaller than the tot-P content found in the stream draining agricultural land use while higher than tot-P content draining a forest. The lower values of tot-P in areas with mixed land use can be due to the effect of non-conservative mixing of forest runoff with agricultural drainage as found by Shekobe (2012). Shekobe (2012) studied the effect of mixing runoff water from a forest dominated stream (Dalen) with water coming mainly from agricultural land-use (Støabekken1). Shekobe found that between 55 to 82% of the PO_4-P and between 50 to 75% of the DOM-P was converted to a particulate form within 5 hours. This was likely due to formation of Al oxy-hydroxides followed by sorption of PO_4 and by complexation of Ca^{2+} to the DNOM followed by sorption to the suspended particle matter. As discussed previously in section 4.4.2, the labile aluminium that was leached out from the forest due to the acid rain precipitates when the water mix downstream with neutral or alkaline runoff water from agricultural fields. This implies that there is formation of Al oxy-hydroxides in the agricultural zone where it finds P rich runoff resulting in co-precipitation of PO_4 due to adsorption to the amorphous Al oxy-hydroxides. This decreases the amount of bioavailable PO_4 in the flowing streams. It is therefore not expected that the runoff found in streams draining watersheds containing a mixed forested and agricultural land use will simply reflect the relative contribution of each of these sources.

The relatively low tot-P concentration in the Dalen stream water, as compared to Støabekken1 and Huggenes, is explained by land use, erosion risk and soil properties especially with the chemistry of Al/Fe. In the case of land use, Dalen is predominantly forest area with no application of P-fertilizer as is in the agriculturally dominated sites. Due to the forest cover and the protection afforded by plant roots the soil erosion is minimal and movement of particles is limited. Furthermore, the aluminium in soil water limits the mobility of PO_4 due to that labile aluminium species (Al_i) bind PO_4 lowering the mobility of PO_4 and thereby its concentration in stream waters is low. Although the concentration of tot-P in the stream draining forests is low compared to the stream draining agricultural land, the levels of tot-P in the runoff from forested sites represents a significant background loading of P to the lake considering that forest land-use constitute 80% of the watershed (Vogt, pers. comm.).

The large spatial variation in tot-P content among the streams draining agricultural land can be explained by difference in amount of agricultural land-use as well as agricultural practices such as application of fertilizers. Furthermore, erosion risk and physico-chemical properties of the soils

(soils being characterized by texture, composition, P content) are factors that govern the P fluxes to the stream waters. The tot-P values are especially high in the streams draining mainly agricultural lands with a high content of sand (Gebreslasse, 2012). This may be due to that sand has a very low sorption capacity which allows P to remain in the water solution. The spatial differences in different factors will be further discussed using multivariate statistics.

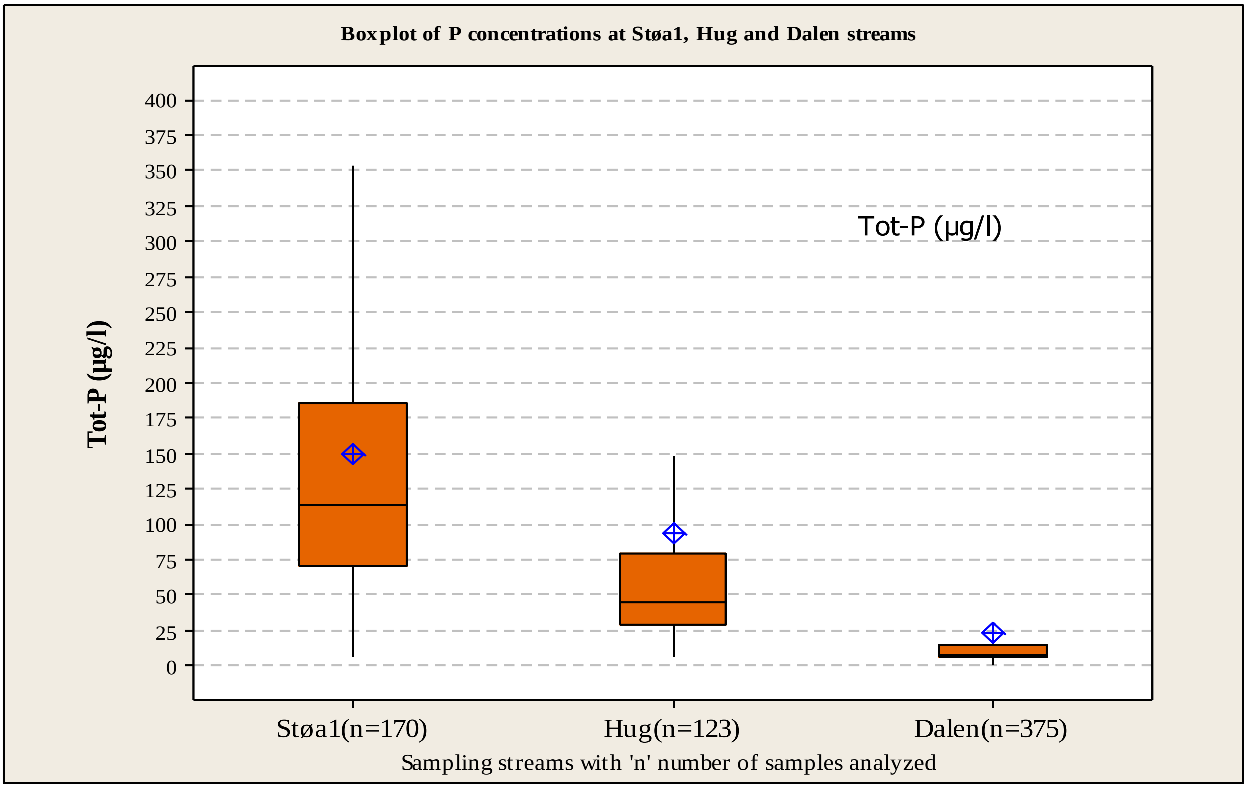

Figure 19: Tot-P concentrations of the three studied streams. Results represent 25th and 75th percentiles of the data sets with 'n' in bracket shows number of samples analysed.

4.5.2 Distribution of P fractions in stream water

Data on tot-P concentration in the stream water is not enough to provide full information on how P is mobilized from agricultural soils and how it is transported to the streams. It is therefore important to further look at the different P fractions and the way these fractions are distributed in time and space. Tot-P and P-fractions in stream water was determined by the operationally defined methods discussed in section 3.4.8. The median contribution of the three P-fractions, PP, DOM-P and PO_4, in the three streams is presented in Figure 20. Contribution of each fraction in percentage is also presented in Appendix-G; Table G-7.

More than half of the tot-P (55 to 60%) is bound to particle matter (PP) in the Støabekken1 and Huggenes streams draining agricultural and mixed land use respectively, whereas dissolved organic bound P (63%) was the dominant fraction in the stream draining forested Dalen sub-catchment.

Higher PP fraction in the streams draining agricultural land suggests that during flow events large amount of P associated soil material is being carried out by erosion and will as such be governed by the particle loading in the stream. The highest contribution of PP (60%) comes from the stream draining mixed land use, Huggenes. This could be due to the fact that the site is categorized as medium high erosion risk (Table 2), coupled with the combined contribution effect of both from agriculture and forest. It is a case when agricultural runoff water is mixing with forest runoff water down streams, causes precipitation of particles and eventually high levels of PP. The positive correlation between total suspended solids and tot-P (section 4.5.4) is also an evidence that enhanced adsorption of dissolved P on the suspended matter may result in the formation of PP. Results are also in agreement to previous reports by Parekh (2012) and Opland (2011) who studied the same streams, though with less data available. Relatively small PP fraction in Dalen can be explained by that the forest land use hinders erosion due to the perennial plant cover and due to the overall lower levels of P. Therefore, the forest is anticipated to influence slightly to the variation of tot-P concentrations in stream. Moreover, sorption of dissolved P is stronger at Dalen since the soils at Dalen contain relatively higher levels of organic matter (section 4.3) leaving PO_4 as a smallest fraction next to PP. It is also due to the rapid assimilation of PO_4 by the plants that availability is small in the stream.

The DOM-P constitutes a relatively large fraction (63%), (Appendix-G; Table G-7) of the tot-P found in the stream draining forest although the tot-P concentration was relatively low compared to the two streams draining agricultural land-use. The dense cover of forest provides high levels of organic matter in the soils due to litter fall. This inherently leads to elevated amounts of DOM-P in the forest stream water (discussed in section 4.3). The presence of relatively high concentration of organic matter in Dalen soil (Mohr, 2010), offers another significant explanation for low concentration of dissolved PO_4. Soil organic matter readily forms strong complex compounds with trivalent cations such as Al and Fe. This soil organic matter-Al/Fe complex has a potential importance in scavenging of PO_4, by forming ternary P-Al-OM/P-Fe-OM complexes (Gerke, 2010). This may lead to low levels of PO_4 in the stream water. PO_4 is also adsorbed on the surfaces of oxides and hydroxides of Al/Fe. However, during periods of reduced redox conditions PO_4 adsorbed to oxides and hydroxides of Fe may constitute a source of PO_4 due to reduction of Fe^{3+} to Fe^{2+}, (Fe^{2+} being subsequently trapped as FeS), allowing free PO_4 to escape to water solution.

DOM-P constitute relatively less of the tot-P in the two streams draining agricultural land accounting for 19% of the tot-P in the Huggenes stream water and only 6% of the tot-P in the Støabekken1 stream water. The relatively higher contribution of DOM-P at Huggenes stream water compared to Støabekken1 is likely due to the ≈30% forest cover in the Huggenes sub-catchment.

The PO_4 fraction constituted the second largest fraction of tot-P at Støabekken1 stream water, accounting for 39% of the total P, where agriculture is by far the largest land use in the sub-catchment. This relatively higher fraction of dissolved PO_4 in this stream is likely due to leaching of inorganic P fertilization applied in the field and some release of internal soil P from the naturally P rich marine clays deposits (Parekh, 2012). Leaching of PO_4 from the soils is accelerated during high flow events. It is legitimate to postulate that the temporal and spatial differences in amount of tot-P in the studied streams is governed by multiple factors and that the spatial differences can mainly be explained by factors related to land use.

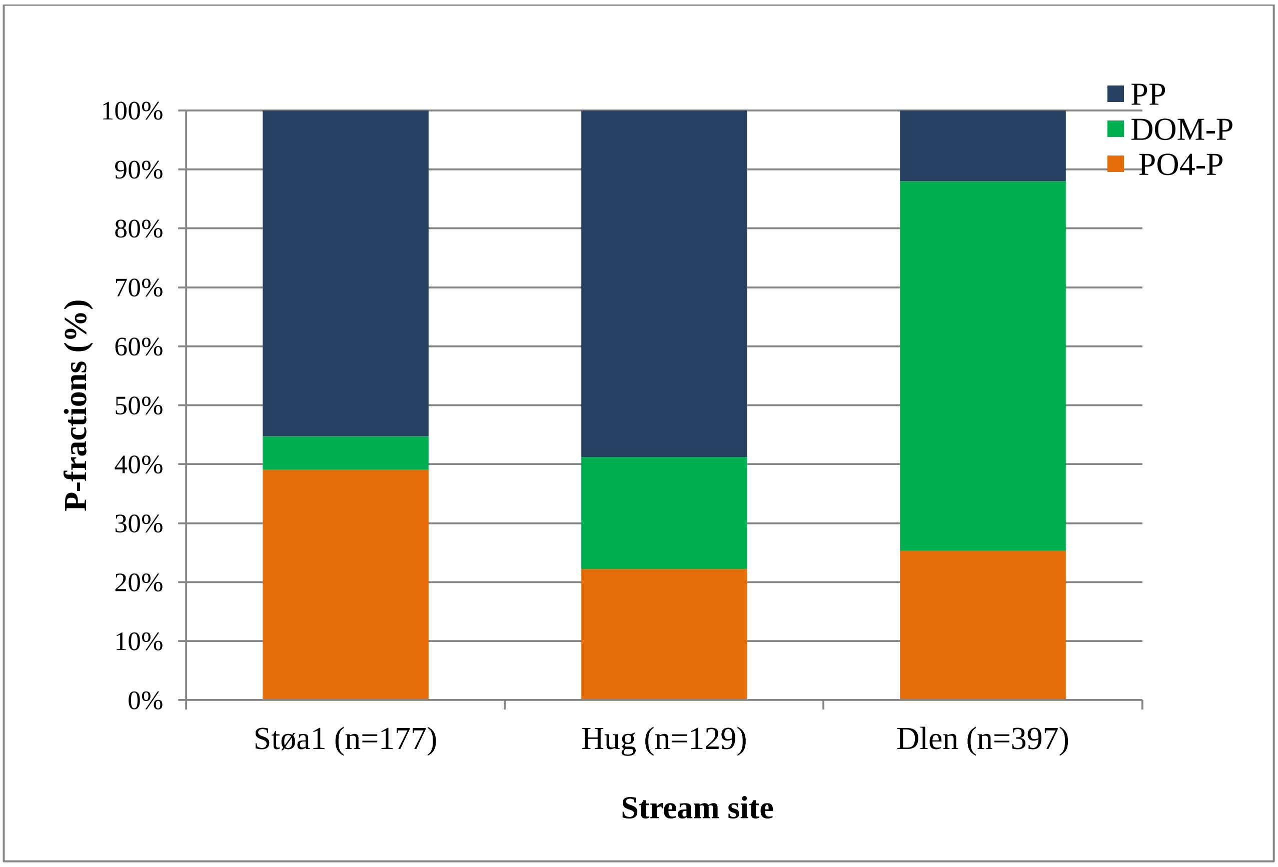

Figure 20: Relative percent distribution of P-fractions in the selected stream waters with numbers 'n' of data samples shown in the bracket of graph analysed for P.

4.5.3 Effect of mixing stream water from different land use

Huggenes stream drains from a mixed land use where tot-P concentration in the stream water is a combined contribution from both forest and agricultural runoff. The concentrations for tot-P and the distribution of P fractions are given in section 4.5.1 and 4.5.2. Figure 21 presents concentrations of P fractions measured in the Huggenes stream along with calculated concentrations of P fractions. The calculated values are a conservative mixture of the Støabekken1 and Dalen water in a ratio similar to the ratio of agricultural to forest land-use in the Huggenes watershed. Assuming that Huggenes stream water is a combination of runoff from Støabekken1 which is agriculture and runoff from Dalen which is completely forest, the water chemistry of the stream is explained by the chemistry of non-conservative mixing. It is expected that the effect of mixing runoff water from forest and agriculture would alter the P chemistry.

Forest runoff with low pH and significant Al_i (Dalen is Al_i rich) was mixed with runoff water from agricultural zone (Støabekken1) having neutral pH and containing higher levels of phosphates. Tot-P content in the Huggenes runoff water was observed to be lower than what is calculated as a conservative mixture. This decrease is due to increased precipitation of P with Al_i as Shekobe (2012) found experimentaly after mixing runoff from Dalen and runoff from Støabekken. This suggests aluminium form oxy Al-hydroxides which adsorbs P to its surfaces decreasing the amount of free PO_4 in the flowing water. More importantly, it is an indication that transport of PO_4 and DOM-P from place to place in the agricultural zones is dependent on the amount of Al_i and the extent at which Al_i precipitates P in the agricultural zones.

Absence of Al leaching from upstream forest watershed is most likely caused enhanced mobility of PO_4 in the agriculture watershed to water bodies. This is due to lack of co-precipitation of P in the pathways. During the acid rain period 1970s and 1980s PO_4 mobility was determined by the amount of labile Al_i and the extent it precipitated PO_4 in the agricultural zones. The decrease of anthropogenic SO_4^{2-} deposition has substantially reduced the concentrations of Al_i in the runoff in the forest catchments since 1980s. Reduced formation of oxy-Al hydroxides in the agricultural zones due to decline in acid rain may lead to elevated levels of bioavailable PO_4 reaching the lake. This may partly explain the lack of effect of abatement actions on reducing the flux of PO_4 to the lake that has been implemented at the same time period.

Higher levels of PO_4-P in the calculated conservative mix as compared to the measured absolute concentrations in Huggenes (Figure 21) can thus be explained by decreased in PO_4 by to the Al_i that precipitates upon the mixing. Decreased SO_4^{2-} concentrations decrease the influence of SO_4^{2-} on Al_i mobility and availability.

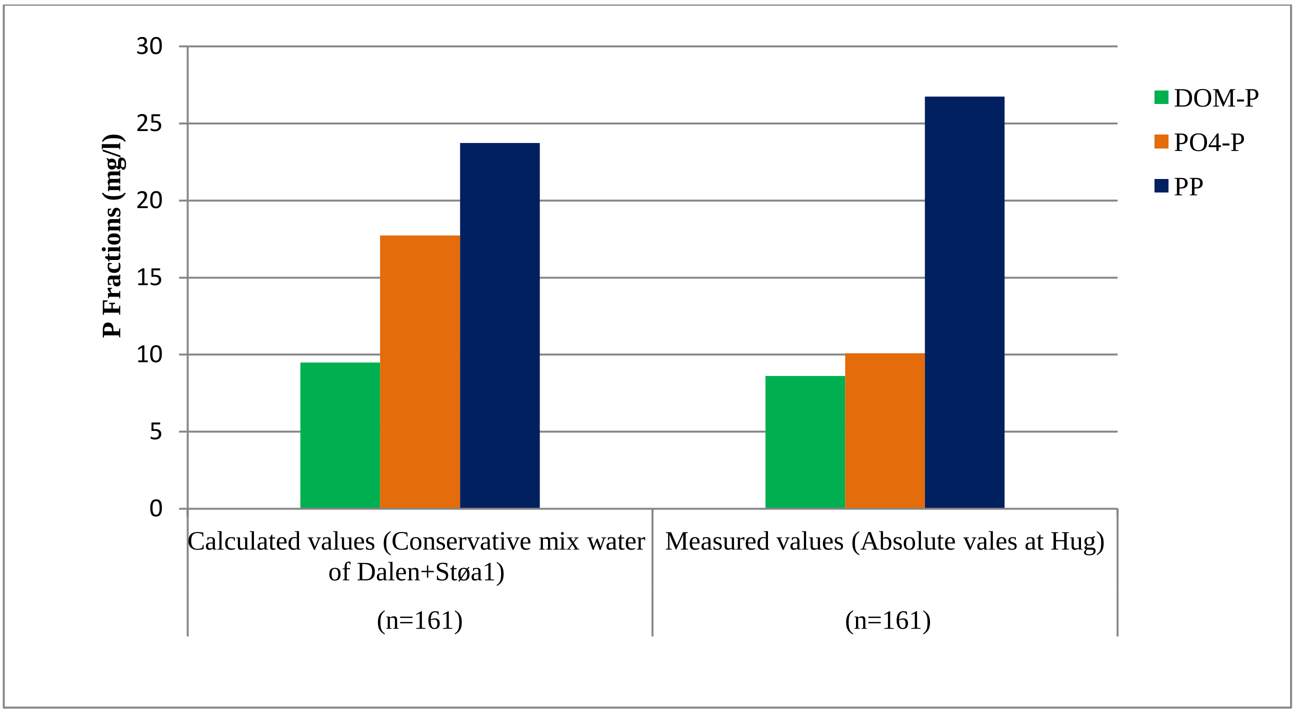

Figure 21: Average P-fractions measured at Huggenes as compared to calculated values of runoff water from Dalen and Støa1 in a ratio similar to agriculture and forest land use.

Figure 22 presents measured and calculated DOC concentrations from the mixing runoff waters in the mixed land-use stream. The results showed that in a calculated conservative mix the DOC was 13% higher than the measured DOC concentration at Huggenes. Increase in DOC concentrations in the mixing runoff waters may be due to different factors.

Firstly, it is studied that reduction in acid rain deposition has led to increased leaching DNOM in south eastern Norway (Monteith et al., 2007; Parekh, 2012). With the increased leaching of DNOM from forested catchments there has likely been an increase in background flux of DOM-P to the lakes. This may be explained by the fact that increased SO_4^{2-} concentration during the acid rain period decreases Al_o concentrations in the agricultural zones. SO_4^{2-} is caused Al to bind to DNOM and thus, preventing organic matter from dissolving. This results in an increase of coagulation and precipitation of organic matter due to the ionic attraction of DONM fractions which keeps DNOM at lower concentrations. This is today the reverse phenomenon that decreased SO_4^{2-} concentrations due to reduction in acid rain produce higher levels of Al_o with reduced ionic attraction between DNOM fractions which allows dissolution of DNOM. This is indirect evidence that there are elevated levels of DNOM today than was during the acid period (Monteith et al., 2007). Shekobe (2012) found that almost linear relation between Al_o, DNOM, and DOM-P in the forest site, Dalen. This implies stream water containing high levels of DNOM likely contain high amounts of DOM-P. DOC increase in the mixing solution can be explained by that partly reduced mineral acidity or enhanced direct discharge from horizons. It is therefore a reason that higher organic matter and Al_o intrinsically lead to increased DMO-P.

The second factor that may be important why there is an elevated level of DOC is related to the hydrological transport of DNOM in the environment. It is speculated that increased precipitation and temperature in recent years has led to increased transport of DOC (Freeman et al., 2001). In southern Norway for instance, DNOM concentrations have been shown to increase almost by two fold after the acid period with the increase in precipitation. Runoff intensity is a decisive factor for increase in levels of humus. This has been observed in runoff for the last decades through increased export of DNOM which depends on conditions of low ionic strength and high anion concentration (Evans et al., 1998).

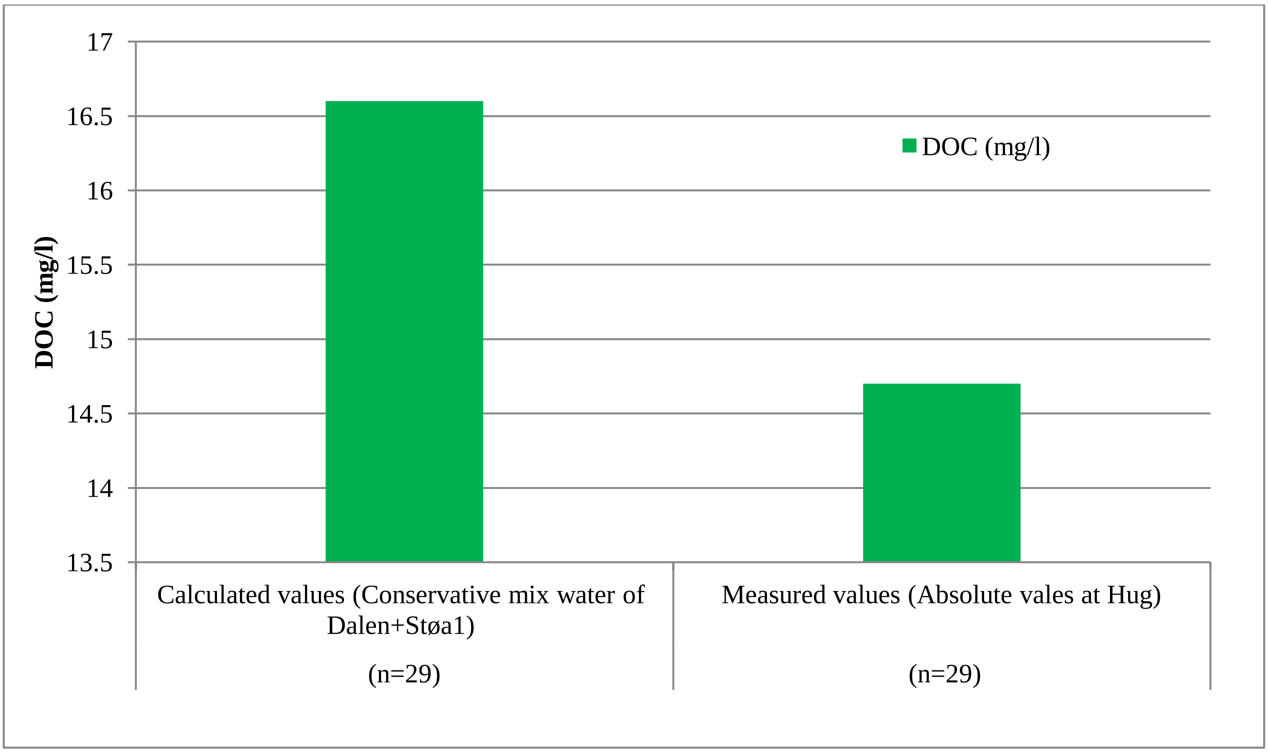

Figure 22: Average DOC concentration of measured values compared to calculated values of mixing of runoff water from Dalen and Støa1 in a ratio similar to agriculture and forest land use at Huggenes.

4.5.4 Effects of variation in runoff intensity in stream water

Variation in runoff intensity and the changes in tot-P concentration over the course of flow events in the streams draining agricultural land is presented in Figure 23. As discussed in previous sections, erosion is much smaller in forests such as Dalen than in agricultural areas. Thus, Dalen is not included here. Furthermore, it is important to look at the different seasonal conditions separately. Seasonal fluctuations create distinct annual hydrological patterns with different flow regimes. Seasonal flow regimes were roughly distinguished as spring snowmelt (March-April), summer baseflow (May-July) and autumn rain flow (August-November, November not included due to lack of samples) periods. Spring snowmelt and autumn rainfall periods are termed as high flow events in this context and mostly accompanied with high flux of all nutrients washed out of agricultural lands with runoff.

The spring snowmelt period, from the end of March to the beginning of April, was accompanied by a series of snowmelt storms causing a large rise in the hydrograph. It was also observed that autumn rainfall storms produce rise in the hydrograph. These high flow events were also characterized with loss of high levels of P. With the increase of rainfall intensity in autumn for instance, there is greater degree of interaction between runoff and surface soils mainly on ploughed soils. Thus, greater mass of soil is eroded and thereby large pool of P is released to stream water at high compared to low rainfall intensities. This results in high tot-P concentrations in the streams. During summer baseflow there is low runoff and river discharge mostly from ground water origin, which make up P transported at significant amounts (Figure 23A and B).

Tot-P loss varied throughout the monitoring periods. Tot-P concentrations in Støabekken1during spring snowmelt varied from 32µg/l in beginning of March to 722µg/l in late March and beginning of April (Figure 23A). Tot-P concentrations at Huggenes stream reached as high as 1461µg/l in October, fall rainstorms (Figure 23B). This high value recorded in the Huggenes stream is likely due to that the agricultural land in the sub-catchment has higher erosion risk, which water flux is much higher than Støabekken1. This implies wash out of soil particles is greater in the Huggenes though P content in the soil is smaller than Støabekken1. High tot-P concentrations in both Støabekken1 and Huggenes streams during periods of high flow indicate that increased runoff intensity has a significant effect on the transport of tot-P. This is mainly due to increased surface and subsurface runoff allowing a flushing of water directly from the P rich Ap layer into the stream, bypassing the sorptive capacity of deeper soil layers, and causing enhanced soil erosion. Furthermore, the high flow velocity allows re-suspension of fine particulate matter with sorbed P to mobilize from the streambed and be transported with stream waters. The temporal variation of tot-P is thus mainly governed by runoff intensity which is controlled by factors such as precipitation and temperature.

Temperature is being a factor which affects the type of precipitation (rainfall) and snowmelt. The increase temperature increases snowpack melting and precipitation depends largely on temperature.

Erosion and transport of the soil particles to streams is the reason for that a large part of the tot-P in the streams draining agricultural land is found to be bound to particle matter. That is why the concentration of tot-P is correlated to the particle loading in the streams. This inherently needs to be the case as particle-bound transport of P (PP) was the predominant P fraction in the runoff. Total suspended solids (TSS) showed strong positive correlation with tot-P in Støabekken1(r=0.881) and Huggenes (r=0.780; Appendix-J). This clearly indicates that erosion and soil losses are important process for transport of tot-P in the catchment area. The correlation also confirms that snowmelt and rainfall induced erosion is a governing factor in the transport of tot-P to streams. Furthermore, the relationship between the ratios of TSS to tot-P (tot-P/TSS) was observed highest in the agriculturally draining streams (9.11‰ in Støabekken1 and 3.33‰ in Huggenes on median, 12.00‰ and 6.74‰ on average, respectively; Appendix-G; Table G-10). A small ratio of tot-P/TSS indicates that for a mass of soil loss small amount of P is transported associated with the soil in the streams. This is also in agreement (on average values) with Bechmann and Øgaard, (in press) who studied in the same streams except for Dalen.

Gebreslasse (2012) documented strong positive correlation between TSS and runoff but weak correlation was observed with the TSS fraction-fractions; TSS fractions being inorganic and organic particulate matter. Gebreslasse also documented that during high flow events the inorganic particle matter was the dominant fraction of TSS in all the streams studied. This was also in accordance with Skarbøvik et al. (2011) who also studied the Huggenes stream as well as Vaskeberget which also drain agricultural fields in western Vansjø area.

During the summer baseflow events (May-July) the estimated tot-P concentrations ranged from 31 to 261µg/l in Støabekken1and from 22 to 120µg/l in Huggenes (with one exceptional value of 560µg/l in Huggenes), showing less variation as compared to results from high flow events. Baseflow season is dominated by ground water discharge flow chemistry. This ground water is characterized by high ion concentration and small temporal differences (section 4.1). It is evident from the Figure 23A and B that there are large temporal variation in amount of tot-P in the two agriculturally dominating sampling streams. For instance, it was observed that 78 to 82% of the tot-P at both Støabekken1and Huggenes is transported in spring (e.g. March) and autumn (e.g. October) seasons. In summer baseflow (e.g. June) 18 to 21% of the tot-P is transported. This suggests that P transport during the high flow storm events is much more significant and much of the tot-P is transported with in this short, vigourious flow events (Appendix-G; table G-8).

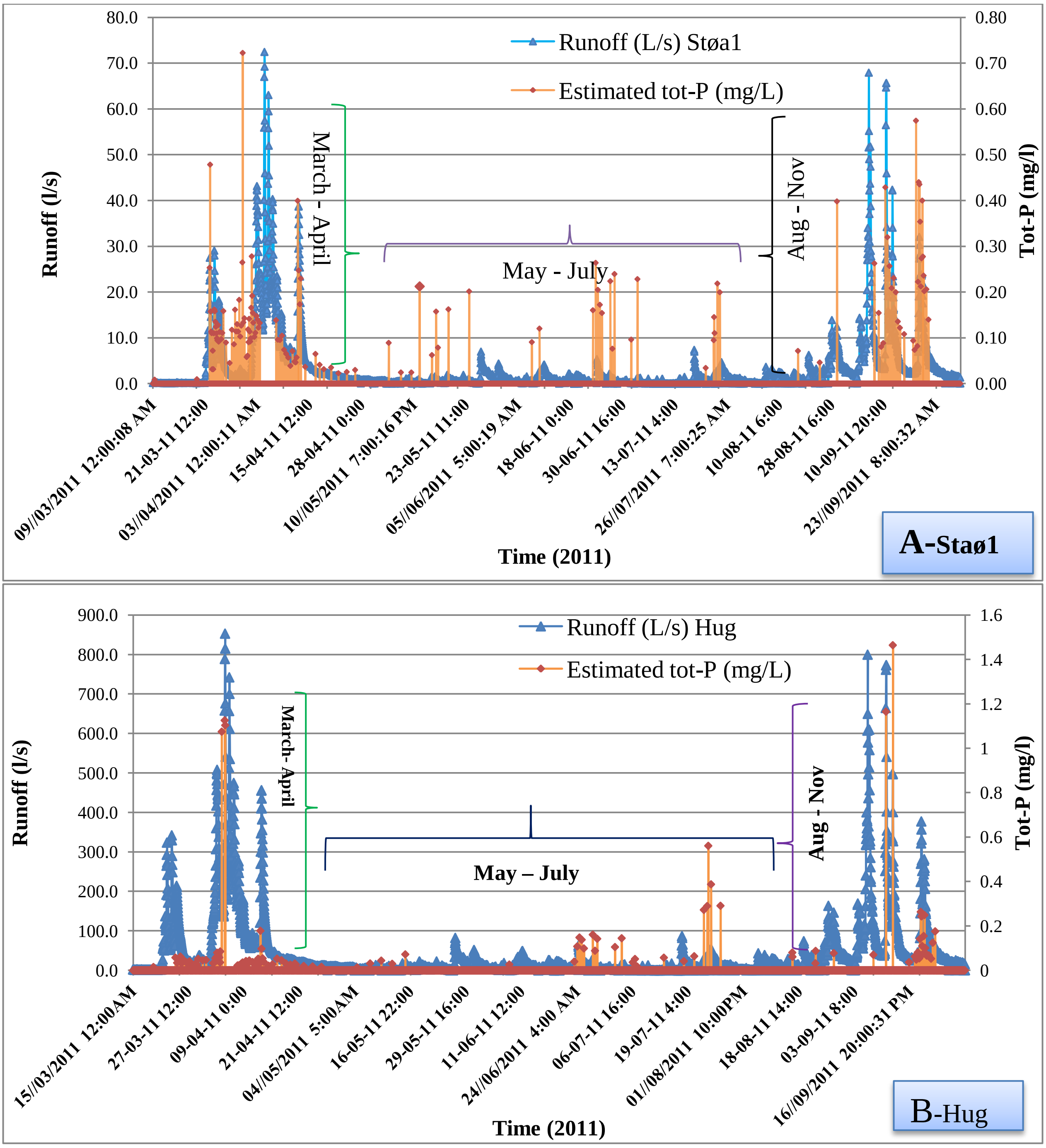

Figure 23: Daily runoff or discharge of streams (Daily runoff data from calculation by my co-supervisor Alexander Engebretsen). The runoff in the distinct seasons is categorized and grouped as snowmelt flow; autumn rain flow and as base flow.

4.5.5 Temporal variation in P-fractions in the stream waters

Figure 24 presents the average distribution values for P fractions in the different snow free months (March through October, of the year 2011) and thereby covering the hydrological regimes discussed above. In Figure 24, a boxplot of tot-P by monthly tot-P concentration show a clear seasonality, with generally high tot-P concentrations occurring in the spring snowmelt and autumn rainy months, and low tot-P concentrations in the summer with very high values in the streams draining agriculture. Generally, there is a very low tot-P value in the stream draining forest. The higher values in the two periods with high flow may be explained by wash-off P from the soil. This is due to surface- and sub-lateral flow flushing directly into the stream and thereby bypassing the assimilation in the rooting zone and adsorptive capacity of the deeper mineral soil layers. Furthermore, macropores allow water during wet periods to drain rapidly down into the sub-soil and in to the drainage pipes, avoiding the contact with the soil. Tot-P concentration during the flow events were characterized with vast variation which is due to the different in storm events of the year. This was observed in Figure 23A and B, that in the two storm events (spring and autumn), at the beginning of the storm events tot-P was higher (rising with hydrograph) and fall again to low concentrations. This can be more explained with hysteresis effect which is beyond this thesis work as it requires more advanced knowledge and sampling techniques (beyond the scope of this thesis).

P-fraction varied markedly during the study period with less variation during baseflow in the dry summers. Less variation is due to stable hydrological conditions. Furthermore, lower concentration values in Huggenes and in Støabekken1 appeared during baseflow in the dry summer. However, average tot-P concentrations are significant during the summer baseflow. This is explained by up-concentration during stagnant flow periods due to evapotranspiration. The significant values may also be due longer residence time allowing for longer interaction time between soil water and the soil material. Similar observation were shown by Shigaki et al. (2007) who studied rainfall intensity and P source effect on P transport in surface runoff from soil trays. Tot-P in August and September appear to have higher values implying there is high loss of P due to the rain events

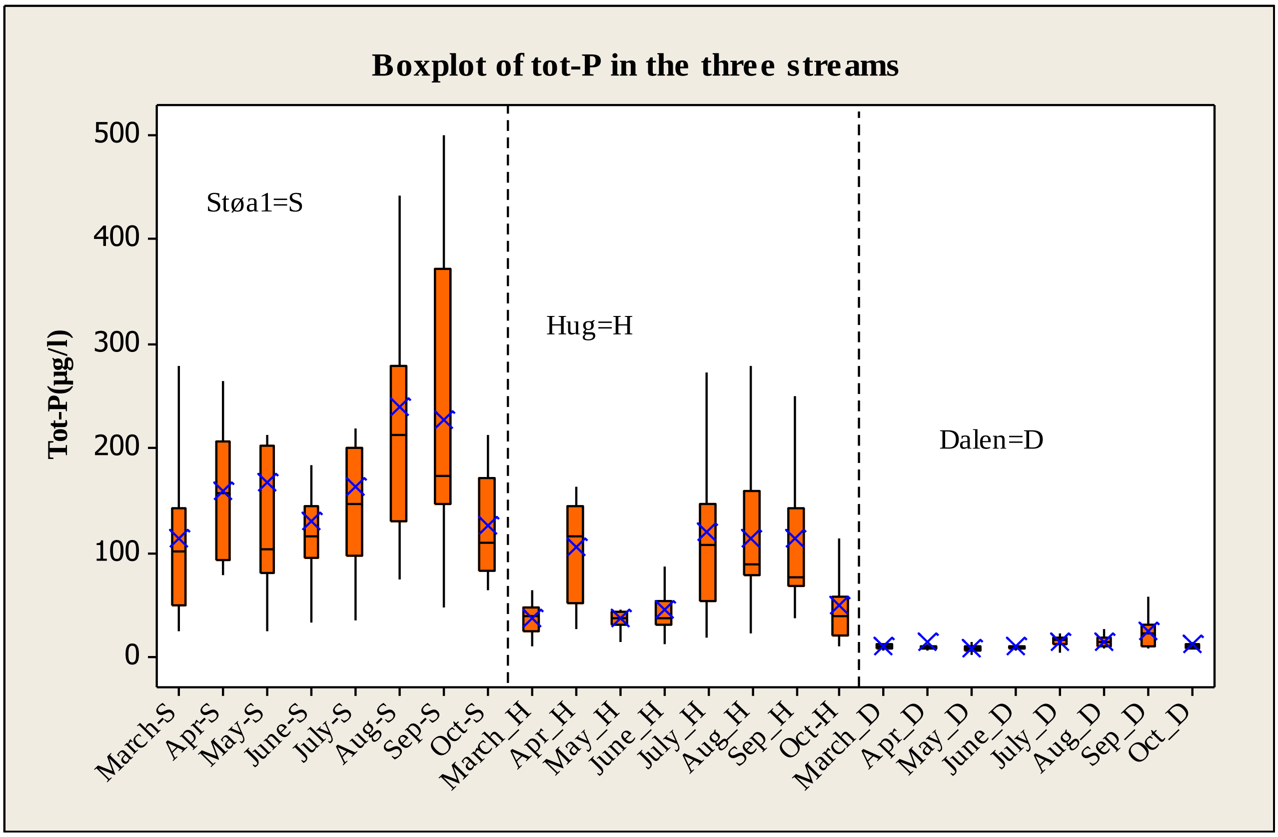

Figure 24: Tot-P in the different hydrological regimes in the snow free periods of (wet year, 2011) in the three studied streams presented as boxplot. 75th percentile above the horizontal median and 25th below the median. Mean is represented with a star in blue colour.

The P fractions in each month for each site are presented in Figure 25. Estimated average values from Figure 24 are presented only to show the variations across the sites and the contribution of each P fraction in the particular months of a year. P fraction results showed pronounced temporal variation with less variation in the stream draining forest. PP concentration was the dominant P fraction in both the streams draining agriculture. Soil and sediment re-suspension and erosion, augmented by soil amendments contribute to the addition of high PP concentrations in the streams. It is documented by Shigaki et al. (2007) that increased PP transport is attributed to the detachment and transport of undissolved P source particles during high flow events. There was elevated absolute concentration and high relative contribution of free PO_4 during April (~40%) and September (37%) at Støabekken. At Huggenes the highest absolute and relative amounts of PO_4 is ranging between 25 to 30% in August through September. Significant levels of P fractions at Støabekken is due to leaching of P from the saturated soils during these wet seasons which reduced condition that releases P bound to Fe(III). It is well known that extended periods under reducing conditions can increase P movement in soils (Scalenghe et al., 2002). It is possible the absence of plant P uptakes, such as during the dormant period in winter, can increase P levels. Low concentrations of PO_4 in May, June and July in all the streams may be due to the growing-season in which much of the PO_4 is assimilated by biological uptakes. Less PO_4 at Huggenes stream water as compared to

Støabekken1 may be due to precipitation reaction with labile inorganic Al from upstream forest runoff mixing with the seepage water from the agricultural land (section 4.5.1). This part of the PO_4 will then be precipitated with the Al and contributes to the PP.

In the Dalen stream water, the perennial vegetation cover efficiently prevents erosion. Therefore, there is much less amounts (below 10%) of PP in all the months. Instead the main P-fraction is DOM-P (50 to 65%). The fractions of P in the Dalen stream are rather constant throughout the year with the exception of higher contribution of DOM-P during June and August. Higher organic matter content contributes to low pH, which allows Al_o to complex with DNOM. In this case, PO_4 is sorbed as Al_o-organic matter phosphate complex and thereby minimize available PO_4 in the stream water. DOM-P accounted for relatively little of the tot-P (7 to 15%) in the Støabekken1and at slightly more in the Huggenes (8 to 23%) with a larger forest land use in the Huggenes catchment. This is related to that large loads of DNOM and inherent DOM-P is exported from the forests (Figure 20). DOM-P in Dalen stream water constituted the largest P fraction in the months indicated. This is mainly due to the higher content of dissolved organic matter with inherent content of P. It is also a contribution through the presence of organically complexed Al (Al_o) and iron which may lead PO_4 to bind to the DNOM as Al-organic matter phosphate complex and thereby minimize the fraction of PO_4 in the stream water.

Major abatement actions conducted in western Vansjø are mainly aimed at reducing PP from agricultural fields. Despite these efforts the dominant P-fraction appears still to be PP in streams draining agricultural land. This implies that agricultural lands remain prone to lose their P by rainfall and snowmelt induced erosion as the most fundamental mechanism in transporting the PO_4 from the terrestrial to the aquatic environment.

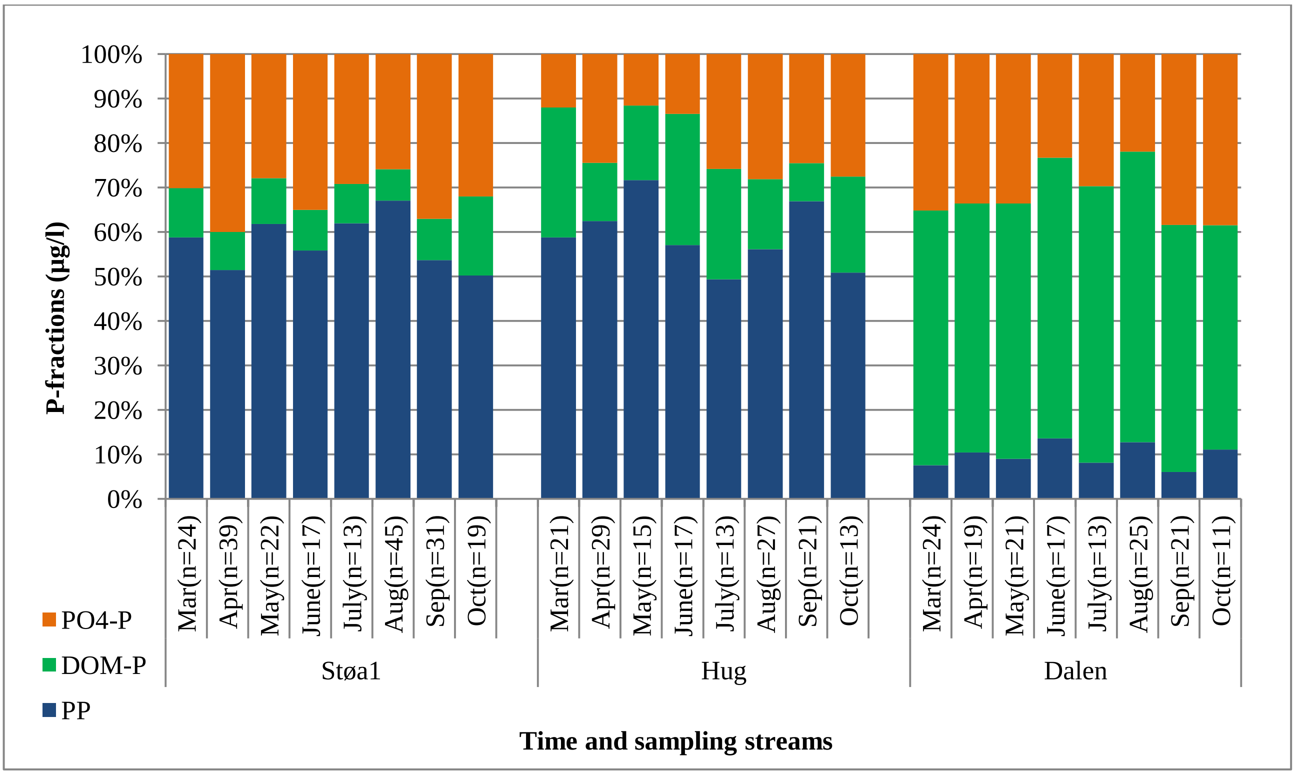

Figure 25: Monthly P-fractions contribution from the three studied stream water during snow free periods (March through October, 2011). Concentration values are based on median values in Figure 24.

4.6 Total suspended solids (TSS) and its role in P transport

Figure 26 presents an overview of the level and range of TSS in the streams. Concentrations of TSS during the sampling periods (mainly the year 2011) in the three studied streams showed variations both in time and space. TSS concentrations generally vary from low (2mg/l) in the low flow periods to as high as 40mg/l during periods of high flow. Variations would mainly be due to fluctuation in amount and energy of runoff in the respective streams. At Støabekken1 and Huggenes the intensity of runoff/discharge were found to be positively correlated (r=0.785, r=0.458, respectively) to TSS supporting that runoff is a driving factor in the transport of soil particles. Gebreslasse (2012) documented that the total suspended solids (TSS) in streams of western Vansjø, including the streams in this study, are highly correlated (r=0.970) with runoff. Gebreslasse concluded that higher flow events results in higher TSS loading which also carried a higher fraction of particulate bound P in the streams. Erosion is best explained by land-use type, topography and soil texture (section 2.2), and amount of TSS in the streams showed not only temporal variation but also large spatial variation. The erosion risk in the sites, as discussed in section 3.1.2, is much smaller in forested fields than is in agricultural fields. Støabekken1 and Huggenes are two streams draining agricultural land with concentration of TSS (12.4mg/l and 13.7mg/l, on median, respectively) that are about two times higher than values obtained from the forest draining site-Dalen (7.0mg/l). Although Dalen is forest dominated area significant amount of TSS is transported in the stream. This may be due to wash-off fine soil particles in forest areas which can be easily carried away even with less energetic flowing water. Gebreslasse (2012) found that the ratio of silt to sand fraction in the stream sediments increased with increasing ratio of forest to agriculture in the catchment. Gebreslasse also found that more of the TSS in the forest draining stream sediments is organic fraction whereas inorganic TSS fraction is dominant in the sediments draining agricultural zones. Results for can be found in (Appendix-G; Table G-9).

Tot-P has strong relationship with TSS in the stream waters (section 4.5.4). Correlations are smaller in the forest draining stream suggesting amount of P in the particles is higher in the streams draining agricultural than is in the stream draining forest. This is due to the perennial plants which highly bound up with the soils in the forest (Skarbøvik et al., 2011) reduces the movement of particles.

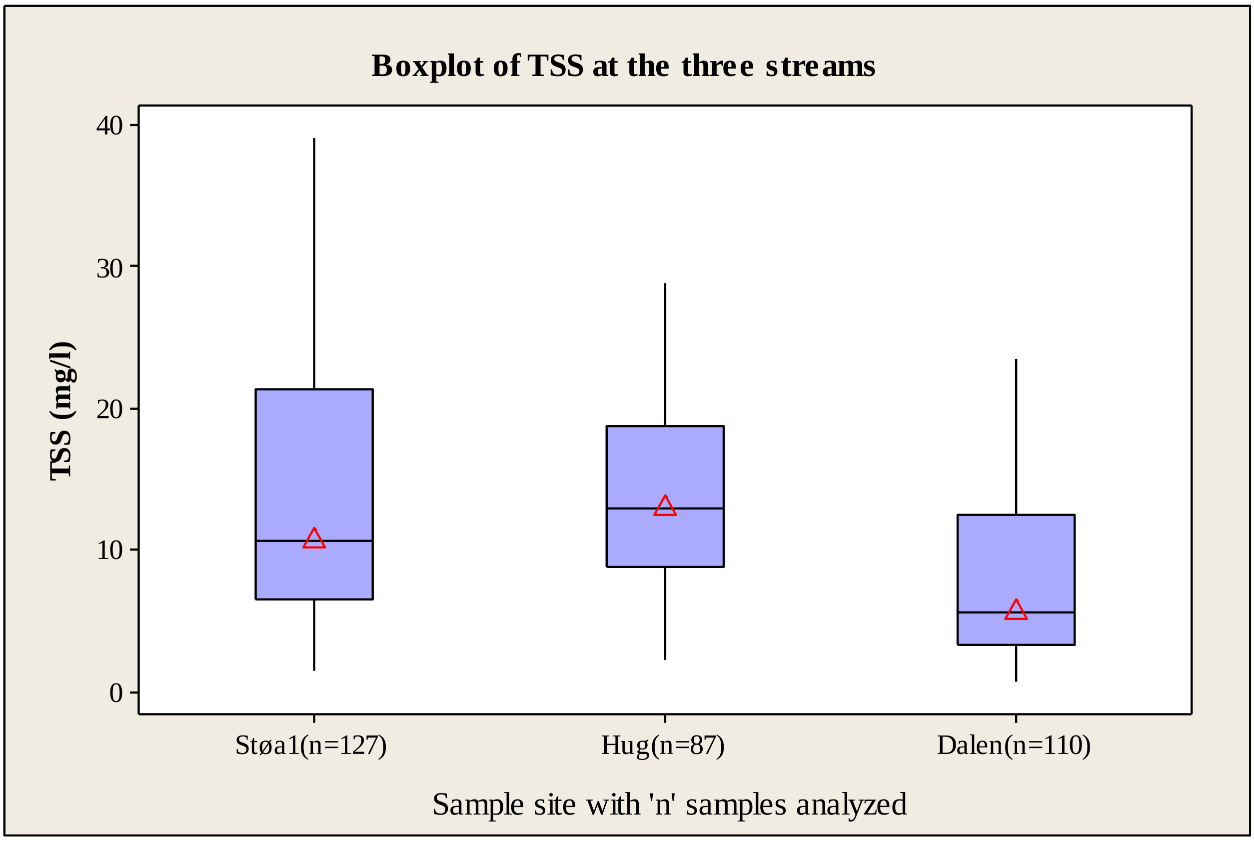

Figure 26: Boxplot of concentration of total suspended solids (mg/l) of stream water samples during study period. Range of data is represented with vertical lines on which the box represents the 25th and 75th percentile of the data series. Median is the black horizontal line inside the box and mean is the triangle inside the box.

Figure 27 presents concentration of total suspended solids (TSS) under high and low flow regimes. High and low flow regimes are distinguished in section 4.5.4. Samples are only for the year 2011. Temporal variation is mainly due to fluctuation in amount and thereby velocity of runoff in the respective streams. In all the streams the concentration of TSS in the high flow regimes are two to three times higher than to that of in the low flow periods (Appendix-G; Table G-9). Slightly higher concentration of TSS in periods of high flow is also found in Huggenes and could be due to the fact that the stream's high flux of water and a case when forest runoff water is mixing with agricultural runoff causes precipitation of particles.

Tot-P is mainly transported as PP (55-60%) and this transport of PP is much related to stream water flow. The role of TSS in the transport of tot-P is therefore best explained by the stream flow. The flow of stream water varies considerably from day to day and from month to month due to variations in weather and runoff. This flow fluctuation in river runoff affects the amount and flux of TSS as it is an important transport process for P to the lake (e.g. Skarbøvik et al., 2011). Large amount of tot-P is loaded into the lake during peak discharge in April and October (section 4.5.4). Therefore, abatement actions aiming at reduction of soil erosion can minimize amount of P-flux to the lake Vansjø.

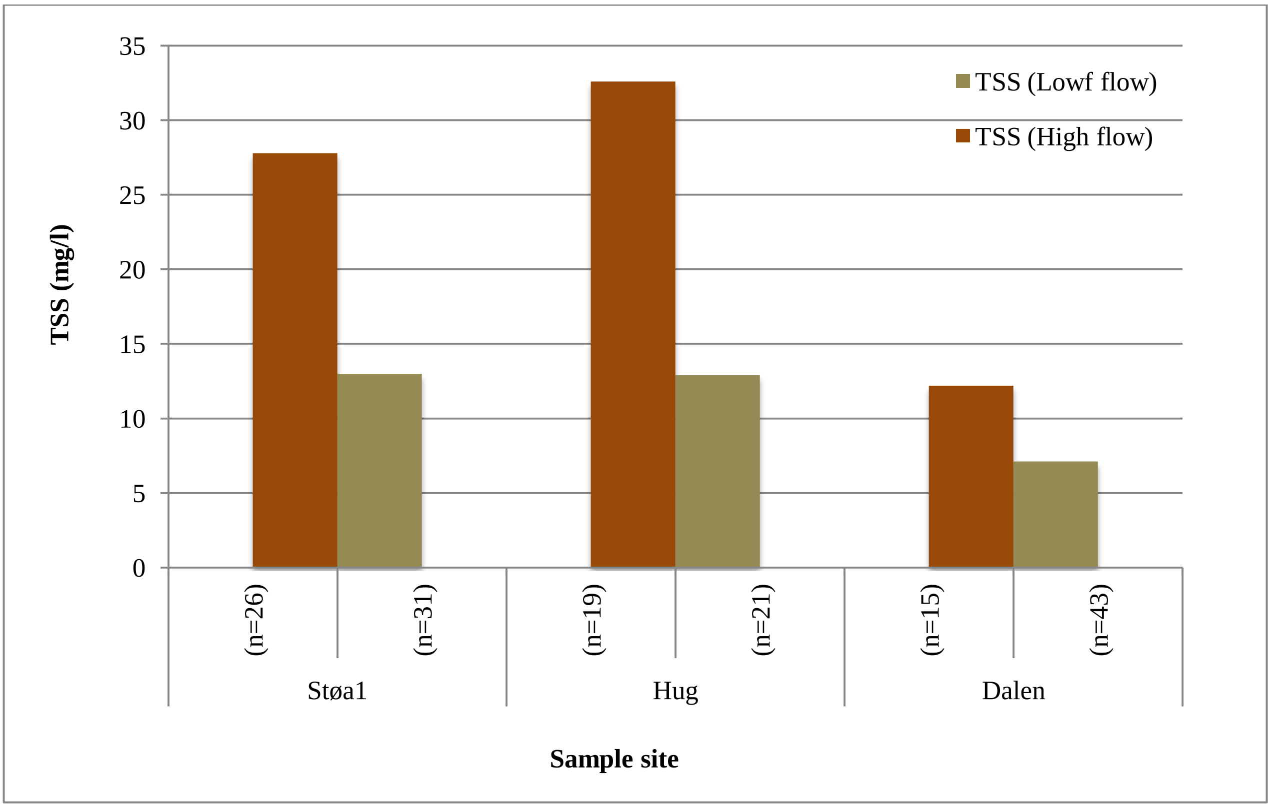

Figure 27: Median concentration of total suspended solids/particles in the three stream waters in periods of high and low flow events. Numbers under bar graphs are samples considered.

4.7 Iron content and effect of flooding

Iron (Fe) content of the soil play a key role in the binding of PO_4 to the soils as discussed in section 2.10. Fe in the environment is redox sensitive element and in reduced soil water environment, where nitrate and MnO_2 is depleted, the Fe^{3+} is reduced to Fe^{2+}. Reduction of Fe^{3+} releases PO_4 adsorbed to Fe(III)hydroxides, PO_4 in Fe(III)PO_4 minerals as well as PO_4 bound to organically complexed Fe(III) through bridging between organic coating and phosphates. The next electron acceptor on the redox ladder is sulphate. Sulphate is reduced to sulphide which binds Fe(II) as pyrite (FeS). Reducing conditions occur within short time in water logged soils by oxidative decomposition and mineralization of organic matter by bacteria. The effect of this was evident in the year 2000 when lake Vansjø experienced a major flood and there were a substantial load of phosphates to the lake. This large loading of PO_4 mainly believed to come from large erosion of stream-banks and overflow of sewage networks (Gebreslasse, 2012). Based on conceptual understanding of the role of iron on PO_4 binding capacity to soils and the effect of reducing conditions on this capacity it is hypothesized that also a considerable loading of PO_4 to the lake after the flood was due to the loss of PO_4 bound originally to Fe(III) in stagnant waterlogged soils. Furthermore, reducing conditions develop also, in the lake sediments which release phosphates bound to Fe(III) in sediments allowing for remobilization of phosphates thus in an internal loading source of phosphates. Where or when this water in reduced condition is exposed to the atmosphere in the stream or after flooded soils are allowed to drain and O_2 is in action, oxidation again takes place. Fe^{2+} is oxidized to Fe^{3+} and phosphate co-precipitates. The effect is evident in the sediments of the Støabekken1 stream, which is fed only by drainage pipes in soils that are especially rich in iron.

XRF[3] and ICP-OES results determined on sediment samples at streams of Morsa documented by Gebreslasse (2012) revealed that the Støa1 stream sediments have high Fe content (Table 6). Gebreslasse found that of the nine streams draining into western Vansjø the Støa1 stream sediment had the second largest Fe content following the neighboring Støa2 stream. Opland (2011) also showed that the soil in soil plot in the agricultural fields at Huggenes were rich in iron contents. This is due to that the Ra appears to have high iron content in the soils. The Ra directly drains to the western Vansjø. It is therefore reported that iron bound P is transported to western Vansjø making the water quality problems and that is why the western Vansjø is reportedly stated as eutrophic.

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[3] (XRF): X-ray fluorescence is a quantitative analytical technique used for the rapid determination of many major and minor elements in soil, rock and sediment samples in solid forms.

Table 6: Iron content in sediment samples collected at the studied streams by Gebreslasse (2012).

Site	Fe_2O_3 content in g/kg
Staø1..	69.0
Hug...	44.0
Dalen..	26.5

4.8 Principal component analysis of P fractions with explanatory variables

A PCA analysis was performed on stream water P fractions along with some explanatory variables. The explanatory variables were: runoff, alkalinity, conductivity, major cations, major anions, TSS, tot-P and P fractions, DOC, bicarbonate, and other. The PCA analysis was weak due to small number of samples and variables. The purpose is only to high light some preliminary impression if there is a possible clustering of variables. This was performed to assess the relationship among explanatory variables and response parameters explaining the factors influencing the concentrations and distribution of P fraction in stream waters. Results are presented in Figure 28.

There are three distinct loading clusters that may be distinguished according to the land-use (agriculture, forest and other) in the watershed. PC1 and PC2 explaining 53% and 22%, of the entire variation in the data set respectively, is mainly governed by the differences in land-use. PC1 (53%) greatly explains the variation between agriculture and forest land-use. Along the PC1 agriculture and forest have opposite loading. In the agriculture loading cluster the variables have moderate correlation. This is due to that the runoff from agricultural land possesses high concentrations of nutrients, such as NO_3^- and K^+ due to the application of KNP fertilizers, and high pH, alkalinity, HCO_3^-, along with Mg^{2+}, Ca^{2+} concentrations due to high base saturation of soils and liming. Tot-P and P fractions (PP, PO4-P) are well correlated and found in the agricultural loading cluster except DOM-P which is found to load as opposed to the agriculture.

PC2 has strong loading of the “other” land–use type which are oppositely loaded to the tot-P and P-fractions. The third loading cluster of variables is the forest. Variables are weakly correlated and yet forest is characterized with having high values of DOM-P, DOC, Al_i and H^+. The weak correlation is manifested between DOC and DOM-P.

Table 7: Eigen analysis of correlation matrix of explanatory variables

Eigen value	12.819	5.262	2.287	1.297	0.925	0.634	0.487	0.289	0.000
Proportion	0.534	0.219	0.095	0.054	0.038	0.026	0.020	0.012	0.000
Cumulative	0.534	0.753	0.848	0.893	0.931	0.957	0.977	0.989	0.989

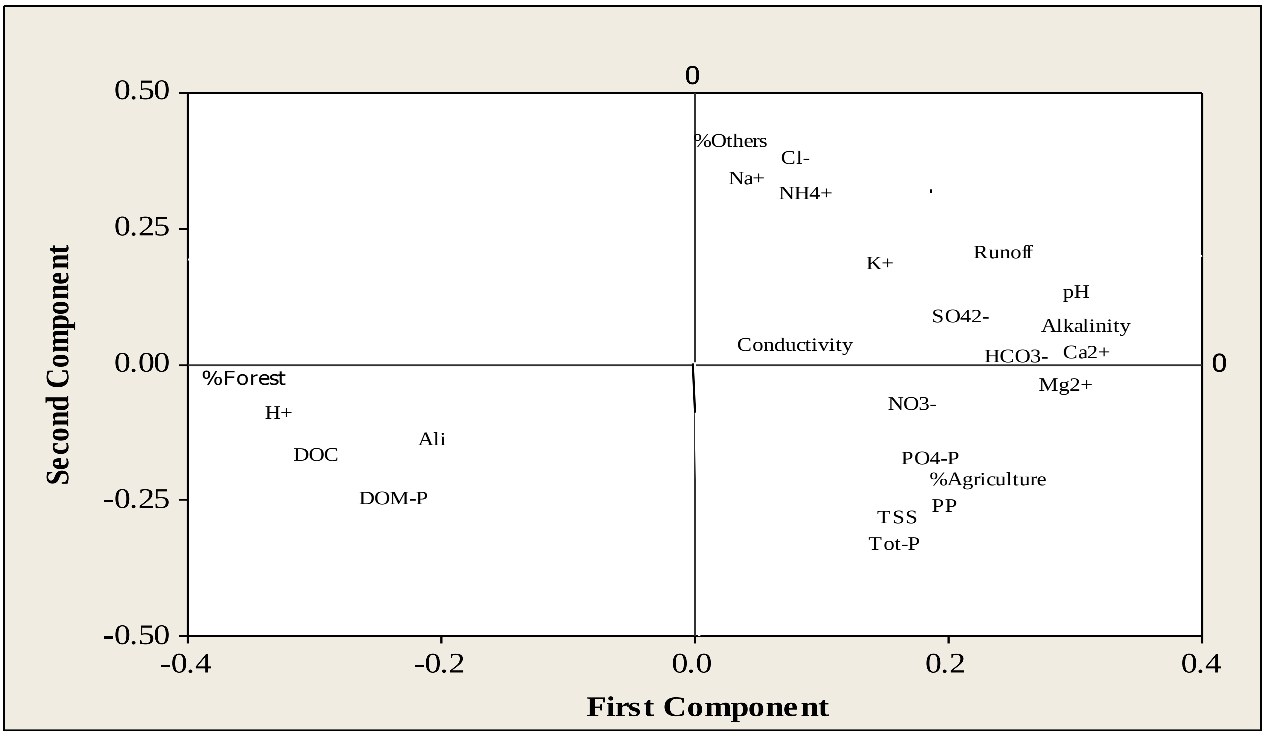


Figure 28: PCA loading plot with respect to the first two PCs showing three groups corresponding to variables. Three loading groups, agriculture, forest and other.

4.9 Impact of particulate bound P loading in to the lake Vansjø

Surface and subsurface lateral runoff play a key role on the transport of huge amounts of soil particles and nutrients to recipient water bodies. Erosion is predominantly of the silt and clay fraction in the top soil due to the energy limitations in transport of larger particles (Sharpley, 1985). Because of the large surface area of the fine particles, a large proportion of tot-P is associated to these eroded soil particles and are transported downstream and deposited in the sediments in streams and lakes. Deposited soil sediments in lower water course/lake might sorb or release PO_4-P which however, depends on the equilibrium established between P in the water column and deposited lake sediments. The tendency of releasing P from their surfaces or retaining on their surfaces is important mechanism from impact perspective. The scavenging of phosphates by sediment particles continues until sorbing capacity is exhausted, or equilibrium is established. It is also likely that sorption/ desorption reactions takes place between particulate and dissolved P pools in the stream sediments.

The main impact is that P can be demobilized and remobilized from sediments in to different P fractions by desorption/adsorption, precipitation/dissolution of precipitates, assimilation into biomass/enzymatic hydrolysis of ester bonds and ligand exchange mechanisms (Boström et al., 1982). During growing seasons when even external sources are not sufficient to cover the demand of P, part of it from sediment may potentially be released to the water column of lakes acting as a source of P to lake biomass and can trigger blooms of cyno-bacteria. Internal loading of P will then determine the eutrophication status of lakes (Ruikai et al., 2012), and cause a time lag of recovering after reduction of external loading (Pettersson, 1998).

Results obtained from three streams assessed in this thesis showed that the dominant fraction of P was the particulate form (PP). This suggests that on a long-term basis it is evident that there will be huge accumulation of particulate bound P in lake sediments. On the other hand, if there is a large sediment loading into the lake the rapid settling and accumulation of sediments will serve to bury the particles so that the diffusion of P does not reach direct contact with the water column. This will thus efficiently prevent any exchange and thereby reduced the contribution of P from PP in the sediments. Results obtained revealed that transport of particulate bound P is much higher from streams draining agricultural land than from forest dominated sites. This is likely due to that arable soils have high susceptibility to be eroded and washed downstream to the recipient lakes. This in turn will have effects on growing seasons due to PP mobilization and transformation within the lake itself for plant and microbial uptake.

5 CONCLUSION

In contrast to the stream draining forest, the streams draining agricultural land show elevated tot-P concentrations. The tot-P found in the stream draining forest was relatively low due to no application of P containing fertilizers in the area. This suggests the importance of P containing fertilizer applications on agricultural soils which is able to leach into the streams during episode of flow events causing water quality problems. Effect of land use distribution pronouncing governs the variation of amounts of tot-P and P fractions. This was supported with the PCA analysis showing that DOM-P, DOC, Al_i and H^+ were negatively loading in the forest, while most of the response variables such as pH, tot-P, TSS and PP have had positive load in the agriculture draining stream.

Reduced Al_i leaching from soils due to reduction of acid rain in recent years results in lack of co-precipitation of P by Al in the agricultural soils. A condition with reduced Al_i and lack of formation of oxy Al-hydroxides favours free movement of phosphates in the environment without any influence and reaches into the lake via the streams. This is the process that has a great contribution to intensification of eutrophication in the lake Vansjø today. Lack of response for implemented abatement actions in lake Vansjø today is the result of reduction in acid rain.

Decreased SO_4^{2-} concentrations due to reduction in acid rain produce higher levels of Al_o in the agricultural zones. This creates reduced ionic attraction between DNOM fractions and allows dissolution of DNOM. DOC increase in the mixing of stream water of different land-use can be explained by that partly reduced mineral acidity. This is indirect evidence that there are elevated levels of DNOM today than was during the acid period, implies stream water containing high levels of DNOM likely contain high amounts of DOM-P. It is therefore a reason that higher organic matter and Al_o intrinsically lead to increased DMO-P.

The amount and distribution of P fractions in the lake is the net result of the continuous P sedimentation and direct flux of dissolved P to the water from the addition of P containing fertilizers from the surrounding agricultural fields. Dissolved P is important as immediate source of P on water which brings quality problems; however, in a long term accumulated PP may also be available to algae. P losses from soil and transport to water bodies are mainly explained by hydrological water flows in a way that runoff from agricultural segments contributes much of the tot-P which has direct consequences in eutrophying lakes. The tot-P losses are dominated with PP in the streams draining agriculture.

Runoff/river discharge was found as an important deriving factor governing the temporal and spatial variations in the transport of large pools of TSS. Losses of TSS are in turn an important transport process for P from agricultural zones to the streams. Results also confirm that seasonal variation has clearly observed with large amount of tot-P leached in the streams draining agriculture during episodes of high flow with large proportion of PP. Therefore, hydrology is an explanatory factor for the temporal variations of P losses in the catchment.

Reference

Akhtar, M.S., Richards, B.K., Medrano, P.A., DeGroot, B., Steenhuis, T.S., 2003. Dissolved phosphorus from undisturbed soil cores. Soil Science American Journal 67, 458-470.

Anderson, D., 1979. Processes of humus formation and transformation in soils of the Canadian great plains. Journal of Soil Science 30, 77-84.

Appelo, C., Postma, D., 2007. Geochemistry, groundwater and pollution, 2nd edition. Balkema publishing, Amsterdam, Netherlands.

Aquarius, 2000. 'Farmers as water managers in a changing climate'. Norwegian pilot area. Østfold Baseline Report.

Barnes, R.B., 1975. The determination of specific forms of aluminum in natural water. Chemical Geology 15, 177-191.

Bechmann, M., 2005. The phosphorus index tool for assessing phosphorus transfer from agricultural areas in Norway. Doctor scientiarum Thesis. Norwegian University of Life Sciences, Department of Plant and Environmental Sciences.

Bechmann, M., Øgaard, A., Larsen, R., 2010. Critical source areas of nutrient losses from agriculture in Norway. Acta Horticulturae, 63-72.

Bechmann, M., Øgaard, A.F., in press. Water quality changes fllowing intensive focus on mitigation methods to reduce phosphorus losses in the catchment of lake Vansjø, Norway. Agrochemistry and soil science.

Bechmann, M., Stålnacke, P., 2005. Effect of policy-induced measures on suspended sediments and total phosphorus concentrations from three Norwegian agricultural catchments. Science of The Total Environment 344, 129-142.

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

Bjørdalen, K., Andersen, T., Færøving, P.J., 2007. Utredninger Vansjø-Kartlegging av vannkvalitet i 2006, NIVA, Norwegian Institute for Water Research.

Bjørndalen, K., Andersen, T., Bechmann, M., Borgvang, S., Brabrand, Å., Delstra, J., Gunnarsdottir, H., Hobæk, A., Saloranta, T., Skarbøvik, E., Solheim, A., 2006. Utredninger Vansjø 2005-Sammendrag og anbefalinger (NIVA) [In Norwegian]. 41

Børresen, T., Uhlen, G., 1991. Soil erosion and phosphorus loss in surface runoff from a field-lysimeter in Ås winter 1989/90 [In Norwegian]. Norwegian Journal of Agricultural Sciences.

Boström, B., Jansson, M., Forsberg, C., 1982. Phosphorus release from lake sediments. Arch. Hydrobiol. 18, 5-59.

Boström, B., Persson, G., Broberg, B., 1988. Bioavailability of different phosphorus forms in freshwater systems. Hydrobiologia 170, 133-155.

Brady, N., Weil, R., 2009. Elements of the nature and properties of soils. Prentice Hall.

Braskerud, B., 2001. The Influence of vegetation on sedimentation and resuspension of soil particles In small constructed wetlands. Journal of Environmental Quality 30, 1447-1457.

Carpenter, S.R., 2005. Eutrophication of aquatic ecosystems: bistability and soil phosphorus. Proc Natl Acad Sci USA 102, 10002-10005.

Carpenter, S.R., Caraco N.F., Correll D.L., Howarth R.W., Sharpley A.N., Smith V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological Applications 8, 559-568.

Christensen, J.H., Räisänen J., Iversen T., Bjøge D., Christensen O.B., Rummukainen M., 2001. A synthesis of regional climate change simulations: A scandinavian perspective. Geophys. Res. Lett. 28, 1003-1006.

Christophersen, N., Wright, R.F., 1981. Sulfate budget and a model for sulfate concentrations in stream water at Birkenes, a small forested catchment in southernmost Norway. Water Resources Research 17, 377-389.

Cordell, D., Rosemarin A., Schröder J.J., Smit A.L., 2011. Towards global phosphorus security: A systems framework for phosphorus recovery and reuse options. Chemosphere 84, 747-758.

Correll, D.L., 1998. The role of phosphorus in the eutrophication of receiving waters: A review. Journal of Environmental Quality. 27, 261-266.

D'Angelo, E.M., Reddy, K.R., 1994. Diagenesis of organic matter in a wetland receiving hypereutrophic lake water: Distribution of dissolved nutrients in the soil and water column. Journal of Environmental Quality 23, 928-936.

Daniel T, C., Sharpley A.N., Edwards D.R., Wedepohl R., Lemunyon J.L., 1994. Minimizing surface water eutrophication from agriculture by phosphorous management. Journal of Soil and Water Conservation 49, 30-38.

Dickson, W., 1978. Some Effects of the Acidification of Swedish Lakes Limnology 20, 851-556.

Dils, R.M., Heathwaite, A.L., 1999. The controversial role of tile drainage in phosphorus export from agricultural land. Water Science and Technology 39, 55-61.

Djodjic, F., Bergström, L., 2005. Conditional phosphorus index as an educational tool for risk assessment and phosphorus management. 34, 296-300.

Dokulil, M.T., Teubner, K., 2011. Eutrophication and climate change: Present situation and future scenarios eutrophication-causes, consequences and control, In: Springer Netherlands, pp. 1-16.

Driscoll, C.T., Schafran, G.C., 1984. Short-term changes in the base neutralizing capacity of an acid Adirondack lake, New York. Nature 310, 308-310.

Driscoll, C.T., Schecher, W.D., 1990. The chemistry of aluminum in the environment. Environmental Geochemistry and Health 12, 28-49.

Eimers, M., Watmough, S., Buttle, J., 2008. Long-term trends in dissolved organic carbon concentration: a cautionary note. Biogeochemistry 87, 71-81.

Elliott, E.T., Coleman, D.C., 1988. Let the soil work for us Ecological Bulletins 39, 23-32.

Evans, C., Cullen, J., Alewell, C., Kopácek, J., Marchetto, A., Moldan, F., Prechtel, A., Rogora, M., Veselý, J., Wright, R., 2001. Recovery from acidification in European surface waters. Hydrology and Earth System Sciences Discussions 5, 283-298.

Foy, R.H., Bailey-Watts, A.E., 1998. Observations on the spatial and temporal variation in the phosphorus status of lakes in the British Isles. Soil Use and Management 14, 131-138.

Freeman, C., Evans, C.D., Monteith, D.T., Reynolds, B., Fenner, N., 2001. Export of organic carbon from peat soils. Nature 412, 785-785.

Gächter, R., Meyer, J.S., 1993. The role of microorganisms in mobilization and fixation of phosphorus in sediments. Hydrobiologia 253, 103-121.

Gachter, R., Meyer, J.S., Mares, A., 1988. Contribution of bacteria to release and fixation of phosphorus in lake sediments. Limnology and Oceanography, 1542-1558.

Gburek, W.J., Sharpley A.N, Folmar G.J, 2000. Critical areas of phosphorus export from agricultural watersheds.

Gburek, W.J., Sharpley, A.N., 1998. Hydrologic controls on phosphorus loss from upland agricultural watersheds. Journal of Environmental Quality 27, 267-277.

Gebreslasse, Y.K., 2012. Particle transport of phosphorus in streams draining catchments with different land uses: Master Thesis, University of Oslo, Blindern, Norway. .

Gerke, J., 2010. Humic (organic matter)-Al/Fe-phosphate complexes: An underestimated phosphate form in soils and source of plant-available phosphate. Soil Science 175, 417-425

Gregorich, E., Monreal, C., Carter, M., Angers, D., Ellert, B., 1994. Towards a minimum data set to assess soil organic matter quality in agricultural soils. Canadian Journal of Soil Science 74, 367-385.

Haaland, S., Hongve, D., Laudon, H., Riise, G., Vogt, R.D., 2010. Quantifying the drivers of the increasing colored organic matter in boreal surface waters. Environmental Science & Technology 44, 2975-2980.

Harrison, A.F., Taylor, K., Scott, A., Poskitt, J.A.N., Benham, D., Grace, J., Chaplow, J., Rowland, P., 2008. Potential effects of climate change on DOC release from three different soil types on the Northern Pennines UK: examination using field manipulation experiments. Global Change Biology 14, 687-702.

Haygarth, P., Wood, F., Heathwaite, A., Butler, P., 2005. Phosphorus dynamics observed through increasing scales in a nested headwater to river channel study. Science of The Total Environment 344, 83-106.

Haygarth, P.M., Chapman, P.J., Jarvis, S.C., Smith, R.V., 1998. Phosphorus budgets for two contrasting grassland farming systems in the UK. Soil Use and Management 14, 160-167.

Haygarth, P.M., Jarvis, S.C., 1999. Transfer of phosphorus from agricultural soil, In: Donald, L.S. (Ed.) Advances in Agronomy. Academic Press, pp. 195-249.

Heckrath, G., Brookes P.C, Poulton P.R, Goulding K.W.T, 1995. Phosphorus leaching from soils containing different phosphorus concentrations in the broadbalk experiment. Journal Environmental Quality 24, 904-910.

Hinesly, T.D., Jones, R.L., 1990. Phosphorus in waters from sewage sludge amended lysimeters. Environmental Pollution 65, 293-309.

Hinsinger, P., 2001. Bioavailability of soil inorganic phosphorus in the rhizosphere as affected by root-induced chemical changes: a review. Plant and Soil 237, 173-195.

Holtan, H., Kamp-Nielsen, L., Stuanes, A., 1988. Phosphorus in soil, water and sediment: an overview. Hydrobiologia 170, 19-34.

Hongve, D., Riise, G., Kristiansen, J., 2004. Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water – a result of increased precipitation? Aquat. Sci. 66, 231-238.

House, W.A., Warwick, M., 1998. Intensive measurements of nutrient dynamics in the River Swale. Science of The Total Environment 210–211, 111-137.

Hutchison, K.J., Hesterberg, D., 2004. Dissolution of phosphate in a phosphorus-enriched ultisol as affected by microbial reduction. Journal of Environmental Quality 33, 1793-1802.

Hyne, R.V., Wilson, S.P., 1997. Toxicity of acid-sulphate soil leachate and aluminium to the embryos and larvae of Australian bass (Macquaria novemaculeata) in estuarine water. Environmental Pollution 97, 221-227.

ISO6878, 2004. Water quality-determination of phosphorus: Ammonium molybdate spectrometric method.

ISO7888, 1985. Water quality-determination of electrical conductivity.

ISO9963-1, 1994. Water quality -determination of alkalinity-Part 1: Determination of total and composite alkalinity.

ISO10204-1, 1992. Water quality-determination of dissolved fluoride, chloride, nitrate, orthophosphate, bromide, nitrate and sulphide ions, using liquid chromatography of ions.

ISO10523, 1994. Water quality-determination of pH.

ISO11923, 1997. Water quality -- Determination of suspended solids by filtration through glass-fibre filters.

ISO22036, 2008. Soil quality-determination of trace elements in extract of soil by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Johnson, D.W., Cole Dale W., Van Miegroet Helga, Horng F.W., 1986. Factors affecting anion movement and retention in four forest soils. Soil Science Society of America journal 50, 776-783.

Jolliffe, I., 2005. Principal Component Analysis, In: Encyclopedia of Statistics in Behavioral Science. John Wiley & Sons, Ltd.

Kalbitz, K., Solinger, S., Park, J., Michalzik, B., Matzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: a review. Soil Science 165, 277-304.

Kalff, J., 2002. Limnology: inland water ecosystems. Prentice Hall.

Kleinman, P., Sharpley Andrew, Saporito Lou, Buda Anthony, Bryant Ray, 2008. Application of manure to no-till soils: phosphorus losses by sub-surface and surface pathways. Nutrient Cycling in Agroecosystems 84, 215-227.

Klif, 2011. Overvåking av langtransportert forurenset luft og nedbør. Årsrapport – Effekter 2010. Statlig program for forurensningsovervåking, Rapport SPFO: 1094/2011, TA-2793/2011.

Leone, A., Ripa, M., Boccia, L., Lo Porto, A., 2008. Phosphorus export from agricultural land: a simple approach. Biosystems Engineering 101, 270-280.

Loeb, R., Lamers Leon P.M., Roelofs Jan G.M., 2008. Effects of winter versus summer flooding and subsequent desiccation on soil chemistry in a riverine hay meadow. Geoderma 145, 84-90.

Lundekvam, H., Skoien, S., 1998. Soil erosion in Norway. An overview of measurements from soil loss plots. Soil Use and Management 14, 84-89.

Lundekvam, H.E., Romstad, E., Øygarden, L., 2003. Agricultural policies in Norway and effects on soil erosion. Environmental Science & Policy 6, 57-67.

MacCarthy, P., 2001. The Principles of Humic Substances. Soil Science 166, 738-751.

McDowell, R., Sharpley, A., Condron, L., Haygarth, P., Brookes, P., 2001. Processes controlling soil phosphorus release to runoff and implications for agricultural management. Nutrient Cycling in Agroecosystems 59, 269-284.

McDowell, R., Srinivasan, M., 2009. Identifying critical source areas for water quality: Validating the approach for phosphorus and sediment losses in grazed headwater catchments. Journal of hydrology (Amsterdam) 379, 68-80.

McDowell, R.W., Sharpley, A.N., 2001. Soil phosphorus fractions in solution: influence of fertiliser and manure, filtration and method of determination. Chemosphere 45, 737-748.

Meyer-Reil, L.A., Köster, M., 2000. Eutrophication of marine waters: Effects on benthic microbial communities. Marine Pollution Bulletin 41, 255-263.

Mohr, C.W., 2010. Understanding geochemical and hydrological process governing the mobilization of P from terrestrial to aquatic environment. Master Thesis, University of Oslo, Blindern, Norway.

Monteith, D.T., Stoddard, J.L., Evans, C.D., de Wit, H.A., Forsius, M., Hogasen, T., Wilander, A., Skjelkvale, B.L., Jeffries, D.S., Vuorenmaa, J., Keller, B., Kopacek, J., Vesely, J., 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature 450, 537-540.

Moore, A., Reddy, K.R., 1994. Role of Eh and pH on phosphorus geochemistry in sediments of Lake Okeechobee, Florida. Journal of Environmental Quality 23, 955-964.

Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27, 31-36.

Nislow, K.H., Armstrong, J.D., McKelvey, S., 2004. Phosphorus flux due to Atlantic salmon (Salmo salar) in an oligotrophic upland stream: effects of management and demography. Canadian Journal of Fisheries and Aquatic Sciences 61, 2401-2410.

Norwegian Forest and Landscape Institute, 2011. Skog landscape, http://www.skogoglandskap.no/en/

NS4725, 1984. Vannundersøkelse - Bestemmelse av totalfosfor - Oppslutning med peroksodisulfat

NS-EN872, 2005. Water quality-determination of suspended solids, method by filtration through glass fibre filters.

NS-EN-ISO15691-1, 2004. Water quality-Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA). Method by flow injection analysis (FIA).

O'Reilly, C., Magette, W., Daly, K., Carton, O., Dunne, E., Reddy, K., 2005. Soil hydrology as a factor in diffuse phosphorus pollution. In: International symposium on' nutrient management in agricultural watersheds: A wetlands solution", Wexford, Ireland., pp. 18-22.

OECD, 2008. Environmental performance of agriculture in OECD (organization for economic commission and devolpment) countries since 1990, Paris, France.

Øgaard, A.F., Bechmann, M., 2010. Integrated project in the region of lake Vansjø, Norway, for reduced phosphorus runoff from vegetable fields. Acta Horticulturae 5, 153-155.

Oliver, B.G., Thurman, E.M., Malcolm, R.L., 1983. The contribution of humic substances to the acidity of colored natural waters. Geochimica et Cosmochimica Acta 47, 2031-2035.

Opland, K., 2011. Processes governing mobility and transport of phosphorus from agricultural soil: Master Thesis, University of Oslo, Blindern, Norway.

Øygarden, L., 2000. Soil erosion in small agricultural catchments, south-eastern Norway: Doctor scientiarum thesis. Agricultural University of Norway, Department of Soil and Water Sciences

Parekh, N.A., 2012. Assessment of phosphorus fractions in streams draining different land use and development of new monitoring method: Master Thesis, University of Oslo, Blindern, Norway.

Patrick, W.H., Khalid, R.A., 1974. Phosphate release and sorption by soils and sediments: Effect of aerobic and anaerobic conditions. Science 186, 53-55.

Pettersson, K., 1998. Mechanisms for internal loading of phosphorus in lakes. Hydrobiologia 373-374, 21-25.

Piccolo, A., 1996. Humic Substances in Terrestrial Ecosystems. Elsevier Science.

Pionke, H.B., Gburek W.J., Schnabel R.R., Sharpley A.N., Elwinger G.F., 1999. Seasonal flow, nutrient concentrations and loading patterns in stream flow draining an agricultural hill-land watershed. Journal of hydrology (Amsterdam) 220, 62-73.

Reddy, K.R., DeLaune, R.D., 2008. Biogeochemistry of wetlands: Science and applications. CRC Press.

Rhue, R.D., Harris, R.G., 1999. Phosphorus sorption/desorption reactions in soils and sediments. In Reddy, K.R., G.A. O’Connor, and C.L. Schleske (eds.). Phosphorus biogeochemistry in subtropical ecosystems. pp 187-206. Lewis Publishers, Boca Raton.

Roden, E., Edmonds, J., 1997. Phosphate mobilization in iron-rich anaerobic sediments: Microbial Fe(III) oxide reduction versus iron-sulfide formation Archiv fuer Hydrobiologie 139, 347-378.

Rouco, M., López-Rodas, V., Flores-Moya, A., Costas, E., 2011. Evolutionary changes in growth rate and toxin production in the cyanobacterium; Microcystis aeruginosa under a scenario of eutrophication and temperature increase. Microbial Ecology 62, 265-273.

Ruikai, X., Vogt, R.D., Lukawska-Matuszewska, K., 2012. Report on Survey of Phosphorus in sediments at Sæbyvannet, (Department of chemistry University of Oslo).

Rummukainen, M., Raisanen J., Bjørge D., Christensen J.H., Christensen O.B., Iversen T., Jylha K., Olafsson H., Tuomenvirta H., 2003. Regional climate scenarios for use in Nordic water resources studies. Nordic hydrology 34, 399-412.

Ryan, M., 1998. Water movement in a structured soil in the south-east of Ireland: preliminary evidence for preferential flow. Irish Geography 31, 124-137.

Scalenghe, R., Edwards, A., Ajmone Marsan, F., Barberis, E., 2002. The effect of reducing conditions on the solubility of phosphorus in a diverse range of European agricultural soils. European journal of soil science 53, 439-447.

Schnitzer, M., 1978. Humic substances (Chapter 1):Chemistry and Reactions In: Schnitzer, M., Khan, S.U. (Eds.) Developments in Soil Science. Elsevier, pp. 1-64.

Sharpley, A., 1985. Depth of surface soil-runoff Interaction as affected by rainfall, soil slope, and management. Soil Science Society America Journal 49, 1010-1015.

Sharpley, A., Ahuja, L., Yamamoto, M., Menzel, R., 1981. The kinetics of phosphorus desorption from soil. Soil Science Society America Journal 45, 493-496.

Sharpley, A., Daniel, T., Edwards, D., 1993. Phosphorus movement in the landscape. Journal of production agriculture 6, 492-500.

Sharpley, A., Daniel, T., Sims, J., Lemunyon, J., Stevens, R., Parry, R., 2003. Agricultural phosphorus and eutrophication. Agricultural Research Service.

Sharpley, A., Kleinman, P., 2003. Effect of rainfall simulator and plot scale on overland flow and phosphorus transport. Journal of environmental quality 32, 2172-2179.

Sharpley, A.N., Chapra, S., Wedepohl, R., Sims, J., Daniel, T., Reddy, K., 1994. Managing agricultural phosphorus for protection of surface waters:Issues and options. Journal of Environmental Quality 23, 437-451.

Sharpley, A.N., McDowell, R.W., Kleinman, P.J., 2001. Phosphorus loss from land to water: integrating agricultural and environmental management. Plant and Soil 237, 287-307.

Sharpley, A.N., Smith, S.J., 1994. Wheat tillage and water quality in the Southern plains. Soil and Tillage Research 30, 33-48.

Sharpley, A.N., Syers, J.K., 1979. Loss of nitrogen and phosphorus in tile drainage as influenced by urea application and grazing animals. New Zealand Journal of Agricultural Research 22, 127-131.

Shekobe, M.R., 2012. Effects of reduction in acid rain on phosphate loss - Mixing of Al rich water from upstream acid forest soils with phosphate rich runoff from agricultural soils. Master Thesis, University of Oslo, Blindern, Norway. .

Shigaki, F., Sharpley Andrew N., Prochnow Luis Ignacio, 2007. Rainfall intensity and phosphorus source effects on phosphorus transport in surface runoff from soil trays. Science of The Total Environment 373, 334-343.

Sims, J.T., Edwards A.C., Schoumans O.F., Simard R.R., 2000. Integrating soil phosphorus testing into environmentally based agricultural management practices. Journal of Environmental Quality 29, 60-71.

Skarbøvik, E., Bechmann, M., 2010. Some characteristics of the Vansjø-Hobøl catchment. Bioforsk Report 5.

Skarbøvik, E., Bechmann M., Rohrlock T., Haande S., 2011. Overvåking Vansjø/Morsa 2009-2010. Resultater fra overvåking av innsjøer, elver og bekker i perioden oktober 2009-oktober 2010 [in Norwegian] Bioforsk Jorg og Miljø 6.

Skjelkvåle, B., Wright, R.F., Henriksen, A., 1998. Norwegian lakes show widespread recovery from acidification; results from national surveys of lakewater chemistry 1986-1997. Hydrology and Earth System Sciences Discussions 2, 555-562.

Smayda, T.J., 2008. Complexity in the eutrophication–harmful algal bloom relationship, with comment on the importance of grazing. Harmful Algae 8, 140-151.

Smith, V.H., 2003. Eutrophication of freshwater and coastal marine ecosystems a global problem. Environmental Science and Pollution Research 10, 126-139.

Smith, V.H., Tilman G.D., Nekola J.C., 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. Environmental Pollution 100, 179-196.

Solheim, A.L., Vagstad, N., Kraft, P., Løvstad, Ø., Skoglund, S., Turtumøygard, S., Selvik, J.-R., 2001. Tiltaksanalyse for Morsa (Vansjø-Hobøl-vassdraget)-Sluttrapport. [In Norwegian]. NIVA Rapport. Available at:.

Spivakov, B.Y., Maryutina T.A., Muntau H., 1999. Phosphorus speciation in water and sediments. Pure Applied Chemistry 71, 2161-2176.

Sporre-Moeny, J., Lanyon, L., Sharpley, A., 2004. Low intensity sprinkler for evaluating phosphorus transport from different landscape positions. Applied engineering in agriculture 20, 599−604.

Syversen, N., 2002. Cold-climate vegetative buffer zones as filters for surface agricultural runoff: Retention of soil particles, phosphorus and nitrogen. Agricultural University of Norway, Department of Soil and Water Sciences

Thuen, G., Buer, J., 2003. Handlingsplan for Morsa 2002-2005 ("Action Plan for Morsa"). Morsa Prosjektet.

Thurman, E.M., 1985. Organic geochemistry of natural waters. M. Nijhoff, Dordrecht.

Uhlen, G., 1989. Surface runoff losses of phosphorus and other nutrient elements from fertilized grassland. Norwegian Journal of Agricultural Sciences 3, 47-55.

Ulén, B., 1997. Nutrient losses by surface run-off from soils with winter cover crops and spring-ploughed soils in the south of Sweden. Soil and Tillage Research 44, 165-177.

Ulén, B., Aronsson H., Bechmann M., Krogstad T., ØYgarden L., Stenberg M., 2010. Soil tillage methods to control phosphorus loss and potential side-effects: a Scandinavian review. Soil Use and Management 26, 94-107.

Ulen, B., Bechmann, M., Ister J., Jarvie H.P., Tunney H., 2007. Agriculture as a phosphorus source for eutrophication in the north-west European countries, Norway, Sweden, United Kingdom and Ireland: a review. Soil Use and Management 23, 5-15.

UN-ECE, 1999. The 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone. Document ECE/EB.AIR/67, United Nations Economic Commission for Europe, New York and Geneva.

vanLoon, G.W., Duffy, S.J., 2007. Environmental chemistry a global perspective, 2nd ed. Edition. New York, Oxford University Press.

Vogt, R.D., 2008. Phosphorus fractionation (unpublished work), Department of Chemistry, UiO, Oslo.

Walling, D., Collins, A., Stroud, R., 2008. Tracing suspended sediment and particulate phosphorus sources in catchments. Journal of Hydrology 350, 274-289.

Withers, P., Jarvie, H., 2008. Delivery and cycling of phosphorus in rivers: A review. Science of The Total Environment 400, 379-395.

Withers, P.J.A., Haygarth, P.M., 2007. Agriculture, phosphorus and eutrophication: An European perspective. Soil Use and Management 23, 1-4.

Wright, R.F., Lotse, E., Semb, A., 1993. RAIN Project: Results after 8 Years of Experimentally Reduced Acid Deposition to a Whole Catchment. Canadian Journal of Fisheries and Aquatic Sciences 50, 258-268.

Zhang, G.-H., Liu, G.-B., Wang, G.-L., Wang, Y.-X., 2011. Effects of vegetation cover and rainfall intensity on sediment-bound nutrient loss, size composition and volume fractal dimension of sediment particles. Pedosphere 21, 676-684.

List of appendices

Appendix

Appendix-A: Types of water

Table A-1. Types of water used in the preparation of reagents and standards which describes types of ion-exchanged water according to the Millipore purification specifications.

Parameter/criteria	Type I water (ultra pure)	Type II water
Resistivity MΩ .cm at 25 °C	>18	>1
TOC(ppb)	< 10	<50
Sodium (ppb)	<1	<5
Chloride (ppb)	<1	<5
Silica (ppb)	<3	<3
Bacteria (CFu/ml)	<10	<100

Appendix-B: Equipments used in the physico-chemical sample measurement

B- 1. pH meter

Orion Research, Expandable ion Analyzer EA920 with 8102 ROSS® head electrode.

B- 2. Electrical conductivity and temperature

Five Go™ (FG3) portable manual operated devices equipped with temperature sensor. Instrument from METTLER-TOLEDO.

B- 3. Alkalinity meter

A Titrino 716 DMS instrument from Metrohm AG.

B- 4. UV-Vis

Digital double beam spectroscopy UV-150-2 instrument with wavelength range of 200-1000nm. Instrument is equipped with Czerny-Turner type grating monochromator and Silicon photo cell detector. Product of SHEMDZU Corporation.

Appendix-C: Standard determination of total suspended solids (TSS)

Standard operating procedure (SOP) is based on the Norwegian Standard NS-EN 872. Glass micro-fiber filters of the type *Whatman 1825-047.47mm* for filtration were used. During each weighing, the *Reference Filter* also weighed.

$$\mathbf{TSS} = \frac{\mathbf{M1-Mo}}{\mathbf{V}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ Equation 9}$$

M_1=*mass of filter paper+ mass of retained solid matter*
M_O = *mass of filter paper*
TSS =Total suspended solid particulate mater
V = volume of sample filtered

Appendix-D: Total organic carbon (TOC) analyzer

D- 1. Instrumentation and calibration solution preparation

All glass equipments were cleaned and baked at 500˚C for 4-5hrs. Potassium hydrogen phthalate ($HOOCC_6H_4COOK$) was used as a calibration solution after dried for 1h at 110˚C, and dissolved in Type 1 water. The following calibration solution were prepared; 0, 5, 10, 50, and 20 mg/l C. The limit of detection (LOD) of the TOC-analyzer was determined to be 0.80 mg/l C at the time of analysis. This was calculated from 3 X standard deviation of 10 repeated measurements of blank sample (Type I water).

D- 2. Instrumental settings

Table D-1. Instrumental settings applied for the TOC-analyzer

Parameters	Setting
Pressure	5bar (500kpa)
Flow rate	150ml/min
Number of injections	3
Max. number of injections	5
Min. number of injections	3
Number of washes	4
Sparage time	1min
Type of catalyst	P/N, 638-920269-01

Appendix-E: Ion Chromatography (IC)

E- 1. Instrumentation and calibration solution preparation

Instrument: ICS-2000, from Dionex Corporation, equipped with chemical suppression and anion self regenerating.

Calibration solutions for IC were prepared from mineral salts of NaF, NaCl, $NaNO_3$, $NaSO_4$ and KH_2PO_4 which dried first at a temperature of 100°C for ≥2hrs (cooled in hexicator) and by dissolving in type I water. Final concentrations of the calibration solutions were then; 0, 1, 10, 20, 40, 50 mg/l of NO_3^-, Cl^-, SO_4^{2-} and 0, 0.1, 0.3, 0.5 and 0.7mg/l of F^-.

Table E-1. Instrumental settings for the IC.

Parameter	Setting
Flow rate	1.0mL/min
Temperature	30 °C
Applied current	5A
Injection volume	5µL
Number of replicate	3
Eluent storage solution	Methanesulfonic acid

E- 2. Limit of detection (LOD) for IC

Table E-2. Limit of detection (LOD) for IC calculated in mg/l

Anion	SO_4^{2-}	NO_3^-	Cl^-	F^-
Detection limit (LOD)	0.021	0.054	0.014	0.0064

LOD determined as 3 X standard deviation of 10 subsequent measurements of blank sample using the IC.

Appendix-F: Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

F- 1. Preparation of calibration standards for ICP-OES

Calibration standard solutions were prepared from an analytical grade 1000±5 mg/l multi-element standard stock solution (Merck, Darmstadt, Germany). Multi-element standard solution UN 2031, 1000mg/l stock solution which contains; Ca, Mg, Na and K standards were used for the preparation which was carried out in the following ways. Equation used in preparing standards was dilution method with type-I water, that is $C_1V_1 = C_2V_2$. The standard solutions and samples were prepared to contain 0.3% (v/v) HNO_3 matrix. Cesium (Cs; 1mg/l) was also added as internal ionization standard solution. The standard calibration method was used, with matrix matching of the standards and quadratic curves were used for Ca, Mg, K and Na.

Table F-1. Standard solutions prepared for major cations (mg/l)

	Prepared standards			
Number	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}
1	1.0	0.5	1.0	0.5
2	2.0	1.0	2.0	1.0
3	5.0	2.5	5.0	2.5
4	10.0	5.0	10.0	5.0
5	25.0	10.0	20.0	10.0
6	60.0	20.0	40.0	20.0

The instrument is calibrated by the standard solutions and samples were analyzed accordingly.

F- 2. Instrumental conditions and procedures used during analysis by ICP-OES

Varian Vista AX CCD simultaneous axial view ICP-OES from Varian Ltd, Australia. Instrument is equipped with Echelle polychromator optical operating system. The following default operating conditions of the spectrometer were used for the analysis of the selected elements. Analysis was done at the department of chemistry, UiO.

Table F-2. ICP-OES operating conditions

Instrument Parameter	Value
RF power	1.20 kW
Plasma gas flow rate	15 l/min
Auxiliary gas flow rate	1.5 l/min
Nebulizer Argon flow	0.75 l/min
Replicate reading time	1.00 s
Instrument stabilization delay	15 s
Sample uptake delay	30 s
Sample flow rate	1.50 ml/min
Rinsing time	30s
Replicates	10

F- 3. Wavelength selection

The selection was done using ISO 22036 (2008) as guideline. Two alternative wavelengths were first selected for each element. Based on the intensity and potential spectral interferences of the element at particular wavelength the computer software provides alternative recommended wavelengths for each element and those lines with high intensity and with low spectral interferences were selected. Finally one wavelength was chosen based on the limit of detection.

Table F-3. The selected wave length of the cations analyzed

Element	Wave length (nm)
Ca^{2+}	396.847
Mg^{2+}	279.553
Na^{+}	588.995
K^{+}	766.491

F- 4. Statistical formulas for limit of detection (LOD) of all measurements

The limit of detection (LOD) is the lowest possible concentration of an element in a blank that is determined to be statistically different from a blank. LOD of each element in table 3 is found by three times the standard deviation of concentrations of the method blank.

LOD= 3*SD(blank)

Average $(X_{Average})=\Sigma X_i/n$

Standard deviation $(SD)=\sqrt{}\ [\Sigma X_i - X_{average})^2/\ (n-1)]$

Relative RSD (%) = $(SD/\ X_{average})*100$

Where SD blank is standard deviation of the blank sample (mg/L),

n=sample size

Table F-4. LOD calculated for ICP-OES results in mg/l

Cation	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}
LOD	0.08	0.08	0.05	0.05

LOD determined as 3x standard deviation of 10 subsequent measurements of blank sample (type 1 water) using the ICP-OES during time of analysis.

Appendix-G. Results

G- 1. Stream water results

Table G-1. Major cations and anions of stream water

Site	**Median concentration of cations and anions (µeq/l)**						
	Ca^{2+}	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**SO_4^{2-}**	**NO_3^{-}**	**Cl^{-}**
Støa1	1602	482	394	173	755	109	284
Hug	1093	444	268	144	818	90	361
Dalen	62	37	150	13.4	31	2.6	141

Table G-2. pH of the studied streams.

	pH of sampling sites			
	Median	Mean	Q3 (75%)	Q1 (25%)
Støa1	7.3	7.3	6.8	7.5
Hug	7.1	7.1	7.2	6.5
Dalen	4.6	4.6	4.6	4.2

Q3 (75%) =75th percentile; Q1 (25%) =25% percentile

Table G-3. Concentration of DOC in mg/l in the studied streams.

DOC concentration				
	Median	Mean	Q3 (75%)	Q1 (25%)
Støa1	10.7	10.1	12.4	5.1
Hug	15.0	15.0	7.0	6.4
Dalen	32.7	32.4	27.5	19.1

Q3=75th percentile; Q1=25th percentile

Table G-4. Alkalinity of the three sampling streams in µeq/l.

Streams	Median	Mean	Q3 (75%)	Q1 (25%)	No of samples
Staø1	1597	1566	1991	885	76
Hug	613	687	845	485	65

Q3 (75%) =75th percentile; Q1 (25%) =25th percentile

Table G-5. Conductivity of the three sampling streams in µS/cm

Stream	Mean	Median
Støa1	447.1	397.0
Hug	321.4	296.2
Dalen	52.3	46.6

Table G-6. Stream water tot-P (µg/l) determined using CNP autoanalyzer.

	Tot-P			
	Median (Tot-P)	Mean (tot-P)	Q3 (75%)	Q1 (25%)
Støa1	113.0	145.9	152.1	64.8
Hug	45.5	93.3	80.9	30.5
Dalen	8.4	23.1	18.2	7.2

	Tot-P			
	Median (Tot-P)	PP	PO_4-P	DOM-P
Støa1	113.0	66.44	44.2	6.37
Hug	45.5	27.71	10.10	8.62
Dalen	8.4	1.01	2.13	5.26

Q3 (75%) = 75th percentile, Q1 (25%) =25th percentile

Table G-7. Stream water P-fractions distribution (%) calculated from table G-6.

	Tot-P			
	Median(Tot-P)	PP%	PO_4-P%	DOM-P%
Støa1	113.0	55	39	6
Hug	45.5	59	22	19
Dalen	8.4	12	25	63

Table G-8. Tot-P during the different flow events.

	Tot-P (µg/l; Mean)			Tot-P (µg/l; Median)		
Site	Spring (Evans et al.)	Summer (June)	Autumn (October)	Spring (Evans et al.)	Summer (June)	Autumn (October)
Støa1	225.5	123.2	229.2	200.5	111.9	210.5
Hug	128.2	90.0	193.4	88.4	35.5	80.2
Støa1 (%)	39.0	21.3	39.7	38.3	21.4	40.3
Hug (%)	31.2	21.9	46.9	43.3	17.4	39.3

N.B. Samples are only for 2011 for this table

Table G-9. TSS of the three stream waters during high and low flow events.

	Median (high flow)	Median (low flow)
Stream	TSS (mg/l)	TSS (mg/l)
Støa1	27.8	12.99
Hug	32.6	12.61
Dalen	12.2	7.11

Table G-10. Ratio of tot-P to TSS (X1000) in the three sampling streams.

	Median			Mean		
Stream	Tot-P(10^-3)	TSS	Tot-P/TSS (‰)	Tot-P	TSS	Tot-P/TSS (‰)
Støa1	113	12.4	**9.11**	153	12.77	**11.98**
Hug	46	13.7	**3.38**	95	14.095	**6.74**
Dalen	8.3	5.17	**1.61**	23	5.64	**4.08**

N.B. Tot-P and TSS in mg/l, percent is in 1000

Table G-11. P-fractions in the conservative mixing of stream waters and measured values (Figure 22 and 23)

	DOM-P	PO4-P	PP	
Calculated values (Conservative mix water of Dalen+Støa1)	9.48	17.74	23.74	(n=161)
Measured values (Absolute vales at Hug)	8.62	10.10	26.74	(n=161)

	DOC (mg/l)	
Calculated values (Conservative mix water of Dalen+Støa1)	16.60	(n=29)
Measured values (Absolute vales at Hug)	14.70	(n=29)

G- 2. Dalen soil water results

Table G-12. Absolute and percentage distribution of P fractions in Dalen soil water samples (+horizons).

Plot	Horizon	PO4-P (µg/l)	DOM-P (µg/l)	%PO4-P	%DOM-P
Ridge	TF	118	22.2	84.2	15.8
	ZT	33	35.0	48.5	51.5
	O	1.5	12.5	10.7	89.3
	E	2.0	9.7	17.1	82.9
	B	0.9	2.1	30.0	70.0
	C1	0.6	1.2	33.3	66.7
	C2	0.5	2.7	15.6	84.4
Slope	TF	307	50	86.0	14.0
	ZT	27	49	35.5	64.5
	O	0.6	3.2	15.8	84.2
	AE	0.8	2.7	22.9	77.1
	B1	0.6	2.9	17.1	82.9
	B2	0.7	3.7	15.9	84.1
	C	1.5	3.0	33.3	66.7
Valley bottom	TF	129	20	86.6	13.4
	ZT	27	49	35.5	64.5
	O	0.9	5.4	14.3	85.7
	A	0.7	4.0	14.9	85.1
	B1	1.0	3.9	20.4	79.6
	B2	1.6	2.1	43.2	56.8
	C	1.0	4.2	19.2	80.8

Table G-13. Concentration of major cations and anions in Dalen soil water (μeq/l).

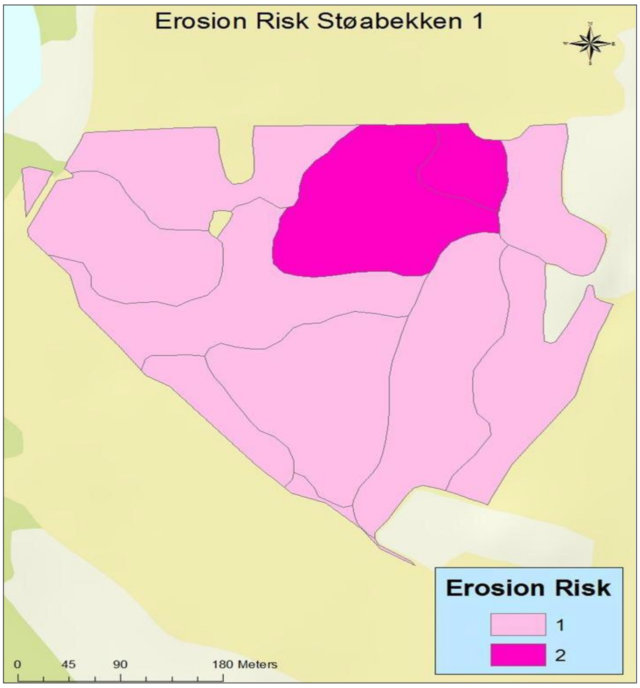
		Cl-	SO42-	NO3-	K+	Na+	Ca2+	Mg2+
Ridge	TF	90.7	25.5	2.7	77.1	87.4	64.5	37.0
	ZT	117.0	25.4	1.9	57.1	135.9	60.0	61.2
	O	164.2	23.1	1.3	18	120.1	73.0	108.2
	E	223.9	115.6	2.6	36.3	148.4	52.3	57.4
	B	148.6	59.7	1.3	26.2	174.4	10.2	14.6
	C1	95.6	61.9	0.9	26.5	186.0	8.5	11.0
	C2	95.6	61.9	0.9	29.2	195.5	14.4	23.8
Slope	TF	145.3	40.5	54.7	75.4	150.2	67.4	60.1
	ZT	311.2	70.4	16.4	76.1	250.5	98.8	115.1
	O	280.8	66.0	3.3	21.6	295.2	32.9	53.8
	AE	293.3	74.3	1.5	26.3	284.0	96.4	51.5
	B1	143.3	86.8	0.9	49.1	257..	29.4	38.2
	B2	226.4	75.4	0.8	31.1	233.8	139.3	74.6
	C	228.7	69.1	0.8	28.6	251	132.0	74.6
Valley bottom	TF	55.3	27.4	35.9	53.9	69.1	169.5	43.6
	ZT	55.3	27.4	35.9	14.8	80.4	98.9	58.0
	O	127.7	85.7	45.2	35.8	212.9	45.6	79.6
	A	164.9	131.8	1.3	28	238.9	110.3	141.3
	B1	165.2	121.7	1.1	42.5	242.5	129.2	154.9
	B2	144.7	90.5	2.4	41.2	439.0	464.0	496.0
	C	164.9	131.8	1.5	54.5	326.0	304.5	301.5

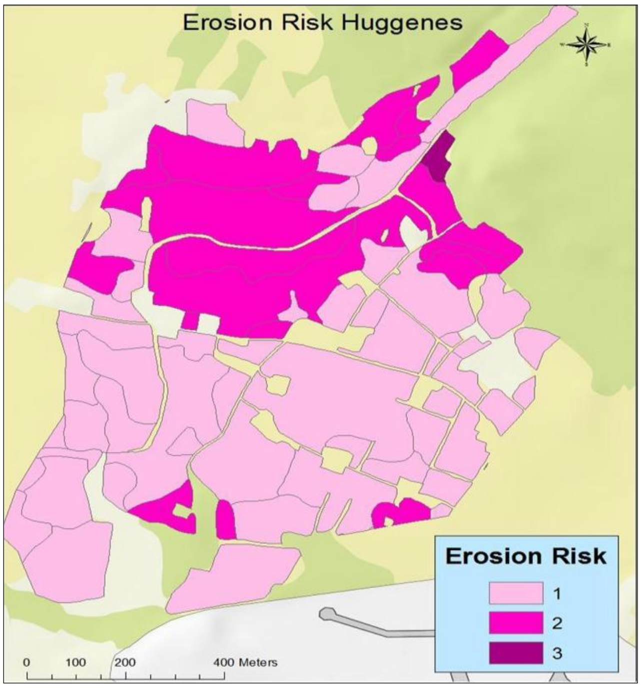
Appendix-H: Land use and erosion risk

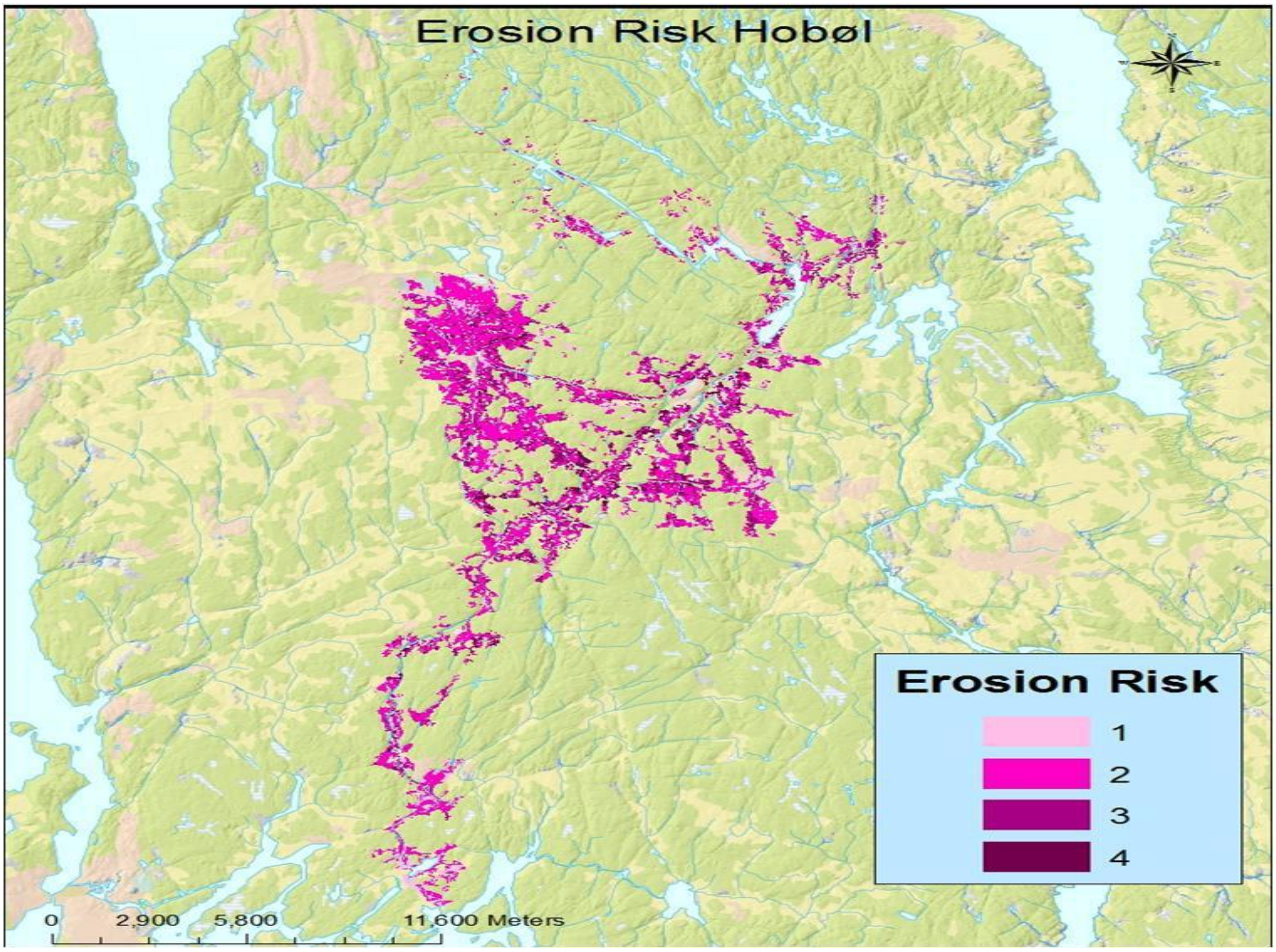
Table H-1. Land use distribution of the three sites (%).

Land use %	Hug	Støa1	Dalen
Agriculture	58.6	86.0	0.0
Forest	28.1	0.0	76.6
Forest and Bogs	28.9	0.0	100.0
Open areas	7.1	12.2	0.0
Transport	1.2	0.0	0.0

H-1: Erosion risk map







Appendix-I: Quaternary deposit types

Table I-1. Percentage distribution of the quaternary deposit types of the streams

Deposit type	Støa1	Hug	Dalen
Bare mountain	5.5	13.4	50.1
Organic soil (bogs and peat)	0.0	0.0	14.6
Sea and fjord deposits, continuous cover	0.0	17.2	0.0
Sea, fjord and beach deposits, discontinues.	80.2	15.4	12.9
Thin humic cover over mountain	0.0	4.3	22.4
Deposits under water, unspecified	0.0	0.0	0.0
Filling material (anthropogenic origin)	0.0	0.0	0.0
Glacial stream deposits	0.0	0.0	0.0
Landslide material, continuous cover	0.0	0.0	0.0
Marine beach deposits, continuous cover	14.3	49.8	0.0
Moraine deposits, continuous cover	0.0	0.0	0.0
Moraine deposits, un continuous cover	0.0	0.0	0.0
Stream and river deposits	0.0	0.0	0.0
Margin moraine, lateral moraine	0.0	0.0	0.0

Appendix- J: Pearson correlation coefficient

	Støa1																				
Hug	Order																				
Order	pH	Runoff	TSS	Tot-P	PP	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	SO4^{2-}	NO$_3$-	Cl$^-$	Agric	H$^+$	EC	HCO$_3^-$	Alk	DOM-P	PO$_4$-P	Forest	DOC
pH		**0**.248 0.481	-0.115 0.673	0.599 0.075	0.460 0.330	0.295 0.441	-0.211 0.441	-0.609 0.586	-0.322 0.082	-0.453 0.398	-0.449 0.211	-0.301 0.431	0.522 0.135	0.519 0.152	0.582 0.312	-0.585 0.771	0.923 0.028	0.784 0.006	0.301 0.444	**-0.768** 0.021	0.953 0.000
Runoff	0.074 0.851		0.685 0.010	**0.881** 0.001	0.035 0.929	-0.331 0.384	-0.254 0.509	-0.538 0.135	0.023 0.953	-0.454 0.219	-0.361 0.341	-0.484 0.187	-0.102 0.794	0.628 0.07	0.594 0.230	0.443 0.089	0.038 0.923	0.099 0.801	0.22 0.569	0.187 0.643	-0.197 0.611
TSS	-0.374 0.322	0.458 0.128		**0.877** 0.001	0.688 0.007	**-0.704** 0.034	-0.069 0.861	-0.522 0.150	0.455 0.218	0.213 0.569	-0.281 0.465	-0.154 0.693	**0.557** 0.119	-0.252 0.513	0.436 0.065	-0.307 0.567	-0.532 0.141	**-0.747** 0.021	0.456 0.217	0.621 0.236	0.153 0.694
Tot-P	0.511 0.098	**0.783** 0.000	**0.778** 0.008		0.914 0.000	-0.541 0.132	0.136 0.885	0.321 0.723	0.443 0.652	-0.134 0.730	-0.225 0.560	0.150 0.701	0.751 0.027	0.342 0.367	-0.123 0.871	-0.135 0.991	0.503 0.168	0.439 0.301	0.921 0.000	0.035 0.564	**0.752** 0.019
PP	0.460 0.330	**0.813** 0.008	0.457 0.122	0.914 0.000		0.458 0.441	0.208 0.783	0.456 0.563	0.827 0.005	0.499 0.687	-0.342 0.368	0.432 0.246	0.877 0.003	0.175 0.653	-0.351 0.354	-0.491 0.179	0.490 0.149	-0.594 0.091	0.683 0.023	-0.607 0.113	-0.250 0.516
Ca^{2+}	-0.230 0.552	**-0.705** 0.034	0.015 0.969	0.393 0.295	0.313 0.412		**0.975** 0.012	0.456 0.781	0.564 0.342	0.666 0.050	0.015 0.969	0.016 0.888	0.238 0.661	0.177 0.561	0.210 0.588	0.773 0.117	**0.821** 0.002	-0.136 0.727	-0.211 0.585	0.468 0.204	0.081 0.837
Mg^{2+}	0.071 0.855	-0.027 0.945	0.336 0.377	0.150 0.700	0.837 0.005	**0.875** 0.000		0.150 0.700	**0.837** 0.005	0.297 0.437	0.282 0.462	0.016 0.967	**0.797** 0.011	0.211 0.754	0.663 0.006	0.287 0.666	0.441 0.345	-0.264 0.552	0.021 0.774	0.404 0.281	-0.369 0.329
Na$^+$	0.054 0.890	**-0.809** 0.008	0.131 0.006	0.017 0.966	-0.367 0.332	0.702 0.008	0.661 0.018		0.441 0.231	0.168 0.666	-0.399 0.287	-0.662 0.053	0.415 0.267	0.078 0.856	0.373 0.362	-0.112 0.882	-0.128 0.783	-0.065 0.623	-0.210 0.711	0.543 0.083	-0.338 0.374
K$^+$	0.393 0.295	0.219 0.572	-0.249 0.519	0.225 0.561	0.798 0.002	0.588 0.078	0.656 0.061	0.112 0.656		0.288 0.452	**0.827** 0.021	-0.207 0.593	0.416 0.265	0.121 0.551	0.025 0.448	0.211 0.554	0.114 0.424	-0.119 0.748	-0.203 0.883	-0.125 0.749	0.312 0.008
SO$_4^{2-}$	0.456 0.774	0.321 0.556	-0.032 0.935	0.354 0.351	**0.756** 0.018	-0.269 0.679	-0.273 0.921	-0.157 0.457	-0.079 0.875		0.332 0.383	-0.501 0.171	0.357 0.206	- 0.351 0.268	-0.195 0.624	0.369 0.200	0.246 0.447	-0.297 0.437	-0.212 0.584	-0.125 0.749	-0.132 0.735
NO$_3^-$	0.419 0.261	0.229 0.462	0.365 0.425	0.125 0.456	0.282 0.462	0.128 0.875	0.165 0.334	-0.159 0.787	**0.718** 0.003	0.363 0.722		-0.527 0.145	0.551 0.067	-0.213 0.161	0.056 0.889	0.014 0.981	-0.217 0.652	-0.229 0.711	-0.198 0.677	**-0.492** 0.179	0.196 0.614
Cl-	0.644 0.035	0.494 0.175	0.121 0.576	0.601 0.037	-0.079 0.840	-0.159 0.921	-0.147 0.947	-0.023 0.950	-0.068 0.856	0.932 0.001	0.403 0.236		-0.345 0.363	-0.498 0.172	-0.088 0.900	0.221 0.660	-0.371 0.375	-0.447 0.400	-0.132 0.483	0.454 0.220	0.313 0.412
Agric	0.468 0.152	-0.125 0.749	-0.505 0.166	0.699 0.039	0.877 0.003	**0.960** 0.000	0.153 0.694	-0.313 0.412	-0.002 0.996	0.464 0.209	0.433 0.382	-0.089 0.823		0.798 0.005	-0.052 0.899	-0.027 0.946	**0.656** 0.017	0.131 0.972	**0.664** 0.017	-0.302 0.430	**-0.559** 0.125
H$^+$	-0.265 0.606	0.508 0.083	0.599 0.088	0.469 0.203	0.457 0.569	0.214 0.581	-0.279 0.466	-0.342 0.368	-0.241 0.533	-0.386 0.305	-0.365 0.113	-0.544 0.171	0.798 0.006		0.687 0.041	**0.724** 0.027	0.018 0.884	0.117 0.894	0.311 0.444	**0.651** 0.101	**0.815** 0.004
EC	0.143 0.714	0.818 0.008	0.181 0.641	0.222 0.565	-0.434 0.243	0.075 0.859	-0.073 0.853	0.099 0.799	-0.187 0.630	-0.222 0.567	0.206 0.595	-0.048 0.902	-0.248 0.520	0.547 0.127		-0.550 0.024	**-0.712** 0.226	-0.102 0.991	-0.115 0.768	-0.162 0.678	-0.226 0.559
HCO$_3^-$	**0.708** 0.033	0.472 0.199	**0.669** 0.049	0.085 0.829	0.151 0.698	0.341 0.369	-0.406 0.278	0.247 0.707	0.332 0.589	**0.487** 0.521	0.223 0.576	0.413 0.713	**0.556** 0.062	0.663 0.065	0.199 0.608		-0.282 0.462	-0.114 0.771	-0.203 0.601	-0.075 0.847	-0.262 0.497
Alk	**0.869** 0.010	-0.207 0.593	0.094 0.811	0.477 0.062	0.424 0.255	0.481 0.197	0.367 0.331	0.505 0.166	-0.266 0.489	0.286 0.456	0.273 0.477	-0.328 0.389	**0.753** 0.031	0.149 0.702	**0.669** 0.049	0.685 0.042		0.419 0.261	0.331 0.153	**-0.883** 0.029	-0.069 0.861
DOM-P	-0.210 0.731	-0.689 0.04	0.117 0.764	**0.748** 0.021	0.411 0.305	0.189 0.666	0.212 0.448	0.410 0.523	0.351 0.153	0.113 0.153	-0.261 0523	-0.564 0.441	0.231 0.972	0.566 0.452	0.298 0.435	-0.323 0.397	-0.652 0.057		0.342 0.302	0.458 0.266	0.354 0.355
PO$_4$-P	0.301 0.444	0.689 0.042	0.471 0.201	0.921 0.000	0.431 0.333	0.105 0.788	0.134 0.770	-0.423 0.223	-0.190 0.477	-0.114 0.414	-0.277 0.683	-0.125 0.711	**0.664** 0.117	0.312 0.421	0.092 0.847	0.461 0.212	0.331 0.153	0.342 0.302		-0.032 0.935	0.225 0.561
Forest	**-0.681** 0.021	0.099 0.799	-0.187 0.631	-0.589 0.223	-0.607 0.113	-0.222 0.567	0.206 0.595	-0.048 0.902	0.087 0.824	-0.094 0.809	-0.655 0.056	0.558 0.118	-0.145 0.711	0.384 0.307	0.297 0.437	**-0.967** 0.000	-0.512 0.256	0.493 0.177	0.517 0.154		0.777 0.011
DOC	0.215 0.468	0.432 0.466	0.119 0.885	0.621 0.014	0.443 0.568	0.111 0.884	0.269 0.668	0.456 0.662	**-0.775** 0.014	0.220 0.479	0.219 0.572	**0.741** 0.022	**-0.521** 0.425	**0.815** 0.004	-0.249 0.519	-0.553 0.122	-0.235 0.542	0.529 0.143	-0.206 0.595	**0.785** 0.013	

Table J-2: Pearson correlation analysis among parameters of the stream waters

Order	Agriculture	Forest	Others	Al_o	Tot-P	DOC	H^+	TSS	pH
Agriculture	1								
Forest	**0.655** 0.043	1							
Others	0.451 0.211	-0.441 0.303	1						
Al_o	-0.223 0.751	0.416 0.551	0.102 0.749	1					
Tot-P	**0.757** 0.092	-0.179 0.865	0.296 0.655	0.216 0.564	1				
DOC	**-0.559** 0.006	**0.717** 0.007	0.015 0.916	**0.897** 0.000	-0.098 0.899	1			
H^+	-0.303 0.151	0.338 0.563	0.071 0.990	0.214 0.745	0.189 0.815	**0.944** 0.000	1		
TSS	**0.589** 0.029	-0.113 0.911	0.212 0.776	0.063 0.933	**0.721** 0.009	0.061 0.943	-0.112 0.885	1	
pH	**0.473** 0.229	-0.216 0.877	0.321 0.338	0.093 0.951	0.591 0.012	**0.658** 0.053	0.217 0.559	-0.231 0.873	1