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degree in chemistry

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Characterization of Forest Soils in the Morsa Watershed in order to assess the background leaching of Phosphorus to the Eutrophic Western Vansjø Lake.

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Abbreviations

Al-P	Aluminium bound phosphorus fraction
AlS	Aluminum saturation
Ali	Labile inorganic aluminium
BS	Base saturation
Ca-P	Calcium bound phosphorus
CECe	Effective cation exchange capacity
DOM	Dissolved organic matter
DOM-P	Dissolved organic bound phosphorus
DNOM	Dissolved natural organic matter
EU WFD	European union water frame work directive
EUTROPIA	Watershed Eutrophication management through system oriented process modelling of Pressures, Impacts and Abatement actions
Fe-P	Iron bound phosphorus
ICP-OES	Inductively coupled plasma optical emission spectroscopy
Inorg-P	Inorganic phosphorus
LOD	Limit of detection
LOI	Loss on ignition
OM	Organic matter
Occl-P	Occluded phosphorus
Org-P	Organic phosphorus
PCA	Principal component analysis
POM	Particulate organic matter
PSD	Particle size distribution
pH	Negative logarithm of hydrogen activities
PO_4-P	Orthophosphates determined as phosphorus
Tot-P	Total phosphorus
Sol-P	Easily soluble phosphorus (NH_4Cl-P)

Type I water	Ultra-pure water
Type II water	Pure water

ABSTRACT

This master thesis is part of the EUTROPIA project funded by Research Council of Norway (RCN) (190028/S30), which aims to obtain a better understanding of the catchment processes governing variation in levels and fluxes phosphorus. This master thesis was conducted in Morsa (Vansjø Hobøl) catchment located in south eastern part of Norway. The catchment area is pilot study area for the implementation of the EU Water Framework Directive (WFD) in Norway. This is therefore a study site where a large number of research studies have been conducted aimed at understanding the governing factors controlling the water quality, including the cause for enhanced influx of phosphorous (P) leading to eutrophication.

Since 85% of the catchment is comprised by forest this thesis has focused on the role of forest soils in providing the background P load to the lake. The aim of this study has thus been to assess the governing factors for the spatial natural variation in soil P pools, and to assess how temporal changes in the environment (deposition loading and climate) may cause changes in the leaching of P from these pools. This has been conducted through sampling of forest soils and analysis of their P pools and physiochemical characteristics. In order to capture the span in soil chemistry the soil samples were collected from different topographies (i.e. ridge, slope and the valley bottom) at sub-catchments located below and above marine limit.

A total of 83 soil samples were collected from generic soil horizons (organic soils the O horizon, mineral soils A- C horizons and soils from bogs H and C horizons) from 8 sub-catchments in the watershed, and analyzed for soil pH, organic matter content (LOI), effective cation exchange capacity (CECe) and base saturation (BS), along with the main total- and inorganic pool of phosphorus. A more detailed fractionation of the inorganic phosphorus pools as well as texture as particle size distribution (PSD) was determined on a set of selected mineral soils.

84.3% of the soils are acidic soils with an average soil pH value below 5. This is a pH in which labile inorganic aluminium (Ali) is soluble in significant concentrations. Over the past 20 – 30 years the deposition of acid rain has been reduced causing a 81% decrease in sulphate concentration in surface waters in south-eastern Norway. Consequently, the concentrations of

labile Ali have decreased from around 150 to 50 µg/L and concentrations of dissolved natural organic matter (DNOM) has more than doubled in these surface waters.

Half of the forest soil samples show base saturation (BS) below 30%. The %BS shows large spatial variation, though average values are found to be high in the forest floor O horizon (57%) and peat H horizon (54%), decrease down into the mineral soil profile to a minimum in the E horizon (20%), and then increase slightly to the B horizon (24%) and C horizon (51%). The %BS is generally found to increases down along topographic gradients, with the highest values in the clay rich soil layers (91%) under the peat bogs in the valley bottom. %BS is thus positively correlated to the fraction of fine particles clay and silt.

The CECe was found to be mainly governed by the amount of soil organic matter with increasing CECe with increasing organic matter content. Average CECe value in the organic and mineral soil horizons were 189 meq/kg and 60 meq/kg, respectively. In the mineral soils the CECe also shows a positive correlation with the amount of clay in the soils.

The levels of total- and organic phosphorus were high in the organic forest floor O-horizons. The pools of organic-phosphorus decrease while the pools of inorganic-phosphorus increases down the soil profile. Organic-P seems thus to be governed by the amount of organic matter while the pool of inorganic-P is governed by the soils content of fine particles.

A significant amount of the inorganic phosphorus fractionation in the organic horizon is comprised by easily soluble phosphorus (Sol P) (14mg/kg). This is likely due to the rapid circulation of phosphate (PO_4) in the forest. Aluminium (Al-P) and Iron (Fe-P) bound phosphorus constitute the main P fraction in especially the O and B horizons. The large Al-P and Fe-P in the O horizon is due to that Al^{3+} and Fe^{3+} forms binding bridges between the negatively charged functional groups on the organic material ($R\text{-}COO^-$, $R\text{-}O^-$ etc) and the negatively charged HPO_4^{2-} (e.g.: $R\text{-}COO^- - Al^{3+} - HPO_4^{2-}$). In addition to forming binding bridges, the Al and Fe may co-sorb phosphate when the ions are sorbed to the soil particles in the B horizon. The absolute and relative amount of calcium bound P (Ca-P) increases down through the soil profile. This reflects the increase in soil pH down through the soil profile.

1 INTRODUCTION

1.1 Cultural eutrophication and global problem

Excessive influx of nutrients, such as nitrates and phosphates, facilitate algal growth leading to plankton blooms which produce obnoxious tastes and odours in water, oxygen loss in the hypolimnion and disrupt aquatic ecology (Evangelou, 1998). In unpolluted lakes, the bioavailable levels of both nitrates and phosphates exist in small quantities and this condition limits plant growth. However, anthropogenic sources can dramatically enhance the concentration of plant nutrients in water bodies. Usually, the main limiting nutrient in freshwater lakes is phosphate. The man-made eutrophication is described as cultural eutrophication. However the condition of eutrophication happens also naturally by the aging of lakes, though this may take thousands of years. Figure 1 below shows the main sources of nutrients to surface waters.

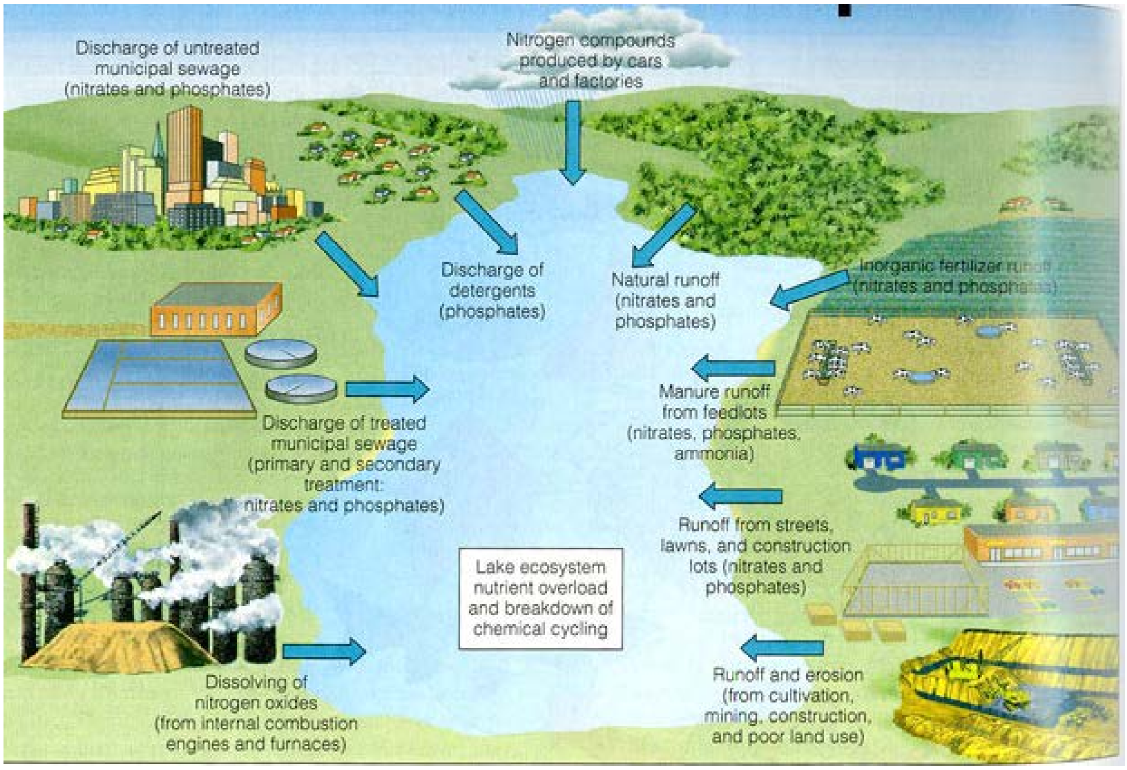

Figure 1: Allochtoneous sources of nutrients leading to cultural eutrophication[1]

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[1] Available at http://library.thinkquest.org/04oct/01590/pollution/culturaleutroph.jpg

Phosphate in the form of dissolved and suspended materials accelerate eutrophication when discharged into a water system. Human-induced diffuse source inputs of phosphate, such as excessive use of inorganic fertilizers and manure in agriculture, and point sources of untreated wastewater effluents containing detergents and sewage, may significantly increase nutrient loading into lakes. This enhances eutrophication beyond natural levels and causes deleterious changes to the natural ecosystem.

Cultural eutrophication of surface water resources is an increasing global problem causing significant environmental and societal damages. Eutrophication is becoming one of the main problems in the world, especially during the last 50 to 60 years. Many lakes and water reservoirs in most of the world are experiencing eutrophic conditions affecting aquatic ecosystem. Eutrophication problem brings both social and economic impacts due to the loss of ecosystem services. For example, where the lake serves as a raw water source of drinking water, the excessive algal bloom causes bad taste and awful odour demanding more expensive filtration and cleansing system. In addition there is a loss of recreational value as people generally prefer to be in a more clear and attractive water than in a turbid (cloudy) waters. Where there is blooming of blue-green algae swimming in the lake causes itching and may cause toxic effect. Moreover, excessive algal growth causes significant deterioration of the biota, e.g. by depletion of dissolved oxygen concentration in the hypoliminion, which render the water uninhabitable for most fauna which needs high levels of dissolved oxygen to survive. Consequently, it harms the fishing industry by decreasing the population of fish in the lake (Carpenter, 2008). Lakes and water reservoirs restored from eutrophic status to environmentally sound condition may take an extended period of time and demands considerable effort. Some of restoration strategies listed by (Leng, 2009) are:

- Hypolimnetic aeration (where water from the bottom of a lake is brought to the surface to be oxygenated then returned to the bottom)
- Bio-manipulation (the manipulation of food webs to enhance grazing on algae)

It is therefore better to have abatement actions decreasing the loading of nutrients to the surface waters. The main abatement actions commonly implemented are listed in the following chapter.

1.2 Western Vansjø and the Morsa catchment: Abatement actions

Morsa catchment (Figure 2) with an area of approximately 700 km^2 is located in south-eastern Norway, and includes large water bodies like Lake Vansjø. Lake Vansjø has two main basins; Storefjorden (eastern basin), which is the largest one with an area of 24 km^2, and Vanemfjorden (western basin), which is the smaller and shallower basin with an area of 12 km^2. Collectively, including Grepperødfjorden (located in between the two basins), this is known as lake Vansjø see Figure 2. The lake flows from Storefjorden to Vanemfjorden, which drains out into the Oslo Fjord through the Moss River (Mosseelva).

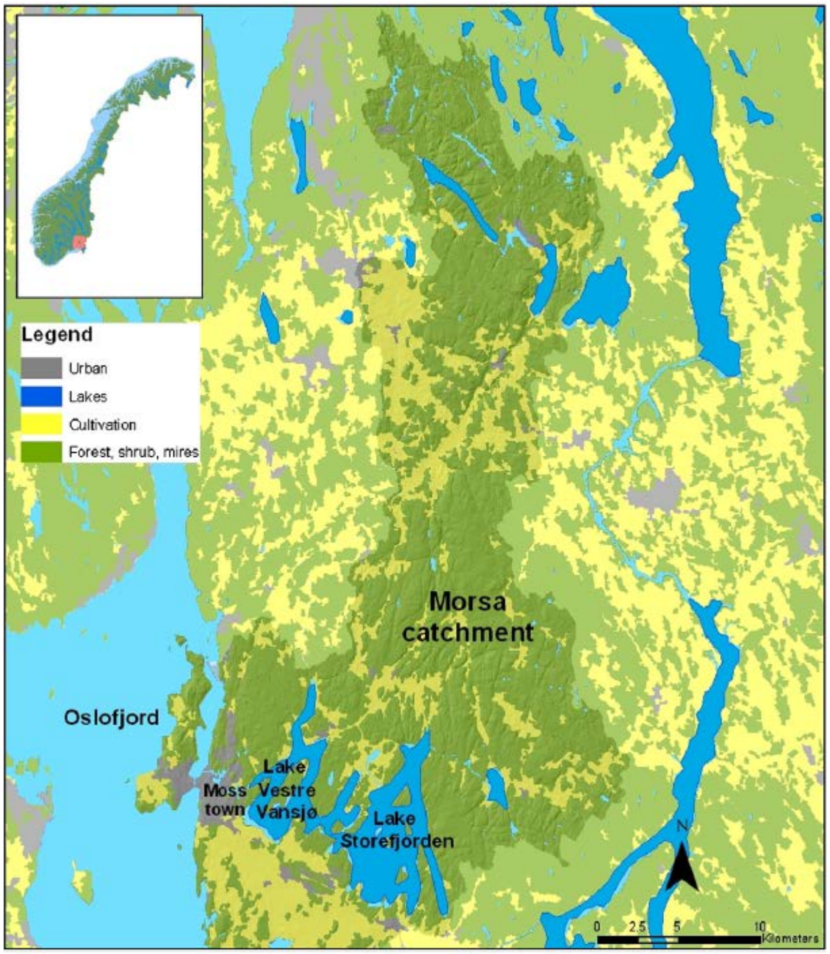

Figure 2: Morsa catchment draining to the Vansjø lakes including Lake Storefjorden map taken from (Barton et al., 2008)

Lake Vansjø in Figure 2, which is the main lake in the Morsa catchment, is at risk of not meeting the EU WFD for good ecological status due to eutrophication (Barton et al., 2008; Skarbøvik and

Bechmann, 2010). The lake covers a surface area of approximately 36 km^2. Most of the area in the Morsa catchment is covered by forest (about 80%), 15% of the area is used for agriculture land, and the remaining about 5% of the total catchment area comprises water bodies, bogs and open areas (Blankenberg et al., 2008). Agriculture originates as the main anthropogenic source of phosphorous (P) input into Norwegian surface waters with a contribution of about 45% of phosphorus loading to the water system[2]. Vanemfjorden is a highly eutrophic lake with frequent cyanobacteria blooms. The main sources of nutrient loading are agriculture (57%), septic tanks from individual households (11%), municipal wastewater (6%) and natural background run-off (26%) (Barton, 2007). Lake Vansjø is a relatively shallow lake for Norwegian conditions, and its morphometric features are given in Table 1below.

Table 1: Morphometric data for Lake Vansjø taken with kind permission from (Skarbøvik and Bechmann, 2010)

Morphometric	Lake Vansjø	Vanemfjorden (Western basin)	Storefjorden (Eastern basin)
Mean depth (m)	7	3.8	8.7
Maximum depth (m)	41	19	41
Surface area (km^2) at 25.5m a.s.l	35.8	12	23.8
Volume (10^6 m^3) at 25.5m a.s.l	252.2	46.1	206.1
Water residence time (years)		0.21	0.85

Lake Vansjø has got a lot of attention from the Norwegian government and environmental authorities due to its eutrophication problem.

To overcome the problem different mitigation actions have been undertaken. These mitigation actions are designed to reduce erosion risk and surface runoff so as to lessen the release of phosphorus from the agricultural areas. This is because erosion and runoff are the most contributory factors that play a major role in the loss of the total phosphorus from the terrestrial environment to the water system. The total erosion risk depends on natural factors such as slope,

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[2] See http://folk.uio.no/rvogt/Eutropia/Eutropia.doc

soil type, precipitation and factors influenced by human activities such as crops and soil management (Skarbøvik and Bechmann, 2010). Some of the mitigation options as described by Bechmann and Øgaard (2010) are:

- **Reduced phosphorus application:** Reduction of phosphorus application in fertilizers can reduce leaching and transporting of dissolved and particulate phosphorus from soils, and this will be also more effective by reducing of transporting soil particles using soil management. This method reduces the availability of phosphorus in runoff.

- **Cover crops**: Usually, phosphorus binds to soil particles and losses of phosphorus associate with soil particles are often linked to soil erosion; therefore, planting cover crops that can reduce soil disturbance are important to protect soil from erosion risk during the autumn and winter period.
- **Vegetated buffers**: Vegetated areas of the land between the agricultural fields and the water bodies contribute to reduce concentrations of suspended sediments and phosphorus in surface runoff from reaching water bodies by allowing more runoff to infiltrate and react with soils, see fig 3.
- **Construction wetlands**: Establishing mitigation options such as sedimentation ponds and construction of wetlands that removes phosphorus from water helps to reduce phosphorus load in the water system, and this can be more effective by including a phosphorus adsorbing filter (Bechmann and Øgaard, 2010).

Figure 3: Buffer zones in the Morsa catchment. Pictures are with kind permission from (Skarbøvik and Bechmann, 2010).

1.3 Geology of Morsa catchment

The highest point of the catchment area is about 346 m above sea level (a.s.l) whereas the lowest is at the sea level. A topographic map is given in Figure 4 below.

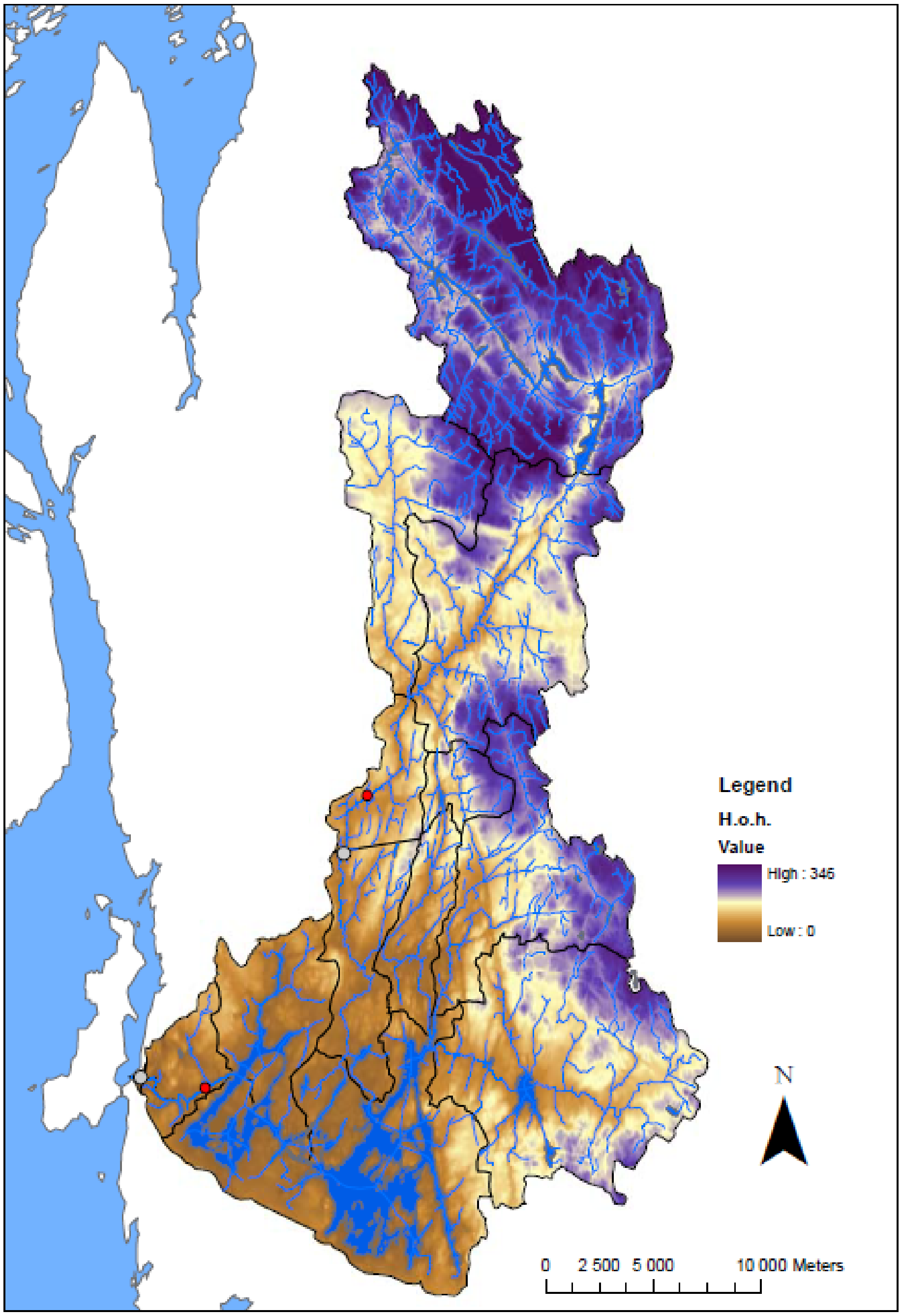

Figure 4: Topography of Morsa catchment (with height above sea level; i.e. H.o.h. in the Figure). Map taken with kind permission from (Skarbøvik and Bechmann, 2010).

The 10% northernmost part of the catchment is dominated by forest and the bedrock is mainly pre-cambrian with predominantly gneiss. In this area, situated above the marine limit of about 214 m a.s.l, the thin moraine soil layers gives relatively poor soil quality for agriculture (Skarbøvik and Bechmann, 2010). The soils in the lower reaches of the rest of the catchment are rich in silt and clay minerals. This is because the area was submerged under the sea during the Pleistocene (epoch of the quaternary) period. Since the last ice age, when the great glacier melted the land has risen from the sea. As the shoreline passed through the landscape it washed the ridges barren leaving rock outcrop, the slopes were beaches leaving sandy deposits and the valley bottom and gently sloping areas accumulated fine marine clay deposits which became the most fertile soil. Due to this geological history of the catchment the soils in the northern forested areas are predominantly coarse moraine, whereas in the southern areas soils are dominated by marine deposits which are rich in clay. Therefore, in the agricultural areas the soils have up to 80% clay and the rest is covered with silt and sand (Skarbøvik and Bechmann, 2010). In the very southern part of the catchment, a huge end moraine is effectively damming the lake. This is the reason why the catchment drains to the west rather than to the south.

1.4 The EUTROPIA Project

This master’s thesis is part of the interdisciplinary research project named EUTROPIA (Watershed Eutrophication management through system oriented process modeling of Pressures, Impacts and Abatement actions) financed by the Research Council of Norway (Project No. 190028/S30). The project was established early in 2009. A main aim of the EUTROPIA project was to study the major processes and their governing pressures controlling fluxes of major phosphorus fractions to Lake Vansjø. Understanding these processes is a prerequisite to understand how changes in environmental pressures will affect the phosphorus fluxes from the terrestrial to the aquatic environment. The Water Framework Directive (WFD) that was adopted by the Norwegian government, has as goal that all surface waters should have a good chemical and ecological condition and to have minimum deviation from their natural condition by 2015. This obliges scientists and environmental managers to assess the initial and current state of the environment, and to predict future changes. Fresh water lake status, according to the WFD, is composed of two elements: ‘chemical status’ and ‘ecological status (Pollard and Huxham, 1998).

The EUTROPIA project is an interdisciplinary research collaboration. The project has partners from the Norwegian Institute for Water Research (NIVA), Norwegian Institute for Nature Research (NINA), Norwegian Institute for Urban and Regional Research (NIBR), Norwegian Institute for Agricultural and Environmental Research (Bioforsk), Norwegian University of Life Science (UMB) and the Departments of Bioscience and Chemistry at the University of Oslo. The project is divided into five work packages. The work of this master's thesis has mainly focused on the work package two (the project plan[3]) in identifying hydro-biogeochemical processes that control the mobilization and transport of phosphorus fractions from terrestrial to aquatic environment. The focus of this thesis is on forest soils. Soils have been collected from forest areas of the catchment and analysed for physiochemical characteristics and phosphorus pools.

1.5 Objective of the master thesis

The main goal of this study is to assess the spatial distribution of physiochemical characteristics and P-pools in soils in the Morsa watershed that are not influenced by agricultural activity. The hypothesis is that the size of P pools may be related to topography and other soil characteristics. It is also an aim to investigate if there is a significant difference in these pools above and below the marine limit. A goal is furthermore to get a measure of the natural characteristics of the soils that today are used as farmland in order to assess the amount of background leaching of P.

Dalen is an area in which many studies have been conducted; an aim of this research is therefore also to investigate how representative the soil in the Dalen catchment is relative to the rest of the forested areas in the Morsa catchment.

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[3] http://folk.uio.no/rvogt/Eutropia/Eutropia.doc

2 THEORY

2.1 Eutrophication

Lakes and water reservoirs are massive sedimentation sinks which not only serve to remove suspended matter from tributary waters but also act as a huge reaction vessels for biological phenomena involving production of both plants and animals (Sawyer, 1966). These lakes and reservoirs also provide ecosystem services to the society and biota by providing clean water to household for drinking and washing, for irrigation in agricultural, for industrial sector and recreation such as bathing, as well as a safe and sound habitat. These water bodies run the risk to become deteriorated and have low quality due to poor management and the way how the society uses them. For example, the discharge of sewage from industrial and urban wastewater, and run-off from agricultural fertilizers and pest-control chemicals into the water bodies (Codd, 2000).

Eutrophication is the rapid biological response to excess input of nutrients into freshwaters, lakes and reservoirs and happens rarely under natural conditions, but is more commonly recognized as a consequence of human activities (Codd, 2000; Smith et al., 1999). Eutrophication is also defined as the natural slow ageing process of lakes and is distinguished geologically as gradual process (Rast and Thornton, 1996). As ageing progresses, the depth to the sediment of the lake gradually decreases so that there no longer exists a hypolimnion. The phosphate released by bacterial decomposition of the materials in the sediment is mixed throughout the water column allowing the lake water to become richer in nutrient materials on which phytoplankton grow. This shift typically is accompanied by changes in species and biotic community composition. Eutrophication results in increase of cyanobacteria, algal blooms and plant biomass and also brings decrease in biodiversity in the aquatic environment (Codd, 2000).

Anthropogenic sources of nutrients have become detrimental to water quality and aquatic ecosystem health. Thus, much research has been done to identify the sources and mechanisms of nutrient supply to lakes. Anthropogenic nutrient inputs are classified as point sources or non-point sources. Point sources generally consists of sewage leakage from scattered dwellings and leakage from manure or animal food storage facilities mainly in association with the farmyard. Controlling of point-sources in agricultural land is relatively simple, though it may be costly. On the other hand, non-point sources are more difficult to control or monitor because they are diffuse. A comprehensive list of possible point and non-point sources are included in Table 2.1 taken from Smith et al. (1999).

Table 2: Point source and nonpoint source

Point sources

- waste water effluent (municipal and industrial)
- storm sewer outfalls from cities
- runoff and leachate from waste disposal sites
- runoff and leachate from animal feeds
- runoff from mines, oil fields, and unsewered industrial sites
- runoff from construction sites

Nonpoint sources

- runoff from agriculture
- runoff from forest
- runoff from pastures and rangelands
- atmospheric deposition over a water surface
- activities on land that generate contaminates such as logging, wetland conversion, construction and development of land or waterways

Table 3: Effects of eutrophication on lakes and reservoirs

- Increased biomass of freshwater phytoplankton and periphyton
- Shifts in phytoplankton species composition to taxa that may be toxic or inedible (e.g. bloom-forming cyanobacteria)
- Changes in vascular plant production, biomass, and species composition
- Reduced water clarity
- Decreases in the perceived aesthetic value of the water body
- Taste, odour, and water supply filtration problems
- Possible health risks in water supplies
- Elevated pH and dissolved oxygen depletion in the water column
- Increased fish production and harvest
- Shifts in fish species composition towards less desirable species

The effects of eutrophication on the environment may have harmful consequences on the health of exposed animal and human population through various mechanisms. Some of the health risks are when freshwater extracted from eutrophic areas is used for drinking water. Table 2 and 3are from (Smith et al., 1999) shows some of the symptoms and impacts of eutrophication.

Figure 5: Lake Vansjø has many user interests - the lake is amongst others used for recreation; picture taken with kind permission from (Skarbøvik and Bechmann, 2010)

2.1.1 Eutrophication status

There are many inorganic minerals that serve as nutrients for plant growth. Minerals containing nitrogen, phosphorus, carbon, potassium, sulphur, calcium, magnesium and many other trace nutrients have an important role in the growth of plants. Of the many mineral resources required for the growth of plants, inorganic nitrogen and phosphorus are the two fundamental nutrients that have been found to limit the growth of terrestrial plants and also the main focus regarding eutrophication (Smith et al., 1999). The two nutrients are most commonly the limiting factor for further growth due to the relatively low availability compared to the high biological demand. It is speculated that the phosphorus is becoming more and more the limiting factor in surface waters due to the on-going deposition of reactive nitrogen.

Phosphorus (P) is a naturally occurring element that exists in minerals, soils, living organisms and in water and is a crucial nutrient supply for plant growth and development (Iyamuremye and Dick, 1996). Phosphorus exists in an undersupply condition in most soils, mainly in soils with acidic properties and highly weathered soils such as Ultisols and Oxisols (Iyamuremye and Dick, 1996). Generally, due to adsorption by Fe or Al oxides or by its precipitation with soluble A1 and Fe in acid soils, P is available to plants in very small amounts, whereas in alkaline soils phosphate readily reacts with Ca to form insoluble precipitates.

Human activities have strong effects on the fluxes of P to surface waters. Large amounts of minerals that are enriched with P are mined and processed to create P containing fertilizers, and these fertilizers are widely used in the world even in agricultural areas where the soils already have more than enough P reserves. In addition to the agricultural sources of N and P, humans use flowing water as convenient wastewater disposal systems. The loading of N and P to the world’s rivers, lakes and oceans is thus very strongly influenced by human population densities, the population densities of livestock, and land-use (Smith et al., 1999). According to the degree of enrichment with nutrients and organic matter, lakes are often classified by their trophic state with the main classes of oligotrophic, mesotrophic, eutrophic, and dystrophic (Salameh and Harahsheh, 2011), in other terms the trophic states are classified as good, moderate, poor and bad where the key parameters are found in an increased level (Direktoratsgruppa, 2009).

2.1.1.1 Oligotrophic

Oligotrophic lakes are poorly nourished with plant nutrients and support little plant growth. As a result, biological productivity is generally low. The waters are clear, and the deepest layers get enough light and oxygen throughout the year.

2.1.1.2 Mesotrophic

Mesotrophic lakes are waters having intermediate nutrient supply. They are moderately well supplied with plant nutrients and support moderate plant growth.

2.1.1.3 Eutrophic

Eutrophic lakes are waters that have relatively large supplies of nutrients and support heavy plant growths. As a result biological productivity is generally high. The waters are turbid because of dense growths of phytoplankton or they contain an abundance of rooted aquatic plants; deepest waters exhibit reduced concentrations of dissolved oxygen during periods of restricted circulation.

2.1.1.4 Dystrophic

Dystrophic lakes are lakes having brownish acidic waters, with a high concentration of humic matter, and a small plant population. Figure 6 below shows the degree of trophy of water bodies and total phosphorus concentration. Many researchers have discussed the details and classification of the trophic status using different physic chemical indicators of the water column. Further readings can be referred to the documents written by (Ferreira et al., 2011; Shannon and Brezonik, 1972; Vollenweider et al., 1998), and many other papers.

Table 4: Eutrophication criteria for lakes and reservoirs and the boundary values for fixed trophic classification systems (Organization for Economic Co-operation and Development (OECD)[4]

Trophic category	Total phosphorus (µg/L)	Chlorophyll a (µg/L)		Secchi depth (m)	
		Mean	Maximum	Mean	Minimum
Ultra-oligotrophic	<4.0	<1.0	<2.5	>12.0	>6.0
Oligotrophic	<10.0	<2.5	<8.0	>6.0	>3.0
Mesotrophic	10 – 35	2.5 – 8.0	8 – 25	6 – 3	3 – 15
Eutrophic	35 – 100	8 – 25	25 – 75	3 – 1.5	1.5 – 0.7
Hypertrophic	>100	>25	>75	<1.5	<0.7

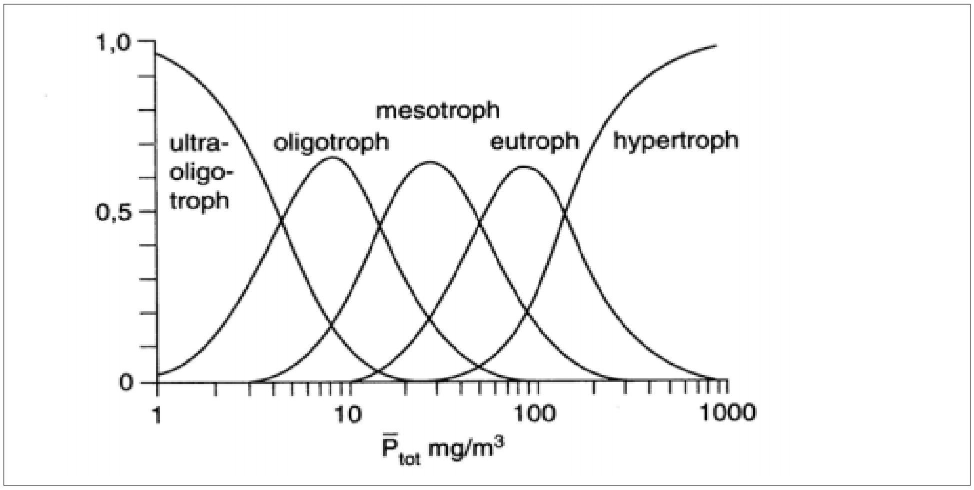

Figure 6: Probable boundaries of the degrees of trophy of waterbodies with differing annual mean values of total phosphorus concentrations picture taken from Organization for Economic Co-operation and Development(OECD)

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[4] Can be found on the web: http://www.chebucto.ns.ca/ccn/info/Science/SWCS/TPMODELS/OECD/trophic.html

2.2 Cause for eutrophication: Governing factors, role of climate, effect of reduced acid rain, background flux of P-DNOM

Organic matter (OM) in water body is found as dissolved (DOM) or particulate (POM) forms, and the proof of their presence is the characteristic of yellow-brown colour of water (vanLoon and Duffy, 2005). The organic matter formed in land and transported into the hydrosphere due to rainfall that runs off or percolates through the soil carrying soluble and particulate OM to water bodies makes up an important fraction of the total OM. OM is also produced within the water bodies (autochthonous). As plant material (for example, leaves) degrade soluble organic compounds are leached from the tissue and these organic compounds are the precursors of natural organic matter (NOM) (Leenheer, 2002). The flux of DNOM has now increased in areas which were previously suffering from a heavy acid rain problem like the south eastern part of Norway, and as a result increasing concentration of DNOM in water bodies are found in these regions. Acid rain leaches out inorganic aluminum species from forest soils, and when the soil water drains into the surface waters, the inorganic aluminum species accumulated in surface waters suppresses the solubility of DOM, especially the hydrophobic fraction. The effect of aqueous inorganic aluminum as a flocculent and coagulant may be clearly envisaged at water treatment works. Flocculation of DNOM by using aluminum sulphate ($Al_2\ (SO_4)_3$) is a commonly used procedure at water treatment work with high levels of DNOM in their raw water. Based on this there is a hypothesis that “the ongoing strong decrease in aluminum concentrations, along with fall in ionic strength, due to the reduction in acid deposition, is a strong underlying driver for the increase in the amount of aquatic DOM and colour in surface waters across much of Europe and North America[5]”.

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[5] available at http://folk.uio.no/rvogt/CV/Publications/Critical%20Review%20-%20Vogt.pdf

2.2.1 The main drivers for mobility of dissolved natural organic matter

There may be a lot of factors that can be the main drivers of DNOM. The following three are discussed below. More information can be found in[6].

2.2.1.1 Change of climate

The increase in temperature accompanied by increasing of precipitation due to global warming is also a factor that has contributed to the increase of DOM in surface waters. Organic matter of the soil decomposes more rapidly as the temperature increases because of the increased rate of microbial decomposition in soils especially in peatlands. It is, therefore, postulated that the observed increasing in concentration of DOC and colour in surface water is partly due to the increase in temperature (Freeman et al., 2001).

2.2.1.2 Change in land use

Spatial variation of land use causes DOM to have different amounts and properties in the watersheds. For example, extensive afforestation and increased proportion of conifers on acid soils lead to increased DOM leaching to surface waters.

2.2.1.3 Anthropogenic atmospheric deposition

During the 70ties and 80ties when acid rain reigns, surface waters had a decreased colour and low concentrations of DOM. Since the mid of 1985, acid rain deposition was decreased by > 50% because of the reduction of deposition sulphur compounds to the atmosphere in Europe and North America. Especially in Norway, the reduction was large. It amounts to about 80%. This decrease in acid rain leads to a up to 90% reduction in the concentration of sulphate anions in the surface water accompanied by decreasing concentrations of the acid cations, especially inorganic aluminum (Al^{3+}), and to some extent also the base cations such as Ca^{2+}, and Mg^{2+}. This results in reduction of ionic strength. A reduced ionic strength also gives more soil erosion and thereby an increased transport of particulate-P. The figures below show the effect of sulphur reduction (acid rain reduction) increases in DNOM (expressed as TOC) through lower aluminum concentration.

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[6] available at http://folk.uio.no/rvogt/CV/Publications/Critical%20Review%20-%20Vogt.pdf

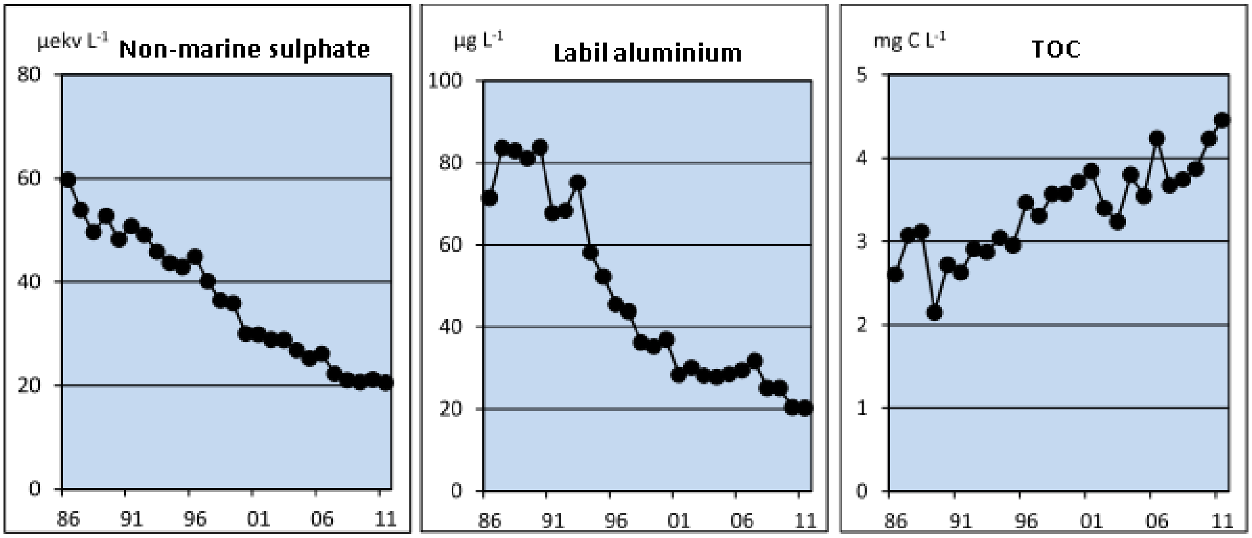

Figure 7: (right to left) reduction of sulphate deposition, decrease in aluminium concentration and increase in TOC at 78 lakes throughout Norway (Skjelkvåle et al., 1999)

2.3 Organic and inorganic forms of Phosphorus in soil-water

Soil phosphorus exists in inorganic and organic forms. Inorganic P is usually associated with aluminum (Al), iron (Fe) and calcium (Ca) compounds of varying solubility and availability to plants in soil. Phosphorus has to be added to most agricultural soils so that adequate levels are available for most favourable crop growth and yield. However, a great part of the phosphate in soils is sorbed to soil particles or incorporated into soil organic matter that cannot be easily available to plants; this depends on soil pH (pH influences Al chemistry, at pH 6 and 8 Al^{3+} hydrolysis and precipitates out as amorphous oxy-hydroxides, see section 2.9) and type of soil constituents (Al, Fe, and Ca content). The solubility of phosphates or the conversion of unavailable to available forms of soil phosphorus is usually controlled by either sorption-desorption or precipitation-dissolution reactions depending on the environment in the soil or sediments (Holtan et al., 1988). Organic Phosphorus compounds range from readily available decomposed plant residues within the soil to stable compounds that have become part of soil organic matter. Wetland soils are inherently characterized by high organic matter content so that organic phosphorus commonly dominates the total phosphorus in wetlands. Peat-dominated wetlands have therefore a higher proportion of organic phosphorus compared to soils with high content of mineral matter (Schlesinger, 1997). Although a large proportion of total phosphorus exists in organic forms, only a small portion of this pool may be bioavailable. Biological processes in the soil, such as microbial activity, tend to control the mineralization and immobilization of organic Phosphorus.

Mineralization is a process of breakdown or conversion of organic phosphorus to inorganic phosphorus. It occurs in soils as a result of microbial decomposition. Immobilization is a process in which any inorganic phosphorus released into water is assimilated into microbial biomass and forms stable organic phosphorus (Molla et al., 1984; Zou et al., 1992). In most soils the phosphorus content of surface horizons is larger than in subsoil.

In acid soils, Al and Fe govern phosphorus sorption, while Ca compounds sorb phosphorus in alkaline soils; as a result phosphorus availability is greatest at soil pH between 6 and 7 (from figure 8 below). The dissociation reactions of the orthophosphoric acid in aqueous system as a function of pH is presented in Table 5 and illustrated in Figure 8.

Table 5: Acid dissociation constants for phosphoric acid (Reddy and DeLaune, 2008; vanLoon and Duffy, 2005).

Forms of the acid	Dissociation constants
$H_3PO_4 = H_2PO_4^- + H^+$	$pKa_1 = 2.15$
$H_2PO_4^- = HPO_4^{2-} + H^+$	$pKa_2 = 7.2$
$HPO_4^- = PO_4^{3-} + H^+$	$pKa_3 = 12.38$

Where pKa1, pKa2 and pKa3 are acid dissociation constant, the Figure 8 below shows the PO_4^{3-} distribution.

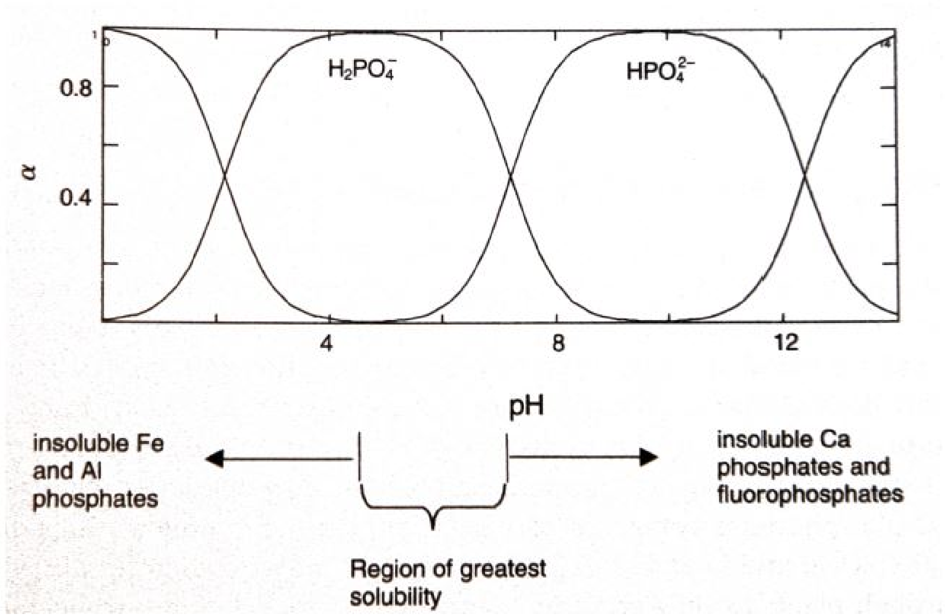

Figure 8: Distribution of Phosphate species in aqueous solution expressed as a function of pH (Loon and Duffy, 2005).

Under most natural conditions, dominant phosphate species are $H_2PO_4^-$ and HPO_4^{2-} (Figure 8). At around pH 7.2 there are approximately equal amounts of $H_2PO_4^-$ and HPO_4^{2-}. $H_2PO_4^-$ is the dominant form of free orthophosphate species in the pH range of most natural acid forest soils (4 - 6.5). The relative de-protonation and protonation of aqueous phosphate species determine their reactivity as inorganic ligands or ions pairs, particularly with iron and aluminum under acidic conditions and with calcium and magnesium under alkaline conditions.

2.4 Processes governing phosphorus release from natural soils

Phosphorus exists in soil both in inorganic and organic forms. The organic forms of phosphorus in soil are present in the range 30 to 65% (Harrison, 1987). The plant available form of phosphorus in the soil solution is a very small fraction of the total phosphorus content in the soil and ranges typically in concentration between 0.01 to 0.3 mg L^{-1} (Frossard et al., 2000). This low concentration affects the growth of plants. In order to fulfil the required flux of bioavailable phosphorus for plant growth, therefore, it must be made available through a combination of chemical and biological processes which release phosphorus from the soil pools. The most important chemical (abiotic) soil processes involved in soil P transformation are precipitation-dissolution and sorption-desorption, whereas the most important biological (biotic) process is mineralization-immobilization.

Dissolved and particulate phosphorus are the two main phosphorus fractions in which it transported from the terrestrial environment to the water bodies. However, the distribution between dissolved and particulate phosphorus forms depends on the main transport pathways, soil properties, management practices, and hydrological features of a particular site (Djodjic, 2001). Erosion is the transport of soil particles from land and the deposition of these materials elsewhere. Erosion depends on variables such as precipitation, overland flow, farming practice, soil texture and topography. Erosion preferentially leads to the transport to aquatic systems of finer-sized soil particles and organic matter, which both have a large capacity to sorb phosphorus. The most important transport pathways of phosphorus losses from agricultural soils are surface run-off (overland flow), interflow (lateral flow below the soil surface), matrix flow and preferential flow. Figure below shows the transport pathways for the particles.

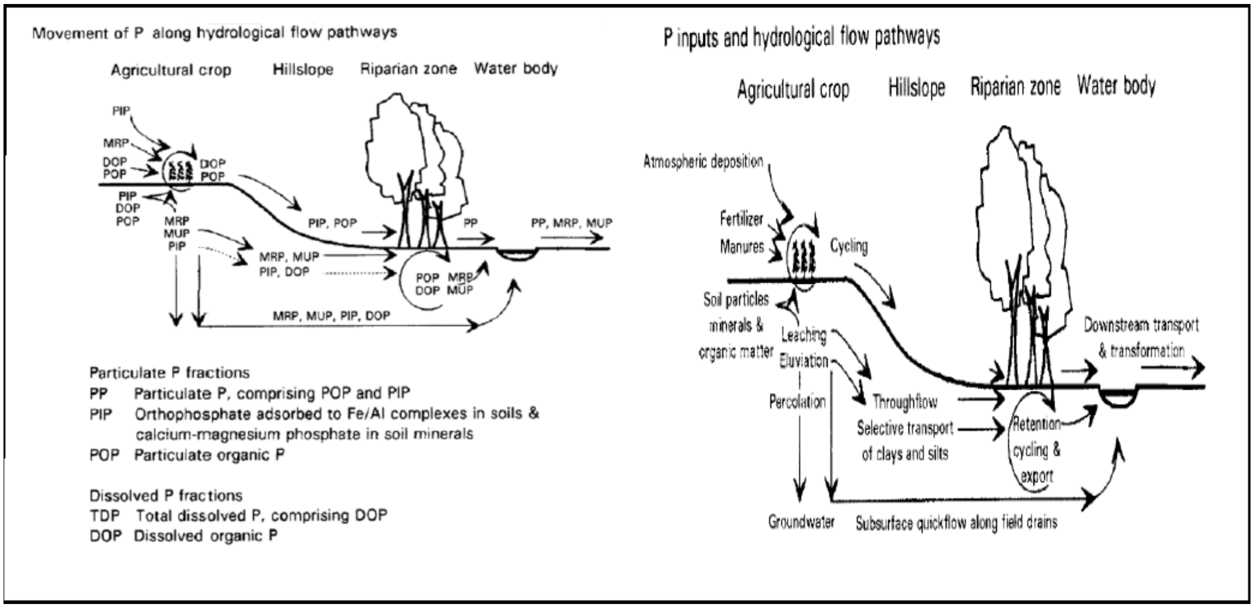

Figure 9: Transport and site management factors influencing the potential for P loss from agricultural land to surface waters (Sharpley et al., 2001)

2.5 Natural Soil (Forest Soil) and agricultural soils: Spatial pattern in distribution of forest and agriculture.

The type of soil in Morsa catchment, where 85% its land area covered by forest is dominated by Podzol type of soil. Podzol are generally located in the temperate forested regions; in which clays, humic acids, iron, and other soluble constituents have been eluviated from the A and E horizons. The eluviated E horizons are characterized by its distinctive light colour found immediately below the black A horizon rich in organic matter. The light colour is formed due to loss of iron/aluminum by leaching. Below the E horizon there is a brightly red/brown coloured zone of iron/aluminum deposition (illuvial Bs horizon) and/or a darker zone of organic deposition (Bh). It is the constituents of the eluviated E soil horizons that have accumulated to form a spodic illuvial Bs horizon.

2.6 Soil profiles

Soil formation usually occurs by transport of weathering products down through the profile in humid regions. Soil profiles are divided into horizons with notations (H, O, A, E, B, C and R) depending on their relative placement and physical and chemical characteristics. The top H and O horizons are organic soils and sub-surface are mineral soils horizons (A – C).

2.6.1 Organic soil horizons

Organic soil horizons are situated on the top of the soil profiles.

- H-layer: Denote a histosol soil horizon. A histosol may be a bog or peat. The histosol is water saturated and also defined as having greater than 40cm organic soil material.
- O-horizons: It is generally the uppermost layer of the mineral soil profile and consists of greater than 35% organic matter. It is dry and found less than 40cm.

2.6.2 Mineral soil horizons:

Mineral soil horizons are soil horizons which contain less than 35% of organic matter.

The properties and notations of mineral soil horizons are discussed below.

- A-horizons: This horizon is on the top of the mineral soil. This horizon is darker coloured than lower horizons and is separated from the O horizon by that it contain less than 35% of organic material. The organic material exists as fine particles or as coating on mineral grains.
- E-horizons: This horizon is characterized by its light colour or bleached appearance. This is a zone which has been strongly leached. It is an eluvial layer that has been washed out of clay, iron, and aluminium by humus. Eluviation is the transportation of dissolved or suspended soil material within the soil by the movement of water.
- B-horizon: This horizon is commonly called subsoil. It is zone of illuviation and accumulation of dissolved or suspended soil materials from A and E horizons as a result of eluviation.
- C-horizon: This horizon is the deepest horizon in the profile. It is considered an unaltered or weathered parent material.
- R-horizon: This horizon denotes the bed rock.

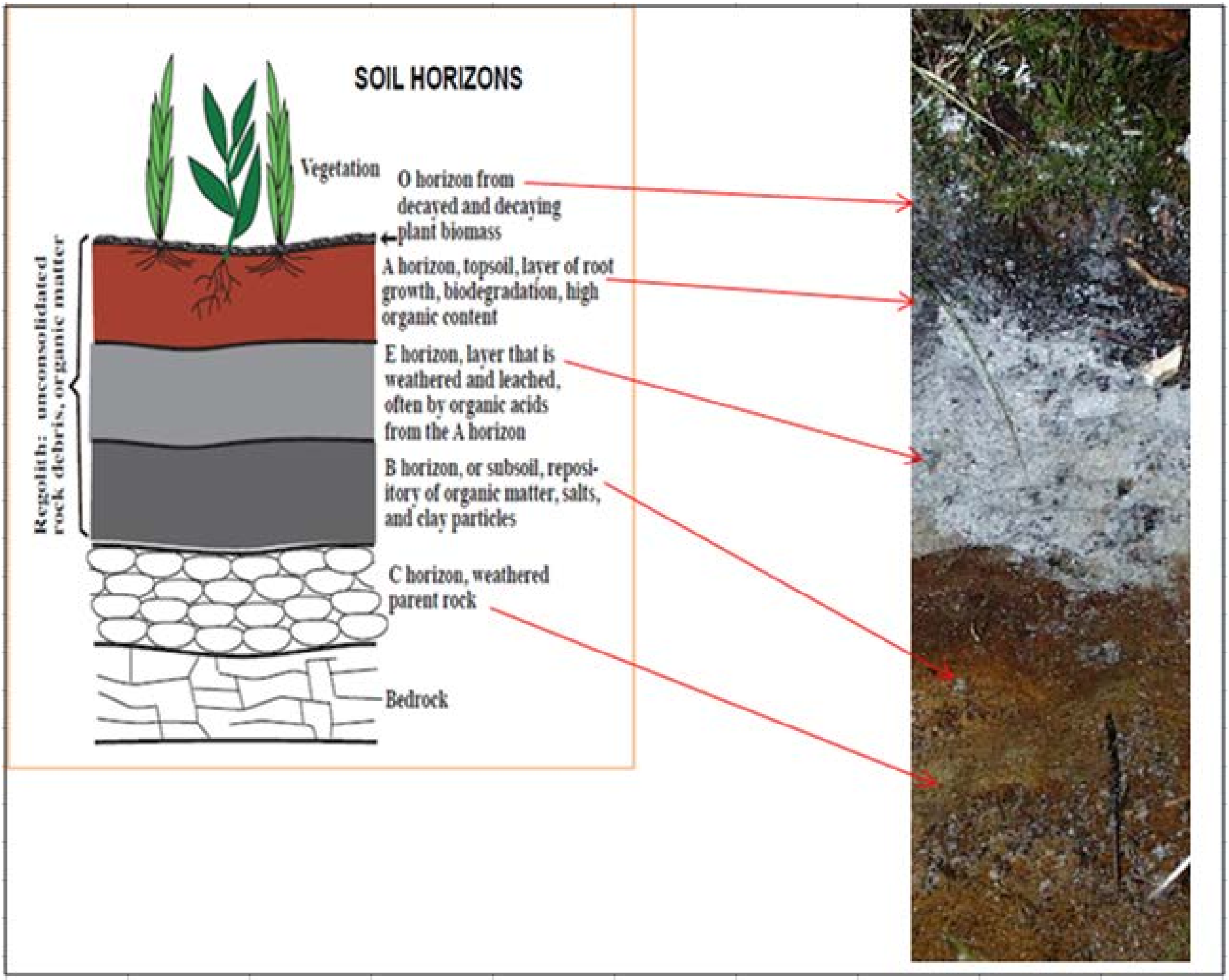

Figure 10: Soil profile showing soil horizon (Manahan, 2004); photo from Vogt (Kjemi 5700, uio).

2.7 Soil properties

The terrestrial environment is comprised of bedrock and soil and the living matter associated with these. Rocks and soil together are referred to as the lithosphere. Soil is a dynamic natural body composed of mineral and organic solids, gases, liquids and living organisms. The terrestrial environment covers 29% of the earth surface; 80% of the land surface is covered by soil (vanLoon and Duffy, 2005). Among the many reasons that scientists concerned about studying soil is that;

1. Soils provide a supporting medium for many forms of life and are the basis of agriculture and forestry.
2. Soils play a major role as key environmental agent;
    - Soil is the locus of input from the atmosphere and output to the hydrosphere.
    - Soil alters water chemistry as it passes through the watershed.
    - Soil plays a central role in global nutrient (C, P, N, and S) cycling.
    - Soil influences transport and fate of pollutants.

Moreover, soils involve chemical processes such as organic matter decomposition, nitrification, denitrification, phosphorus fixation, and sulphide oxidation.

2.7.1 Physical properties of soils

Soil physical properties profoundly influence how soils function in an ecosystem and how they can best be managed. The occurrence and growth of many plant species are closely related to soil physical properties, as is the movement over and through soils of water and its dissolved nutrients and chemical pollutants. Soil scientists use the colour, texture and other physical properties of soil horizons in classifying soil profiles. Soil texture is determined by the particle size distribution and is an important explanatory variable of the soil as it reflects both the soil permeability for water and the soils ability to adsorb chemical constituents. The texture of the soil is therefore a parameter that is included in this study.

2.7.2 Chemical properties of soils

Organic matter and clay content play a major role in determining the chemical properties of a given soil sample. Soil pH and cation exchange capacity are key soil chemical properties governing the spatial variation in P pools and are thus included in this study.

2.7.2.1 Soil pH

Soil pH affects the mobility of many pollutants in soil by influencing the rate of their biochemical breakdown, their solubility, and their adsorption to colloids (Brady and Weil, 2008). Carbonic acid is a weak acid which produces hydrogen ion to the soil when carbon dioxide gas from soil generated by the root respiration and decay of labile organic matter dissolves in water

(Appelo and Postma, 2005). Soils rich in carbonate minerals have a high pH which means that they are somewhat alkaline. On the other hand, soils rich in organic matter usually are acidic with a low pH. The acidity is to a large part generated by weak acid functional groups on the soil organic humic material. This material is derived from the microbial decomposition of organic matter. Soil with only poorly weatherable parent material are more acid than soils containing carbonate minerals as they are not able to neutralize the humic matter acidity. Vegetation (particularly conifers which produces organic acids) and climate along with acid rain are important factors that affect soil pH. Acid soils have a dominance of adsorbed aluminium and iron on its cation exchanger (see section 2.7.2.2.). Changes in redox status affects the soil pH, hence, flooded soils exhibits higher pH values than their upland counterparts (vanLoon and Duffy, 2005), see section 2.9. Through governing and reflecting the solubility and thereby the concentrations of Al, Fe and Ca the soil pH is a key explanatory variable for the availability of nutrients in the soil. Furthermore, the soil pH affects the activity of microorganisms which are responsible for breaking down organic matter and most chemical transformations of the soil.

2.7.2.2 Effective cation exchange capacity (CECe)

The effective cation exchange capacity is a key soil property. It is defined as the sum of total cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+, Al^{3+}, Fe^{3+}, Mn^{2+}) that a soil can absorb and exchange (Eq. 3.5). CECe is highly dependent up on the nature and content of clay minerals (the type of soil texture) and the content and degree of decomposition of organic matter (vanLoon and Duffy, 2005). In general, Sandy soils with low content of organic matter have very low CECe values, while soils with high clay content and or organic matter have a significant CECe values. Dissociation of organic acids results in a negative net charge on the soil organic matter, and again this negative charge is balanced by the amount of ion exchangeable cations in the soil. Because the dissociation of organic acids depends on the pH, the CECe associated with the organic matter is known as pH dependent CECe, therefore, the value of the pH dependent CECe will increase with pH. Usually, CECe is expressed as number of moles of positive charge per unit mass (meq/100g). Base saturation percentage is the proportion or percentage of cation exchange site occupied by non-acid cations, defined in Eq. 3.6.

2.8 Effect of decreased acid rain: Increased DNOM, reduced Al_i

Primary sources of sulphur in the environment consist of mineral weathering, atmospheric loading of acid rain (precipitation and dry deposition) and acid mine seepage, runoff from agriculture and urban land uses, and ground water interactions (Lehr et al., 2008). Lower pH and enhanced concentrations of sulphate allows enhanced mobilization of Al from the acid sensitive areas which complexed the organic matter causing the DNOM to precipitate. Therefore, acid rain decreased solubility of humus compounds by protonation of the weak acids and by complexing the organic matter compounds with Al comes from leaching.

$$R\text{-}COO^- + H^+ \leftrightarrow R\text{-}COOH, \text{ protonation} \quad (2.1)$$

$$3R\text{-}OO^- + Al^{3+} \leftrightarrow Al(R\text{-}OO)_3, \text{ complexation} \quad (2.2)$$

With the decrease in acid rain deposition since the 1980s, the dissolved organic matter (DOM) has again increased in stream water and fresh water lakes. Due to this increase in the DNOM-quantity, the water has become browner. Hence, a reduction in acid rain causes the DNOM compounds to become more soluble in water and be transported into stream waters and eventually drain into lakes. Figure 7 shows the relation of reduction in acid rain with reduction in Al leaching increasing the TOC. More information about the effect of acid rain and DNOM can be found in Vogt et al. (2003).

2.9 The role of Fe and Al in soils and sediments in retaining and release of phosphorus

The biogeochemistry of phosphorus in flooded soils and sediments differ from oxidized upland and other terrestrial soils, since phosphorus adsorption and mobilization are strongly affected by hydrology governing the redox potential. The soil capacity to adsorb phosphorous is dependent on the soils content of Fe/Al oxides and hydroxides, clay and dissolved organic matter (Kuo and Mikkelsen, 1979; Reddy and DeLaune, 2008). Al and Fe ions form positively charged oxy-hydroxides that sorb PO_4 anions. Furthermore, the Al^{3+} and Fe^{3+} constitute a binding bridge between the net negative charged surfaces of clay or organic matter coating on minerals and the PO_4 anion.

Ferric iron (Fe^{3+}) and sulphate (SO_4^{2-}) are reduced under anaerobic condition to ferrous iron (Fe^{2+}) and sulphide (S^{2-}), eq. 2.3 and 2.5. This plays a major role in the movement of phosphorus in the environment. According to Mortimer (1941) and Roden and Edmonds (1997) the reduction of ferric ion (Fe^{3+}) to more soluble ferrous ion (Fe^{2+}), and the reduction of sulphate to sulphide with subsequent capturing of the Fe^{+2} as FeS, leads to the release of previously bound phosphorus eq. 2.7. Therefore, in flooded environments P fluxes can occur from sediments/soils to surface waters. The P released by the reduction of Fe^{3+} can again be precipitated by re-oxidation of the reduced Fe^{2+} upon entering an oxidizing environment through sorption to the newly formed iron oxides. This serves to decrease the amount of phosphorus released (Patrick and Khalid, 1974). Change of climate is believed to bring more precipitation (heavy rainfall, increasing surface runoff, and flooding), and higher winter temperature. This will serve to increase the extent and frequency of reducing conditions in the soils and results in more flushing of P from soil horizons to the surface water system.

$$Fe(OH)_3 + 3H^+ + e^- \leftrightarrow Fe^{2+} + 3H_2O \qquad (2.3)$$

$$FePO_4 + 2H^+ + e^- \leftrightarrow Fe^{2+} + H_2PO_4^- \qquad (2.4)$$

$$CH_4 + SO_4^{2-} + 2H^+ \leftrightarrow H_2S + 2H_2O + CO_2 \qquad (2.5)$$

$$CH_4 + SO_4^{2-} + H^+ + Fe(OH)_3 + e^- \leftrightarrow FeS + 4H_2O + CO_3^{2-} \qquad (2.6)$$

$$CH_4 + SO_4^{2-} + H^+ + FePO_4 + e^- \leftrightarrow FeS + H_2O + HCO_3^- + H_2PO_4^- \qquad (2.7)$$

Aluminium sulphate (alum) is used as phosphate precipitant in some strongly eutrophic lakes and sewage treatment plants (Cooke et al., 1993) due to the strong binding between Al and PO_4. When alum ($Al_2(SO_4)_3$) is dissolved in circumneutral water the aluminium ions rapidly hydrolyse, leading to the formation of aluminium hydroxides ($Al(OH)_3$). The amorphous form of $Al(OH)_3$ dominates at a circumneutral pH. The colloidal and amorphous flocs of $Al(OH)_3$, have high coagulation and P adsorption properties. This reduces the P transport to the surface water system. The amorphous aluminium hydroxide with adsorbed phosphate will slowly age into strongly insoluble hydrous Al-PO_4 mineral (Cooke et al., 1993; Moore and Reddy, 1994).

$$[AlOH_2^{+}]OH + H_2PO_4^{-} \leftrightarrow [AlOH_2^{+}]H_2PO4^{-} + OH^{-} \tag{2.8}$$

$$Al^{3+} + H_2PO_4^{-} + 2\ H_2O \leftrightarrow 2\ H^{+} + Al\ (OH)_2H_2PO_4\ (s) \tag{2.9}$$

Acidity of forest soils is basically governed by the parent material ability to neutralize the natural acid production (weak carbonic and natural organic acids) through weathering. The acidification can be augmented due to acid deposition. This is especially the case in acid sensitive catchments where poor weathering leads to limited replenishment of base cations that are leached out of the soils causing a decrease in base saturation. The direct effect of soil acidification is to lower the pH of the soils. The combined effect of reduced base saturation, lowered pH and increased concentration of sulphate as a mobile counter anion, allow for a significant amount of labile aluminium in solution.

Decline in acid rain deposition over Norway has reduced the leaching of Al from the forest soil into surface water (Skjelkvåle et al., 1999). Less labile aluminium is thus washed out of acid head water catchments and down into the agricultural lowlands. There is therefore less labile aluminium where the acid water mix with circumneutral pH and P rich seepage water from the agricultural fields causing less precipitation of phosphate. This has resulted in more free movement of phosphate in the water system. More information can be found in Orderud and Vogt (2013).

3 MATERIALS AND METHODS

In this section the materials, methods and sampling employed in conducting the study are described. A brief description of the study site, with emphasis on the forest soils and plot of the eight sampling sites, are given in section (3.1).

Soil sample collection was conducted in the mid of August 2011. The unconsolidated deposits in 90% of the catchment area were deposited under the marine limit at the end of the last glacial epoch for about 10 000 years ago (Skarbøvik and Bechmann, 2010). Marine sediments are known to contain elevated levels of phosphorus as this is the final sink of phosphorus in the global phosphorus cycle. It is therefore hypothesized that there is a considerable natural background flux of P to the surface waters. The Vansjø Lake was as such most likely a naturally eutrophic system, which, due to an additional anthropogenic phosphorus loading, now experiences large eutrophication problems. Soils and water samples from the forested sub-catchment Dalen have previously been analyzed for physiochemical properties (Gebreslasse, 2012; Mohr, 2010). These studies showed that the soils and sediments in this forested catchment are acid sensitive. During the acid rain period in the 70ties and 80ties inorganic labile aluminium (Al_i) was eluted out from such acid forest soils into their acid first order streams. In the watercourse this water was mixed downstream with well buffered water causing the Al_i to precipitate out as Al-oxy-hydroxides. Ortho-phosphate in the water was co-precipitated. Alum ($Al_2(SO_4)_3$) is used by sewage treatment plants to precipitate out phosphate, it is also spread out over eutrophic lakes as an abatement action. It is therefore likely that reduced in co-precipitation of phosphorus due to the decrease in leaching of labile aluminium, caused by the up to 90% decrease in sulphate concentration since the end of 1970s, and has partly counteracted the effect of the abatement actions over the same periods.

3.1 Site description

The study area is known as Morsa watershed with focus on the sub-catchment of western Vansjø. Morsa catchment is an important catchment for many reasons. It is one of the catchments in Norway which is most affected by agricultural runoff and therefore also eutrophication and harmful algal blooms. It has been a pilot catchment in the implementation of the EU Water Framework Directive (WFD), and has a number of different user interests

(Skarbøvik and Bechmann, 2010). Morsa watershed covers an area of 700 km^2, of which 80% is comprised by forest, 15% by agriculture and 5% by others land-use. The morphology and soils in the area is characterized by quaternary geological characteristic of marine unconsolidated deposits rich in clay (Skarbøvik and Bechmann, 2010). The lake is a source of drinking water for more than 60,000 people and it receives pollution from human activities in the watershed.

Soils from Dalen has previously been analysed in our laboratory for physico-chemical properties (Mohr, 2010). The soils were collected from ridge, slope and valley bottom, and the results shows that; the largest soil P pools was found in the organic matter dominated soil floor which is the O horizon where organically bound P. The P pools in the O horizon shows decrease down the topography slope possibly due to the sub-lateral flow of water that washes out the soil horizon during periods of high runoff. E horizon which is located at the ridge shows low pool of P, this is because of the soil horizon is depleted of iron and Aluminum sesquioxides and clay content which have the ability to bind P. A significant amount of P bound to Ca and Fe was also found in the B and C soil horizons. The soils in Dalen also found to be acidic with pH well below 6 in all horizons and plots. The pH increases typically down through the soil profile as well as down along the topographic gradient. Sampling sites shown in figures 12, 13 and 14

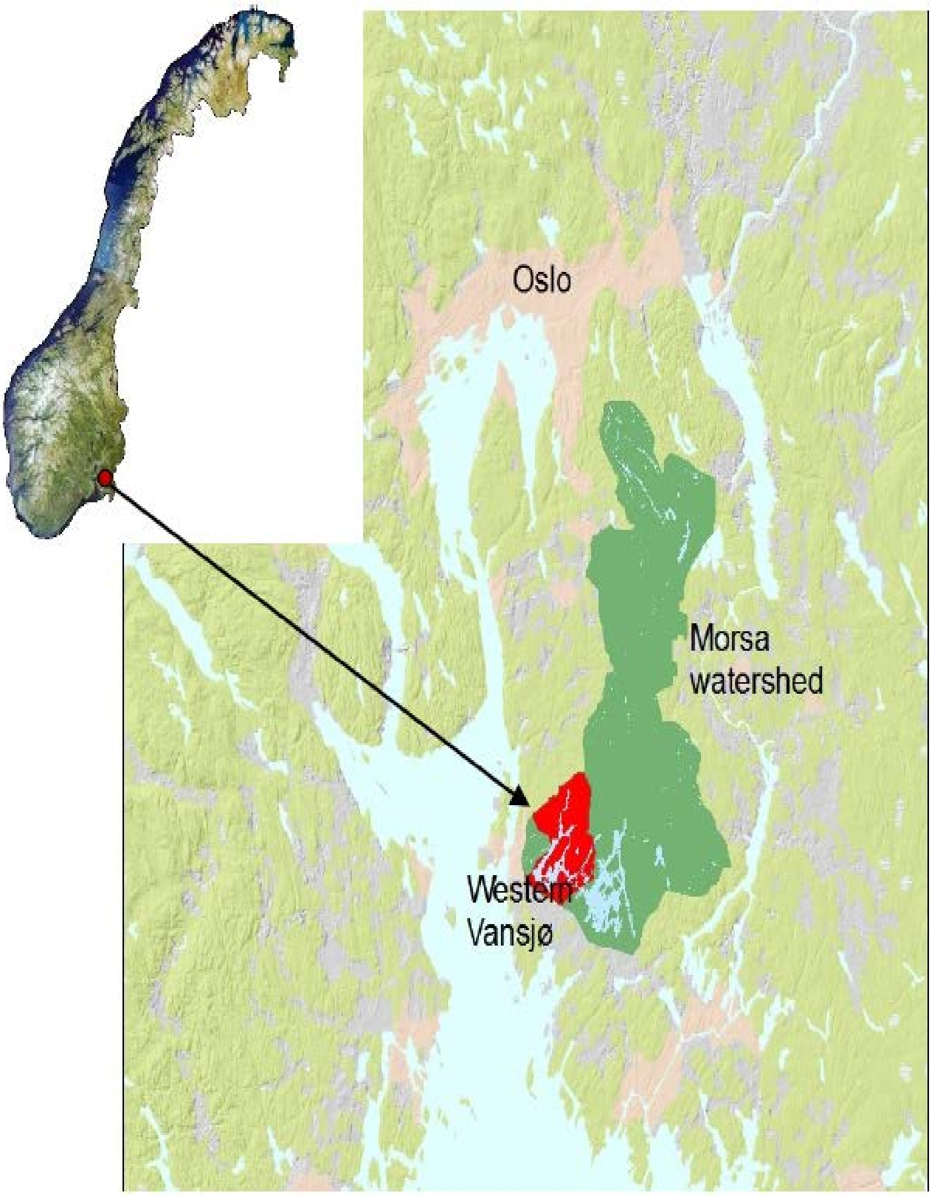

Figure 11: The Morsa watershed (dark green) with the sub-catchment of Western Vansjø (red) from (AQUARIUS, 2010)

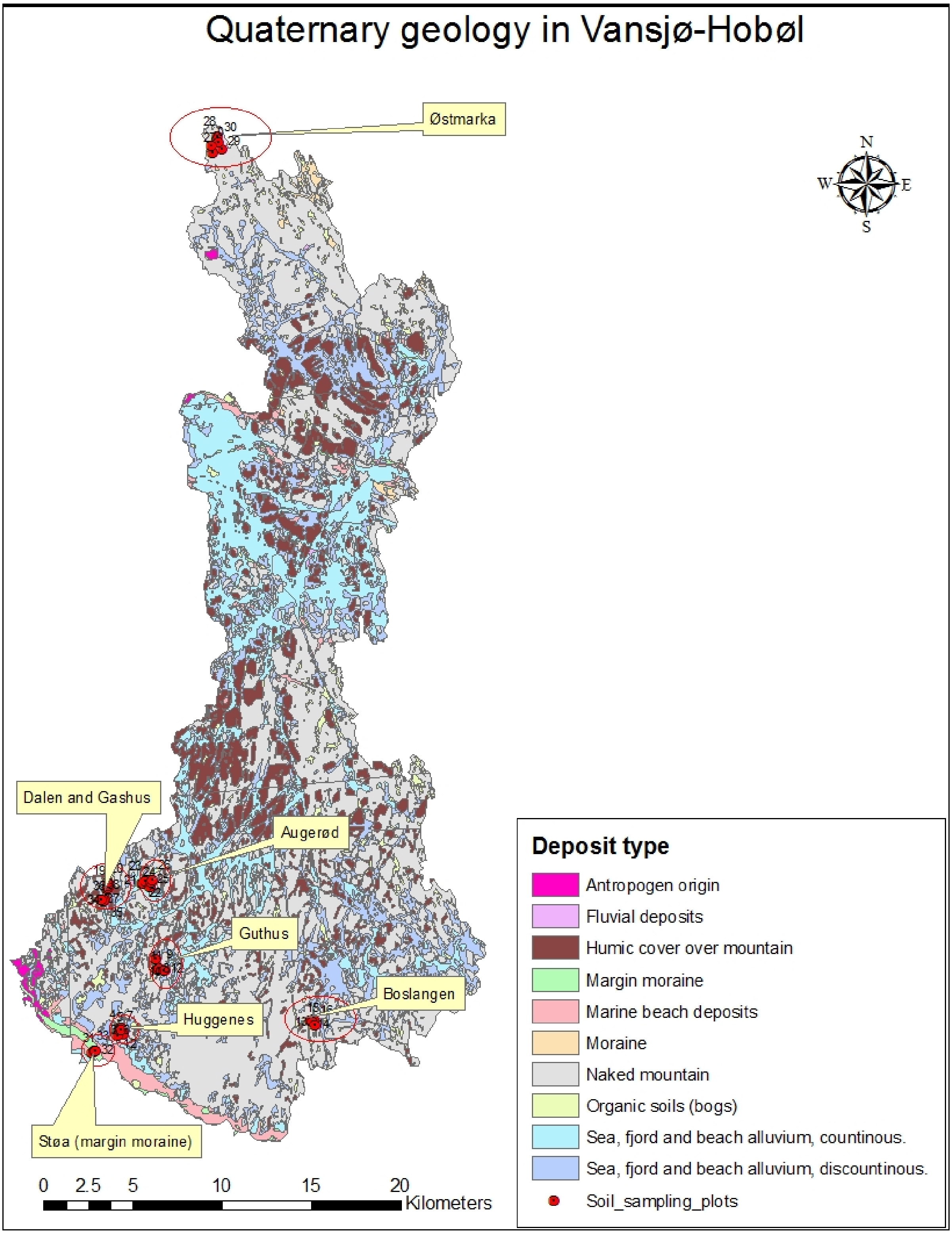

Figure 12: Sediment deposit types in the Morsa watershed including the eight sampling sites for soil (red dots) [7].

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[7] The map used is a quaternary map, 1:50000 produced by Geology for Society (NGU) (http://www.ngu.no/no/hm/Kart-og-data/nedlasting/), map is modified by Alexander Engebretsen.

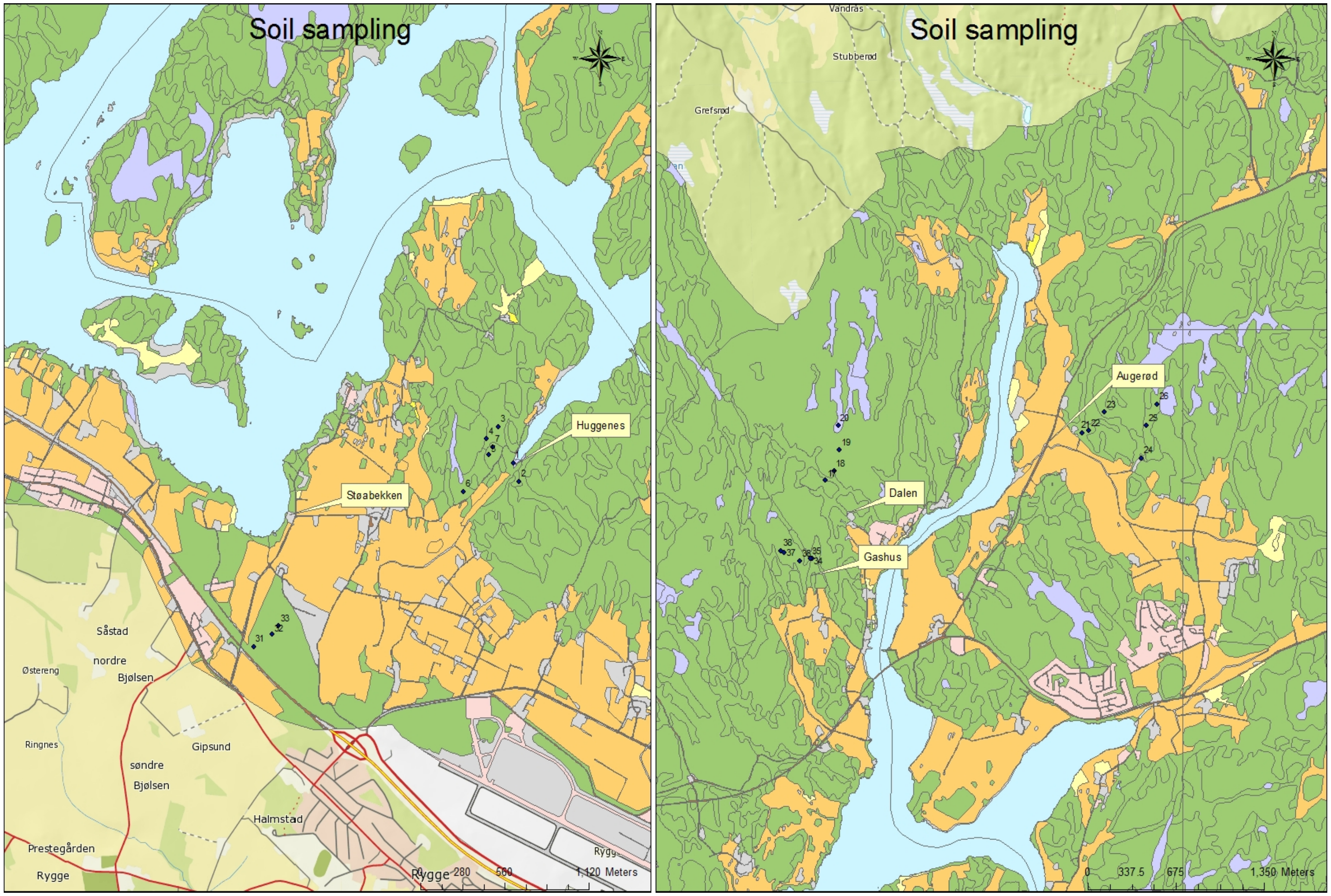

Figure 13: Soil sampling maps for sites of Dalen, Augerød, Gashus, Støa and Huggenes, the numbers and black dots in each site represents plot numbers where the soils are sampled[8].

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[8] . see next page

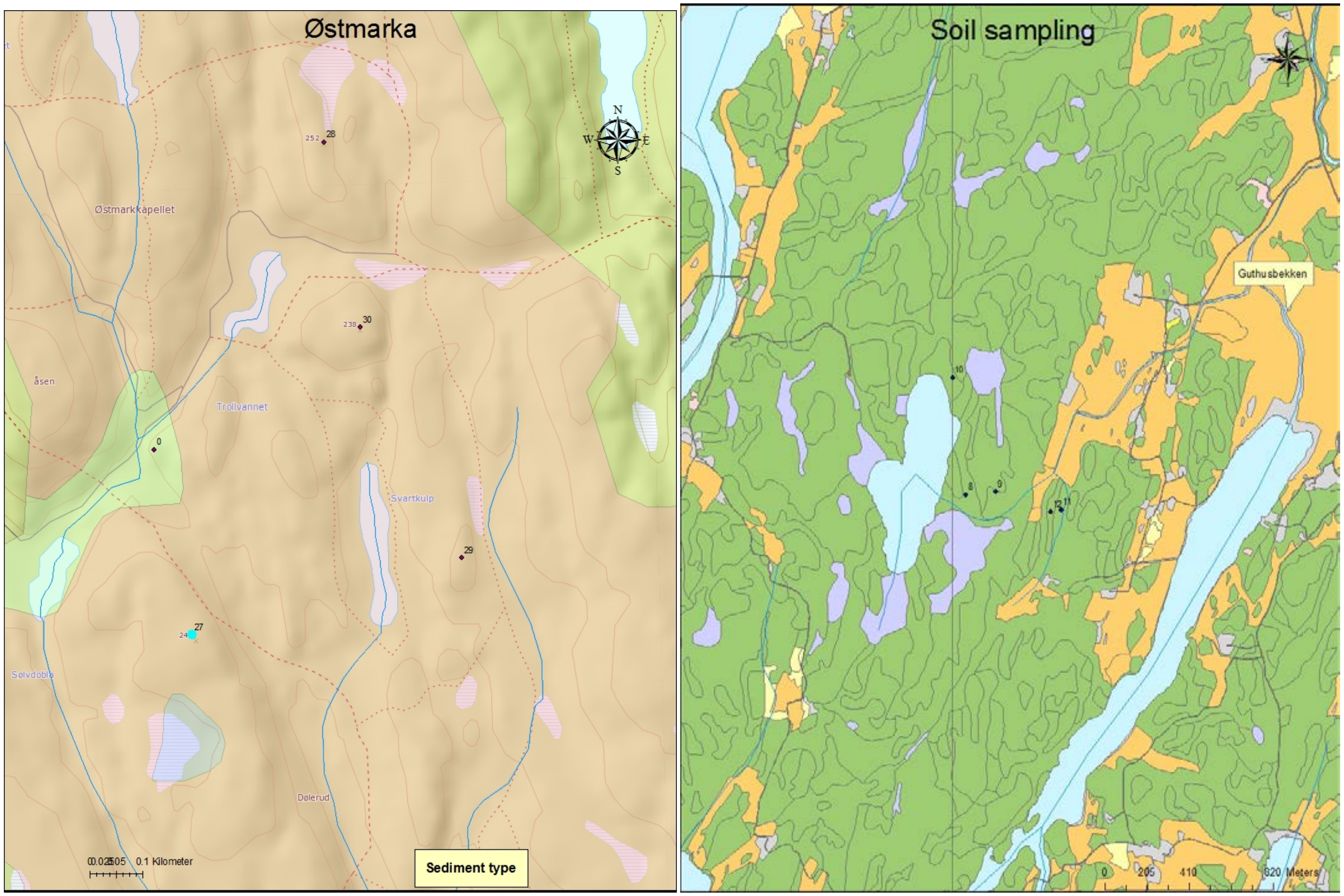

Figure 14: Soil sampling maps for the sites of Guthus and Østmarka; the numbers and black dots in each site represents plot numbers where the soils are sampled[9].

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[9] More information about the plot numbers are given in table 3.1 and see figure 12 for the legends description. The map used is a quaternary map, 1:50000 produced by Geology for Society (NGU) (http://www.ngu.no/no/hm/Kart-og-data/nedlasting/), modified by Alexander Engebretsen.

3.2 Soil sampling

Soil samples were collected from eight conifer forested sub catchments in the Morsa watershed (see Figures 12, 13 and 14). The plots in the sub-catchments have different type of unconsolidated deposits (Table 6). The coordinates and elevations of each plot numbers in (figures 13 and 14) was inserted in to GPS map 62s (GARMIN) instrument, to find the exact sampling site, and 83 Soils samples were collected from these sub-catchments (Huggenes, Dalen, Augerød, Støa, Østmarka, Guthus, Boslangen and Gashus). All the samples are collected from forest using an auger (soil sampler) and placed in a Ziploc plastic bag for transport. All sub-catchments are located below the marine limit except the Østmarka site. See appendix G also for maps of the quaternary deposits of the study area.

Table 6: Type of unconsolidated deposits, morphology and soil horizons at the sampling sites. The information is extracted from each sub-catchment from the map in Figure12 and appendix G. The maps are provided by the Norwegians Forest and Landscape Institute (2011) and revised by Alexander Engebretsen, UiO.

Sub-catchment	Plot number (see Figure 13 and 14)	Deposit type	Morphology	Soil horizons
Huggenes	5	Naked mountain	Ridge	O
	3	Sea fjord and beach alluvium continuous	Ridge	O,AE,B
	7	Naked mountain	Slope	O,A
	4	Sea fjord and beach alluvium discontinuous	Slope	O,E,B
	2	Sea fjord and beach alluvium discontinuous	Slope	O,E,Bs,B,C
	6	Organic soils (bogs)	Valley bottom	H,C
	1	Sea fjord and beach alluvium continuous	Valley bottom	H1
Guthus	12	Naked mountain	Ridge	O
	9	Naked mountain	Ridge	O,A,E,Bs
	11	Sea fjord and beach alluvium discontinuous	Valley bottom	A,B,C
	10	Sea fjord and beach alluvium discontinuous	Valley bottom	H1,H2,C
	8	Organic soils (bogs)	Valley bottom	H1,H2,C
Boslagen	16	Naked mountain	Ridge	O
	15	Naked mountain	Slope	O,E

	14	Organic soils (bogs)	Valley bottom	H,A,C
	13	Sea fjord and beach alluvium discontinuous	Valley bottom	O,A,B
Dalen	19	Humic cover over mountain	Ridge	O
	18	Humic cover over mountain	Slope	O
Augerød	23	Humic cover over mountain	Slope	O,B
	22	Naked mountain	Slope	O,A,B
	25	Humic cover over mountain	Valley bottom	O
	24	Sea fjord and beach alluvium discontinuous	Valley bottom	A,B,C
	21	Sea fjord and beach alluvium discontinuous	Valley bottom	O,A,B,C
Støa	33	Margin moraine	Ridge	O,E,Bs,B
	32	Margin moraine	Slope	O,AE,B
	31	Margin moraine	Valley bottom	O,A,B,B2
Gashus	38	Naked mountain	Ridge	O
	36	Naked mountain	Ridge	O
	35	Sea fjord and beach alluvium discontinuous	Slope	O,Bh,B,C
	34	Organic soils (bogs)	Valley bottom	H,A
Østmarka	30	Naked mountain	Ridge	O,E,B
	29	Naked mountain	Slope	O,B,C
	27	Naked mountain	Valley bottom	O,B,C

3.2.1 Soil from different horizons

Soils from the sites were sampled from different generic horizons, approximately from 1cm below the top surface to 120 cm depth. The soil horizons O, H, A, AE, E, B, Bs and C were found in the Morsa watershed. In some sampling sites, especially on the bare rock mountains, only O horizons were sampled as other horizons were lacking. The H horizons, denoting Histosols, were inherently found on waterlogged areas. Below the organic peat layer, typically at around 80cm depth, a clay soil layer (C-horizon) was commonly found. Figure 15 below shows the sampling strategy to capture soils from different topography.

Soil samples were collected from the ridges, slopes and valley bottom in order to capture the topographic gradient found within each site. All sites were located below the marine limit, except Østmarka, which was situated above the marine limit. The main span in soil structure was thereby sampled due to the redistribution of the unconsolidated deposits as the shoreline passed through the watershed. Emphasis was given in the sampling strategy to capture fertile soils in the valley floors that have not been exposed to agricultural practices.

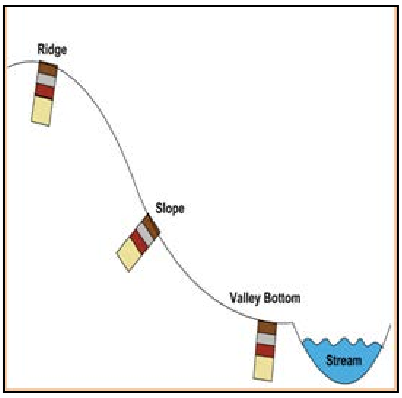

Figure 15: Soil profile from the different topographic presentation from (Mohr, 2010).

Figure 16: Picture from sampling site from ridge topography and the ridges show also bare mountain, Photo was taken during sample collection.

Figure 17: Picture from soil sampling site from slope topography. In this figure it shows the lighter soil colour. Photo was taken during sample collection.

Figure 18: Picture from soil sampling site from the valley bottom topography, near a stream. The water shows a brown colour. Photo was taken near the stream during sample collection.

3.3 Soil sample pre-treatment

After the soils were brought to the chemistry laboratory at the Department of Chemistry, University of Oslo, the necessary sample pre-treatments such as drying, sieving, homogenizing and storing has been conducted according to ISO-11464 (2006) method. Figure 19 shows pictures from the sample drying process.

Figure 19: Drying of soil samples from various soil types and horizons (upper panel). During the drying the samples were covered as shown in the lower panel.

3.3.1 Grinding and sieving of soil samples

The collected soil samples were placed on cardboard plates covered with a cardboard (as shown in figures 19 and dried at a room temperature for about three weeks. The dried samples were then crushed gently using a mortar and a pestle, and sieved through a 2mm mesh. During the grinding process care was taken not to crush the individual soil minerals ensuring that only large soil aggregates were broken. Grinding and sieving are essential part of homogenizing the sample and is consistent with the internationally accepted standard for soil chemical analysis (ISO-11464, 2006). The soil fractions that passed through the 2mm sieve was collected and stored for physicochemical analysis.

3.3.2 Storage and homogenization of the soil samples

Sieved soil samples were stored in cardboard boxes (of approx. 0.5L volume) and placed in a dry shelf at room temperature. Homogenization of soil samples is very important to get a good analytical result. Thus, before withdrawal of samples from the boxes, the samples were mixed using a spoon.

3.3.3 Cleaning procedures

Plastic and glassware used for the analysis of the samples were cleaned in a Miele Mielabor G 7783 Mutitronic washing machine (Miele, Germany), which performs HNO_3 acid wash and Type II water rinse in accordance with Miele Mielabor G 7783 Mutitronic washing machine standard wash procedure. The sample bottles were also cleaned with diluted 5-10% HCl overnight. All glass equipment used in the experimental work had been top filled or soaked in 10 % (w/w) HNO_3 and then rinsed with Type II and Type I water to minimize contamination prior to analysis unless otherwise stated. See appendix D for characteristics of type I and type II water.

3.4 Physicochemical Soil analysis

The soil samples were analyzed for soil physiochemical properties such as soil moisture, soil pH, organic matter content, effective Cation Exchange Capacity (CECe) including Base Saturation (BS%) and Aluminum Saturation (AlS%), particle size distribution (% of clay, silt and sand) and phosphorus pools (total-P, inorganic-P and organic-P) and inorganic P-fractionations (easily soluble-P, P bound to Al, P bound to Fe, P bound to Ca and occluded-P). The preparations of samples and standard solutions for the physicochemical analysis of the samples were conducted at the laboratories at the Departments of Chemistry and Geosciences, UiO.

3.4.1 Soil pH

Soil pH was measured according to a method described in ISO-10390 (1994) both in water and 1M $CaCl_2$ (1:5, soil to 1M $CaCl_2$) extract. Sample solutions were shaken repetitively, and left for two hours for sedimentation. The purpose of extracting with a salt solution is to provide pH values that are more comparable as the salt masks the variability in the salt content of soils and serves to maintain the soil in a flocculated condition as well as to decrease the junction-potential effect on the electrode (Beery and Wilding, 1971; Coleman et al., 1950). The measurement of pH was done using an Orion pH-meter with a ROSS pH electrode. Two replicates per sample were measured. All the analysis results are given in appendix A and appendix C, table C1.

3.4.2 Dry matter content

Dry matter of the air dried soil samples was conducted according to a method described in ISO-11465 (1993). About 10g of soil was weighed accurately (M_1) using an analytical balance (Sartorius LC3201D, accuracy ± 0.1 mg), and put into a pre-weighed container (M_0). The container with the soil sample was placed in a drying oven at a constant temperature of $105^oC \pm 5^oC$ overnight, and then placed in a desiccator for cooling. The cooled and dried soils were weighed again (M_2) on the analytical balance. The mass difference is used to calculate the dry matter and water content of the soil according to Eq. 3.1 and 3.2. Results are given in appendix A.

$$W_{H2O} = \left(\frac{M1-M2}{M1-M0}\right) \times 100\% \qquad (3.1)$$

$$W_{dm} = \left(\frac{M2-M0}{M1-M0}\right) \times 100\% \qquad (3.2)$$

Where, W_{H2O} is water content

W_{dm} is dry matter

M_0 is mass of the empty container

M_1 is mass of the air dried soil + container

M_2 is mass of the oven dried soil at $105^oC \pm 5^oC$ + container

3.4.3 Organic matter content

Organic matter of the soils was determined by loss on ignition (LOI) according to the modified ISO standard by Krogstad (1992). For this purpose, 5-10g of soil was weighed on an analytical balance into a quartz container and placed at 550°C in furnace for 4 hours for high temperature combustion of the organic matter to CO_2. After burning the containers with the ash content were placed in desiccator for cooling and then the mass was determined. The LOI was determined according to Eq. 3.3. Results are given in appendix A and appendix C, table C1.

$$LOI\ = \left(1 - \frac{M2 - M0}{M1 - M0}\right) \times 100\% - WH2O \qquad (3.3)$$

Where

LOI is Loss on Ignition

W_{H20} is water content from Eqn 3.1
M_0 is mass of empty container
M_1 is mass of air dried soil + container
M_2 is mass of ignited soil + container

3.4.4 Particle size distribution (PSD) for mineral soils

Particle-size distribution analysis is a measurement of the size distribution of soil particles in a soil sample. The major features of soil particle size analysis is the dispersion of soil aggregates into distinct units by removal of organic matter, salts, carbonates and oxides, by using chemicals, mechanical shaker (electrical mixer), and ultrasonic vibrator machine according to ISO-11277 (1998). Sieving, sedimentation and laser diffraction was applied as methods for the separation of the particles according to their size.

Determination of particle size distribution was performed at Dept. of Geosciences, University of Oslo, using a Beckman-Coulter LS 13 320 Laser diffraction particle size analyser. The principle of the Laser Diffraction Method (LDM) is that particles of a given size diffracts light at a given angle when a parallel beam of light passes through the suspension kept in the sample cell. The angle of diffraction increases with decreasing particle size and vice versa (Di Stefano et al., 2010). Only mineral soils from (A, E, B, C) horizons were selected for the determination of the particle size distribution and soils were included from both the above and below marine limits.

The selected soils were pre-treated according to a method described in ISO-11277 (1998) to destroy oxides and organic content of the soil using hydrogen peroxide (H_2O_2) 30% (v/v). The selected soil samples for PSD analysis was placed in a glass container, and 30ml of water followed by 30ml of 30% (v/v) hydrogen peroxide was added to moisten and remove organic matter, salts, oxides and carbonate content of the soil. Any vigorous reaction was avoided by adding drops of 2-Octanol solution, and contents of the vessel was continously stirred. Finally the container was covered and left over night for sedimentation. After the removal of the organic matter content, salts, oxides and carbonates; the samples were dried using vacuum freeze dryer. A small amount of each samples free of organic matter were taken for size distribution measurement. Results are given in appendix A.

3.4.5 Determination of Effective Cation Exchange Capacity, soil pH and Base and Aluminium saturation

Effective cation exchange capacity (CECe) of a soil is simply a measure of the amount of exchangeable sites on soil surfaces that can hold positively charged ions by electrostatic forces (Schwertfeger and Hendershot, 2009). Cations which are bound by electrostatic force are exchangeable with other cations when the soil is in contact with a solution and are thus readily available for plant uptake.

Determination of effective cation exchange capacity (CECe) is based on the method described by Hendershot et al. (2007). The method is comparable to ISO 11260 and ISO/TC190/SC3 standards, using spectrophotometric determination of Al. The main deviation is that exchangeable H^+ is determined by measuring pH directly in the supernatant solution and that iron and manganese is determined in addition to the Al. The soil extraction was conducted with soils that have been air-dried and passed through a 2.00mm aperture sieve. About 1.50g of soil sample for organic soils and 4.50g of soil for mineral soils were accurately weighed into polycarbonate centrifuge tubes. About 30.0mL of 0.1M $BaCl_2$ extracting solution was added to each of the soil samples. The samples were shaken for 2hrs in a Nalgene and Edmund KS-15 shaking machine at a slow speed of 50strokes/minute. After shaking, the mineral soil samples were centrifuged for 10 minutes at 3000 rpm in a Jouan B4i (Thermo fisher scientific Inc.) centrifuge. The solution was decanted and then filtrated under vacuum pressure through a Whatman No. 42 filter paper [10]for quantitative analysis. Organic soil samples were not centrifuged. They were only filtered with a Whatman No. 42 filter paper in the same way as the mineral soils. For CECe and base and aluminium saturation calculations see chapter 3.4.5.3.

3.4.5.1 Exchangeable H^+ using pH- measurement

The filtrate was transferred to a scintillation bottle which was stored cool and dark before analysis. The pH of extracted soil sample was measured using pH-meter. The measurement was conducted in order to determine exchangeable hydrogen ions [H^+]. The concentration of H^+ ([H^+]) was calculated based on the measured activity of the H^+ by dividing with the activity coefficient for H^+.

3.4.5.2 Cation analysis using inductively coupled plasma optical emission spectroscopy

The concentration of basic- and acidic cations calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), aluminium (Al^{3+}), iron (Fe^{3+}) and manganese (Mn^{2+}) in the extracts were determined according to the method described in ISO-22036 (2008), using VISTA AX CCD Simultaneous Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The instrument is equipped with an Echelle polychromator, a Charge Coupled Device (CCD) for detection, and the emission was measured axially. Prior to analysis, all sample and standard solutions were acidified to 1% (m/v) nitric acid. Concentrations of each cation obtained from the instrument in mg/L were converted to CEC in meq/kg of the cations in soil as explained in section 3.4.5.3 and results are given in appendix A and appendix C, table C3.

3.4.5.3 Calculations of CECe, base- (%BS) and aluminum saturation (%AlS)

All concentrations in the supernatants were translated into meq/kg of dry soil (see Eq. 3.4). The exchangeable amount of the different cations per kg soil was calculated from the concentration in the extracts ([X]), the amount of soil (1.5 or 4.5g) and volume (30mL) of extractant solution according to eq. 3.4.

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[10] . Provides fine retention and slow flow rate. Suitable for general filtration of many types of samples

$$(\mathrm{X})\ (\mathrm{in\ cmol_e/kg_{soil}}) = [\mathrm{X}]\ (\mathrm{in\ cmol_e/L}) \cdot \frac{30\mathrm{mL}}{\mathrm{g_{soil}} \cdot \frac{w_{dm}}{100}} \tag{3.4}$$

Where, [X] is concentration of cations (cmole)

g $_{soil}$ is weight of dry soil sample in (g)

W_{dm} is dry matter correction factor

The sum of all cations in meq/kg of the soil gives the CECe

$$CEC_E = \sum (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Al^{3+}, Fe^{3+}, Mn^{2+}, H^{+})\mathrm{cmol_e\ kg_{soil}}^{-1} \tag{3.5}$$

The percentage of sum base cations (Ca2+, Mg2+, K+, Na+) relative to the CECe gives the Base Saturation (BS%) (eq. 3.6)

$$\%BS = \frac{\sum (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+})}{CEC_E} \cdot 100 \tag{3.6}$$

The percentage of aluminum relative to the CECe gives the Aluminium saturation (AlS) (eq. 3.7).

$$\%AlS = \frac{\sum (Al^{3+})}{CEC_E} \cdot 100 \tag{3.7}$$

Results for CEC_e and BS are found in appendix A and appendix C, table C4.

3.5 Analysis of phosphorus pools in soil extracts

The soil samples were analyzed for total and inorganic phosphorus according to the method by Møberg and Petersen (1980). The sequential fractionation of inorganic phosphorus was analyzed for easily soluble-P, P bound to Al, P bound to Fe, P bound to Ca and occluded-P based on the method developed by Chang and Jackson (1957). The method is discussed in section 3.5.1and 3.5.2 below.

3.5.1 Total-phosphorus

Measurement of the total phosphorus is based on the method described by Møberg and Petersen (1980). About 1.0g of soil was ignited according to section 3.4.3, and of each the ignited sample was transferred to acid washed 250mL volumetric flask and added 5mL of 6M H_2SO_4. After the contents of the flask were mixed well, the mixture was heated in a water bath at 70^0C for 10 minutes. Further 5.0 mL of 6M H_2SO_4 was added and left for cooling for one hour. The sample was diluted to a total volume of 250mL using Type I water. After dilution, the sample was left for two days for sedimentation so that a clear solution is formed. Total-P of the sample solution was measured at Dept. of Geosciences UiO, on a SEAL Orthophosphate Auto Analyzer 3 using the application of Molybdenum blue method described by Murphy and Riley (1962). See the method in appendix F, figure F4.

3.5.2 Inorganic- and Organic phosphorus

Inorganic phosphorus was extracted following the same procedure as total phosphorus, except the soil was 1g of air dried. Organic-P (Org.-P) was calculated by difference between Total-P and Inorganic-P as shown below. Results for inorganic phosphorus and organic phosphorus are found in appendix A and appendix C, table C5 and C6 respectively.

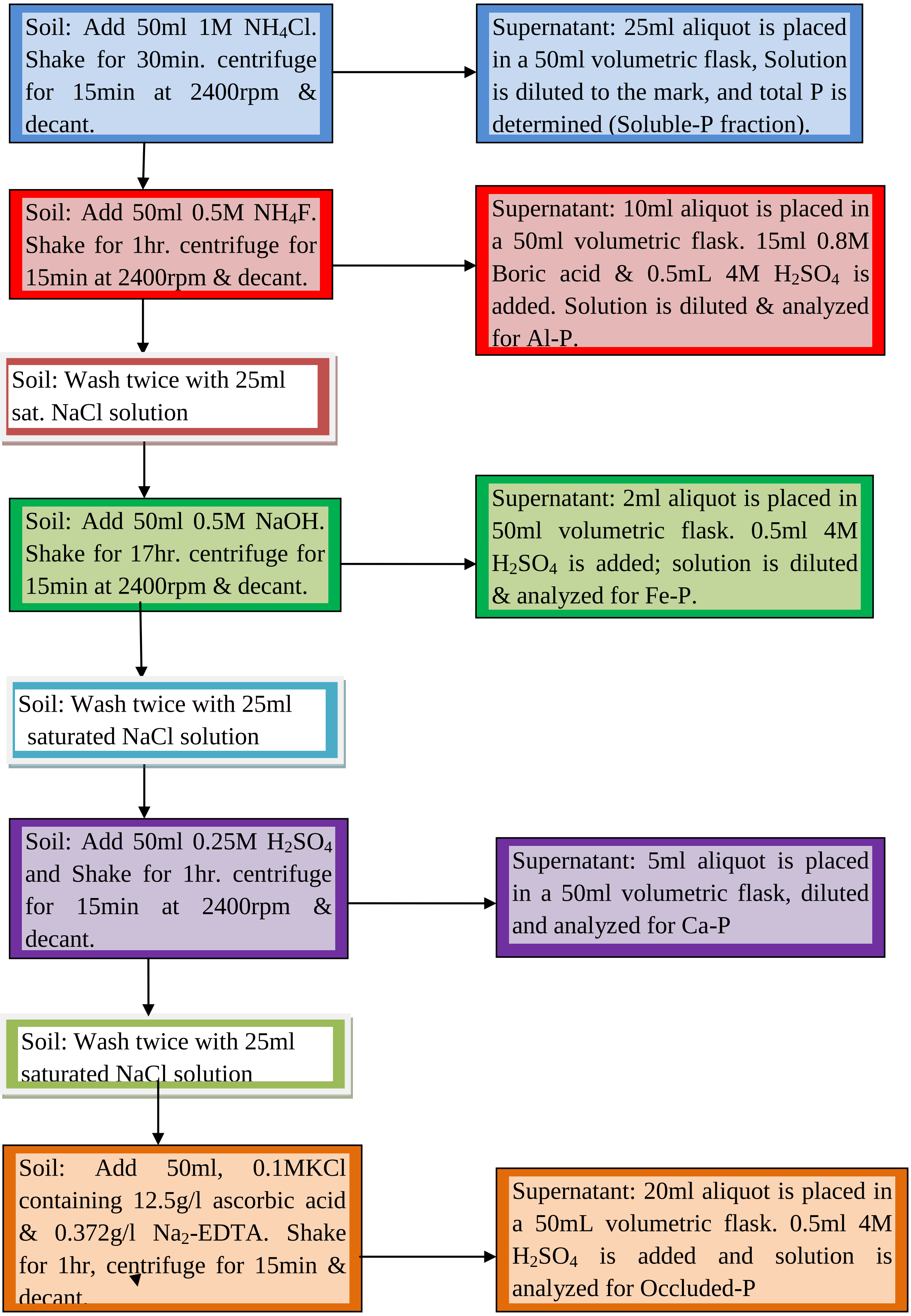
3.5.3 Sequential extraction of inorganic phosphorus in soils

Sequential extraction schemes were developed to search out additional information on the levels of soil phosphorus fractions in soils. A single sample of soil is extracted sequentially by adding stronger extracting solvents to separate the phosphorus into fractions based on the chemical solubility (Turner et al., 2005). The method of the sequential extraction of Inorganic-P was performed according to the method explained by Chang and Jackson (1957). According to the sequential extraction method, five inorganic P-pools are defined; easily soluble phosphorus, P bound to Al, P bound to Fe, P bound to Ca and occluded phosphorus. Fractionation of these five inorganic phosphorus pools was conducted as outlined below and shown in Figure 20. Results are given in appendix F, table F3.

3.5.3.1 Procedures of the sequential extraction and preparation method

About 1g sample of soil was placed in an 85mL centrifuge tube and extracted with 50mL of 1M NH_4Cl for 30 min on a mechanical shaker (Edmund Bühler KS-15). The suspension was centrifuged and the supernatant solution was saved for the determination of the soluble and loosely bound phosphorus. A 50mL of neutral 0.5M NH_4F was added to an 85mL centrifuge tube again and the suspension extracted on a mechanical shaker for 1 hour. The suspension was centrifuged and the supernatant solution was decanted for determination of aluminium bound phosphate. The soil sample left after the extraction of aluminium phosphate was washed twice with 25mL of saturated NaCl solution. It was then extracted with 50mL of 0.1M NaOH on the shaker for 17 hours. The soil suspension was centrifuged for 15 minutes at 2400 rpm and centrifuged again to obtain a clear solution that was decanted into another centrifuge tube for determination of iron phosphate. The soil sample after extracting iron phosphate was washed with two successive aliquots of 25mL of saturated NaCl solution. It was then extracted with 50mL of 0.25M H_2SO_4 for 1 hour on a mechanical shaker (Edmund Bühler KS-15). The suspension was centrifuged and the clear supernatant solution is decanted for determination of calcium phosphate. The soil sample left after the extraction of calcium phosphate was again washed twice with 25mL of saturated NaCl solution and it was then extracted with 50mL of 0.1MKCl that contains ascorbic acid and Na2-EDTA for 1 hour on the mechanical shaker. The suspension was then centrifuged for 15minutes and the clear supernatant was analyzed for occluded phosphate (see Figure 20).

The SEAL Autoanalyzer 3 at the Department of Geosciences, UiO, was used to determine the Tot-P and Inorganic-P fractions from the soil extracts acquired from the Chang and Jackson (1957) and Møberg and Petersen (1980) methods. The instrument was set with the parameters given in appendix F.



Soil: Add 50ml 1M NH_4Cl. Shake for 30min. centrifuge for 15min at 2400rpm & decant.

Supernatant: 25ml aliquot is placed in a 50ml volumetric flask, Solution is diluted to the mark, and total P is determined (Soluble-P fraction).

Soil: Add 50ml 0.5M NH_4F. Shake for 1hr. centrifuge for 15min at 2400rpm & decant.

Supernatant: 10ml aliquot is placed in a 50ml volumetric flask. 15ml 0.8M Boric acid & 0.5mL 4M H_2SO_4 is added. Solution is diluted & analyzed for Al-P.

Soil: Wash twice with 25ml sat. NaCl solution

Soil: Add 50ml 0.5M NaOH. Shake for 17hr. centrifuge for 15min at 2400rpm & decant.

Supernatant: 2ml aliquot is placed in 50ml volumetric flask. 0.5ml 4M H_2SO_4 is added; solution is diluted & analyzed for Fe-P.

Soil: Wash twice with 25ml saturated NaCl solution

Soil: Add 50ml 0.25M H_2SO_4 and Shake for 1hr. centrifuge for 15min at 2400rpm & decant.

Supernatant: 5ml aliquot is placed in a 50ml volumetric flask, diluted and analyzed for Ca-P

Soil: Wash twice with 25ml saturated NaCl solution

Soil: Add 50ml, 0.1MKCl containing 12.5g/l ascorbic acid & 0.372g/l Na_2-EDTA. Shake for 1hr, centrifuge for 15min & decant.

Supernatant: 20ml aliquot is placed in a 50mL volumetric flask. 0.5ml 4M H_2SO_4 is added and solution is analyzed for Occluded-P

Figure 20: Sequential extraction method of soil analysis for inorganic phosphorus fractionation (Pierzynski, 2000).

Results obtained from the determination of phosphorus pools, i.e. Inorganic and organic phosphorus and the inorganic-P fractionation (easily bound phosphorus to soils, Al-bound phosphorus, Fe-bound phosphorus, Ca-bound phosphorus and occluded phosphorus) are found in appendices A, C and F.

3.6 Statistical analysis

The Minitab 16 statistical programme was used to perform a hierarchical cluster analysis and principal component analysis. In addition individual Pearson correlations were performed in order to find the strength of association between variables.

3.6.1 Hierarchical cluster analysis

Cluster analysis is a method of modelling groupings, or clusters of similar parameters or objects. The clusters are presented with a dendogram, a two-dimensional chart where the y-axis shows the similarity (where 100 % is very similar and 0 % no likeness between the clusters and the horizontal lines denotes the clusters (BRIDGES JR, 1966).

3.6.2 Principal component analysis

A Principal Component Analysis (PCA) is a way of identifying patterns in large data matrix in which observations are described by several inter-correlated quantitative dependent variables (Abdi and Williams, 2010). Its goal is to extract the important information from the data, to represent it as a set of new orthogonal variables called principal components, and to display the pattern of similarity of the observations and of the variables as points in maps.

4 Result and Discussion

83 soil samples collected from soil profiles on ridges, slopes and valley bottoms in the forests of the Morsa catchment were analyzed for physicochemical properties such as soil pH, organic matter (LOI), effective cation exchange capacity and base saturation and pools of phosphorus, as well as particle size distribution on the mineral soils. This section describes the result and discusses empirical and conceptual relationships between the analyzed parameters.

4.1 Soil pH and Organic matter content

4.1.1 Soil pH

Results of soil pH measured in water and in $CaCl_2$ suspension are given in Appendix A. The pH measured in $CaCl_2$ is approximately one unit lower than the pH measured in water, and this is because of ion exchange process. The calcium chloride provides Ca^{2+} ion in the solution to replace some of the H^+ ions on the soil particles, forcing the hydrogen ions on to the solution. The Ca^{2+} is a strong competing cation binding negatively charged groups. Figures 21 and 22 show the trend in soil pH with topography and down through the soil profiles, respectively. The soil pH_{CaCl2} varies from pH=2.73 in the O horizon located on the top surface of the mineral soil profile on the ridge to pH=5.45 in the deep C horizon in the bottom of the bogs on the valley floor. There is, as commonly found, an increase of soil pH down the soil horizons. The increase pH down the soil profile is in the literature commonly explained by the neutralization through acid consuming weathering down through the B and C horizons. Observing to Figures 22 and 23, it indicates that the pH of the soils is to a large extent governed by the organic matter content. The O and H horizons are acidic with high organic matter content while the deep soil horizons (A, B and C) have highest pH value with low organic matter content. The measured pH[11] in H_2O and $CaCl_2$ is also observed positively correlated with Loss on Ignition (LOI, chapt. 4.1.2) with correlation coefficient r=0.663 and 0.658 respectively, (see appendix B). Organic matter of a soil contains many acid functional groups, which is the main source of H^+ at pH below 5.5. These weak acid functional groups cause soil acidity upon their dissociation. Accumulation of organic matter in the soil and

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[11] pH is expressed as H^+ (H_2O) and H^+($CaCl_2$), it is explained as the [H^+] appendix B.

dissociation of weak organic acids are thus one of the most important contributors of hydrogen ions in acid soils. Furthermore, the upper surface part of the soil is exposed to different pressures that can enhance the acidity. For example, the input of strong mineral acid from long-range transported acid rain, the nitrification of ammonium and the decomposition of plant litter falling on the soil surface are among the contributing factors that cause lower pH values in the upper part of the soil horizons.

Within the mineral B and C horizons, where the levels of organic matter are low, most of the variation in soil H^+ was found to be explained by the % Base saturation of the soil sample (r = -0.606 and -0.877 for $10^{-pH(H2O)}$ vs. %BS). This is due to that the amount of exchangeable acidity decreases with increasing %BS.

The soil pH within each genetic soil horizon was found to increase down the topographic gradient although the increase was not clear. Average lowest pH_{H2O} (3.95, n=23) was found in the forest soil on the floor O horizon, while the highest average pH_{H2O} value (5.6) was found in the 4 samples collected from the clay rich soil C horizon found beneath the bogs in the valley bottoms.

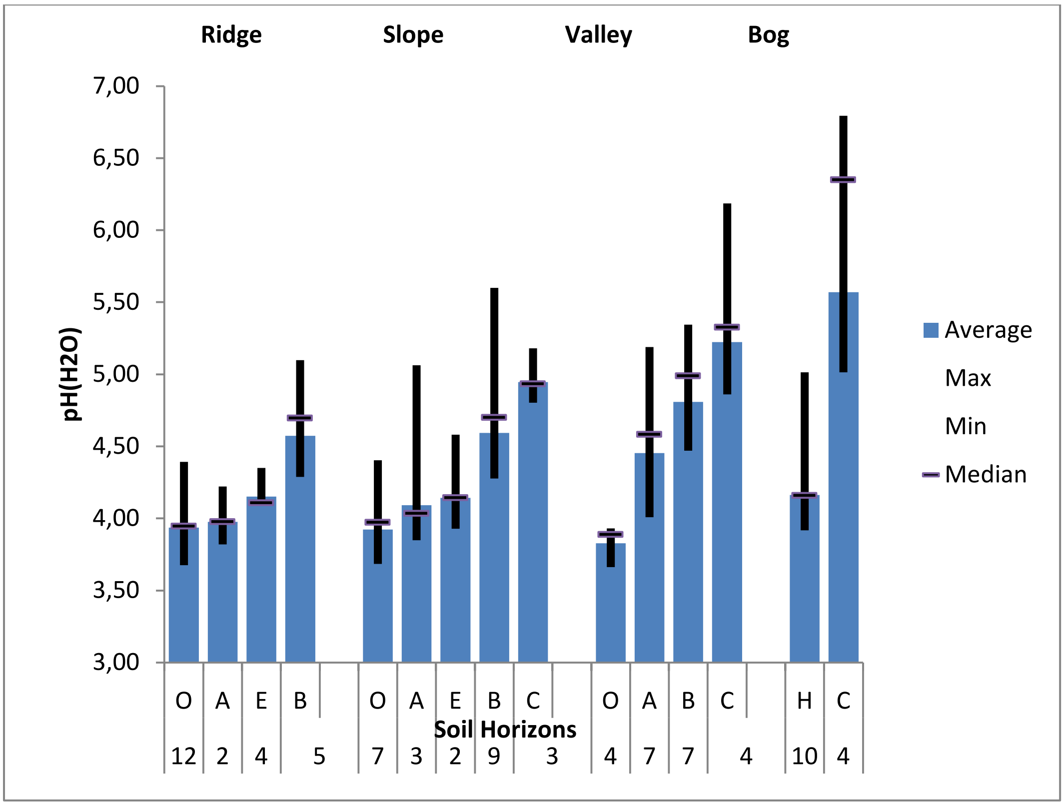


Figure 21: pH shows an increase down through the soil profile as well as down the slope along a topographic gradient - although the increase down the topographic gradient is not so clear

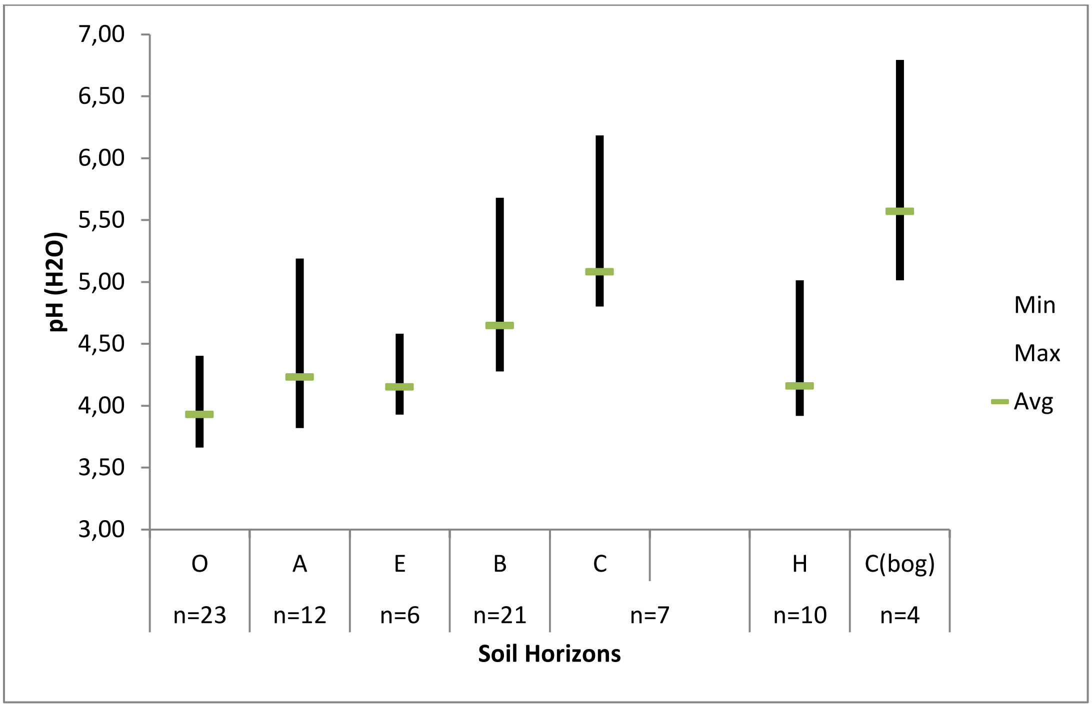


Figure 22: Low pH in the top horizons and increasing pH down into the soil profile

4.1.2 Organic matter content

Loss on Ignition (LOI), reflecting the organic matter content of the soil, decreases as inherently expected from the organic O and H horizons down into the mineral B and C soil horizon. On the ridge and slope the eluvial E horizon has lower LOI than the illuval B horizon due to accumulation of organic matter leached through the E horizon. Figures 23 and 24 show the trends of organic matter within soil profiles and topographic transect. No clear trend in organic content was found between the generic soil horizons along the topographic gradient.

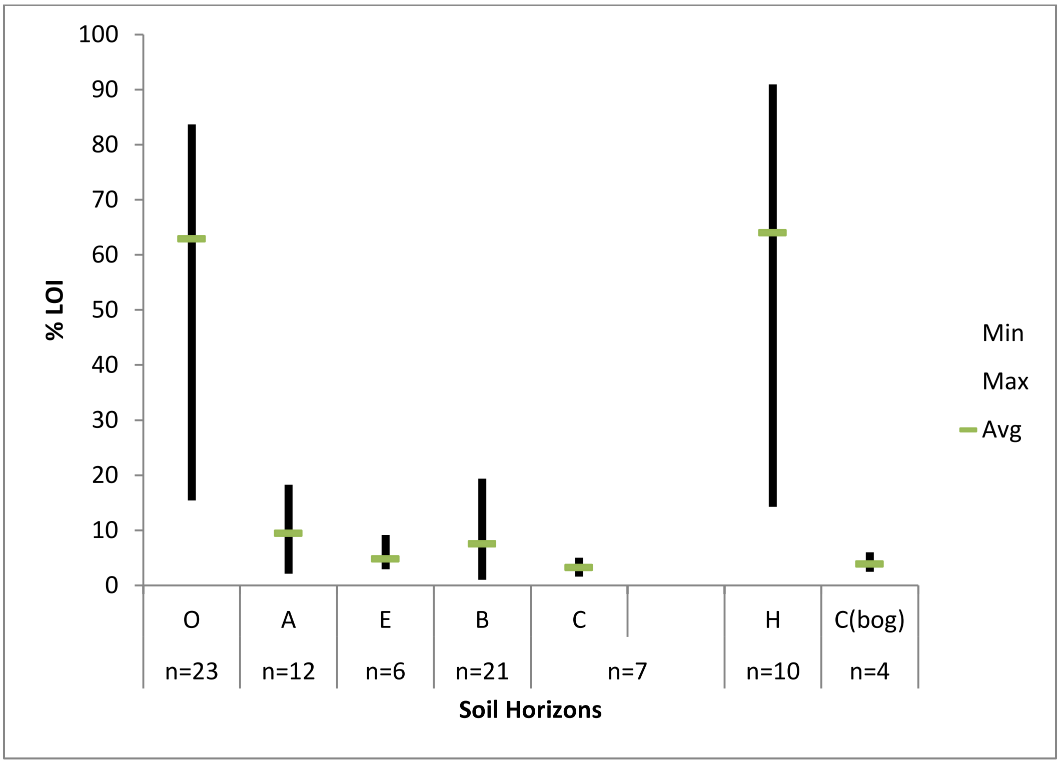


Figure 23: Organic content of soils decreases down through the soil profile

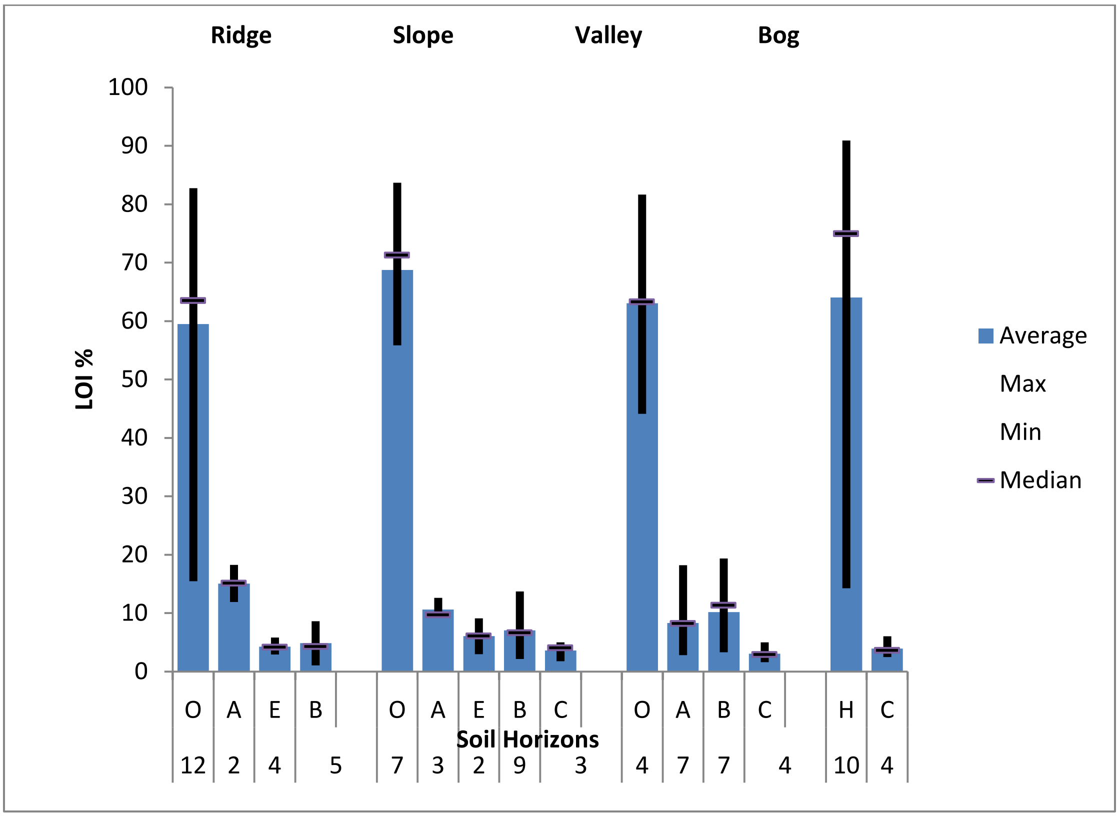


Figure 24: Organic content of the soil in different topography and genetic soil horizons

4.1.3 Representativeness of the Dalen site

The Dalen site, a small forested catchment draining into the western Vansjø basin, is used by Mohr (2010) as a case study of processes governing the dissolution and transport of phosphorous (P) fractions from natural forested soils into the surface waters. These studies have made it clear that a significant amount of aluminium is leached out of these rather acid forest soils. It is therefore postulated that during the acid rain period in the 70ties and 80ties a considerable amount of labile aluminium was leached out of the headwater catchment. The runoff mixes downstream with alkaline seepage from agriculture containing high levels of phosphate. A study by Shekobe (2012) mixing water from Dalen with drainage water from agriculture (Støa) showed that between 50% to 80% of the dissolved phosphate was converted to particulate phosphate along with 60 – 100% of the labile aluminium. A aim of this current study is therefore to determine how representative the acidity of the Dalen site is to the greater forested areas in the Morsa watershed in order to warrant an extrapolation of these findings. In Chapter 4.4.4 the representativeness of Dalen in respect to P pools is discussed.

Data presented in Figures 25 and 26 are compiled data from the study in the Dalen site by Mohr (2010) and Figure 21 from this study. These Figures are used for comparison of the soil acidity and organic content of the soils from Dalen to the rest of the forested sites in the watershed. The soil pH of Dalen is found to lie within the range found in the Morsa watershed, though slightly less acid than the rest of the forest in the watershed. The organic content of the soils of Dalen is much the same as found in the forests of the whole Morsa watershed, except that the forest floor on the ridge is in the upper range, and the Histosol in the valley bottom lies in the lower part of the range of LOI values found in Morsa. Based only on pH and LOI, as key soil physiochemical characteristics, the soils studied in the Dalen watershed appear to be generally representative for the soils in the Morsa watershed.

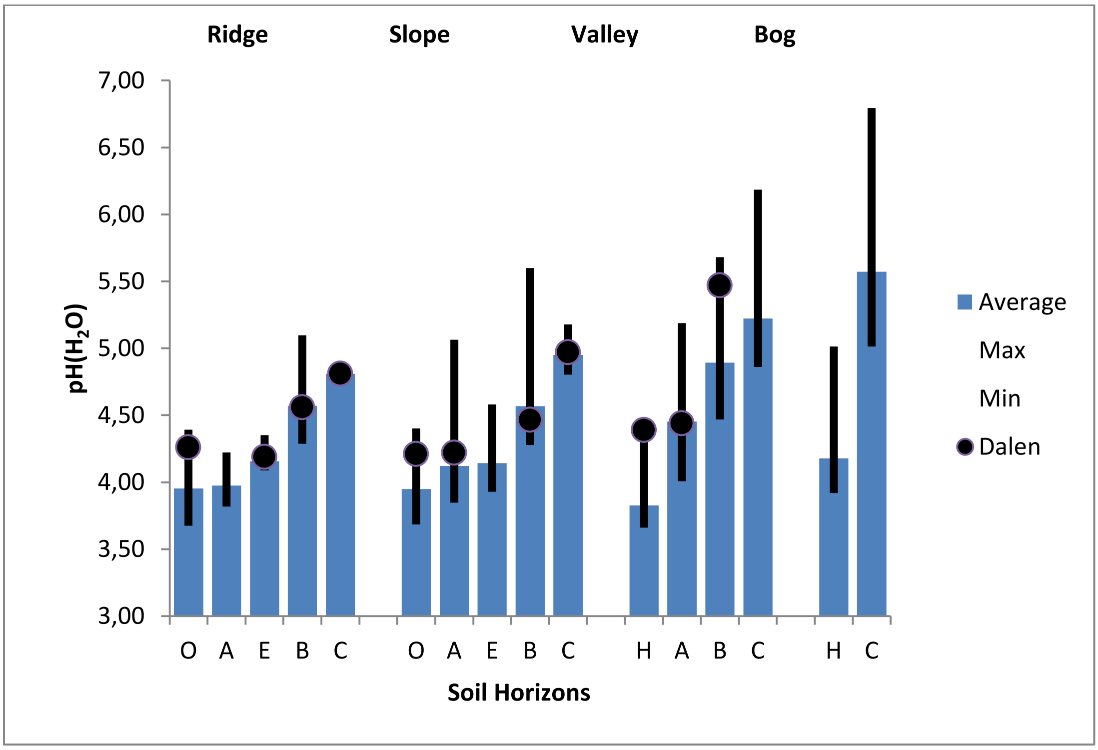


Figure 25: pH of the soils from Dalen versus the rest of the forested sites in the watershed

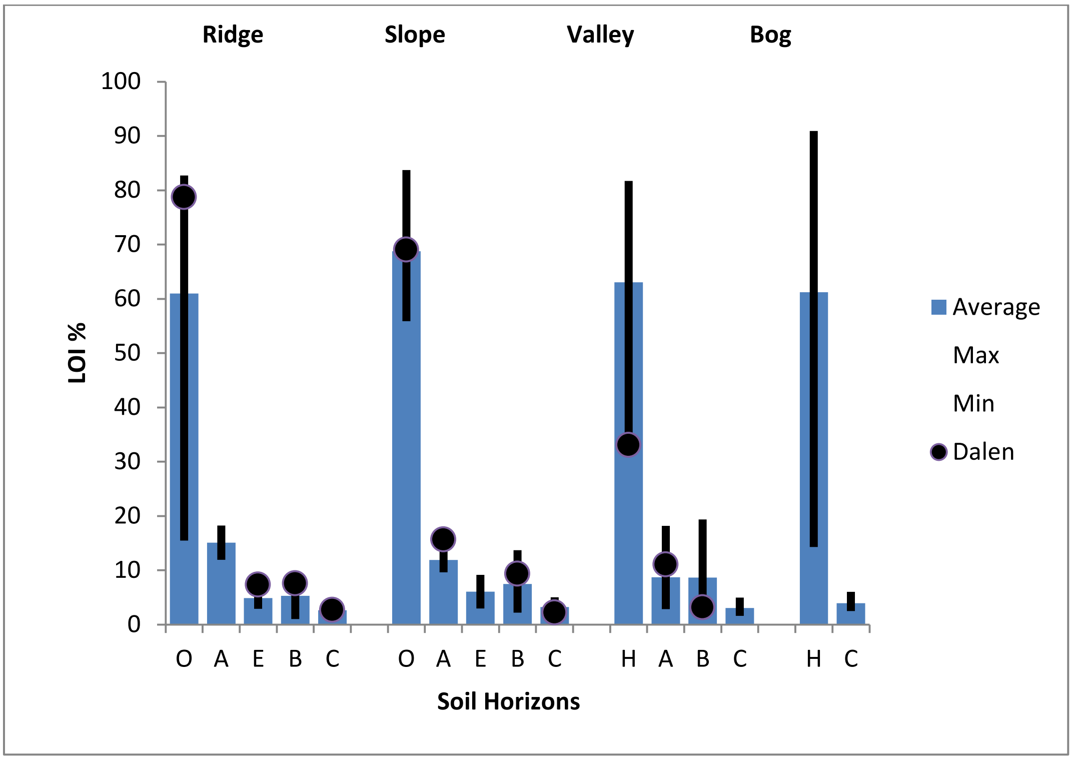


Figure 26: Organic content of soils from Dalen versus the rest of the forested sites

4.2 Soil texture Particle Size Distribution (PSD)

Figures 27 show the percentage distribution of particle size (sand, silt and clay fractions) of the selected mineral soils. According to Loon and Duffy (2005) sand ranges from 0.02-2mm, silt ranges from 0.002-0.02mm, and clay ranges less than 0.002mm. Samples from both above and below marine limits was analysed for PSD, and the samples from above marine limit show sand domination. The soil texture is mainly a sandy loam. The soil texture in the region below marine limit, comprising 90% of the watershed is strongly influenced by the erosion of the seashore upon passing through the landscape. The ridges are washed clean of unconsolidated deposits leaving basically rock outcrops with patches of sand. On the slopes the wave actions left sandy beaches while in the flat valley bottom finer materials accumulated leaving deep deposits of marine clays. Lowest content of the fine particles are thus found in the A and E horizons on the ridge, with an increase in fine material (clay and silt) down the topographic gradient. In the soil on the ridges there is an increase in finer particles down through the profile. This is mainly due to the soil profile forming (pedological) processes transporting particles down through the soil profile. On the slope the top horizons are richer in finer material relative to the deeper soil horizons. This may be due to the higher content of organic matter enhancing the ability to hold finer material.

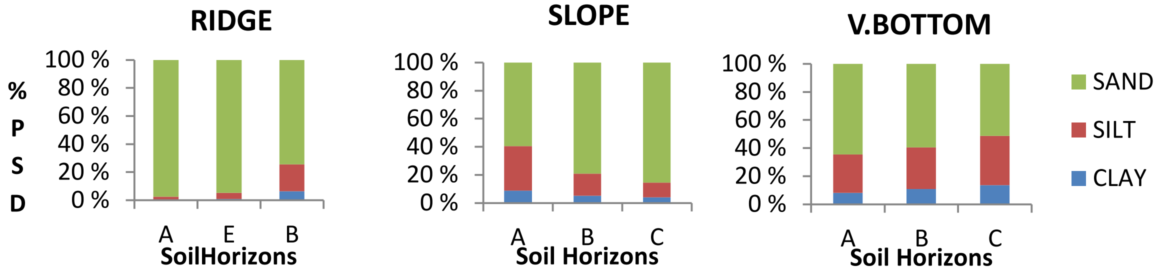


Figure 27. % PSD with in Soil profile and topography (Ridge, Slope and V.bottom, respectively.)

4.3 Effective Cation exchange capacity (CECe) and Base saturation (BS)

4.3.1 Content on the CECe and effect of organic matter and clay

CECe is found in elevated amount in the organic soil horizons with increasing CECe with increasing organic matter content (Figure 28). The average CECe value in the organic soil horizons was 189meq/kg. The mineral soil horizons show CECe value about 60meq/kg. These CECe values are comparable to what was found in pristine forest soils in mid-Norway (Carpenter, 2008) and western Norway, in an acid rain influenced site in southern Norway (Vogt et al., 2003), and in strongly acid rain impacted catchments in Poland (Cooke et al., 1993; Dunne et al., 2005; Patrick and Khalid, 1974). Relatively high CECe values in the mineral soil horizons are found in the soils rich in silt and clay materials (Figure 28). Samples in the red circle in Figure 28 are among the samples rich in fine particles from valley bottoms and shows high CECe values.

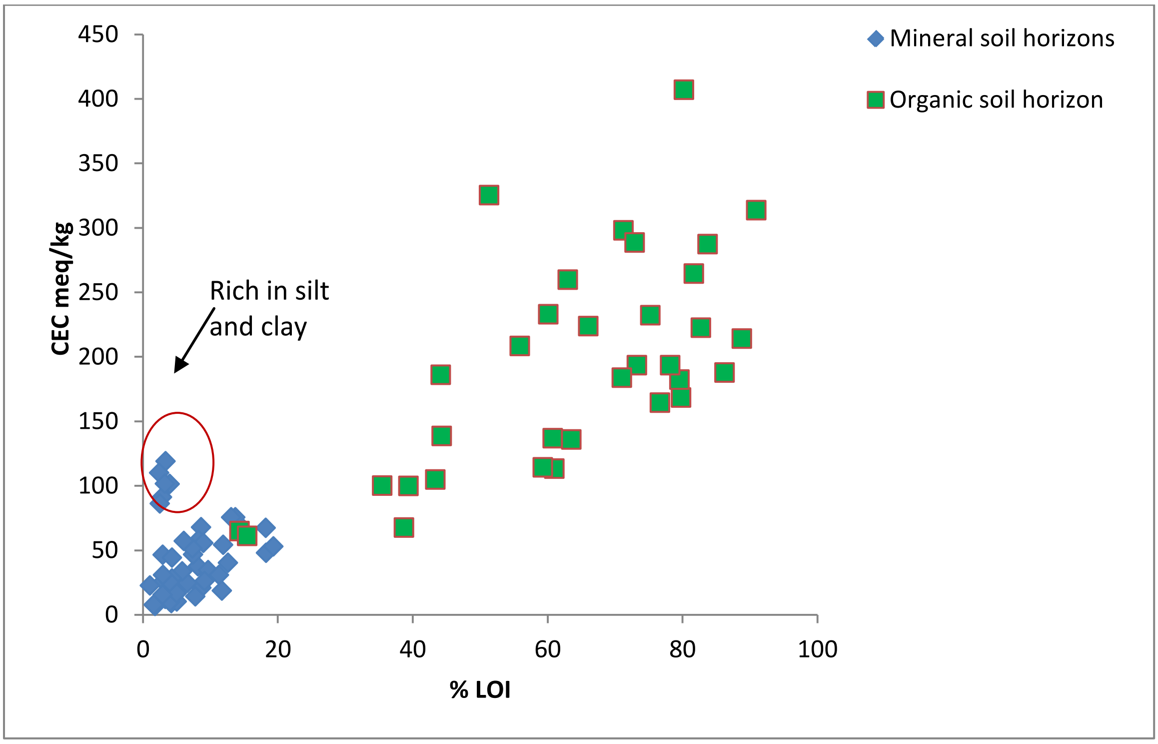


Figure 28: Variation of mineral soil horizons and organic soil horizons with CEC and LOI. Blue diamonds denote mineral soil horizons and green squares denote organic soil horizons

Clay rich soils and soils with high organic content are commonly found to have high CECe. This is due to pH independent charge and large surface area of the clay and the low density and large number of weak organic acid functional groups of the organic matter. A sandy soil with low organic matter content will thus typically have a very low CEC. This is corroborated in the data from Morsa in which CECe is found to be negative correlated with the sand fraction (r = -0.439). CECe is positively correlated with organic matter content (LOI) (r= 0.872). Assigning a value of 0 % clay content in organic soils (due to lack of PSD data on organic soils) the CECe in the soils from Morsa are found to be empirically linked to both the soil organic - and clay content, giving the following multiple linear regression:

CECe = 8.6 + 2.89 % LOI + 2.28% Clay, with an r = 0,868

CECe is thus found to decrease down through the soil profile (Figure 29) mainly due to decrease in organic content (Figure 23). However, CECe increases again in the deep mineral soils down the slope and valley bottom due to increase in clay content (Figures 27 and 29 respectively). In Figure 29 the eluvial E horizon in the soil plot shows lowest CECe value. This is because of the eluviation causing low content of organic matter and clay in this horizon.

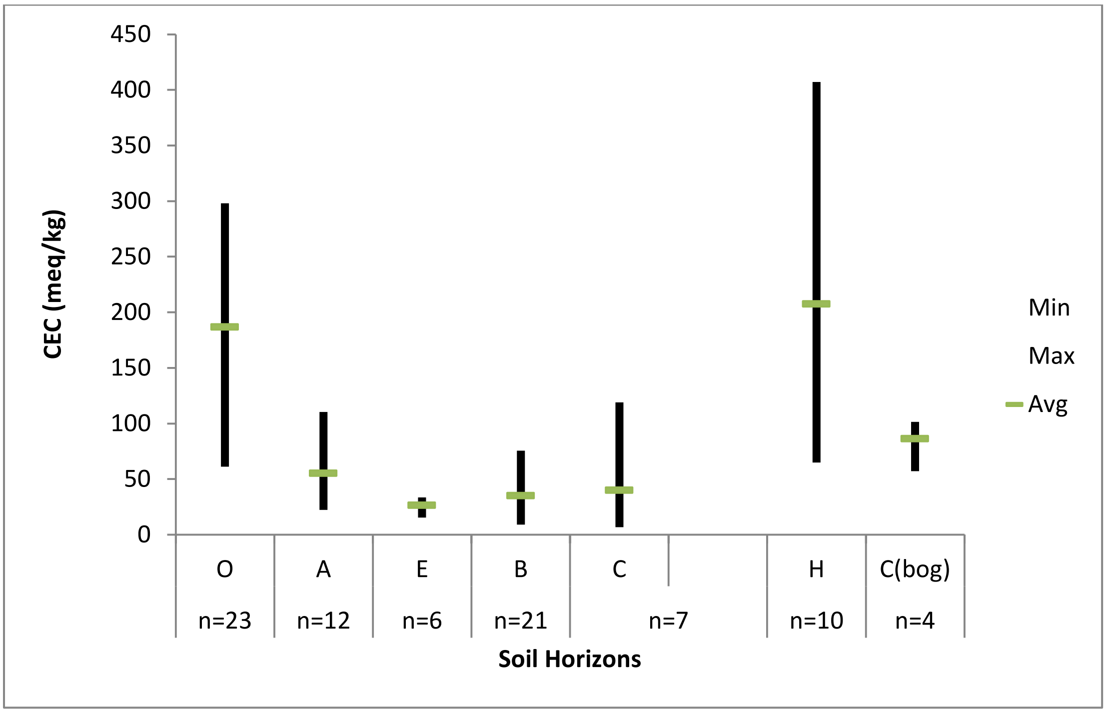


Figure 29: CEC of soils with genetic soil horizons

No clear trend in CECe was found down through the topographic gradient, except a possibly greater variation in the CECe in the valley bottom soils (Figure 30). This greater variation is most likely due to the somewhat larger variation in soil organic content in the horizons in the valley floor as seen in Figure 24.

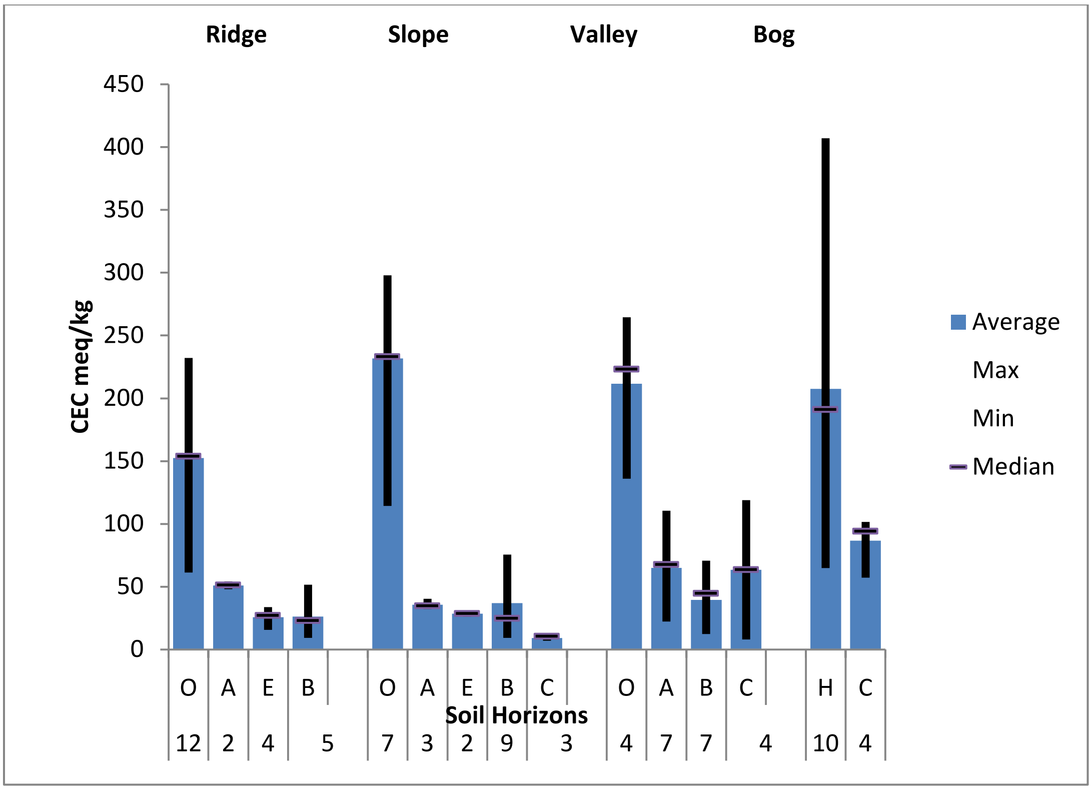


Figure 30: CECe of soils with topography

4.3.2 Variation of Base saturation (BS) with clay and silt

Figures 31 and 32 show that the trends in %BS down into soil profiles and along a topographic gradient, respectively. The %BS shows large spatial variation, though average values are found to be high in the forest floor O horizon (57%) and peat H horizon (54%), decrease down into the mineral soil profile to a minimum in the E horizon (20%), and then increase slightly to the B horizon (24%) and C horizon (51%). Comparing the same generic soil horizons the %BS is generally found to increases down along the topographic gradient, with the highest values in the clay rich soil layers (91%) under the peat bogs in the valley bottom. %BS is thus positively correlated to the fraction of fine particles clay and silt with correlation coefficient of (r=0.616 and 0.561 respectively). The decrease in %BS down to the E horizon is mainly due to natural soil acidification caused by humic acids dissolving, complexing and leaching base cations from the top soil horizons down into the B horizon. The illuviation in the B horizons gives rise to the slight increase in %BS into the B horizon. High %BS in the deeper clay rich C horizons is due to that these soil layers are marine unconsolidated deposits inherently rich in base cations. Furthermore, there has been very little leaching of base cations from these soils due to very poor water permeability through compact clay layers.

%BS in valley bottoms and bogs shows a higher value than on the ridge and slopes. This higher average %BS in the valley floor is conceptually explained by water flow-paths through the watershed. The flow of water down through the soil profile in the recharge zone (ridge and slope) causes a net downwards leaching of base cations, leading to a flux of base cations passing through, and partially being sorbed, to the soils in the discharge zone.

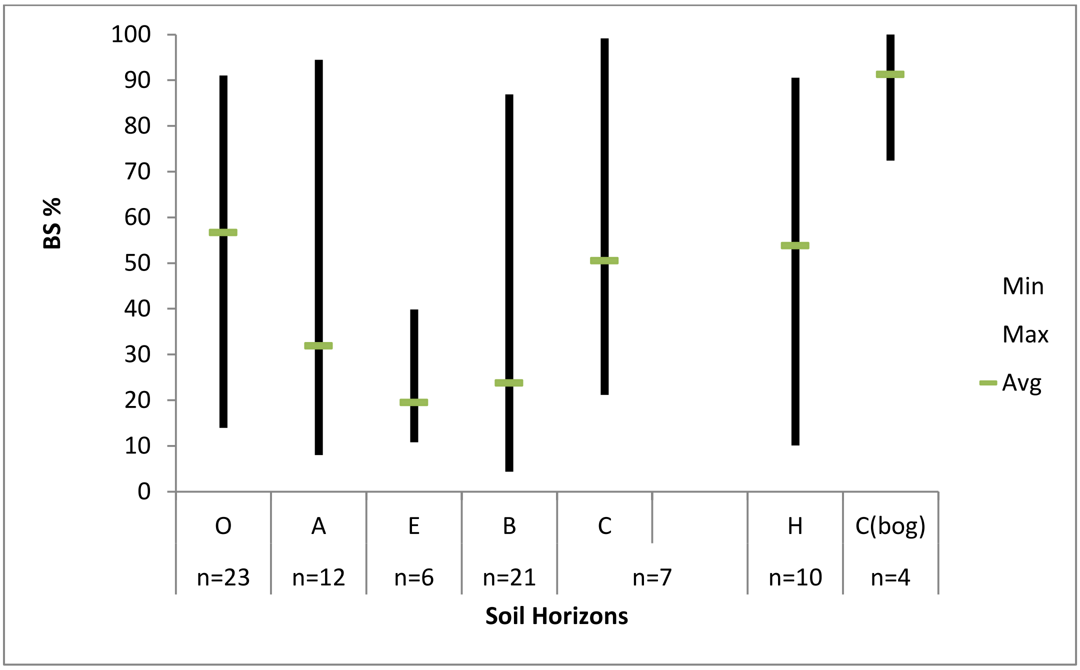


Figure 31: Base saturation (%) of soil in different soil genetic horizons

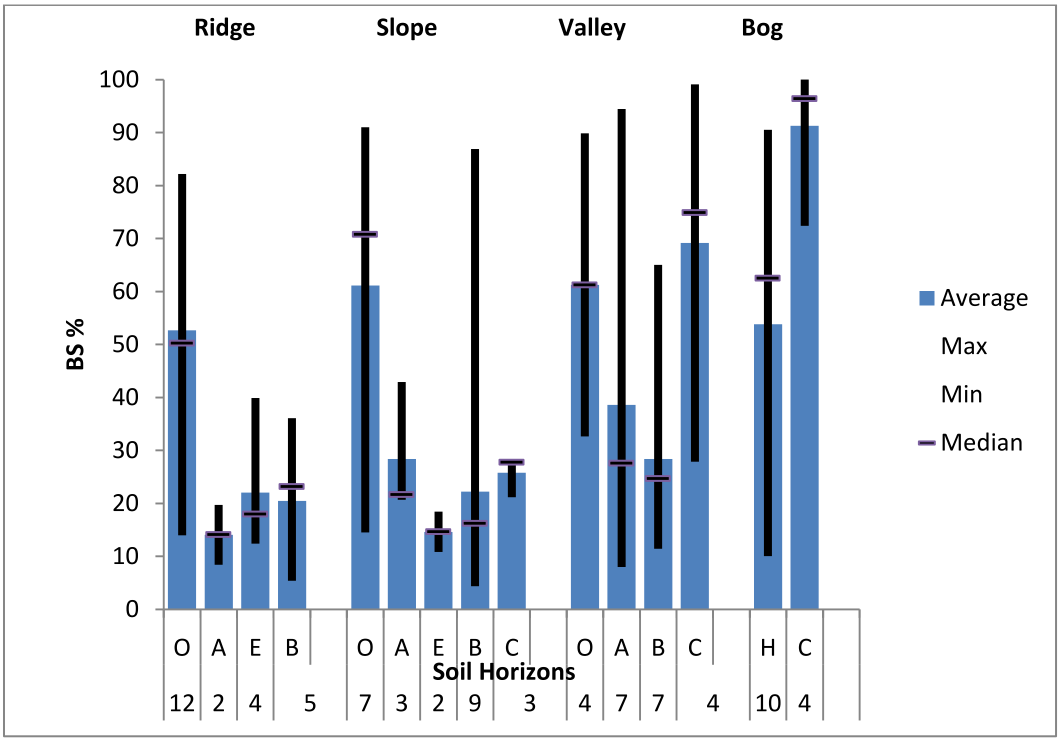


Figure 32: Base saturation (%) of soils in genetic soil horizons along a topographic gradient

4.3.3 Implications regarding aluminium leaching

According to Møberg and Petersen (1982) the soil ion-exchanger releases significant amounts of aluminium when the %BS drop below 20 – 30%. With the presence of a mobile anion, such as sulphate from acid rain, this aluminium may remain labile in solution and be leached out of the soil and into the stream and surface waters. About a third of the soil samples had %BS less than 20% and half of the samples had values less than 30%. Furthermore, the measured %BS levels on the ridge and slopes in the forest soils of Morsa are comparable to sites with documented severe leaching of labile aluminium during the acid rain period (Cooke et al., 1993). On the other hand, the relatively high %BS in the riparian zone in the valley floor implies that labile aluminium in soil water will be immobilized upon passing through this soil en-route to the stream. Nevertheless, during periods of high runoff, such as during spring snowmelt or rainfall episodes during the fall, the peat rich riparian zone becomes water saturated forcing runoff to discharge over its surface directly into the stream. It is therefore clear that these acid soils on the ridges and slopes leached water with high concentrations of labile aluminium during the acid rain period. This led to that at least 42 fish stocks in Østfold were lost due to acid rain in the 1970ies and -80ties (DN, 2006). This spurred a massive liming of 212 lakes in the Østfold County. Acid deposition in this region is since then reduced by up to 90% . This has led to a decline in the leaching of toxic aluminium so that liming is no longer required in 82 of these lakes (Møberg and Petersen, 1982). The remaining watercourses are typically draining forested headwater catchments. Weldehawaria (2013), studying the present soil water and stream water chemistry in the Dalen catchment, found on average around 30µM labile aluminium (Ali) in the E horizons, decreasing down to between 10 and 20µM in the B and C horizons on the slopes. In the stream draining the Dalen catchment the Ali during episodes approaches 10 µM (90% percentile is 7.4 µM). The average sea-salt corrected sulphate is only 22µeq/L (90% percentile is 40µeq/L). This is close to the average value reported for lakes in the southern part of East Norway (Østlandet – Sør) . In 1986 the average sea-salt corrected sulphate concentration in this region was almost 5 times higher (98µeq/L). This has led to an overall 70% decline in labile aluminium from average values close to 5.6µM down to 1.8µM. The Birkenes catchment in southernmost Norway is comparable to the Dalen site in respect to topography, geology, soil and vegetation (see in Vogt et al. (2003) and Mohr (2010)). This site has received a heavier load of acid rain, decreasing form around 2 in 1980 to 0.5 g S m^{-1} in 2011 (Brady and Weil, 2004). In 2011 the average labile Al concentration in the stream was 5.5µM. Episodes studies in this site in 1989 showed that the Ali concentration could surge from around 5µM during base flow to above 20µM during the first episode after a prolonged dry period (Vogt et al., 2003). A major sea-salt episode in 2011 only caused the Ali to increase to 10µM. A conservative assumption is therefore that the volume weighted average Ali concentration in the streams draining forested headwaters in the Morsa watershed during the acid rain period was around 15 µM.

4.4 Soil phosphorus pools

Total phosphorus, Inorganic phosphorus (Inorg-P), Organic phosphorus (Org-P) and P-fractionations were determined on the soil samples according to the methods described in section 3.5. The Organic phosphorus was obtained by difference of the Total-P and Inorganic-P as described in Section 3.5.2, using eq. 3.8.

4.4.1 Spatial variation in Inorganic and Organic phosphorus pools in soil profiles

Very high average Tot-P levels (up to 1370 mg P kg^{-1}) are found in the forest floor (Figure 33). Except for the E horizon the amount of Tot-P lies around 500 mg P kg^{-1} in the mineral soil. High Inorg P levels are found in the C horizon and bogs. The eluvial E horizon shows the lowest concentration due to very poor sorption capacity. The ratio of Inorg P to Org P increases down through the soil profile, especially upon entering the B and C horizons (Figure 34).

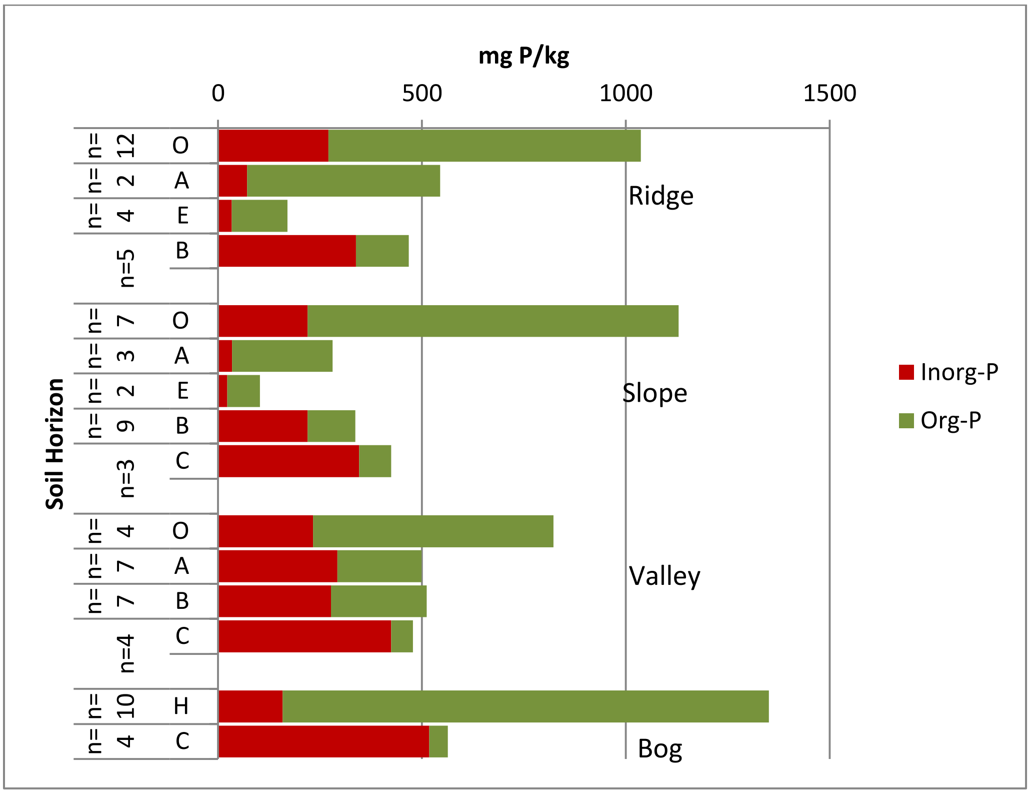


Figure 33: Inorganic and organic phosphorus with topography and soil profile

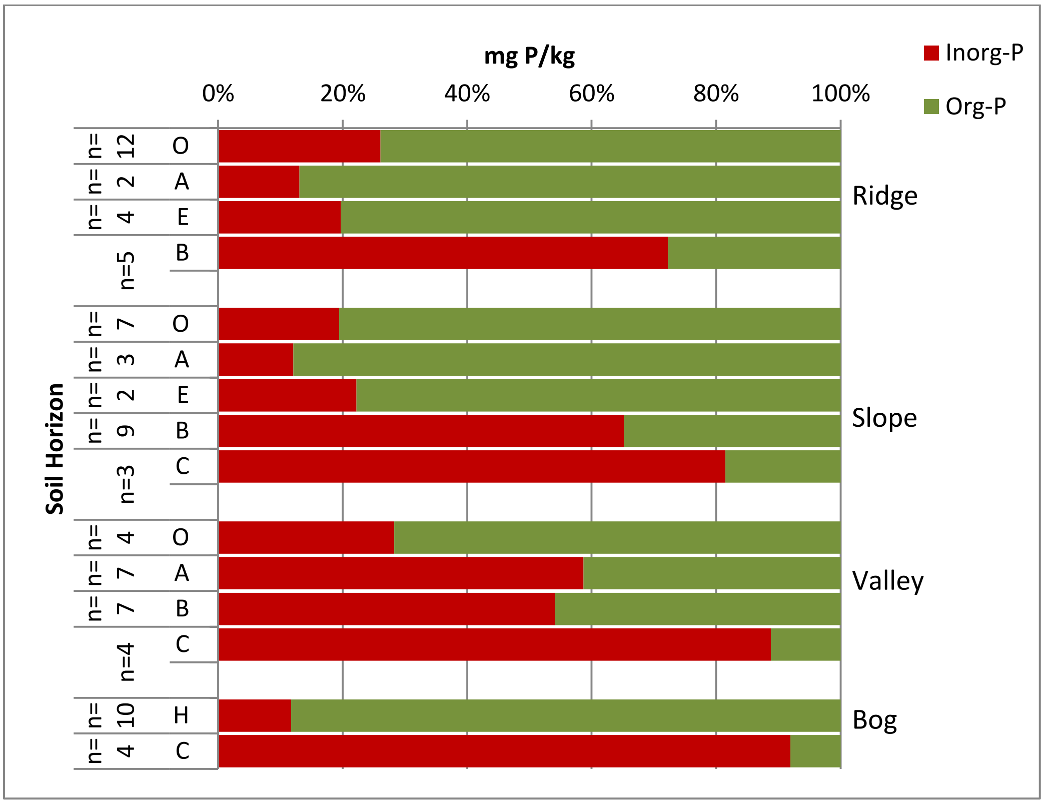


Figure 34: Ratio of inorganic-P to organic-P with soil profiles and topography

The average amount of Inorganic and Organic phosphorous (Inorg P and Org P) was around 250 and 1000mg P kg^{-1} in the forest floor O horizons (Figure 35 and 36). The high levels of Org P is comparable to what was found in the top Ap horizon in a local agricultural field (Opland, 2011). These large pools of P in the forest floor horizons are due to a substantial internal P cycling. Both Inorg-P and Org-P in the eluvial E horizon is low. This is due to that the eluvial horizons have very poor sorption capacity in this bleached horizon due to little organic matter and low content of aluminium and iron in addition to the lack of silt and clay. There is an increase in Inorg-P into the deeper C horizon, especially in the fine material under the bogs, with an average Inorg-P of 500 mg P kg^{-1}. The increase into the B horizon is likely due to accumulation of organic matter (Bh) and/or iron (Fe) and aluminium (Al) (Bhs/Bs) in this illuvial horizon. The trivalent positively charged Fe^{3+} and Al^{3+} form bridging ions between the negatively charged surface functional groups on the mineral and organic soil and the negatively charged HPO_4^{2-} ions. The deep soil C horizons are rich in clay and silt particles which have high sorption capacity to sorb compounds like phosphate. Moreover, these marine clay deposits are inherently rich in phosphate. (Gebreslasse, 2012), studying clay deposits in the streambeds in streams in western Vansjø that were fed by drainage pipes in agricultural fields, found the mineral apatite ($Ca_3(PO_4)_2$) in this clay material. Due to poor water percolation capacity this fossil P has remained in the material and is thus found as increased levels of Inorg P in these deposits. Inorganic phosphorus shows a positive correlation with clay and silt particles with coefficient value of (r = 0.498 and 0.503 respectively, Appendix B). Organic-P follows the amount of organic matter measured as LOI. Figures 33 and 36 show a clear decreasing trend in Org-P down through the soil profile. Organic phosphorus shows positively correlation to organic matter content (LOI) and CEC with correlation coefficient of (r = 0.574 and 0.547 respectively, Appendix B).

Large span in Inorg-P and especially Org-P were also found within the generic soil horizons (Figures 35 and 36).

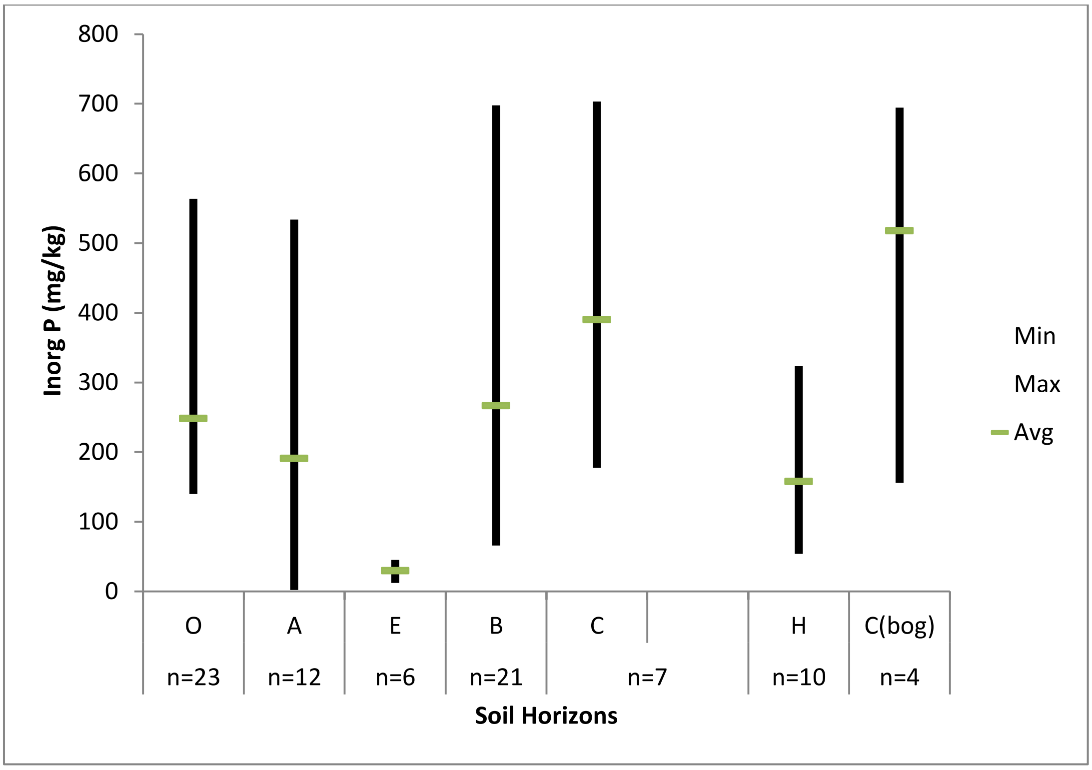


Figure 35: Variation of inorganic phosphorus with soil profiles

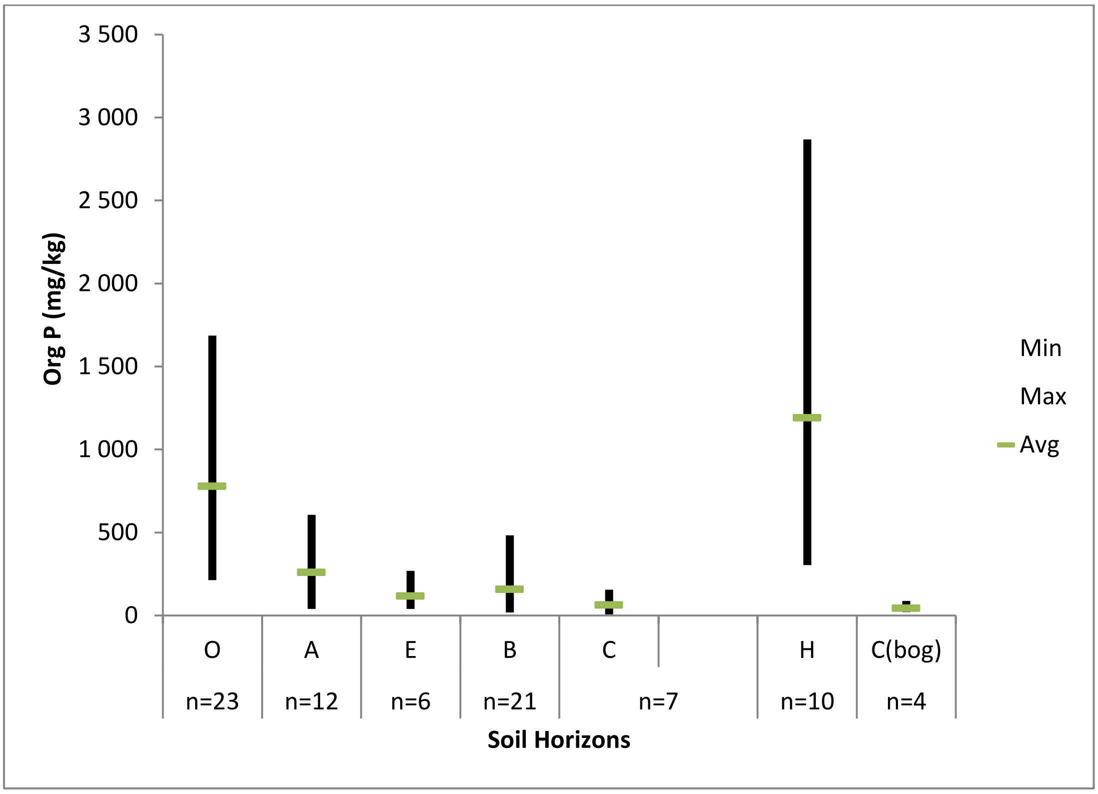


Figure 36: Variation of organic phosphorus with soil profiles

4.4.2 Variation of organic and inorganic phosphorus with topography

There is no clear trend in the size of the Inorg P pool along the topographic gradient from the ridge, through the slope down into the valley floor (Figure 37). The main difference is found in the A horizon, with an increase in the pool down slope. Highest average and median Inorg P levels were found in the marine clay deposits under the peats in the valley bottom.

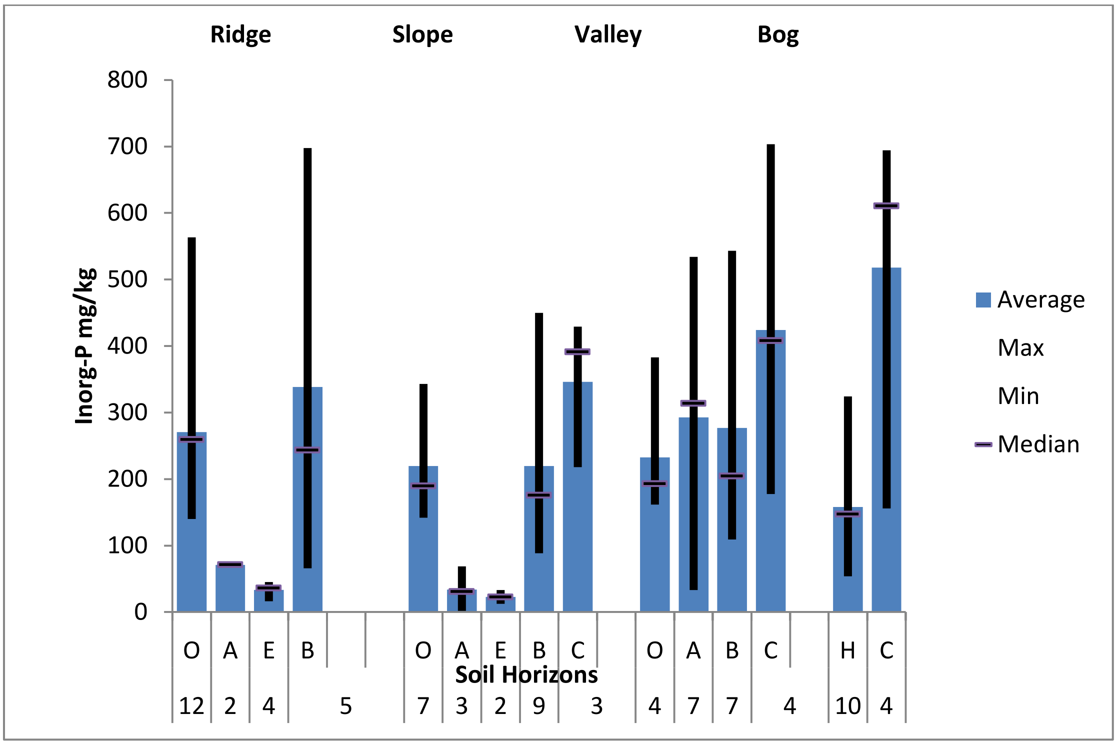


Figure 37: Variation of inorganic phosphorus with topography

No clear topographic gradient was found in the average and median values of the Org P pools (Figure 38), though there is a decrease down slope in the span of size of the pools in the O horizon, despite no such trend in the amount of organic matter in the horizon (Figure 24). This is therefore likely due to that the Org P pool in the surface horizon in the riverine region in the valley bottom is in equilibrium with the overland and sub-lateral flow of water from the slope.

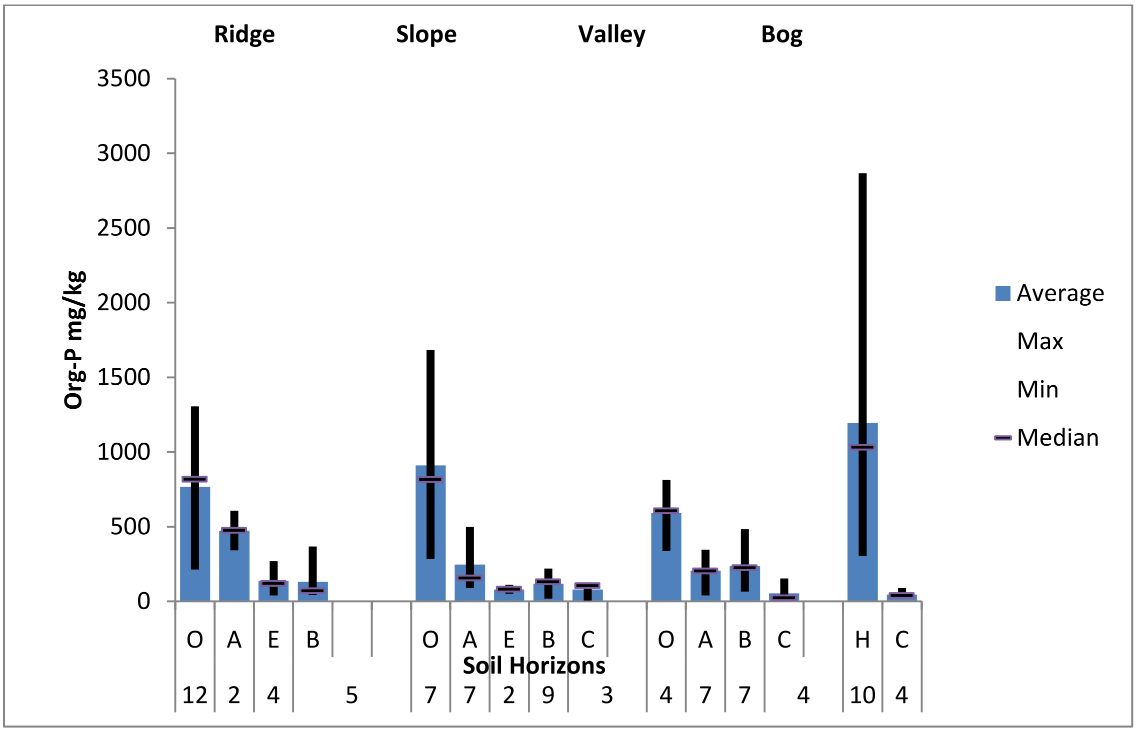


Figure 38: Variation of organic phosphorus with topography

4.4.3 Variation of Inorg-P and Org-P with soil texture (PSD) and OM (LOI)

Clay and silt particles, due to large surface area, have a large ability to bind phosphate compounds. Furthermore, this marine clay material is found to contain significant amount of apatite minerals (Gebreslasse, 2012). Inorganic phosphorus is thus positively correlated to clay and silt particles (r = 0.498 and 0.503, respectively, Appendix B). A significantly higher amount of inorganic phosphorus was thus found in mineral soils than in the organic soils. In Section (4.4.2) the relation of the phosphorus pools with respect to the genetic soil horizons was explained. The spatial variation in Org P is empirically found to be mainly governed by organic matter content (measured as LOI) and CEC. A positive correlation is found between the amount of Org P with LOI and CEC (r = 0.574 and 0.547, respectively. Appendix B). Figures 39 and 40 illustrate how the Inorg P and Org P correlate with particle size distribution and organic matter respectively.

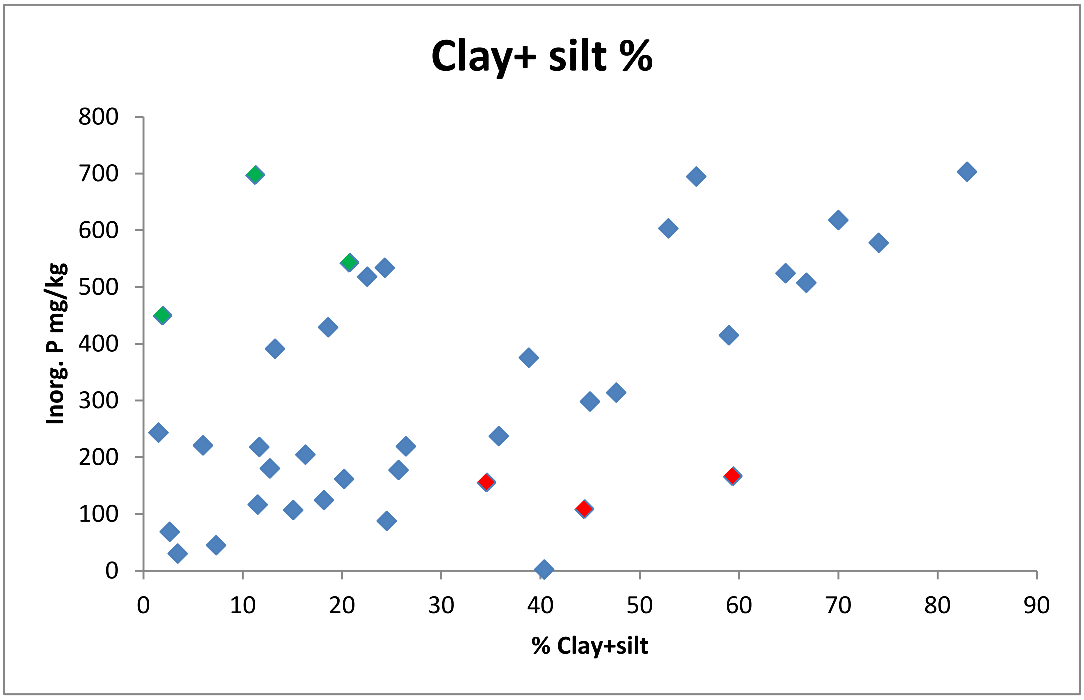


Figure 39: Distribution of inorganic phosphorus with clay and silt particles (how inorganic phosphorus governed by particle size distribution. Samples in green are soils with low psd and high Inorg-P, in red are high in psd and low inorg-P. Both samples show distribution of inorg-P with texture.

From Figure 39 it can be seen that a significant amount of Inorg P (100 to 700mg P kg^{-1}) was found in the clay rich soils, while small amount of Inorg P was found in the soils that have low content of the fine particles. A high level of Inorg P is also found in soils with low clay content. Samples with high and low ratio of Inorg P / %Clay have high and low content of organic matter, although none of the measured parameters offers a clear explanation for this variation at low content of clay.

Figure 40, shows that large pools of Org P (>500mg P kg^{-1}) was found in the soils with a high organic matter content (%LOI) and small pools of org P (<500 mg P kg^{-1}) was found in soils with less organic matter content.

Organic soil horizons show inherently high organic matter content and thereby high content of organically bound phosphorus. Whereas mineral soil horizons, which have less organic matter content, shows less amount of organic phosphorus. This shows that organic matter (LOI) is the main factor governing the P content in these soils as the overall content of Org P is much larger than the Inorg P (Figure 33).

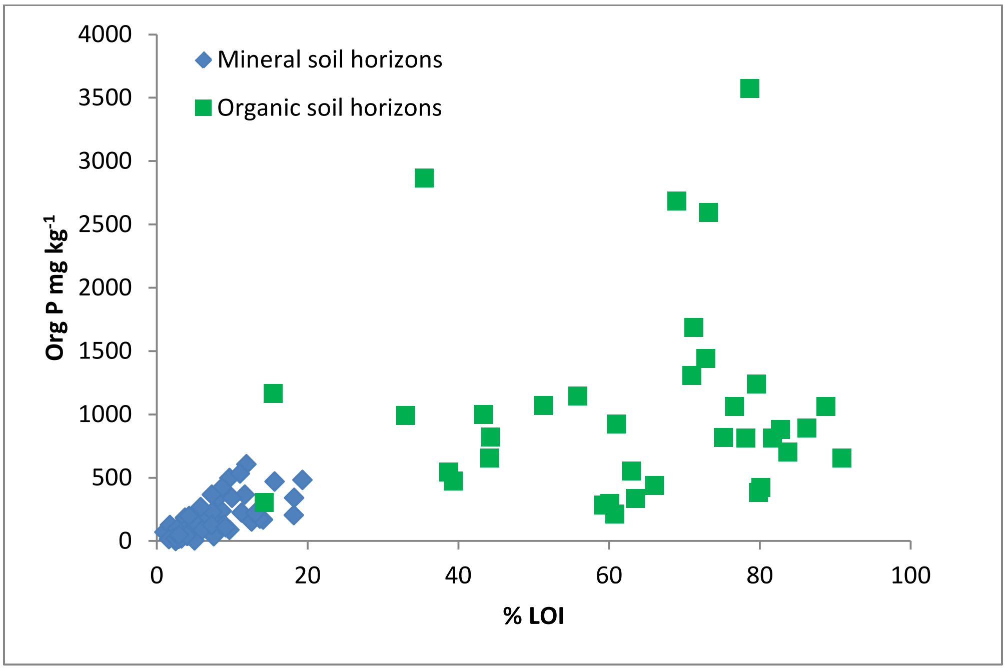


Figure 40: Organic-P distribution with mineral and organic soil horizons

Figure 41 shows that the mineral soils with relatively high amount of Inorg P have a low acidity (measured as high pH (H_2O) value. This is the opposite of what is to be expected due to the effect of the pH dependent charge, causing a more net negative charge at higher pH. It therefore more likely reflects illuviated Al, Fe and organic matter in the less acid soil.

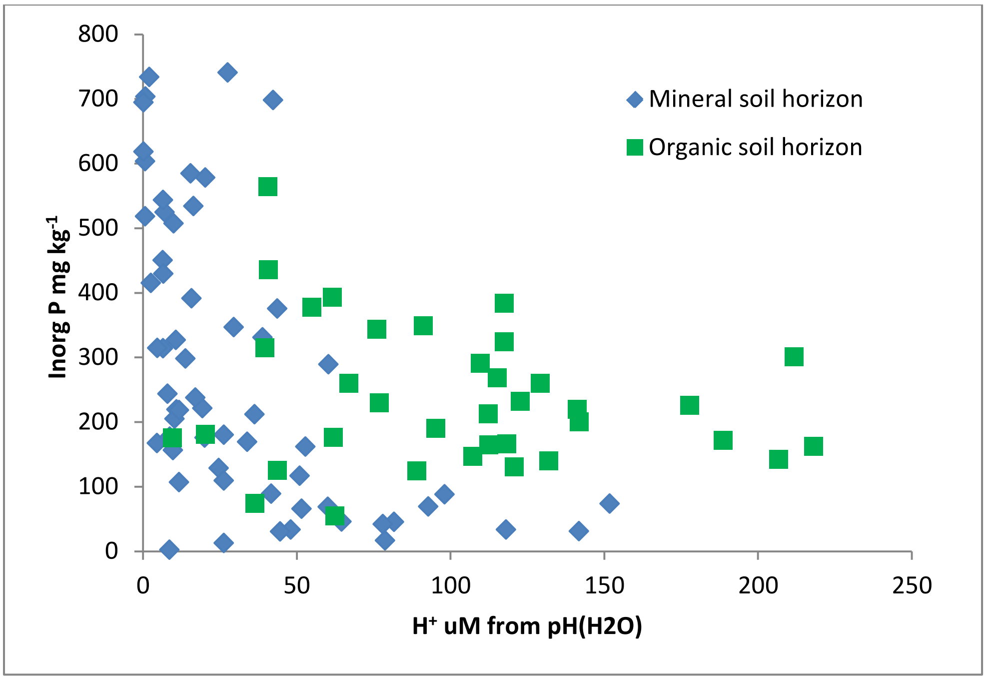


Figure 41: Distribution of inorganic-P within inorganic and organic soil horizons with soil acidity

4.4.4 Org-P and Inorg-P in Dalen versus the rest sites

comparison data for the levels of Org P and Inorg P in Dalen taken from (Mohr, 2010) with the rest of the Morsa catchments. The result shows that the Dalen site has much higher Org P and somewhat higher Inorg P levels in the soil than what is generally found in the forests of the Morsa watershed. The Dalen site is therefore somewhat special in terms of Org P content in the soils.

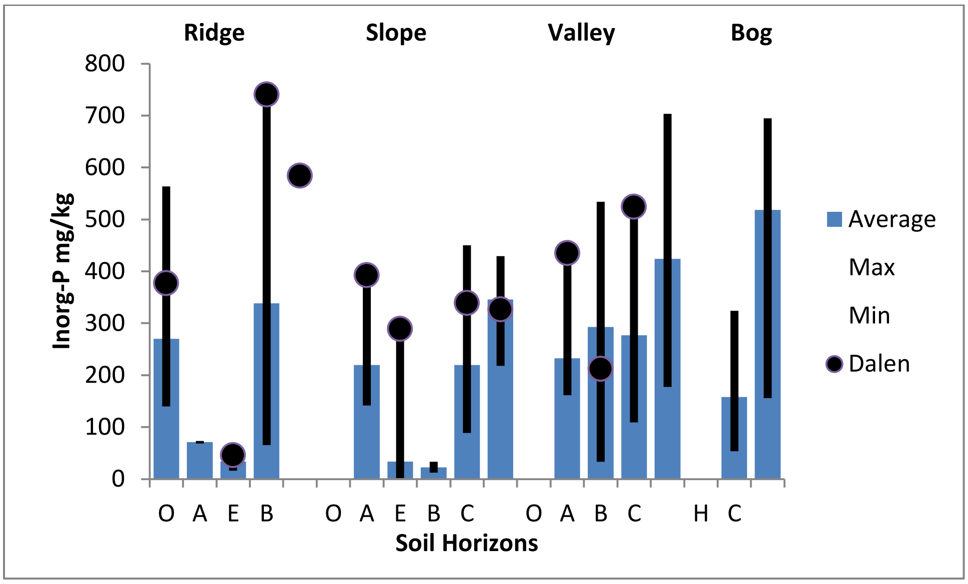


Figure a. Inorg-P of forest soils in Dalen Vs forest soils of the Morsa watershed

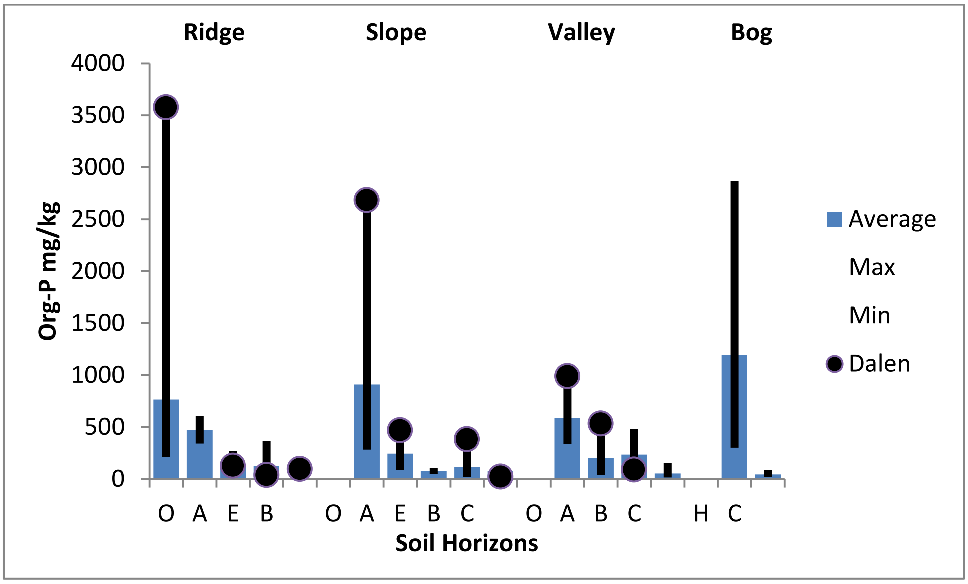
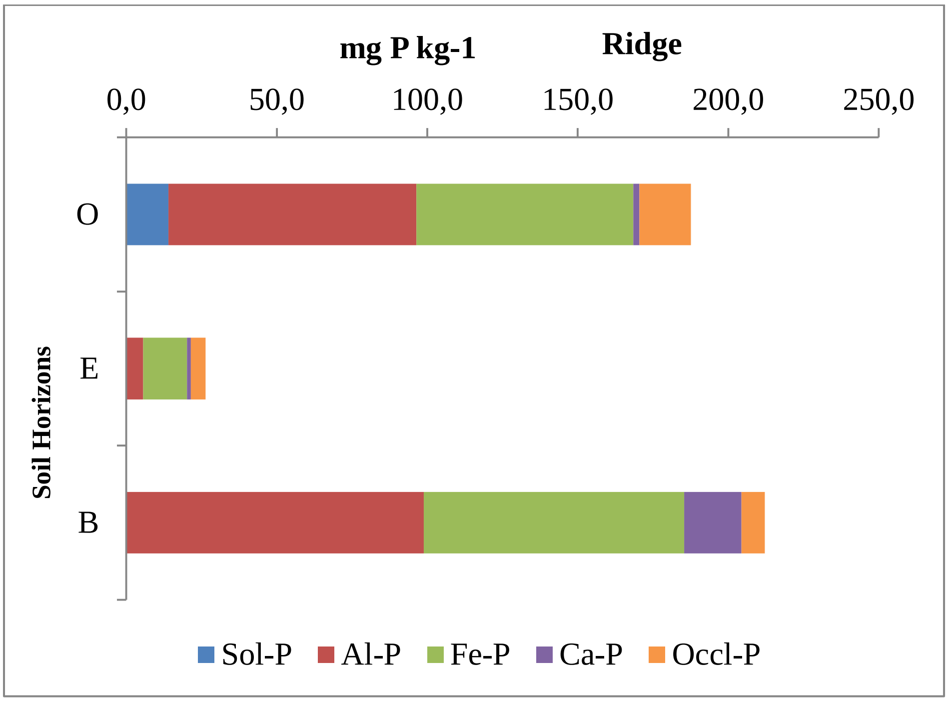


Figure b. Org-P of forest soils in Dalen Vs forest soils of the Morsa watershed

4.4.5 Inorganic phosphorus fractionation in soils.

Figure 42 show the soil content of inorganic phosphorous in the ridge profile taken from Østmarka. The sum of inorganic P fractions do not add up to the amount of total Inorg P determined for these soils, though reflect the relative amount of Inorg P between the horizons as discussed in Chapter 4.4.1. A significant amount (14 mg kg^{-1}) of easily soluble phosphorus (Sol P) was found in O horizon. This is likely due to the rapid circulation of PO_4 in the forest. This is also seen as very high concentrations of free orthophosphate in through fall (between 125 and 300 µg L^{-1}) in Dalen (Weldehawaria, 2013). Aluminium (Al-P) and Iron (Fe-P) bound phosphorus constitute the main Al fraction in especially the O and B horizons, as well as the E horizon. The large Al-P and Fe-P in the O horizon is due to that Al^{3+} and Fe^{3+} forms binding bridges between the negatively charged functional groups on the organic material ($R-COO^-$, $R-O^-$ etc) and the negatively charged HPO_4^{2-} (e.g.: $R-COO^-$ - Al^{3+} - HPO_4^{2-}). The illuvial B horizon have accumulation of aluminium and iron that are leached from the A and E horizons. In addition to forming binding bridges as discussed above the Al and Fe may co-sorb phosphate when the ions are sorbed to the soil particles in the B horizon. The large and dominating Al-P and Fe-P fraction in this horizon is thus to be expected. The absolute and relative amount of calcium bound P (Ca-P) increases down through the soil profile. This reflects the decrease in soil pH down through the soil profile as discussed in Chapter 4.1.1. The fraction of occluded P (Occl-P) is what is found within the crystal lattice of soil minerals. This faction constitutes the largest fraction of P in the eluvial E horizon since all other P fractions are eluted. There is also a significant amount found in the organic O horizon, though this is likely due to sand grains in the forest floor horizons.

Figure 43 shows the soil content of inorganic phosphorous in the valley bottom profile from Hugness, Guthus and Østmarka, and the sum up of each horizon relatively reflects their total inorg-P. The composition of inorganic P fractions in the valley bottom horizons is substantially different from what was seen on the ridge as discussed above. The Al-P and Fe-P fraction dominate in the H histosol horizon. This is for the same reason as argued for the organic O horizon on the ridge. In the B and C horizon under the peat the calcium bound P (Ca-P) is by far the dominant fraction. This is most likely due to the presence of Apatite in these marine clay deposits, as found by Gebreslasse (2012).



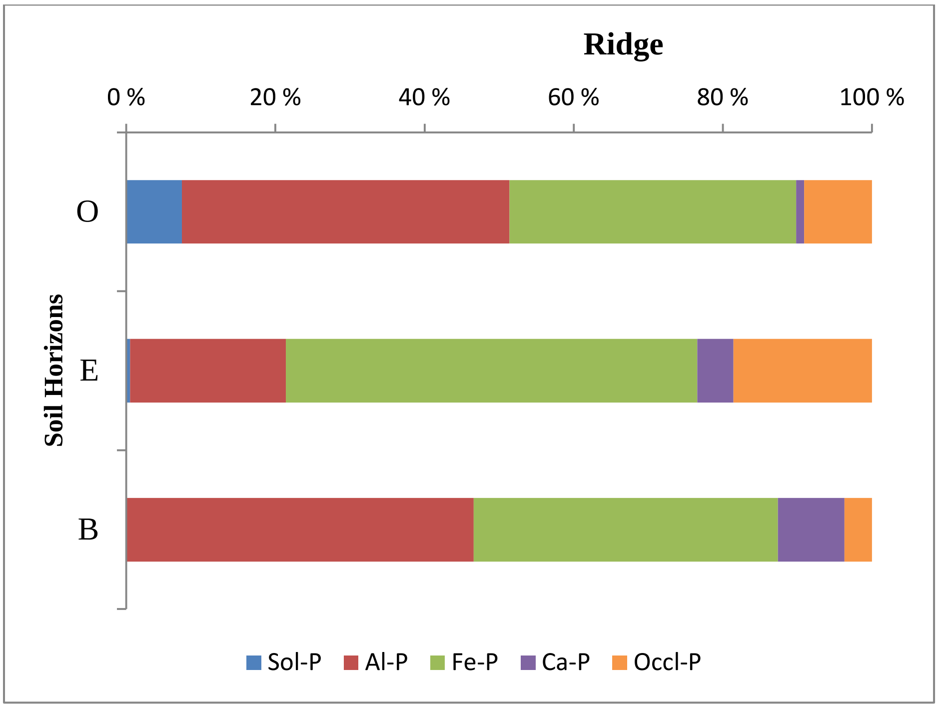
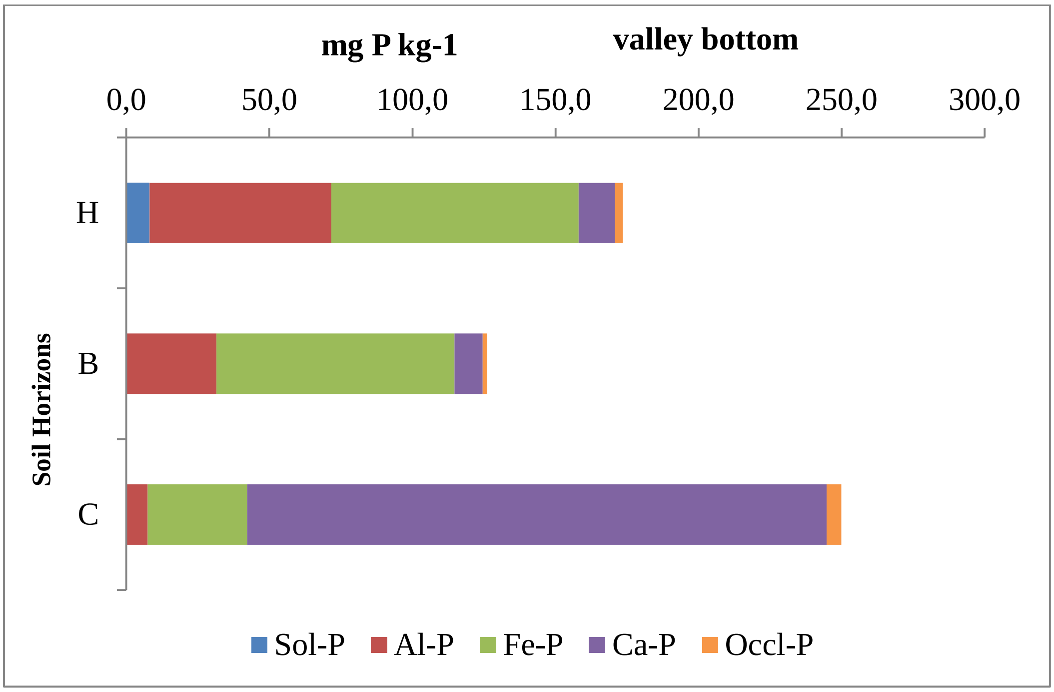


Figure 42: Inorganic-P fractionations Østmarka from ridge samples



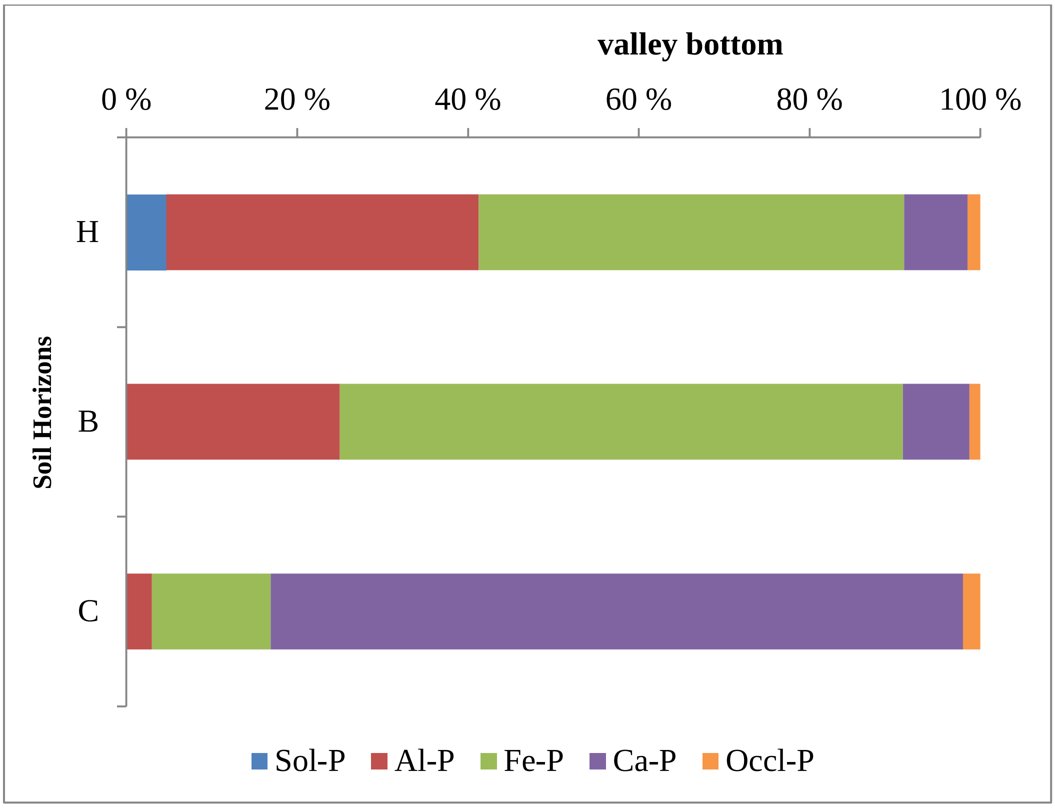


Figure 43: Inorganic-P fractionations at Valley bottom from Hugness, Guthus and Østmarka

4.4.6 Factors governing the spatial distribution of P pools

Principal component analysis and Hierarchy cluster analysis was performed on the explanatory parameters.

4.4.6.1 Hierarchy cluster analysis

Cluster analysis has the purpose of grouping objects that have similar character into respective categories. Results of a hierarchy cluster analysis of the data matrix of 8 explanatory and 2 response parameters for analysed parameters 96 soil samples are shown in Figure 44. Parameters are clustered based on their similarities/dissimilarities, and the parameters in the same group reflects high similarities (correlations), while different groups show less correlation. Soil horizons are given an arbitrary rank number down through the soil profile (i.e. O=1, A=2, E=3, etc.). Topography reflects the samples position along the topographic gradient (i.e.: ridge (=1), slope (=2) or valley bottom (=3)).

The Dendrogram shows that Inorg P and Org P belong to two different clusters. Inorg-P is clustered with fine particles as silt and clay while Org-P is clustered with organic content and therefore acidity and CEC.

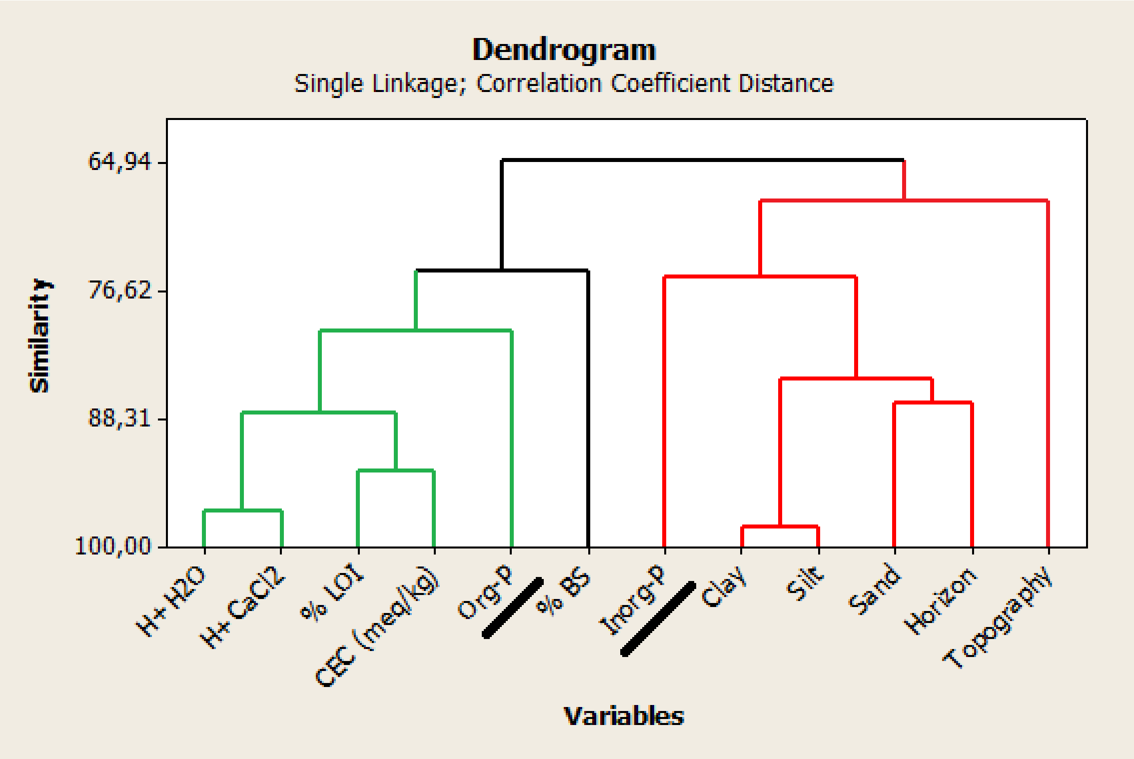


Figure 44: Dendrogram for phosphorus pools with all explanatory variables

4.4.6.2 Principal component analysis

Principal component analysis is a way of identifying patterns in data, and expressing the data in such a way as to highlight their similarities and differences. Figure 45 below show that Org-P and Inorg P have opposite loading along the 1st Principal component (PC1), explaining more than half of the variation in the data set. This component is many governed by the differences between soil generic horizons. The Org P is clustered with high content of organic matter (%LOI) governing high acidity (H+) and CEC, reflecting generic conditions of the top soils. The Inorg P is also governed by the 2nd PC which reflects the position along the topographic gradient and thus the soil base saturation (%BS). In general this PCA indicates that the Org P mainly is governed by the content of organic matter in the soil, while the Inorg P is influenced by the topography, soil acidity and amount of silt and clay.

Figure 46 shows the sample scores divided according to soil horizons. This figure illustrates clearly the role of organic vs. inorganic soil horizons in governing the PC1. Within the inorganic soil horizons the PC2, reflecting basically the soil acidity, is an important explanatory factor.

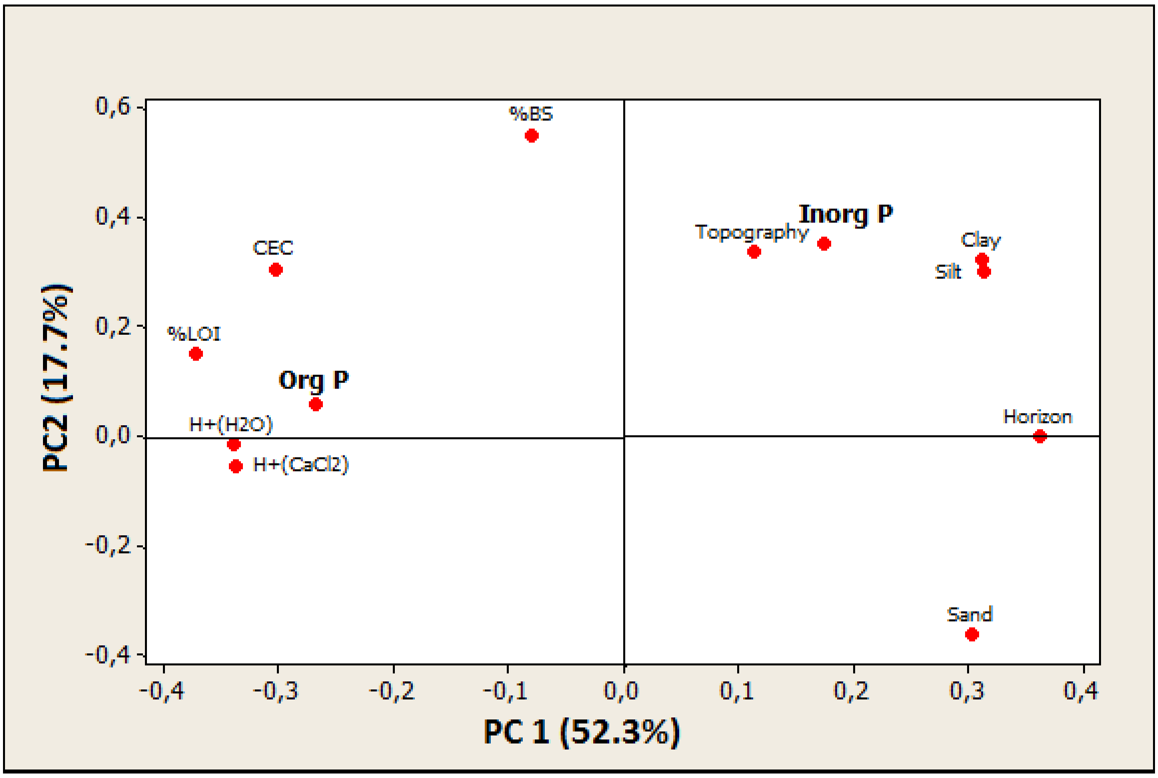


Figure 45: Principal component analysis of the P-pools with the explanatory variables

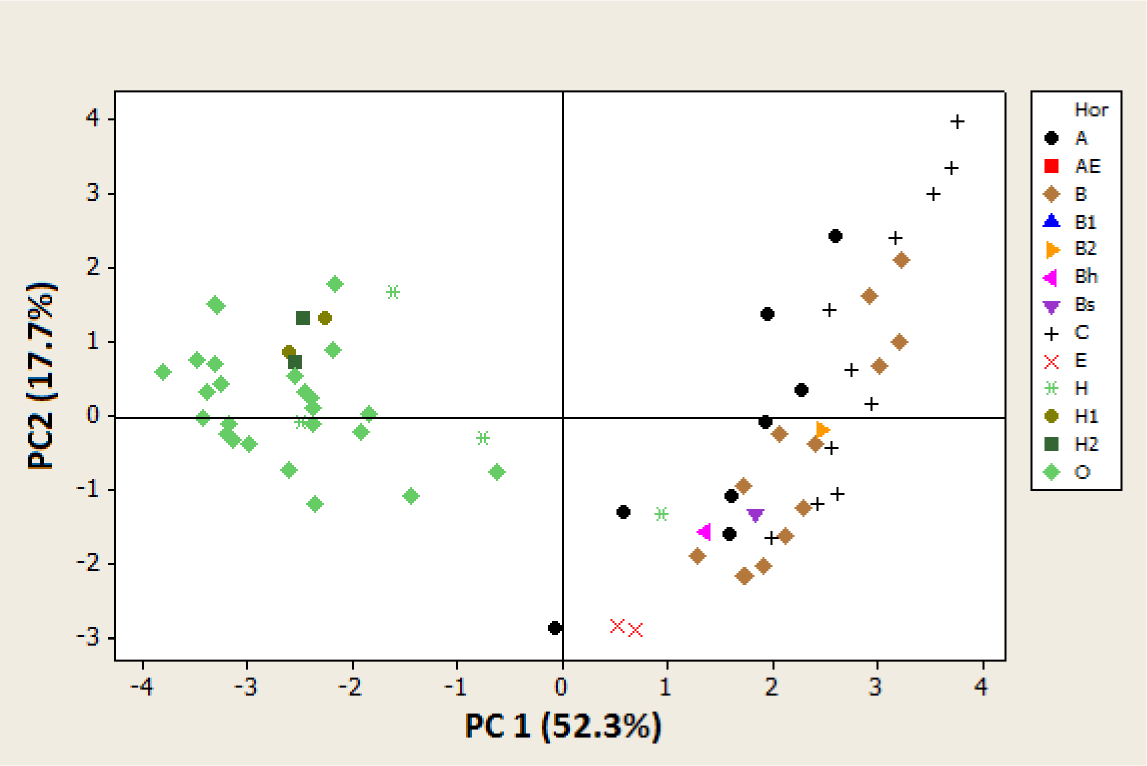


Figure 46: Sample scores in the PCA divided into sub groups of soil horizons

5 Conclusions

Large pools of organic bound phosphorous were found in the upper forest floor horizon, though the size of the pool decrease sharply down into the soil profiles (horizons B and C). This is partly due to the enhanced capacity of the O horizon to bind P, and to the large internal cycling of P in the forest ecosystem. These large P pools are also reflected by elevated concentrations of especially the organic bound P fraction in the O horizon soil water, as studied by Mohr (2010) in Dalen, one of the studied sub-catchments. During intensive rain fall, which enhances surface runoff and sub-lateral flow through the upper surface part of the soil, the soil water rich in phosphate fractions by-pass the absorptive capacity of the deeper mineral soil and flushes directly into the stream. This leads to elevated concentrations of organic bound P fractions in the stream during periods of high runoff. The amount of precipitation and the frequency of heavy precipitation events in eastern Norway (Østlandet) have increased and been above the norm during the past 20 years. Increased runoff intensities will lead to more flushing of the high P pools in the forest floor into surface waters. The increased amount and intensities of precipitation may therefore have led to an increased background flux of P during the same time period as abatement actions towards eutrophication have been conducted. Particle bound P constitute only a small proportion of the total P in the runoff from forested areas due to the thick organic soils held firmly in place by the roots of perennial plants limiting erosion. The inorganic phosphorus pool was found in an elevated amount in the deep soil horizons along with an increasing amount of fine soil particles. Large pools of inorganic P were especially found in the deep clay layers in the valley bottom. This P pool is likely fossil P from when the soils clay material was deposited in calm marine waters. It is therefore not conceived to be mobilized unless the soils are ditched or drained using tiles.

The spatial variation in pools of organic- and inorganic phosphorus in the soil appears therefore to be mainly governed by the amount of organic matter and fine soil particles, respectively. This is supported by a Principal component analysis which shows that the organic phosphorus is clustered with organic matter content (%LOI), governing high acidity (H^+) and CECe, reflecting generic conditions of the top soils. The inorganic phosphorus is found to be clustered together with the position along the topographic (increasing attributed value downslope), and the amount of silt and clay. Increase in fine material downslope are covaried with inorganic P, both due to that the inorganic P is transported down from the ridge, accumulating in the lower grounds, and due to the enhanced capacity of finer material to hold inorganic P. Therefore, in general the PCA indicates that the organic phosphorus is mainly governed by the content of organic matter in the soil, while the inorganic phosphorus is influenced by the topography and amount of silt and clay.

This study shows that the forest mineral soils on the ridge and slopes in the region are generally acid with base saturation in the range (<30%) known to release inorganic labile aluminium in exchange for H^+ or base cations. The soil pH is also acid (<5.5) allowing for significant amounts of labile aluminium to not precipitate as oxy-hydroxides. In the presence of a mobile inorganic counter anion this inorganic labile aluminium may be leached out and into the streams during runoff episodes where the seepage water flush over the water saturated and clay rich riparian zone in the valley bottom. During the acid rain period it is therefore likely that a significant flux of inorganic labile aluminium was leached out of these forest soils and drained down through the watercourse into agricultural land. Upon mixing with phosphorus rich seepage with higher pH, the labile inorganic aluminium precipitated as aluminium oxy-hydroxides and co-precipitated the phosphorus. The decline in acid rain over the past decades has resulted in reduced leaching of the inorganic labile aluminium and thereby a decrease in the precipitation of oxy aluminium hydroxide downstream. This has thereby led to a loss of an efficient removal mechanism of inorganic phosphorous in the stream. Instead the phosphorus is enabled to remain in solution and be flushed down into waterbodies where it fuels the eutrophication problem.

Furthermore, there has been a doubling of the concentration of dissolved natural organic matter (DNOM) in this region of the country over the last 30 years. The cause for this increase is believed to be partly due to increased amount and intensity of precipitation, and partly due to the decrease in acid rain. The increase due to increased precipitation is explained through changes water flow-paths, with increased leaching directly from organic rich soil organic horizons into the stream. The role of decreased acid rain is through both a decreased ionic strength of the water as well as lower concentrations of labile aluminium. Both these factors lead to an increased solubility of DNOM. The concentration of the organically bound phosphorous fraction is inherently and empirically linked to the amount of DNOM, causing a concurrent increase in the flux of organic bound P to the surface waters.

This study documents that the forest floor contains a large pool of organic P, which we know from previous studies are indicative of elevated concentrations of organically bound P in soil solution. Furthermore, the study shows that the soils are prone to have leached inorganic labile aluminium during the acid rain period. It is therefore conceived as likely that the increased precipitation amount and intensity along with the reduction in acid rain have directly and indirectly caused an increase in the mobility of phosphorous and thereby disguising the effect of coinciding abatement actions.

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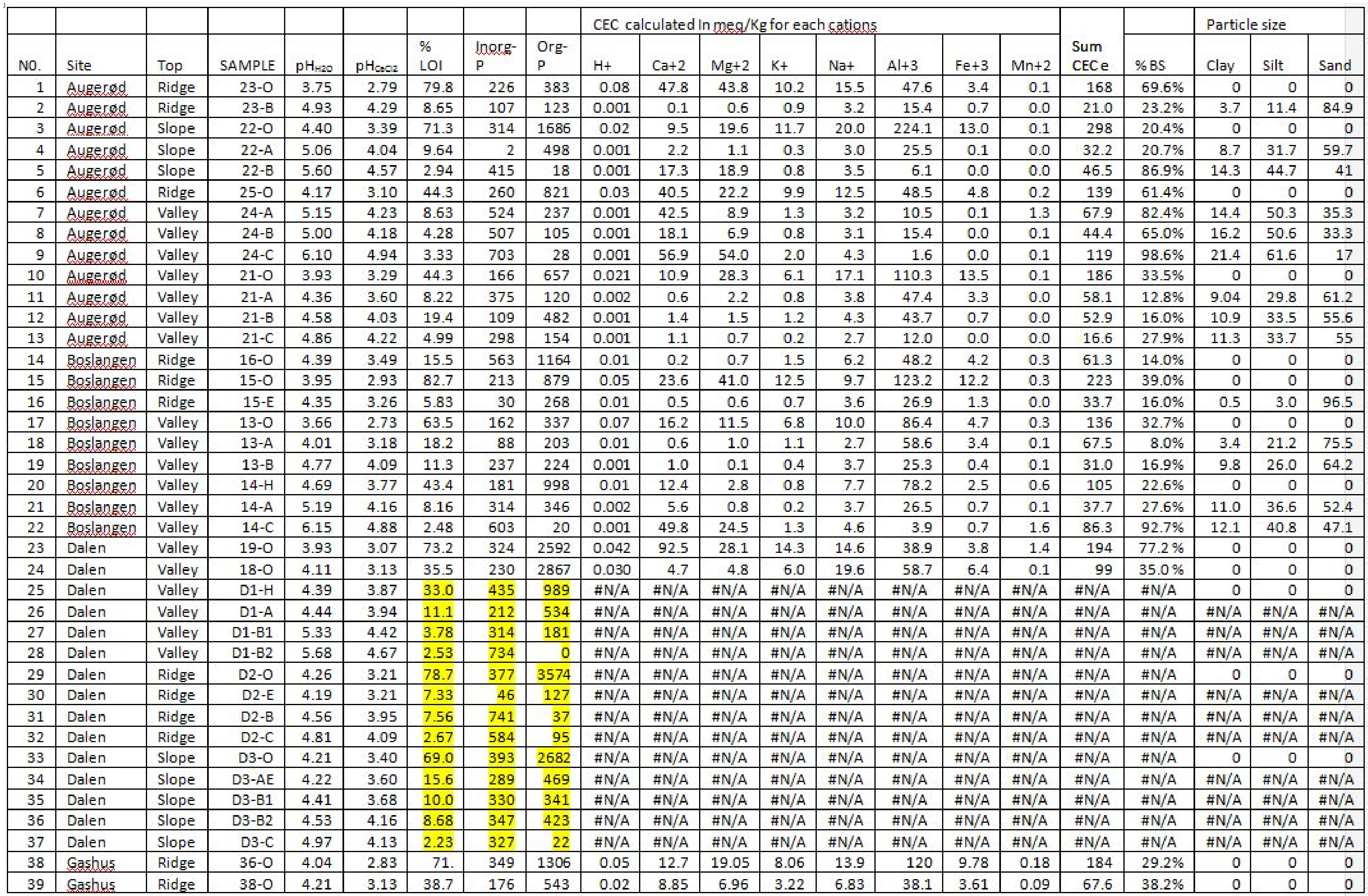
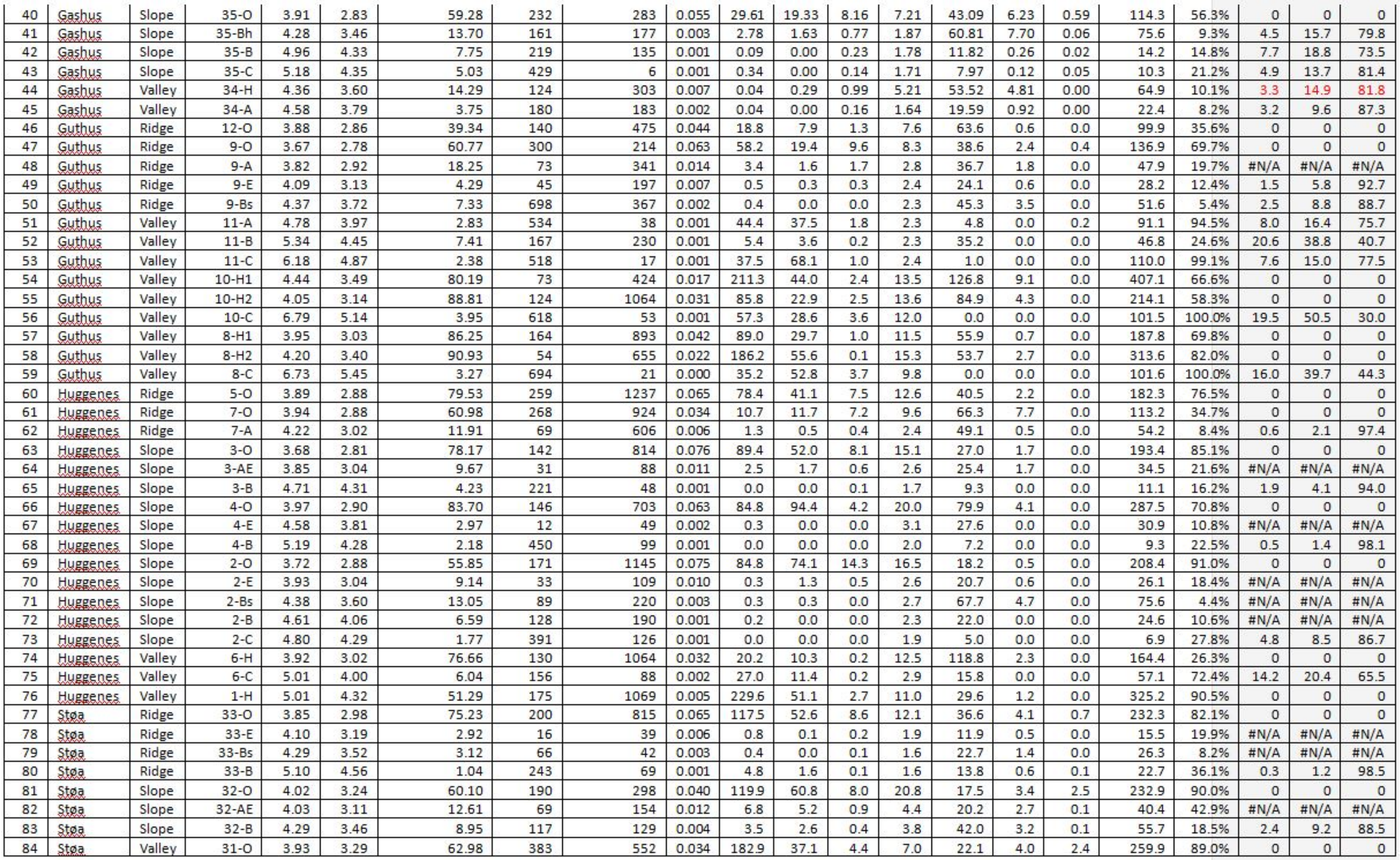
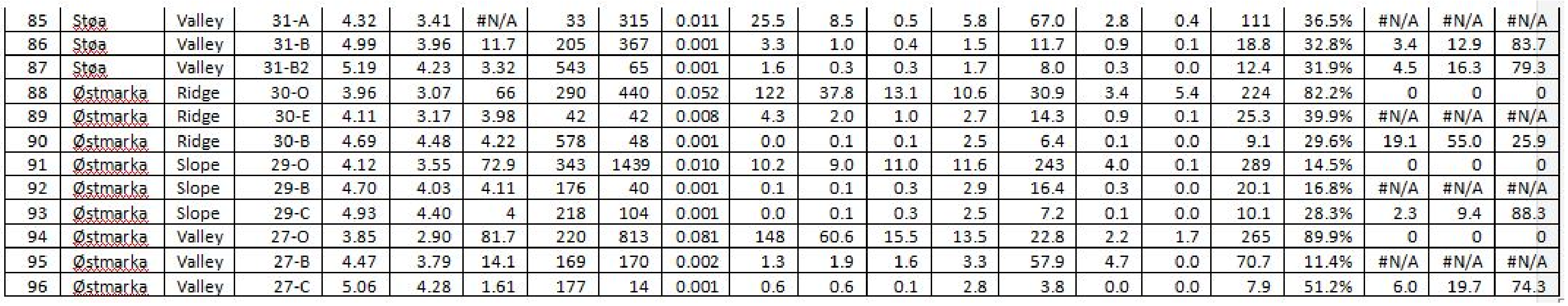
Appendix A: All results for the analysis



									CEC calculated In meq/Kg for each cations										Particle size		
NO.	Site	Top	SAMPLE	$\mathrm{pH_{H2O}}$	$\mathrm{pH_{CaCl2}}$	% LOI	Inorg-P	Org-P	H+	Ca+2	Mg+2	K+	Na+	Al+3	Fe+3	Mn+2	Sum CECe	% BS	Clay	Silt	Sand
1	Augerød	Ridge	23-O	3.75	2.79	79.8	226	383	0.08	47.8	43.8	10.2	15.5	47.6	3.4	0.1	168	69.6%	0	0	0
2	Augerød	Ridge	23-B	4.93	4.29	8.65	107	123	0.001	0.1	0.6	0.9	3.2	15.4	0.7	0.0	21.0	23.2%	3.7	11.4	84.9
3	Augerød	Slope	22-O	4.40	3.39	71.3	314	1686	0.02	9.5	19.6	11.7	20.0	224.1	13.0	0.1	298	20.4%	0	0	0
4	Augerød	Slope	22-A	5.06	4.04	9.64	2	498	0.001	2.2	1.1	0.3	3.0	25.5	0.1	0.0	32.2	20.7%	8.7	31.7	59.7
5	Augerød	Slope	22-B	5.60	4.57	2.94	415	18	0.001	17.3	18.9	0.8	3.5	6.1	0.0	0.0	46.5	86.9%	14.3	44.7	41
6	Augerød	Ridge	25-O	4.17	3.10	44.3	260	821	0.03	40.5	22.2	9.9	12.5	48.5	4.8	0.2	139	61.4%	0	0	0
7	Augerød	Valley	24-A	5.15	4.23	8.63	524	237	0.001	42.5	8.9	1.3	3.2	10.5	0.1	1.3	67.9	82.4%	14.4	50.3	35.3
8	Augerød	Valley	24-B	5.00	4.18	4.28	507	105	0.001	18.1	6.9	0.8	3.1	15.4	0.0	0.1	44.4	65.0%	16.2	50.6	33.3
9	Augerød	Valley	24-C	6.10	4.94	3.33	703	28	0.001	56.9	54.0	2.0	4.3	1.6	0.0	0.1	119	98.6%	21.4	61.6	17
10	Augerød	Valley	21-O	3.93	3.29	44.3	166	657	0.021	10.9	28.3	6.1	17.1	110.3	13.5	0.1	186	33.5%	0	0	0
11	Augerød	Valley	21-A	4.36	3.60	8.22	375	120	0.002	0.6	2.2	0.8	3.8	47.4	3.3	0.0	58.1	12.8%	9.04	29.8	61.2
12	Augerød	Valley	21-B	4.58	4.03	19.4	109	482	0.001	1.4	1.5	1.2	4.3	43.7	0.7	0.0	52.9	16.0%	10.9	33.5	55.6
13	Augerød	Valley	21-C	4.86	4.22	4.99	298	154	0.001	1.1	0.7	0.2	2.7	12.0	0.0	0.0	16.6	27.9%	11.3	33.7	55
14	Boslangen	Ridge	16-O	4.39	3.49	15.5	563	1164	0.01	0.2	0.7	1.5	6.2	48.2	4.2	0.3	61.3	14.0%	0	0	0
15	Boslangen	Ridge	15-O	3.95	2.93	82.7	213	879	0.05	23.6	41.0	12.5	9.7	123.2	12.2	0.3	223	39.0%	0	0	0
16	Boslangen	Ridge	15-E	4.35	3.26	5.83	30	268	0.01	0.5	0.6	0.7	3.6	26.9	1.3	0.0	33.7	16.0%	0.5	3.0	96.5
17	Boslangen	Valley	13-O	3.66	2.73	63.5	162	337	0.07	16.2	11.5	6.8	10.0	86.4	4.7	0.3	136	32.7%	0	0	0
18	Boslangen	Valley	13-A	4.01	3.18	18.2	88	203	0.01	0.6	1.0	1.1	2.7	58.6	3.4	0.1	67.5	8.0%	3.4	21.2	75.5
19	Boslangen	Valley	13-B	4.77	4.09	11.3	237	224	0.001	1.0	0.1	0.4	3.7	25.3	0.4	0.1	31.0	16.9%	9.8	26.0	64.2
20	Boslangen	Valley	14-H	4.69	3.77	43.4	181	998	0.01	12.4	2.8	0.8	7.7	78.2	2.5	0.6	105	22.6%	0	0	0
21	Boslangen	Valley	14-A	5.19	4.16	8.16	314	346	0.002	5.6	0.8	0.2	3.7	26.5	0.7	0.1	37.7	27.6%	11.0	36.6	52.4
22	Boslangen	Valley	14-C	6.15	4.88	2.48	603	20	0.001	49.8	24.5	1.3	4.6	3.9	0.7	1.6	86.3	92.7%	12.1	40.8	47.1
23	Dalen	Valley	19-O	3.93	3.07	73.2	324	2592	0.042	92.5	28.1	14.3	14.6	38.9	3.8	1.4	194	77.2 %	0	0	0
24	Dalen	Valley	18-O	4.11	3.13	35.5	230	2867	0.030	4.7	4.8	6.0	19.6	58.7	6.4	0.1	99	35.0 %	0	0	0
25	Dalen	Valley	D1-H	4.39	3.87	33.0	435	989	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	0	0	0
26	Dalen	Valley	D1-A	4.44	3.94	11.1	212	534	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
27	Dalen	Valley	D1-B1	5.33	4.42	3.78	314	181	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
28	Dalen	Valley	D1-B2	5.68	4.67	2.53	734	0	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
29	Dalen	Ridge	D2-O	4.26	3.21	78.7	377	3574	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	0	0	0
30	Dalen	Ridge	D2-E	4.19	3.21	7.33	46	127	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
31	Dalen	Ridge	D2-B	4.56	3.95	7.56	741	37	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
32	Dalen	Ridge	D2-C	4.81	4.09	2.67	584	95	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
33	Dalen	Slope	D3-O	4.21	3.40	69.0	393	2682	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	0	0	0
34	Dalen	Slope	D3-AE	4.22	3.60	15.6	289	469	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
35	Dalen	Slope	D3-B1	4.41	3.68	10.0	330	341	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
36	Dalen	Slope	D3-B2	4.53	4.16	8.68	347	423	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
37	Dalen	Slope	D3-C	4.97	4.13	2.23	327	22	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
38	Gashus	Ridge	36-O	4.04	2.83	71.	349	1306	0.05	12.7	19.05	8.06	13.9	120	9.78	0.18	184	29.2%	0	0	0
39	Gashus	Ridge	38-O	4.21	3.13	38.7	176	543	0.02	8.85	6.96	3.22	6.83	38.1	3.61	0.09	67.6	38.2%	0	0	0



40	Gashus	Slope	35-O	3.91	2.83	59.28	232	283	0.055	29.61	19.33	8.16	7.21	43.09	6.23	0.59	114.3	56.3%	0	0	0
41	Gashus	Slope	35-Bh	4.28	3.46	13.70	161	177	0.003	2.78	1.63	0.77	1.87	60.81	7.70	0.06	75.6	9.3%	4.5	15.7	79.8
42	Gashus	Slope	35-B	4.96	4.33	7.75	219	135	0.001	0.09	0.00	0.23	1.78	11.82	0.26	0.02	14.2	14.8%	7.7	18.8	73.5
43	Gashus	Slope	35-C	5.18	4.35	5.03	429	6	0.001	0.34	0.00	0.14	1.71	7.97	0.12	0.05	10.3	21.2%	4.9	13.7	81.4
44	Gashus	Valley	34-H	4.36	3.60	14.29	124	303	0.007	0.04	0.29	0.99	5.21	53.52	4.81	0.00	64.9	10.1%	3.3	14.9	81.8
45	Gashus	Valley	34-A	4.58	3.79	3.75	180	183	0.002	0.04	0.00	0.16	1.64	19.59	0.92	0.00	22.4	8.2%	3.2	9.6	87.3
46	Guthus	Ridge	12-O	3.88	2.86	39.34	140	475	0.044	18.8	7.9	1.3	7.6	63.6	0.6	0.0	99.9	35.6%	0	0	0
47	Guthus	Ridge	9-O	3.67	2.78	60.77	300	214	0.063	58.2	19.4	9.6	8.3	38.6	2.4	0.4	136.9	69.7%	0	0	0
48	Guthus	Ridge	9-A	3.82	2.92	18.25	73	341	0.014	3.4	1.6	1.7	2.8	36.7	1.8	0.0	47.9	19.7%	#N/A	#N/A	#N/A
49	Guthus	Ridge	9-E	4.09	3.13	4.29	45	197	0.007	0.5	0.3	0.3	2.4	24.1	0.6	0.0	28.2	12.4%	1.5	5.8	92.7
50	Guthus	Ridge	9-Bs	4.37	3.72	7.33	698	367	0.002	0.4	0.0	0.0	2.3	45.3	3.5	0.0	51.6	5.4%	2.5	8.8	88.7
51	Guthus	Valley	11-A	4.78	3.97	2.83	534	38	0.001	44.4	37.5	1.8	2.3	4.8	0.0	0.2	91.1	94.5%	8.0	16.4	75.7
52	Guthus	Valley	11-B	5.34	4.45	7.41	167	230	0.001	5.4	3.6	0.2	2.3	35.2	0.0	0.0	46.8	24.6%	20.6	38.8	40.7
53	Guthus	Valley	11-C	6.18	4.87	2.38	518	17	0.001	37.5	68.1	1.0	2.4	1.0	0.0	0.0	110.0	99.1%	7.6	15.0	77.5
54	Guthus	Valley	10-H1	4.44	3.49	80.19	73	424	0.017	211.3	44.0	2.4	13.5	126.8	9.1	0.0	407.1	66.6%	0	0	0
55	Guthus	Valley	10-H2	4.05	3.14	88.81	124	1064	0.031	85.8	22.9	2.5	13.6	84.9	4.3	0.0	214.1	58.3%	0	0	0
56	Guthus	Valley	10-C	6.79	5.14	3.95	618	53	0.001	57.3	28.6	3.6	12.0	0.0	0.0	0.0	101.5	100.0%	19.5	50.5	30.0
57	Guthus	Valley	8-H1	3.95	3.03	86.25	164	893	0.042	89.0	29.7	1.0	11.5	55.9	0.7	0.0	187.8	69.8%	0	0	0
58	Guthus	Valley	8-H2	4.20	3.40	90.93	54	655	0.022	186.2	55.6	0.1	15.3	53.7	2.7	0.0	313.6	82.0%	0	0	0
59	Guthus	Valley	8-C	6.73	5.45	3.27	694	21	0.000	35.2	52.8	3.7	9.8	0.0	0.0	0.0	101.6	100.0%	16.0	39.7	44.3
60	Huggenes	Ridge	5-O	3.89	2.88	79.53	259	1237	0.065	78.4	41.1	7.5	12.6	40.5	2.2	0.0	182.3	76.5%	0	0	0
61	Huggenes	Ridge	7-O	3.94	2.88	60.98	268	924	0.034	10.7	11.7	7.2	9.6	66.3	7.7	0.0	113.2	34.7%	0	0	0
62	Huggenes	Ridge	7-A	4.22	3.02	11.91	69	606	0.006	1.3	0.5	0.4	2.4	49.1	0.5	0.0	54.2	8.4%	0.6	2.1	97.4
63	Huggenes	Slope	3-O	3.68	2.81	78.17	142	814	0.076	89.4	52.0	8.1	15.1	27.0	1.7	0.0	193.4	85.1%	0	0	0
64	Huggenes	Slope	3-AE	3.85	3.04	9.67	31	88	0.011	2.5	1.7	0.6	2.6	25.4	1.7	0.0	34.5	21.6%	#N/A	#N/A	#N/A
65	Huggenes	Slope	3-B	4.71	4.31	4.23	221	48	0.001	0.0	0.0	0.1	1.7	9.3	0.0	0.0	11.1	16.2%	1.9	4.1	94.0
66	Huggenes	Slope	4-O	3.97	2.90	83.70	146	703	0.063	84.8	94.4	4.2	20.0	79.9	4.1	0.0	287.5	70.8%	0	0	0
67	Huggenes	Slope	4-E	4.58	3.81	2.97	12	49	0.002	0.3	0.0	0.0	3.1	27.6	0.0	0.0	30.9	10.8%	#N/A	#N/A	#N/A
68	Huggenes	Slope	4-B	5.19	4.28	2.18	450	99	0.001	0.0	0.0	0.0	2.0	7.2	0.0	0.0	9.3	22.5%	0.5	1.4	98.1
69	Huggenes	Slope	2-O	3.72	2.88	55.85	171	1145	0.075	84.8	74.1	14.3	16.5	18.2	0.5	0.0	208.4	91.0%	0	0	0
70	Huggenes	Slope	2-E	3.93	3.04	9.14	33	109	0.010	0.3	1.3	0.5	2.6	20.7	0.6	0.0	26.1	18.4%	#N/A	#N/A	#N/A
71	Huggenes	Slope	2-Bs	4.38	3.60	13.05	89	220	0.003	0.3	0.3	0.0	2.7	67.7	4.7	0.0	75.6	4.4%	#N/A	#N/A	#N/A
72	Huggenes	Slope	2-B	4.61	4.06	6.59	128	190	0.001	0.2	0.0	0.0	2.3	22.0	0.0	0.0	24.6	10.6%	#N/A	#N/A	#N/A
73	Huggenes	Slope	2-C	4.80	4.29	1.77	391	126	0.001	0.0	0.0	0.0	1.9	5.0	0.0	0.0	6.9	27.8%	4.8	8.5	86.7
74	Huggenes	Valley	6-H	3.92	3.02	76.66	130	1064	0.032	20.2	10.3	0.2	12.5	118.8	2.3	0.0	164.4	26.3%	0	0	0
75	Huggenes	Valley	6-C	5.01	4.00	6.04	156	88	0.002	27.0	11.4	0.2	2.9	15.8	0.0	0.0	57.1	72.4%	14.2	20.4	65.5
76	Huggenes	Valley	1-H	5.01	4.32	51.29	175	1069	0.005	229.6	51.1	2.7	11.0	29.6	1.2	0.0	325.2	90.5%	0	0	0
77	Støa	Ridge	33-O	3.85	2.98	75.23	200	815	0.065	117.5	52.6	8.6	12.1	36.6	4.1	0.7	232.3	82.1%	0	0	0
78	Støa	Ridge	33-E	4.10	3.19	2.92	16	39	0.006	0.8	0.1	0.2	1.9	11.9	0.5	0.0	15.5	19.9%	#N/A	#N/A	#N/A
79	Støa	Ridge	33-Bs	4.29	3.52	3.12	66	42	0.003	0.4	0.0	0.1	1.6	22.7	1.4	0.0	26.3	8.2%	#N/A	#N/A	#N/A
80	Støa	Ridge	33-B	5.10	4.56	1.04	243	69	0.001	4.8	1.6	0.1	1.6	13.8	0.6	0.1	22.7	36.1%	0.3	1.2	98.5
81	Støa	Slope	32-O	4.02	3.24	60.10	190	298	0.040	119.9	60.8	8.0	20.8	17.5	3.4	2.5	232.9	90.0%	0	0	0
82	Støa	Slope	32-AE	4.03	3.11	12.61	69	154	0.012	6.8	5.2	0.9	4.4	20.2	2.7	0.1	40.4	42.9%	#N/A	#N/A	#N/A
83	Støa	Slope	32-B	4.29	3.46	8.95	117	129	0.004	3.5	2.6	0.4	3.8	42.0	3.2	0.1	55.7	18.5%	2.4	9.2	88.5
84	Støa	Valley	31-O	3.93	3.29	62.98	383	552	0.034	182.9	37.1	4.4	7.0	22.1	4.0	2.4	259.9	89.0%	0	0	0



85	Støa	Valley	31-A	4.32	3.41	#N/A	33	315	0.011	25.5	8.5	0.5	5.8	67.0	2.8	0.4	111	36.5%	#N/A	#N/A	#N/A
86	Støa	Valley	31-B	4.99	3.96	11.7	205	367	0.001	3.3	1.0	0.4	1.5	11.7	0.9	0.1	18.8	32.8%	3.4	12.9	83.7
87	Støa	Valley	31-B2	5.19	4.23	3.32	543	65	0.001	1.6	0.3	0.3	1.7	8.0	0.3	0.0	12.4	31.9%	4.5	16.3	79.3
88	Østmarka	Ridge	30-O	3.96	3.07	66	290	440	0.052	122	37.8	13.1	10.6	30.9	3.4	5.4	224	82.2%	0	0	0
89	Østmarka	Ridge	30-E	4.11	3.17	3.98	42	42	0.008	4.3	2.0	1.0	2.7	14.3	0.9	0.1	25.3	39.9%	#N/A	#N/A	#N/A
90	Østmarka	Ridge	30-B	4.69	4.48	4.22	578	48	0.001	0.0	0.1	0.1	2.5	6.4	0.1	0.0	9.1	29.6%	19.1	55.0	25.9
91	Østmarka	Slope	29-O	4.12	3.55	72.9	343	1439	0.010	10.2	9.0	11.0	11.6	243	4.0	0.1	289	14.5%	0	0	0
92	Østmarka	Slope	29-B	4.70	4.03	4.11	176	40	0.001	0.1	0.1	0.3	2.9	16.4	0.3	0.0	20.1	16.8%	#N/A	#N/A	#N/A
93	Østmarka	Slope	29-C	4.93	4.40	4	218	104	0.001	0.0	0.1	0.3	2.5	7.2	0.1	0.0	10.1	28.3%	2.3	9.4	88.3
94	Østmarka	Valley	27-O	3.85	2.90	81.7	220	813	0.081	148	60.6	15.5	13.5	22.8	2.2	1.7	265	89.9%	0	0	0
95	Østmarka	Valley	27-B	4.47	3.79	14.1	169	170	0.002	1.3	1.9	1.6	3.3	57.9	4.7	0.0	70.7	11.4%	#N/A	#N/A	#N/A
96	Østmarka	Valley	27-C	5.06	4.28	1.61	177	14	0.001	0.6	0.6	0.1	2.8	3.8	0.0	0.0	7.9	51.2%	6.0	19.7	74.3

NB: data for sample 25 through 37 are taken from (Mohr, 2010).

Appendix B. Pearson correlation analysis data

	Topography	SAMPLE	Soil Hor	H+(H2O)	H+(BaCl)	LOI	Inorg-P	Org-P	CEC	BS	Clay	Silt
SAMPLE	-0.097											
	0.382											
Soil Hor	0.022	0.081										
	0.835	0.466										
H+(H2O)	-0.277	-0.147	**-0.630**									
	0.006	0.185	**0.000**									
H+(BaCl)	-0.367	-0.130	**-0.623**	**0.936**								
	0.000	0.240	**0.000**	**0.000**								
LOI	-0.080	-0.102	**-0.774**	**0.663**	**0.658**							
	0.439	0.364	**0.000**	**0.000**	**0.000**							
Inorg-P	0.058	0.044	0.185	-0.242	-0.209	-0.081						
	0.572	0.696	0.071	0.017	0.041	0.434						
Org-P	0.031	-0.103	**-0.636**	0.387	0.419	**0.574**	-0.027					
	0.768	0.355	**0.000**	0.000	0.000	**0.000**	0.792					
CEC	0.117	-0.132	**-0.687**	0.442	0.413	**0.872**	-0.041	**0.547**				
	0.291	0.235	**0.000**	0.000	0.000	**0.000**	0.710	**0.000**				
BS	0.233	-0.110	-0.176	0.173	0.164	0.385	0.381	0.113	**0.536**			
	0.034	0.322	0.112	0.119	0.138	0.000	0.000	0.310	**0.000**			
Clay	0.467	-0.085	0.258	-0.486	-0.470	-0.132	0.498	-0.241	0.447	**0.616**		
	0.003	0.612	0.117	0.002	0.003	0.429	0.001	0.145	0.005	**0.000**		
Silt	0.457	0.054	0.128	-0.389	-0.406	-0.030	0.503	-0.168	0.428	**0.561**	**0.936**	
	0.004	0.748	0.442	0.016	0.011	0.857	0.001	0.314	0.007	**0.000**	**0.000**	
Sand	-0.466	-0.017	-0.166	0.421	0.429	0.059	-0.508	0.190	-0.439	**-0.583**	**-0.966**	**-0.995**
	0.003	0.922	0.320	0.009	0.007	0.727	0.001	0.253	0.006	**0.000**	**0.000**	**0.000**

Appendix C. Results of all parameters with topography and horizons

Table C1: results for pH $_{H20}$

pH H_2O	n	Horizon	Average	Max	Min	Median
Ridge	12	O	3.95	4.39	3.67	3.95
	2	A	3.98	4.22	3.82	3.98
	4	E	4.16	4.35	4.09	4.11
	5	B	4.57	5.10	4.29	4.62
Slope	7	O	3.95	4.40	3.68	3.99
	3	A	4.12	5.06	3.85	4.12
	2	E	4.14	4.58	3.93	4.14
	9	B	4.57	5.60	4.28	4.61
	3	C	4.95	5.18	4.80	4.95
Valley	4	O	3.83	3.93	3.66	3.89
	7	A	4.45	5.19	4.01	4.50
	7	B	4.89	5.68	4.47	5.00
	4	C	5.22	6.18	4.86	5.33
Bogs	10	H	4.18	5.01	3.92	4.20
	4	C	5.57	6.79	5.01	6.35

Table C2: results for Organic matter content

LOI	n	Horizon	Average	Max	Min	Median
Ridge	12	O	60.9	82.7	15.5	66.0
	2	A	15.1	18.3	11.9	15.1
	4	E	4.9	7.33	2.92	4.29
	5	B	5.32	8.65	1.04	5.78
Slope	7	O	68.8	83.7	55.9	70.1
	4	A	11.9	15.6	9.64	11.1
	2	E	6.05	9.14	2.97	6.05
	9	B	7.47	13.70	2.18	7.75
	3	C	3.26	5.03	1.77	3.12
Valley	4	O	63.1	81.69	44.14	63.24
	7	A	8.7	18.21	2.83	8.22
	7	B	8.64	19.35	2.53	7.41
	4	C	3.08	4.99	1.61	2.85
Bogs	10	H	61.3	90.9	14.3	73.2
	4	C	3.94	6.04	2.48	3.61

Table C3: results for CEC

CEC	n	Horizon	Average	Max	Min	Median
Ridge	12	O	152	232	61.3	153
	2	A	51.1	54.2	47.9	51.1
	4	E	25.7	33.7	15.5	26.7
	5	B	26.2	51.6	9.13	22.7
Slope	7	O	232	298	114	233
	3	A	35.7	40.4	32.2	34.5
	2	E	28.5	30.9	26.1	28.5
	9	B	37	75.7	9.25	24.6
	3	C	9.13	10.3	6.93	10.1
Valley	4	O	212	265	136	223
	7	A	65.0	111	22.4	67.5
	7	B	39.6	70.7	12.4	44.4
	4	C	63.4	119	7.87	63.3
Bogs	10	H	208	407	64.9	191
	4	C	86.6	102	57.1	93.9

Table C4: results for Base Saturation

BS	n	Horizon	Average	Max	Min	Median
Ridge	12	O	52.7	82.2	13.9	50.2
	2	A	14.1	19.7	8.4	14.1
	4	E	22.1	39.9	12.4	17.9
	5	B	20.5	36.1	5.37	23.2
Slope	7	O	61.2	91.1	14.5	70.8
	3	A	28.4	42.9	20.7	21.6
	2	E	14.6	18.4	10.8	14.6
	9	B	22.2	86.9	4.37	16.2
	3	C	25.8	28.3	21.2	27.8
Valley	4	O	61.3	89.6	32.7	61.2
	7	A	38.6	94.5	7.99	27.6
	7	B	28.4	65.1	11.5	24.7
	4	C	69.2	99.1	27.7	74.9
Bogs	10	H	53.8	90.5	10.1	62.5
	4	C	91.3	99	72.4	96.4

Table C5: results for inorganic phosphorus

Inorg-P	n	Horizon	Average	Max	Min	Median
Ridge	12	O	279	563	140	260
	2	A	70.9	73.2	68.6	70.9
	4	E	35.9	45.8	16.4	41.7
	5	B	405	741	65.8	411
Slope	7	O	241	393	142	211
	3	A	97.6	289	1.87	49.8
	2	E	22.7	33.1	12.3	22.7
	9	B	241	450	88.6	219
	3	C	341	429	218	359
Valley	4	O	233	383	162	193
	7	A	283	534	33.2	263
	7	B	332	734	109	237
	4	C	424	703	177	408
Bogs	10	H	183	435	53.9	164
	4	C	518	695	156	611

Table C6: results for organic phosphorus

Org-P	n	Horizon	Average	Max	Min	Median
Ridge	12	O	983	3574	214	821
	2	A	474	606	341	474
	4	E	135	268	38.9	127
	5	B	114	367	36.7	58.5
Slope	7	O	1131	2682	283	980
	3	A	302	498	88.1	312
	2	E	79.5	109	49.5	79.4
	9	B	165.4	423	18	135
	3	C	64.5	126	5.73	63.1
Valley	4	O	590	813	337	605
	7	A	247	534	38.5	220
	7	B	203	482	0.00	181
	4	C	53.6	154	14.5	22.9
Bogs	10	H	1174	2867	303	998
	4	C	45.5	88.3	19.9	36.8

Appendix D: water quality

Table D1: water quality information

Type of water	Water purification system	Resistivity (MΩ cm at 25 ^{0}C)	TOC (µg C/L)	Product of
Type I water	Milli-Q water	18.2	≤ 5	Millipore
Type II water	Elix UV deionized water	5-10	< 30	Millipore

Appendix E: ICP-OES analysis

Varian Vista AX CCD simultaneous axial view ICP-OES product of Varian was used. The following default operating conditions of the spectrometer were used for the analysis of the selected elements. This was operated by Christian Wilhelm Mohr department of chemistry, UIO. All samples were acidified with 1% HNO_3

Table E1: ICP-OES instrumental conditions used for analysis

Parameters	
RF power	130kW
Plasma Argon flow rate	15 L/min
Auxiliary Argon flow rate	1.5 L/min
Nebulizer Argon flow	0.75 L/min
Sample flow rate	1.5 mL/min
Reading time	10s
Rinse time	30s
Sample update delay	60s
Rump rate	20

Table E2: wave length selection and Limit of Detection

Wavelength selection for the determination of the major cations (calcium, potassium, magnesium, sodium, aluminum, iron and manganese) using the ICP-OES. Wavelengths were selected based on the concentration of the analytes.

Element	Wavelength	LOD (mg/L)
Na	588.995	0.5
K	769.897	0.05
Ca	396.847	0.1
Mg	280.270	0.04
Fe	238.204	0.03
Al	396.152	0.04
Mn	257.610	0.03

LOD of each element in table E2 is found by three times the standard deviation of concentrations of the method blank. LOD = 3*SD blank

Where, SD is standard deviation of the sample blank, calculated as

$X = \sum X_i / n$, where X is average blank concentration, and n is number of samples

$SD = \sqrt{[(X-X_i)^2 / (n-1)]}$

Appendix F: SEAL Autoanalyzer for phosphate determination

The SEAL Autoanalyzer 3 at the Department of Geosciences, UiO, was used to determine the Tot-P and Inorganic-P fractions from the soil extracts acquired from the Chang and Jackson (1957) and Mørberg and Petersen (1982) methods. The instrument was set with the parameters given in Table F1

Table F1: seal autoanalyzer 3 parameters

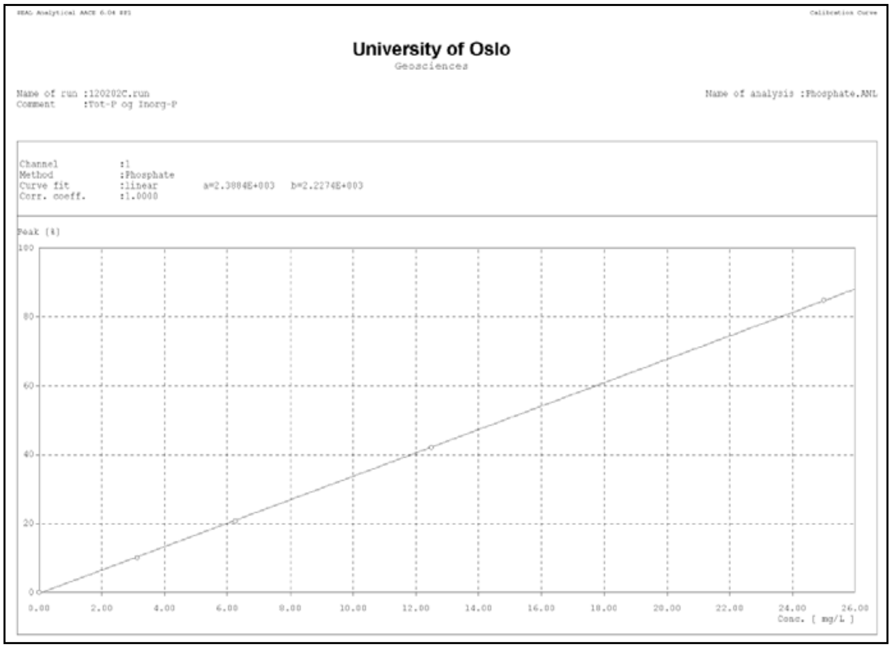
Parameters	Description
Detection range	0.12 – 6000ug/l for phosphate in water solution
Flow cell	10mm
Wavelength	660nm
Reagents	Ammonium molybdate solution, sulphuric acid and sodium dodecyl sulfate solution, ascorbic acid solution
Wash solution	Same matrix as the extraction solution in table 3.3

Table F2: Preparation of reagents used for the extraction method and standard phosphorus solution

Reagents	Amount dissolved per liter type I water
1M NH4Cl	53.3g
0.5M NH4F	18.5g
0.8M H3BO3	50g
0.1M NaOH	4.1g
0.25M H2SO4	15ml
0.1M KCl, Ascorbic acid and EDTA	7.5g, 12.5g and 0.372g respectively
saturated NaCl solution	400g
phosphorus standard solutions 0.78, 1.56, 3.125, 6.25, 12.5, 25 and 50ppm	0.2195g KH2PO4

Table F4: Inorganic phosphorus fractionation results (mg/Kg)

Topography	Horizon	Sol-P	Al-P	Fe-P	Ca-P	Occl-P
Ridge	O	14.0	82.4	72.1	2.0	17.1
	E	0.1	5.5	14.5	1.3	4.9
	B	0.0	98.8	86.6	19.0	7.8
	C	0.0	36.1	38.3	38.3	6.1
Valley bottom	H	1.6	79.6	101.4	19.2	3.0
	B	0.0	31.9	24.1	274.0	5.4
	C	0.0	8.7	22.1	386.0	3.0



SEAL Analytical AACE 6.04 SP1

Calibration Curve

University of Oslo

Geosciences

Name of run :120202C.run

Comment :Tot-P og Inorg-P

Name of analysis :Phosphate.ANL

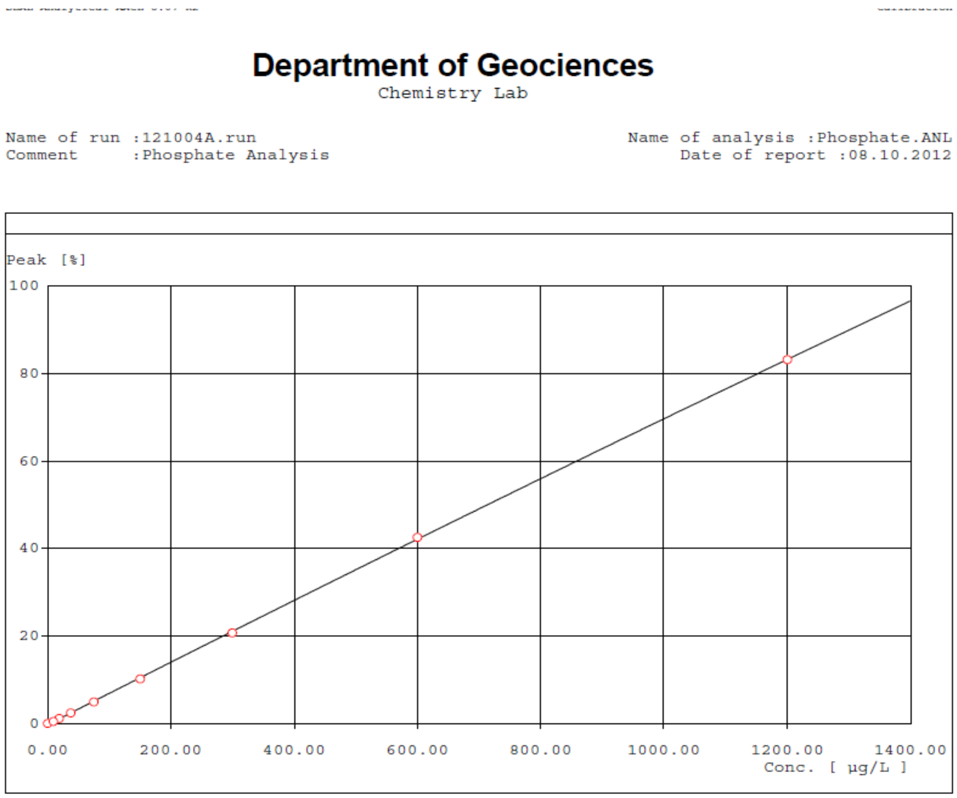
Channel :1

Method :Phosphate

Curve fit :linear a=2.3884E+003 b=2.2274E+003

Corr. coeff. :1.0000

Figure F1: calibration curve for total and inorganic phosphorus analysis



Department of Geociences

Chemistry Lab

Name of run :121004A.run
Comment :Phosphate Analysis

Name of analysis :Phosphate.ANL
Date of report :08.10.2012

Figure F2: Calibration curve for Inorganic-P fractionation

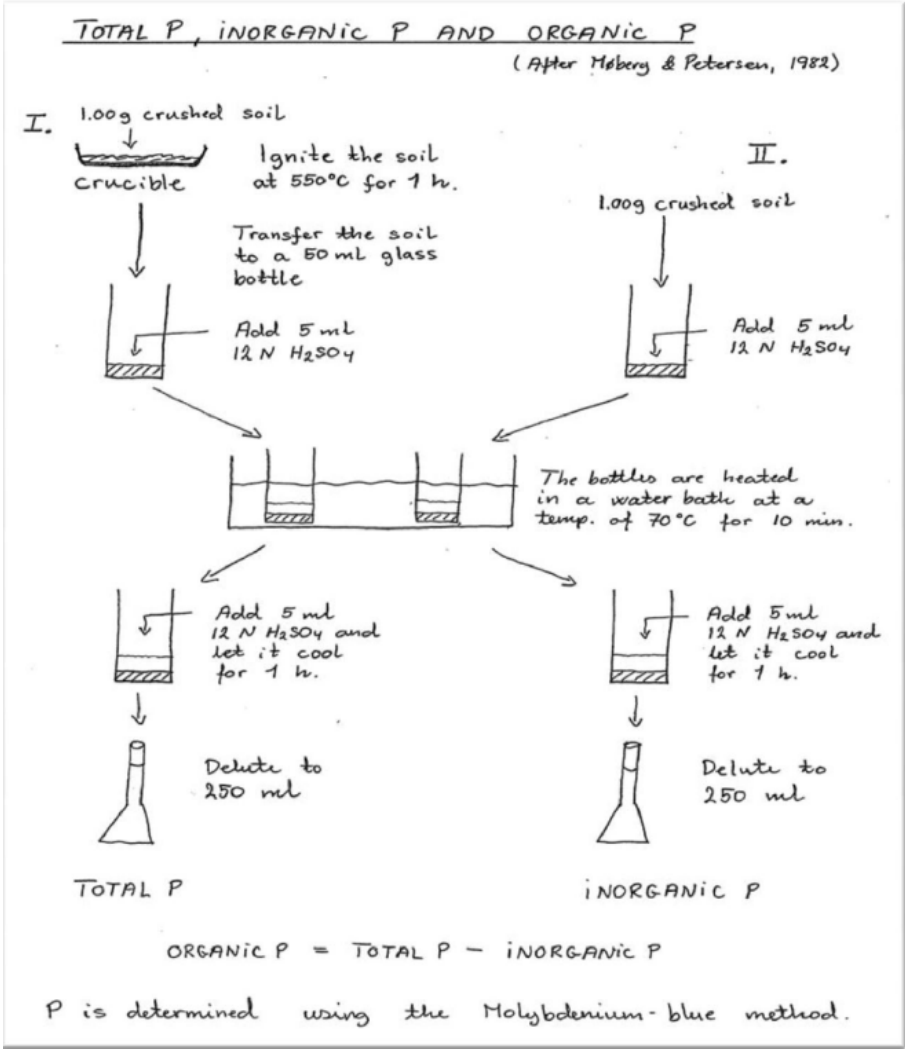


Figure F3: Møberg and Petersen Method- Sample digestion method for determination of Tot-P, Ing-P.

Appendix G: Maps of the quaternary deposits of the study area

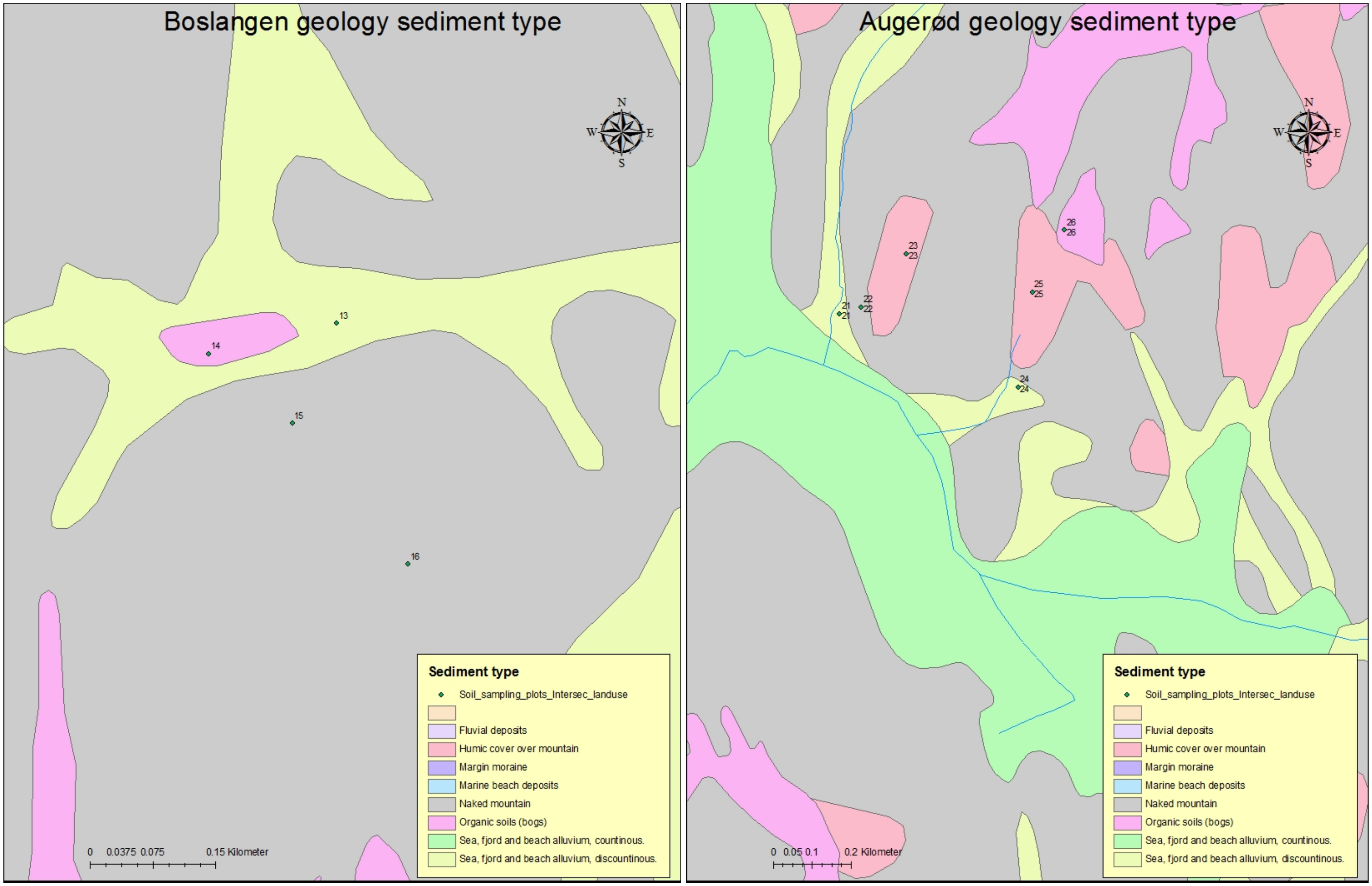


Figure G1: Maps for the quaternary deposits of study are for Boslangen and Augurød.

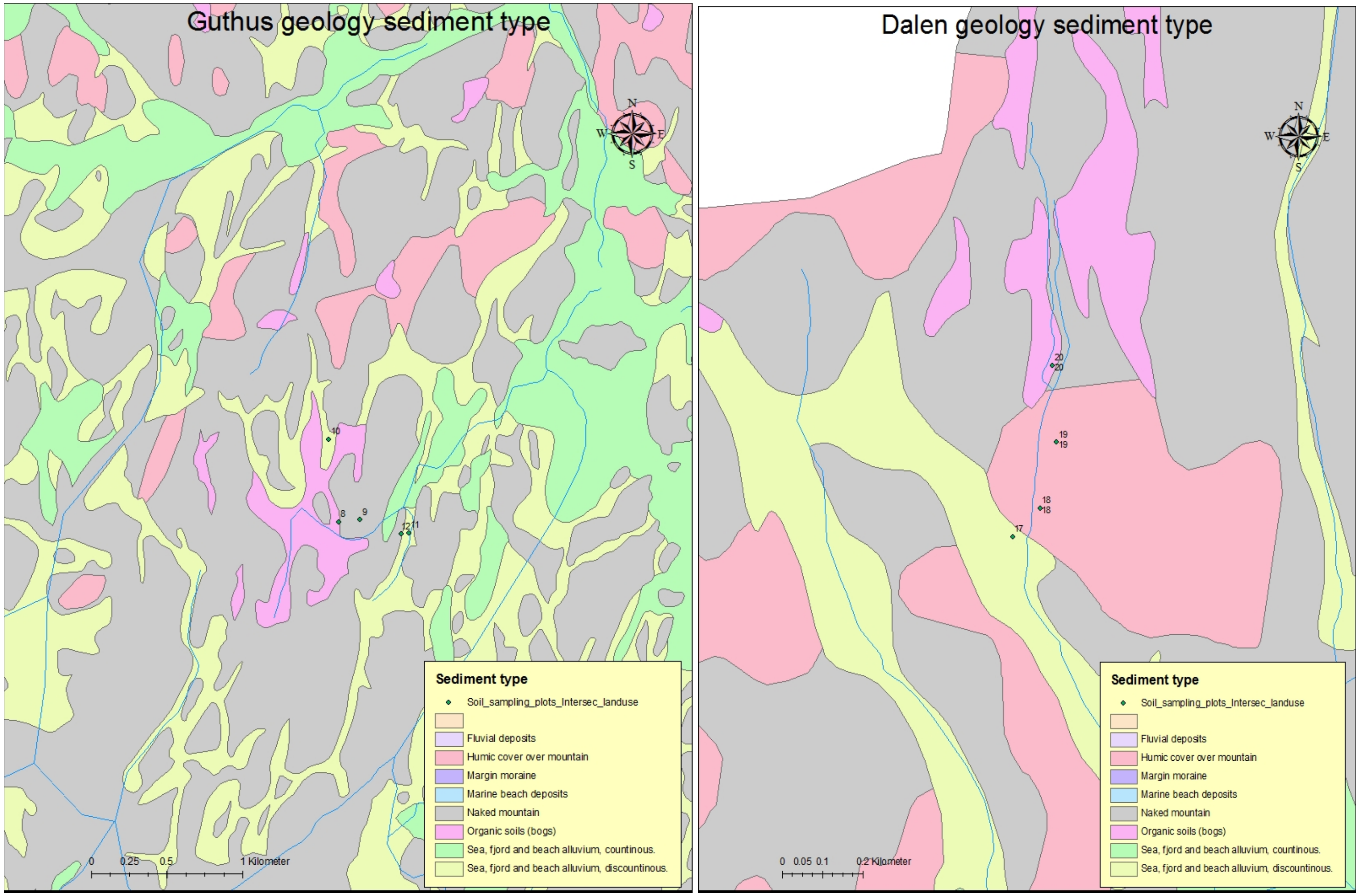


Figure G2: Maps for the quaternary deposits of study are for Guthus and Dalen.

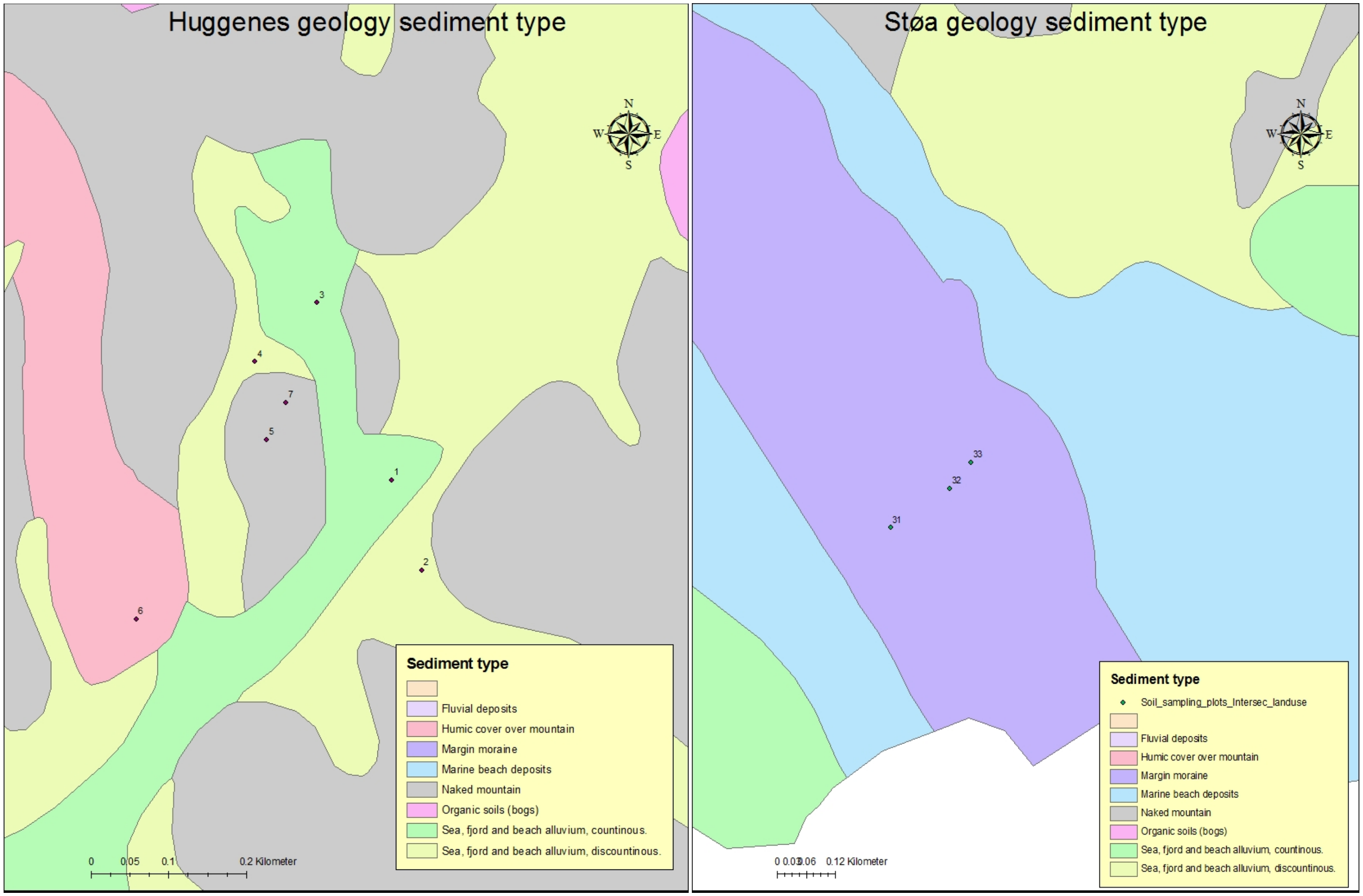


Figure G3: Maps for the quaternary deposits of study area for Huggenes and Støa.

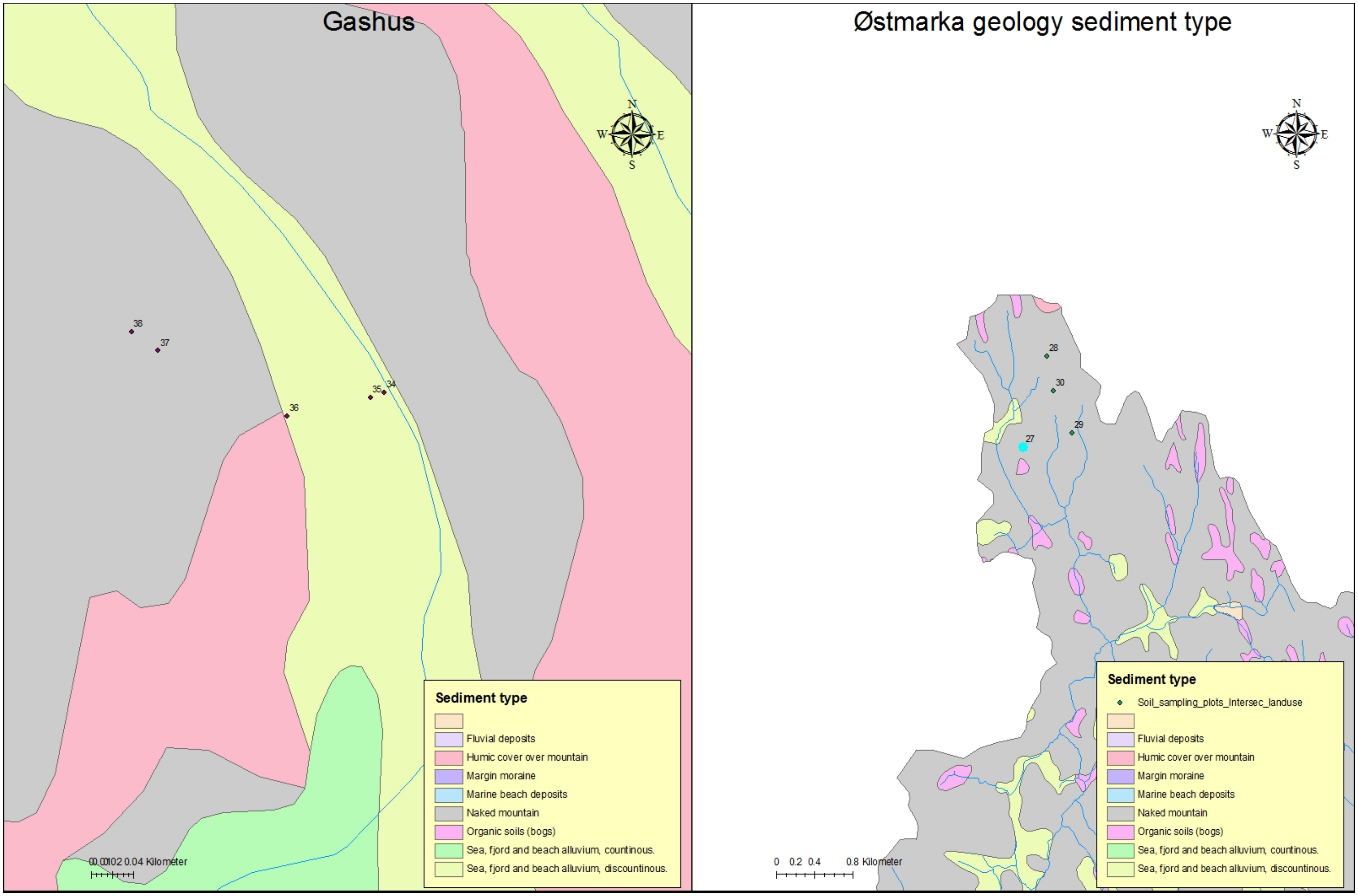


Figure G4: Maps for the quaternary deposits of study are for Gashus and Østmarka.

In the given maps, the numbers and black dots in each site represents plot numbers where the soils are sampled. More information about the plot numbers are given in table 6 and see figure 12 for the legends description. The map used is a quaternary map, 1:50000 produced by Geology for Society (NGU) (http://www.ngu.no/no/hm/Kart-og-data/nedlasting/), modified by Alexander Engebretsen

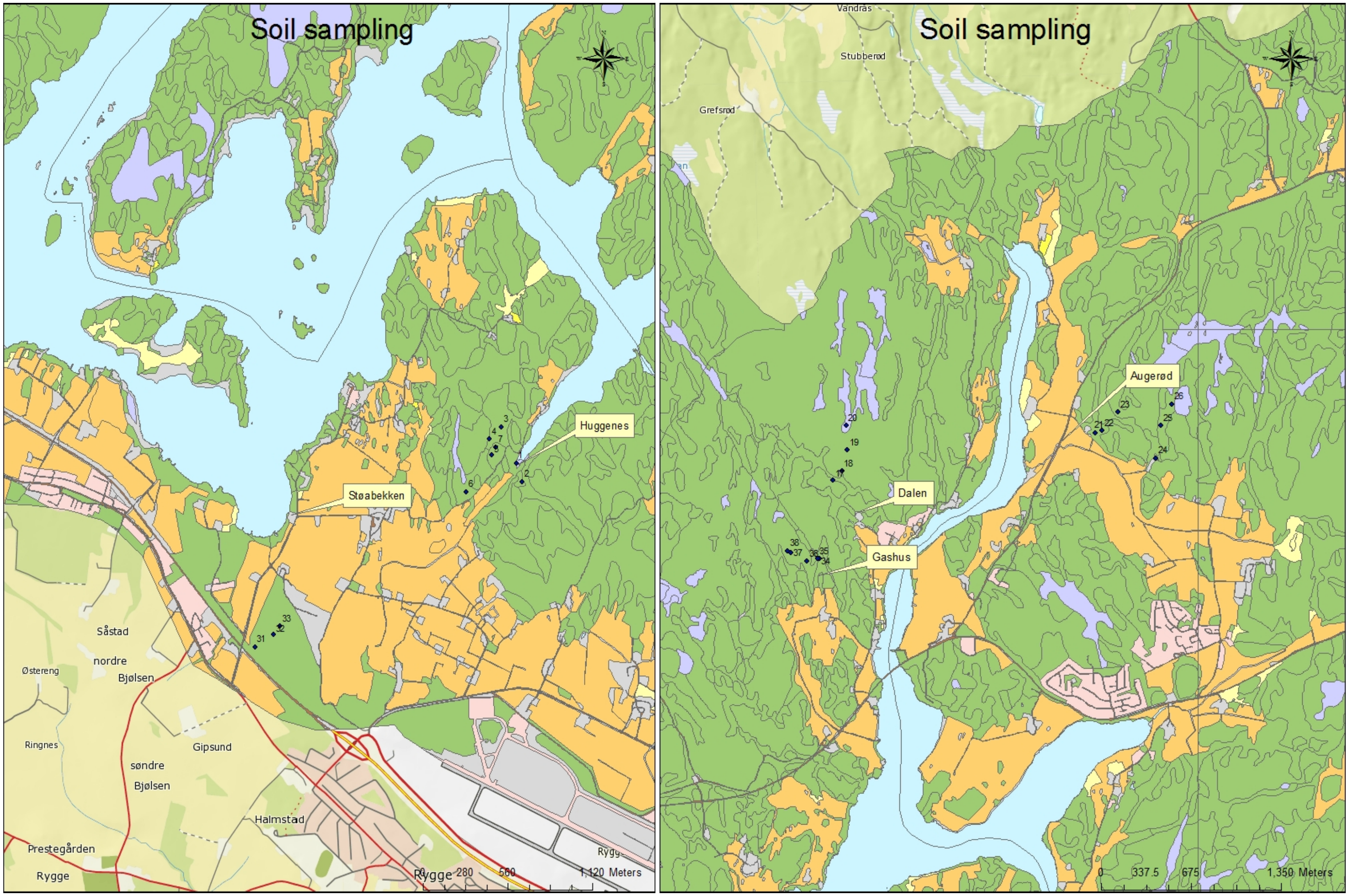


Figure G5: Soil sampling maps for Hugeness, Støa, Gashus, Dalen and Augurød.

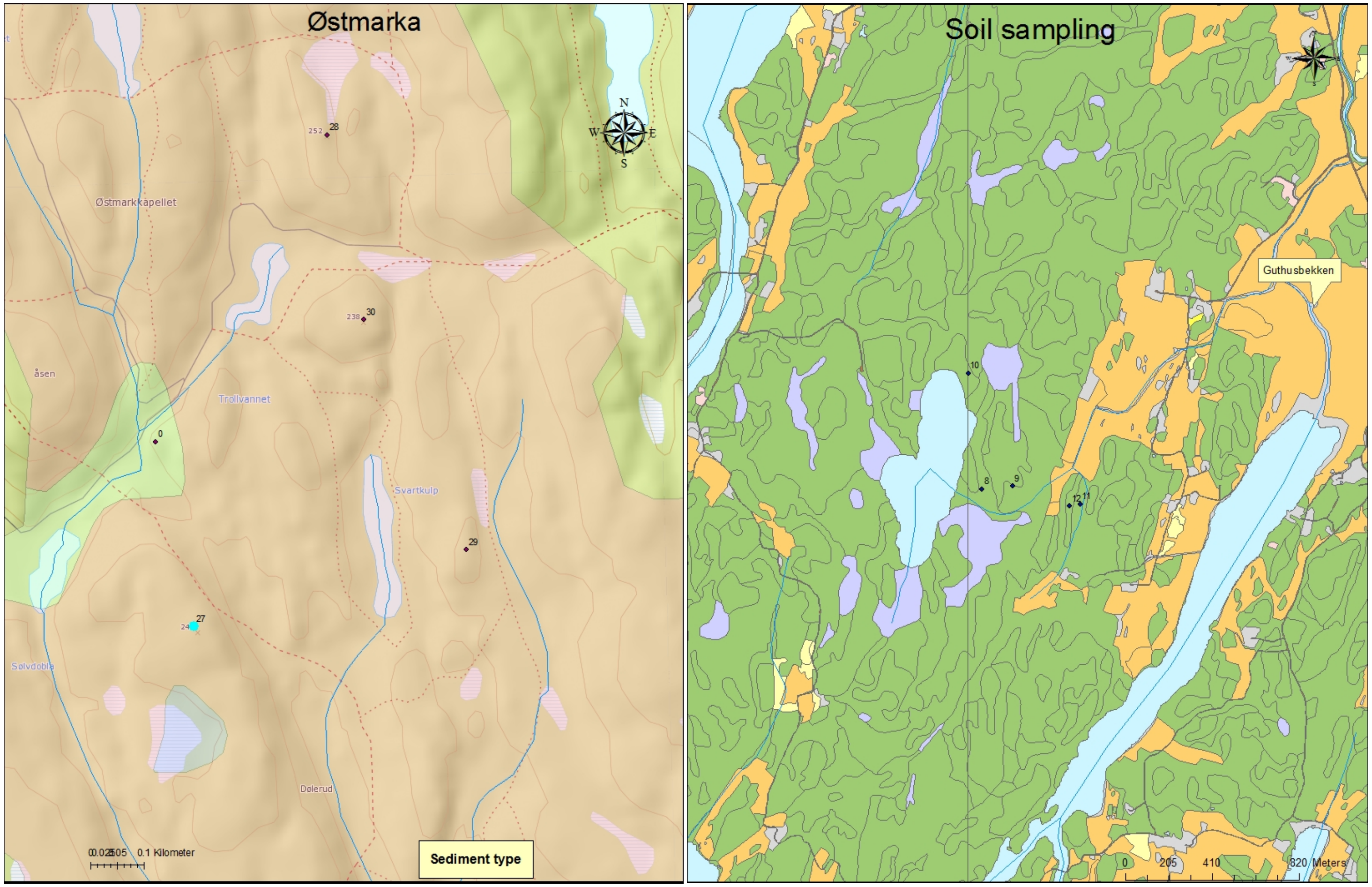


Figure G6: Soil sampling maps for Østmarka and Guthus.

In the given maps, the numbers and black dots in each site represents plot numbers where the soils are sampled. More information about the plot numbers are given on table 6 and see Figure 12 for the legends description. The map used is a quaternary map, 1:50000 produced by Geology for Society (NGU) (http://www.ngu.no/no/hm/Kart-og-data/nedlasting/), modified by Alexander Engebretsen