Thesis for the Master’s
degree in chemistry

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Soil phosphorus pools and their relation to land-use and soil physiochemical properties – A case study of an agricultural watershed in north-eastern China.

60 study points

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Preface

First of all I would like to thank my supervisor prof. Rolf D. Vogt for making it possible for me to conduct the master thesis at the group of environmental analysis, and contributing to the thesis with invaluable comments and suggestions. Also, thanks to my co-supervisors prof. Grethe Wibetoe and PhD candidate Bin Zhou for all help, guidance and comments and advice throughout this process. I would also express my greatest appreciation to Bin Zhou for being a great translator and travel companion during my stay in China.

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My 6 years at the University of Oslo would never be the same without all my friends from LAP and the chemistry programme, so I would like to thank them for sharing so many great moments full of laugher and fun. Especially to the people that I meet every day in the lab and office the past two years; Andreas, Frøydis, Alexis, Bård, Lena and Wycliffe – it would never be the same without you, and I will miss your happy faces and the crazy humour!

To my boyfriend Stian for believing in me, for reminding me that there is a life outside the office and for making me laugh every day. Thank you for being so patient.

And at last I would like to dedicate this thesis to my family; without you support and believe in me I would never been where I am today, and you are the reason I have gotten this far. Thank you.

Abstract

This thesis was carried out as a part of the MILJØ2015-CHINOR bilateral Sino-Norwegian Sinotropia research project funded by the Research Council of Norway (project 209687/E40), which aims at generating knowledge needed in order to select the optimum abatement actions for improving the water quality in a eutrophic reservoir in one of Chinas largest municipalities. The study site was the agricultural watershed around the Yuqiao reservoir, and the focus of the work has been the soil characteristics in the area, and how land-use practises influences the hydro geochemical processes.

As a follow-up to a preceding study done by master student Bishnu P. Joshi samples were collected in order to achieve a better geographical distribution, but also an improved representation of different land-use and soil horizons. The samples were analysed for several physiochemical parameters like pH, organic matter content, cation exchange capacity, sorption capacity, particle size distribution and mineralogy, in addition to the inorganic and organic phosphorus pools. These parameters are assessed in relation to land-use practises at the sampling sites and data on soil-water chemistry in order to better understand the processes governing the mobilization and transport of phosphorous fractions in the soils.

The study revealed that the physiochemical characteristics of the soils from different land-use categories in general do not differ much in any of the parameters. The low amount of organic matter, silt loam texture and relatively low cation exchange capacity suggested that the soils have a low ability to adsorb phosphorus. This was confirmed by a low phosphorus sorption capacity in the range between 200 and 300 mg P/kg. The total phosphorus concentrations in the soils exceeds this capacity, and lies between ca. 450 and 850 mg P/kg soil. It is thus clear that the soils are oversaturated with phosphorus, which is also reflected by a high concentration of free phosphate in the soil-water. Field observations of a compact clay layer under the plough layer (A_p) in the lowland region and the identified dominance of 1:1 clay indicates that vertical flow of water is limited. Furthermore, the soil texture and low organic matter content renders the soil prone to erosion. Thus, the main mobilization process is erosion and the main transport mechanism for phosphorous is through shallow sub-lateral flow and overland runoff.

The study of the physiochemical differences between the soil horizons did not reveal any clear trends, except for the high phosphorus concentration in the A_p horizon, which reflects the extensive application of fertilizers and manure in the area.

Table of Contents

List of Figures

Abbreviations

A_p	Plough layer A horizon
ATP	Adenosine triphosphate
CAS	Chinese Academy of Science
CEC_e	Effective Cation Exchange Capacity
CHINOR	Research Cooperation with China
DNA	Deoxyribonucleic acid
DOM	Dissolved Organic Matter
DOM-P	Dissolved Organic Phosphorus
DPSIR	Drivers, Pressures, State, Impacts and Responses
EDTA	Ethyleneaminetetraaceticacid
EPB	Environmental Protection Bureau
EU	European Union
EUTROPIA	Watershed EUTRophication management through system oriented modelling of Pressures, Impacts, and Abatement actions
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
JOVA	Norwegian programme for monitoring soil and water in agricultural land.
LOI	Loss on ignition
Miljø2015	Norwegian environmental research towards 2015
NIBR	Norwegian Institute for urban and regional Research
NIVA	Norwegian Institute for Water Research
NMR	Nuclear Magnetic Resonance
PC	Principal Component
PC1	First Principal Component
PC2	Second Principal component
PCA	Principal Component Analysis
PCA	Principal Component Analysis
pH_{PZC}	pH at Point of Zero Charge
PO_4-P	Phosphorus on the form of phosphate
PP	Particulate phosphorus
PSD	Particle Size Distribution
PZC	Point of Zero Charge

RCEES	Research Centre for Eco-Environmental Sciences
RCN	The Research Council of Norway
Sinotropia	Watershed EUTROphication management in China through system oriented process modelling of Pressures, Impacts and Abatement actions.
TAES	Tianjin academy of Environmental Science
TIP	Total Inorganic Phosphorus
TOP	Total Organic Phosphorus
Tot N	Total Nitrogen
Tot P	Total Phosphorus
UiO	University of Oslo
USDA	US Department of Agriculture
$\mathbf{W_{dm}}$	Weight of dry matter
$\mathbf{W_{H2O}}$	Weight of water
$\mathbf{-X-OH_2^+}$	Protonated oxide on mineral surface
$\mathbf{-X-O^-_s}$	Deprotonated oxide on mineral surface
XRD	X-Ray Diffraction

1. Introduction

1.1 Water quantity and quality

Water shortage is a serious problem in China. The amount of naturally available freshwater from all surface and underground water sources in China is ranked sixth in the world, however, compared to the population the levels is one of the lowest (per capita) (Shalizi, 2006) and is around one quarter of the world average (Liu & Diamond, 2005). The water is not distributed evenly throughout the country, and according to Shalizi (2006) , Liu and Diamond (2005) and Jiang (2009) the problem is biggest in the north (The Yangtze river is considered to be a natural divide between north and south (Varis & Vakkilainen, 2001), while in the south the problem is moreover flooding. The water shortage in northern China is not only due to the dry climate, but also due to an increase in demand of water and the deterioration of water resources. According to the World Water Council (2012) accelerating population growth and increasing use of water due to life style, agriculture and industry will lead to a further increase in demand in the future. Freshwater is also important for energy production. It is required in every step; extraction, production, refining, processing, transportation and storage, and in some cases electric power generation itself, and it is estimated that the demand of water for energy will double over the next 40 years (World Energy Council, 2010). The lack of freshwater will therefore also lead to a global challenge in energy production. In China agricultural activity is the largest consumer of water, but the growth in demand is largest for urban and industrial use (Shalizi, 2006).The conflicting stakeholder interests of the global water resources, i.e. for energy production, agriculture and recreational activities, as a recipient of waste and a habitat for indigenous species, will lead to an global challenge in meeting the demand of freshwater sources and it is essential to reduce the deterioration of freshwaters around the world to not further escalate the problem.

The water shortage in China and elsewhere is not only due to the availability of freshwater and increased demand, but also a result of water pollution (Jiang, 2009). The water quality is deteriorating due to pollutants, and especially the use of fertilizers and lack of sewage treatment around the world (World Water Council, 2012). The United Nations established eight development goals in 2000 where they include a goal to ensure environmental sustainability. This goal includes a sub target 7. C which aims at reducing the proportion of the world population without access to safe drinking water and basic sanitation by 2015"(United Nations, 2013). Knowledge about processes governing the deterioration of surface waters is therefore crucial for solving the world's challenges with water supply, and to reach millennium goal no 7.C. According to Smith, Tilman, and Nekola (1999) eutrophication is the most widespread water quality problem, and it is considered to be one of the main environmental challenges in China (Jin, Xu, & Huang, 2005).

1.2 Freshwater eutrophication

Eutrophication is a process where the flux of nutrients such as nitrogen or phosphorous increases, causing alterations to the aquatic ecosystem. Phosphorus is considered to be the limiting nutrient in most freshwaters (Welch, 1978) and by increasing the loading of bioavailable phosphorus, or phosphorus compounds that can be made bioavailable, primary production will increase (Weiss, 1969). The sources of phosphorus are mainly anthropogenic, and usually stem from agricultural activities and untreated waste water. According to Chen, Chen, and Sun (2008) the main source of phosphorus input in China stems from diffuse runoff from agriculture (fertilizers and manure), and the most important transport mechanism to freshwater lakes are overland runoff due to soil erosion (Bechmann & Deelstra, 2006; Gburek, Barberis, Haygarth, Kronvang, & Stamm, 2005).

The increase in primary production is associated with several problems; it changes the colour, odour and taste of the water, which is undesirable for people that use it as source for drinking water and recreational activities. It can result in blooms of toxic cyanobacteria which in large enough amounts are harmful to humans that use it for drinking water and other organisms associated with the water (Yang, Wu, Hao, & He, 2008). Furthermore, the algae blooms reduce the light penetration and thereby the photic zone. In the hypolimnion the bacteriological decomposition of the drizzle of dead organic matter leads to anoxic conditions unsuitable as habitat for fish and many other indigenous species. The structure and function of the freshwater ecosystem is thereby altered, ultimately leading to decreased biodiversity. Eutrophication can also be an economical issue because of increased treatment costs due to difficulties meeting standards for drinking water.

The quality status of freshwater lakes can be classified according to the trophic state which is related to the primary production of the lake. The terms used are oligotrophic (nutrient poor), mesotrophic (intermediate nutrient supplies), eutrophic (well nourished) and hypertrophic (Smith et al., 1999). The trophic state is difficult to determine by quantitative measures (like the ones presented in Table 1), because different lakes react differently to the nutrient input. The biological productivity in the lake is therefore used as a classification parameter;

Eutrophic lakes have excessive biological productivity, oligotrophic lakes have limited growth of aquatic organisms, and mesotrophic lakes are somewhere in between (vanLoon & Duffy, 2011). The European Union has developed a quantitative classification scheme for the ecological status of surface waters (European Commision, 2003), and some of the parameters that are linked to the trophic state are given in Table 1 and visualized in Figure 1. Figure 1 is a flow chart for determining the quality of surface waters based on the parameters and boundary values given in Table 1.

Table 1 Classification of surface waters based on chlorophyll A, secchi depth, total phosphorus and total nitrogen. The reference value is the natural state of water without any anthropogenic input (Vannportalen, 2009), and the numbers are the upper limits for each category.

Items	**Surface water quality classification**				
	Reference value	Very poor /poor	Poor /moderate	Moderate /good	Good /very good
Chlorophyll A (µg/L)	3.5	40	20	10.5	7
Secchi depth (m)	5	0.5	1	2	3
Tot P(µg/L)	7	65	35	19	13
Tot N (µg/L)	300	1500	900	550	450

The EU water framework directive is an integrated river basin management plan for Europe that aims at achieving a good status for all waters within 2015 to ensure access to drinking water, bathing water and the protection of aquatic ecology and unique habitats, among other things (European Commission, 2014; Vannportalen, 2009) . The values given in Table 1 is retrieved from a guidance published by the Norwegian directorate group for implementation of the water framework directive (Vannportalen, 2009) and gives the upper limits for each category. The reference value presented in the table is the “natural value”, or the natural state of the water without any anthropogenic influence.

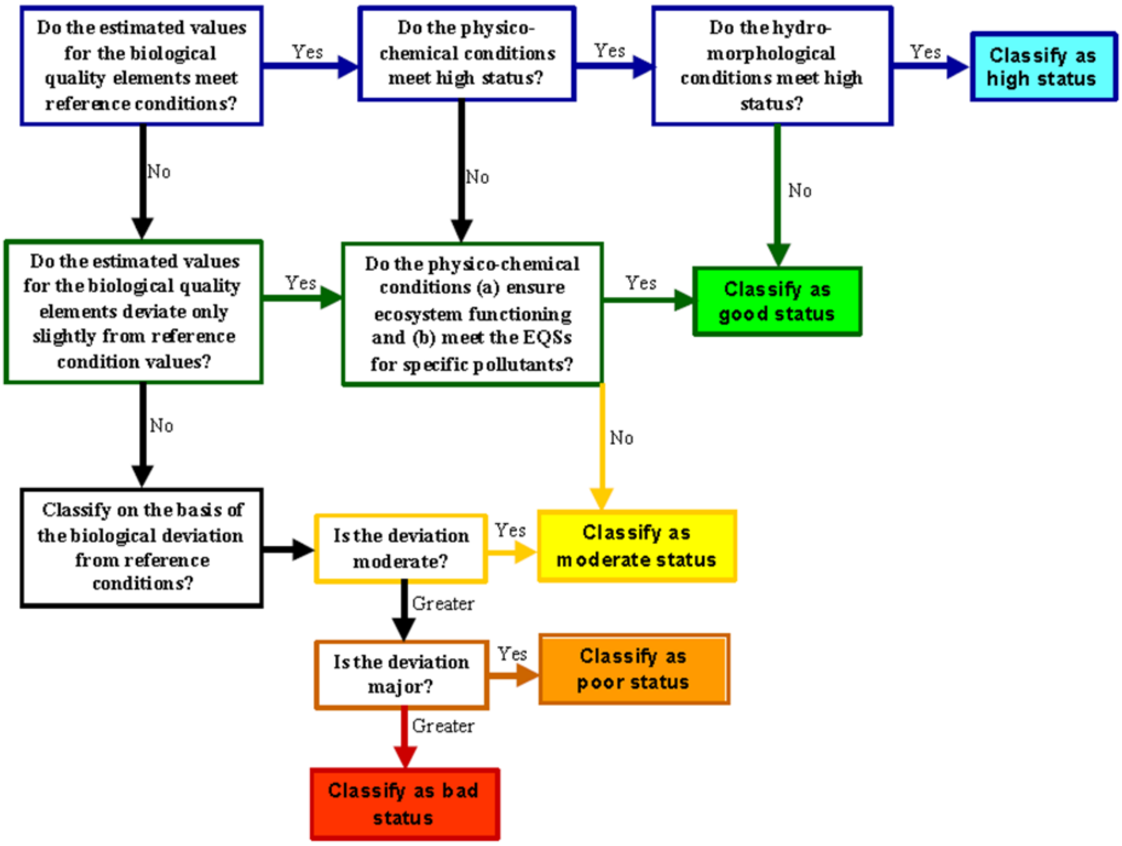


Figure 1 Indication of the relative roles of biological, hydro morphological and physiochemical quality elements in ecological status classification (retrieved from European Commision (2003))

1.3 The Sinotropia research project

This study is an integral part of the MILJØ2015-CHINOR bilateral Sino-Norwegian Sinotropia research project jointly funded by the research council in Norway (RCN) (209687/E40), and Chinese Academy of Sciences (CAS). SinoTropia is inter-disciplinary research collaboration between UiO, NIVA, NIBR, RCEES, CAS and TAES, studying mechanisms and processes governing eutrophication and how they are influenced by different pressures. By using a DPSIR approach (Driving forces, Pressures, States, Impacts and Responses) on the eutrophication problem the project aims at describing the interactions between society and the environment (European Environment Agency, 1999). The project will address the hydro-biogeochemical processes that govern the transport of nutrients to the reservoir, and the results will be incorporated into different models for simulation of watershed and lake response to changes in pressures. The findings in these studies will ultimately be used to provide decision makers with better knowledge regarding appropriate abatement actions to improve the water quality in the reservoir. This master thesis, focusing on the soil characteristics, is conducted in parallel with the master study by Wycliffe O.

Ojwando which emphasizes on the water chemistry in rivers and streams. Both studies build on the preceding master study conducted by Bishnu P. Joshi (Joshi, 2014). The project is divided into five work packages, and this study is a part of Work Package 1; Field sampling and chemical analysis.

SinoTropia is inspired by the completed EUTROPIA project, which focused on gaining the knowledge needed to make abatement actions to reach a good water quality as defined by the EU water framework directive. The study area in the Eutropia project was the local catchment Morsa (consisting of 15 % agricultural land and 80% forest) around the Vansjø Lake, which has suffered from eutrophication since the 1950s. Approx. 20 years have been used to coordinate abatement actions to solve the eutrophication problem, without any significant reduction (Orderud & Vogt, 2013). The project focused on better understanding the processes governing the leaching of phosphorus from forest soils and agricultural land, and the project was completed in May 2013. Results from two master thesis (Opland (2011) and Desta (2013)) will be discussed in the result section.

1.4 The Yuqiao Catchment

The Yuqiao reservoir lies in Ji County, Tianjin, situated northeast of Beijing in north-eastern part of China (Figure 2). Tianjin is the fourth largest municipality in China in terms of urban population. The Yuqiao reservoir was originally constructed as flood protection and for agricultural irrigation in 1959. In the 1980's Tianjin was facing a shortage of drinking water, and as a solution the reservoir was enlarged through the Luan River Diversion Project. The Luan River was diverted through a 234 km long diversion channel, and mainly enters the reservoir through the Li River. The water is diverted mainly in the dry periods, but also when there is a need for more water. In the dry periods the water in the reservoir is only replenished from the Luan river diversion channel. The Yuqiao reservoir acts as the main source of drinking water for about 6.3 million people and water for industry located downstream from the reservoir as well as a place for recreational activity and fishing.

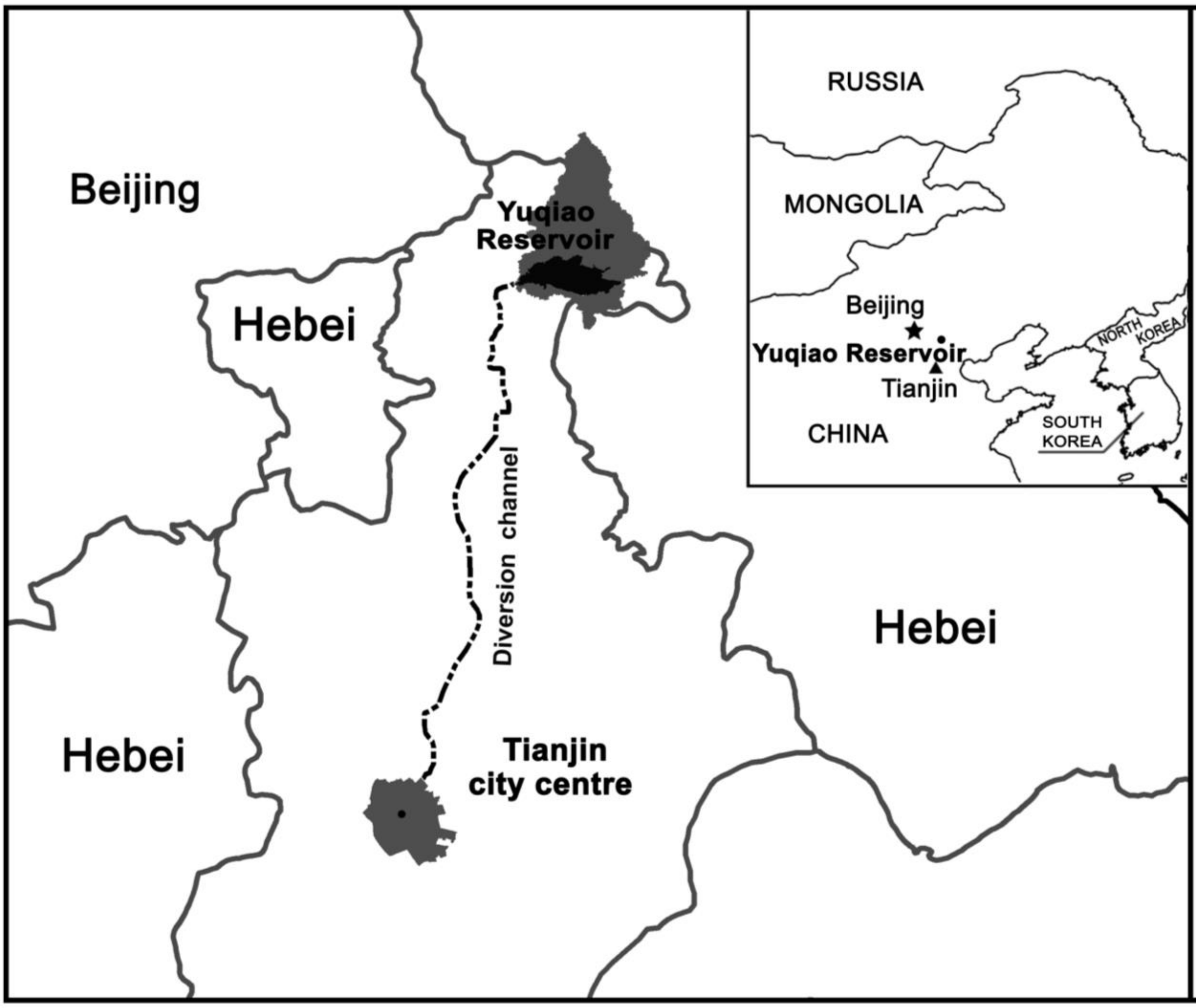


Figure 2 Location of the Yuqiao reservoir and its local watershed

The monitoring data shows an increasing trend of eutrophication (Ji County EPB, 2012), causing water quality problem for the water work. Yuqiao is a shallow reservoir with an average depth of 4 m. Shallow lakes are generally more prone to eutrophication because the sunlight will reach the deeper layer, enabling algae in all water levels to do photosynthesis which is in turn increasing the primary production.

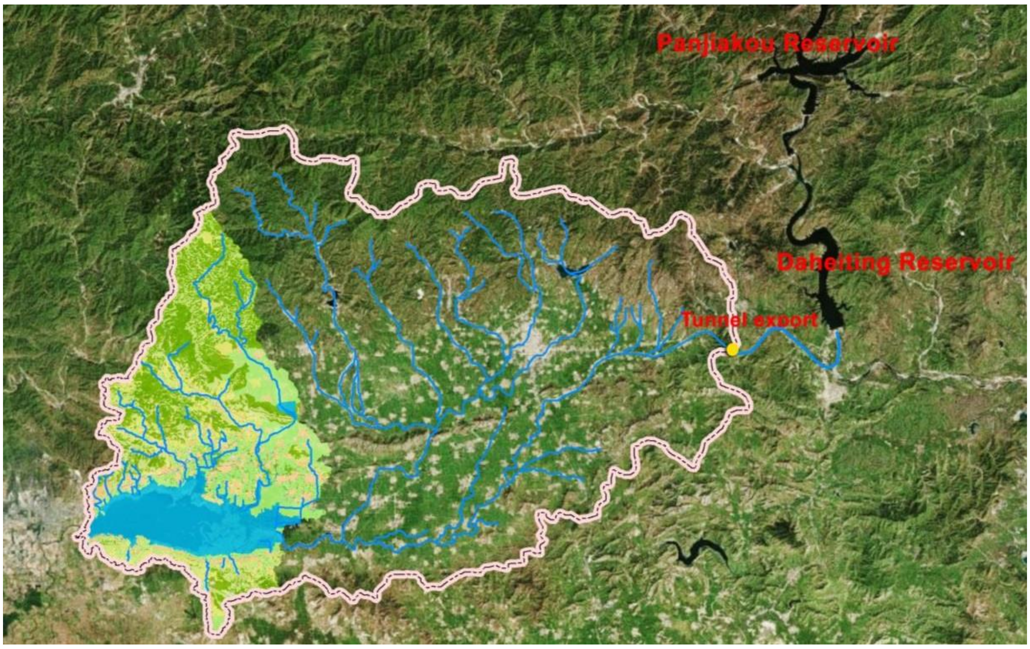


Figure 3 The local and external watershed

The reservoir catchment is divided into two different parts; the internal and external watershed (Figure 3). The external watershed is the source of water coming from the Luan river diversion project. This watershed is outside the boundary line shown on the map (Figure 3), with the channel entrance marked by a yellow dot. The internal watershed is indicated with a boundary line. The major tributaries in the local watershed are the Lin, Sha and Li rivers (Figure 4), but the Lin and Sha rivers are seasonal and are usually dry. The Li River is constant flowing, due to the water input from the external watershed/diversion project.

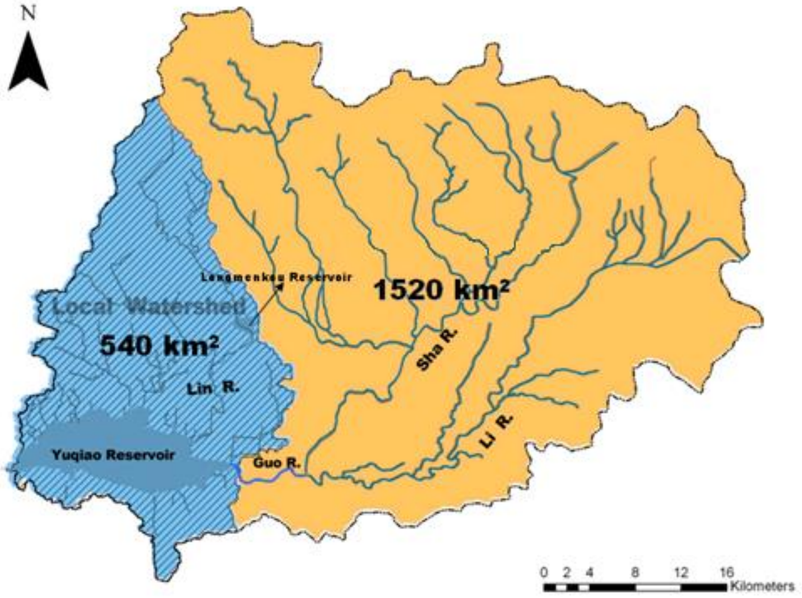


Figure 4 The internal watershed marked with main rivers and the boundary of the local watershed (blue area) (map: modified from Bin Zhou)

Even though the largest part of the internal watershed is not included in the local watershed (area marked with orange in Figure 4), the local watershed is the area of interest in the SinoTropia project. This is due to the fact that around 60% of the total phosphorus (TP) in Yuqiao reservoir stems from the local catchment (Ji County EPB, 2012), while the rest of the total phosphorus (about 40%) stems from the remaining part of the internal watershed. The numbers are based on an average value in the summer months, and are calculated with data from several monitoring sites in the lake.

1.5 Aim of study

The aim of this study is to contribute to a better understanding of the processes governing mobilization of phosphorus fractions from soil to water by studying the physiochemical properties of the soil. Organic matter content, pH, soil texture, mineral composition and phosphorus pools are important parameters governing the mobilization of phosphorus from soil to water. These parameters are therefore central in the assessment of processes leading to phosphorous leaching, and thereby to achieve a better understanding of the key factors influencing phosphorus loading to the reservoir. Hydrology and water flow paths plays an important role in the mobilization of phosphorous through erosion and leaching, and the variation in rainfall intensity is thus also discussed to assess the risk of phosphorus loss from soil. Data from lysimeter sample analysis (soil-water) are compared to the soil composition to get a better understanding of the mobilization processes in the soil. This thesis will also study the spatial variation of phosphorus pools, and how it is related to land-use management. The final results are used for a general comparative analysis between the local watershed and the Vansjø catchment which was studied in the Eutropia project.

2. Theory

2.1 Phosphorus in agricultural soil

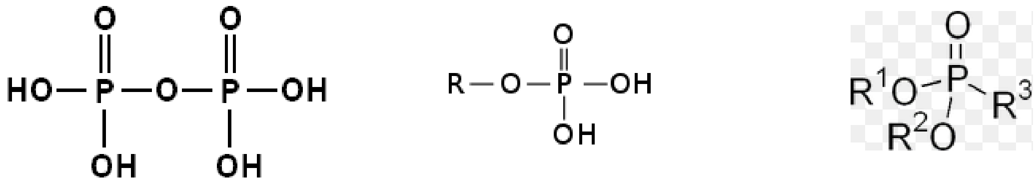
Phosphorus is an essential part of DNA and the energy production in cells (the ATP molecule), and therefore plays an essential role in all living organisms. Phosphorus in the environment is generally found bound to oxygen as orthophosphate, and originally stem from weathering of bedrock. Apatite ($Ca_5(PO_4)_3(F/Cl/OH)$) and Vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) are the most important phosphate minerals, whereof 95 % of the mineralized phosphorus is bound up in Fluorapatite, which is common in most types of rocks (Holtan, Kamp-Nielsen, & Stuanes, 1988). There are three types of bedrock; igneous, sedimentary and metamorphic bedrock. Igneous bedrock is formed from magma or lava, and is mostly made up of silicate. Sedimentary bedrock is made up by sediments that have been exposed to pressure (often from water), and the most common types are limestone, shale and sandstone. Metamorphic bedrock is formed when igneous or sedimentary bedrock is transformed by a change in temperature or pressure, and common types of metamorphic rock are marble, gneiss, slate and schist. The uppermost bedrock in the study area is sedimentary from the pre-Cambrian period (Lu, Lu, Zhao, Wang, & Hao, 2008), as the area has been covered by water for a long period of time.

The gaseous form of phosphorus, phosphine, only exists in extreme anoxic conditions (Dévai, Felfoldy, Wittner, & Plosz, 1988), and is therefore only associated with aerosols in the atmosphere (Schlesinger, 1997; vanLoon & Duffy, 2011).

Phosphorus is closely cycled between soil and biota in natural terrestrial ecosystems (Smil, 2000) as the dissolved bioavailable phosphorus is rapidly assimilated or adsorbed (Tiessen, Ballester, & Salcedo, 2011). This allows little excess phosphorus to be leached from the soil to water. In agricultural ecosystems human input of access phosphorus opens this cycle, making transport processes important. Excess phosphorus will be transported from the soil to the lake, causing eutrophication in phosphorus limited waters (Smil, 2000). The anthropogenic phosphorus sources that causes eutrophication in freshwater lakes is typically divided into two groups; point sources and nonpoint sources. Point sources like municipal waste water or discharge from factories are easy to locate and control, while nonpoint sources are more difficult to locate and control, and usually stems from diffuse urban and agricultural runoff (vanLoon & Duffy, 2011).

Phosphorus in the soil exists in a variety of organic- or inorganic compounds which are either in the solid phase or in dissolved form (Weiss, 1969). The prevailing forms depend on the soil conditions and origin. Plants and microorganisms in the soil assimilate the biologically available form of phosphorus, which is mostly the dissolved inorganic orthophosphate. Phosphorus has the valence state 5+ and the combination with oxygen (and hydrogen) is called orthophosphate. Orthophosphate is defined as the ion PO_4^{3-}, but the term is also commonly used to refer to any hydrated form of the ion (HPO_4^{2-} , $H_2PO_4^-$ or H_3PO_4). The dissolved orthophosphate continuously have to be replenished from the solid phase to sustain the plant growth (Condron, Turner, & Cade-Menun, 2005) and the dissolved inorganic phosphorus fraction is a more bioavailable fraction than the dissolved organic phosphorous fraction (Darch, Blackwell, Hawkins, Haygarth, & Chadwick, 2013). The solid phosphorous pool consists mainly of sorption products with clay or aluminium/iron oxides, or secondary minerals (calcium-, aluminium- or iron phosphates) (Pierzynski, McDowell, & Sims, 2005).

The organic phosphorus are humic compounds that originates from animal and plant remains (both naturally and from organic fertilizers), or can be synthesized by organisms in the soil. The organic phosphorous compounds can be divided into three groups: orthophosphate esters, phosphonates and anhydrides (Figure 5)(Condron et al., 2005). A large proportion of the organic phosphorus in soil are difficult to characterize due to the complex chemical structure (Haygarth & Jarvis, 1999) of humic compounds. The main orthophosphate ester compound in agricultural runoff is the inositol hexaphosphate (an orthophosphate monoester), or phytic acid. This compound is produced in plants and functions as a phosphorous storage. Generally the phytic acid is rather immobile as it absorbs strongly to soils due to its high charge density. According to Magid, Tiessen, and Condron (1996) the inositol hexaphosphate in soils can account for up to 50% of all the organic phosphorus in both natural and agricultural ecosystems, because they are strongly retained, and do not participate easily in the biological cycle. Inositol hexaphosphate is therefore a large contributor to the organic phosphorus pool in the soil (Darch et al., 2013), because organic phosphorus compounds which is not so strongly adsorbed will participate in the biological cycle to a larger extent.



Pyrophosphate (an anhydride)

Orthophosphate monoester

Phosphonates

Figure 5 Structure of anhydrides, orthophosphate esters and phosphonates. The anhydride is exemplified by the pyrophosphate compound.

Due to the strong sorption and the fact that phytic acid can only be made soluble through microbial activity (Sharma, Sayyed, Trivedi, & Gobi, 2013), it is not thought to be readily available for plants, and the transport to the watercourse is mainly associated with particle transport. The phytic acid is therefore less important for eutrophication than other organic phosphorus compounds. On the other hand, application of manure containing high levels of phytic acid (especially from pigs and poultry) can increase the mobility of inorganic orthophosphate in the soil (Condron et al., 2005), because it has a high concentration of strongly sorbing organic phosphorus which may replace sorbed inorganic phosphorus. This may increase the mobility of labile phosphorus and thereby transport to the lake.

2.2 Processes controlling phosphorus in soil and soil-water

The main process governing the mobilization of phosphorus from soil to water is dependent on hydro-biogeochemical factors (Condron et al., 2005; Schlesinger, 1997). Key parameters are therefore soil texture governing hydrology, plant uptake and availability of organic matter governing assimilation and decomposition, and metal oxides along with pH and redox potential governing sorption mechanisms. Soils with a high sorption capacity are usually soils with high clay and organic material content (Gburek et al., 2005; Holtan et al., 1988). The amount of clay in the soil is important due to that clay has a high specific surface area on which P-binding constituents, such as metal oxides, are sorbed (Gburek et al., 2005). At pH above 4.6 the prevailing kaolinite clay minerals have a net negative charge due to isomorphic substitution in the crystal lattice providing a pH independent charge (Section 2.2.1). This causes the clays to strongly adsorb polyvalent cations, such as iron and aluminium, on the surface of the clay particles. These ions are able to constitute a binding bridge to negatively charged phosphate groups due to their polyvalent charge. The clay soils are therefore considered to have a high sorption capacity for phosphate (Holtan et al., 1988). Sorption of phosphorus removes the inorganic phosphorus from the soil water. On the other hand, they constitute a very important factor for the mobilization and transport of phosphorus from soil to water due to the fact that small particles are more easily eroded and transported through overland flow.

When phosphorus is applied to or removed from the soil there will be an imbalance in the equilibrium between soil and water. New equilibrium will commence a process where phosphorus will be sorbed or desorbed dependent on the phosphorus saturation or sorption capacity and the concentration of phosphate in solution. Sorption, precipitation and immobilization remove phosphate from the soil solution. The sorbed or precipitated phosphorus can be released back to the soil water by desorption and dissolution. The assimilated phosphorous is released back to solution through mineralization (Figure 6) (Leader, Dunne, & Reddy, 2008; Pierzynski, McDowell, et al., 2005).

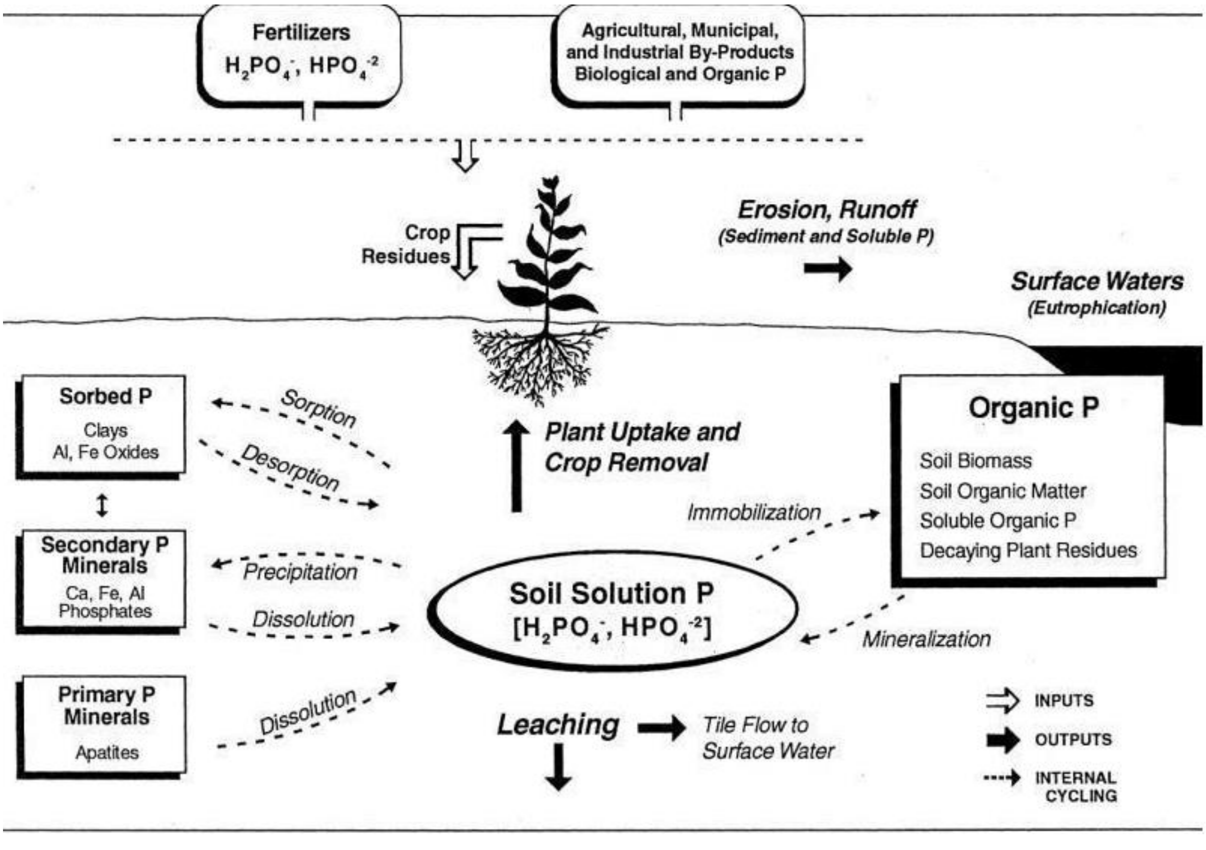


Figure 6 The phosphorus cycle in soil. The figure shows the main mobilization processes in soil as well at the sources and sinks. Retrieved from Pierzynski, McDowell, et al. (2005).

Orthophosphates adsorb to the surface of metal oxides and carbonates by replacing H_2O or OH^- (Pierzynski, McDowell, et al., 2005). The metal oxides form a coating on mainly clay minerals, carbonates and organic material, making sorption possible for these net negatively charged surfaces. Sorption and precipitation processes are dependent on the physical and chemical properties of the soil, and is divided into three different categories: physical sorption, chemisorption and precipitation. Physical sorption can be an anion exchange process. The anion exchange involves electrostatic attraction between phosphate anions and a positively charged surface, which can be pH dependent or permanent (Matocha, 2006). The permanent charge is indifferent to the conditions in the soil, and is due to isomorphic substitution within the crystal lattice (Matocha, 2006). Isomorphic substitution involves a replacement of metal ions in the lattice; the "new" cations with a lower charge create a net negative charge on the mineral, and this is not affected by the surrounding pH (Figure 7).

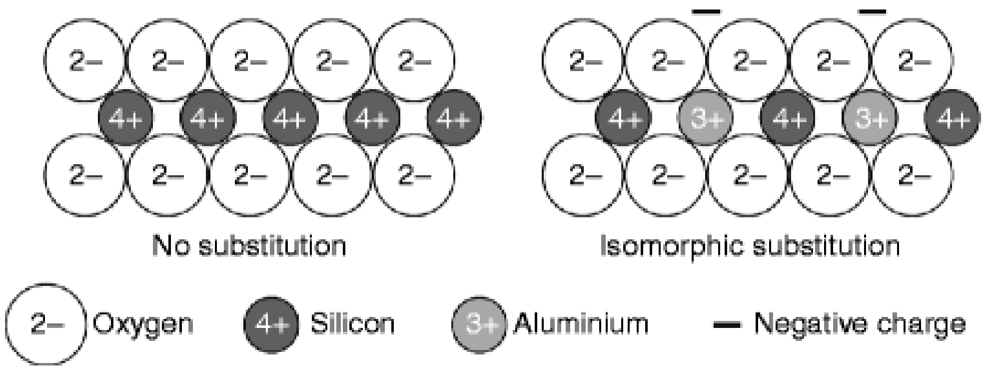


Figure 7 Example of isomorphic substitution in the crystal lattice. Retrieved from Józefaciuk (2011).

The pH dependent charge is due to ion adsorption on the surface (Madrid, Diaz, & Cabrera, 1984), i.e. when the hydroxide groups on the surface of the mineral under acidic conditions has a positive charge, and attracts anions that can undergo ion exchange with phosphate (Figure 8).

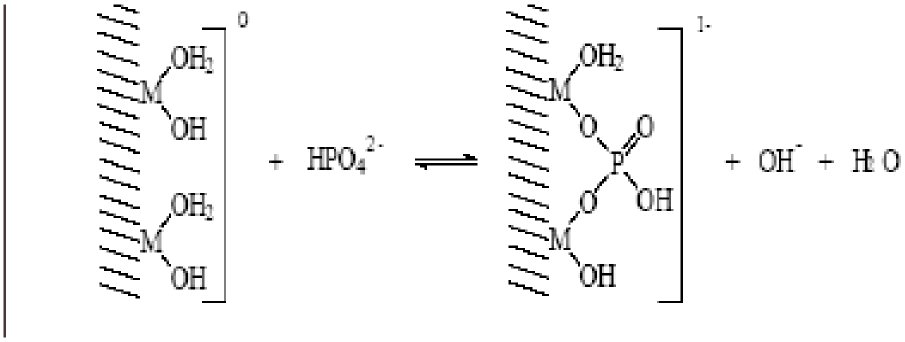


Figure 8 Ion exchange with hydroxide and orthophosphate on a clay surface. Reprinted from Memon (2008)

These ion exchange processes are dependent on the pH, point of zero (PZC) charge (section 2.2.1), and the type of clay mineral (section 2.2.4). Ion exchange reactions are reversible and rapid, and accounts for a small part of the adsorbed phosphorus in soils (Rhue & Harris, 1999).

Chemisorption is a ligand exchange mechanism where phosphate displace a functional group on the surface, and binds directly with the oxide (Manahan, 2005). The most reactive surfaces are iron and aluminium oxyhydroxides followed by the edges of silicate minerals (Rhue & Harris, 1999), while carbonates are according to Rhue and Harris (1999) not very important for the sorption capacity, even when they are coated with iron oxides. Precipitation is when the orthophosphate combine with commonly occurring metal cations such as iron, aluminium and calcium (Rhue & Harris, 1999). The solubility of phosphorus is greatest between pH 4.5 and 7, and the dominant species are then $H_2PO_4^-$ (Figure 9). When the pH is below the range of greatest solubility the concentration of labile aluminium and iron is commonly so high that the solutions are usually saturated in respect to the solubility product of their phosphate salt ($AlPO_4$ and $FePO_4$). Likewise, when the pH is above 7 the concentration of calcium is generally so high that the solubility product of $Ca_3(PO4)_2$ is reached (vanLoon & Duffy, 2011).

If sorption products do not undergo dissolution, they will eventually age into secondary minerals (precipitation products). Immobilization is the process where inorganic phosphorus is converted to organic phosphorus by plant uptake, and mineralization is when organic phosphorus is converted to the inorganic phosphate. This process is rapid, and will sustain plant growth.

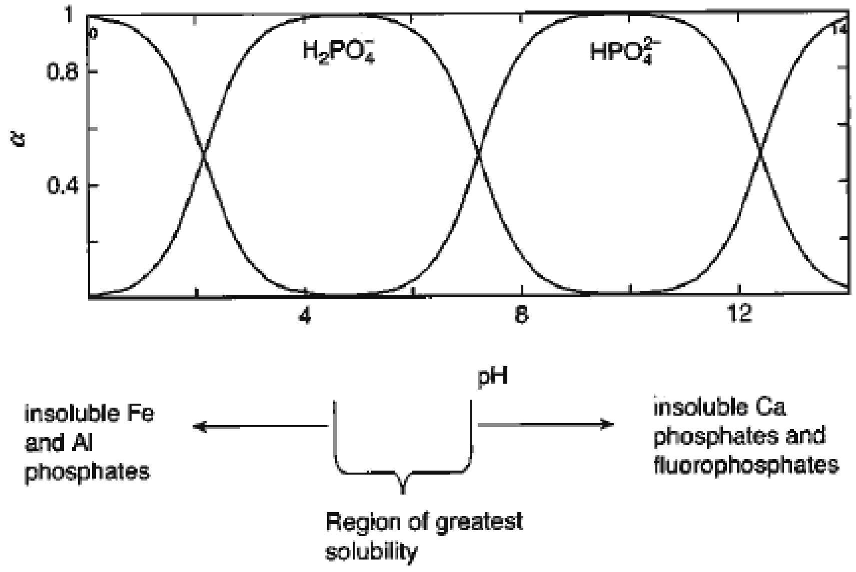


Figure 9 Phosphate speciation in an aqueous solution and factors controlling the solubility. Retrieved from vanLoon and Duffy (2011).

2.2.1 Point of zero charge and pH

The solubility of phosphorus is greatest between pH 4.5 and 7, and the dominant species are then $H_2PO_4^-$ (Figure 9). When the pH is outside the range of greatest solubility, phosphorus will form insoluble precipitates with available iron/aluminium and calcium/fluoride respectively (vanLoon & Duffy, 2011). At low pH aluminium iron becomes soluble, and the concentration of these cations in soil solution increases. If there are large enough amounts of orthophosphate in the solution, the soil water may become supersaturated with regards to the solubility product of $AlPO_4$ and $FePO_4$, and precipitate phosphate out of the solution. At pH above the region of greatest solubility calcium carbonate becomes soluble, and form $Ca_3(PO4)_2$ precipitates with phosphate.

Clay, primary minerals and organic matter are important for the sorption capacity, but they have a negatively charged surface. Metal oxides (such as iron and aluminium) are making sorption possible by constructing a coating on the soil particles. Iron and aluminium oxides are positively charged at the pH range found in soil, due to the high pH value at the Point of Zero Charge. PZC denotes the pH value where the sum of positively charged sites is equal to the negatively charged sites on the mineral surface. When the pH is above PZC the surface is negatively charged due to deprotonation of the surface, and when pH is below PZC the surface becomes positive due to protonation.

- At $pH > pH_{pzc}$
  $(\text{I-O-I})^- + \{\text{-X-O}^-_s\} > \{\text{-X-OH}_2{}^+_s\} \rightarrow \text{net} - \text{charge}$
- At pH_{pzc}:
  $(\text{I-O-I})^- + \{\text{-X-O}^-_s\} = \{\text{-X-OH}_2{}^+_s\} \rightarrow \text{no net charge}$
- At $pH < pH_{pzc}$
  $(\text{I-O-I})^- + \{\text{-X-O}^-_s\} < \{\text{-X-OH}_2{}^+_s\} \rightarrow \text{net} + \text{charge}$

Where (I-O-I) is 1:2 clay lattice structure, -X-O^-_s is the deprotonated oxide on the mineral surface, and $\text{-X-OH}_2{}^+_s$ is the protonated oxide on the mineral surface.

Table 2 PZC of common clays and metal oxides (Appelo & Postma, 2010) and charge at soil pH (around 6).

Clay/metal oxide	pH_{PZC}	Net charge
Feldspar	2,2	-
Smectite **Montmorillonite**	2,5	-
Quartz	2,9	-
Kaolinite	4,6	-
Gibbsite (α-$Al(OH)_3$)	5,0	-
Halloysite	7,1	+
Goethite (α-FeOOH)	7,8	+
γ-Al_2O_3	8,5	+
Vermiculite	8,6	+
Illite	8,8	+
Iron oxides	8,5 – 9,3	+
α-Al_2O_3	9,1	+
Calcite	9.5	+

This means that at the pH range that is commonly found in soils (between pH 4 to 8) the metal oxides have a positive charge, and phosphate can undergo anion exchange with sorbed anions on the surface (Manahan, 2005). At high pH metal oxides on the surface of soil particles is negatively charged, making anion exchange impossible. The phosphate anions may then instead displace the hydroxide and bond directly to the oxide surface (Kudeyarova, 2010; Manahan, 2005).

2.2.2 Effect of redox potential

Under most conditions in the environment phosphate reactions do not involve electron transfer, and the redox potential therefore does not directly affect orthophosphate speciation (Reddy & DeLaune, 2008). Reducing conditions in the soil occurs when the soil is flooded with water, and O_2 is depleted due to oxygen respiration and slow diffusion of O_2 between air and water (O_2 is not replenished). When the redox potential decreases, phosphate sorption decreases due to a change in the iron speciation in soil (Baldwin, Mitchell, & Olley, 2002). Under normal conditions iron has the oxidation state Fe^{3+}, and is able to sorb phosphate ($FePO_4$). When iron is reduced to Fe^{2+} the iron can undergo to processes: phosphate is released and Fe^{2+} recombine with sulphide (S^{2-}) to FeS, or iron and phosphate forms an insoluble complex e.g. vivianite - $Fe_3(PO_4)_2$ (Roden & Edmonds, 1997).

2.2.3 Soil texture and organic matter

Soil texture is an important parameter for sorption of phosphorus. Soil consisting of small sized particles have a higher sorption capacity due to a larger surface area (Holtan et al., 1988). As previously discussed in Section 2.2, the clay minerals are dependent on metal oxides to be able to sorb phosphorus, and He et al. (2009) showed in a study of suspended particles in an estuary and how the phosphate cations and particle size varied. They found that there was a correlation between amount of metal oxides and decreasing particle size (increasing surface area) and adsorbed phosphorus, implying that the particle size and the negatively correlated surface area are important for the sorption capacity. On the other hand, clay sized particles are usually aggregated together in the soil reducing the transport because they form heavier aggregates that are not as easily transported (see Section 2.3).

Mineral particles are divided into three categories according to diameter: clay (< 0.002 mm), silt (0.002 – 0.063 mm) and sand (0.063 – 2.00 mm) (ISO11277, 2009) according to Friedman and Sanders (1978) classification system. Soil texture is classified using the soil texture triangle (Figure 10).

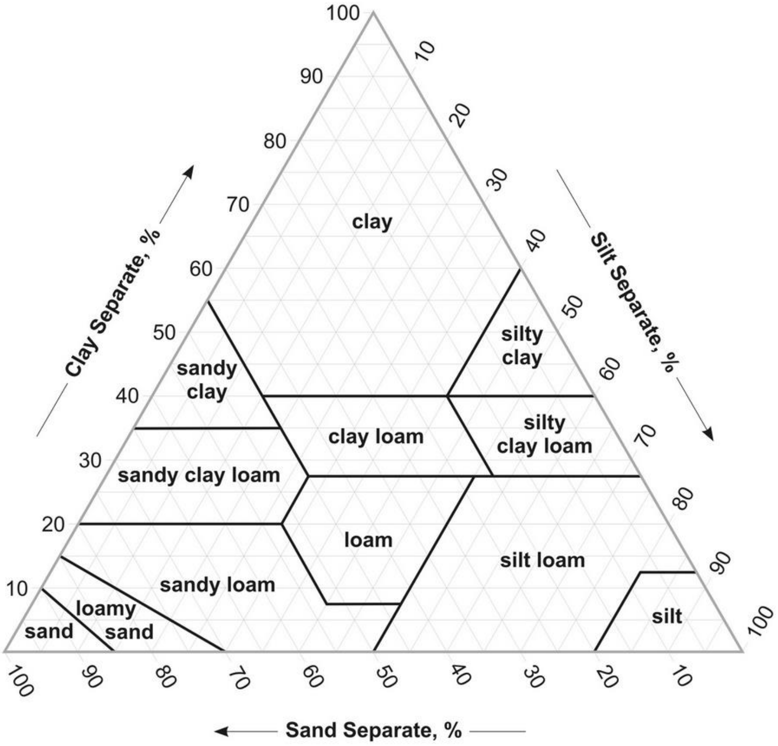


Figure 10 The soil texture classification triangle. Figure retrieved from USDA ((n.d)).

Organic matter is acting in the same way as clay minerals. They are negatively charged, and are dependent on metal oxides to sorb phosphate to the surface. But, unlike clay, they consist of a dissolved organic anion fraction which can compete with phosphate for positively charged sorption sites in the soil, and thereby decreasing the sorption of phosphate (Stuanes, 1982). Soil organic matter in mineral soils (i.e. containing metal oxides) is therefore thought to contribute to the sorption of phosphate but may also have a contradictory effect due to their production of dissolved organic fraction, making the clay sized particles more important for the soils sorption capacity.

2.2.4 Clay minerals

Clay minerals are important for the sorption capacity and the hydrological flow in soil. The clay minerals are common weathering products, and can be divided into two groups based on their structure which is built up by tetrahedral silicate sheets and octahedral hydroxide sheets in a 1:1 or 2:1 ratio.

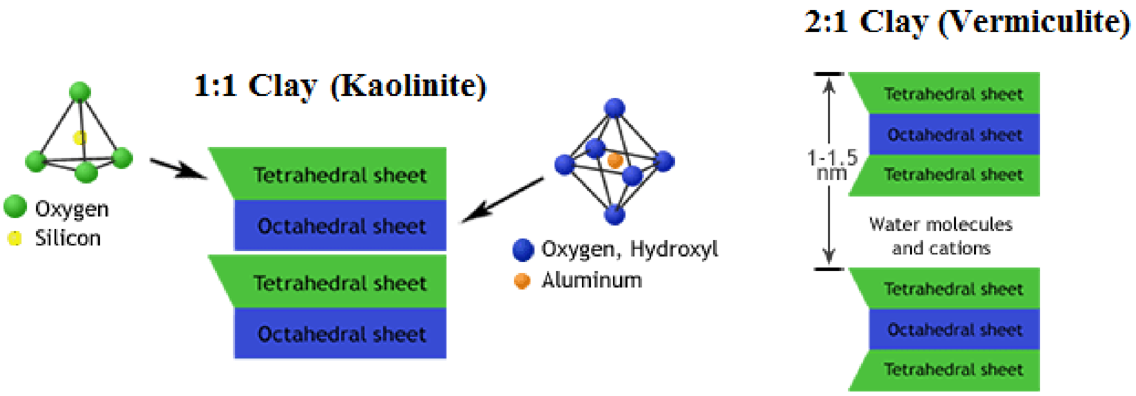


Figure 11 Clay structure, here represented by Kaolinite (1:1) and Vermiculite (2:1). Illustration modified from Missouri Soil Survey (2014)

1:1 types of clay are the different types of Kaolinite (i.e. Kaolinite, Dickite and Halloysite). Kaolinites are non-expanding due to tightly packed sheets (see Figure 11) which means that they will not shrink and swell and make it possible for water to percolate through the surface. Soils with large amounts of kaolin clays are relatively impermeable, making overland flow dominant.

2:1 types of clays are Illites, Smectites (Montmorillonite), Vermiculites and Chlorites. They have a large space in the interlayers with room for water and ions (Figure 11). They shrink and swell, and are more permeable than the Kaolinite group. The 2:1 clays have different sized spacing between the sheets, making them differ somewhat in expansion capacity; Illite (and Chlorite) does not expand due to a very small or no gap between the sheets, Vermiculite (Figure 11) is moderately expansive, while Smectite is highly expansive.

Cation exchange capacity (CEC) of soils is conventionally given as cmol/kg, and expresses the soils ability to adsorb and exchange cations. A soil with high CEC can hold more nutrients compared to soils with low CEC. This also accounts for the negative charged phosphate because it means that the negatively charged clay can become positive through isomorphic substitution – making anion exchange possible on the surface of the mineral (see section 2.2 and 2.2.1). The clay minerals have a wide range of cation exchange capacities, which it is dependent on mineral structure, structural substitutions and the specific surface of the mineral that is accessible to water (Carroll, 1959). The CEC of some clay minerals is given in Table 3, together with quartz (a common sand-sized silicate mineral) and organic matter for comparison. As you can see, the 2:1 clays with large space between the sheets (Smectite and Vermiculite), has the highest CEC, followed by Illite and Chlorite and then the 1:1 type of clays. Organic matter is considered to have a high CEC, which is in the same range as for vermiculite and Smectite.

Table 3 The cation exchange capacities of some clay minerals, quartz and organic matter (Appelo & Postma, 2010; vanLoon & Duffy, 2011)

Mineral	CEC (cmol/kg)
Kaolinite	3-15
Halloysite	4-10
Smectite (Montmorillonite)	80-150
Vermiculite	100-200
Illite	20-50
Chlorite	10 – 40
Quartz	1 – 2
Organic matter	150 – 500

2.3 Water flow paths and transport from soil to water

The transfer of phosphorus from soil to water involves two processes: mobilization and transport (Gburek et al., 2005). Mobilisation denotes both dissolution and physical detachment, while transport is defined as the movement of phosphorus by convective transport of flowing water (hydrological transport).

Hydrological transport includes both overland and subsurface flow (Gburek et al., 2005), and includes the transport of phosphorous bound to particles and dissolved phosphorus species. The main flux of phosphorus in the natural global phosphorus cycle is by rivers and streams (Schlesinger, 1997), and phosphorus bound to particles constitute the major fraction of total phosphorus in surface runoff (Gburek et al., 2005). (Runoff is a general hydrological term used to describe the movement of water from land above and below the ground.) This is probably due to the fact that the major part of phosphorus in soil is particle bound, and because the transport of dissolved phosphorus is minimal compared to the particulate fraction.

Under the soil surface the water flows horizontally and vertically. Horizontal movement under the surface transports dissolved phosphorus species to the surface water and/or groundwater. The vertical movement of water through soil layers can be divided into matrix flow and preferential flow; the first denotes the water flow through porous soils, while the second is water movement through larger pores made from wormholes or cracks (Gburek et al., 2005). Water movement through soil is mainly by preferential flow through macro- and micro pores, rather than matrix flow. Soil texture is an important parameter for the porosity and cracking of the soil. Sandy soils are porous, and allow water to flow through the horizons by matrix flow. Porous soils can be saturated with water, and the phosphorus in the soil solution may be retarded during transport downwards through the soil horizons (Haygarth & Jarvis, 1999). Soil aggregates increase the amounts of cracks and fissures generating macro pores. Clay soils are compact and do not allow matrix flow, but they easily crack during dry periods (i.e. Smectite, Montmorillonite and Vermiculite), allowing preferential flow (Haygarth & Jarvis, 1999). Some clay minerals do not crack (i.e. Kaolinite and Illite), denying water flow through the soil layers.

Surface runoff, or overland flow, is a downslope movement happening due to input of water to soils which only allows slow percolation rate, or to soils already saturated with water. Incidental overland flow happens after heavy rain or snowmelt, and is considered to be the main phosphorus pathway from soil to water (Pärn, Pinay, & Mander, 2012). In section 2.2.3

it is stated that small particles can sorb more phosphorus than large particles due to the larger surface area. In terms of surface runoff, the small silt and clay size particles are also more prone to be eroded from the soil to water and transported with the water because they remain suspended longer in the water than the larger sand particles, making them very important for the flux of phosphorous to surface waters. Clay is the smallest sized particles, but because of their tendency to aggregate and thereby erode less easily, silt particles may become more easily transported with water than clay (Bissonnais, 1998). The hydrological flow rate is important for overland phosphorus transport because when the water has a high flow rate, heavier particles can be transported, and all the particles are transported for a longer distance before they are suspended (He et al., 2009). This means that storm flows contribute more to the phosphorous flux than slow flowing water, because it is delivering more particle bound phosphorus to the water. Overland flow carries more phosphorus to the water also due to the fact that it is not draining through soil layers with higher sorption capacity, and that the surface horizons in agricultural soil contains more phosphorus in the top layer.

In agricultural areas the land-use practice is affecting the flux of phosphorus to the water. Soils that are tilled have a higher particle loss than non-tilled fields, especially if the soils are tilled a long time before sowing so that it is exposed for erosion for a longer period, e.g. over winter. Tilling of the soil makes the soil more loosely attached because of the disturbance and lack of vegetation that covers the soil, and the loss of particulate phosphorus will increases due to more erosion (Haygarth & Jarvis, 1999). On the other hand, tilling of the soil incorporates the phosphorus into the soil, making the concentration of phosphorus lower in the top layer compared to the non-tilled soils, which means that in the non-tilled soils incidental transfer of phosphorus is a concern in the first days after application, because the phosphorus in the fertilizers has not yet been translocated into the soil (Haygarth & Jarvis, 1999; Verbree, Duiker, & Kleinman, 2010; Withers, Nash, & Laboski, 2005).

3. Materials and methods

3.1 Site description

The site description is divided into five parts, according to the DPSIR framework used by the European Environment Agency; Drivers, Pressures, State, Impact and Responses. Drivers, through production and consumption, exert pressure on the environment. Pressures describe the release of substances, use of resources and use of land, and the pressures exerted by the society manifest themselves into changes in the environmental conditions. The state gives a description of the physiochemical state in a defined area, and impacts describe how the changes affects the social and economic functions on the environment such as health conditions, resources availability and biodiversity. Responses describes the societal responses to the changes in the environment (Smeets & Weterings, 1999).

3.1.1 Drivers

There are between 120 000 – 140 000 people living in the 152 villages distributed in the watershed. The locations of the villages can be seen in Figure 12, and as shown in the figure the villages are mostly located around the reservoir, and some in the mountain areas north of the Yuqiao reservoir. The main source of income for the residents comes through agriculture, aquaculture, fishing, and small businesses' like restaurants, hotels, industry etc. (Ji County Bureau of Statistics, 2012). As the majority of the people in the area are living of farming and husbandry, the use of inorganic fertilizers and discarding of livestock manure are extensive according to Ji County EPB (2012) This suggests that the enrichment of nutrients in the reservoir is strongly influenced by the agricultural activities.

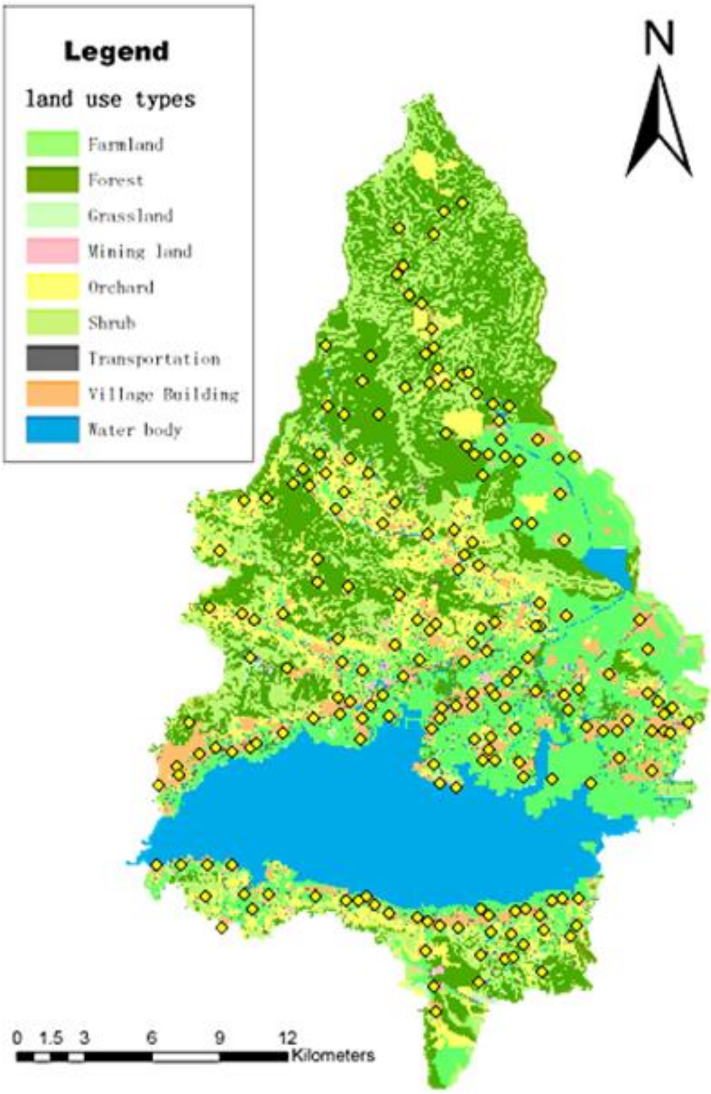


Figure 12 Distribution of land-use practice and villages. The village locations are marked with a yellow diamonds. (Map: courtesy of PhD candidate Bin Zhou)

The different land-use practises are shown in Figure 12. The watershed covers a total area of 540 km^2. In this thesis the agricultural activities are divided into for main groups: farmland, forest, orchard and vegetable. The forest areas are not agricultural areas but are included because it covers a large area in the local watershed. Farmland, forest and orchards covers around 108 km^2, 138 km^2 and 61 km^2, respectively. The vegetable fields are mostly managed as private gardens, and their crops are usually grown for personal consumption, but there are also some large vegetable and grain fields. These two vegetable farming practices differ in the use of fertilizers: In the private gardens they generally apply no chemical fertilizers because it is thought not to be healthy (Zhou, 2012), while in the fields there is an extensive use of manure and chemical fertilizers to a large extent (around 3~5 times compared to farmlands with crop rotation between maize and wheat). The farmland management practice in the fields focus mainly on crop rotation between winter wheat and summer maize. In the vegetable gardens they grow vegetables such as tomato cucumber and Chinese nut. The orchards are used to grow different kinds of fruits such as apples, persimmon, pear, chestnuts and walnuts. In the orchards they use mainly manure and not inorganic fertilizers, and the farmer usually put the manure in pits around the tree. Forests are divided in two; natural forest is located in the north, while the forests situated in the lowland areas are used for commercial purposes like lumbering. Table 4 provides an example of when the fertilizers are applied on the fields for the different land management practices. This information is obtained through preliminary field interviews conducted by PhD candidate Bin Zhou (Pers. Comm. and Zhou (2012))

Table 4 Example of common land management practice and fertilizer application. The information is gathered through a field survey in Dajugezhuang village. Table modified from Zhou (2012)

Planting Pattern		**Sowing Time**	**Time for top addressing**	**Harvest time**	**Fertilizer application**		**TP (g/ m^2)**
					Basic fertilizer	**Top addressing**	**TP**
Farmland	Corn	Beginning of July	Middle of August	Beginning of October	Fertilizer: 45-75 g/m^2	Urea：30 g/ m^2	2
					High efficient fertilizer（non top addressing）：60-75 g/ m^2		2.7
	Wheat	Middle of October	Beginning of December	Middle of June	Fertilizer: 30-75 g/m^2	Ammonium Hydrogen Carbonate:75-150 g/ m^2	1.9
Vegetation	Tomato	Tomato: Plant in March and harvest in middle June. Cucumber: plant in July and harvest in the beginning of October			Chicken manure 6 kg/m^2	$(NH_4)_2HPO_4$ 100 g/ m^2	50.2
	Cucumber				Chicken manure 5 kg/ m^2	$(NH_4)_2HPO_4$ 90 g/ m^2	46.3
Orchard	Apple	Applies fertilizer in the end of February			Cow manure 8 kg/ m^2	-	9.6
	Persimmon	Applies fertilizer in the middle of January			Cow manure 7.5 kg/ m^2	-	8.8

The farmers in the area are also holding animal husbandry, and the manure produced by the animals are normally discarded on waste land or used as fertilizers. In 2012 it was reported that there are around 106 000 pigs, 6 000 cattle, 16 000 sheep and 805 000 poultry in the area (Ji County EPB, 2012).

When the Yuqiao reservoir was constructed in the 1950s and expanded in the 1980s many farmers were relocated to higher areas in the watershed. Because of the loss of land, some of these farmers started aquaculture or fishing instead. There are two different aquaculture practises in the area; constructed fish ponds along the shore of the reservoir and fish tanks. Fish tanks were banned, due to the large release of nutrients to the reservoir. While many fish ponds are still in use, although they also were banned in 2013. According to the Ji County EPB (2012) only ca. 4% of the total phosphorus loading to the reservoir stems from fish farming, and since the focus of this thesis is phosphorus in soil and its mobilization and transportation the fishing practises will not be discussed any further.

3.1.2 Pressures

The contribution of phosphorus from the soil to the lake is dependent on several factors. There is no general control of the animal manure in the area. Some is used for fertilizing, while in other cases it is deposited in piles on wasteland. What is clear is that the extensive agricultural management and husbandry contributes substantially to the phosphorous loading in the runoff. Crop rotation is reducing the excess nutrient in the soils top layer by incorporating it evenly through the plough layer and thus decreasing the amount of nutrients in the surface runoff, while tilling is increasing erosion because it makes the soil loosely attached. The livestock mentioned in section 3.1.1 produced about ~372 tonnes of phosphorus in 2012 through manure (Tianjin Ji County Statistical Bureau, 2010). The average load of phosphorus from animal manure to agricultural area in one year is thus 15 g P/m^2 , and in addition they applied 30 kg/m^2 year of inorganic fertilizers (Tianjin Ji County Statistical Bureau, 2010). The farmers in the area use different kinds of fertilisers, but a common one is the 18 - 18 - 18 of N - P_2O_5 - K_2O, so this will be used as an example. In 30 g fertiliser/m^2, P_2O_5 accounts for ~ 5.5 g/m^2 and of this 2.4 g /m^2 are phosphorus. In total the farmers adds 17.4 g P/m^2 to the soil every year. In comparison, Bioforsk Jord & miljø (2013) states through their report from the monitoring programme JOVA (Monitoring of soil and water in agricultural land) that the phosphorus loading from manure and inorganic fertilizers is on average 1.9 g P/m^2 in Norway.

Sewage and waste from human households are dealt with in various ways. The sewage system is not very well developed in the area, and there is little or no waste water treatment. Some people are still using human manure for fertilizing. All households have containers in the ground where they collect the sewage. These containers are usually emptied every other year depending on the size, and discarded into fish ponds, fields, wasteland or directly into the rivers due to lack of treatment facilities. It is therefore reason to assume that a lot of the human waste ends up in the reservoir. The household garbage is usually collected by the county government (Zhou, 2012), but the waste is stored outside in piles before collection (Figure 13). The Tianjin Ji County Statistical Bureau (2010) reported that the sewage and garbage contributes with ~1 g P/m^2 to the area every year. This amount is small compared to the contribution by manure, and is therefore not included in the discussion.

Figure 13 Example of garbage storage in study area (photo: Ellen Pettersen)

3.1.3 State

The region has a sub humid continental monsoon climate, with an annual mean temperature of 14 °C, and an average annual precipitation of 653 mm. The rainy season is between July and September, and accounts for about 60 % of the precipitation. The topography of the area is shown in the digital elevation model map in Figure 15. The northern part is characterized by mountains and steep hills, while the central and north eastern part close to the shoreline is a flat low land of deltaic alluvial sediments. The rest of the area (marked with grey in the map) has a hilly morphology. Calcaric and eutric cambisol covers most of the study area (Figure 14). On the hills and mountains the soils are developed through weathering of the parent sedimentary bedrock consisting of sandstone and limestone. The soil texture is considered to be sandier in the mountain areas and finer grained soils are located near the reservoir in the lowlands (Wang, 1982).

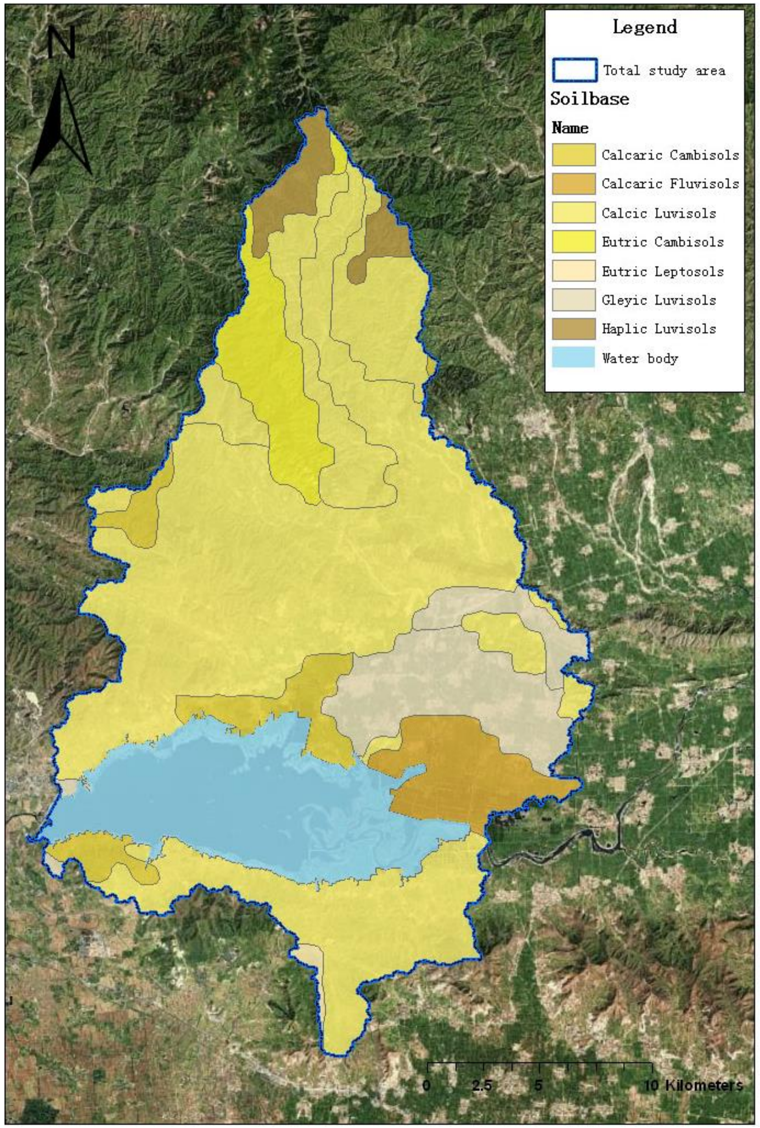


Figure 14 Soil type in the study area (Map: courtesy of PhD candidate Bin Zhou)

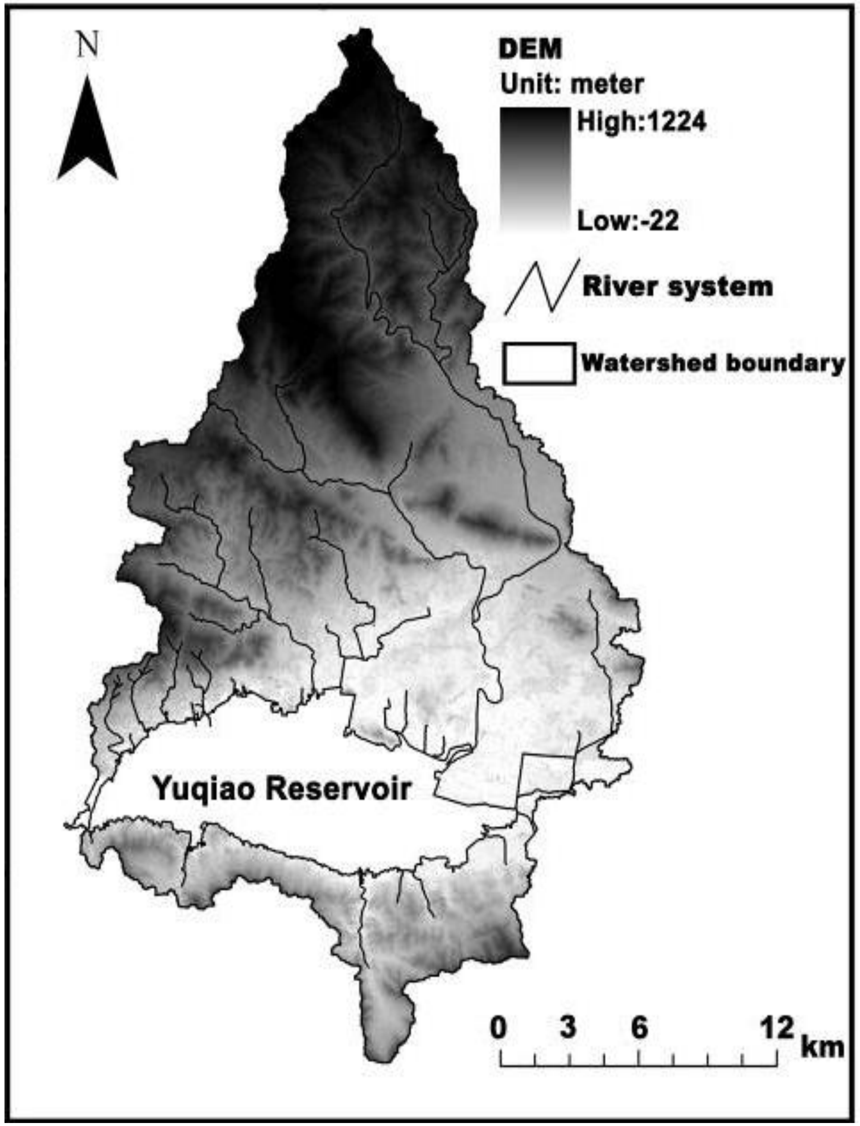


Figure 15 Digital elevation model showing the topography in the local watershed (map: courtesy of PhD candidate Bin Zhou)

In the study conducted by Joshi (2014) for his master degree it is shown that the phosphorus pools in the soil are largest for the vegetable fields with an average total phosphorus concentration of 640 mg P/kg soil, followed by orchard and farmlands with averages of 600 mg P/kg soil and 570 mg P/kg soil, respectively. The forest area had an average value of total phosphorus concentration around 400 mg P/kg soil. Furthermore, he found that the inorganic phosphorus fraction is the main phosphorus pool in the local watershed, and that the area of highest loss risk of phosphorus was around the shore and in the central-east part of the catchment due to the proximity to the lake and land management practice in the area.

3.1.4 Impacts

The loading of phosphorus to the agricultural areas affect the natural processes in the soil, and the balance between sorption and desorption governs the equilibrium of phosphorus between soil and soil-water (Reddy & DeLaune, 2008). The soil in the local watershed have been studied and described by (Joshi, 2014). He found that the average soil pH lies between 7 and 8 for all the different land-use practices, which is the area where phosphate precipitates with Ca^{2+} (see section 2.2.1). The organic matter content is generally between only 5-10%, and the degree of phosphorus saturation indicates that the soils have few available sites for phosphorus sorption (Joshi, 2014). The large application of fertilizers and manure, combined with the poor ability of the soils to adsorb phosphorous, augmented by the flash floods during the wet season, is believed to be the main cause for the large flux of nutrients to the reservoir.

3.1.5 Responses

As mentioned in Section 0 the Yuqiao reservoir shows an increasing trend of eutrophication, presumably due to the agricultural activities in the area (Ji County EPB, 2012). The total phosphorus content in the lake (calculated as the average between different monitoring sites in the reservoir) increased from 2002 to 2012, and has on several occasions exceeded the total phosphorus boundary value for poor ecological status (Figure 16) (Vannportalen, 2009).

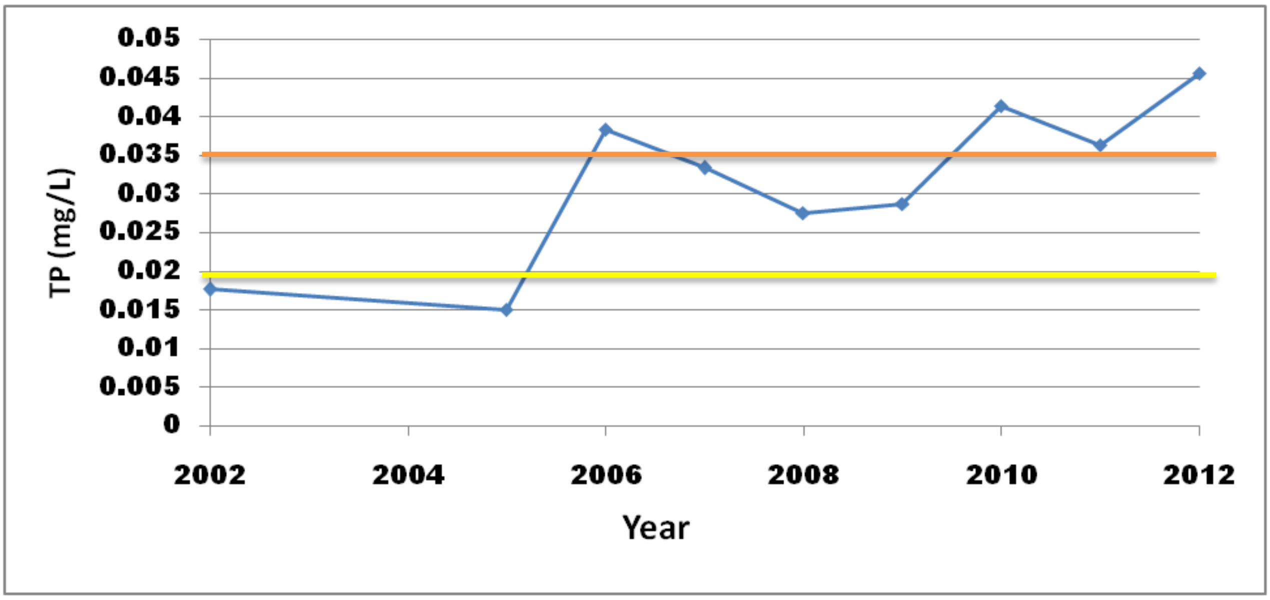


Figure 16 Average total phosphorus concentration in the lake (blue line) (Ji County EPB, 2012), and total phosphorus boundary for poor/moderate (orange) and moderate /good (yellow) ecological status set by the European commission (Vannportalen, 2009).

Figure 17 Duckweed and ducks in a water basin connected to the YuQiao reservoir (photo: Ellen Pettersen)

A few abatement actions have been implemented in order to reduce the flux of nutrients to the lake. In sometimes a 15 cm high berm is constructed around the area around newly sown crop, such as winter wheat to keep the water in the field, and thus preventing runoff. A terraced farmland around the south shore is constructed to limit runoff/erosion (Figure 19). There are not many erosion channels but the ones that are constructed lead to the low land areas around the reservoir, and there are in some areas constructed flood dams (Figure 18).

Figure 18 Flood dam in the low land area in the south shore of the reservoir (photo: Ellen Pettersen).

The central eastern part is a low land area (Figure 15) and is annually flooded during the raining season. The reservoir elevates a few meters during the rainy season, and manure and fertilizers applied to these fields may therefore be flushed out and be directly introduced to the reservoir.

Figure 19 Terraced farmland in the south shore constructed to reduce runoff and erosion. (Photo: Dr. Xueqiang Lu).

3.2 Sampling

The overall soil sampling strategy was to cover the span in presumably important explanatory variables for the spatial distribution of phosphorous pools in the local watershed. A good geographical distribution of the sampling sites throughout the local watershed was also important in order to map the spatial variation in soil phosphorous pools. Master student Bishnu P. Joshi and PhD candidate Bin Zhou collected 109 samples from 78 sites (no SS001 to SS078) during the summer of 2012. In 31 of the sample sites soil from both A and B horizon was collected (in total 62 samples). The results from these samples are described and discussed in Joshi (2014). This study reviled that more focus, and thus more samples, were needed on specific land-use practice and topography as well as from different soil horizons. The main sampling strategy in this study was therefore aimed at improving the representation of the whole watershed by filling the blank spaces and knowledge gaps that had been disclosed by the study of Joshi (2014) (see Figure 20 & Figure 21). 11 samples from 11 sites (number SS079 to SS089) were collected during the winter period (07.01.2013 – 14.01.2013), while 110 samples from 75 sample sites (SS090 to SS164) were collected during the summer (22.06.2013 – 30.06.2013). All of the 230 samples were collected in plastic bags and marked with serial number. The locations were recorded using a GPS tracker.

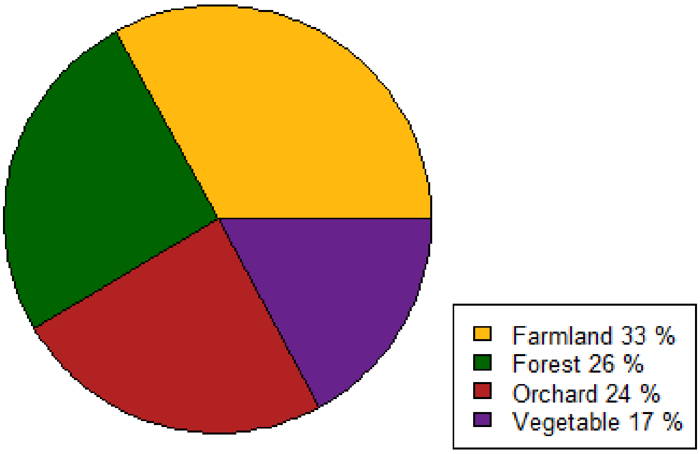


Figure 20 Sample site distribution between different land-use. In total there are 230 samples from 164 sites.

At 14 sample sites the samples were collected from several generic horizons; A, B and C. The A_p horizon is only collected in the agricultural fields and is from the plough layer (typically between 0-20 cm). The B horizon is the alluvial horizon (20 to 30 cm). The C horizon (from 30 cm and down) is only collected from the low land area and is from an apparent compact clay layer. The sampling was performed by thoroughly mixing a composite sample of 5 sub-samples from a representative area of about $1m^2$ at each site.

After collecting the samples in plastic bags, they were marked with a serial number on the form "SS001". SS stands for Sinotropia Soil while the following number is specific for each sample site. Samples collected below the A horizon were marked with a "B" or "C" following their generic sequence. The samples were also given a corresponding UiO number (i.e. U001), which was specific for each sample. This meant that samples from the same site, but from different horizons received an individual number and was not marked with "A", "B" or "C" (see Appendix A for more details).

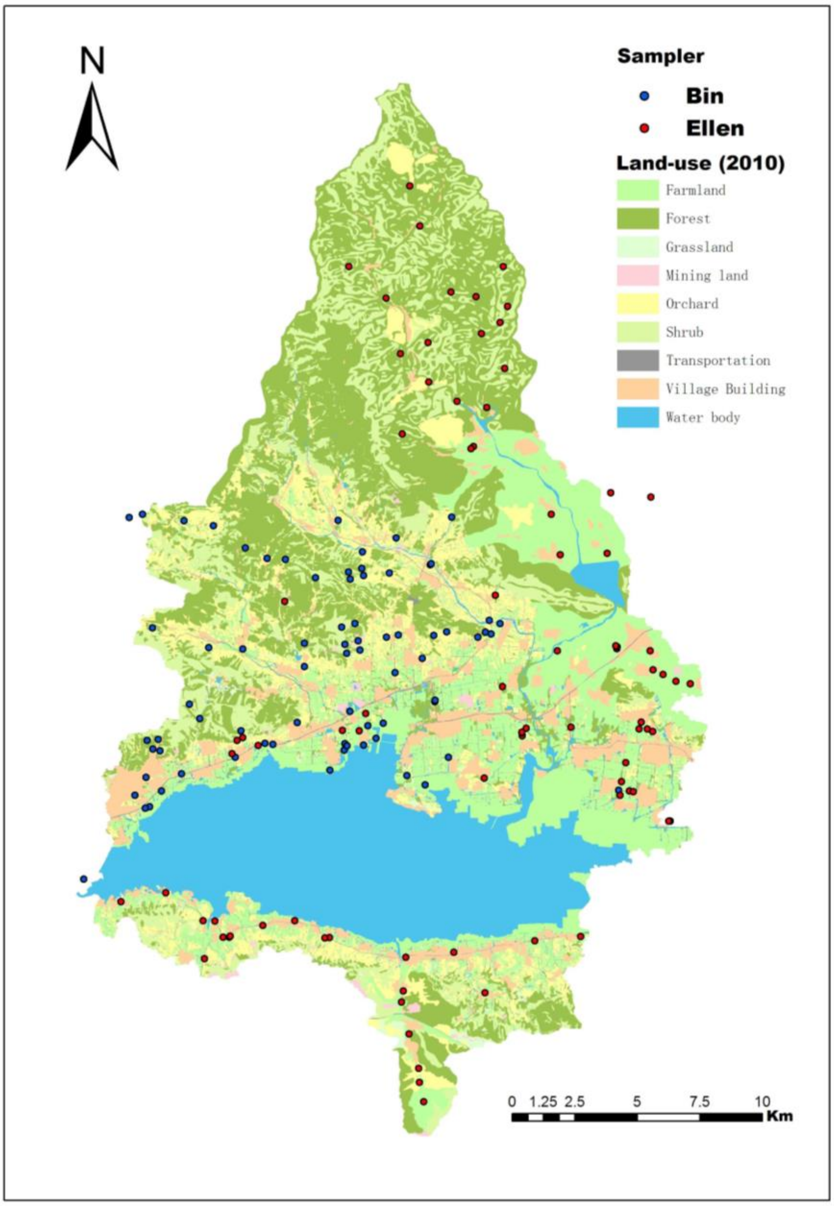


Figure 21 Spatial distribution of all sample sites. Samples (Joshi, 2014) are marked with a blue dot, while samples added in this study is marked with red. The land-use practice is shown with different colours which are explained by the legend. (map: PhD candidate Bin Zhou)

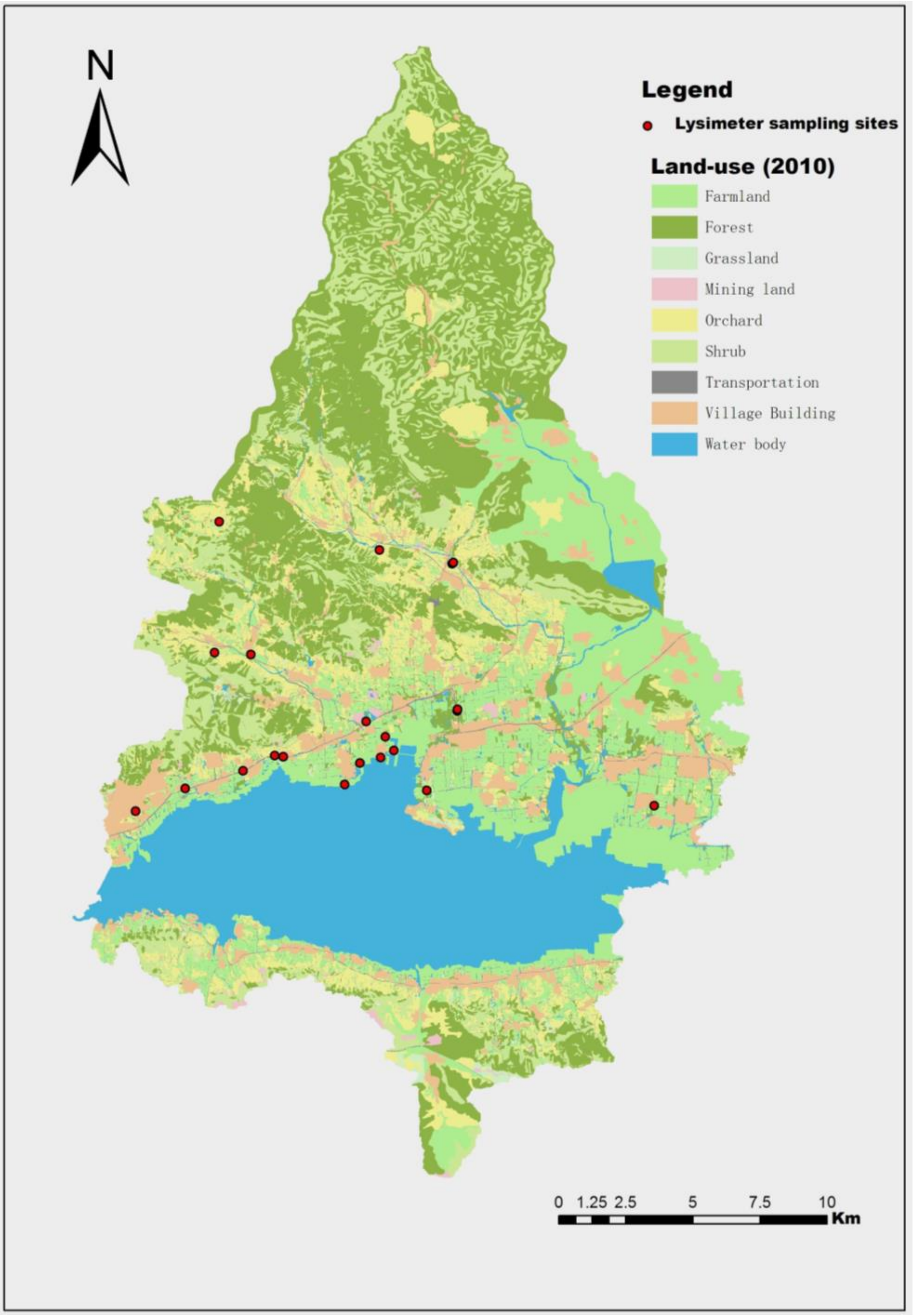


Figure 22 Map showing the distribution of the soil - water sampling sites. The lysimeters where only installed in the A horizon (map: courtesy of PhD candidate Bin Zhou)

Ceramic lysimeters and vacuum sampling flask where installed in several places in the area by PhD candidate Bin Zhou and Master student Bishnu P. Joshi (Figure 22). Soil water was collected in April, July and August of 2012. Many of the lysimeters did not collect any soil water even after periods with heavy rain. The lysimeters where checked, and there was not found anything wrong with them. The lack of water in the faulty lysimeters was therefore assumed to be due to that they were installed in clay layers, which do not allow any percolation of water.

3.3 Sample pre-treatment

Sample pre-treatment was conducted according to ISO11464 (2006). The soil samples were air-dried on top of waxed paper plates in the laboratory, with a waxed paper plate on top in order to avoid dust contamination from the air.

The air-dried sample was weighed, and then sieved through a 2 mm grating, carefully using a mortar and pestle to crush soil aggregates. The >2 mm fraction was weighed before incineration and discharging. The < 2 mm fraction is referred to as the soil sample in the following discussion.

3.4 Storage

The air dried and sieved soil samples were collected in cardboard boxes marked with serial number, and stored dark at room temperature in the laboratory until analysis.

3.5 Soil analysis

Sample SS001 to SS089 were pre-treated at TAES, while samples SS090 – SS164 were pre-treated at Department of Chemistry, UiO. Soil analysis on all the samples was performed at the Department of Chemistry, UiO, except for the determination of particle size distribution. This was determined in the Sedimentology lab at the Department of Geosciences, UiO.

Detailed information regarding pre-treatment and analysis of samples SS001 to SS089 is given in Joshi (2014). Pre-treatment and analysis performed on sample SS090 to SS164 was conducted using the same methods as described in Joshi (2014) if nothing else is stated. The soil analysis using XRD and the determination of PSD were not performed by Joshi. The methods used are therefore the ones described in this thesis.

3.5.1 Dry matter

Air dried soil samples were used for analysis. To be able to express the quantitative results based on the dry weight of the soil, the percentage of dry weight relative to air dried weight (W_{dm}) of each soil sample needs to be determined. This was done gravimetrically by drying the air dried soil at 105°C and assessing the weight ratio before and after drying. The determination of W_{dm} was done according to ISO11465 (1993). See Appendix B for more details.

3.5.2 pH

The pH in both deionized water and 1.0 M KCl solution was determined following ISO10390 (2005). The pH meter used was an Orion Research Expandable IonAnalyser EA 920, with a Thermo Scientific pH-electrode. See Appendix B for details and results.

3.5.3 Loss on ignition

A proxy for organic matter content was found by determining the loss on ignition (in %), according to the method described in Krogstad (1992). Loss on ignition is found gravimetrically by incinerating the soil for 3 hours at 550 $^{\circ}$C, and calculating the weight loss. See Appendix B for details and results.

3.5.4 Effective cation exchange capacity

Effective cation exchange capacity (CEC_e) was determined by PhD candidate Bin Zhou after the method described by Hendershot and Duquette (1986), which is comparable to the (ISO11260, 1994). The method deviates from the ISO standard by measuring the pH directly in the supernatant solution and that iron and manganese is also determined. The extracts was analysed using Inductively Coupled Plasma Optic Emission Spectroscopy (ICP-OES).

3.5.5 Particle Size distribution

Soil texture of the samples was determined by analysing the particle size distribution (PSD) of the soil. Sample preparation for the PSD followed the procedure described by ISO11277 (2009) The PSD on the prepared soil samples were conducted with a laser diffraction particle size analyser. The samples were prepared with several reagents in order to remove organic matter, iron oxides, soluble salts, and carbonates (see Appendix C for more detailed information). This is important as these constituents ‘glue’ the particles together forming soil aggregates. Prior to analysis the samples were set in an ultrasonic bath with 5% sodium metaphosphate solution to ensure complete dispersion. Each sample was analysed twice, and the average values are used to calculate the weight percent of sand, silt and clay.

The principle behind laser diffraction particle size analysis method is that the particle reflects the laser light in a specific diffraction pattern according to their size. The intensity of the lines with a specific pattern is dependent on the amount of particles with a given size. A Fourier lens is used to filter the reflected laser light as it is only sensitive to the angle of incidence of the diffracted light, and not the position or speed of the particle. The lens thereby diffracts the signal in the same way for the same particles (see Figure 23). The diffracted light from the Fourier lens reach the detectors, and the light is measured as flux (intensity/area). The instrument used has 126 detectors, and the particle sizes are calculated by dividing the pattern into groups which corresponds to different particle sizes. The relative amplitude of each group is then used to decide the relative amount of particles with the corresponding size.

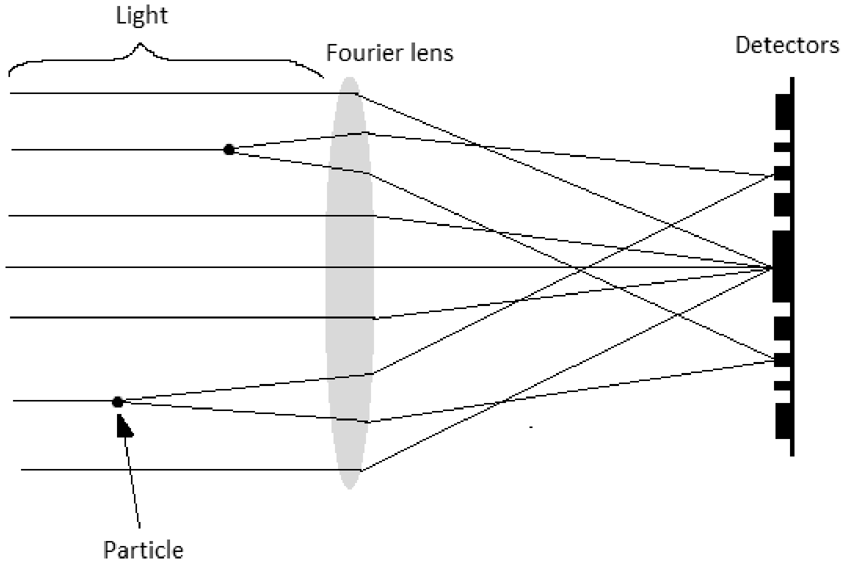


Figure 23 Fourier lens and detector. Particles with the same size diffract the light in the same way independent of position and speed.

The Beckmann Coulter single wavelength instrument is used to determine the grain size between 0.00045 mm (particles are defined to be > 0.00045 mm) and 2.00 mm, and the results are given as a cumulative distribution according to the volume of the grains. This method is based on the assumption that the particles all have the same density (volume % = mass %) and that they are spherical.

The particle size distribution was determined on soil samples from 49 sample sites. The samples are mainly of the Ap horizon but some samples from the B and C horizon are included (in total 68 samples). The selection of samples was aimed at capturing the span in soil pH and organic content, as well as to spatial distribution within the watershed and between different land-use.

3.5.6 Mineralogy

The mineralogy of the soil was determined using an X-Ray Diffraction (XRD) analyser. XRD is an analytical technique for identification and quantification of crystalline or powder materials (Harris & White, 2008). The principle behind the method is based on Bragg’s equation (Equation 1). It expresses the condition for diffraction and in result the reason why different minerals will give different signals; every type of crystalline mineral present in the sample will give a characteristic diffraction pattern because of their characteristic distance between the crystal planes. The wavelength and diffraction angle is measured and used in Bragg's equation to calculate the d-spacing which is substance-specific.

$$n\lambda = 2dsin\theta \qquad \textit{Equation 1}$$

Where d is the distance between the atomic planes in the crystal (d-spacing), λ is the wavelength of the diffracted beam and θ is the diffraction angle. This distance between the planes in the crystal is used to identify the minerals.

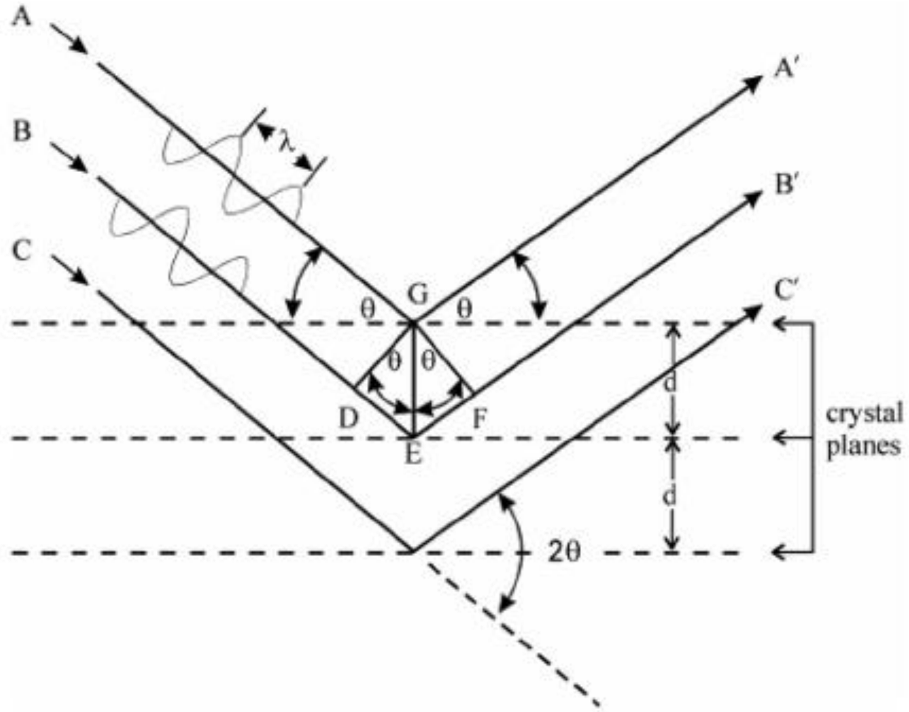


Figure 24 Schematic presentation of diffraction. Retrieved from Harris and White (2008).

Fourteen soil samples were chosen for analysis. Samples were chosen to have a good geographical distribution and to be evenly distributed between different land management practices. The soil was placed onto a sample holder, and smeared gently to make the surface as smooth as possible. During analysis the machine rotates the sample between 3° and 70°, while sending X-ray beams onto the samples, and the different surface of the minerals gives diffraction patterns which are used to identify the minerals present in the sample. The software used to interpret the signals was TOPAS version 4 – 2.

3.5.7 Phosphorus fractions

3.5.7.1 Extraction of organic and inorganic phosphorus

Extraction of organic and inorganic phosphorus pools in the soil samples was conducted according to the method described by Møberg and Petersen (1982). The method is based on the assumption that the inorganic phosphorus will be released in the presence of 6.0 M sulphuric acid, while the organic phosphorus will not because the acid is not an oxidizing agent. The acid dissolves all the iron and aluminium oxides and sesquioxides, as well as carbonates that are binding the phosphate. To determine the total amount of phosphorus the soil is incinerated at 550 °C before extraction with sulphuric acid. The ignition will convert the organic phosphorus to inorganic phosphorus which then is released by the extraction with 6.0 M sulphuric acid. The organic phosphorus fraction is determined as the difference between the inorganic fraction and the total phosphorus. See Appendix D for more details.

3.5.7.2 Determination of total and inorganic phosphorus

The inorganic phosphorous fraction was determined spectrophotometrically following the method described in ISO6878 (2004). The orthophosphate in the soil extract reacts with an acid solution containing molybdate and antimony ions, and forms an antimony phosphomolybdate complex. This complex is then reduced with ascorbic acid to form a coloured molybdenum blue complex, which can be measured spectrophotometrically at λ=880nm. The absorption at this wavelength is then proportional to the concentration of orthophosphate in the soil extracts. An UV-1800 SHIMADZU UV-visible spectrophotometer was used to measure the absorbance of the complex, and the concentration of orthophosphate was determined using a standard curve and linear regression. The total phosphorus was determined using ICP-OES. The instrument settings and standard curves can be found in Appendix D. A correlation check between ICP-OES and the molybdenum blue method was performed, see Appendix D for results and operating conditions.

The reason for using two different methods for the determination of phosphorus in the soil extracts are mainly due to practical reasons, but it can be supported scientifically. In the comparison of the two methods it is important to divide between the total and inorganic phosphorus fractions. A correct determination of phosphorus is dependent on a successful extraction of phosphorus. For the inorganic fraction this means that no organic phosphorus must be dissolved, and for the total it means that all the phosphorus in the soil should be dissolved (except for the minerals). The molybdenum blue method will only be able to detect dissolved phosphate, the method is rather specific for this compound. When using the ICP-OES for determination of phosphorus in a solution you measure all the phosphorus that is in the solution. The different digestion methods seems to have some challenges with dissolving some organic phosphorus compounds making the total phosphorus underestimated with the colorimetric method, while with ICP-OES this fraction can be detected because they are released in of the high temperature plasma (Pierzynski, Zhang, et al., 2005). This is an advantage in using ICP-OES for determination of total phosphorus. On the other hand it will be a disadvantage when determining the inorganic fraction because you are not interested in detecting the organic phosphorus that will be present in the solution.

3.5.8 Phosphorus sorption capacity

The phosphorus sorption capacity is determined as a combination of two methods; phosphorus sorption index and Mehlich 3, both described by Sims (2000) in Methods of Phosphorus Analysis for Soils, Sediments, Residuals and Waters. Phosphorus sorption index (PSI) is an approximation of the soils capacity of sorbing phosphorus that was developed by Bache and Williams (1971). The principle behind the determination is to add a known amount of phosphorus to a solution, shake it for 18 hours, and then measure the amount of phosphate in the supernatant spectrophotometrically by the molybdenum blue method. To calculate the soils phosphorus sorption capacity, the phosphorus that is already sorbed to the soil in the sample needs to be determined, and added to the PSI. This is done by the Mehlich 3 method where you add a extraction solution to 2.0 g of soil, shake and filter it and then measure the phosphate in the extract spectrophotometrically with the molybdenum blue method (Sims, 2000). Both determinations were performed by PhD candidate Bin Zhou.

3.5.9 ^{31}P- NMR analysis

^{31}P- NMR analysis was performed on 2 forest and 2 vegetable garden samples. The Analysis was performed by Bin Zhou at the Department of Chemistry, UiO.

3.0 g of pre-treated soil was extracted with 0.25 M NaOH and 0.11 M EDTA and shaken overnight (Cade-Menun & Preston, 1996; Turner, 2008) The extract is then centrifuged and added a 5% (v/v) mixture of sodium carbonate and sodium dithionite before freeze drying (Turner, Cade-Menun, & Westermann, 2003) The freeze dried soil was then transferred to a NMR tube and added NaOH and D_2O. The spectra were obtained at a 400Hz NMR spectrometer.

3.6 Soil – water analysis

The soil water analysis where performed by Ye Ping at TAES. The method used is shortly referred to in the sections below.

3.6.1 pH

The determination of pH was done as described in ISO10523 (1994).

3.6.2 TOC

The absorbance of the soil water was measured spectrophotometrically in a 10mm quartz cuvette at 254 nm, as a proxy for content of dissolved organic matter. The samples were filtered through a 0.45µm membrane filter prior to analysis to avoid interference from particles in the soil-water, and the results are reported in mg C/L.

3.6.3 Cations

The concentration of Na^+, K^+, Ca^{2+} , Mg^{2+} and NH^{4+} was determined using ion chromatography as described in ISO14911 (1998).

3.6.4 P-fractionation

Figure 25 shows the fractionation on phosphorus in a water sample. The phosphorus are determined by the molybdenum blue method for all the groups, but in group B and C the water is digested with potassium peroxidisulfate as described in NS4725 (1984). Group A and B are filtered before analysis to remove particles. After determination of the phosphorus in the different groups, the fractions were calculated according to the equations below.

- Particulate phosphorus (PP) = group C – group B
- Organic phosphorus (DOM-P) = group B – group A
- Free phosphate (PO_4-P) = group A

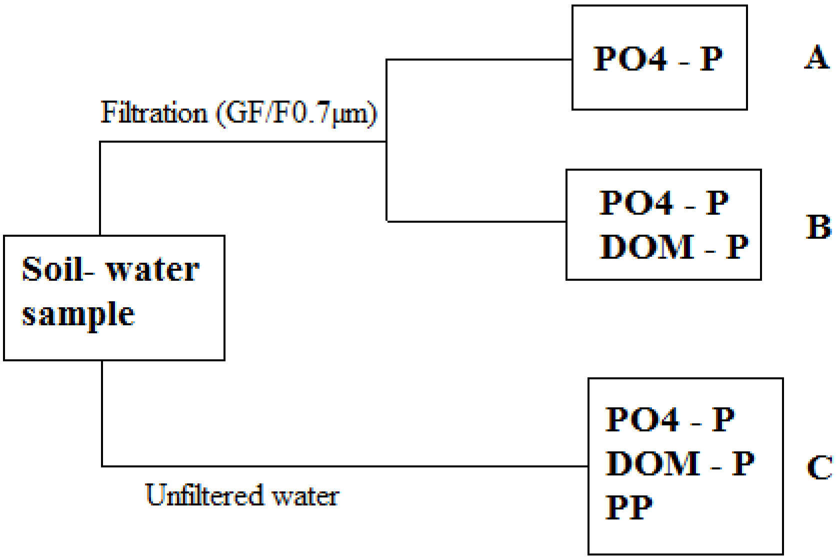


Figure 25 phosphorus fractionation (modified from (Mohr, 2010)

3.7 Multivariate statistics

Multivariate analysis is used when a comparison of several variables measured for several samples is of interest. Variables usually correlate and covariates in respect to each other and the outcome, and there is a need to simplify the picture to be able to detect the underlying structure (Rencher, 2002).

3.7.1 Cluster analysis

Cluster analysis search for patterns in a dataset, and shows them by grouping correlated or similar observations. Variables within a cluster are more similar to each other than to the variables in another cluster, and the similarities are based on a measure of the Euclidean distance, which is the distance between two points in two or more dimensions as given by the Pythagorean formula. It is common to visualize the clustering with a dendrogram, and in the dendrogrammes presented in this thesis the distance is the minimum Euclidean distance between two observations within a variable (single linkage). A small distance between the variables is an indication of similarity and vice versa.

To be able to include horizons in the cluster they are given arbitrary increasing numbers (A=1, B=2 and C=3). Land-use is included by numerating them with a binary matrix with farmland, forest, orchard and vegetable (Personal comm. Tom Andersen 2014).

3.7.2 Principal component analysis

Principal component analysis (PCA) reduces the amount of dimensions in a dataset which consists of many interrelated variables, without removing the variation in the dataset (Jolliffe, 2002). The variables are transformed into principal components that are uncorrelated, but are ordered so that the first few components explain most of the variation present in all the original variables.

The land-use parameter is excluded in the PCA because the analysis does not handle categorical variables, only continuous (Jolliffe, 2002)

4. Results and discussion

Multivariate statistical analyses on the data matrix are used as a first approximation in order to provide an overview of the relationships between the explanatory parameters and the phosphorous pools. Based on this soil physiochemical ‘landscape’ the main explanatory variables for the spatial variation in pools of organic and inorganic phosphorous are identified. The underlying factors governing the spatial differences are subsequently addressed by assessing the physiochemical data of soils within similar categories of the main explanatory factors.

4.1 PCA and cluster analysis

A cluster analysis was performed on 68 samples and the variables organic matter, soil texture (clay, silt and sand), pH_{H2O}, numerical horizons and land-use (Figure 27). A preliminary test showed that the two pH measures (water and salt) are so closely clustered that they are considered to provide the same information (Appendix G). The pH_{KCl} was therefore excluded from the multivariate statistical analysis. Mineralogy is not included in the cluster analysis because the data only represents 14 samples, and the eight minerals that were detected greatly increase the number of variables. A cluster analysis based on 14 samples and 17 variables is weak, and the use of this information would possibly lead to incorrect conclusions. CEC_e and phosphorus sorption capacity is also not included because these parameters are not determined in soils from the B and C horizons, making it impossible to include the horizons parameter in the cluster analysis.

4.1.1 Land use and soil horizons as main explanatory factors

The dendrogram of the land-use, organic matter content, soil pH_{H2O}, PSD% and soil horizon is given in Figure 26. This dendrogram shows that these parameters are grouped into two main clusters; one cluster includes forest and orchard together with organic matter and sand. The grouping with sandy soils reflects that the soils with lower quality class are left as forest or that the farmers use these areas to grow fruit trees. The relation with organic matter is likely due to that soils with perennial vegetation commonly have higher content of organic matter than agricultural soils. The second cluster includes the vegetable gardens along with soil pH and the finer soil particles (silt and clay). Higher pH in agricultural soils is partly due to the soils natural content of carbonates along with finer particles successfully buffering the pH as well as the direct application of lime by the farmer. The clustering of finer soil particles with the vegetable gardens is the reason why the farmers use these soils for growing vegetables; soils with high content of finer particles are more fertile. Farmland is outside both these clusters, and appears to be explained by something else. The soil horizons are clustered with soil pH and the finer soil particles, reflecting the co-varied increase in these parameters down the into the soil profile. The clustering of different land-use with different soil physiochemical parameters implies that the biogeochemical processes differ between them.

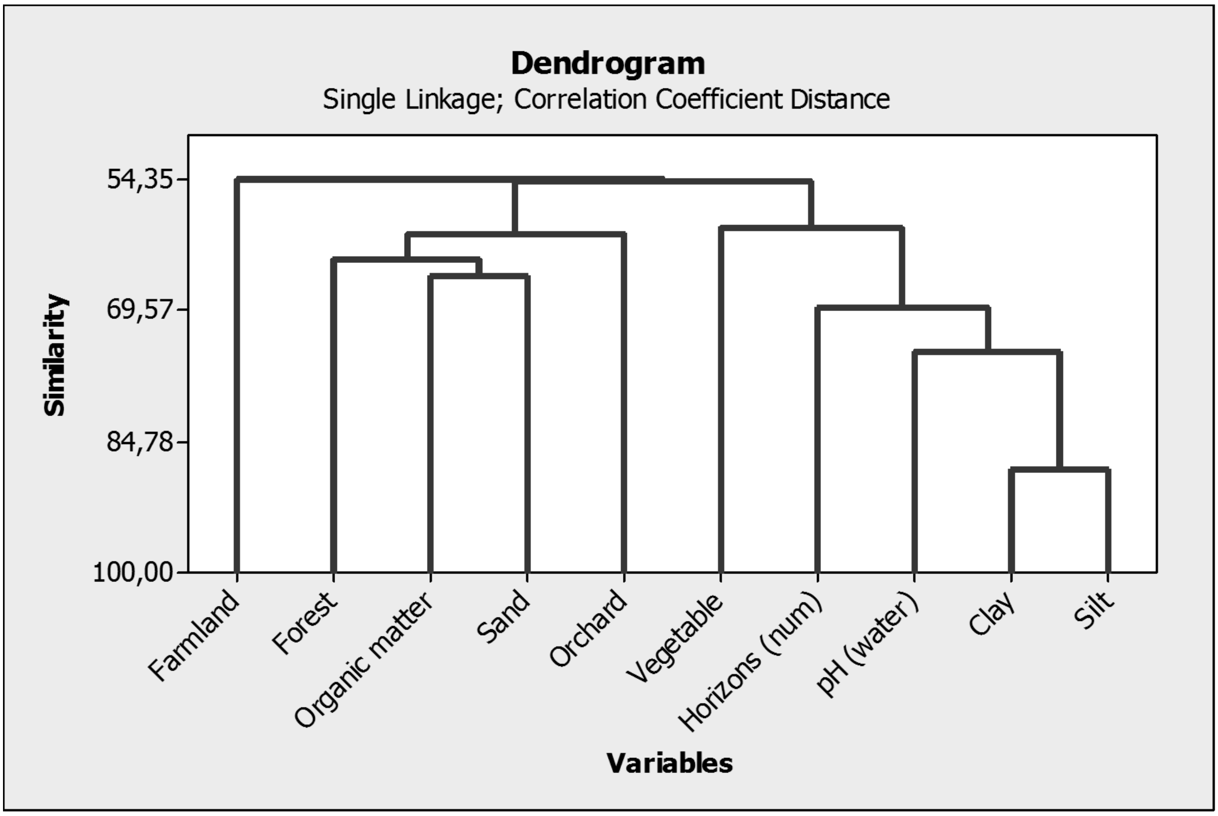


Figure 26 Dendrogram of all parameters (68 samples)

When the organic and inorganic phosphorus pools (TOP and TIP, respectively) are included to the cluster analysis, the dendrogram is affected with respect to the clustering of orchards and vegetable garden (Figure 27). The phosphorous pools may therefore be assessed as relatively independent variables in the analysis in regards to the soils physiochemical parameters. The dendrogram shows that the organic phosphorus pool (TOP) is strongly connected to organic matter content. This is inherent as organic matter contains organic phosphorous, and that the soils with higher organic matter content have a higher capacity to sorb phosphorous. The inorganic phosphorous pool (TIP) is thereby also related to the organic content. The vegetable gardens have shifted to the cluster with phosphorous pools and the orchards have become closer linked to forests. The shift in the dendrogram for vegetable gardens and orchards is due to that both have large pools of phosphorus in the soils. Orchards is now situated between the forest and organic matter likely due to the use of manure as fertilizer in the orchards, giving locally very large phosphorous pools in the orchards soils. The dendrogram further suggests, rather in conflict with conceptual reasoning, that the soil horizon, soil pH and content of finer particles appear to have low explanatory value for the phosphorous pools.

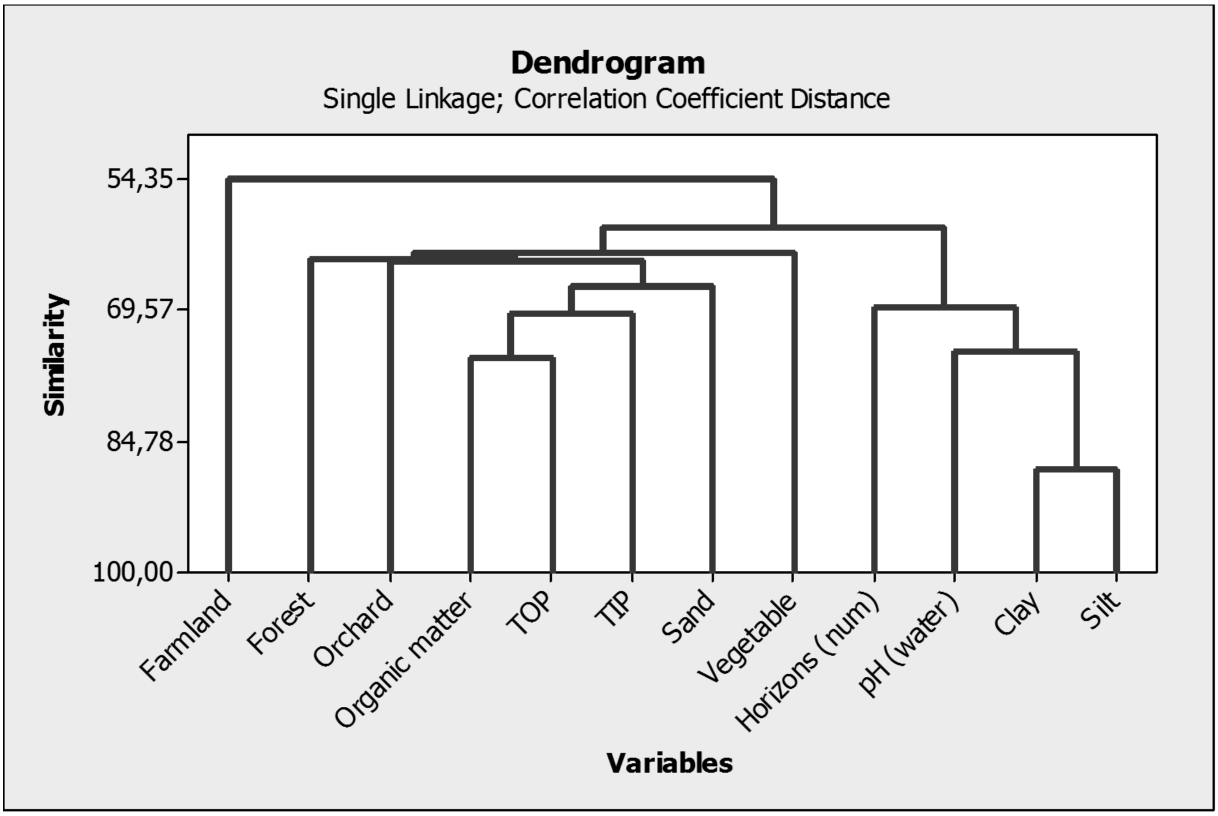


Figure 27 Dendrogram of explanatory variables and phosphorus-pools (68 samples)

4.1.2 Soil horizon as main explanatory factor

The parameter loadings along the two main principal components in a PCA of explanatory soil physiochemical parameters, including the phosphorous pools and soil horizons (i.e. without the land-use categories) are shown in Figure 28 (68 cases). The first principal component (PC1), describing almost half (46.7%) of the variation in the dataset, is governed by soil texture divided between the cluster of silt and clay on the one side and sand on the other. The second principal component (PC2), accounting for 16.4% of the variation, appears to be describing the soil depth assigned by the soil horizons (increasing with depth). The third principal component (PC3), explaining an additional 12.3% of the variation, is strongly positively loaded along with inorganic phosphorus and negatively loaded to soil pH. This analysis modifies the cluster analysis in pointing out the strong opposite loading between soil horizon and the phosphorous pools in the plane of the two main principal components. This relationship is perpendicular on the soil texture gradient, implying that effect PSD has on the phosphorous pools is independent of the relationship between soil horizons and phosphorous pools. It is surprising that the pools of phosphorous have negative loading to the finer particle sizes. Generally clay and silt has large capacity to adsorb phosphorous due to large surface area. The cause for this may be that the clays are mainly found to be 1:1 clays, which have very poor adsorption capacity.

The figure implies that the main explanatory factor for the size of phosphorous pools is the soil horizon. This agrees with the data as the sizes of the phosphorous pools are found to decrease down through the soil. This is partly due to the application of phosphorous fertilizers and manure in the A_p horizon as well as its greater ability to adsorb phosphorous due to higher content of organic matter. The increase in clay content with depth has a confounding effect due to the very poor adsorption capacity of the prevailing 1:1 type clays.

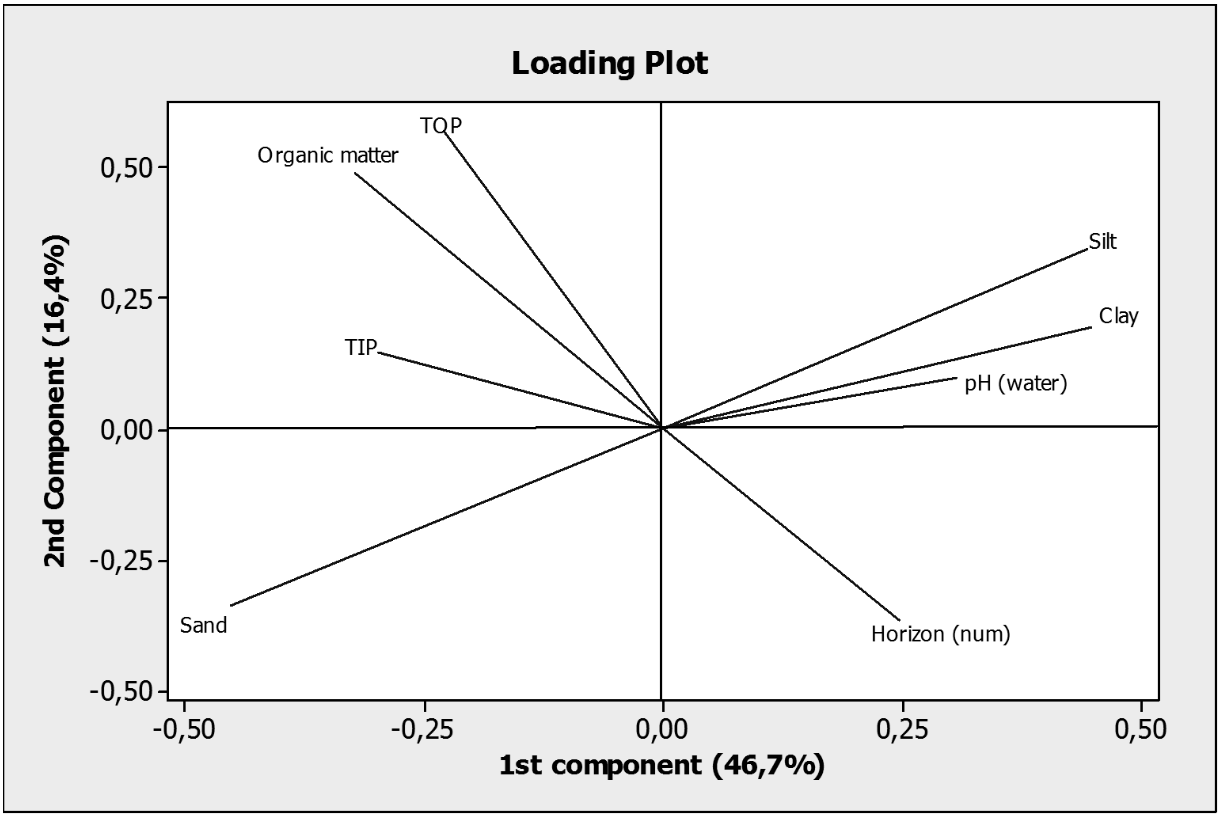


Figure 28 PCA parameter loading plot of the 1st and 1nd principal component (68 samples) without the categorical variable land-use.

A PCA where the PSD% data were dropped in order to increase the number of cases to 205 (Figure 29), further emphasises the role of soil horizons as the main explanatory factor for the differences in phosphorous pools between the soil samples. The PC1, explaining 36.9% of the variation in the dataset, is strongly explained by the increasing soil horizons (A – B – C), which is negatively loaded to the organic phosphorus. This is clearly due to the higher phosphorous content of the upper horizons. The clustering of the phosphorous pools with the soil organic content may simply be due to that both co-vary as both are dependent on the soil horizon. On the other hand it is reasonable to assume that the higher organic content contains more soil organic phosphorous as well as sorb more phosphorous because it increases the soils sorption capacity. The fact that the pH is negatively loaded to organic matter content along the first PC may be due to the acid effect of humic material, though it is more likely that it is due to that both parameters co-vary with soil horizon (i.e. increasing pH with decreasing organic content with depth) and land-use (higher pH and lower soil organic matter content in agricultural soils compared to forest soils). The second PC, explaining an additional 20.2% of the variation, is also partly explained by the soil horizons. In the plane of the 1st and 2nd PC the inorganic phosphorus (TIP) is negatively loaded against pH. This may be reflecting that rather independent of soil horizon the soil pH appears to be an important parameter explaining the spatial differences in the pools of inorganic phosphorous within each horizon. Largest phosphorus pools are found in uppermost soil horizon (A) and in the soils with the highest organic matter content.

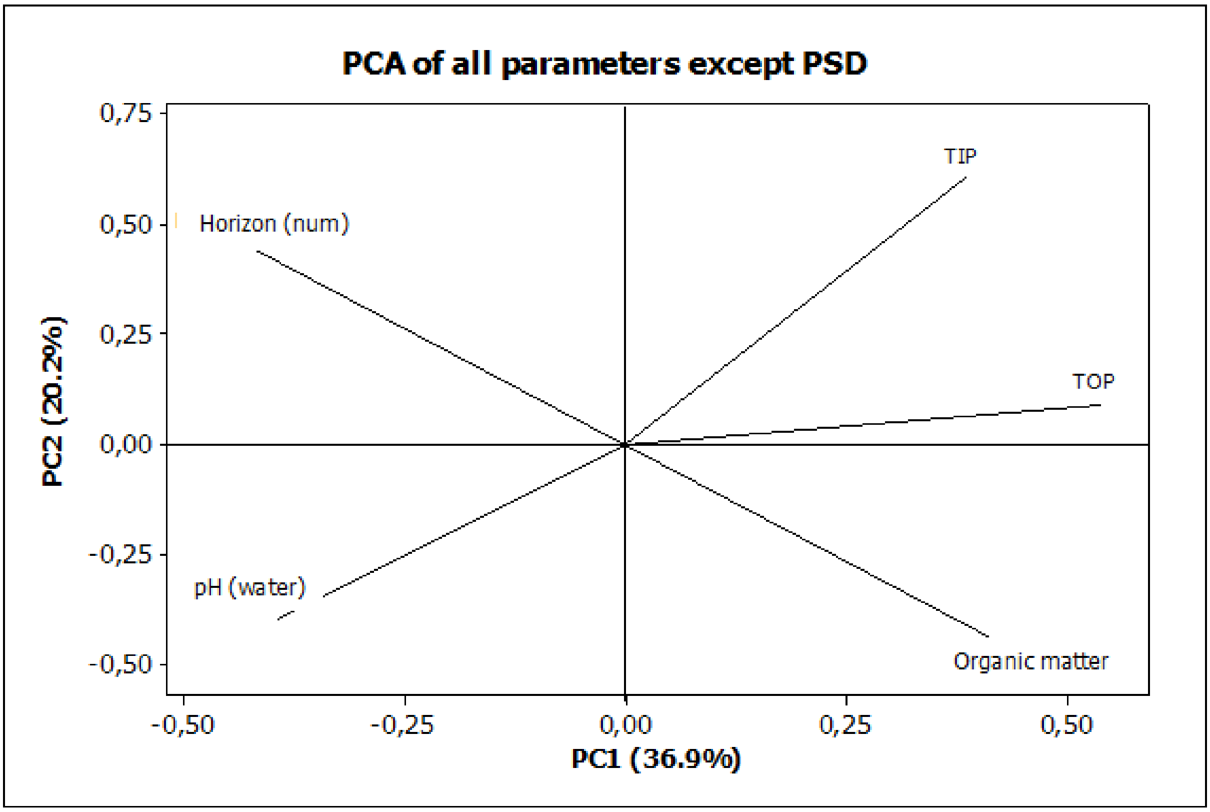


Figure 29 A PCA parameter loading plot of the 1st and 2nd principal component. Soil texture data is excluded to increase the number of samples to 205.

4.1.3 Underlying explanatory variables

A dendrogram showing the clustering of parameters in the A horizon for all land-use practices is given in Figure 30 (49 cases). The two same clusters as seen in the dendrogram using all the data (Figure 27) are still apparent. This means that within the A horizon the spatial variation in the size of the phosphorous pools is mainly explained by the organic matter content.

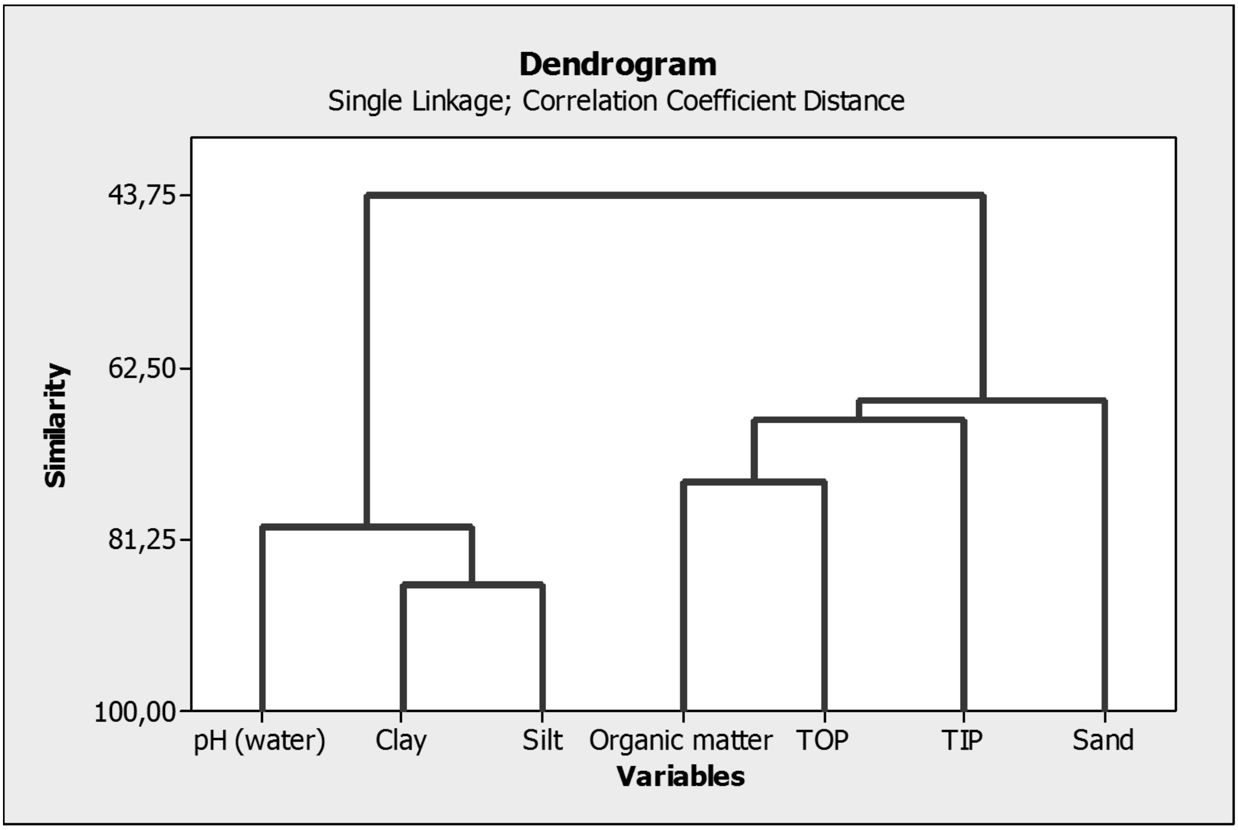


Figure 30 A dendrogram of variables in the A horizon (49 samples)

Likewise, the PCA of only the A horizon data (49 cases; Figure 31) resembles the PCA of all the data (Figure 31). The parameters with greatest loading along the PC1 (50.9 %) remains to be the PSD, while the variation along the PC2 is manly governed by the soils content of organic matter. The pools of inorganic P appear to be governed by the mainly the relative amount of sand, while the organic phosphorous pool is governed by the soils content of organic matter.

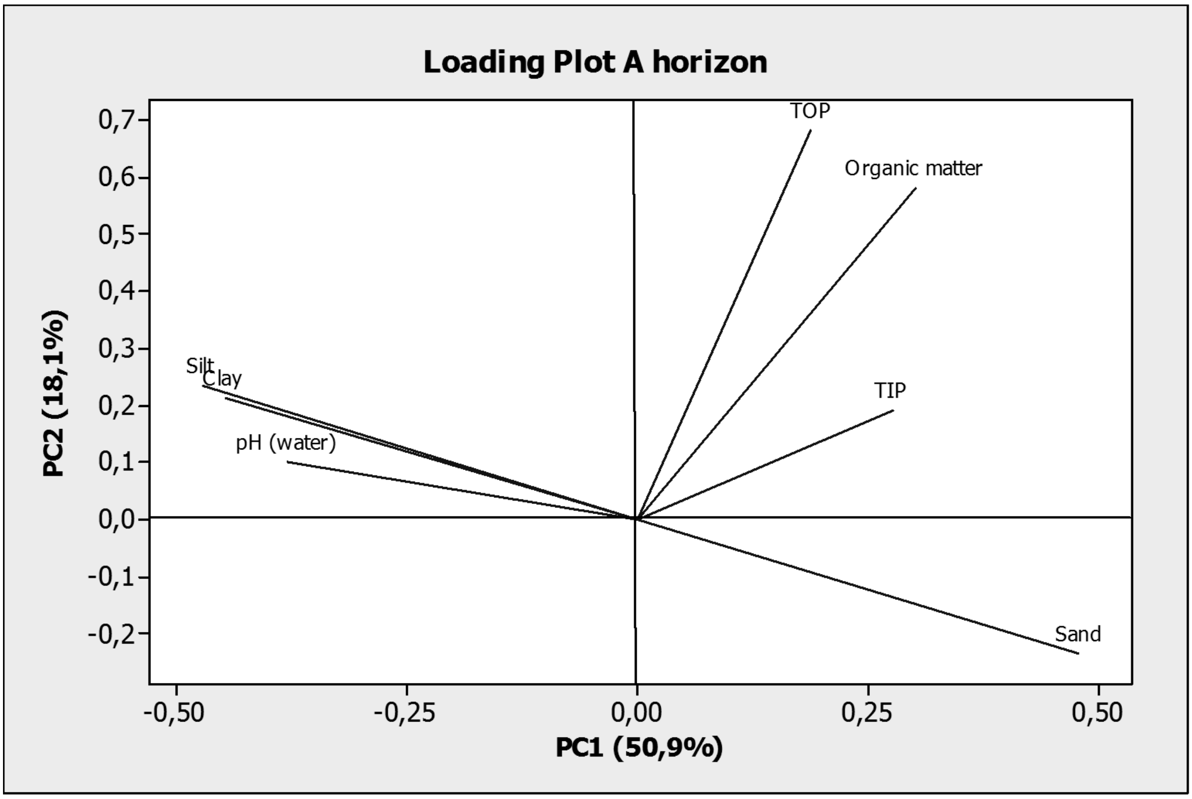


Figure 31A PCA parameter loading plot of the 1st and 1nd PC in the A horizon (49 samples).

4.2 Physiochemical properties of the A horizon soil and soil-water relative to land-use

The results and discussion in this section (4.2) is based on results obtained from soil sampled in the A horizon in farmland, forest, orchard and vegetable if nothing else is stated. As discussed in Section 3.1.1, the Ji County EPB (2012) states that the nutrient enrichment of the reservoir is strongly influenced by the agricultural activities, and the results will therefore be discussed in terms of types of land-use and the corresponding management practices.

4.2.1 pH

The soil pH_{H2O} for the A horizon lies in the region between 6 and 8 (Figure 32), and can thus be defined as neutral. The pH_{H2O} is below pH_{PZC} for goethite, halloysite, vermiculite, illite, calcite, $\gamma/\alpha\text{-}Al_2O_3$ and iron oxides (with the exception of goethite in some cases), and the surface charge of these minerals are net positive making sorption of phosphate through ion exchange possible with these minerals. For orthoclase (K-feldspar) the pH is above $pH_{PZC,}$ and the surface is thus negative. The pH_{KCl} is on average one unit lower than for pH measured with water due to the process where K^+ ions replace H^+ on the soil surface, making the solution more acidic. Based on that the pH_{H2O} is generally above the region of greatest solubility (Figure 9) we can assume that the phosphorus solubility is controlled by the solubility of calcium phosphate precipitates.

Soil pH can be buffered by carbonates to pH around 8 (Dahlgren, 2008) which may stem from natural processes like weathering of sedimentary bedrock, or liming in agricultural soil (the process of adding calcium carbonate to agricultural soil in order to elevate the pH and make the soil more fertile). This indicates that carbonates are present in the soil in the study area, buffering the pH to between 6 and 8.

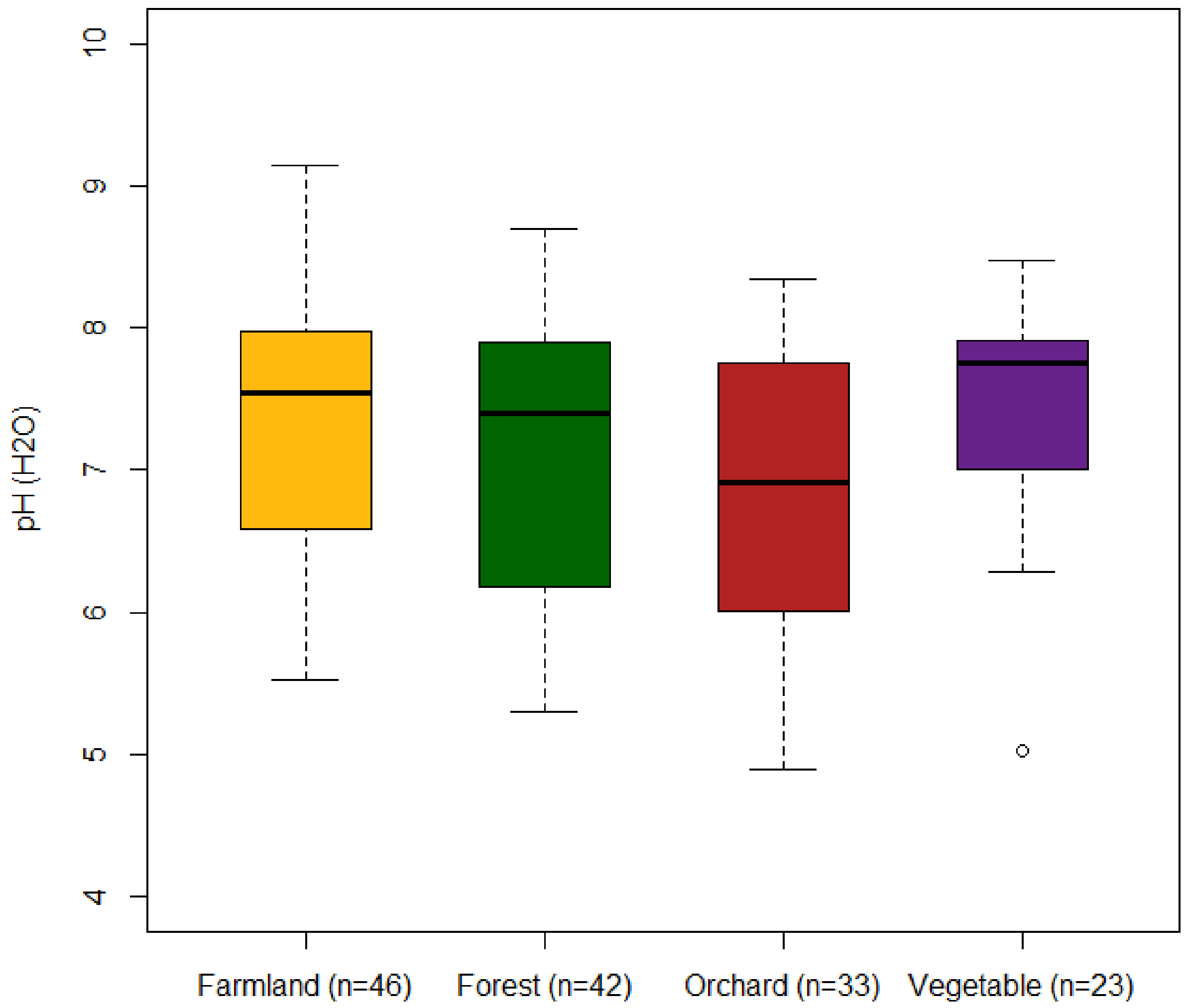


Figure 32 Soil pH$_{H2O}$ in the A horizon. The boxplot show the median and the 25th and 75th percentiles (Q1 and Q3). The whiskers show the minimum and maximum value. The dots in the figure represents outliers in the dataset; they are defined as Q1±1.5*IQR, where IQR = Q3 - Q1.

There is no apparent significant difference in the pH for the different land-use, but orchards have a somewhat lower average pH value than the pH in forest, farmlands and vegetable fields. This may be due to the humic material which originates from decay of leaves and other plant material, because humic material lowers the pH through the release of H^+ from the acid functional group. The fact that forest have about the same pH as the farmland and vegetable implies that the soils are naturally rich in carbonates because the forest area is not affected by human activities and liming. Farmland and vegetable gardens have a slight tendency to higher pH than orchards and forest. This is probably due to the fact that the land used for agricultural activities has soil with a good buffering capacity, and thus higher fertility, and that they are limed.

The pH_{H2O} for soil and soil-water (lysimeter samples) in the A horizon is given in Figure 33. The figure shows that the pH in the soil-water is generally higher compared to the soil pH in the farmland and forest areas, while in orchards and vegetable gardens the pH is higher in the soil than in the soil-water. The differences here are very small. In concentration we are talking about differences of 0.1µM and 0.01µM H^+. Overall the pH in soil and soil water is almost the same.

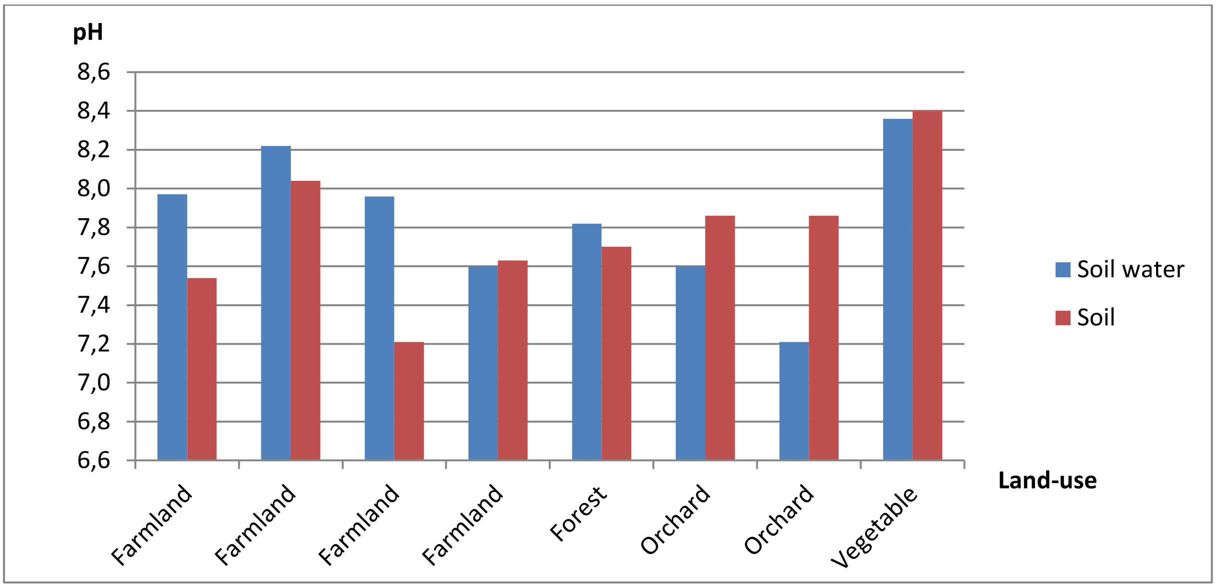


Figure 33 pH_{H2O} measured in soil and soil water (lysimeter), according to land-use.

These differences indicate that there are different biogeochemical processes governing the soil water chemistry in the farmland and forest compared to orchards and vegetable. In all cases the pH is higher in the soil than what is expected to be in the rain which is due to alkaline compounds in the soil that neutralize the rainwater (Rain usually has a naturally low pH value 5.64 because of CO_2, and due to acidic compounds in the atmosphere for instance SO_2 and NO_2. Anthropogenic dust again increases the pH). Soils rich in carbonates usually give a soil solution high in pH and alkalinity due to consumption of H^+. The equilibrium reaction in an aqueous solution is given below.

$$CO_3^{2-} + H^+ \Leftrightarrow HCO_3^- + H^+ \Leftrightarrow H_2CO_3$$

In the orchards and vegetable areas the pH in the soil water is slightly lower than in the soil, which may stem from the organic matter that release H^+ and lower the pH. The sample sites have organic matter content around 4% and 2% respectively, which is quite low, and the pH cannot be explained by the organic matter content. This also account for the forest sample site which has a content of organic matter around 3.5 %.

4.2.2 Organic matter content

The organic matter content (in %) is generally low (between 2% and 7.5%) for the Ap horizon soils from agricultural areas (farmland fields, orchard and vegetable garden) while the soils in the forests have a significant higher median value (Figure 34), and a range between 2% and 12%. The large span between the minimum and maximum organic matter content for forest indicates that these sites show large natural diversity.

The organic matter content is as generally expected higher in the forest and orchard than in farmland fields and vegetable gardens. This is mainly due to large supply of litter fall of leaves, needles and root residues from the trees, while the organic matter content in farmlands and vegetable gardens are lower because they are greatly affected by cultivation speeding up the decomposition and crop removal (Condron et al., 2005).

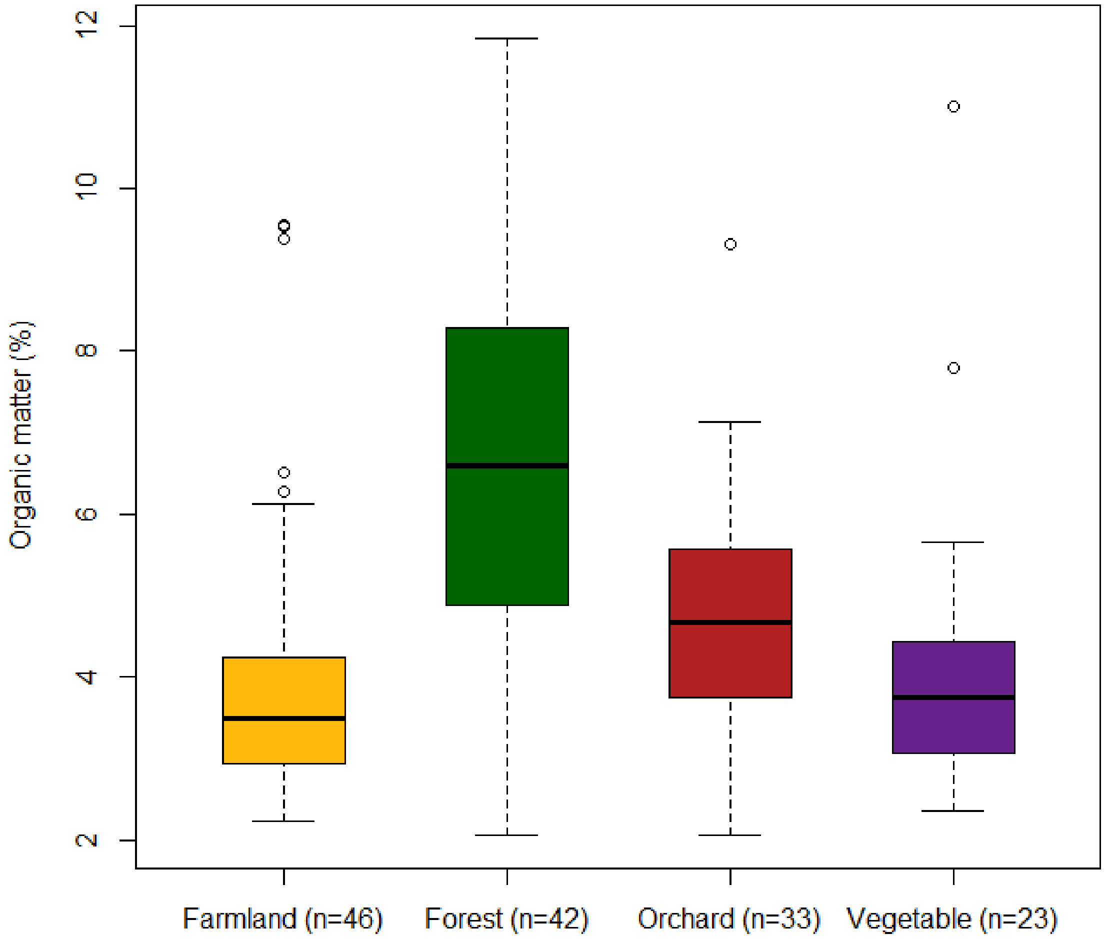


Figure 34 Organic matter content in the A horizon. The boxplot show the median and the 25th and 75th percentiles (Q1 and Q3). The whiskers show the minimum and maximum value. The dots in the figure represents outliers in the dataset; they are defined as Q1±1.5*IQR, where IQR = Q3 - Q1.

Organic matter contains inherently organic phosphorous and will enhance the sols capacity to sorb phosphate if the conditions are right. The organic matter content is higher in the forest and orchard soils compared to the farmland and vegetable gardens, suggesting that the sorption capacity of phosphorous might be higher in these two categories. The farmers in the area are adding phosphorus to the soil in the orchards (as manure) which mean that this might be sorbed to a higher degree than in the other areas. Dissolved organic matter from the manure may also compete for sorption sites on the mineral particles, decreasing the phosphorus sorption capacity of the orchard soils. On the other hand, if high concentrations of calcium are present in the soil this will immobilize the dissolved organic matter, making the competition between organic matter and phosphorus limited.

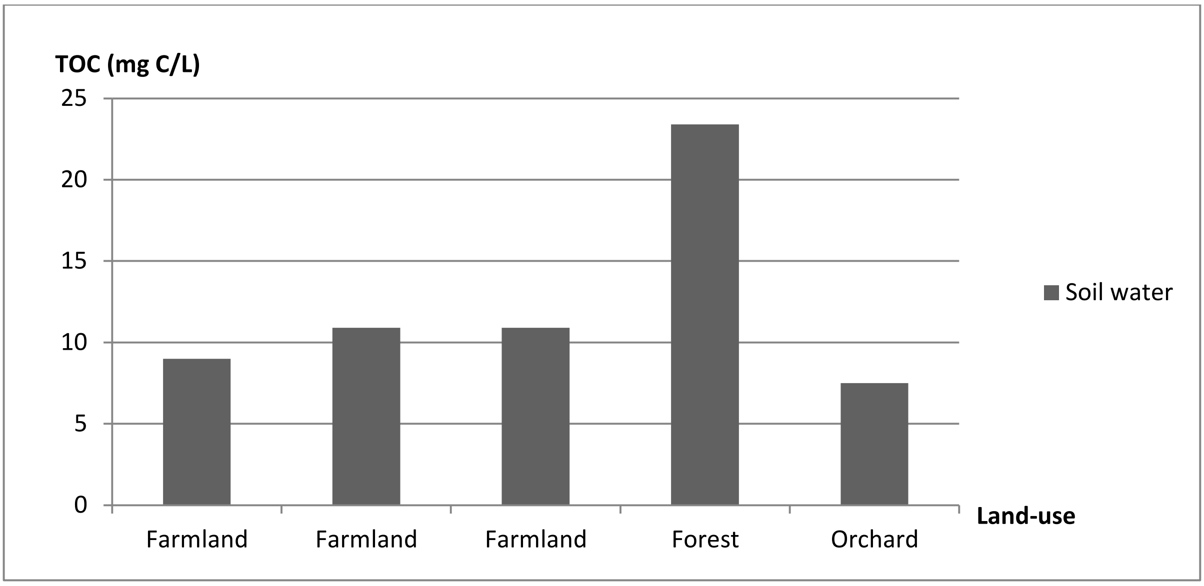


Figure 35 Total organic carbon content of soil water.

The dissolved organic carbon (DOC) concentration in soil-water (Figure 35) show a similar trend as the organic matter content of soil (Figure 34), where forest have the highest content compared to farmland and orchard. The levels of DOC are relatively high, especially in the forest soil, considering the high calcium concentration (avg. 3.75mM). Competition for sorption sites between organic anions and phosphorous is therefore possible.

4.2.3 Soil texture and mineral composition

Based on the PSD analysis the soil texture in the area is generally found to be silt loam. There are no clear spatial trends in the soil texture: the south part, the eastern plain areas and the mountain areas in the north all have the same soil texture. In a few sites they soil have a silt texture while others have sandy loam, but these appear randomly distributed.

Medium textured soils (silt/loamy soils) are in general more easily eroded (Bissonnais, 1998), which means that the soil in the study area may be very unstable. Erosion is more likely to happen during heavy rain events, which is common in the study area during the rainy season. In addition to the soil texture, organic matter plays an important role in preventing soil erosion, because it acts as a bonding agent between the mineral particles (Bissonnais, 1998) by aggregating the soil particles and giving a granular structure. The combined effect of texture and low organic content render the soil from the A horizon in the study area prone to erosion.

The crystalline mineral composition of the soils was rather homogeneous, with the main components (with ranges) being quartz (33 – 39%), halloysite (21 – 24%) and muscovite (20 – 27 %). Between 4 – 7% albite is also identified in most of the samples. In addition some small amounts of orthoclase (k-feldspar), microcline and illite are found. The phosphorus containing minerals apatite and vivianite were not found in the soils. Moreover, field observations showed that the A horizon in the plain lowland area was usually lying on top of a clay soil layer. This is likely a non-swelling 1:1 type clay considering the age of the soils and that the main clay type found in the A horizon is Halloysite. This clay is impermeable for water forcing all the drainage through or over the shallow A horizon.

4.2.4 Effective cation exchange capacity

The effective cation exchange capacity (CEC_e) is generally expected to be high for soils with high organic matter and clay content, with values typically above 100 cmol/kg. Sandy soils with low organic matter content are considered to have a low CEC_e, even less that 5 cmol/kg (vanLoon & Duffy, 2011). Clays have few pH dependant charged sites and the 1:1 clays, which dominate in the study area, have usually a limited amount of permanent negative charge. Moreover, the 1:1 structure limits the absorption capacity as there is less surface area and no interlayer. The clays in the studied soils are therefore considered to not enhance the CEC_e.

Soils with high CEC_e are considered to be more fertile than soil with low CEC_e because they can retain nutrients (i.e. calcium, magnesium, sodium and potassium) through cation exchange. Furthermore, the capacity to adsorb phosphate is also enhanced due to the charge bridging by polyvalent cations in the diffuse double layer. It is therefore common to find that soils with high CEC_e are used for agricultural purposes. Fe^{3+} likely plays an important role in these soils based on the strong red colour apparent in most of the soils.

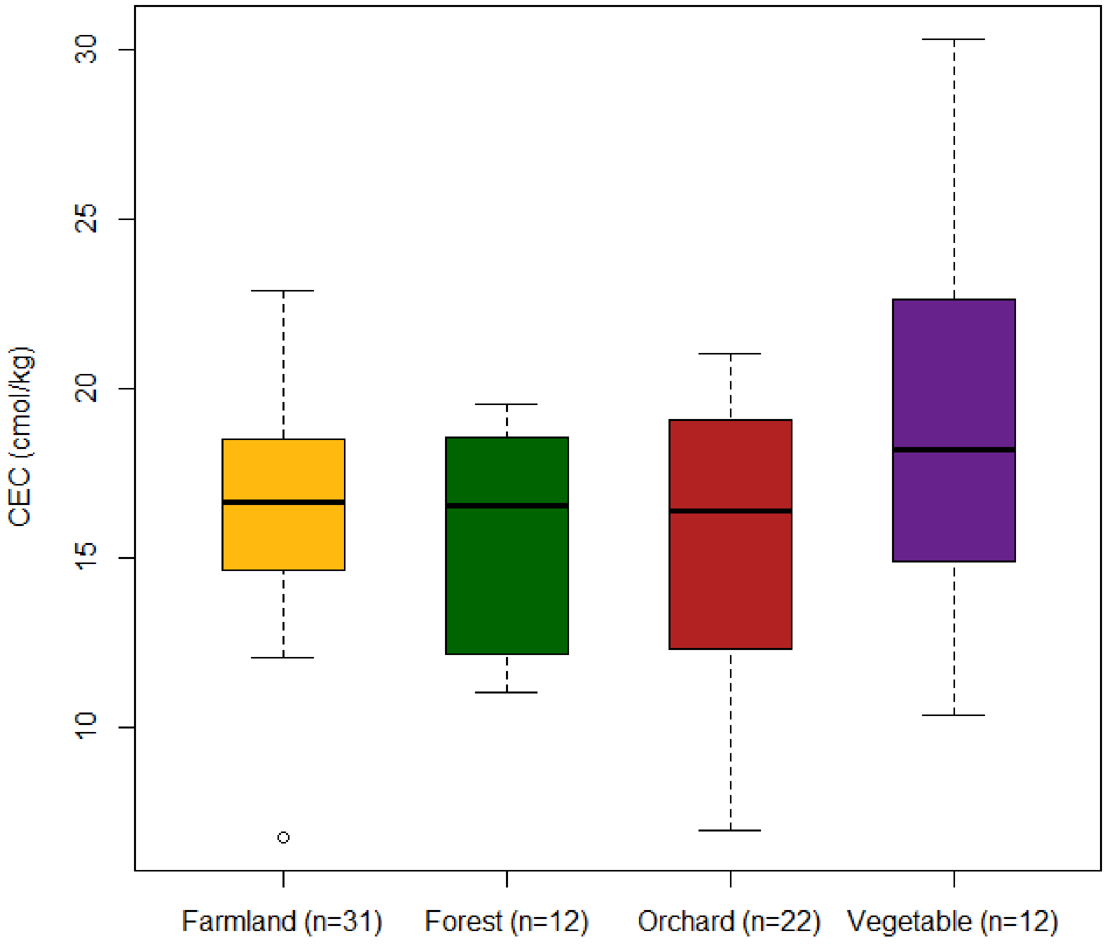


Figure 36 Effective cation exchange capacities of soils according to land-use. The boxplot show the median and the 25th and 75th percentiles (Q1 and Q3). The whiskers show the minimum and maximum value. The dots in the figure represents outliers in the dataset; defined as Q1±1.5*IQR, where IQR = Q3 - Q1.

The soils CEC_e in farmland, forest and orchards appear similar in the study area, though the median value is somewhat higher in the vegetable gardens. This is not in accordance with the low organic matter content in the vegetable gardens (as reported in Section 4.2.2 and 4.2.3 respectively) but it indicates that the soils with highest CEC_e and thus highest fertility, is used for growing vegetables which requires more fertile soils than grain. Generally the soil in the area has a medium to low CEC_e compared to soils around the world (vanLoon & Duffy, 2011). The low CEC_e, especially in the farmland fields, indicates a poor ability to adsorb phosphorous.

4.2.5 Phosphorus pools and phosphorus sorption capacity

The total phosphorus concentration in the soil in farmland fields, forest, orchards and vegetable gardens is shown in Figure 37, and the median concentrations are 680 mg P/kg, 446 mg P/kg, 833 mg P/kg and 783 mg P/kg, respectively.

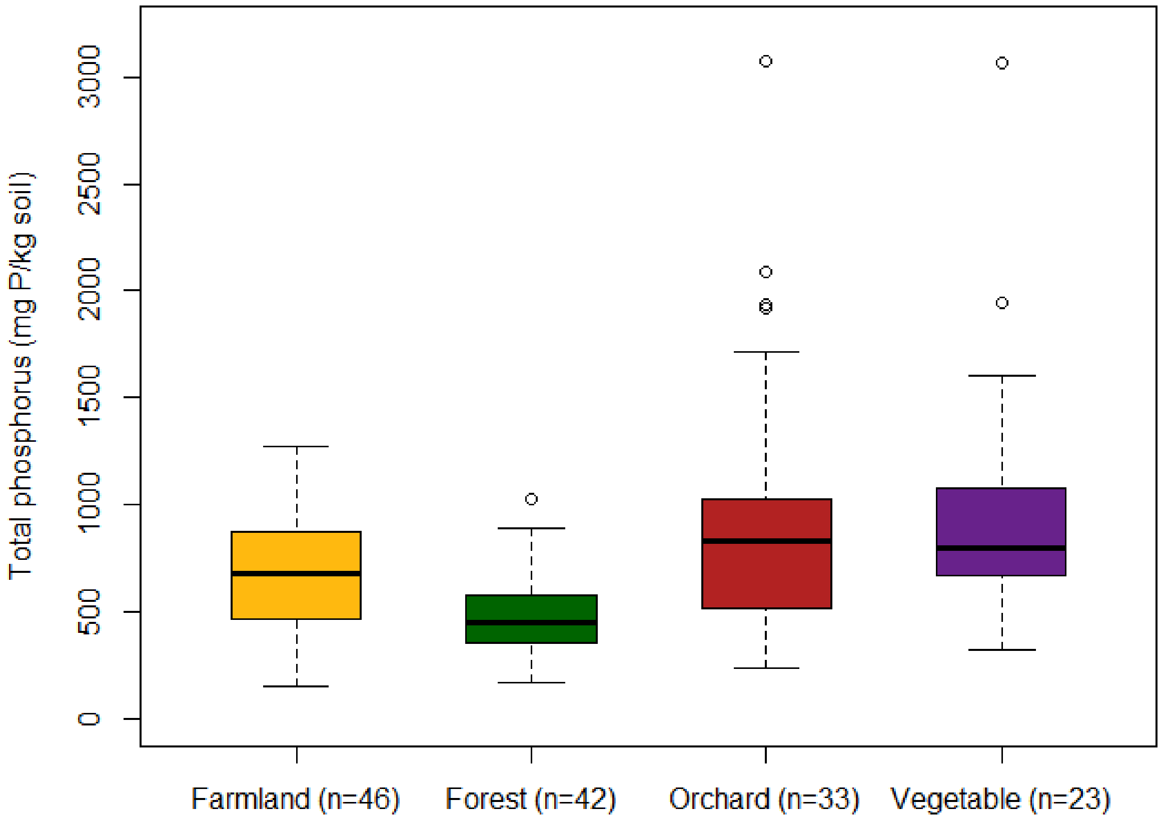


Figure 37 Total phosphorus concentration in the A horizon. The boxplot show the median and the 25th and 75th percentiles. The whiskers show the minimum and maximum value. The dots in the figure represents outliers in the dataset; defined as Q1±1.5*IQR, where IQR = Q3 - Q1.

Globally the total phosphorus concentrations in soil varies widely, usually somewhere between 100-3000 mg/kg (Condron et al., 2005). In the Morsa Watershed, which was studied in the Eutropia project (Section 1.3) (using the same analytical methods), the total phosphorus concentration in the A_p horizon in agricultural soil was between 1000 and 2000 mg P/kg (Opland, 2011). In the A horizon of forest soils the concentration was somewhat lower, with values between 750 and 1370 mg P/kg (Desta, 2013). The total phosphorus concentrations in the A horizon in the local catchment are rather low compared to the concentrations reported by Condron et al. (2005), Opland (2011) and Desta (2013), with median and 75th percentile below 1100 mg P/kg soil (Figure 37) for all land management practises and forest areas. This is somewhat surprising thinking about the excessive use of manure and fertilizers in the local watershed, i.e. ~9 times larger than the average in the Norway (Section 3.1.2). A plausible cause for the low amount of phosphorus in the soil, despite the excessive application of phosphorous fertilizer, is the low capacity of the soil to adsorb phosphorus. The agricultural soil in the Morsa watershed the soils are rich in organic matter and thus have a high phosphorous sorption capacity. On the other hand, the soils in the study area around Yuqiao reservoir have a low sorption capacity and thus low phosphorus concentration due to low organic matter content and silt loam texture with 1:1 type clays. The phosphorus sorption capacity of the soil in the local watershed was determined, and the results are given in Figure 38.

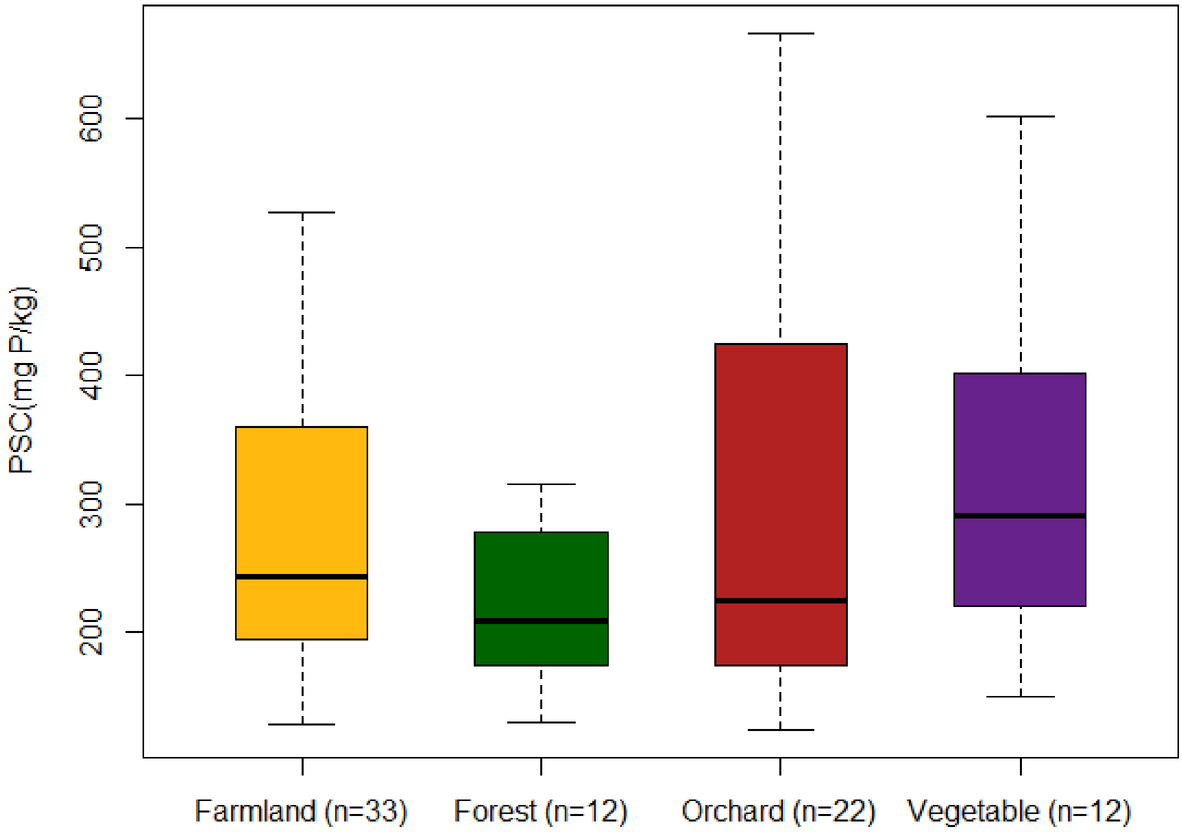


Figure 38 The phosphorus sorption capacity of farmland, forest, orchard and vegetable soils. The boxplot show the median and the 25th and 75th percentiles. The whiskers show the minimum and maximum value.

The average phosphorous sorption capacity between the different land-use categories shown in Figure 38 is similar to differences in the total phosphorus concentrations shown in Figure 37. The total phosphorus is higher than the phosphorus sorption capacity, which implies oversaturation of phosphorus in the soil. The differences in phosphorous sorption capacity between the different land-use categories do not appear to be explained by differences in soil organic content (Figure 34). On the contrary, soils with the highest organic content have the lowest capacity to sorb phosphorous. The differences in phosphorous sorption capacity appear instead to follow the CEC_e (Figure 36), though the dissimilarities are small. It is likely that adsorbed iron (III), acting as a charge bridge, may play an important role in governing the adsorption capacity, though there exists no data to substantiate this. The contribution of inorganic and organic phosphorus pools in the soil is shown in Figure 39. The largest fraction is inorganic phosphorus for all land-use practices; the average percentage of inorganic phosphorus is 74%, 59%, 72% and 69% for farmland, forest, orchard and vegetable. The organic phosphorus fraction is the same in orchard and forest, and somewhat higher in the vegetable fields. Farmland has the lowest concentration. The differences between the organic phosphorus is not significant (see error bars in Figure 39), so the assumption is that they are practically the same.

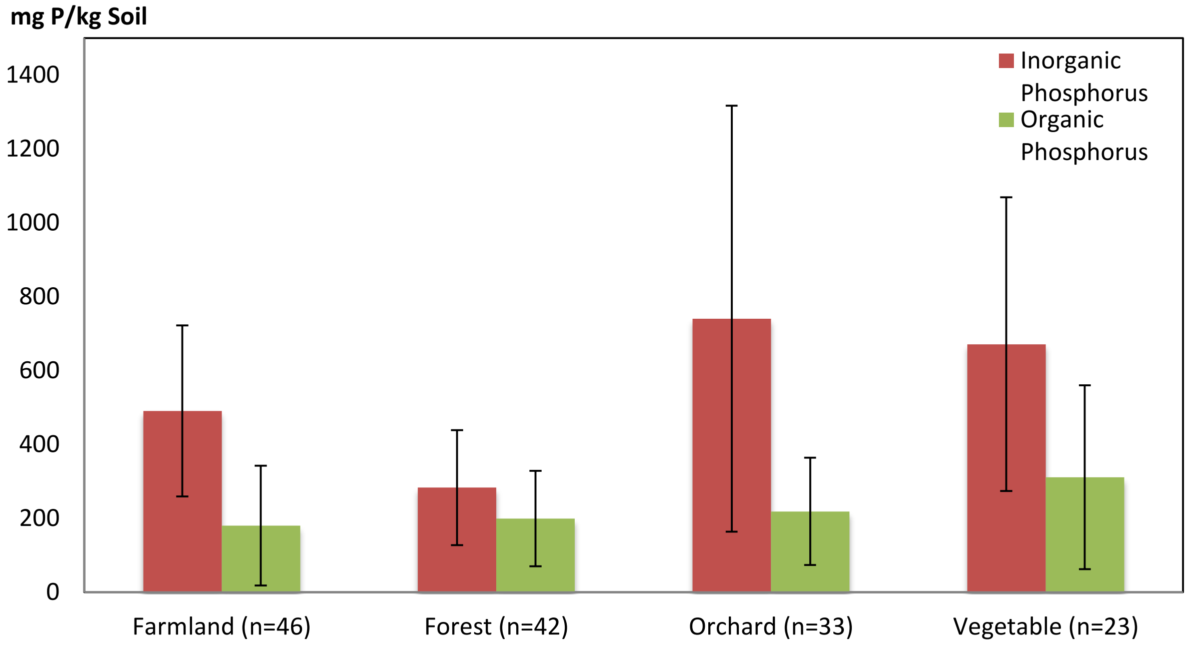


Figure 39 Average concentration of inorganic and organic phosphorus in the A horizon. The error bars shows the standard deviation expressing the spatial variation.

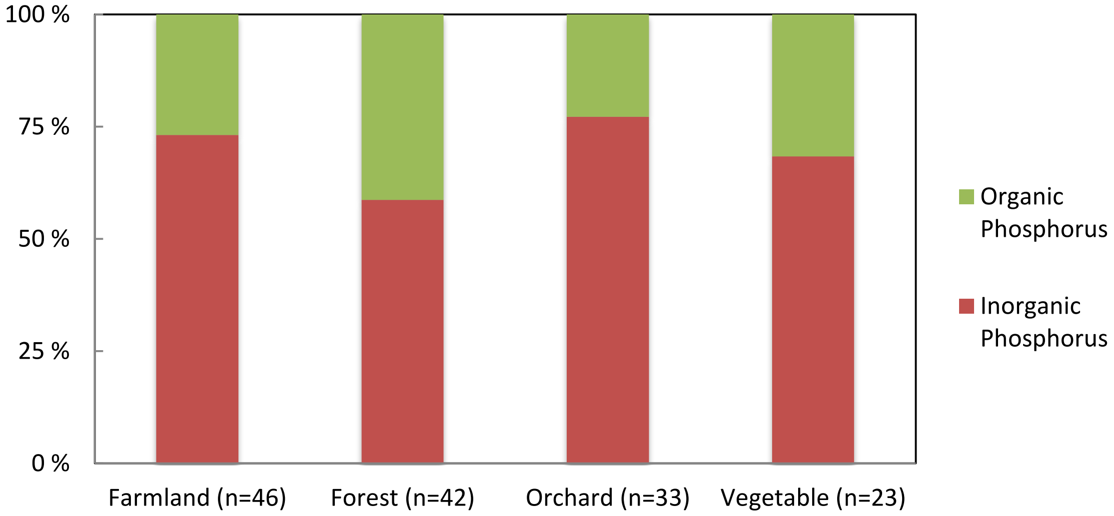


Figure 40 The relative contribution of inorganic and organic phosphorus in the A horizon.

The farmland soils have the lowest average concentration of inorganic phosphorus, as well as a smaller spatial variation (shown by the error bars in Figure 39) compared to orchards and vegetable fields. This is possibly due to the fact that the management practice for farmland is more uniform compared to vegetable and orchards.

The inorganic and organic phosphorous pool in forest soils are quite similar, comprising 59% and 41%, respectively (Figure 39). The relatively large organic phosphorus pool is most likely explained by the relatively high organic matter content in the forest soils (Figure 34). The forest soil samples where mainly collected by Joshi (2014), and in his thesis he argues that the inorganic fraction is this high in the forests because some of the samples are taken from forests that are used for production of timber. The timber production sites are somewhat fertilized to increase the growth, and the farmers in some cases remove unwanted plants – both practices interfering with the natural cycle, increasing the amount of inorganic phosphorus and decreasing the amount of organic phosphorus. The phosphorus pools in the orchards and vegetable garden soils are quite similar. The inorganic fraction contributes with 72 % and 69 %, respectively, of the total phosphorus. Both are fertilized with manure, and are much heavier fertilized than farmlands (Table 4, page 25). The vegetable fields show a somewhat larger amount of organic phosphorus (41%) compared to the other land-use practices, which can be explained by the manure application.

A ^{31}P-NMR study was performed on four soil samples from forest and orchards to identify the different organic phosphorus compounds in the soil. The result showed the same compounds forest and orchard, and the results for one forest sample are shown in Figure 41.

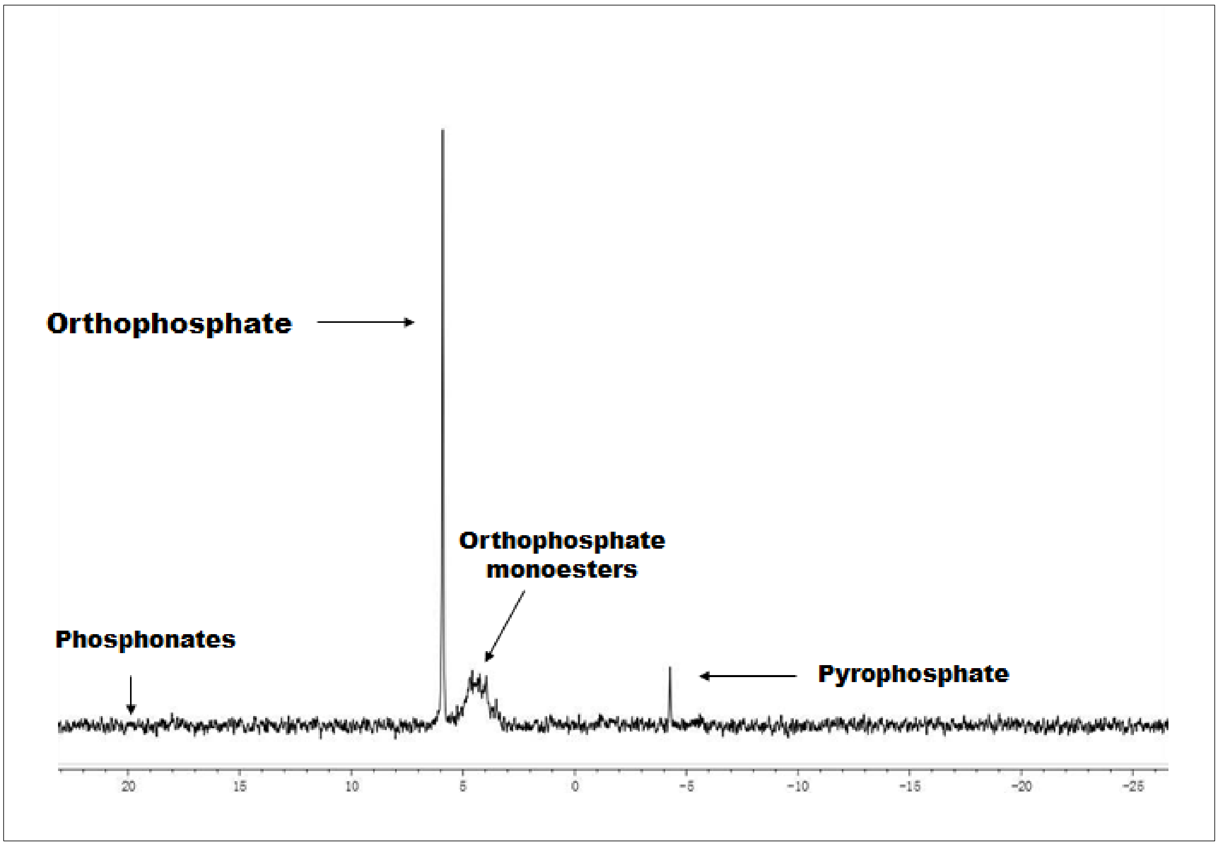


Figure 41 A ^{31}P-NMR spectra of a forest sample (NaOH-EDTA extracts, 400 Hz), with arrows indicating the position of different organic phosphorus compounds.

In addition to the orthophosphate peak, an orthophosphate monoester peak and pyrophosphate peak were detected. The area where phosphonates should be detected is marked in the spectra, but this compound is not present in the sample. The orthophosphate monoester and pyrophosphate are rather common in soils because they both are relatively stable.

4.2.6 Phosphorus fractions in soil solution

The phosphorus fractions in soil-water are presented in Figure 42. The phosphorus concentrations in the agricultural soil solutions are very high compared to the average total phosphorous concentration in the reservoir (33µg P/L). In the surface waters the median concentration is 200µg P/L (n=357). This illustrates the large potential for leaching and phosphorous flux to the reservoir. All agricultural land-use categories show a huge span in the concentration of phosphorous. A few samples have extremely high concentrations may have been collected following the application of fertilizer or manure. Other samples have concentrations below 60µg P/L. The one sample collected from forest soil has a relatively low concentration of phosphorous. The dominant phosphorous fraction in the soil-water is free inorganic phosphate. An exception is a sample from an orchard soil with high turbidity (137 NTU) and dominant colloidal phosphorus fraction.

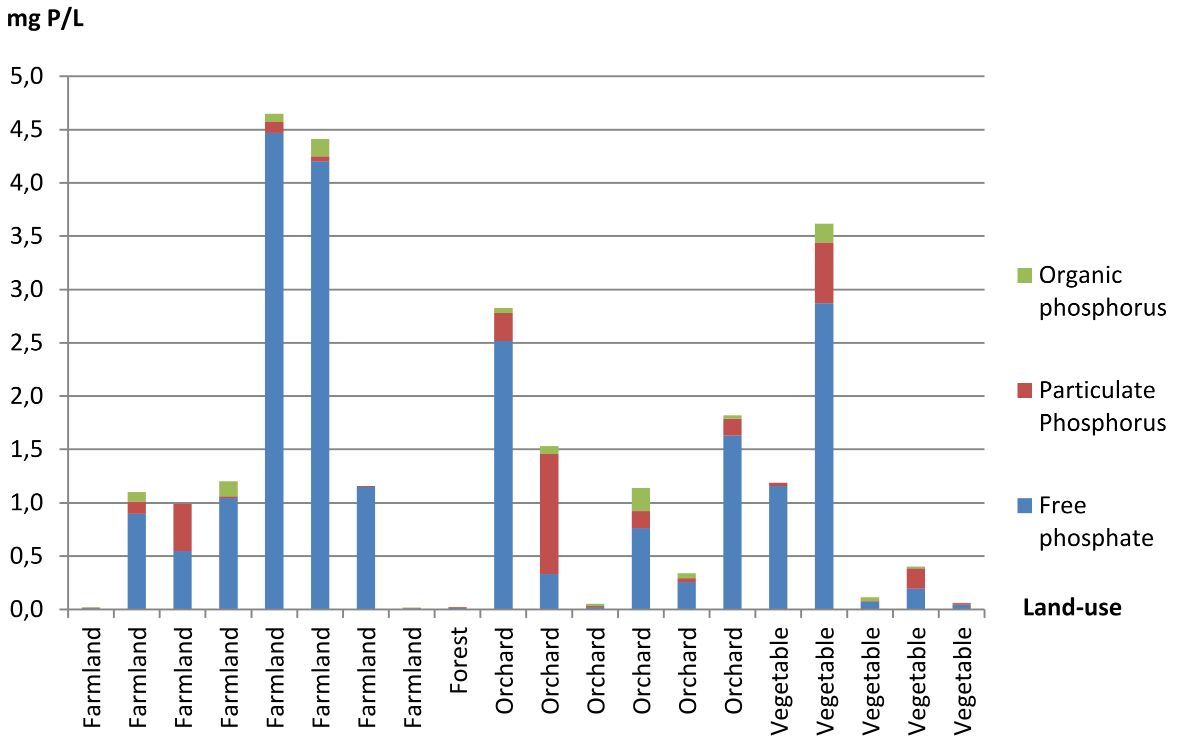


Figure 42 Phosphorus fractions in soil water (in mg P/L).

Generally the relative fraction of free phosphorous (dissolved inorganic phosphorus) increases with increasing concentration of total phosphorus, while the relative amounts of colloidal and organic phosphorus are highest in samples with relatively low total phosphorus (Figure 43). This suggests that the main process governing the high total phosphorus concentrations are the release of inorganic free orthophosphate. Orthophosphate is usually not found in high concentrations in soil solution due to that it is rapidly assimilated and efficiently adsorbed to the soil. The existence of very high concentrations of free phosphate in the agricultural soil solutions implies that the farmers are adding too much fertilizer relative to what can be assimilated by the crops, and that the adsorption capacity of phosphorous is exceeded allowing no more phosphorous to be adsorbed to the soils.

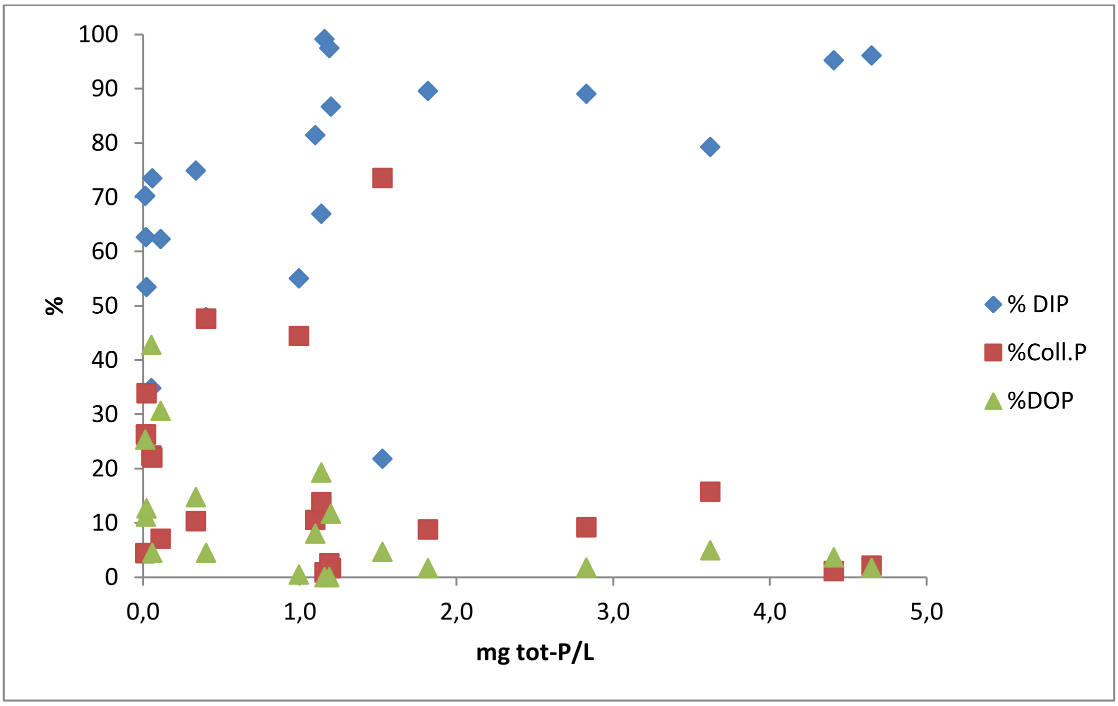


Figure 43 Distribution of phosphorus fractions with increasing total phosphorus concentration in soil water.

4.3 Physiochemical properties of the soil horizons relative to land-use.

In the previous section only the A horizon in the different land-use categories was addressed. In this section the spatial differences in physiochemical properties and phosphorus concentrations between soil horizons (A, B and C) within the different land-use categories are discussed. The variables assessed are pH, organic matter content, phosphorus fractions and soil texture. For the first three variables there are samples from 3 farmland fields, 3 orchards, and 4 vegetable gardens (only three sites were PSD analysed). The forest soil profiles did not have a C horizon, and are therefore not included in this assessment. Soil profiles in the study area had no clear distinction of the horizon boundaries. The collection of the three generic horizons was therefore collected mainly based on depth (Section 3.2).

In general, the soil chemistry changes downwards through the soil horizons. The different horizons are affected by different processes, and are affected by the local environment. The A_p soil layer in farmland areas are greatly affected by human activity, and are not in its natural state, while the B and C horizon is covered by the upper layer and are mostly influenced by the above soil layer due to vertical water flow, and the physiochemical characteristic of the soil itself.

4.3.1 pH

The soil pH in natural systems is increased by carbonate weathering (in carbonate rich soils) and lowered by acid production through humic and carbonic acid deprotonation (Section 4.2.1). In agricultural soils the carbonates also stems from artificial liming. In soil systems the balance between the proton consumption by weathering and proton production by weak acids (carbonic and humic acids) dictate the soil pH. The organic content of the soil are usually higher in the A horizon then in the deeper horizons. This is due to the crop remains and manure that is ploughed into or accumulated on top of this horizon. Organic rich soils would be expected to have a lower pH in the uppermost horizon and increase downwards through the soil horizons. This is because of the dominance of acidic humic compounds producing protons in the A horizon. Liming of agricultural soils generates an alkaline solution depending on the type of lime (carbonate, oxide or hydroxide). If the soils are limed regularly, the pH would therefore be expected to be higher in the A_p layer compared to B and C. Figure 44, Figure 45 and Figure 46 show no clear trends in the pH value through the A, B and C horizon for different sampling sites according to land use practice.

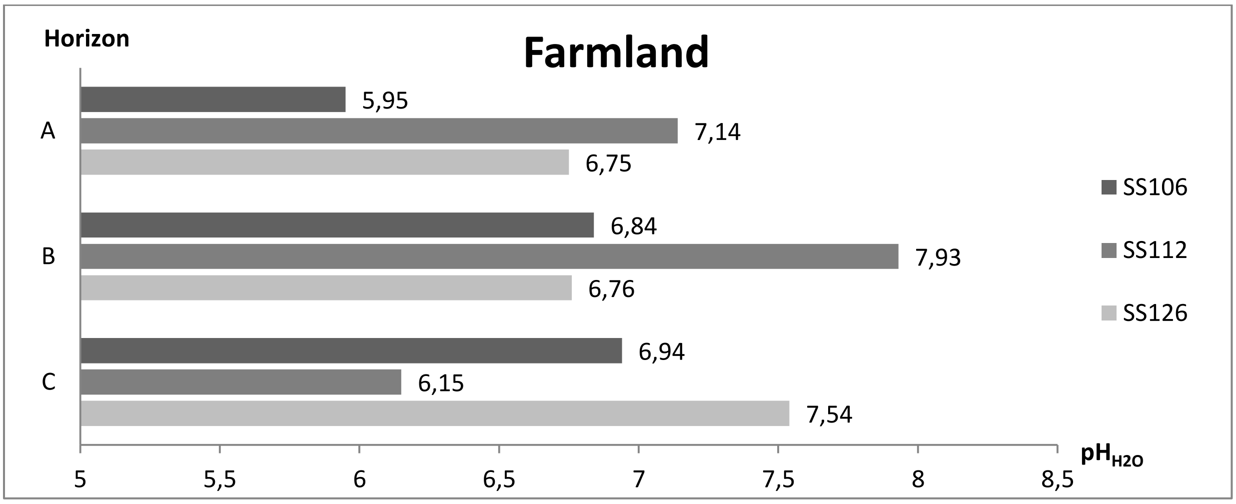


Figure 44 The pH value for each horizon (A_p, B and C) in three different farmland sampling sites.

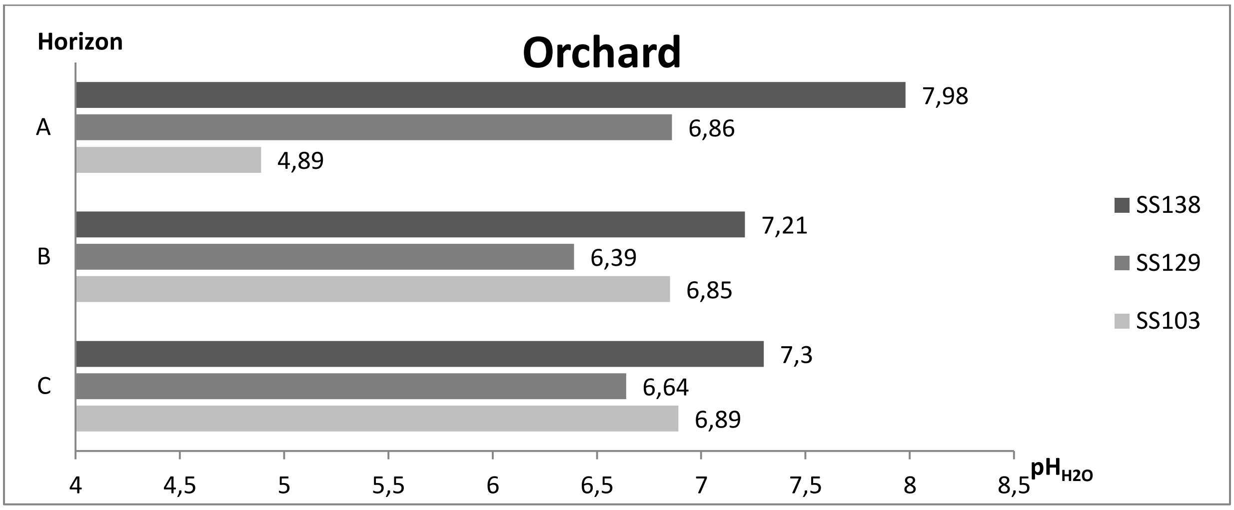


Figure 45 The pH value for each horizon (A, B and C) in three different orchard sampling sites.

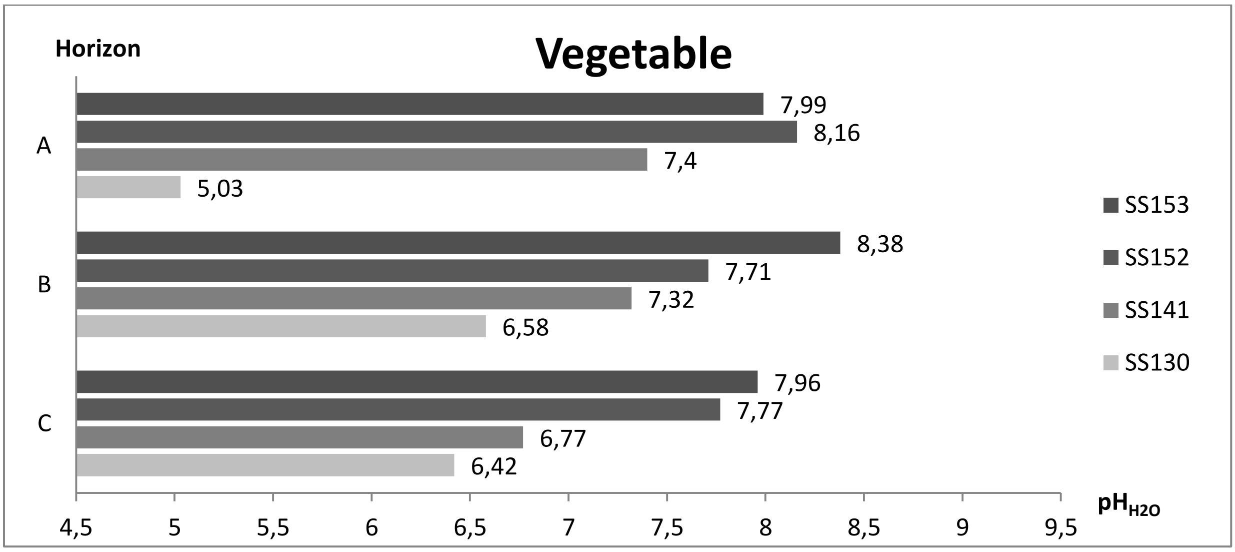


Figure 46 The pH value for each horizon (A_p, B and C) in four different vegetable sampling sites.

4.3.2 Organic matter content

The organic matter content is expected to be higher in the A horizon, compared to B and C horizon in natural and agricultural soils. In orchards the downfall of leaves etc. increases the organic matter content, together with the use of manure in pits around the trees. The content of organic matter in the vegetable gardens is explained by multiple agricultural practises. Manure is mostly used as a fertilizer, and it is a common practice to discard the plant litter back to the soils after the harvest (Zhou, 2012), both increasing the organic matter content in the A_p horizon. Farmlands on the other hand, are not fertilized with manure, and crop removal prevents the accumulation of organic matter in the A_p horizon. Only limit amount of harvest remains are left in the fields, and do not contribute much to the organic matter content.

In general Figure 47 and Figure 48 shows that due to the removal and enhanced decomposition of organic matter in the farmland fields and vegetable garden, the soil organic matter content is kept very low in the A_p horizon despite addition of plant remains (only vegetable fields) and manure. All the vegetable garden soils shows and overall decrease from A_p to C horizon, SS141 shows a rapid decrease from A_p to B, but increases almost up to A_p levels in the C horizon.

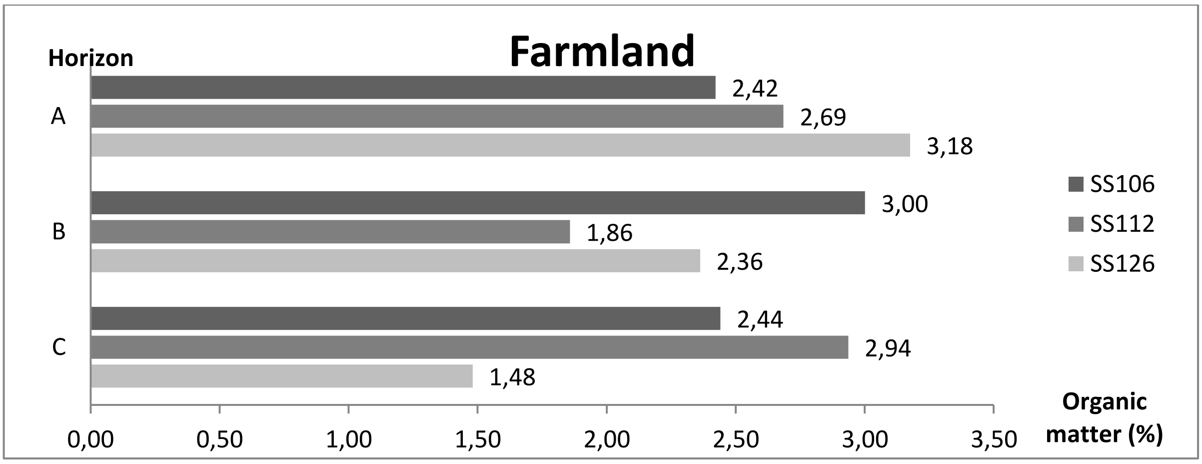


Figure 47 The organic matter content (%) for each horizon (A_p, B and C) in three different farmland sampling sites.

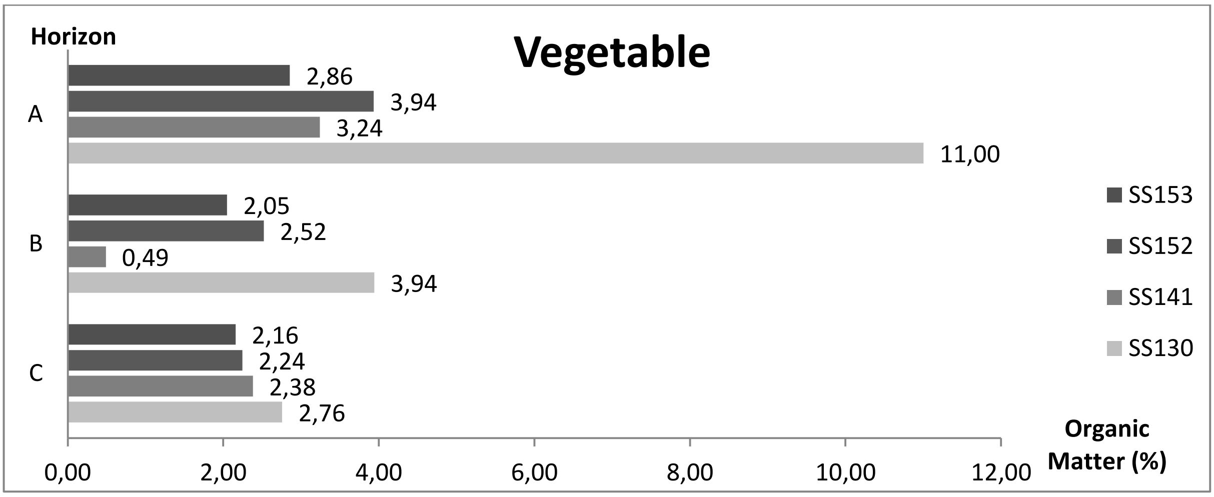


Figure 48 The organic matter content (%) for each horizon (A_p, B and C) in four different vegetable sampling sites.

In Figure 49 we can see an expected trend in two of three cases where the organic matter content is largest in the A horizon, and decreases through B and C, due to the lack of tilling and contribution of litter fall.

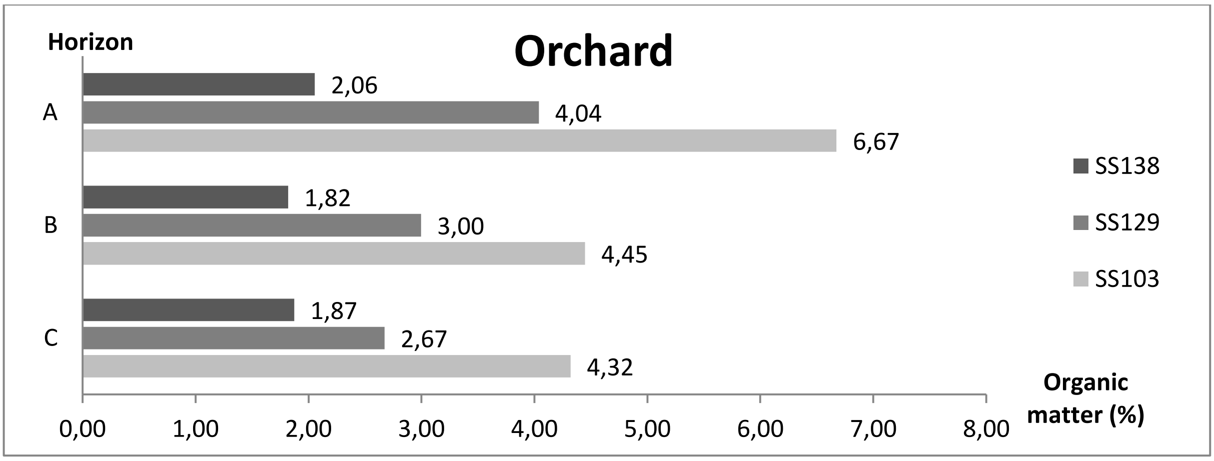


Figure 49 The organic matter content (%) for each horizon (A_p, B and C) in three different orchard sampling sites.

4.3.3 Soil texture

In general the soil texture is finer in the A layer than further down through the soil profile. In the case where the unconsolidated material is derived by weathering of the underlying bedrock the uppermost layer is usually the most weathered soil, while the soil just above the bedrock has a more coarse texture with sandier soil and some pebbles and larger rocks. Figure 52, Figure 50 and Figure 51 shows the particle size distribution for farmland, orchard and vegetable sites, and show no trend as described above. This is likely due to that the samples are collected in the lowland area of the local watershed, which has a deltaic alluvial soil.

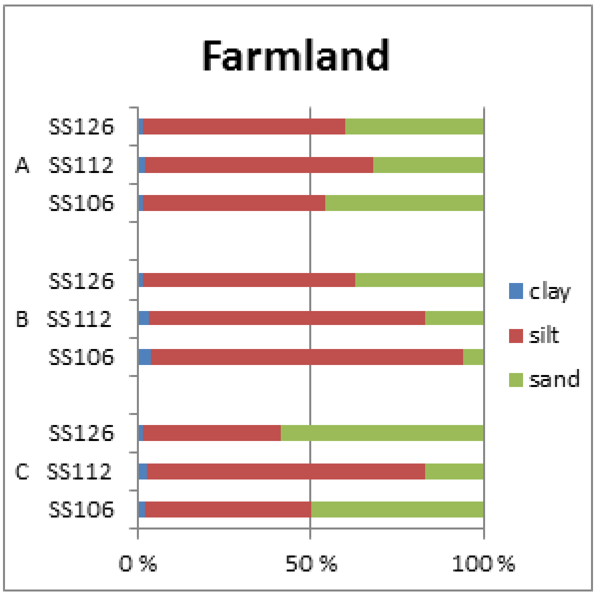


Figure 52 Soil texture in three farmland sites

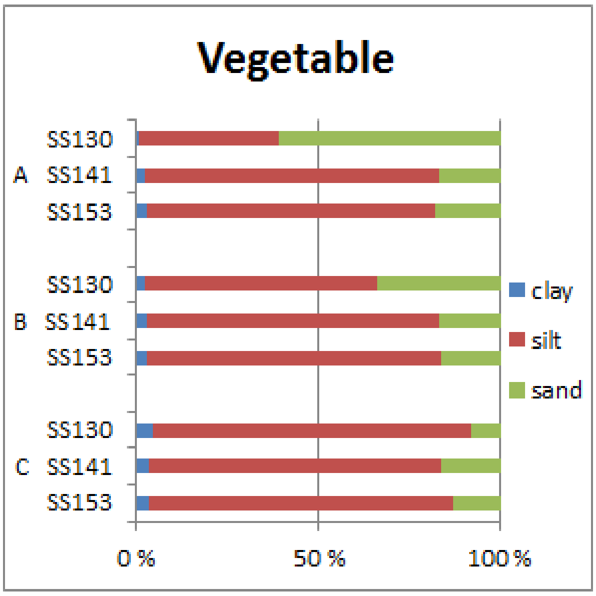


Figure 50 Soil texture in three vegetable sites

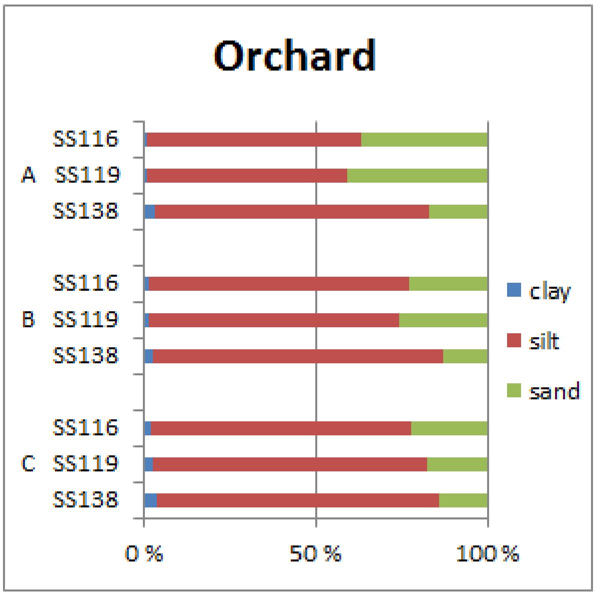


Figure 51 Soil texture in three orchard sites

4.3.4 Phosphorus fractions

The phosphorus concentration in agricultural soil is greatly influenced by the application of inorganic fertilizers and manure. The concentration of phosphorus divided into inorganic and organic phosphorus in the A, B and C horizon is shown in Figure 53, Figure 54 and Figure 55. As previously stated the inorganic phosphorus is the main constituent in the total phosphorus pool. This is also valid for the B and C horizon, which can be seen from the figures below. Generally the phosphorus concentration decreases through the horizons for all land-use practices, indicating that application of phosphorus to the top layer is an important parameter for the total phosphorus concentration in the soil.

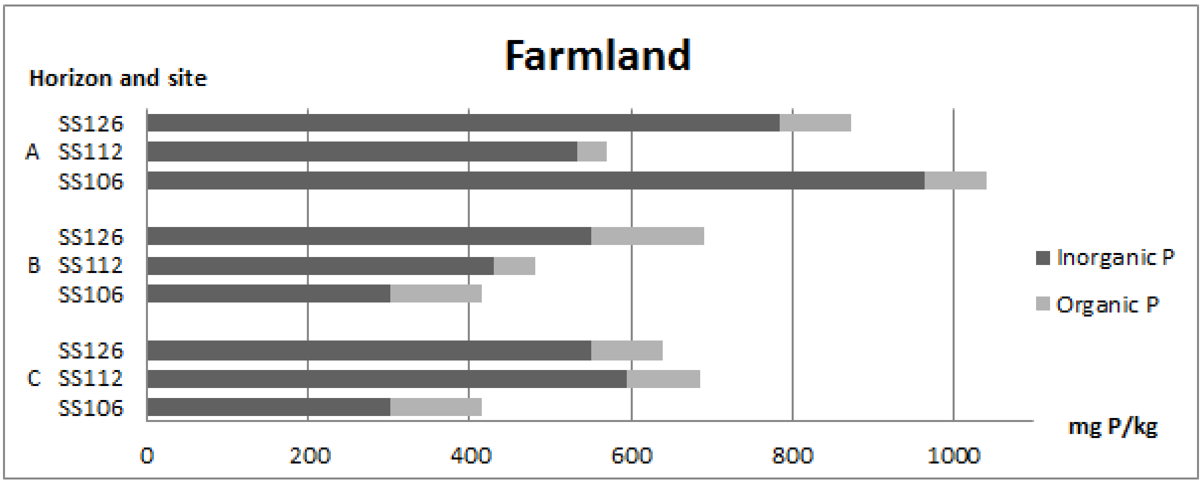


Figure 53 The concentration of total phosphorus in A_p, B and C horizon for farmland sites

In the farmlands (Figure 53) the percentage of inorganic phosphorus decreases slightly from the A_p to the C horizon. This reflects the use of inorganic fertilizers in these areas, which increases the inorganic fraction in the A_p layer. The ratio between the % organic phosphorus and % inorganic phosphorus increases from A_p to B for all the samples, and both decrease and increase from B to C.

Orchards have more variability between the sites, and SS129 is clearly different with 98 % inorganic phosphorus in the A horizon, compared to 71 % and 40 % for SS103 and SS138 respectively. The percentage of organic phosphorus decreases from A to B, and increases in C for SS103 and SS138. The percentage of organic phosphorus in sample site SS129 increases up to the same level as the two other samples, indicating that the A layer most likely is fertilized with inorganic fertilizers, and not manure which is common. The figure also shows us that the relative content of inorganic phosphorus increases with total phosphorus, as previously discussed

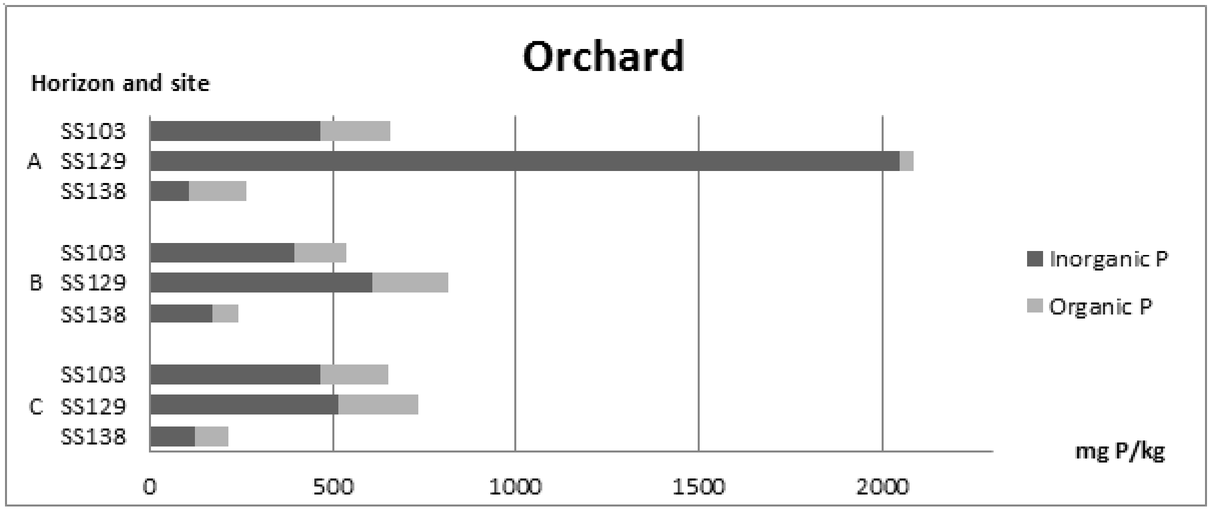


Figure 54 The concentration of total phosphorus A, B and C horizon for orchard sites.

In the vegetable gardens the organic phosphorus fraction is between 30 % and 50 %, and is large compared to farmland and orchards; In farmlands and orchards this fraction is commonly below 30% (not including SS138 which has 60% organic phosphorus in the A layer).

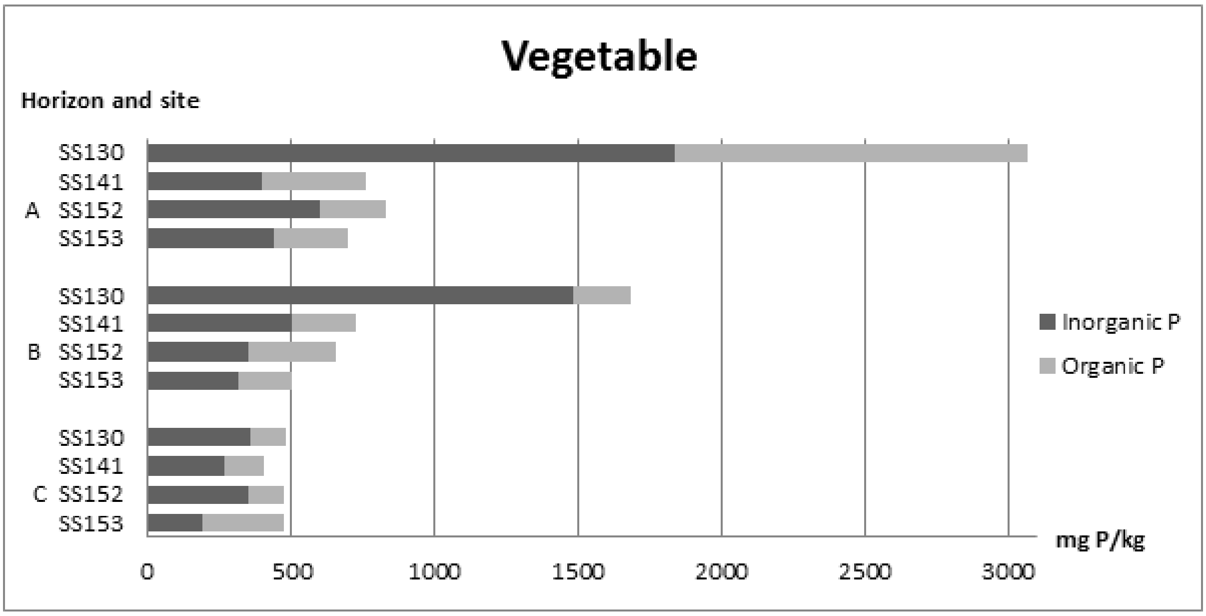


Figure 55 Total phosphorus concentration divided into inorganic and organic fraction in A_p, B and C horizon for vegetable sites

5. Conclusions

A cluster analysis of the soils physiochemical properties and land-use shows that forest and orchard land-use are related to relatively high sand and organic matter content, while the vegetable gardens are related to soils with relatively high pH and content of finer soil particles. This reflects that soils with high quality (most fertile) are used for growing vegetables, while the areas with poor soil quality are either used to grow fruit trees, produce timber, or just left in the natural state (forest). The phosphorus pools are found to be relatively independent variables regarding the studied soils physiochemical characteristics. A Principal component analysis (PCA) indicates that the spatial variation in phosphorus pools cannot be explained by the soil horizon, pH or content of finer particles. This might imply that the different land-use is the most important explanatory factor.

In general the soils from different land-use do not differ significantly with regards to the studied physiochemical parameters. The median pH is between seven and eight, indicating that the calcium concentration is controlling the concentration of orthophosphate in solution through the solubility of calcium phosphate. The pH is governed by the carbonate weathering and the organic matter content in the soil. The soils have a silt loam texture with a predominance of 1:1 clays, a relatively low organic matter content (generally between 2 and 7.5%), and a medium to low cation exchange capacity. This implies that the soil have a poor ability to adsorb phosphorus, which is also shown by the low phosphorus sorption capacity.

The concentration of total phosphorus was found to be between ca 450 mg P/kg soil and 850 mg P/kg, where the highest concentration is found in orchards and vegetable gardens, even though the differences are not large. Comparing the total phosphorus concentration to the phosphorus sorption capacity it is clear that the soils are oversaturated with phosphorus. This is reflected by a high concentration of phosphorus in soil-water, with a predominant fraction of free phosphate in the solution. The silt loam soil texture and low organic matter content render the soil in the area susceptible for erosion. This, combined with high phosphorus content in the A horizon, and a limited vertical percolation of water through the horizons, due to type 1:1 clay, makes erosion and surface runoff important mobilization and transport factors of phosphorus from agricultural land to the reservoir.

The soils physiochemical parameters generally exhibit no clear trends down through the soil horizons (i.e. from A, through B to C). An important exception is for the sizes of inorganic and organic phosphorus pools, which clearly decreases downwards through the soil profiles. This reflects the application of fertilizers and manure in the A layer of agricultural soils

The level of phosphorous in the soils from the local catchment around the Yuqiao reservoir is rather low compared to the amounts measured in the soils from the Morsa watershed in Norway. This is surprising considering that the amount of phosphorus applied to the fields around Yuqiao is estimated to be about 7 times larger than the average amount of phosphorus added to the soils through fertilizing in Norway. The explanation of the relatively low concentrations is probably the low sorption capacity of the soils in the study area.

The extreme over-application of phosphorous, relative to what the crop production can assimilate, along with the soils lack of ability to adsorb more phosphorous leads to that most of the applied phosphorous is washed out of the soil. Limiting the application of phosphorous fertilizers in the local watershed is thus an abatement action that will significantly reduce the flux of phosphorous to the watershed. Although this may appear as a ‘low-hanging-fruit’ the practical implementation is not trivial. Lack of agricultural literacy on best-management-practices and means of disposal of waste from husbandry are major thresholds.

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List of appendices

Appendix A. Sample sites, land-use practice and coordinates

UiO no.	Sinotropia no.	Soil Horizon	Land-use	Coordinates	
				x	y
U110	SS079	A	Orchard	117.5881	40.27607
U111	SS080	A	Forest	117.5593	40.2473
U112	SS081	A	Orchard	117.5767	40.23575
U113	SS082	A	Forest	117.5833	40.21578
U114	SS083	A	Forest	117.5965	40.20564
U115	SS084	A	Orchard	117.6097	40.19848
U116	SS085	A	Farmland	117.6172	40.18232
U117	SS086	A	Farmland	117.6535	40.15769
U118	SS087	A	Farmland	117.7002	40.16361
U119	SS088	A	Farmland	117.6814	40.16525
U120	SS089	A	Farmland	117.6301	40.09593
U121	SS090	A	Farmland	117.4898	39.9988
U122	SS091	A	Farmland	117.4947	40.0123
U123	SS092	A	Farmland	117.532	40.0122
U124	SS093	A	Farmland	117.5817	39.9828
U125	SS094	A	Farmland	117.5817	39.9828
U126	SS095	A	Farmland	117.5896	39.9589
U127	SS096	A	Forest	117.5628	40.0804
U128	SS097	A	Farmland	117.6442	40.0044
U129	SS098	A	Orchard	117.6236	40.1963
U130	SS098	A	Orchard	117.6236	40.1963
U131	SS099	A	Vegetable	117.6321	40.2103
U132	SS100	A	Orchard	117.6212	40.2228
U133	SS101	A	Orchard	117.63	40.2268
U134	SS102	A	Orchard	117.6337	40.2326
U135	SS102	A	Orchard	117.6337	40.2326
U136	SS103	A	Orchard	117.6318	40.2469
U137	SS103	B	Orchard	117.6318	40.2469
U138	SS103	C	Orchard	117.6318	40.2469
U139	SS104	A	Orchard	117.6071	40.2378
U140	SS105	A	Vegetable	117.6188	40.2361
U141	SS106	A	Farmland	117.6795	40.1435
U142	SS106	B	Farmland	117.6795	40.1435
U143	SS106	C	Farmland	117.6795	40.1435
U144	SS107	A	Vegetable	117.6575	40.1432
U145	SS108	A	Farmland	117.5659	40.0866
U146	SS109	A	Vegetable	117.6837	40.1092
U147	SS110	A	Farmland	117.6838	40.1099
U148	SS111	A	Vegetable	117.6831	40.1103
U149	SS111	A	Vegetable	117.6831	40.1103

UiO no.	**Sinotropia no.**	**Soil Horizon**	**Land-use**	**Coordinates**	
				x	**y**
U150	SS112	A	Farmland	117.6992	40.1084
U151	SS112	B	Farmland	117.6992	40.1084
U152	SS112	C	Farmland	117.6992	40.1084
U153	SS113	A	Vegetable	117.7005	40.1015
U154	SS114	A	Farmland	117.7053	40.0998
U155	SS115	A	Farmland	117.7113	40.0973
U156	SS116	A	Orchard	117.7179	40.0964
U157	SS116	B	Orchard	117.7179	40.0964
U158	SS116	C	Orchard	117.7179	40.0964
U159	SS116	A	Orchard	117.7179	40.0964
U160	SS116	B	Orchard	117.7179	40.0964
U161	SS116	C	Orchard	117.7179	40.0964
U162	SS117	A	Farmland	117.6938	40.0803
U163	SS118	A	Vegetable	117.6948	40.0828
U164	SS119	A	Orchard	117.6977	40.0803
U165	SS119	B	Orchard	117.6977	40.0803
U166	SS119	C	Orchard	117.6977	40.0803
U167	SS120	A	Farmland	117.7001	40.0794
U168	SS120	B	Farmland	117.7001	40.0794
U169	SS120	C	Farmland	117.7001	40.0794
U170	SS121	A	Farmland	117.6875	40.0682
U171	SS122	A	Vegetable	117.6854	40.0614
U172	SS123	A	Farmland	117.6847	40.0565
U173	SS124	A	Farmland	117.689	40.058
U174	SS125	A	Vegetable	117.6909	40.0578
U175	SS126	A	Farmland	117.6619	40.0811
U176	SS126	B	Farmland	117.6619	40.0811
U177	SS126	C	Farmland	117.6619	40.0811
U178	SS127	A	Farmland	117.641	40.0809
U179	SS128	A	Vegetable	117.6391	40.0782
U180	SS129	A	Orchard	117.6389	40.0792
U181	SS129	B	Orchard	117.6389	40.0792
U182	SS129	C	Orchard	117.6389	40.0792
U183	SS130	A	Vegetable	117.639	40.0795
U184	SS130	B	Vegetable	117.639	40.0795
U185	SS130	C	Vegetable	117.639	40.0795
U186	SS131	A	Forest	117.5155	40.0753
U187	SS132	A	Vegetable	117.4508	40.0194
U188	SS133	A	Farmland	117.4718	40.0226
U189	SS134	A	Farmland	117.4891	40.0124
U190	SS135	A	Farmland	117.4985	40.0065

UiO no.	**Sinotropia no.**	**Soil Horizon**	**Land-use**	**Coordinates**	
				x	**y**
U191	SS136	A	Orchard	117.5014	40.0065
U192	SS137	A	Vegetable	117.5018	40.0068
U193	SS138	A	Orchard	117.5172	40.0106
U194	SS138	B	Orchard	117.5172	40.0106
U195	SS138	C	Orchard	117.5172	40.0106
U196	SS139	A	Vegetable	117.5482	40.0061
U197	SS140	A	Orchard	117.5461	40.006
U198	SS141	A	Vegetable	117.5461	40.006
U199	SS141	B	Vegetable	117.5461	40.006
U200	SS141	C	Vegetable	117.5461	40.006
U201	SS142	A	Farmland	117.5839	39.9988
U202	SS143	A	Farmland	117.5826	39.9867
U203	SS144	A	Farmland	117.5851	39.9712
U204	SS145	A	Orchard	117.5898	39.9538
U205	SS146	A	Orchard	117.5918	39.9469
U206	SS147	A	Farmland	117.6063	40.0005
U207	SS148	A	Orchard	117.0161	38.9851
U208	SS148	A	Orchard	117.0161	38.9851
U209	SS149	A	Orchard	117.6208	39.9859
U210	SS150	A	Farmland	117.6657	40.0059
U211	SS151	A	Farmland	117.708	40.0471
U212	SS152	A	Vegetable	117.7074	40.0471
U213	SS152	B	Vegetable	117.7074	40.0471
U214	SS152	C	Vegetable	117.7074	40.0471
U215	SS153	A	Vegetable	117.5549	40.0805
U216	SS153	B	Vegetable	117.5549	40.0805
U217	SS153	C	Vegetable	117.5549	40.0805
U218	SS154	A	Orchard	117.5838	40.187
U219	SS155	A	Orchard	117.616	40.1815
U220	SS155	A	Orchard	117.616	40.1815
U221	SS156	A	Orchard	117.5962	40.2197
U222	SS157	A	Orchard	117.5927	40.2617
U223	SS158	A	Orchard	117.6269	40.1288
U224	SS159	A	Vegetable	117.6558	40.1086
U225	SS159	A	Vegetable	117.6558	40.1086
U226	SS160	A	Vegetable	117.6212	40.0631
U227	SS161	A	Vegetable	117.5283	40.1271
U228	SS162	A	Orchard	117.5055	40.0772
U229	SS163	A	Forest	117.5082	40.0782
U230	SS164	A	Farmland	117.5032	40.0724

Appendix B. Determination of pH, dry matter and loss on ignition.

B.1 pH

5 mL of soil was mixed with 25 mL deionized H_2O, and put on a shaking table for 1 hour (250 times back and forth) before measuring pH in the suspension. The same procedure was done to determine pH in a 1M KCl solution. The KCl solution was made by dissolving 74.5 KCl in 1000 mL deionized water. The pH meter was calibrated with a standard with pH 4 and pH 7 before use.

Table B.1 pH results

Sinotropia no.	Horizon	pH (H_2O)	pH (KCl)	Sinotropia no.	Horizon	pH (H_2O)	pH (KCl)
SS090	A	7.93	7.16	SS112	A	7.14	6.02
SS091	A	8.03	7.54	SS112	B	7.93	6.53
SS092	A	7.68	7.35	SS112	C	6.15	4.90
SS093	A	7.52	6.15	SS113	A	7.25	6.30
SS094	A	7.66	7.18	SS114	A	5.86	4.60
SS095	A	7.87	7.24	SS115	A	6.28	5.02
SS096	A	8.69	8.37	SS116	A	6.71	6.28
SS097	A	7.98	7.42	SS116	B	6.70	6.34
SS098	A	8.18	7.09	SS116	C	6.25	5.34
SS098	A	8.09	6.9	SS116	A	7.98	7.60
SS099	A	6.28	5.19	SS116	B	7.05	6.47
SS100	A	5.08	4.17	SS117	A	6.16	5.07
SS101	A	6.01	5.12	SS118	A	6.69	6.36
SS102	A	5.81	4.82	SS119	A	6.21	5.99
SS102	A	6.02	4.85	SS119	B	6.56	5.79
SS103	A	4.89	3.78	SS119	C	6.81	5.56
SS103	B	6.85	5.42	SS120	B	8.16	7.54
SS103	C	6.89	5.49	SS120	C	7.93	6.69
SS104	A	6.04	5.16	SS121	A	5.87	4.51
SS105	A	7.73	7.23	SS122	A	7.28	7.04
SS106	A	5.95	4.83	SS123	A	6.77	5.31
SS106	B	6.84	5.89	SS124	A	7.8	6.41
SS106	C	6.94	5.61	SS125	A	7.92	7.47
SS107	A	7.52	7.03	SS126	A	6.75	5.8
SS108	A	6.71	5.56	SS126	B	6.76	5.58
SS109	A	6.39	5.80	SS126	C	7.54	5.87
SS110	A	5.53	4.51	SS127	A	6.28	5.46
SS111	A	6.76	6.56	SS129	A	6.86	6.31
SS111	A	7.60	7.14	SS129	B	6.39	5.24

Table B.2 pH results

Sinotropia no.	Horizon	pH (H_2O)	pH (KCl)	Sinotropia no.	Horizon	pH (H_2O)	pH (KCl)
SS129	C	6.64	5.35	SS147	A	8.02	7.38
SS130	A	5.03	4.82	SS148	A	7.43	6.79
SS130	B	6.58	6	SS148	A	7.01	6.16
SS130	C	6.42	5.12	SS149	A	7.98	7.41
SS131	A	7.89	7.14	SS150	A	7.17	6.63
SS132	A	8.04	7.17	SS151	A	7.39	6.49
SS133	A	7.71	6.9	SS152	A	8.16	7.85
SS134	A	7.51	6.46	SS152	B	7.71	6.82
SS135	A	8.23	7.53	SS152	C	7.77	6.85
SS136	A	7.36	6.7	SS153	A	7.99	7.47
SS137	A	7.73	7.05	SS153	B	8.38	7.91
SS138	A	7.98	6.92	SS153	C	7.96	7.31
SS138	B	7.21	6.1	SS154	A	5.23	4.44
SS138	C	7.3	5.84	SS155	A	6.97	6.83
SS139	A	7.75	6.82	SS155	A	7.01	6.8
SS140	A	7.35	7.17	SS156	A	5.79	4.62
SS141	A	7.81	7.4	SS157	A	5.4	4.49
SS141	B	7.98	7.32	SS158	A	6.01	5.54
SS141	C	7.69	6.77	SS159	A	5.9	5.81
SS142	A	7.44	7.19	SS159	A	6.08	4.86
SS143	A	7.86	7.48	SS160	A	6.29	6.15
SS144	A	7.55	7.16	SS161	A	7.84	7.61
SS145	A	5.43	4.92	SS162	A	7.47	7.49
SS146	A	7.01	6.21	SS163	A	8.05	8.08
				SS164	A	7.99	7.44

B. 2 Dry matter %

About 10-15 g of soil was weighed into a dry container, and dried overnight at 105 °C. The balance used is an Ohaus Discovery analytical balance. The Ohaus Discovery analytical balance used for weighing was checked using a reference item with known weight and a control chart (Shewart chart). After cooling the soil in a desiccator it was weighed again, and the dry matter of the soil was calculated by using the equation:

$$W_{dm} = \frac{m_2 - m_0}{m_1 - m_0} * 100$$

m_0 = weight in grams of dry container and lid.

m_1 = weight in grams of soil before drying

m_2 = weight in grams of container, lid and soil after drying

B. 3 Loss on ignition %

About 3 gram soil was weighed into a porcelain crucible using the Ohaus discovery analytical balance, and ignited in the oven at 550°C ± 25 °C for 3 hours. The Ohaus Discovery analytical balance used for weighing was checked using a reference item with known weight and a control chart (Shewart chart). After ignition the soil was put in a desiccator for cooling, and weighed in an analytical balance after approximately 1 hour. The loss on ignition was then calculated by the equation (Krogstad, 1992):

$$LOI\% = 100 - \frac{m_5 - m_3}{m_4} * 100 - W_{H_2O}$$

m_3 = weight of crucible.

m_4 = weight of air dried soil before ignition

m_5 = weight of soil and container after ignition

W_{H2O} equals

$$W_{H_2O} = \frac{m_1 - m_2}{m_2 - m_0} * 100$$

Table B.3 Dry matter, pH and loss on ignition results.

UiO no.	Sinotropia no.	Horizon	W dm%	LOI %	UiO no.	Sinotropia no.	Horizon	Wdm %	LOI %
U122	SS091	A	98.3	3.70	U175	SS126	A	98.4	3.18
U126	SS095	A	98.2	3.15	U176	SS126	B	98.4	2.36
U127	SS096	A	97.6	4.79	U177	SS126	C	98.7	1.48
U128	SS097	A	97.7	3.91	U178	SS127	A	98.2	4.24
U133	SS101	A	97.7	5.46	U180	SS129	A	98.1	4.04
U136	SS103	A	97.6	6.67	U181	SS129	B	97.4	3.00
U137	SS103	B	97.7	4.45	U182	SS129	C	97.3	2.67
U138	SS103	C	97.8	4.32	U184	SS130	B	99.7	3.94
U141	SS106	A	98.9	2.42	U185	SS130	C	96.9	2.76
U142	SS106	B	97.6	3.00	U186	SS131	A	97.9	4.50
U143	SS106	C	98.5	2.44	U194	SS138	B	97.6	1.82
U145	SS108	A	98.2	2.93	U195	SS138	C	97.4	1.87
U147	SS110	A	98.9	2.60	U199	SS141	B	95.8	0.49
U150	SS112	A	98.0	2.69	U200	SS141	C	98.5	2.38
U151	SS112	B	97.3	1.86	U211	SS151	A	97.5	3.59
U152	SS112	C	97.3	2.94	U212	SS152	A	97.8	3.94
U155	SS115	A	98.3	3.03	U213	SS152	B	97.8	2.52
U156	SS116	A	97.8	6.88	U214	SS152	C	97.5	2.24
U157	SS116	B	97.8	5.30	U215	SS153	A	97.9	2.86
U158	SS116	C	98.5	2.51	U216	SS153	B	98.1	2.05
U159	SS116	A	97.8	6.71	U217	SS153	C	97.8	2.16
U160	SS116	B	98.3	2.99	U220	SS155	A	98.0	7.12
U162	SS117	A	98.2	3.27	U221	SS156	A	98.5	3.62
U164	SS119	A	97.8	5.30	U222	SS157	A	97.7	6.24
U165	SS119	B	98.4	2.51	U223	SS158	A	98.4	4.99
U166	SS119	C	98.1	6.71	U227	SS161	A	97.6	5.66
U168	SS120	B	98.4	2.99	U228	SS162	A	98.0	4.81
U169	SS120	C	97.9	7.05	U229	SS163	A	98.4	6.95
					U230	SS164	A	98.0	3.03

Appendix C. Particle size distribution

C. 1 Procedure and method check

The particle size distribution of the soil samples was determined using a combination of ISO11277 (2009) and laser diffraction particle size analysis. To determine the PSD it is important to ensure complete dissolution of soil aggregates. According to the ISO-standard organic matter, carbonates, soluble salts and iron oxides contributes to the soil aggregation, and these compounds must therefore be removed prior to analysis to give a good dispersion of the soil particles.

Table C.1 PSD% pre-treatment procedure

Compound dissolved/removed	Solution	Procedure
Organic matter	H_2O 30 % v/v H_2O_2 2-octanol	2 g soil was mixed with H_2O to become thoroughly wet. 10 mL H_2O_2 was added to the solution, and the mix was left over night (A few drops of 2-octanol was added to avoid sputtering). The solution was centrifuged and decanted. If the supernatant was coloured the procedure was repeated.
Soluble salts and gypsum	H_2O	The soil was added water to produce a 1:5 volume ratio of soil and water. The solution was shaken end-over-end for 1 hour, and then centrifuged. The conductivity of the supernatant was measured; If $E_c > 0.4$ dS/m, the procedure was repeated (This was not necessary for the samples).
Iron oxides	40g/L sodium dithionite, 41 g sodium acetate in 1000 mL H_2O. Buffered to pH 3.8 with Acetic acid	The soil was added the solution in a 1:40 volume ratio of soil:solution, and shaken overnight. The solution was centrifuged and decanted. This was done 2-3 times to ensure complete removal.
Carbonates	82.8 mL HCl, 37% (v/v) diluted to 1000 mL	Around 25 mL 1 M HCl and 50 mL H_2O was added to the soil and heated in a water bath at 80°C for 15 minutes. The suspension was stirred from time to time. After heating in water bath the solution was left over night. The E_c was then measured; if $E_c > 0.4$ dS/m repeat.

The procedure to remove all the above mentioned compounds is a time consuming procedure, so to check if the procedure was necessary, 12 samples were analysed twice, once without any treatment (no treatment), and once where all the compounds where removed (ISO treatment). Sample replicates for both ISO treatment and no treatment where homogenized and transferred to a container, and dried overnight at 105 °C. A small amount of sample (0.100 – 0.250 g) where then weighed into a 50 mL beaker, added about 10 mL of 5% sodium metaphosphate solution (formerly known as Calgon (Yaalon, 1976)) and put in an ultrasonic bath for 5 min. After dissolving the sample in the solution it was transferred to the instrument and analysed. The results are given in Table C.2.

Table C.2 Raw data for both treatments.

UiO no.	ISO treatment			No treatment		
	Clay (volume %)	Silt (volume %)	Sand (volume %)	Clay (volume %)	Silt (volume %)	Sand (volume %)
U110	0,64	61,0	38,4	0,64	61,0	38,4
U128	4,92	74,7	20,4	3,26	72,1	24,6
U140	0,95	68,7	30,4	0,59	64,3	35,1
U145	2,06	82,2	15,7	2,13	84,9	13,0
U148	0,93	38,8	60,3	0,99	38,5	60,5
U183	1,04	46,5	52,5	0,74	38,5	60,8
U187	2,37	74,6	23,0	3,03	74,1	22,9
U193	3,37	83,1	13,5	3,21	79,9	16,9
U196	3,29	76,0	20,7	2,09	73,0	24,9
U204	3,11	84,5	12,4	2,35	82,1	15,6
U230	2,54	79,3	18,2	2,90	75,9	21,2

Table C.3 Absolute and relative difference for samples treated according to ISO11277 and samples with no treatment

Sample ID	Absolute Difference			Relative Difference (%)		
	Clay	Silt	Sand	Clay	Silt	Sand
U110	0,0	0,0	0,0	0,00	0,00	0,00
U128	1,7	2,5	-4,2	25,3	2,29	-12,8
U140	0,4	4,3	-4,7	28,9	4,31	-9,80
U145	-0,1	-2,6	2,7	-2,24	-2,11	12,2
U148	-0,1	0,3	-0,2	-4,21	0,45	-0,22
U183	0,3	8,0	-8,3	21,3	12,2	-10,0
U187	-0,7	0,6	0,1	-17,0	0,50	0,29
U193	0,2	3,2	-3,4	3,22	2,63	-15,5
U196	1,2	3,0	-4,2	27,7	2,67	-12,7
U204	0,8	2,4	-3,2	17,7	1,94	-15,8
U230	-0,4	3,4	-3,0	-9,02	2,87	-10,4

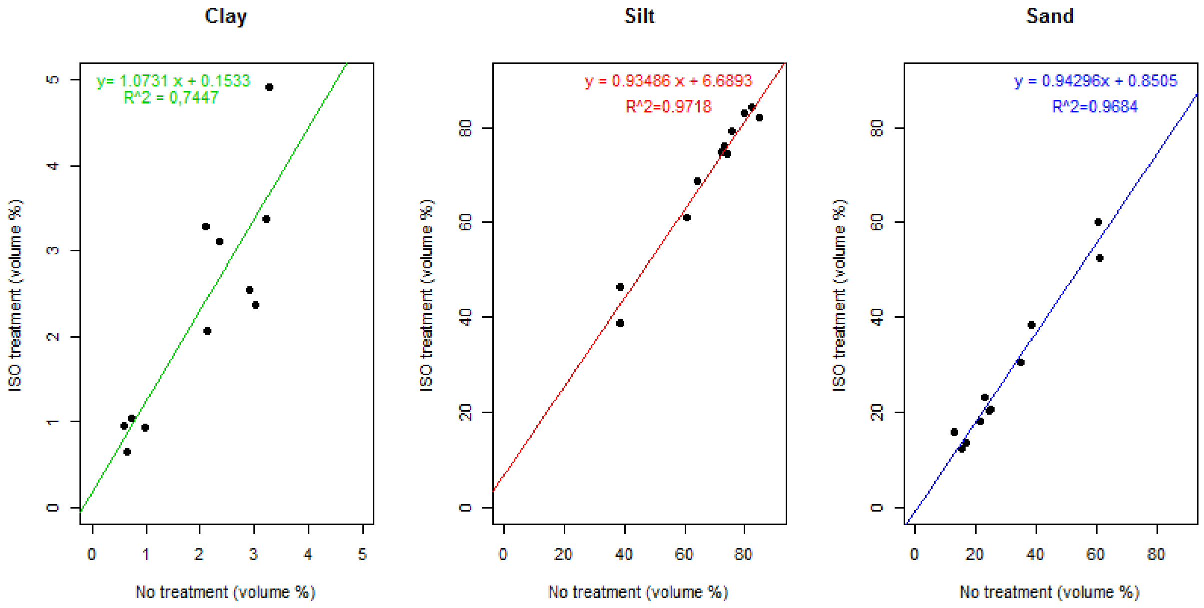


Figure C.1 Correlation

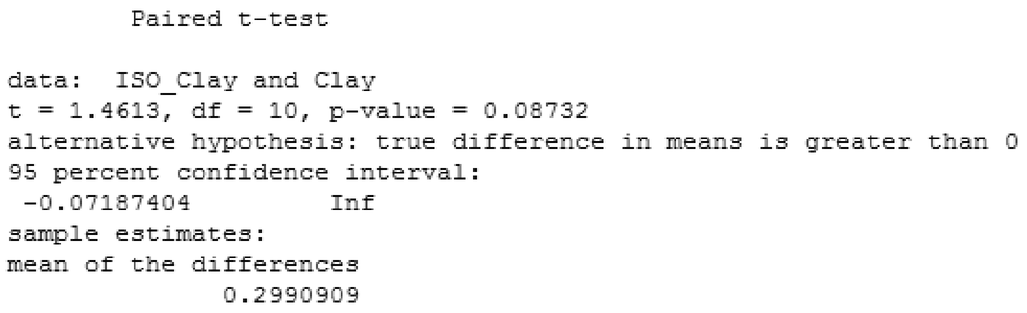
C.2 Paired t-test

A paired t-test where performed in order to check if the differences was significant on a 95 % significance level.

- **Comparing mean differences of clay (ISO treatment) and clay (no treatment)**

H_0: $\mu = 0$ (Mean differences are equal to zero)

H_α: $\mu > 0$ (ISO treatment gives larger clay volume % than no treatment)



```
        Paired t-test

data:  ISO_Clay and Clay
t = 1.4613, df = 10, p-value = 0.08732
alternative hypothesis: true difference in means is greater than 0
95 percent confidence interval:
 -0.07187404         Inf
sample estimates:
mean of the differences
              0.2990909
```

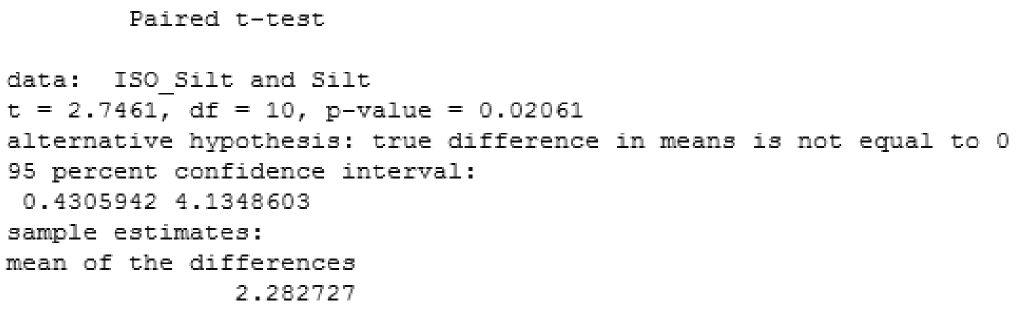
Figure C.2 R output for paired t-test of clay fraction

We cannot reject the null hypothesis at a 95% confidence level. The clay fraction is not significantly larger for ISO treatment compared to no treatment.

- **Comparing silt (ISO treatment) and silt (no treatment)**

H_0: $\mu = 0$ (Mean differences are equal to zero)

H_0: $\mu \neq 0$ (mean difference are not equal to zero)



```
        Paired t-test

data:  ISO_Silt and Silt
t = 2.7461, df = 10, p-value = 0.02061
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
 0.4305942 4.1348603
sample estimates:
mean of the differences
               2.282727
```

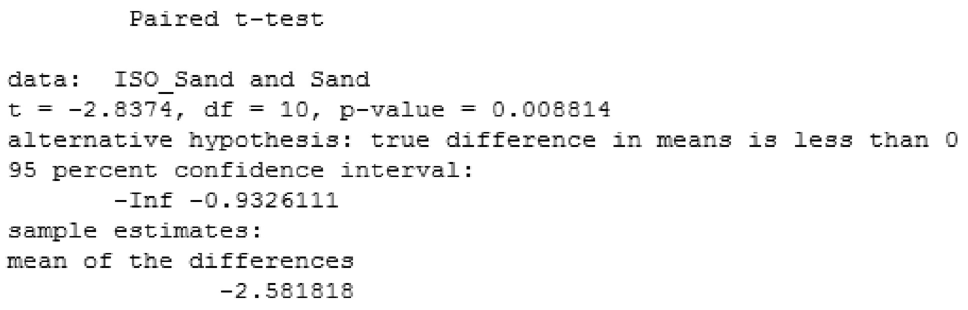
Figure C.3 R output for paired t-test of silt fraction

The null hypothesis can be rejected at a 95% confidence level. The difference lies between 0,43 % and 4,13 %, meaning that the silt fraction is somewhat larger for ISO-treatment compared to no treatment.

- **Comparing sand (ISO treatment) and sand (no treatment)**

H_0: $\mu = 0$ (Mean differences are equal to zero)

H_0: $\mu < 0$ (ISO treatment gives smaller sand volume % than no treatment)



```
        Paired t-test

data:  ISO_Sand and Sand
t = -2.8374, df = 10, p-value = 0.008814
alternative hypothesis: true difference in means is less than 0
95 percent confidence interval:
       -Inf -0.9326111
sample estimates:
mean of the differences
              -2.581818
```

Figure C.4 R output for paired t-test of silt fraction, showing the confidence interval, t- and p-value for the paired t-test

The null hypothesis can be rejected at a 95% confidence level, which means that the sand fraction is somewhat smaller for ISO-treatment compared to no treatment.

For the use in this thesis the differences for ISO treatment and no treatment is not large enough, and the results for no treatment will be used.

Sample ID	**Horizon**	**Particle size distribution %**			**Soil texture**
		Clay	**Silt**	**Sand**	
SS079	**A**	0,64	60,96	38,4	silt loam
SS080	**A**	0,7	49,4	49,9	sandy loam
SS082	**A**	2,47	61,93	35,6	silt loam
SS086	**A**	2,04	53,56	44,4	silt loam
SS091	**A**	2,85	66,15	31	Silt loam
SS095	**A**	2,1	82,1	15,8	silt
SS096	**A**	4	75,8	20,2	Silt loam
SS097	**A**	3,26	72,14	24,6	Silt loam
SS099	**A**	1,57	59,63	38,8	silt loam
SS101	**A**	0,85	59,15	40	silt loam
SS105	**A**	0,59	64,31	35,1	silt loam
SS106	**A**	1,67	52,23	46,1	silt loam
SS106	**B**	3,79	89,91	6,3	silt
SS106	**C**	1,92	48,18	49,9	silt/sandy loam
SS108	**A**	2,13	84,87	13	silt
SS109	**A**	0,8	50,1	49,1	silt/sandy loam
SS110	**A**	1,08	44,92	54	sandy loam
SS111	**A**	0,99	38,51	60,5	sandy loam
SS112	**A**	2,03	65,97	32	silt loam
SS112	**B**	3,17	79,73	17,1	silt loam
SS112	**C**	2,43	80,77	16,8	silt
SS115	**A**	1,64	64,46	33,9	silt loam
SS116	**A**	1	62,1	36,9	silt loam
SS116	**B**	1,76	75,24	23	silt loam
SS116	**C**	1,98	75,82	22,2	silt loam
SS117	**A**	2,08	77,12	20,8	Silt loam
SS118	**A**	1,41	60,49	38,1	Silt loam
SS119	**A**	0,82	58,28	40,9	Silt loam
SS119	**B**	1,67	72,73	25,6	Silt loam
SS119	**C**	2,58	80,02	17,4	silt
SS120	**B**	1,75	58,15	40,1	silt loam
SS126	**A**	1,47	58,23	40,3	Silt loam
SS126	**B**	1,72	60,78	37,5	Silt loam
SS126	**C**	1,41	39,99	58,6	sandy loam

Sample ID	**Horizon**	**Particle size distribution %**			**Soil texture**
		Clay	**Silt**	**Sand**	
SS127	**A**	1,73	66,57	31,7	Silt loam
SS129	**A**	2,01	63,19	34,8	Silt loam
SS130	**A**	0,74	38,46	60,8	sandy loam
SS130	**B**	2,2	63,9	33,9	Silt loam
SS130	**C**	4,64	87,36	8	silt
SS132	**A**	3,03	74,07	22,9	Silt loam
SS133	**A**	2,46	74,04	23,5	Silt loam
SS138	**A**	3,21	79,89	16,9	silt loam
SS138	**B**	2,81	84,09	13,1	silt
SS138	**C**	3,7	82,1	14,2	Silt
SS139	**A**	2,09	73,01	24,9	silt loam
SS140	**A**	1,89	72,41	25,7	silt loam
SS141	**A**	2,52	80,58	16,9	silt loam
SS141	**B**	2,81	80,39	16,8	Silt
SS141	**C**	3,29	80,51	16,2	Silt
SS143	**A**	1,75	68,95	29,3	Silt loam
SS144	**A**	1,92	72,68	25,4	Silt loam
SS145	**A**	2,35	82,05	15,6	Silt loam
SS146	**A**	2,02	79,48	18,5	Silt loam
SS147	**A**	2,06	65,24	32,7	Silt loam
SS150	**A**	2	76,6	21,4	Silt loam
SS151	**A**	3,14	77,26	19,6	silt loam
SS152	**A**	1,74	59,86	38,4	silt loam
SS153	**A**	2,82	79,38	17,8	silt loam /silt
SS153	**B**	2,89	80,71	16,4	silt
SS153	**C**	3,58	83,42	13	silt
SS155	**A**	1,02	52,48	46,5	silt loam
SS156	**A**	1,09	46,61	52,3	sandy loam
SS157	**A**	1,67	68,63	29,7	silt loam
SS158	**A**	1,53	63,67	34,8	silt loam
SS161	**A**	3,23	77,57	19,2	silt loam
SS162	**A**	2,82	77,38	19,8	silt loam
SS163	**A**	1,14	51,56	47,3	silt/sandy loam
SS164	**A**	2,9	75,9	21,2	silt loam

Appendix D. Mineralogy

The data obtained by TOPAS interpretation is given in Table D.1.

Table D.1 Raw data mineralogy (in %)

Sample ID	Quartz	Halloysite	Clinochlore	Muscovite	Albite	Illite	Orthoclase	Microcline
U111	33.6	32.4		20.8	5.17	9.08	10.0	
U122	31.4	23.0	4.26	18.7	4.66	6.43	4.73	6.84
U127	36.2	21.0		19.8	5.50	9.10	6.9	5.10
U131	39.0	21.6		26.7	6.30			6.40
U145	35.0	23.2		25.9	5.70		10.1	
U156	38.5	21.7		26.4	7.01			6.30
U183	36.3	22.9		24.6	5.90		10.3	
U187	35.0	22.5		24.1	5.90		5.10	7.30
U196	34.0	22.7		20.8	5.20	8.00	9.40	
U202	33.0	22.4		19.9	5.20	8.90	10.5	
U210	33.6	21.6		21.2	5.70	8.00	9.80	
U212	33.9	23.7		20.2	4.90	7.40	9.70	
U220	35.0	21.7		22.4		9.40		11.4
U222	33.7	23.7	5.2	22.2	5.30		10.0	
U227	34.0	21.8	5.6	23.4	5.50		9.8	
U230	36.7	23.1		25.6	4.60		10.0	

Appendix E. Phosphorus fractionation

E. 1 Extraction of total and inorganic phosphorus

About 1 g of soil was weighed accurately using an Ohaus Discovery analytical balance, added 5 mL 6M H_2SO_4 and then heated at 70 °C for 10 minutes in a water bath. The Ohaus Discovery analytical balance used for weighing was checked using a reference item with known weight and a control chart (Shewart chart). After heating, the solution was added 5 mL 6M H_2SO_4 and left to cool for 1 hour. The soil used for determination of the total phosphorus fraction was ignited for 1 hour at 550 ±25 °C before the extraction with acid.

After cooling the extract was transferred to a 250.0 mL volumetric flask, and diluted to the mark with distilled water. Before analysis the soil extract was filtered through S&S 589^3 blue ribbon ash less filter paper. Soil extracts were stored dark at 4 °C prior to analysis.

Three samples were weighed in, extracted three times and then analysed to check the methods accuracy. The results for inorganic phosphorus are given in Table E.1 while the results for total phosphorus are given in Table E.2.

Table E.1 The average, standard deviation and relative standard deviation for extraction method and measurements with MBM.

	U164 (mg P/kg)	**U180 (mg P/kg)**	**U181 (mg P/kg)**
Replicate 1	2835	2049	607
Replicate 2	2646	2189	562
Replicate 3	2545	1946	617
Average	2675	2061	595
St.dev	147	122	29
RSD %	5.5	5.9	4.9

Table E.2 The Average, standard deviation and relative standard deviation of the extraction method for total phosphorus and ICP-OES determination.

	U164 (mg P/kg)	**U180 (mg P/kg)**	**U181 (mg P/kg)**
Replicate 1	3072	2089	814
Replicate 2	3200	2216	789
Replicate 3	2696	2431	871
Average	2989	2245	825
St.dev	262	173	42
RSD %	8.8	7.7	5.1

E.2 Determination of total and inorganic phosphorus using MBM.

The sample extracts were diluted 50 times with deionized H_2O by transferring 2.0 mL to a 100.0 mL volumetric flask, and adjusted to the pH range 3-10 with NaOH. 2.0 mL ascorbic acid and 4.0 mL acid molybdate (solution 2) was added to the extract solution for colour development. The absorbance was measured at 880 nm within 10-30 min after adding reagents.

Calibration solutions were made from a 2.0 mg P/L stock solution and the concentrations 0 mg P/L, 0.08 mg P/L, 0.2 mg P/L, 0.3 mg P/L and 0.4 mg P/L, matrix matched and adjusted to pH 3-10 with NaOH. The calibration solutions were added 1 mL ascorbic acid, and 2 mL acid molybdate (solution 2) . The calibration curves are shown in Figure E.1, E.2 and E.3

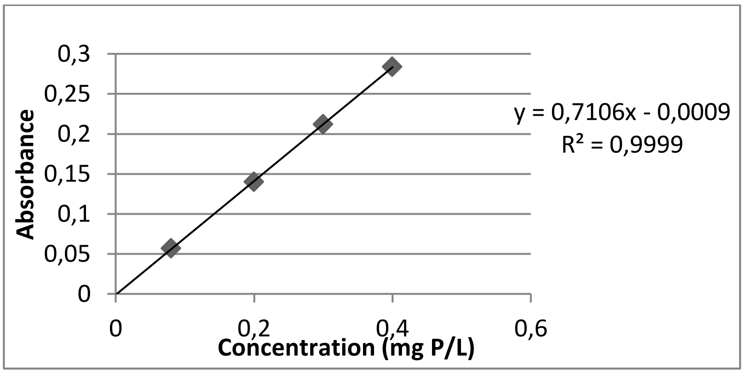


Figure E.1 Standard curve no. 1 for determination of inorganic phosphorus with MBM.

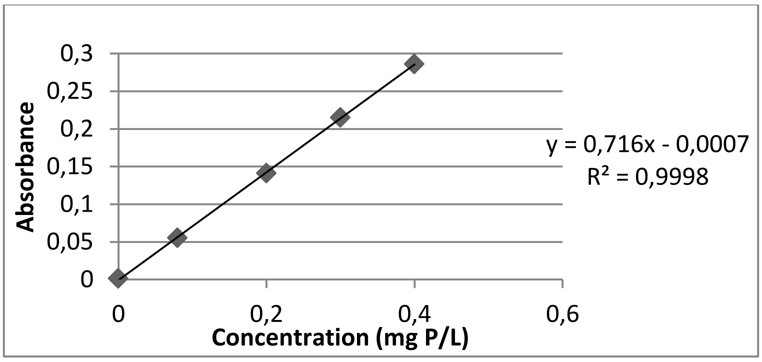


Figure E.2 Standard curve no. 2 for determination of inorganic phosphorus with MBM

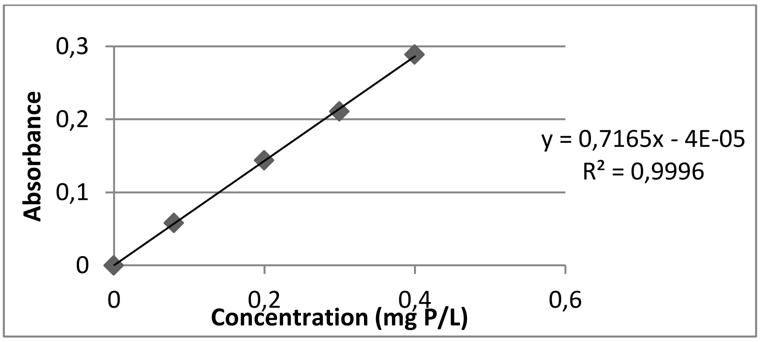


Figure E.3 Standard curve no. 3 for determination of inorganic phosphorus with MBM.

Three sample extracts were measured with three replicates to check the precision of the dilution, colour development and measurements. The results, standard deviation and relative standard deviation are shown in Table E.3.

Table E.3 Average, standard deviation and relative standard deviation of the measurements of inorganic phosphorus with MBM.

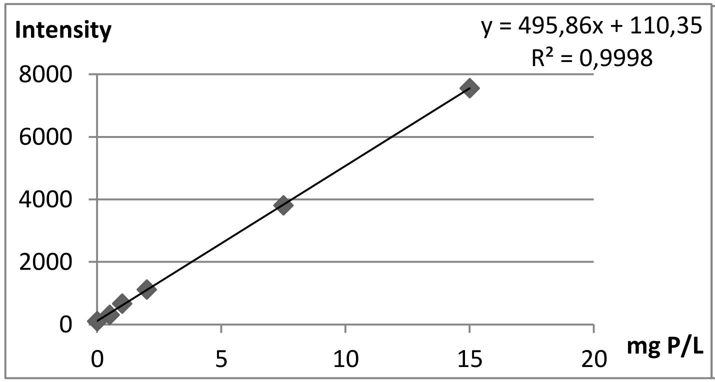
U164 (mg P/kg)		U180 (mg P/kg)		U181 (mg P/kg)	
Replicate 1	2835	Replicate 1	2013	Replicate 1	589
Replicate 2	2817	Replicate 2	2066	Replicate 2	607
Replicate 3	2781	Replicate 3	2049	Replicate 3	607
Average	2811	Average	2043	Average	601
St.dev.	27	St.dev	27	St.dev	10
RSD %	1.0	RSD %	1.3	RSD %	1.7

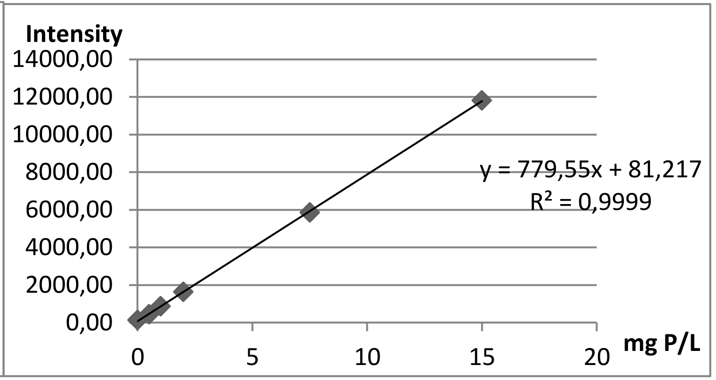
E3. Determination of total and inorganic phosphorus using ICP-OES

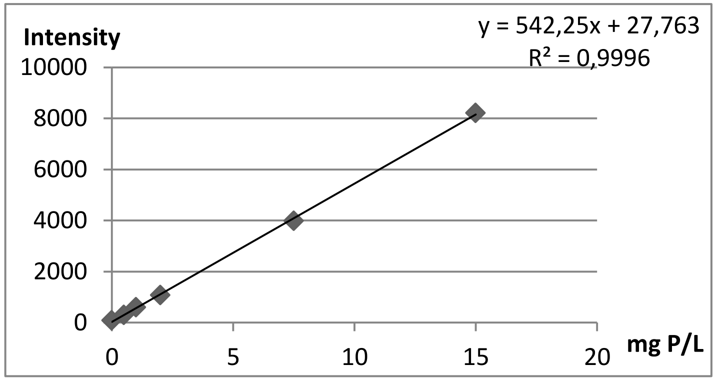
Calibration solutions was made with 0 mg P/L, 0.5 mg P/L, 1 mg P/L, 2 mg P/L 7.5 mg P/L and 15 mg P/L from a 100 mg P/L stock solution. The solutions were matrix matched by adding H_2SO_4 to the same concentration as the sample extracts. Calibration curves are shown on the next page. Calibration was run again every 20 sample, and a blank test was run after each calibration to check the carry over. See Table E.4 for instrument settings. 3 replicates for each sample were analysed and the average intensity was used to calculate the concentration in mg/L (done by the instrument).

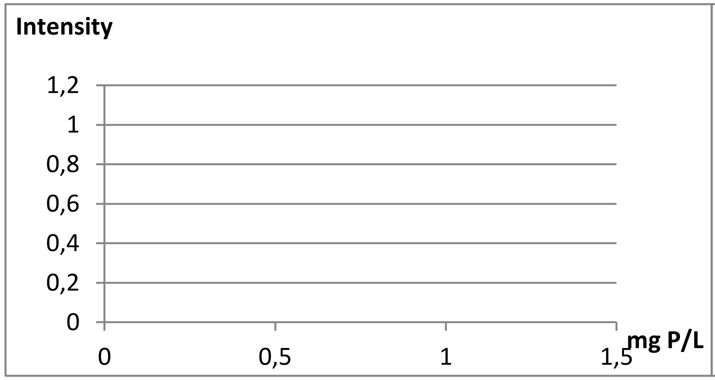
Table E.4 instrument settings for ICP-OES analysis

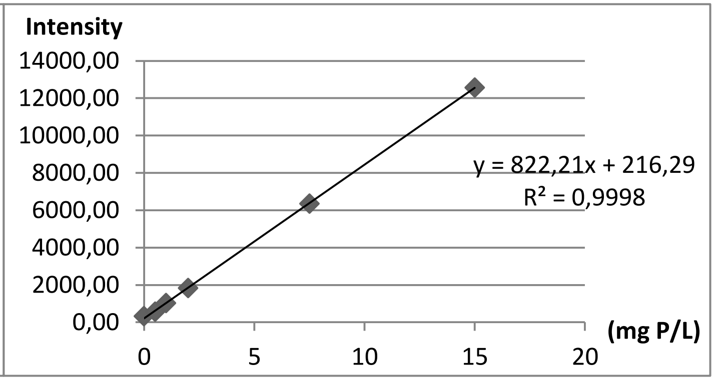
Instrument settings for Varian Vista AX CCD simultaneous axial view ICP-OES	
RF Power	1 kW
Plasma flow	15 L/min
Auxiliary flow	1.5 L/min
Nebulizer flow	0.75 L/min
Replicate read time	1 s
Stabilization delay	15 s
Sample uptake delay	30 s
Pump rate	15rpm
Rinse time	10 s
Replicates	3
Wavelength	213.618

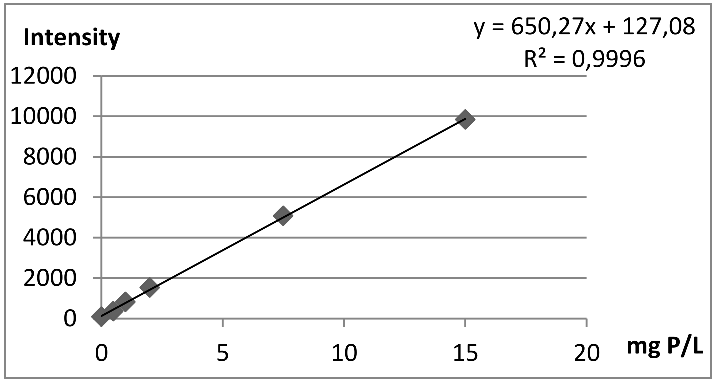

Intensity
y = 495,86x + 110,35
R² = 0,9998
8000
6000
4000
2000
0
0
5
10
15
20
mg P/L

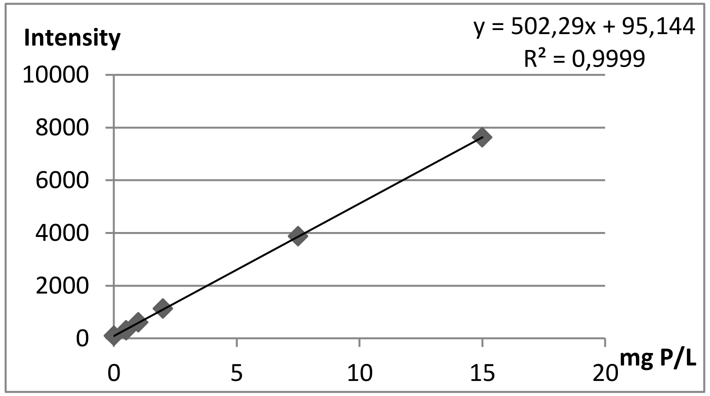

Intensity
14000,00
12000,00
10000,00
8000,00
6000,00
4000,00
2000,00
0,00
y = 779,55x + 81,217
R² = 0,9999
0
5
10
15
20
mg P/L


Intensity
y = 542,25x + 27,763
R² = 0,9996
10000
8000
6000
4000
2000
0
0
5
10
15
20
mg P/L


Intensity
1,2
1
0,8
0,6
0,4
0,2
0
0
0,5
1
1,5
mg P/L


Intensity
14000,00
12000,00
10000,00
8000,00
6000,00
4000,00
2000,00
0,00
y = 822,21x + 216,29
R² = 0,9998
0
5
10
15
20
(mg P/L)


Intensity
y = 650,27x + 127,08
R² = 0,9996
12000
10000
8000
6000
4000
2000
0
0
5
10
15
20
mg P/L


Intensity
y = 502,29x + 95,144
R² = 0,9999
10000
8000
6000
4000
2000
0
0
5
10
15
20
mg P/L

E. 4 Limit of Detection

The limit of detection (LOD) for phosphorus as wavelength 213.618 was determined by analysing a method blank ten times during one analysis and calculating the standard deviation.

LOD = 3* standard deviation

The methods LOD were calculated to be 9.10 mg P/ kg (or 0.0425 mg P/L).

E. 5 Correlation check between ICP-OES and Molybdenum blue method – total phosphorus

The correlation between results obtained by MBM and ICP-OES are good with $R^2 = 0.9955$ (Figure E.4)). ICP-OES gives a somewhat higher concentration (Figure E.5). The results obtained with ICP-OES are used in the thesis.

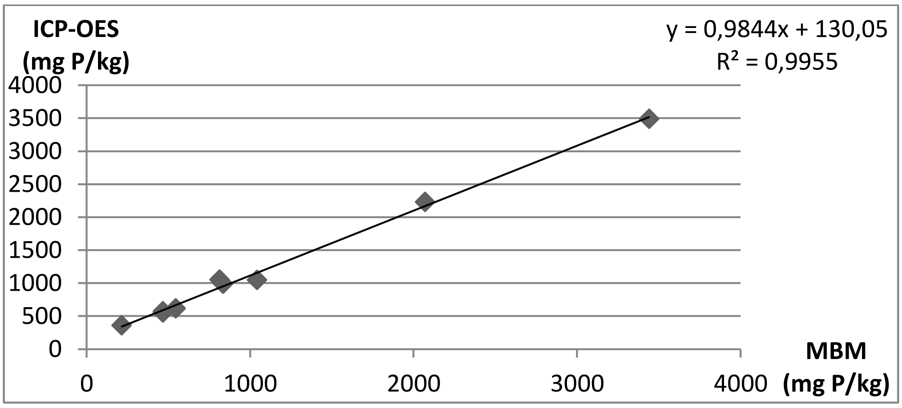


Figure E.4 Correlation between total phosphorus results obtained with ICP-OES and MBM

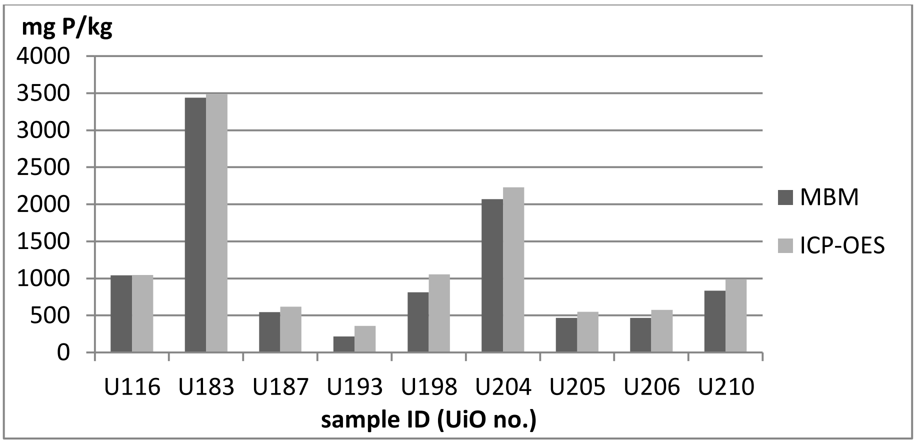


Figure E.5 Comparison of total phosphorus results obtained with ICP-OES and MBM

E. 6 Correlation check between ICP-OES and Molybdenum blue method – inorganic phosphorus

Good correlation between the two methods (Figure E.6).

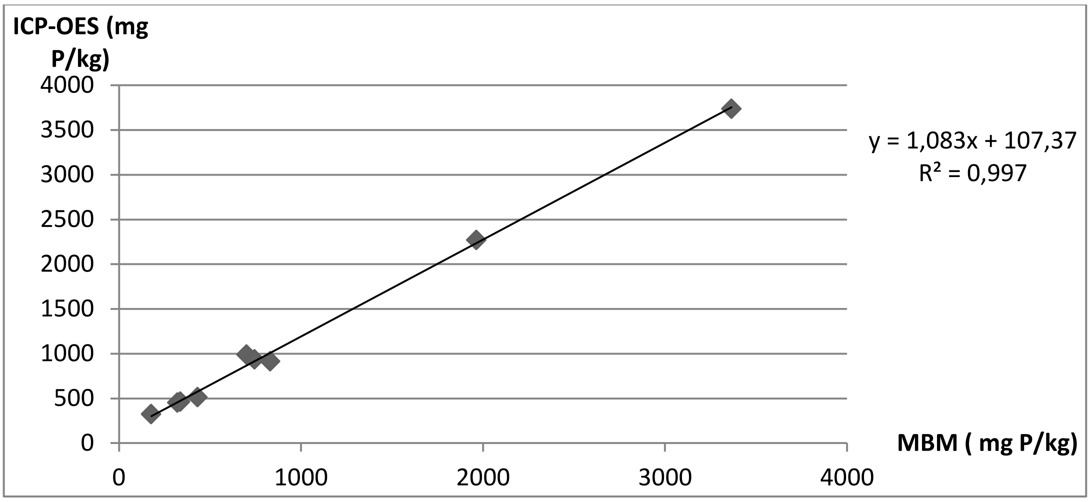


Figure E.5 Correlation between results obtained for inorganic phosphorus by ICP-OES and MBM

The concentrations measured for inorganic phosphorus with ICP-OES were almost the same as for total phosphorus (Figure E.6), sometimes even larger, making it difficult to calculate the organic fraction. The results obtained by MBM were used in this thesis.

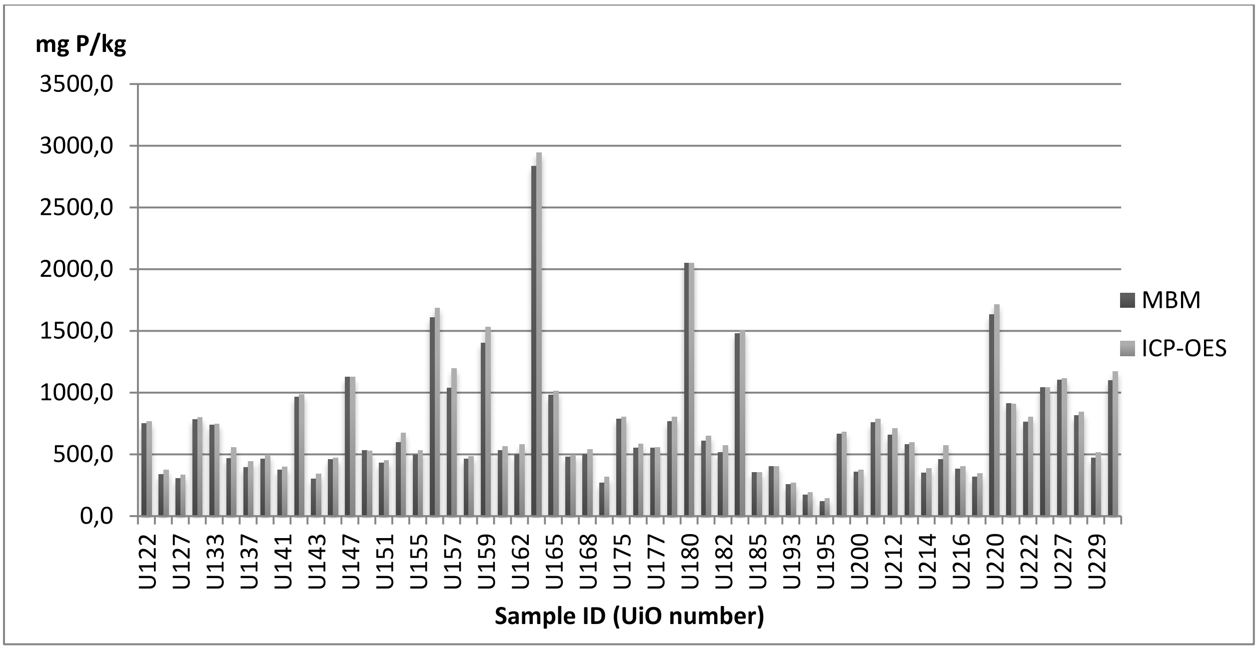


Figure E.6 Concentration of inorganic phosphorus measured by ICP-OES and MBM.

E. 7 Compilation of data: Quality control of the determination of total phosphorus by comparing results obtained by B.P. Joshi and author.

Nine representative samples, with different concentrations where chosen to run a check the quality of the data obtained by B. P. Joshi (MBM) and by the author (ICP-OES). The correlation of the data can be seen in Figure E.7, and the concentrations in Figure E.8.

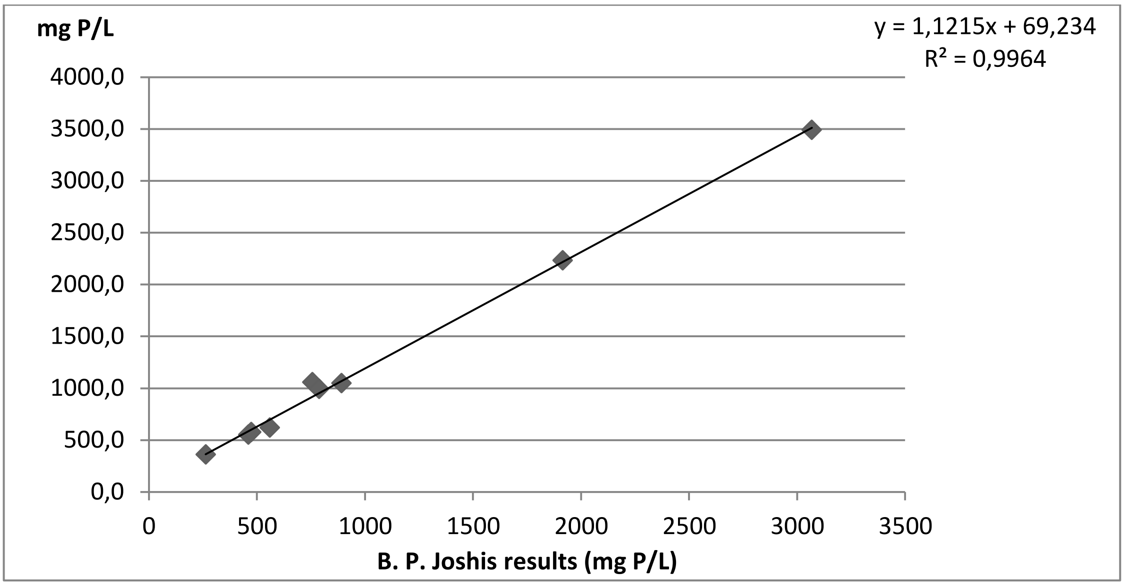


Figure E.7 Correlation of total phosphorus concentration determined by B. P. Joshi (MBM) and author (ICP-OES).

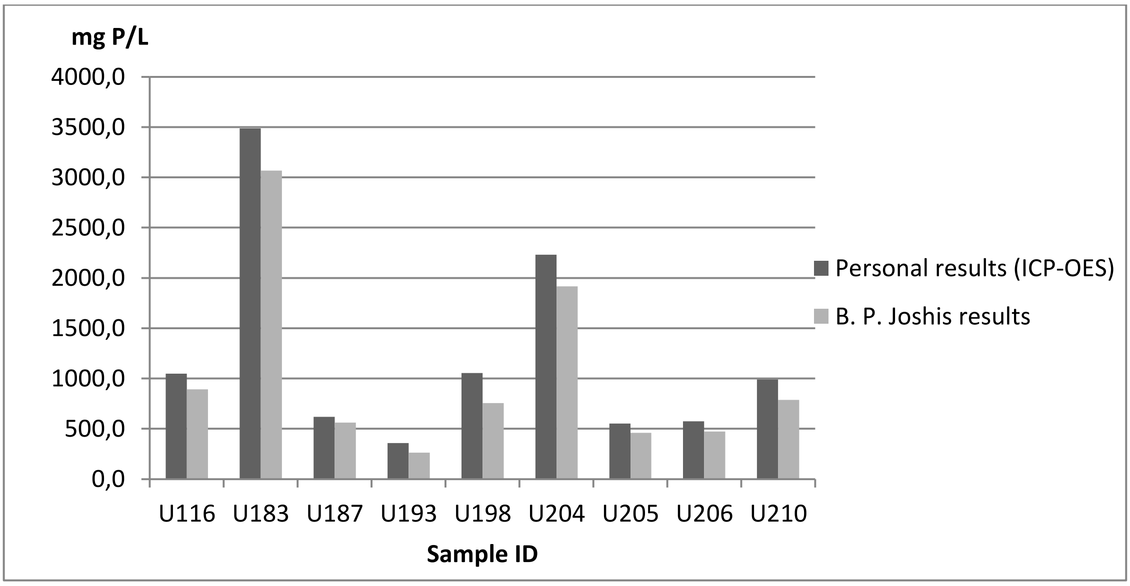


Figure E.8 Comparison of total phosphorus concentration obtained by B. P. Joshi (MBM) and author (ICP-OES).

E. 8 Compilation of data: Quality control of the determination of inorganic phosphorus by comparing results obtained by B.P. Joshi and author.

Nine representative samples with different concentrations where chosen to run a check the quality of the data obtained by B. P. Joshi (MBM) and by the author (MBM). The correlation of the data can be seen in Figure F.1, Figure F.2 shows the concentrations obtained.

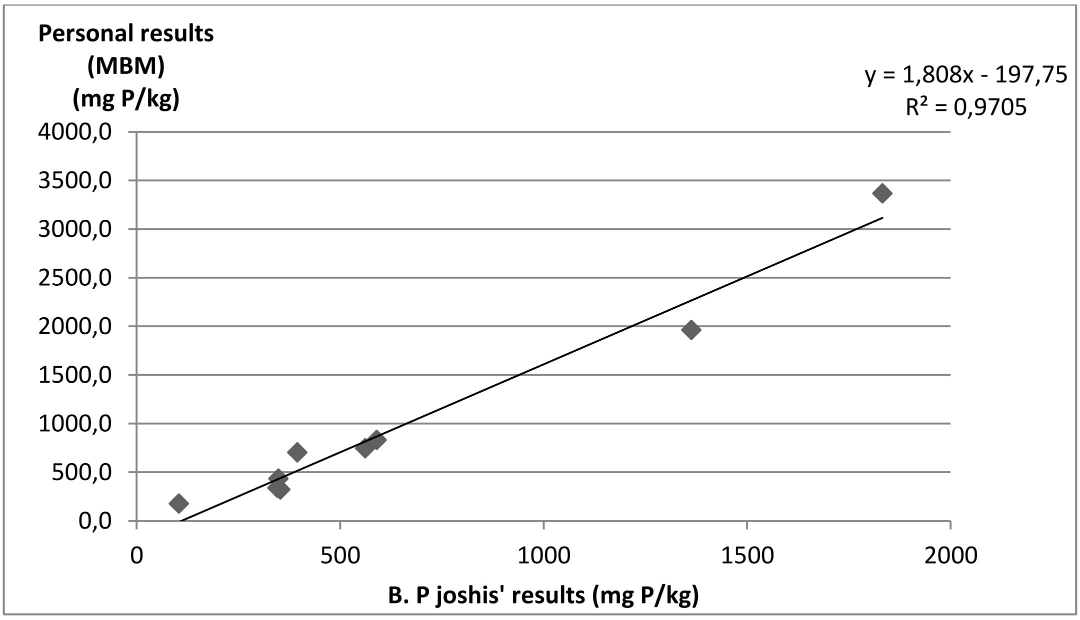


Figure E.9 Correlation of inorganic phosphorus concentration determined by B. P. Joshi and author.

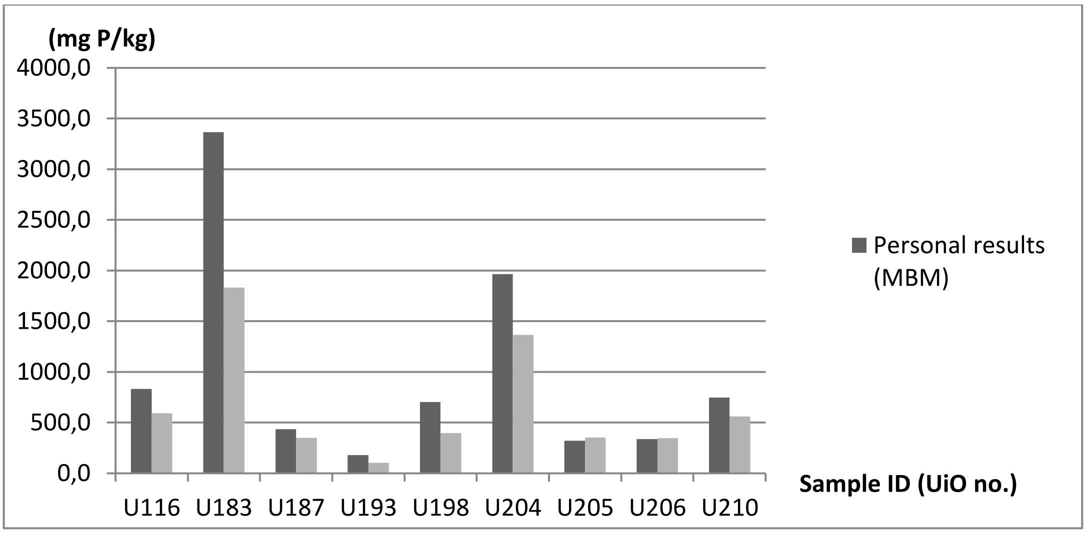


Figure E.10 Comparison of total phosphorus concentration obtained by B. P. Joshi and author.

Appendix F. Phosphorus results

Table F.1 Phosphorus concentrations in farmland and forest.

UiO no.	Sinotropia no.	Horizon	Land-use	Phosphorus (mg P/kg)		
				Total	Inorganic	Organic
U122	SS091	A	Farmland	871	748	123
U126	SS095	A	Farmland	410	338	72
U128	SS097	A	Farmland	861	783	78
U141	SS106	A	Farmland	438	371	67
U142	SS106	B	Farmland	1040	965	75
U143	SS106	C	Farmland	414	301	113
U145	SS108	A	Farmland	545	460	85
U147	SS110	A	Farmland	1133	1125	8
U150	SS112	A	Farmland	570	532	38
U151	SS112	B	Farmland	481	430	51
U152	SS112	C	Farmland	687	594	93
U155	SS115	A	Farmland	601	495	106
U162	SS117	A	Farmland	973	499	474
U168	SS120	B	Farmland	566	498	68
U169	SS120	C	Farmland	346	268	78
U175	SS126	A	Farmland	874	784	89
U176	SS126	B	Farmland	690	550	140
U177	SS126	C	Farmland	639	550	90
U178	SS127	A	Farmland	920	765	155
U211	SS151	A	Farmland	765	757	8
U230	SS164	A	Farmland	1253	1098	155
U127	SS096	A	Forest	387	304	83
U186	SS131	A	Forest	560	403	157
U229	SS163	A	Forest	847	469	377

Table F.2 Phosphorus concentrations in orchard and vegetable fields.

UiO no.	Sinotropia no.	Horizon	land-use	Phosphorus (mg P/kg)		
				Total	Inorganic	Organic
U133	SS101	A	Orchard	770	736	35
U136	SS103	A	Orchard	655	466	189
U137	SS103	B	Orchard	539	394	145
U138	SS103	C	Orchard	653	464	189
U156	SS116	A	Orchard	1718	1609	109
U157	SS116	B	Orchard	1352	1038	314
U158	SS116	C	Orchard	553	462	92
U159	SS116	A	Orchard	1502	1400	102
U160	SS116	B	Orchard	592	530	63
U164	SS119	A	Orchard	3072	2835	237
U165	SS119	B	Orchard	1190	980	210
U166	SS119	C	Orchard	507	479	28
U180	SS129	A	Orchard	2089	2049	40
U181	SS129	B	Orchard	814	607	207
U182	SS129	C	Orchard	734	515	219
U193	SS138	A	Orchard	357	256	100
U194	SS138	B	Orchard	244	172	72
U195	SS138	C	Orchard	212	120	92
U220	SS155	A	Orchard	1938	1632	306
U221	SS156	A	Orchard	974	910	64
U222	SS157	A	Orchard	988	761	227
U223	SS158	A	Orchard	1145	1041	104
U228	SS162	A	Orchard	976	814	163
U184	SS130	B	Vegetable	1684	1480	204
U185	SS130	C	Vegetable	485	354	131
U199	SS141	B	Vegetable	725	663	62
U200	SS141	C	Vegetable	402	356	46
U212	SS152	A	Vegetable	830	655	175
U213	SS152	B	Vegetable	655	580	75
U214	SS152	C	Vegetable	475	350	125
U215	SS153	A	Vegetable	700	456	244
U216	SS153	B	Vegetable	501	383	118
U217	SS153	C	Vegetable	477	314	162
U227	SS161	A	Vegetable	1535	1100	435

Appendix G. PCA and cluster analysis

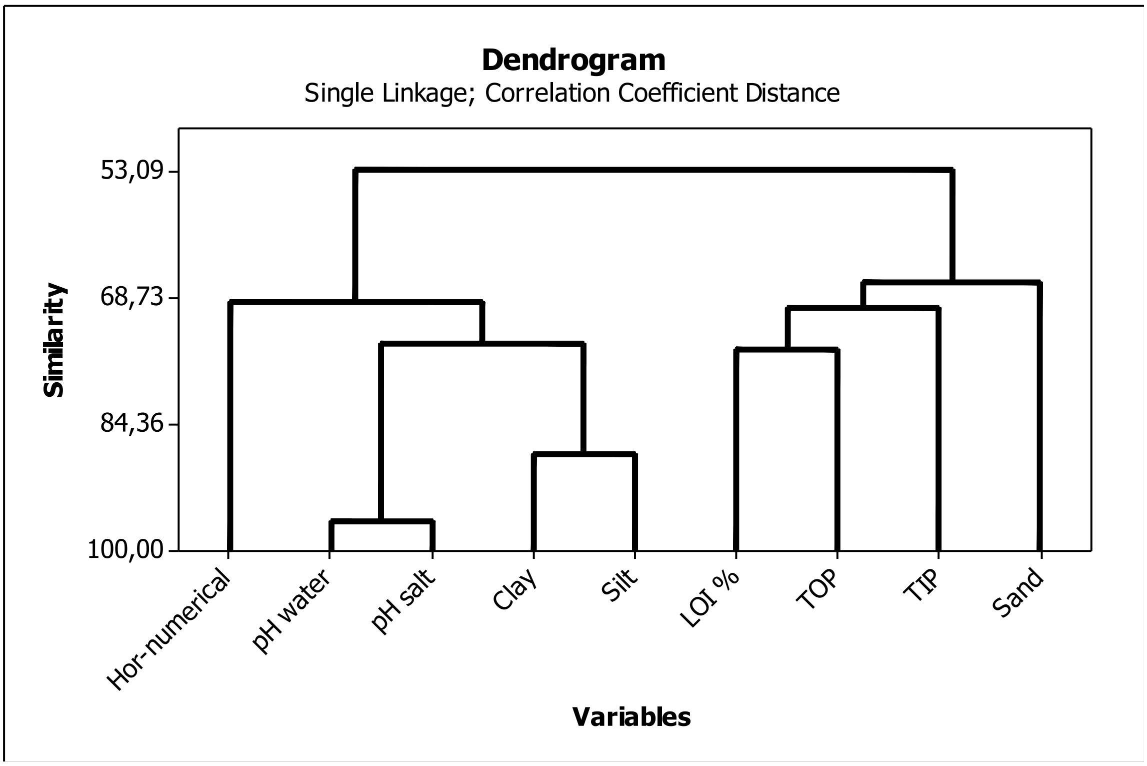


Figure G.1 Preliminary cluster analysis

	pH (H_2O)	pH KCl	pH ($CaCl_2$	pH salt	LOI %	Water%	TP	TIP	TOP	Clay	Silt
pH KCl	0,956										
pH Cacl2	0,834	0,636									
	0,000	0,011									
pH salt	0,880	1,000	0,981								
	0,000	*	0,000								
LOI %	0,101	0,464	-0,032	0,117							
	0,484	0,019	0,844	0,419							
Water%	0,334	0,362	0,247	0,287	0,119						
	0,018	0,075	0,124	0,044	0,409						
TP	-0,207	-0,229	0,021	-0,089	0,201	-0,132					
	0,168	0,319	0,902	0,557	0,180	0,383					
TIP	-0,286	-0,538	0,045	-0,207	0,073	-0,258	**0,819**				
	0,054	0,012	0,792	0,168	0,628	0,083	**0,000**				
TOP	0,048	0,328	-0,030	0,140	0,246	0,138	**0,576**	0,003			
	0,753	0,146	0,864	0,355	0,099	0,360	**0,000**	0,986			
Clay	**0,666**	**0,625**	0,323	**0,597**	0,438	0,219	0,022	-0,232	0,301		
	0,002	**0,006**	0,397	**0,007**	0,061	0,367	0,929	0,338	0,211		
Silt	**0,554**	0,476	**0,636**	**0,539**	0,419	0,292	-0,136	-0,470	0,385	0,550	
	0,014	0,046	**0,066**	**0,017**	0,074	0,225	0,579	0,042	0,104	0,015	
Sand	-0,572	-0,495	-0,653	-0,554	-0,430	-0,295	0,131	0,468	-0,389	-0,587	**-0,999**
	0,010	0,037	0,057	0,014	0,066	0,220	0,594	0,043	0,099	0,008	**0,000**

Appendix H. Samples and results from Bishnu P. Joshi

UiO No.	Sinotropia no.	Land-use	Coordinates		Horizon	pH (H2O)	pH (CaCl2)	LOI %	Water %	Phosphorus (mg P/kg)		
			X	Y						Total	Inorganic	Organic
U002	SS002	Farmland	117.5669	40.0821	A	7.54	6.62	2.83	2.09	234	232	2
U003	SS002	Farmland	117.5669	40.0821	B	7.90	6.57	2.52	2.39	258	159	99
U012	SS007	Farmland	117.4577	40.0577	A	7.68	6.40	3.2	2.52	264	173	92
U013	SS007	Farmland	117.4577	40.0577	B	7.61	6.18	2.69	1.99	288	183	105
U018	SS010	Farmland	117.5085	40.11	A	8.09	7.12	5.09	1.94	481	295	186
U019	SS010	Farmland	117.5085	40.11	B	8.06	7.14	3.23	1.85	345	199	147
U030	SS016	Farmland	117.5983	40.0907	A	8.04	4.88	4.59	2.42	1000	837	163
U031	SS016	Farmland	117.5983	40.0907	B	6.80	4.65	4.4	2.52	427	338	89
U032	SS017	Farmland	117.5985	40.0912	A	7.21	6.58	3.85	1.61	701	688	13
U033	SS017	Farmland	117.5985	40.0912	B	7.82	6.92	3.08	1.65	216	163	54
U034	SS018	Farmland	117.5557	40.0734	A	7.63	6.96	3.78	1.6	619	525	94
U035	SS018	Farmland	117.5557	40.0734	B	8.06	7.26	2.65	1.45	525	382	144
U046	SS026	Farmland	117.4645	40.0535	A	8.18	7.44	2.53	1.69	548	415	133
U049	SS028	Farmland	117.47	40.0592	A	7.73	6.77	3.87	2.19	709	683	26
U050	SS028	Farmland	117.5694	40.0913	B	8.21	7.17	2.89	2.15	624	518	106
U051	SS029	Farmland	117.5935	40.0608	A	7.94	6.87	3.48	2.59	437	313	124
U053	SS031	Farmland	117.5561	40.0758	A	7.65	6.95	3.44	2.37	744	590	153
U054	SS032	Farmland	117.5561	40.0758	A	8.52	7.61	2.23	1.89	369	253	116
U055	SS032	Farmland	117.5561	40.0758	B	8.33	7.59	3.24	2.18	683	500	183
U057	SS034	Farmland	117.4628	40.0641	A	9.14	7.52	2.85	2.49	371	275	96
U072	SS045	Farmland	117.5373	40.1036	A	8.08	7.66	6.05	3.08	481	356	125
U073	SS045	Farmland	117.5373	40.1036	B	7.18	6.69	5.37	3.08	454	324	130
U079	SS050	Farmland	117.4557	40.1575	A	8.11	7.59	9.54	3.08	1270	812	458

UiO No.	Sinotropia no.	Land-use	Coordinates		Horizon	pH (H2O)	pH (CaCl2)	LOI %	Water %	Phosphorus (mg P/kg)		
			X	Y						Total	Inorganic	Organic
U083	SS053	Farmland	117.557	40.1082	A	7.73	6.90	9.37	3.59	661	337	324
U087	SS057	Farmland	117.556	40.1115	A	6.92	4.65	4.84	2.57	153	103	51
U088	SS058	Farmland	117.563	40.1127	A	6.58	5.13	5.72	3.55	277	177	100
U091	SS061	Farmland	117.559	40.1349	A	5.75	4.50	6.51	2.37	1191	853	338
U103	SS072	Farmland	117.593	40.1062	A	7.53	6.63	6.27	2.19	743	560	183
U104	SS073	Farmland	117.581	40.1147	A	7.80	7.23	9.52	2.37	514	394	120
U189	SS134	Farmland	117.489	40.0124	A	7.51	6.46	3.36	6.39	465	305	160
U190	SS135	Farmland	117.499	40.0065	A	8.23	7.53	2.93	5.91	494	402	92
U201	SS142	Farmland	117.584	39.9988	A	7.44	7.19	3.75	3.52	899	458	442
U202	SS143	Farmland	117.583	39.9867	A	7.86	7.48	3.41	2.16	700	286	414
U203	SS144	Farmland	117.585	39.9712	A	7.55	7.16	3.71	3.29	1000	660	340
U206	SS147	Farmland	117.606	40.0005	A	8.02	7.38	3.48	6.04	474	346	127
U210	SS150	Farmland	117.666	40.0059	A	7.17	6.63	3.40	3.67	787	562	226

UiO No.	Sinotropia no.	Land-use	Coordinates		Horizon	pH (H2O)	pH (CaCl2)	LOI %	Water %	Phosphorus (mg P/kg)		
			X	Y						Total	Inorganic	Organic
U061	SS037	Mineral land	117.464	40.0773	A	8.43	7.92	2.88	1.08	311	258	53
U062	SS038	Mineral land	117.469	40.0777	A	8.15	7.14	2.19	3.63	359	313	46
U063	SS038	Mineral land	117.469	40.0777	B	8.35	7.38	4.68	4.76	194	105	90
U069	SS043	Mineral land	117.534	40.0835	A	7.87	6.58	6.92	3.85	244	158	86

UiO No.	Sinotropia no.	Land-use	Coordinates		Horizon	pH (H2O)	pH (CaCl2)	LOI %	Water %	Phosphorus (mg P/kg)		
			X	Y						Total	Inorganic	Organic
U006	SS004	Forest	117.5965	40.1399	A	5.93	5.40	3.52	1.91	311	140	172
U007	SS004	Forest	117.5965	40.1399	B	5.82	4.70	3.24	0.96	153	105	48
U010	SS006	Forest	117.5706	40.0776	A	7.44	6.71	3.68	2.08	888	800	88
U011	SS006	Forest	117.5706	40.0776	B	7.74	6.84	2.19	2.03	482	411	71
U022	SS012	Forest	117.5186	40.0761	A	7.70	6.17	3.66	2.98	371	244	127
U023	SS012	Forest	117.5186	40.0761	B	7.68	6.12	3.16	2.91	325	204	121
U036	SS019	Forest	117.549	40.0663	A	6.66	5.65	4.37	2.47	507	338	169
U037	SS019	Forest	117.549	40.0663	B	7.18	6.20	3.72	2.99	282	156	125
U043	SS023	Forest	117.629	40.1185	A	6.80	6.06	10.34	2.76	654	194	460
U047	SS027	Forest	117.4625	40.053	A	8.53	7.44	3.51	2.25	289	213	76
U048	SS027	Forest	117.4625	40.053	B	8.26	7.39	4.09	2.3	377	268	109
U052	SS030	Forest	117.6044	40.0706	A	6.37	4.91	6.46	3.16	485	327	158
U056	SS033	Forest	117.5571	40.075	A	8.52	7.70	2.05	1.63	435	277	157
U058	SS035	Forest	117.4695	40.0736	A	7.95	6.64	6.48	3.42	384	181	203
U059	SS036	Forest	117.4661	40.0743	A	7.69	6.06	8.33	4.09	291	245	47
U060	SS036	Forest	117.4661	40.0743	B	7.97	6.70	8.46	4.27	430	285	145
U064	SS039	Forest	117.4882	40.0851	A	8.05	7.10	5.4	5.4	233	95	138
U065	SS039	Forest	117.4882	40.0851	B	8.09	6.49	4.39	7.52	178	115	63
U066	SS040	Forest	117.4833	40.0903	A	7.72	6.85	7.06	3.51	497	152	345
U067	SS041	Forest	117.5074	40.0806	A	7.38	6.55	10.73	3.87	879	502	377
U068	SS042	Forest	117.5741	40.083	A	8.33	7.81	2.9	1.59	355	263	92
U070	SS044	Forest	117.5373	40.1119	A	7.95	6.91	8.49	3.26	250	218	32
U071	SS044	Forest	117.5373	40.1119	B	8.10	7.04	6.92	4.15	194	109	85

UiO No.	**Sinotropia no.**	**Land-use**	**Coordinates**		**Horizon**	**pH (H2O)**	**pH (CaCl2)**	**LOI %**	**Water %**	**Phosphorus (mg P/kg)**		
			X	**Y**						**Total**	**Inorganic**	**Organic**
U074	SS046	Forest	117.5427	40.1355	A	5.30	4.60	8.29	2.57	418	156	262
U075	SS047	Forest	117.5287	40.1421	A	7.90	7.31	8.03	2.78	419	225	194
U076	SS048	Forest	117.5201	40.1425	A	8.22	7.30	8.35	4.08	1025	702	323
U077	SS049	Forest	117.5099	40.1463	A	5.84	4.89	11.85	3.16	352	144	208
U078	SS049	Forest	117.5099	40.1463	B	6.18	5.00	7.62	3.96	198	109	89
U080	SS051	Forest	117.4619	40.1587	A	7.74	6.44	6.17	3.53	254	183	71
U081	SS052	Forest	117.4662	40.1178	A	8.32	7.25	7.95	4.08	481	364	117
U082	SS052	Forest	117.4724	40.119	B	8.51	7.68	4.93	3.16	484	450	34
U084	SS054	Forest	117.5633	40.1094	A	7.46	6.20	8.23	4.26	199	105	94
U085	SS055	Forest	117.5571	40.1082	A	6.25	5.10	6.05	2.68	392	209	182
U086	SS056	Forest	117.5633	40.1094	A	6.45	4.89	8.28	2.89	401	198	203
U089	SS059	Forest	117.5549	40.1177	A	7.43	6.32	8.18	3.99	475	292	183
U090	SS060	Forest	117.5611	40.1189	A	6.17	4.84	4.88	1.89	168	81	87
U096	SS066	Forest	117.6248	40.1149	A	6.90	6.17	7.54	2.35	372	195	177
U097	SS066	Forest	117.6159	40.1143	B	8.05	7.20	4.7	1.6	225	75	150
U098	SS067	Forest	117.6221	40.1155	A	5.93	4.67	7.37	3.09	578	401	177
U099	SS068	Forest	117.5979	40.1145	A	5.90	3.95	6.08	2.59	211	209	2
U100	SS069	Forest	117.6041	40.1157	A	6.82	6.43	10.68	2.77	815	499	317
U101	SS070	Forest	117.6068	40.1569	A	5.91	4.93	11.55	3.29	531	128	403
U102	SS071	Forest	117.5797	40.1012	A	6.18	5.23	9.08	2.5	782	428	354
U105	SS074	Forest	117.5758	40.1139	A	6.27	5.09	5	2.4	508	357	151
U107	SS076	Forest	117.5807	40.1496	A	6.16	4.89	5.19	2.2	578	402	176
U108	SS077	Forest	117.5807	40.1496	A	7.60	6.29	4.91	2.16	599	494	105
U109	SS078	Forest	117.5535	40.1561	A	7.82	7.33	7.96	2.38	594	462	132

UiO No.	Sinotropia no.	Land-use	Coordinates		Horizon	pH (H2O)	pH (CaCl2)	LOI %	Water %	Phosphorus (mg P/kg)		
			X	Y						Total	Inorganic	Organic
U004	SS003	Orchard	117.5585	40.0873	A	7.86	6.92	4.41	2.28	833	664	169
U005	SS003	Orchard	117.5585	40.0873	B	7.86	6.79	3.18	2.35	313	189	124
U008	SS005	Orchard	117.5971	40.1403	A	5.92	4.52	2.87	1.29	238	132	105
U009	SS005	Orchard	117.5971	40.1403	B	6.18	4.54	2.4	1.78	543	409	134
U016	SS009	Orchard	117.5047	40.0711	A	8.14	7.28	4.32	2.28	900	763	137
U017	SS009	Orchard	117.5047	40.0711	B	7.94	6.70	2.94	3.93	239	207	32
U020	SS011	Orchard	117.4925	40.1106	A	7.78	6.82	5.3	2.89	415	306	108
U021	SS011	Orchard	117.4925	40.1106	B	7.58	6.42	3.8	3.17	434	274	160
U026	SS014	Orchard	117.495	40.1544	A	7.72	7.52	3.53	2.17	575	392	183
U027	SS014	Orchard	117.495	40.1544	B	7.49	6.25	2.5	1.82	247	133	114
U028	SS015	Orchard	117.5649	40.1446	A	8.34	6.59	5.47	2.46	515	393	122
U029	SS015	Orchard	117.5649	40.1446	B	8.10	6.32	3.88	2.69	165	107	58
U038	SS020	Orchard	117.5849	40.0641	A	7.76	7.21	4.58	2.07	1000	804	196
U039	SS020	Orchard	117.5849	40.0641	B	7.56	6.52	3.14	1.98	438	320	118
U042	SS022	Orchard	117.6241	40.1198	A	6.92	5.65	2.99	1.86	678	579	99
U044	SS024	Orchard	117.4813	40.1562	A	7.75	6.40	4.02	3.09	501	332	169
U093	SS063	Orchard	117.5582	40.1375	A	7.70	6.84	5.56	2.87	792	703	89
U094	SS064	Orchard	117.5644	40.1387	A	6.68	5.78	6.94	3.47	463	333	130
U095	SS065	Orchard	117.6186	40.1137	A	5.62	4.54	9.32	2.88	1029	597	431
U106	SS075	Orchard	117.5773	40.137	A	6.56	5.15	4.21	1.76	558	439	120
U204	SS145	Orchard	117.5898	39.9538	A	5.43	4.92	5.73	6.36	1915	1364	552
U205	SS146	Orchard	117.5918	39.9469	A	7.01	6.21	2.96	2.10	460	353	107
U191	SS136	Orchard	117.5014	40.0065	A	7.36	6.70	3.75	4.09	1431	1131	300
U193	SS138	Orchard	117.5172	40.0106	A	7.98	6.92	2.06	3.28	263	104	159

UiO No.	Sinotropia no.	Land-use	Coordinates		Horizon	pH (H2O)	pH (CaCl2)	LOI %	Water %	Phosphorus (mg P/kg)		
			X	Y						Total	Inorganic	Organic
U001	SS001	Vegetable	117.5648	40.0752	A	8.40	7.71	2.35	2.27	874	781	94
U014	SS008	Vegetable	117.4795	40.0653	A	7.86	7.10	3.71	1.85	899	743	156
U015	SS008	Vegetable	117.4795	40.0653	B	7.32	6.48	2.81	2.26	272	171	101
U024	SS013	Vegetable	117.5223	40.0757	A	7.83	7.24	3.98	2.09	323	241	82
U025	SS013	Vegetable	117.5223	40.0757	B	6.37	7.34	3.13	1.73	435	346	89
U040	SS021	Vegetable	117.684	40.0584	A	6.74	5.46	4.43	2.43	590	409	181
U041	SS021	Vegetable	117.684	40.0584	B	7.35	5.79	4.74	3.7	284	176	107
U045	SS025	Vegetable	117.4335	40.0276	A	8.47	7.62	2.99	2.52	792	697	95
U092	SS062	Vegetable	117.5653	40.1361	A	7.89	7.31	5.56	2.88	490	355	135
U163	SS118	Vegetable	117.6948	40.0828	A	6.69	6.36	3.52	4.35	1146	902	244
U171	SS122	Vegetable	117.6854	40.0614	A	7.28	7.04	3.13	2.37	1112	957	156
U192	SS137	Vegetable	117.5018	40.0068	A	7.73	7.05	3.80	1.96	732	292	440
U198	SS141	Vegetable	117.5461	40.006	A	7.81	7.40	3.24	2.08	756	395	361
U187	SS132	Vegetable	117.4508	40.0194	A	8.04	7.17	2.74	3.90	560	349	211
U179	SS128	Vegetable	117.6391	40.0782	A	5.85	#N/A	12.9	5.99	3245	1927	1318
U183	SS130	Vegetable	117.639	40.0795	A	5.03	4.82	11.0	8.75	3068	1833	1235
U146	SS109	Vegetable	117.6837	40.1092	A	6.39	5.80	3.75	2.18	1603	1289	313
U131	SS099	Vegetable	117.6321	40.2103	a	6.28	5.19	5.60	2.00	967	439	527
U144	SS107	Vegetable	117.6575	40.1432	A	7.52	7.03	3.36	2.39	765	466	299
U153	SS113	Vegetable	117.7005	40.1015	A	7.25	6.30	4.32	2.99	773	604	169
U140	SS105	Vegetable	117.6188	40.2361	A	7.73	7.23	7.79	2.99	3463	2455	1008
U174	SS125	Vegetable	117.6909	40.0578	A	7.92	7.47	4.45	3.49	1946	1470	476
U148	SS111	Vegetable	117.6831	40.1103	A	6.76	6.56	2.62	1.39	1042	606	436