Phosphorus leaching from agricultural soils with different tillage

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Period	September 2009-June 2010

On the cover image
of agricultural fields surrounding Ås

Acknowledgements

One year ago I was in Spain preparing myself to come to Norway. I was thinking during a long time if I was doing the correct, thinking in the positive that this experience could be for me, but also in the negative things. All the people that I have surrounding me told me: “take the chance”. That´s what I did, now I want to use this space to thank all of them the big support that they gave me:

My parents Mª Dolores and Gunnar because without them my experience here would not be the same, for all their unconditional love and his moral support during my sad days; **My aunt Josefina** for her good and wise advice and in general to all **My familie**; **My boyfriend Vicente** for his love and hours and hours of help that he has given me. I can´t forget also my supervisor in Spain, **Prof. Raul Crespo,** for all the information and for all attention on me during registration process.

Now at the end of my stay here I can not forget all the people that had help me here. Since the first moment I have had the sensation of being like at home, for their kind greeted and knowledge that I have learned from them. Thanks to:

My supervisor, **Prof. Rolf D. Vogt**, for giving me the opportunity of studying environmental chemistry and for all his support and help; My mate and supervisor at Bioforsk **Rikard Pedersen**, for all the new things that he has shown me and for all the help that he has given me to make this project possible; **Alex, Christian, Asfaw, Yemane, Nosa**, mates in the environmental chemistry group for all the help that they have provided me with my samples analysis.

It was a pleasure for me being here, meeting and working with you.

Ana Mª Skeide Caplliure

June 2010

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Abstract

Through this report one can realized about the importance of good agricultural practices in order to preserve the environment. The main aim of this report has been study the behavior of phosphorus flux through different type of agricultural soils. **Chapter 1** Along this chapter situation of the agriculture in Norway has been explained in addition to the grade of eutrophication problems that the country has nowadays. **Chapter 2** Here I have gone through the basis of the chemistry agriculture, explaining the behavior of phosphorus in soils, the different tillage techniques used to minimize the loss of phosphorus and the problems of the use of high amounts of pesticides and fertilizers. **Chapter 3** Is based on the impacts of losses of phosphorus, that means eutrophication problems. **Chapter 4** In this chapter I have related all the leaching procedure, from the sampling time, through the experiment until the analysis done to the samples collected. **Chapter 5** This is the part of the report were all the results from the analysis done to the samples are explained and discussed. In the last chapter **Chapter 6** conclusions from the experiment are reflected.

Introduction

Nowadays agricultural pollution for water bodies has gained higher interest because of the implementation of the EU´s water framework directive. To reduce the agricultural pollution, strategies to mitigate it are necessary and prerequisite for all efficient mitigation are: comprehensive knowledge and understanding of the transport processes and pathways for pesticides, nutrients and soil.

Different areas have different risk of pesticide transport. The effects of soil management on pesticide transport differ for different soil types. Soil erosion will contribute to the transport of particulate bound pesticides and soil tillage is known to have a great impact on this transport mechanism (Lundekvam, 1997).Transport of soil particles through soil profile comprise a large part of the total particle transport of clayey soil in South-eastern Norway (Lundekwam, 1997, Øygarden, 2000).

Soil texture and soil management are determining conditions for the development of soil macropores (Børresen and Njøs, 1993) and hence, may influence the risk of transport of pesticides sorbed to particles. Pesticides like Fluazinam, wich is strongly sorbed to soil (Pest Management Regulatory Agency, 2003) may be more prone to surface runoff and leaching through macropores in reduced tillage systems while Glyphosate is being mainly sorbed to mineral material. Glyphosate has been shown to potentially leach to deeper soil layers (Sims et al., 1998).

This pesticides content Phosphorus and P is a fundamental constituent of the metabolism and biochemistry of living organism and as Nitrogen is generally understood as the most limiting nutrient for terrestrial plant growth, the element that commonly limits productivity in freshwater and other ecosystems (Golttermann and de Oude, 1991; Correl, 1998). Elevated P levels have led to Eutrophication in sensitive surface waters mainly from diffuse, nonpoint sources of agriculturally related P. (Sims et al., 1998).

Eutrophication is usually the main cause for not fulfilling the requirement for good ecological quality in agricultural districts. South-eastern Norway more than 30% of water bodies are characterized as being at risk of Eutrophication. Excessive fertilization over long periods has produced

large P pools in agricultural soils. As a date 45% of the anthropogenic P input to Norwegian surface water originates from agricultural areas (Eutropia project).

For this reasons much research has been done, but significant and growing problems of P contamination still exist today. The goal of this project is examine the relationship between soil properties and P soil capacities, moreover investigate leaching of P as affected by pesticide sources.

1 An overview of the agriculture in Norway

1.1 Agriculture in Norway

Norway comprises the western part of the Scandinavian Peninsula. Its borders are shared with Sweden, Finland and Russia. The geography of the country has an important influence on the land use. A relatively long and narrow country, a mountain range divides the country into an Atlantic western and a Continental eastern part. The climate varies from nemo-boreal along south coast to sub-arctic in the mountains and in the north.

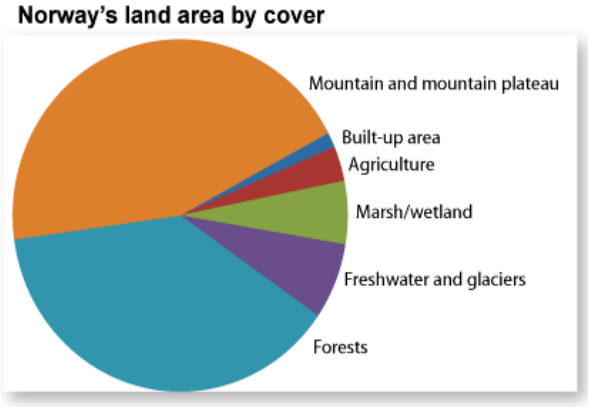


Figure 1. Distribution of the land area in Norway

As is possible see in the figure 1only 3% more or less of the country is under agricultural cultivation, the other main land use being 22% in production forest and more or less and the 75% as mountain land, glaciers, lakes and built areas.

This elongated country is cultivated land in more northern latitudes than in any other country, thus avoiding that conditions vary greatly depending on the region in which agriculture is practiced.

Agriculture in Norway accounts for about 2 % of annual GDP, and including associated activities, agriculture accounts about 10% of Norwegian employment (Royal Ministry of Agriculture, 2006).

Cereals, potatoes and grasses are the main agricultural crops. Production possibilities are related to climate (temperature, length of the growing season and rainfall distribution), soil type, and factors influencing workability (slope and stoniness) (Arnoldussen, Norwegian Institute of Land Inventory).

Grains are grown only in the south while western Norway has some livestock raising and dairy farming. The leading crops in 1998 were cereals—particularly barley, wheat, and oats (total output of 1.3 million metric tons)—and potatoes (400,320 tons). Norway is still a major fishing nation and is self-sufficient in many agricultural products, but fruits, vegetables, and most grains are all imported.

In yellow is shown the agricultural areas, figure 2, cereal production is mainly located in the south east and in the center of the country. Østfold county accounted for 21% of Norway's grain production in 2001; Hedmark county for 34% of potato production that year.

Moreover than the number of larger farms has increased, most farms in 1990 were still small, with about 99% of the 84,635 farm holdings (including meadows) consisting of less than 50 ha (124 acres) of arable land. Because of the small size of the holdings, many farm families pursue additional

Figure 2. Distribution of agriculture

occupations, mainly in forestry, fishing, and handicrafts.

Although the agricultural areas that Norway has, the country continues importing most of its grain and large quantities of its fruits.

1.2 Use of fertilizers and pesticides

With steep slopes and heavy precipitation, Norway requires substantial quantities of fertilizers to counteract soil leaching. Smallholders and those in marginal farming areas in the north and in the mountains receive considerable government assistance for the purchase of fertilizers.

Although this, in general Norwegian agriculture uses relatively low amounts of pesticides. Pesticide uses has declined substantially over the past two decades and at the present only about 7% of planted areas are treated. The only pesticide approved for use in Norway is glyphosate (Inger Sundheim et al., Norwegian institute for Agricultural and Environmental research).

However, leaching of pesticides to surface and ground water is increasingly as a problem (Tiberg, 1998). In 2005/2006, the amounts of fertilizer and pesticides used on agricultural land totaled about 104, 100 tones of nitrogen and about 12, 400 tones of phosphorus. These nutrients are an essential basis for increased agricultural production, but if they are lost from the nutrient cycle, they may cause pollution by eutrophication of lakes, rivers and coastal waters (State of the Environment, Norway).

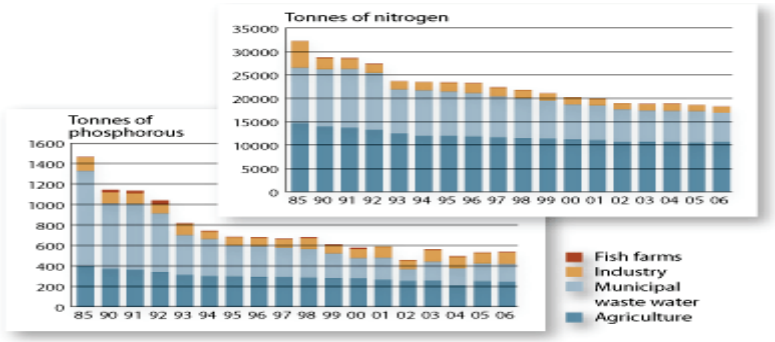


Figure 3. Imputs of nutrients in Norway

1.3 Causes of using fertilizer and pesticides: Eutrophication

Fertilizer from farmland pollutes water in the same way as discharges of nutrients from domestic waste water, aquaculture and certain types of industry. Locally, agriculture alone can cause eutrophication in a watercourse.

Water Eutrophication occurs due to runoffs of nutrients into echo systems which, as a result, experience “algae blooms” or excessive, abnormal algae growth, which leads to a depletion of oxygen in the body of water. Lack of oxygen can lead to fish death and nutrient run-offs may cause bacterial, viral and parasitic diseases (Food and Agriculture Committee, Norway). In Advanced chapters (Chapter 3) Eutrophication problems will be treated in a huge way.

In addition, agriculture can contribute to eutrophication of coastal waters in certain parts of the North Sea, in combination with domestic waste water, discharges from industry and long-range pollution. In 1988/1989 an algae disaster caused the death of many marine biota in the North Sea and Skagerrak. The pollution of the water by N and P was identified as the cause for the huge increase of poisons algae. Since that moment the European countries bordering the North Sea agreed on a plan to reduce this pollution (North Sea Declaration). Inland, the coastline from the Swedish border to Lindesnes (the southern tip of Norway) has also been vulnerable to excessive phosphorous loads. And two areas from the Swedish border to Strømtangen lighthouse near Fredrikstad, and the inner Oslofjord, have received nitrogen loads for several years.

The catchments of these areas are identified as vulnerable zones according to the EU nitrates directive. In these zones, as is possible to see in the figure 4, Norway is required to establish action programs to reduce nitrogen and phosphorus pollution from agriculture.

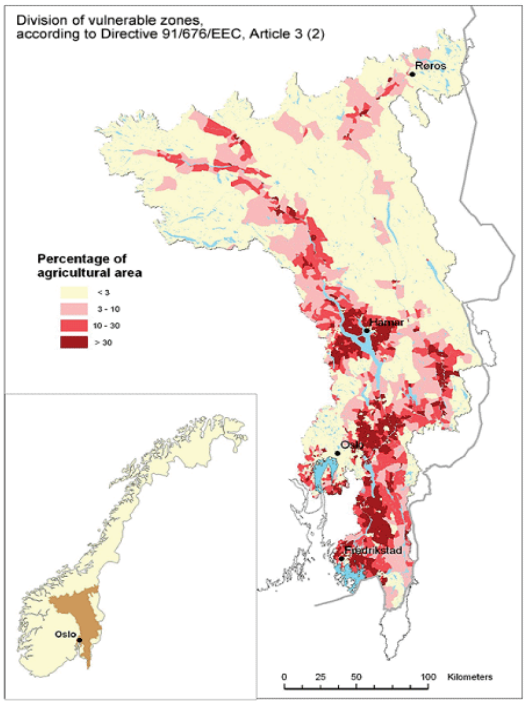


Figure 4. Vulnerable areas

Areas designated as vulnerable zones according to Council Directive 91/676/EEC, Article 3(2). The percentage of agricultural land within a basic unit, which is the smallest geographical unit Statistics Norway uses for statistical purposes, has been used as an indicator of the risk of pollution caused by nutrients from agriculture. Is consider the whole catchment area as a vulnerable zone

1.4 Regulations

To limit discharges of nutrients from agriculture and the environmental damage they can cause, different sets of regulations have been laid down pursuant to the Pollution Control Act and the Soil Protection Act.

The regulations relating to manure and to silage effluent are intended to reduce point discharges from storage facilities and runoff when manure is used on agricultural land, and a regulation relating to the leveling of agricultural land are to help control runoff from areas that have been leveled.

Also to reduce erosion, the government has set as a priority the reduction of the area under autumn ploughing in regions susceptible to soil erosion. Farmers received compensation for ploughing their land in spring. The amount of compensations is related to the erosion risk level of the particular areas (Arnoldussen, Norwegian Institute of Land Inventory)

In addition to these regulations, the Ministry of Agriculture has used other regulations and grant schemes to reduce excessive nutrient inputs. These include the regulations relating to fertilizer management and a number of grant schemes that encourage conversion to more environmentally-friendly cultivation techniques such as:

- altering soil management regimes so that farmers avoid leaving areas with no plant cover in winter
- applying fertilizer in such a way that there is no surplus of nutrients
- maintaining strips of vegetation along the edges of fields
- constructing grassed waterways to prevent erosion

Until 1997, grants were provided for technical facilities to improve environmental conditions in agriculture, and point discharges were considerably reduced as a result.

The Ministry of Agriculture has been responsible for drawing up action programs as required by the EU nitrates directive. When these have been completed, it is expected that further measures will be taken to reduce nutrient inputs from agriculture (Miljostatus).

2 Agricultural chemistry

In areas with intensive livestock farming, soils are often enriched with Phosphorous as a result of continued applications of fertilizers, pesticides and animal manures (Pautler and Sims, 2000). The P accumulation in soil and subsequent loss of it from soils to waterways can accelerate Eutrophication of surface waters (Sharpley et al., 2003).

The potential desorbability of soil P has been well correlated with soil P saturation which estimates the degree to which P sorption sites have been filled (Beauchemin and Simard, 1999). In chemical terms, P saturation is defined as the amount as the amount of P as a fraction of total P sorption capacity of a soil. The p sorption capacity, a measure of the ability of soil to retain p mainly by adsorption and precipitation, is therefore an important factor controlling the release of P from soil water.

Phosphorous usually shows limited mobility in soils and its contribution to accelerated water Eutrophication is mostly attributable to surface flow rather than subsurface flow (Sims et al., 1998; Elliot et al., 2002). However areas of intensive agriculture can be susceptible to deep leaching of P due to a long history of over fertilization and uses of pesticides (Ham, 1999; Novak et al., 2000).

To understand better this flux of P is needed knowledge in its behavior.

2.1 Phosphorus chemistry in soil

Phosphorus (P) (atomic weight 30.974) is the 12th most abundant element in the lithosphere (Biogeochemistry of wetlands). Is a naturally element, which exists in mineral, soil, living organism and water. Opposite to N that can be incorporate to the soil from the atmosphere, all the P present in the soils, come from decomposition of the bedrock during the process of weathering and represents round 0.1% of the earth crust (Quimica Agricola).

The P cycle is dynamic and involves interaction or exchange between biotic and abiotic pools. Understanding for abiotic components, non-living

chemical and physical factors in the environment, and as biotic components as living organism.

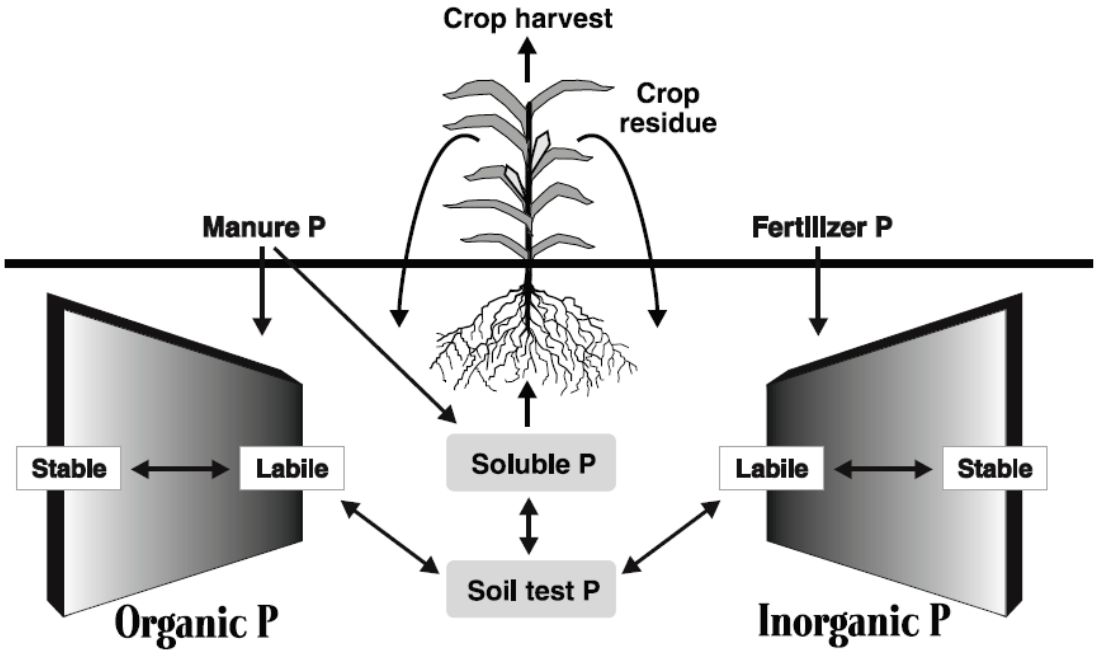


Figure 5. The phosphorus cycle

The forms of P present in soil can include organic, soluble or bound forms. Understanding the relationship among these forms of P is necessary to understand plants utilization of it and the extent to which P can move within the environment (Wiederhoft and Johnson, NSDU, 2005).

2.1.1 Different forms of phophorus in soil

Phosphorus comes from a polyprotic acid, the phosphoric acid (H_3PO_4) and the class of phosphate ion that we can find en the soil depends of pH of it. Between the limits of pH that normally are in the soil is possible to find three forms of phosphates groups:

$[H_3PO_4] \leftrightarrow [H_2PO_4^-] + [H^+]$ log Kº = -2.15 (primary ionization)

$[H_2PO_4^-] \leftrightarrow [HPO_4^{2-}] + [H^+]$ log Kº = -7.20 (secondary ionization)

$[HPO_4^{2-}] \leftrightarrow [PO43^-] + [H^+]$ log Kº = -12.35 (tertiary ionization)

Under acid soil conditions (pH=4), the dominant phosphate species is ortophosphoric acid (H_3PO_4) which is a weak acid, colorless and freely

soluble in water. Dominant specie under alkaline soil conditions (pH=9) is $PO4_3^-$. In the pH range of most soils (pH 4-6.5) $H_2PO_4^-$ is the dominate form of orthophosphate, easier absorb form by plants.

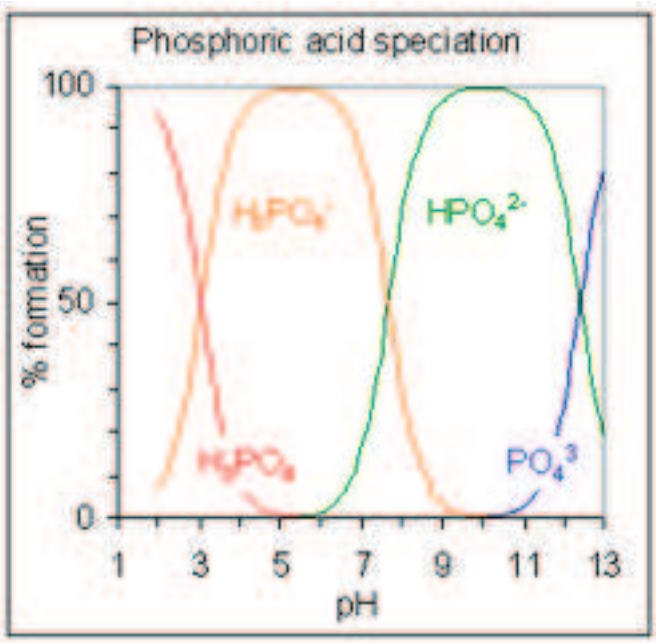


Figure 6. Relative distribution of phosphate species as a function of pH

The relative protonation and deprotonation determine their reactivity as inorganic ligands or ion pairs particularly with iron (Fe^{3+}) and Aluminum (Al^{3+}) in acidic conditions. And with alkalinity pH reacts with calcium, sodium or magnesium, but the presence of sodium in soil is rarely, we were talking then about saline soils.

Category	Subcategory	Examples	References
Inorganic	Ionic	PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$	Aslyng (1954)
	Mineral	Apatite, tinticite	Frossard et al. (1995)
Organic	Monoesters	Inositol hexaphosphate	Anderson et al. (1974)
	Diesters	Phospholipids	Newman and Tate (1980); Hawkes et al. (1984)
		Nucleic acids	Newman and Tate (1980); Hawkes et al. (1984)
	Biomass P	Microbial P	Brookes et al. (1982, 1984)
		Adenosine triphosphate	Jenkinson et al. (1979)
	Humic P		Tiessen et al. (1994)

Table 1. Some categories of phosphates in the soil

Both organic and inorganic phosphates are to be found (Table 1), but neither category is ever present to the exclusion of the other, and neither could be said to be the dominant category in soils worldwide. This is in contrast to nitrate, which is found in the soil only as an anion and is never combined chemically with organic matter. There is also usually about 50 times as much organic nitrogen in a soil as there is nitrogen as nitrate.

2.1.1.1 Inorganic phosphate

Orthophosphoric acid is tribasic, but the first dissociation constant is very much greater than the second or third. The proportions of the three orthophosphate ions depend on the pH of the solution but all are likely to be present at the pH values likely to be found in most soils (Aslyng, 1954). All the dihydrogen phosphates are soluble in water, but of the other orthophosphates, only those of the alkali metals (except lithium) are water-soluble. Plants reportedly show a preference for the dihydrogen phosphate (Moser et al., 1959), and (Aslyng, 1954) gave a table showing the proportion of the total orthophosphate present in this form at various pH values. This proportion will be relevant to phosphate leaching where the dihydrogen phosphate is sorbed or precipitated preferentially or when plant uptake is likely to diminish leaching significantly.

Inorganic phosphate is found in a variety of insoluble forms, of which the commonest in the earth's crust is apatite (Frossard et al., 1995). This has the general formula $Ca_{10}X_2(PO_4)_6$, where X is OH^- or F^-, giving hydroxyapatite or fluoroapatite, respectively.

$3(PO_4)_2Ca_3F_2Ca$ Fluoroapatite
$3(PO_4)_2Ca_3CaCO_3$ Carbonate apatite
$3(PO_4)_2Ca_3Ca(OH)_2$ Hidroxi apatite
$3(PO_4)_2Ca_3CaO$ Eloxi apatite
$(PO_4)_2Ca_3$ apatite, tricalcium phosphate
PO_4HCa Calcium monophosphate
PO_4H_2Ca Calcium dihydrogen phosphate

Calcium may be substituted by sodium or magnesium and phosphate by carbonate. Monocalcium, dicalcium and octocalcium phosphates are also found in soils in which calcium predominates over aluminum and iron.

Where the latter metals dominate the system, the phosphate compounds formed are not usually well crystallized (Frossard et al., 1995). Reaction with aluminium oxides may give an amorphous phosphate or an organized phase such as sterrerite, $(Al(OH)_2)_3HPO_4H_2PO_4$, while iron oxides may give tinticite, $Fe_6(PO_4)_4(OH)_6 \cdot 7H_2O$ or griphite, $Fe_3Mn_2(PO_4)_2(OH)_2$.

Among all the calcium phosphates, fluoropatite is the most insoluble compound of the group and the product group that contains the phosphorus in the least taken up by plants of all phosphate groups. The only soluble in water and therefore assimilated by plants are calcium monohydrogen phosphates.

2.1.1.2 Organic phosphate

The organic component usually comprises 30–70% of the phosphate in mineral soils (Hedley and Tiessen). It is found in a wide range of forms in the soil (Table 1), which is not surprising, given its role in metabolic energy transfer and other life processes.

2.1.1.2.1 Monoesters

The term monoester-phosphate is used to describe compounds with the general structure ROH_2PO_3, of which the commonest in soils is inositol hexaphosphate. Inositol is essentially a hexane ring on which each carbon atom carries a hydrogen atom and a hydroxyl group. Its hexaphosphate, also known as phytin or phytic acid, results from the esterification of each hydroxyl group. It has been known to soil scientists for many years (Anderson and Arnold), studied its hydrolysis, finding that the ester linkages were not all broken at the same time. The presence of the organic group in the molecule does not prevent the phosphate group from being sorbed by the soil, and this plays an important part in the compound's behavior in the soil (Anderson et al., 1974).

2.1.1.2.2 Diesters

Diesters have the general structure $(RO)(R'O)HPO_3$, but this simplified structure covers a wide range of compounds that include fragments of RNA (Anderson and Newman), phospholipids and teichoic acid, a compound

which consists of sugar units linked by phosphate groups and which may originate from bacterial cell walls (Ward, 1981).

2.1.1.1.3 Microbial biomass phosphate

The term microbial biomass has evolved as a collective term for the bacteria, fungi and small soil animals that between them effect the turn-over of organic matter in the soil (Jenkinson and Powlson, 1976). Phosphate is a constituent of phospholipids, DNA and RNA in these organisms and is also involved in their metabolic energy transfers. Brookes et al. (1984) estimated the microbial biomass phosphate in six arable soils to be between 6 and 24 kg ha^{-1}, i.e., about 3% of the organic phosphate, and that in eight grassland soils to be between 18 and 101 kg ha^{-1}, about 14% of the organic phosphate.

2.1.1.1.4. Humic phosphate

The term humic phosphate is used to describe phosphate associated with dead organic matter that does not fall into either of the ester categories. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. Some of it will be susceptible to mineralization by microbes in the soil and some inert. (Hedley et al.,1982).

2.2 Effects of tillage in phosphorus losses

Tillage operations fall into three categories, primary tillage, secondary tillage and subsoiling. Primary tillage usually aims to loosen compacted soil and it often involves total or partial inversion of the top 250 mm of soil, which buries weeds and incorporates crop residues so that they can be broken down by microbes. Secondary tillage causes further soil fragmentation intended to produce a seedbed. Both types of tillage are part of the annual routine for many farmers, but subsoiling is usually done only on an occasional basis. It goes well below the depth of the other operations to loosen dense or compacted subsoils or to provide more drainage channels.

Tillage has a very important effect on the structure of the soil (Dexter, 1988). In particular, it changes the size distribution of the aggregates in the top-soil and the water pathways through it. The fragmentation may also

lessen the porosity of the aggregates; their mass is conserved, but their porosity is not (Currie, 1966). It also usually compact the soil at the base of the plough layer, making it more impermeable, and this can have significant consequences for flows of water and pollutants from the soil.

2.2.1 Leaching of phosphorus through different tillage

Fields with high losses of phosphorus must have a high source potential and a mechanism to transport phosphorus to bodies of water. Phosphorus can travel to surface water attached to particles as soil or manure. But also can dissolve into runoff water as it passes over the surface of the field.

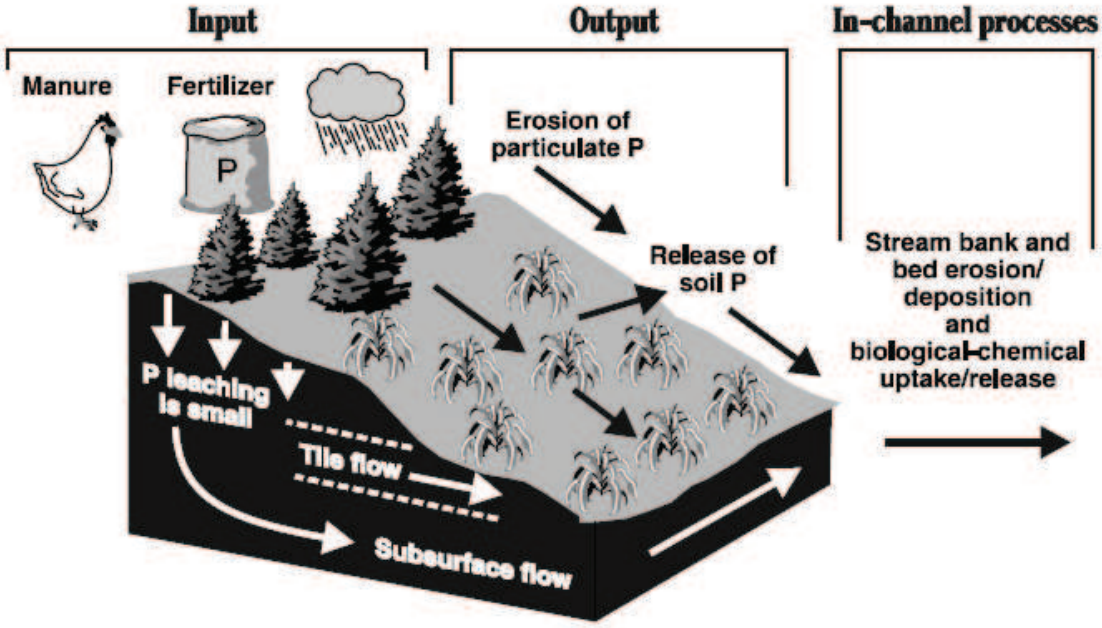


Figure 7. Phosphorus movement

Leaching of phosphorus usually is not a significant concern. Soil particles strip soluble phosphorus from the water as it leaches through the soil profile. The concentration of phosphorus leachate is significantly less than surface runoff concentrations (section 2.2.2). However, special situations can allow higher concentrations of phosphorus into groundwater. The capacity of soil to absorb phosphorus can be overwhelmed on sandy soils or when the water table is close to soil surface. Also, cracking is soil creates channels allowing surface water to travel directly to groundwater.

Tillage increases surface roughness and thence the capacity to store water in surface depressions. This will encourage infiltration into the soil matrix rather than surface run-off or preferential flow, both of which are likely to carry solutes, including phosphate, rapidly from the soil surface into water bodies in which they are not wanted. Tillage also lessens the bulk density of the top-soil and thus increases its overall porosity, which will have broadly the same consequences. These effects will lessen phosphate leaching and will also interact in a beneficial way (Addiscott and Dexter, 1994). Tillage and other operations leave wheelings in the soil in which cracks form subsequently. Cracks so formed could act as preferential flow pathways for phosphate loss.

Ploughing can leave a smeared or compacted layer at the base of the top-soil. This could have a beneficial effect, by delaying downward water movement and increasing the 'exposure integral' for phosphate sorption. But it will, however, encourage horizontal flow of water, and if this flow is fairly rapid, phosphate losses to surface waters could be accelerated in some circumstances. Much will depend on the topography and the intensity of the rainfall.

Ploughing can seal-off the larger continuous pores in the soil, while direct drilling or minimum tillage leaves them open and should encourage preferential flow, making any phosphate on the surface vulnerable to rapid leaching, whether it comes from fertilizer or other sources.

Tillage that inverts the soil moves any phosphate or crop residues on the surface to a depth of up to 250 mm (Figure 8). This could be significant in some circumstances. What may be more significant, however, is that practicing minimum tillage and not inverting the soil while continuing to broadcast phosphate fertilizer can lead to a build-up of phosphate in the soil at the surface. Such phosphate is very vulnerable to loss in the preferential flow described in the preceding paragraph or to being carried off in surface run-off

Figure 8. Phosphate accumulated at the soil surface is protected by inversion tillage against loss by preferential flow or surface run-off

Clearly, good tillage practice can lessen phosphate losses by leaching, just as bad practice can make them worse. Fortunately, practices that retain water in the soil matrix and so help to store water in the soil for use by crops also seem likely to restrain losses of phosphate by leaching.

2.2.2 Surface run-off of phosphorus

Run-off and erosion are considered to be the main mechanisms by which phosphate is lost from agricultural land, so the effects of tillage on these processes are important (Sharpley et al.,1992). Phosphorus is almost considered entirely associated with soil particles. When run-off water gains sufficient energy to cause soil erosion, the amount of phosphorus lost from the field increases dramatically. Reducing or eliminating tillage to control erosion can reduce total phosphorus losses significantly.

One of the measures that nowadays has been taken to minimize erosion losses of phosphorus is the inversion tillage (figure 8), can be useful as a means of removing phosphate from the critical top 25 mm of soil, where it tends to accumulate. Sharpley et al. (1994) cite several papers showing that incorporating phosphate, from fertilizer or manure, beneath the soil surface lessened the loss by run-off. This practice will remain effective, of course, only until long-term fertilizer use and cultivation bring about a uniformly large concentration of phosphate in the top-soil. The risk of losses by run-off should generally be lessened by tillage practices designed to retain water within the soil. The most basic of these is simply to plough across the slope rather than up and down it (Catt et al., 1994).

Figure 9. Field with inversion tillage
Is possible to show how the soil is removed.

2.3 Fertilizers and pesticides: Sources of phosphorus

As has been introduce in this chapter fertilizers and pesticides are one of the main source of phosphorus, that is why an overview of them is necessary to understand how they can affect to the eutrophication problem.

2.3.1 Fertilizers

Fertilizers are soil amendments applied to promote plant growth; the main nutrients present in fertilizer are nitrogen, phosphorus, and potassium (the 'macronutrients') and other nutrients ('micronutrients') are added in smaller amounts. Fertilizers are usually directly applied to soil, and also sprayed on leaves .Fertilizers are roughly broken up between organic and inorganic fertilizer, with the main difference between the two being sourcing, and not necessarily differences in nutrient content.

Organic fertilizers and some mined inorganic fertilizers have been used for many centuries, whereas chemically-synthesized inorganic fertilizers were only widely developed during the industrial revolution. Along this section only some of phosphates fertilizers are going to be mention, as examples of sources of phosphorus.

2.3.1.1 Phosphate fertilizers

The development of modern phosphate fertilizer industry began in 1842 when was patent a process by which a natural phosphorus mineral is treated with sulfuric acid to provide a product that has a high efficiency in phophorus, began then a continuous period of superphosphate until 1950, when they began to market fertilizer products with a higher phosphorus content, better management and greater economy in its manufacture.

Currently fertilizer phosphorus fertilizers industry has an output of approximately 100 - 120 million metric tons of phosphate fertilizer colliding with the production that were in the 1955 only 6 million metric tons. All part of a phosphate fertilizer raw materials comes from natural deposits of phosphorite, which are popularly known as apatite, are extensive sedimentary deposits found near the surface and pit exploited discovered, an analytical study has shown that most of the phosphorus found in the sea and all deposits of phosphorus derived from marine

organic remains, that by tectonic lavas have emerged abroad. (Quimica Agricola).

Any part of the natural phosphate comes from tricalcium phosphate, and natural products will always be accompanied by considerable portions of clay, calcium carbonate, organic matter, magnesium carbonate, fluoride, iron and aluminum oxides. These natural products undergo a series of treatments in order to become phosphate fertilizer, today phosphorus fertilizers are classified into three broad groups, depending on the treatment that natural phosphorites had suffered:

- Ground phosphates, which are those obtained a selection and a more or less fine grind natural phosphates.
- Roasted, calcined phosphate, phosphate here is subjected to heat treatment at various temperatures, followed by addition of stabilizing agents.
- Finally we have those treated with acid, obtained by treatment of phosphorite with various acids with a natural right to solubilize tricalcium phosphate, from phosphate to mono or dicalcium, or to obtain phosphoric acid.

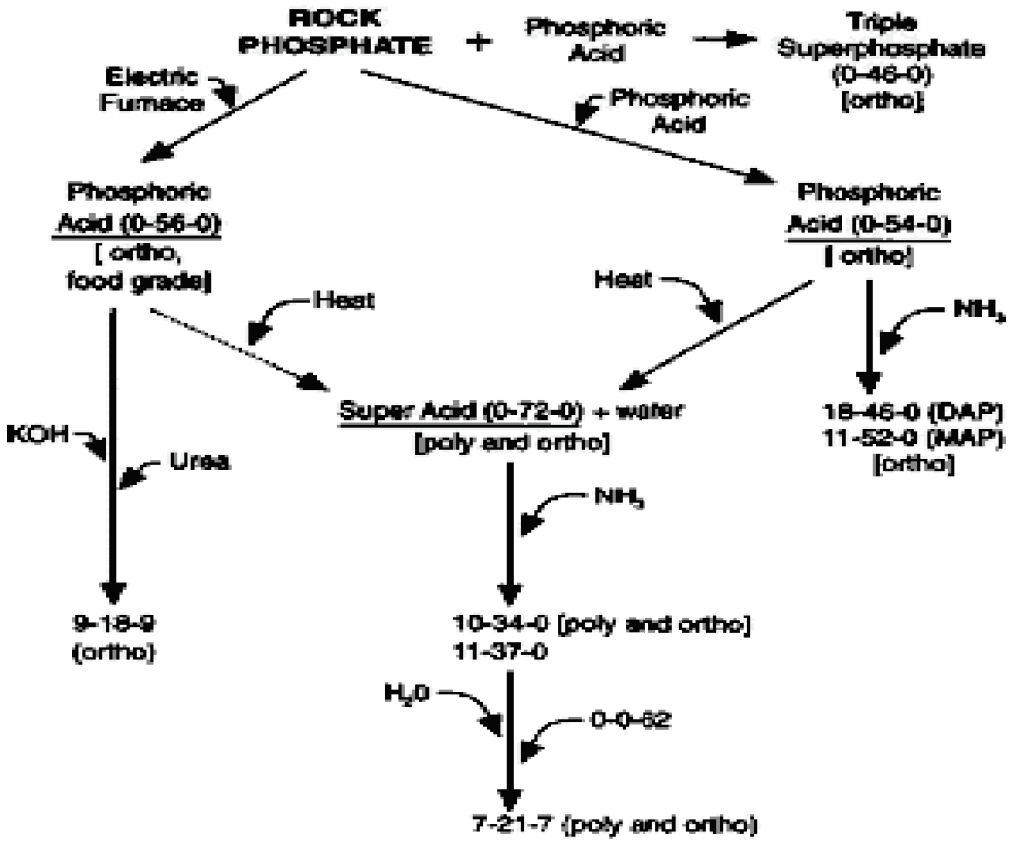


Figure 10. Obtaining of different phosphorus fertilizers

2.3.2 Pesticides

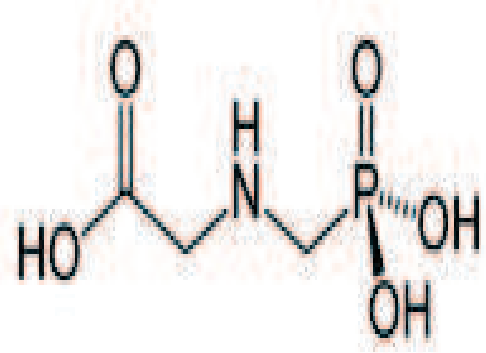
As FAO (Food and Agriculture Organization of the United Nations) has defined:

Pesticide is any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. The term includes substances intended for use as a plant growth regulator, defoliant, desiccant or agent for thinning fruit or preventing the premature fall of fruit, and substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport.

But behind these benefits, pestices raise a number of environmental concerns.

2.3.2.1 Glyphosate: an example of phosphate pesticide

As was mention in the first chapter (Overwiew of the agriculture in Norway), Glyphosate is the only pesticide that can be use nowadays in Norway.



Glyphosate (N-(phosphonomethyl) glycine) is a broad-spectrum systemic herbicide used to kill weeds, especially perennials. It is typically sprayed and absorbed through the leaves, injected into the trunk, or applied to the stump of a tree, or broadcast or used in the cut-stump treatment as a forestry herbicide.

Figure 11. Glyphosate structure

Glyphosate is an aminophosphonic analogue of the natural amino acid glycine and the name is a contraction of *glycine*, *phos*-, and *-ate*. The molecule has several dissociable hydrogens, especially the first hydrogen of the phosphate group. The molecule tends to exist as a zwitterion where a phosphonic hydrogen dissociates and joins the amine group. Technical grade glyphosate is a colourless, odourless crystalline powder, formulated as water-soluble concentrates and granules. Glyphosate was first discovered to have herbicidal activity in 1970 by John E. Franz. Commonly known by its original trade name Roundup™ (manufactured by Monsanto) (PANAP, 2009).

Glyphosate is believed to be the world's most heavily used pesticide (Duke and Powles, 2008), with over 600 thousand tonnes used annually (CCM International 2009). It is a broad spectrum (non-selective), systemic, post-emergence herbicide used to control annual and perennial plants including grasses, sedges, broadleaf weeds and woody plants. It is used for crops, orchards, glasshouses, plantations, vineyards, pastures, lawns, parks, golf courses, forestry, roadsides, railway tracks, industrial areas, and home gardening. It is used for pre-harvest desiccation of cotton, cereals, peas, beans, and other crops; for root sucker control; and for weed control in aquatic areas.

2.3.2.1.1 Mode of action

The commonly accepted explanation of glyphosate's mode of action is as follows: glyphosate inhibits the enzyme 5-enolpyruvyl-shikimate 3-phosphate synthase, which is essential for the formation of aromatic amino acids (phenylalanine, tyrosine, tryptophan) in plants, by what is commonly referred to as the shikimic pathway. Without amino acids the plants cannot make protein; growth ceases, followed by cellular disruption and death. The shikimic pathway is not found in the animal kingdom, hence glyphosate was thought to be "relatively non-toxic to mammals" (Anadón 2009). However, there may be more to it than that: after glyphosate is absorbed through the foliage, it is translocated within the plant, down to the roots and released into the rhizosphere (soil surrounding the roots) (Kremer and Means, 2009), where it disrupts the soil and root microbial community

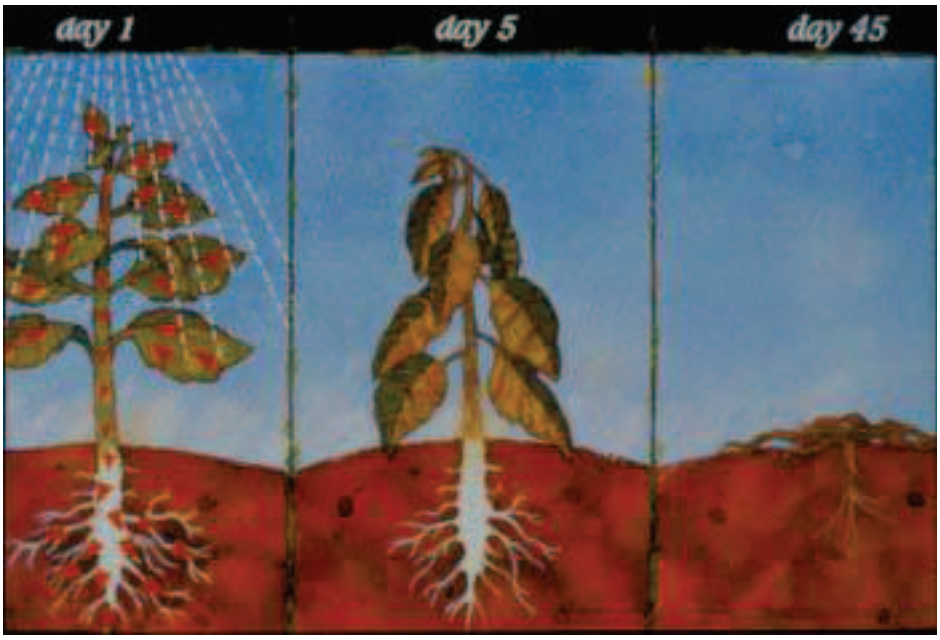


Figure 12. How Roundup works

2.3.2.1.2 Environmental fate

Soils

Glyphosate is relatively persistent in soil, with residues still found up to 3 years later in cold climates. It is less persistent in warmer climates, with a half-life between 4 and 180 days. It is bound onto soil particles, and this was once thought to mean that glyphosate is not biologically active within soil, nor will it leach to groundwater. However it is now known that it can easily become unbound again, be taken up by plants or leach out, indicating a greater risk of groundwater contamination. It can reduce nitrogen and phosphate fertility of soils.

Water

Glyphosate is soluble in water, and slowly dissipates from water into sediment or suspended particles. Although it does break down by photolysis and microbial degradation, it can be persistent for some time in the aquatic environment, with a half-life of up to nearly 5 months, and still be present in the sediment of a pond after 1 year.

Residues of glyphosate have been found in a wide range of drains, streams, rivers, and lakes, in many countries including Canada, China, France, Netherlands, Norway, USA, and the UK (Widelfalk et al.,2008). The structure and composition of natural aquatic communities, the diversity of species, and the balance and interactions between them are of profound importance for ecosystem functioning right through all the trophic levels (Pérez et al 2007); and Roundup has been shown to have profound impacts on such communities. The effects on microorganisms, algae and amphibia vary considerably between species, raising concerns about how contamination of freshwater environments with glyphosate can tip the ecological balance, possibly giving rise to harmful algal blooms (Pérez et al, 2007) and reducing species richness (Relyea, 2005).

3 Eutrophication: consequence of the use of phosphorus

Phosphorus can be a major limiting nutrient in many freshwater aquatic ecosystems such as lakes or streams. Phosphorus loads from uplands to many aquatic systems rapidly increased during the industrial and green revolution as a result of heavy fertilizer use. Wetlands usually work as buffers for phosphorus retention between uplands and adjacent aquatic systems. Converting wetlands to agricultural and urban lands decreased the capacity of existing wetlands to retain phosphorus. As consequence, has increased the enrichment of many lakes, rivers, estuaries, and coastal waters with phosphorus.

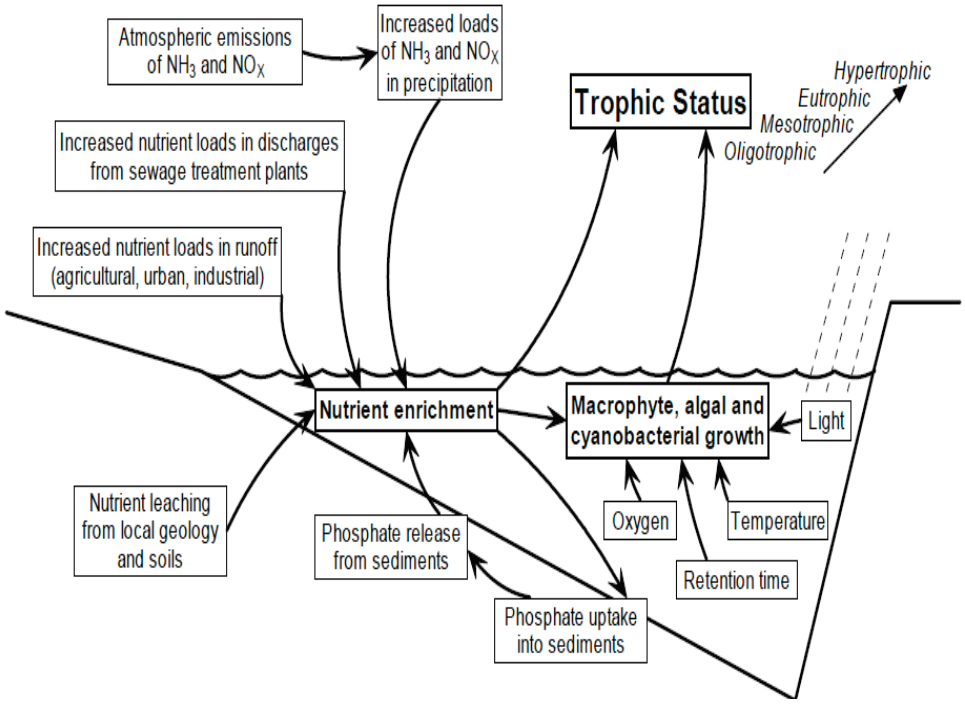


Figure 13. Most important factors driving Eutrophication process

Typically, phosphorus is added in various forms to a watershed (figure11). These include fertilizers, nonhazours wastes (animal manures), and nutrient enriched waters.

3.1 Eutrophication definition

"Eutrophication" is the enrichment of surface waters with plant nutrients. While eutrophication occurs naturally, it is normally associated with anthropogenic sources of nutrients. Understanding as anthropogenic: effects, processes or materials derivation from human activities, as opposed to those occurring in biophysical environments without human influence.The "trophic status" of lakes is the central concept in lake management. It describes the relationship between nutrient status of a lake and the growth of organic matter in the lake. Eutrophication is the process of change from one trophic state to a higher trophic state by the addition of nutrient (table 2). Agriculture is a major factor in eutrophication of surface waters.

Trophic status	Organic matter mg/m^3	Mean total phosphorus[1] mg/m^3	Chlorophyll maximum[1] mg/m3	Secchi depth[1] m
Oligotrophic	low	8.0	4.2	9.9
↓				
Mesotrophic	medium	26.7	16.1	4.2
↓				
Eutrophic	high	84.4	42.6	2.45
↓				
Hypertrophic	very high	750-1200		0.4-0.5

Table 2. Relationship between trophic levels and lake characteristics

The sequence of trophic state, from oligotrophic (nutrient poor) to hypertrophic (nutrient rich) is shown in table 3. Is possible realized showing the table that in the eutrophic state the amount of total phosphorus is really huge in comparison with the oligrotrophic state.

3.1.1 What is meant by Trophic State?

The trophic state of a lake is a hybrid concept with no precise definition. Originally, trophic referred to nutrient status. Eutrophic water was water with high concentrations of nutrients and by extension, a eutrophic lake was a lake that contained eutrophic water. Now a eutrophic lake may not only be a lake with high levels of nutrients, but also a very shallow pond, full of rooted aquatic plants, that may or may not have high levels of nutrients. Lakes are divided into three trophic categories: oligotrophic, mesotrophic, and eutrophic.

- Oligotrophic lake is a large deep lake with crystal clear waters and a rocky or sandy shoreline. Both planktonic and rooted plant growth are sparse, and the lake can support a cold water fishery.
- Eutrophic lake is typically shallow with a soft and mucky bottom. Rooted plant growth is abundant along the shore and out into the lake, and algal blooms are not unusual. Water clarity is not good and the water often has a tea color.
- Mesotrophic is an intermediate trophic state with characteristics between the other two.

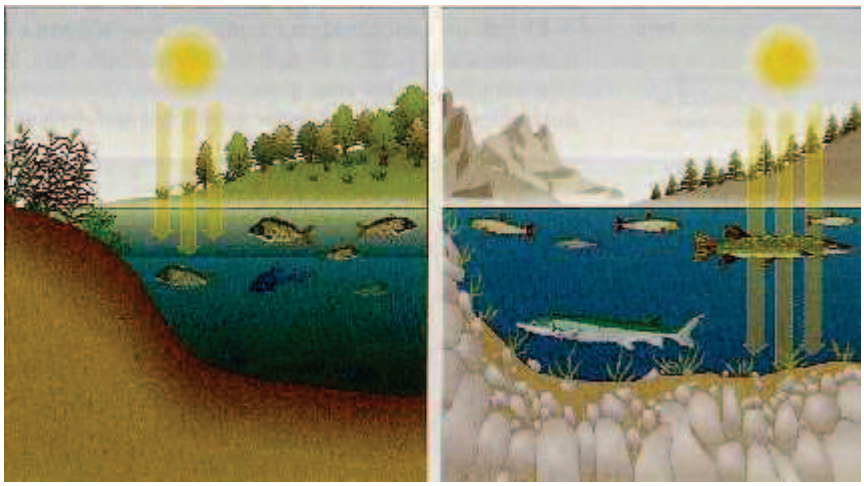


Figure 14. Eutrophic lake and oligotrophic lake

3.1.2. Symptoms and impacts of eutrophication

Below is show some impacts causes by the eutrophication effect, is a recompilation from those which FAO(FAO, 1997) consider more important:

- Increase in production and biomass of phytoplankton, attached algae, and macrophytes.
- Shift in habitat characteristics due to change in assemblage of aquatic plants.
- Replacement of desirable fish (e.g. salmonids in western countries) by less desirable species.
- Production of toxins by certain algae.
- Increasing operating expenses of public water supplies, including taste and odour problems, especially during periods of algal blooms.

- Deoxygenation of water, especially after collapse of algal blooms, usually resulting in fish kills.
- Infilling and clogging of irrigation canals with aquatic weeds (water hyacinth is a problem of introduction, not necessarily of eutrophication).
- Loss of recreational use of water due to slime, weed infestation, and noxious odour from decaying algae.
- Impediments to navigation due to dense weed growth.
- Economic loss due to change in fish species, fish kills, etc.

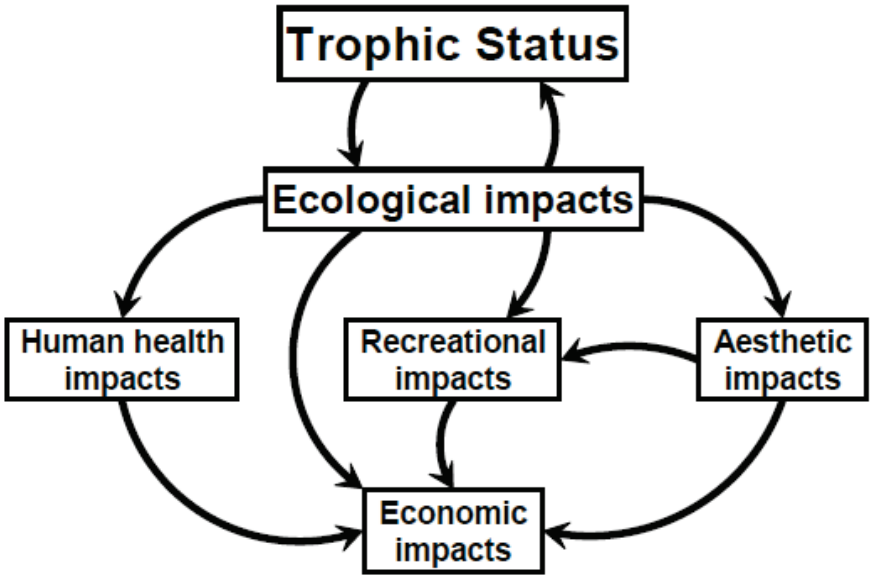


Figure 15. Summary of potential negative impacts of high level trophic state

3.1.3 Managing eutrophication

The basis of eutrophication management is often the 'limiting nutrient concept' (Walmsley, 2000). The rate and extent of aquatic plant growth is dependent on the concentration and ratios of nutrients present in the water. Plant growth is generally limited by the concentration of that nutrient that is present in the least quantity relative to the growth needs of the plant. Minimisation of eutrophication-related impacts therefore tends to be focussed on efforts to reduce nutrient (particularly phosphorus) inputs. This approach therefore deals directly with the primary cause of eutrophication (namely, nutrient enrichment).
Typically, limiting nutrients entering an impoundment exhibiting a high degree of eutrophication will first focus on point sources. These are easier to quantify, simpler to manage and often contribute the highest nutrient

load. Following this, non-point sources are managed and then internal ("in-lake") management options can be implemented.

3.1.3.1 Reducing eutrophication

There are two possible approaches to reducing eutrophication:

1. Reduce the source of nutrients (e.g. by phosphate stripping at sewage treatment works, reducing fertilizer inputs, introducing buffer strips of vegetation adjacent to water bodies to trap eroding soil particles).
2. Reduce the availability of nutrients currently in the system (e.g. by removing plant material, removing enriched sediments, chemical treatment of water).

3.1.3.1.1 Reducing the nutrient source

Europe is the continent that has suffered most from eutrophication, and increasing efforts are being made to restore European water bodies damaged by nutrient enrichment. If the ultimate goal is to restore sites where nature conservation interest has been damaged by eutrophication, techniques are required for reducing external loadings of nutrients into ecosystems.(Environmetal agency)

Although algal production requires both nitrogen and phosphorus supplies, it is usually sufficient to reduce only one major nutrient. As phosphorus is the limiting nutrient in most freshwater systems, phosphorus has been the focus of particular attention in attempts to reduce inputs. In addition, nitrogen is less easily controlled: its compounds are highly soluble and can enter waterways from many diffuse sources. It can also be 'fixed' directly from the atmosphere. Phosphorus, on the other hand, is readily precipitated, usually enters water bodies from relatively few point sources (e.g. large livestock units or waste-water treatment works) and has no atmospheric reserve. However, efforts to reduce phosphorus loadings in some lakes have failed due to ongoing release of phosphorus from sediments. In situations where phosphorus has accumulated naturally (e.g. in areas with phosphate-rich rocks) and nitrogen increases have driven eutrophication, it may be necessary to control nitrogen instead.

Diversion of effluent

In some circumstances it may be possible to divert sewage effluent away from a water body in order to reduce nutrient loads. The sewerage system was redesigned to divert effluent away from the lake. Diversion of effluent should be considered only if the effluent to be diverted does not constitute a major part of the water supply for the water body. Otherwise, residence times of water and nutrients will be increased and the benefits of diversion may be counteracted.

Phosphate stripping

It has been estimated that up to 45% of total phosphorus loadings to freshwater from sewage treatment works. This input can be reduced significantly (by 90% or more) by carrying out phosphate stripping. The effluent is run into a tank and dosed with a product known as a precipitant, which combines with phosphate in solution to create a solid, which then settles out and can be removed. It is possible to use aluminium salts as a precipitant, but the resulting sludge contains toxic aluminium compounds that preclude its secondary use as an agricultural fertilizer. There are no such problems with iron salts, so Fe(II) ammonium sulfate is frequently chosen as a precipitant. The chemicals required as precipitants constitute the major cost, rather than installations or infrastructure, and the process is very effective: up to 95% of the phosphate can be removed easily, and it is possible to remove more. Despite its effectiveness, however, phosphate stripping is not yet used universally in sewage treatment (Environmental agency).

Buffer strips

Buffer strips are used to reduce the amounts of nutrients reaching water bodies from runoff or leaching. They usually take the form of vegetated strips of land alongside water bodies: grassland, woodland and wetlands have been shown to be effective in different situations. The vegetation often performs a dual role, by reducing nutrient inputs to aquatic habitat and also providing wildlife habitat. A riparian buffer zone of between 20 and 30 m width can remove up to 100% of incoming nitrate. The plants take up nitrogen directly, provide a source of carbon for denitrifying bacteria and also create oxidized rhizospheres where denitrification can occur. Uptake of nitrogen by vegetation is often seasonal and is usually

greater in forested areas with sub-surface water flow than in grassland with predominantly surface flow. The balance between surface flow and sub-surface flow, and the redox conditions that result, are critical in determining rates of nitrate removal in buffer strips (Figure 14).

Figure 16. A field experiment investigating the effectiveness with which a grass buffer strip prevents nutrients applied to the arable field beyond from reaching the stream

Wetlands

Wetlands can be used in a similar way to buffer strips as a pollution control mechanism. They often present a relatively cost-effective and practical option for treatment, particularly in environmentally sensitive areas where large waste-water treatment plants are not acceptable

3.1.3.1.2 Reducing nutrient availability

Once nutrients are in an ecosystem, it is usually much harder and more expensive to remove them than tackle the eutrophication at source. The main methods available are:

- Precipitation (e.g. treatment with a solution of aluminium or ferrous salt to precipitate phosphates).
- Removal of nutrient-enriched sediments, for example by mud pumping.
- Removal of biomass (e.g. harvesting of common reed) and using it for thatching or fuel.

In severe cases of eutrophication, efforts have been made to remove nutrient-enriched sediments from lakes.

Nutrient-rich sediment can be sucked from the lake and used as fertilizer. Water extracted with the sediment can be treated with aluminium salts and run back into the lake. This action reduced phosphorus concentrations and improved the clarity and oxygenation of the water. However, removal or sealing of sediments is an expensive measure, and is only a sensible option in severely polluted systems (Rast and Thorton, 1996).

Removal of fish can allow species of primary consumers, such as the water-flea, *Daphnia*, to recover and control algae. Once water quality has improved, fish can be re-introduced.

Mechanical removal of plants from aquatic systems is a common method for mitigating the effects of eutrophication (Figure 15). Efforts may be focused on removal of existing aquatic 'weeds' such as water hyacinth that tend to colonize eutrophic water. Each tonne of wet biomass harvested removes approximately 3 kg N and 0.2 kg P from the system.

Figure 17. Harvesting methods

Alternatively plants may be introduced deliberately to 'mop up' excess nutrients. Submerged plants are not always as efficient as floating ones at assimilating nitrogen and phosphorus due to their slower growth, resulting from poor light transmission through water (particularly if it is turbid) and slow rates of CO_2 diffusion down through the water column.

4 Leaching phosphorus experiment: materials and methods

This experiment is a participation in a project called "*Reduced Pesticide loads and Risks in cropping systems* (Reduced)" which has being performed since 2007 by Bioforsk (Norwegian Institute for Agriculture and Environmental Research). This is a big project which includes different work packages, more specifically this experiment is related with the work package called "*Identification of process contributing to high risk of pesticide transfer on different soils and soil management"*. And inside this work package, to the activity called "*Leaching of glyphosate, fluazinam, phosphorus and soil particles trough soil profiles with different tillage*".

Through this part of the report only the study of leaching phosphorus is going to be explain. We will go through a basic explanation about what leaching phosphorus means and site description, sampling, experiment procedure and analysis of the samples will be presented.

4.1 Background

Surface application of phosphate as fertilizer, pesticide or manure is common practice in agriculture. The transport of phosphorus from the agricultural production systems to the surrounding water systems has received increased attention because acceleration of eutrophication of surface waters (Levine and Schindler, 1989). To reduce agricultural pollution some strategies are necessary and prerequisites for an efficient mitigation strategy are comprehensive knowledge and understanding of the transport processes and pathways for nutrients, pesticides and soil. These mitigation strategies depend on the transport process. Soil erosion and subsurface runoff have typically been focused on as the primary mechanism of phosphorus loss from soil to receiving waters. Although, significant phosphorus leaching can occur where certain combinations of

land use practices (i.e, overfertilization), soil properties (i.e sandy subsoil) and climatic conditions (i.e precipitations) exist (Eghball et al, 1996).

The objectives of this study are to characterized and quantify the phosphorus leaching from different types of soils under different tillage through different weather stations (autumn, winter and spring).

4.2 Sampling sites

Soil samples were collected from agricultural areas in two different Norwegian counties; Akerhus and Østfold. Exactly three sites where inside Akerhus county: Askim, Syverud and Solør, and the other site Rygge belongs to the Østfold county.

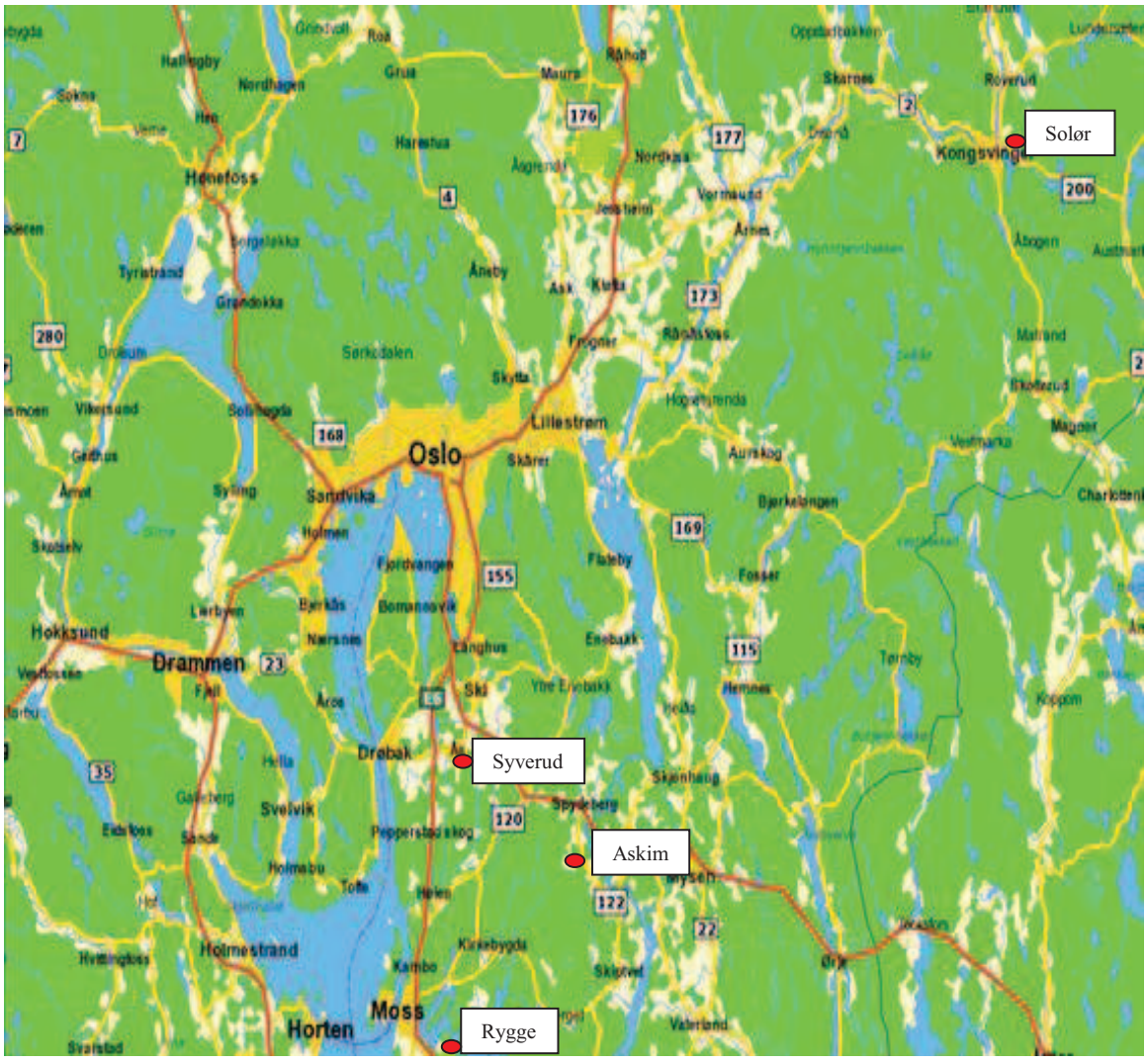


Figure 18. Location of the different sample sites

4.2.1 Characteristics of the sampling sites

Askim

Agricultural field situated 60 km south-east of Oslo

Autumn deep harrowing and spring shallow harrowing, corn site

Levelled silty clay loam

Figure 19. Situation Askim agricultural field

Syverud

Agricultural field situated 37 km south of Oslo

Autumn plowing and spring harrowing, corn site

Structured silt loam

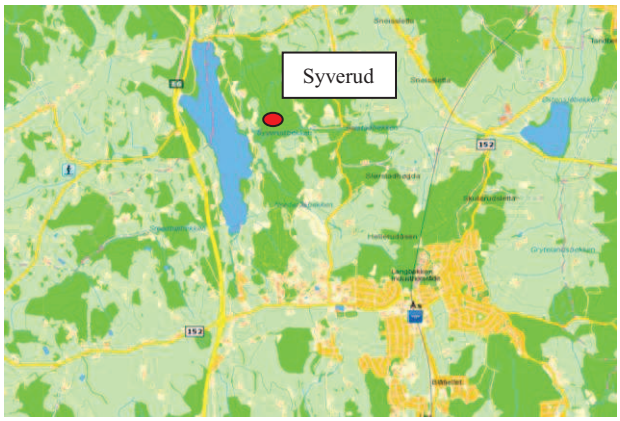


Figure 20. Situation Syverud agricultural field

Rygge

Agricultural field situated 70 km south of Oslo

Potato crop field

Sandy field

Figure 21. Situation Rygge agricultural field

Solør

Agricultural field situated 110 km north-east of Oslo

Potato crop field

Silt field

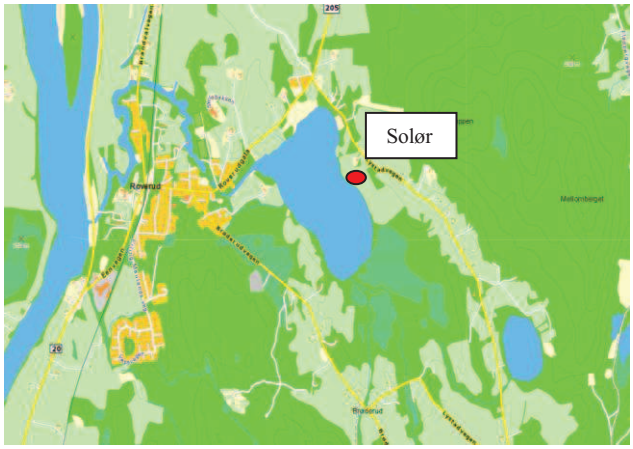


Figure 22. Situation Solør agricultural field

4.3 Soil sampling

Soil sampling took place during the first weeks of October 2009. Twenty four samples were collected in total.

First samples were picked up from Syverud field 8th of October. From this location 8 samples were picked up in total, 4 from samples from an autumn plowing part of the field and 4 others from a spring harrowing part.

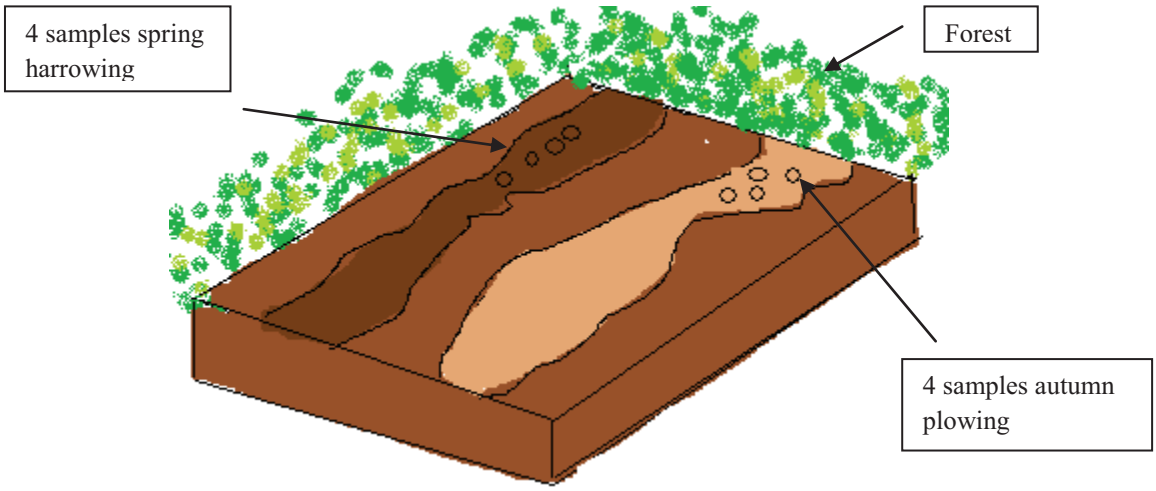


Figure 23. Field profile and sampling sites for Syverud field

Second samples were picked from Askim 12th of October. From this location again 8 samples were collected, 4 from a part of the field with autumn deep harrowing and 4 from another part with shallow harrowing.

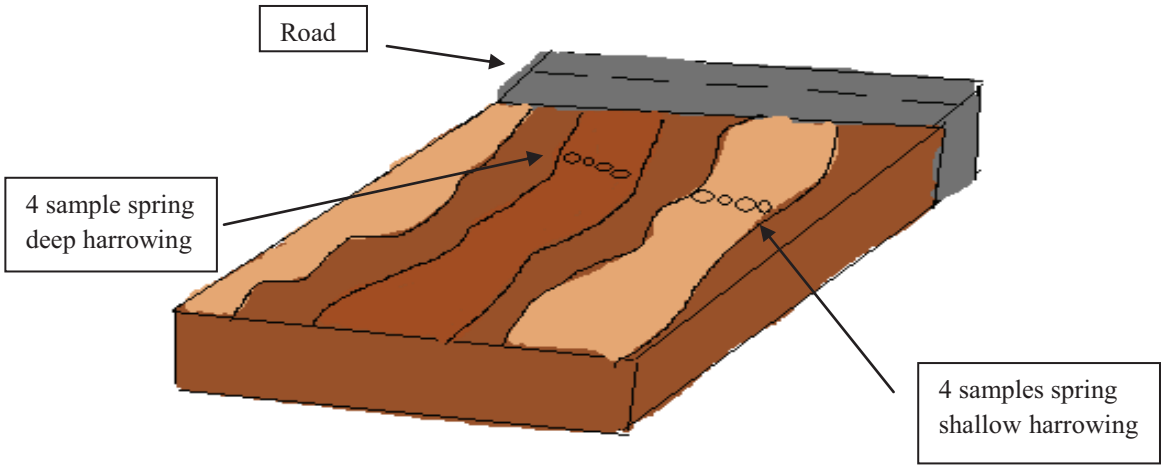


Figure 24. Field profile and sampling sites for Askim field

Solør was the third field being sampling (13th October), in this case only four samples from this potato field where collected. (No information about the field profile).
Last 4 samples were collected from Rygge field (15th October), also a potato site.

Figure 24. Rygge field

4.3.1 Sampling procedure

The twenty-four soil samples were collected from the different fields through the following process:

Soil samples were collected in stainless steel cylinders, 20 cm of diameter and 20 cm of height (figure 23a). The cylinders were driven into the soil using two wooden bars, one with approximately the same length as the diameter of the cylinder, which was on the top and another one longer which function was hit the small one in order to push the cylinder through the soil (figure 23b).
When 1 cm, more or less, of the cylinders was above the ground they were dug out trying not to disturb the soil samples inside (figure 23c). After the cylinders became out of the ground the bottoms were cleaned, taken out all the possible stones and cutting the roots.
Once we had the samples cleaned they were sealed with plastic (figure23d), in order to conserve them until the leaching experiment they were stored in the dark at 4ºC.

In addition to the soil columns also pF-rings were taken out at 5 and 15 cm below the soil surface to measure actual soil water content in each plot (figure23e).At the end some other samples from each digging were taken in order to analyze the characteristics of the different soils (see appendix).

a)

b)

c)

d)

e)

Figure 25. Pictures of cylinders shape a), dug cylinders b), dug out cylinders c), conserving samples d) and pF-rings e)

4.3.2 Numbering and naming of the samples

In order to distinguished the different soil columns a reference numbers and names were given to them.

Syverud		Askim	
Number sample	Name sample	Number sample	Name sample
HARROWING		AUTUMN HARROWING	
1	SH 1	9	AVH 1
2	SH 2	10	AVH 2
3	SH 3	11	AVH 3
4	SH 4	12	AVH 4
PLOWING		SPRING HARROWING	
5	SP 1	13	AHV 1
6	SP 2	14	AHV 2
7	SP 3	15	AHV 3
8	SP 4	16	AHV 4

Solør		Rygge	
Number sample	Name sample	Number sample	Name sample
17	SOL 1	20	RY 1
18	SOL 2	21	RY 2
19	SOL 3	22	RY 3
20	SOL 4	23	RY 4

4.4 Leaching experiment

Laboratory leaching experiment was performed with the columns during autumn, winter and spring in order to compare how the meteorological conditions affected in the flux of the nutrients through the soils.

The procedure was the same along the two first rounds (autumn and winter 2009), only some specific modifications were done along the third round (spring 2010).

The two first rounds were conducted at the lysimeter lab at "Plantehelse" building, which is place at Norwegian institute for Agricultural and Environmental Research (Ås). Third round was performed at a lab in the Bioforsk institute building. The only difference between the two labs was the temperature conditions. While in the lysimeter lab all the experiment was conducted under 10ºC, in the other lab was under normal conditions (20ºC).

4.4.1 Leaching procedure

Leaching experiment was conducted through three soil columns (figure 23c) each day using a well establish order. First columns of each sampling site where use as blanks and that ones were always the first conducted.

	Station 1	Station 2	Station 3
Day 1	SH 1	SP 1	AVH 1
Day 2	AVH 1	SOL 1	RY 1
Day 3	SH 2	SH 3	SH 4
Day 4	SP 2	SP 3	SP 4
Day 5	AVH 2	AVH 3	AVH 4
Day 6	AHV 2	AHV 3	AHV 4
Day 7	SOL 2	SOL 3	SOL 4
Day 8	RY 2	RY 3	RY 4

Table 3. Order leaching experiment was conducted

Three days before each leaching experiment, the different soil columns were sprayed with pesticides. Soil columns from Syverud (SH and SP) and Askim (AVH and AHV) were sprayed with glyphosate (ROUNDUP) and those from Solør (SOL) and Rygge (RY) with fluazinam (see APPENDIX B, Pesticide concentrations). As the normal dose of these pesticides is 1,44 Kg/ha for glyphosate and 0,38 Kg/ha fro fluazinam, soil columns were

sprayed with 10 ml of a solution containing 45µg/l glyphosate and 12 µg/l fluazinam.(The Pesticide Manual, 12th Edition, 2000)

	Glyphosate	Fluazinam
Solubility in water	11,6 g/l	1,7 mg/l
Solubility in organic solvents	insoluble	soluble
Vapour pressure	1,31 x 10-7 mPa	1,5 mPa
Henry's Law constant	<2,1 x 10-7 Pa m3 mol-1	4,10 x 10-1 Pa m3 mol-1
Kow	log P <-3,2 (pH 2-5)	log P = 3,56
Hydrolysis	stable at pH 3, 6 and 9	
pKa	5,77 +/- 0.03, 2,18 +/- 0,02	

Table 4. Properties of the using pesticides

Once the soil columns were sprayed with the pesticides they were prepared for the leaching experiment.

First each cylinder was weight in order to quantify the amount of soil inside. After the weight process, cylinder was placed with extremely care in a steel collecting pan, which has a diameter of 24 cm. Between the pan and the bottom of the cylinder two sieves with two different pore are placed. Then the cylinder and the support were placed in the workbench ready for receive the artificial rain.

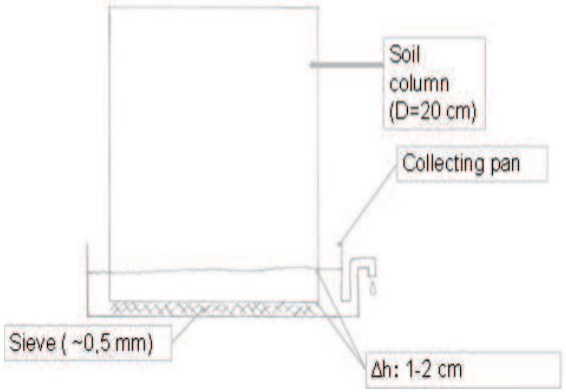
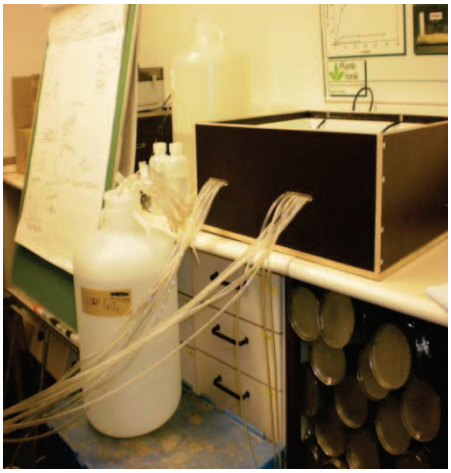


Figure 26. Scheme of cylinder and collecting pan

Artificial rain was prepared as similar as possible to the natural rain measured in a meteorological station in Hurdal (see APPENDIX C, ionic strength).A 20 l container (figure25a) was filled each time that is needed with a solution of 0.03mM $CaCl_2$.The rain was applied using a peristaltic pump which had connected silicon tubes through whose the rain was dripped to the top of the columns. To be close to the natural conditions, the artificial rain was dripped along the soil columns with a volume flow of 314 ml/h. Each time that a new round was conducted, measurements of the flow were done in order to control the pressure of the peristaltic pump (figure25b) to have the correct flow. Tubes tips were cover with some tissues for controlling the drips (figure 25d).

A couple of minutes before rain had started the columns were sprayed with 10 ml of a KBr solution (31.4 g/l) which actuated as a conservative tracer to identify the water flow through the soil columns.


a)


b)


c)


d)

Figure 27. Rain artificial water a), peristaltic pump b), three stations c) and tubes and tips d)

For the columns which were blanks, samples with a volume of 100 ml were taking consecutive along the three hours of the experiment, scoring the time that was spent in obtaining the 100 ml, 30 ml of each 100 ml sample was sampled for the Bromide analysis. In addition from each 100 ml extraction also 30 ml was sample for the analysis of T- phosphorus and other 30 ml for dissolved phosphorus analysis. The samples used for

analyzed dissolved phosphorus were filtered before. These samples were conserved until the analysis adding 0.25 ml of H_2SO_4 (4M).The rest of the water samples was stored in 500 ml bottles (figure26) for the other analyses (ph, conductivity, suspended solids, etc).

Figure 28. Water samples in 500 ml bottles

For the other soil columns the sampling water procedure was a little bit different. All the water that went through one column was collected in 1 l volume bottle and from this one; samples for Bromide, T-phosphorus and dissolved phosphorus were separated.

When the three hours of experiment were finished, the artificial rain was stopped and the tubes were removed from the top of the columns. Then after 30 min without the artificial rain, the soil columns were removed from the steel pan, weighed again and sealed with some tissues and plastic on the bottom in order to be conserved for the other rounds. The soil columns were storage after each round in a parcel of land outside the "Plantehelse" building, covered with sand waiting until next rounds.

The leaching experiment during the third round (spring 2010) was held in another way. In this case the peristaltic pump was not used; the artificial rain was poured in the columns directly. To avoid the splash erosion a filter paper (Wahtman filter No.1) was placed on the soil surface (figure 27). The rain was poured in amounts of 157 ml each five minutes until arrived to a volume of 942 ml in total. Again samples for Bromide, T-phosphorus and dissolved phosphorus were separated for analysis.

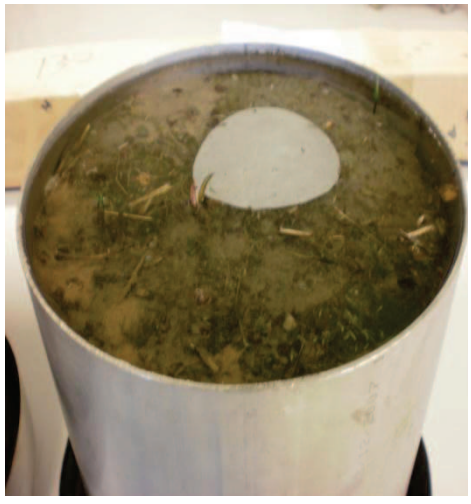


Figure 29. Soil surface with filter paper

4.5 Analysis plan

The water samples collected along the three rounds of the leaching experiment were subjected to various analysis such as measure of pH, conductivity, absorbency UV/Vis, suspended solids, T-phosphorus, dissolved phosphorus, etc. Below all methods of analysis will be accounted.

4.5.1 pH measurement

In the process world, pH is an important parameter to be measured and controlled.
The pH of a solution indicates how acidic or basic (alkaline) it is.
The pH term translates the values of the hydrogen ion concentration which ordinarily ranges between about 1 and 10^{-14} gram-equivalents per liter, into numbers between 0 and 14.

On the pH scale a very acidic solution has a low pH value such as 0, 1, or 2 which corresponds to a large concentration of hydrogen ions, while a very basic solution has a high pH value, such as 12, 13, or 14 which corresponds to a small number of hydrogen ions. A neutral solution such as water has a pH of approximately 7.

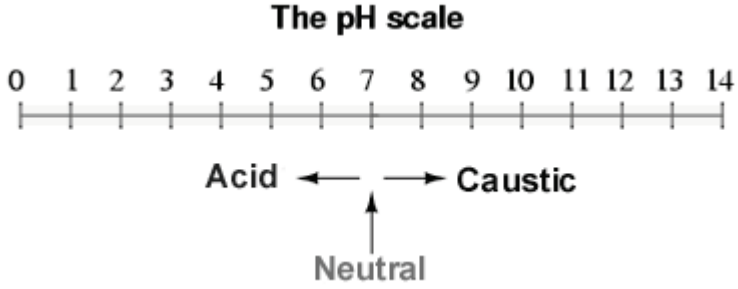


Figure 30. pH scale

4.5.1.1 Mathematical definition

pH is defined as minus the decimal logarithm of the hydrogen ion activity in a solution (IUPAC). By virtue of its logarithmic nature, pH is a dimensionless quantity.

$$\mathrm{pH} = -\log_{10}(a_{\mathrm{H}^+}) = \log_{10}\left(\frac{1}{a_{\mathrm{H}^+}}\right)$$

Where a_H is the (dimensionless) activity of hydrogen ions. The reason for this definition is that a_H is a property of a single ion, which can only be measured experimentally by means of an ion-selective electrode which responds, according to the Nernst equation, to hydrogen ion activity. pH is commonly measured by means of a combined glass electrode, which measures the potential difference, or electromotive force, E, between an electrode sensitive to the hydrogen ion activity and a reference electrode, such as a calomel electrode or a silver chloride electrode. The combined glass electrode ideally follows the Nernst equation:

$$E = E^0 + \frac{RT}{nF}\ln(a_{H^+}); \qquad \mathrm{pH} = \frac{E^0 - E}{2.303RT/F}$$

Where E is a measured potential, E^0 is the standard electrode potential, that is, the electrode potential for the standard state in which the activity is one. R is the gas constant, T is the temperature in kelvins, F is the Faraday constant and n is the number of electrons transferred, one in this instance. The electrode potential, E, is proportional to the logarithm of the hydrogen ion activity.

This definition, by itself, is wholly impractical, because the hydrogen ion activity is the product of the concentration and an activity coefficient. The single-ion activity coefficient of the hydrogen ion is a quantity which cannot be measured experimentally. To get around this difficulty, the electrode is calibrated in terms of solutions of known activity.

The operational definition of pH is officially defined by International Standard ISO 31-8 (International Organization for Standardization) as follows: For a solution X, first measure the electromotive force E_X of the galvanic cell

reference electrode | concentrated solution of KCl || solution X | H_2 | Pt

and then also measure the electromotive force E_S of a galvanic cell that differs from the above one only by the replacement of the solution X of unknown pH, pH(X), by a solution S of a known standard pH, pH(S). The pH of X is then

$$\mathrm{pH(X)} - \mathrm{pH(S)} = \frac{E_S - E_X}{2.303RT/F}$$

The difference between the pH of solution X and the pH of the standard solution depends only on the difference between two measured potentials. Thus, pH is obtained from a potential measured with an electrode calibrated against one or more pH standards; a pH meter setting is adjusted such that the meter reading for a solution of a standard is equal to the value pH(S). Values pH(S) for a range of standard solutions S, along with further details, are given in the IUPAC recommendations (Pure appl. Chemistry, 1985). The standard solutions are often described as standard buffer solution. In practice, it is better to use two or more standard buffers to allow for small deviations from Nernst-law ideality in real electrodes. Note that because the temperature occurs in the defining equations, the pH of a solution is temperature-dependent.

Measurement of extremely low pH values, such as some very acidic mine waters, requires special procedures. Calibration of the electrode in such cases can be done with standard solutions of concentrated sulfuric acid, whose pH values can be calculated with using Pitzer parameters to calculate activity coefficients.

4.5.1.2 Components and function

A pH measurement loop is made up of three components, the pH sensor, which includes a measuring electrode, a reference electrode, and a temperature sensor; a preamplifier; and an analyzer or transmitter.
A pH measurement loop is essentially a battery where the positive terminal is the measuring electrode and the negative terminal is the reference electrode. The measuring electrode, which is sensitive to the hydrogen ion, develops a potential (voltage) directly related to the hydrogen ion concentration of the solution. The reference electrode provides a stable potential against which the measuring electrode can be compared.

When immersed in the solution, the reference electrode potential does not change with the changing hydrogen ion concentration.
A solution in the reference electrode also makes contact with the sample solution and the measuring electrode through a junction, completing the circuit. Output of the measuring electrode changes with temperature (even though the process remains at a constant pH), so a temperature sensor is necessary to correct for this change in output. This is done in the analyzer or transmitter software.

The pH sensor components are usually combined into one device called a combination pH electrode. The measuring electrode is usually glass and quite fragile. Recent developments have replaced the glass with more durable solid-state sensors. The preamplifier is a signal-conditioning device. It takes the high-impedance pH electrode signal and changes it into allow impedance signal which the analyzer or transmitter can accept. The preamplifier also strengthens and stabilizes the signal, making it less susceptible to electrical noise.

The sensor's electrical signal is then displayed. This is commonly done in a 120/240 V ac-powered analyzer or in a 24 V dc loop-powered transmitter.

Keep in mind, application requirements should be carefully considered when choosing a pH electrode. Accurate pH measurement and the resulting precise control that it can allow, can go a long way toward process optimization and result in increased product quality and consistency. Accurate, stable pH measurement also controls and often lowers chemical usage, minimizing system maintenance and expense.

4.5.1.3 Keeping the system up and running

A system's pH electrodes require periodic maintenance to clean and calibrate them. The length of time between cleaning and calibration depends on process conditions and the user's accuracy and stability expectations. Overtime, electrical properties of the measuring and reference electrode change. Calibration in known-value pH solutions called buffers will correct for some of these changes. Cleaning of the measuring sensor and reference junction will also help. However, just as batteries have a limited life, a pH electrode's lifetime is also finite.

The most common approach is the use of a specially-prepared electrode designed to allow hydrogen ions in the solution to migrate through a selective barrier, producing a measurable potential (voltage) difference proportional to the solution's pH:

The design and operational theory of pH electrodes is a very complex subject, explored only briefly here. What is important to understand is that these two electrodes generate a voltage directly proportional to the pH of the solution. At a pH of 7 (neutral), the electrodes will produce 0 volts between them. At a low pH (acid) a voltage will be developed of one polarity, and at a high pH (caustic) a voltage will be developed of the opposite polarity.

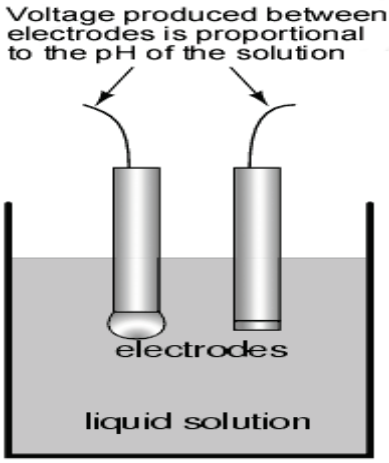


Figure 31. pH electrodes

An unfortunate design constraint of pH electrodes is that one of them (called the measurement electrode) must be constructed of special glass to create the ion-selective barrier needed to screen out hydrogen ions from all the other ions floating around in the solution. This glass is chemically doped with lithium ions, which is what makes it react electrochemically to hydrogen ions. Of course, glass is not exactly what you would call a "conductor;" rather, it is an extremely good insulator.
This presents a major problem if our intent is to measure voltage between the two electrodes. The circuit path from one electrode contact, through the glass barrier, through the solution, to the other electrode,and back through the other electrode's contact, is one of extremely high resistance**.**

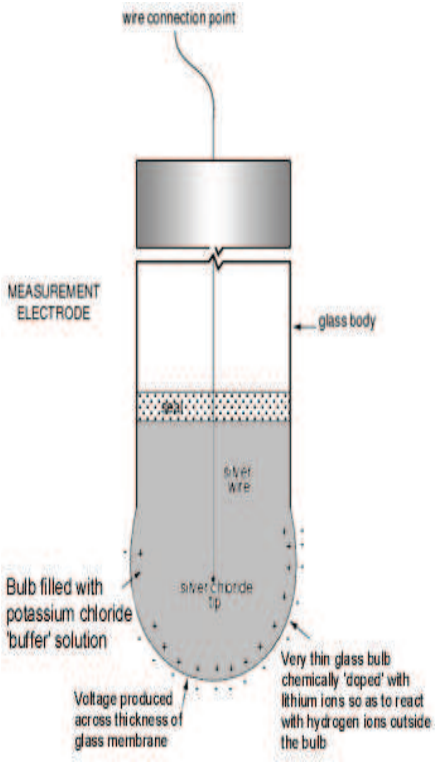


Figure 32. pH Electrode

The other electrode (called the reference electrode) is made from a chemical solution of neutral (7) pH buffer solution (usually potassium chloride) allowed to exchange ions with the process solution through a porous separator, forming a relatively low resistance connection to the test liquid.

The measurement electrode's purpose is to generate the voltage used to measure the solution's pH. This voltage appears across the

thickness of the glass, placing the silver wire on one side of the voltage and the liquid solution on the other. The reference electrode's purpose is to provide the stable, zero-voltage connection to the liquid solution so that a complete circuit can be made to measure the glass electrode's voltage. While the reference electrode's connection to the test liquid may only be a few kilo-ohms, the glass electrode's resistance may range from ten to nine hundred mega-ohms, depending on electrode design.

If a pH measurement system "drifts," creating offset errors, the problem likely lies with the reference electrode, which is supposed to provide a zero-voltage connection with the measured solution.
Because pH measurement is a logarithmic representation of ion concentration, there is an incredible range of process conditions represented in the seemingly simple 0-14 pH scale. Also, due to the nonlinear nature of the logarithmic scale, a change of 1 pH at the top end (say, from 12 to 13 pH) does not represent the same quantity of chemical activity change as a change of 1 pH at the bottom end (say, from 2 to 3 pH). Control system engineers and technicians must be aware of this dynamic if there is to be any hope of controlling process pH at a stable value.

The following conditions are hazardous to measurement (glass) electrodes: high temperatures, extreme pH levels (either acidic or alkaline), high ionic concentration in the liquid, abrasion, hydrofluoric acid in the liquid (HF acid dissolves glass), and any kind of material coating on the surface of the glass. Temperature changes in the measured liquid affect both the response of the measurement electrode to a given pH level (ideally at 59 mV per pH unit), and the actual pH of the liquid.

Water samples were measured for pH using an ORION RESEARCH (expandable ion analyzer EA920) pH-meter. The device was calibrated before using two buffers, pH 7.00 and pH 4.00. These two buffers were selected because the pHs of the samples were expected to be around 5 and 7 (water normal pH).

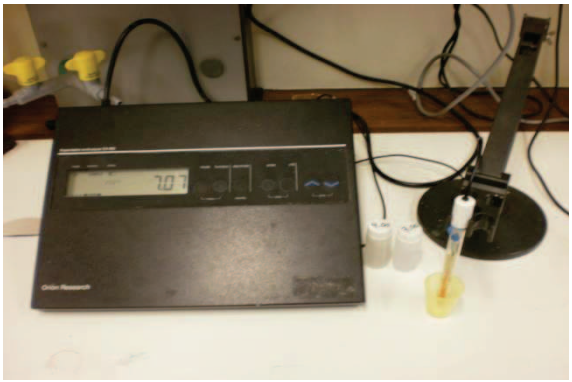


Figure 33. pH-meter ORION RESEARCH

4.5.2 Conductivity measurement

The electrical conductivity is defined as the ability of inorganic salts in solution (Electrolytes) to conduct electrical current.
Pure water, practically does not conduct current, but water with dissolved salts conduct an electric current. The positively and negatively charged ions are leading the current, and the number conducted on the number of ions present and their mobility.
In most aqueous solutions, the larger the amount of dissolved salts, the greater the conductivity (table 5), this effect continues until the solution is so full of ions that restricts freedom of movement and conductivity may decrease rather than increas , with cases of two different concentrations with the same conductivity.
All conductivity values are referred to a reference temperature 25 ° C

Sample temperatura 25ºC	Conductivity, µS/cm
Boiler feed water	1 a 5
Potable water	50 a 100
Sea water	53,000
5 % NaOH	223,000
50 % NaOH	150,000
10 % HCl	700,000
32 % de HCl	700,000
31 % HNO_3	865,000

Table 5. Conductivity for different solutions

Some substances are ionized more fully than others and therefore lead to better power.

They are good conductors: acids, bases, and inorganic salts: HCl, NaOH, NaCl, Na2CO3, etc.
They are bad drivers: The molecules of organic substances which by their nature are non-ionic bonds: such as sucrose, benzene, hydrocarbons, carbohydrates, etc, these substances do not ionize in water and therefore do not conduct electrical current.
An increase in temperature decreases the viscosity of water and allows ions to move more quickly, leading more electricity. The effect of temperature is different for each ion, but typically for dilute aqueous solutions, the conductivity varies from 1-4% per ° C.
Knowing these factors, the conductivity measurement allows us to have a very rough idea of the amount of dissolved salts.

4.5.2.1 Scope

This test method is applicable to the detection of impurities and in some cases the quantitative measurement of the ionic components dissolved in water:

Verification of the purity of distilled and deionized water.
Quickly verify the change in the content of dissolved salts in surface water, domestic and industrial use. Quantitatively analyze total dissolved solids in a water sample. This can be obtained by multiplying the value of the conductivity by a factor of empirical correlation may vary from 0.5 to 0.9, depending on the soluble and the temperature of the sample. This factor can be determined by comparative analysis of total dissolved solids through evaporation and determinations of the corresponding conductivity value. The correlation factor is only valid when the sample has a pH between 5 and 8 to values higher or lower pH, the results are not reliable.

4.5.2.2 Principles

Electrical conductivity is the reciprocal of the ac resistance in ohms measured between opposite faces of a cube of 1.0 cm of an aqueous solution at a specified temperature. This solution acts as an electrical conductor where you can apply the physical laws of electrical resistance. The units of electrical conductivity are Siemens / cm (old units were the mhos / cm which are numerically equivalent to S / cm).
In practice it is measured conductivity between electrodes of 1 cm3, but with different size electrodes, rectangular or cylindrical, so making the measurement, instead of the conductivity, conductance is measured, which when multiplied by a constant (k) of each particular cell, the conductivity becomes in S / cm.

$$\text{Conductivity} = \text{Conductance of the sample} * k$$
$$k = d / A$$

k: constant cell
d: distance of separation of the electrodes
A: Area of the electrodes

Thus, an electrode separation of 1 cm and 1 cm area, will have a k = 1
The electrical measurement is made through a Wheastone bridge to measure resistance.
The resistors R1 and R2 are fixed and its value is according to the range of

conductivity to be measured. The resistance Rx is what gives the solution to that is going to measure the conductivity. The resistance R3 is varied continuously up to balance the bridge, so that no current flowing into the meter (American society for testing and materials, annual book of Standards, 1994).

4.5.2.3 Interference

The exposure of the sample to atmospheric air, can cause changes in conductivity, due to loss or gain of dissolved gases, especially CO_2. This is especially important for high purity water with low concentrations of ionized gases and substances. To prevent this you must have an inert atmosphere of nitrogen and helium on the sample.
Undissolved substances or materials that slowly precipitate in the sample, can cause fouling on the surface of the electrodes and cause erroneous readings.
The contamination by organic substances and corrosion of the electrodes could cause unstable or erroneous readings.
The correlation factor for quantitative values of total dissolved solids is only valid when the sample has a pH between 5 and 8, to values higher or lower pH, the results are not reliable. You will need to adjust the pH to about 7.0 by using a weak acid or base as needed.

4.5.2.4 Device

Conductivity was measured in our water samples using a portable conductivity meter, Conductivity meter FE30/FG3 (METTLER TOLEDO)

Figure 34. Conductivity meter

4.5.2.5 Procedure

First the device was calibrated using a standard solution of KCl Potassium chloride: Dissolve 0.7440 g of KCl in distilled water, ASTM Type I and dilute to 1 liter, which was already prepared. This solution gave a conductivity of 1413 µS / cm.

Cell was cleaned always before and after each measurement. The cell was suspended in the solution trying that was separated from the walls and bottom of the container, at least 0.5 cm. Once the cell was inside the container, the device showed the conductivity for the sample.

4.5.3 UV-Vis Absorbance

Ultraviolet-visible spectroscopy refers to absorption spectroscopy in the UV-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions (Skoog et al., 2007).

The instrument used in ultraviolet-visible spectroscopy is called a UV/vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I / I_o is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance:

$$A = -\log (\%T / 100\%)$$

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating or monochromator to separate the different wavelengths of light, and a detector. The radiation source is often a Tungsten filament (300-2500 nm), a deuterium arc lamp, which is continuous over the ultraviolet region (190-400 nm) or more recently, light emitting diodes (LED) and Xenon Arc Lamps for the visible wavelengths. The detector is typically a photodiode or a CCD. Photodiodes are used with monochromators, which filter the light so that only light of a single wavelength reaches the detector. Diffraction gratings are used with CCDs, which collects light of different wavelengths on different pixels.

A spectrophotometer can be either single beam or double beam. In a single beam instrument (such as the Spectronic 20), all of the light passes through the sample cell. I_o must be measured by removing the sample. This was the earliest design, but is still in common use in both teaching and industrial labs.

In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam.

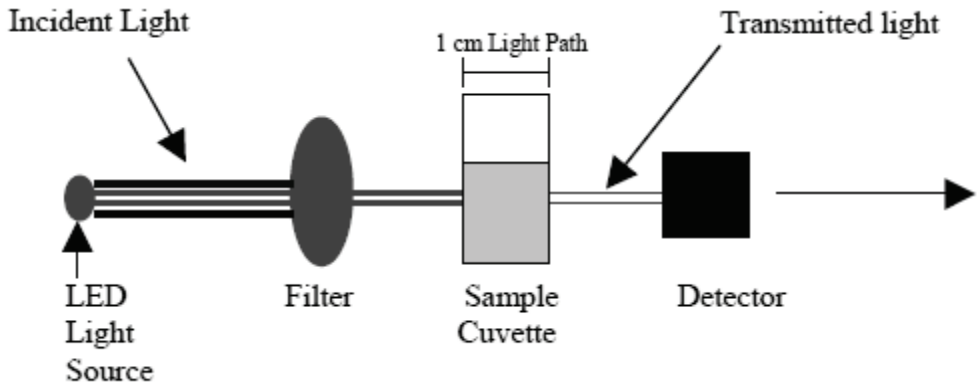


Figure 35. Absorption measurement scheme

Samples for UV/Vis spectrophotometry are most often liquids, although the absorbance of gases and even of solids can also be measured. Samples are typically placed in a transparent cell, known as a cuvette. Cuvettes are typically rectangular in shape, commonly with an internal width of 1 cm. (This width becomes the path length, L, in the Beer-Lambert law.) The type of sample container used must allow radiation to pass over the spectral region of interest. The most widely applicable cuvettes are made of high quality fused silica or quartz glass because these are transparent throughout the UV, visible and near infrared regions. Glass and plastic cuvettes are also common, although glass and most plastics absorb in the UV, which limits their usefulness to visible wavelengths.

Our samples absorbance was measured along two different wavelengths, 254 nm and 400 nm. The device used was a UV-Vis spectrophotometer (SHIMADZU, UV-1201).

Figure 36. Spectrophotometer

Our purpose measuring absorbance, was arrived to obtain the amount of TOC in our samples, due to absorbance of ultraviolet light (specifically at a wavelenght of 254 nm) is a surrogate indicator of organic content (Kirk S. Westphal, 2004.)

4.5.4 Suspended solids

Total suspended solids is a water quality measurement usually abbreviated TSS. As is defining by Norks Standard NS-EN 872:

Suspended solids

Solids removed by filtration or centrifugation under specific conditions

And also a definition of Dissolved solids is given in the same standard as:

Dissolved solids

Substances that remaining, after filtration and evaporation to dryness of a sample, under specific conditions.

TSS was measured in our samples using the procedure describing in NS-EN 872. This European standard describes a method for the determination of suspended solids in raw waters, waste waters and effluents through glass fiber filters. The lower limit of determination is about 2mg/l.

4.5.4.1 Principle

Using a vacuum or pressure device the sample is filtered through a glass fiber filter. The filter is then dried at 105ºC and the mass of the residue retained on the filter is determined by weighing.

4.5.4.2 Devices

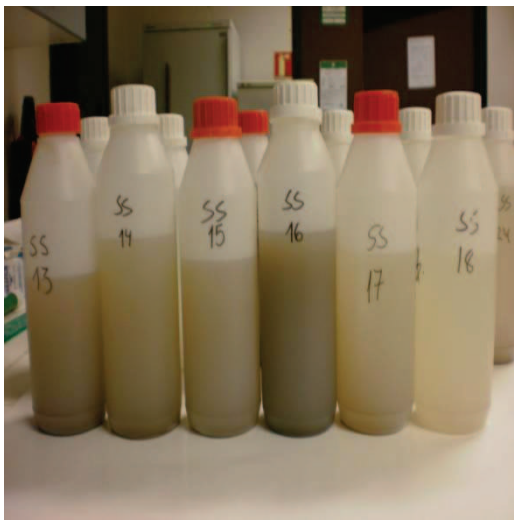
To perform measurements we used:

- Equipment for vacuum or pressure filtration, were the filters were accommodated.
- Borosilicate glass fiber filters (WHATMAN GF/F Ø 47mm).
- Drying oven, capable to maintaining a temperature of 105ºC.
- Analytical balance.
- Drying support of suitable surfaced material, to support the filters in the drying oven.

4.5.4.3 Procedure

First step was putting the fiber filters inside the drying oven around 1h in a 105ºC constant temperature (one of it was weight before in order to use it as blank of lost mass).During all the drying process filters were placed in an aluminum drying support. After the drying process they were weighted.

Next step was the filtration. Filters were placed in the funnel of the filtering device. Water samples were sacked and an amount of 100 ml more or less was poured to the funnel for each sample (typically one liter is pour; but less if the particulate density is high).



Note: some samples has a big amount of solids in side, as is possible to observed in the figure 35, (our water samples were not clear water) and was difficult to filter them so, the amount poured was reduce sometimes to 50 ml.

Figure 37. Water samples

Figure 38. Funnel and filters

Once the filter was almost dry the vacuum was released. Carefully the filters were removed from the funnel with a pair of forceps, put them on the drying support again and dried in the oven for 1h more at a 105ºC. Past the hour they were weighted again.

Besides the measure of TSS, filters were subjected to ignition at 500ºC during 4h, in order to register also the Total Organic content.

4.5.4.4 Problems relation with the measure

Although TSS appears to be a straightforward measure of particulate weight obtained by separating particles from a water sample using a filter, it suffers as a defined quantity from the fact that particles occur in nature in essentially a continuum of sizes. At the lower end, TSS relies on a cut-off established by properties of the filter being used. At the upper end, the cut-off should be the exclusion of all particulates too large to be "suspended" in water. However, this is not a fixed particle size but is dependent upon the energetic of the situation at the time of sampling: moving water suspends larger particles than does still water. Usually it is the case that the additional suspended material caused by the movement of the water is of interest.

These problems in no way invalidate the use of TSS

4.5.5 Alkalinity titration

After measuring pH of our water samples, those which had a pH over 5.5 were subjected to Alkalinity titration.

An aqueous solution of carbon dioxide produces a mixture of carbonate and bicarbonate ions. Determining the carbonate and bicarbonate ions in each other's presence is often important in environmental chemistry.

$$CO_{2\,(g)} + H_2O_{\,(l)} \longrightarrow H_2CO_{3\,(aq)}$$
$$H_2CO_{3\,(aq)} \longrightarrow HCO_3^-{}_{(aq)} + H^+{}_{(aq)}$$
$$HCO_3^-{}_{(aq)} \longrightarrow H^+{}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

The alkalinity of water is the capacity of solutes to act as a base by reacting with protons. There exists a fundamental difference between the expression of acid-base properties of pH and alkalinity. Whereas the pH can be considered to be an intensity factor which measures the concentration of alkali or acids immediately available for reaction, the alkalinity is a capacity factor which is a measure of the ability of water sample to sustain reaction with added acids (in a sense, it is the ability of a water body to neutralize added acids). In practice, it may be determined by measuring the number of moles of H^+ required to neutralize all bases dissolved in one liter of water leaving no further capacity for neutralization of additional protons. We say that alkalinity can be determined by titration of one liter of a water sample to the end point.

Alkalinity is therefore a useful measure of the capacity of water to resist acidification from acid addition (e.g. acid precipitation). The presence of carbonate, bicarbonate, and hydroxide ions usually imparts most of the alkalinity of natural or treated waters.

The importance of the carbonate/bicarbonate system in natural waters stems from its ability to act like a buffer in natural waters. The oceans are described as being buffered since relatively large quantities of acid or base can be added to seawater without causing much change to its pH. However, many freshwater lakes do not have a large buffer capacity and consequently a small addition of acid (e.g. from acid precipitation or industrial effluent) can cause large changes in pH without warning. The carbonate alkalinity and the total alkalinity are useful for the calculations of chemical dosages required in the treatment of natural water supplies.

The total alkalinity can be presented as (Standard Methods for the Analysis of Water and Waste Water, 16th Edition):

Total Alkalinity (mmoles/L) =(c(HCl) x ml (HCl) x1000)/ml sample

4.5.5.1 Measurement

Total alkalinity was measured using 702 SM Titrino device. Alkalinity was measured by titrating (step-wise addition of reagent) using as standard a sulfuric acid HCl 0.02 M solution to a pH end-point of 4.5. Volume of sample for the titration was around 50 ml.

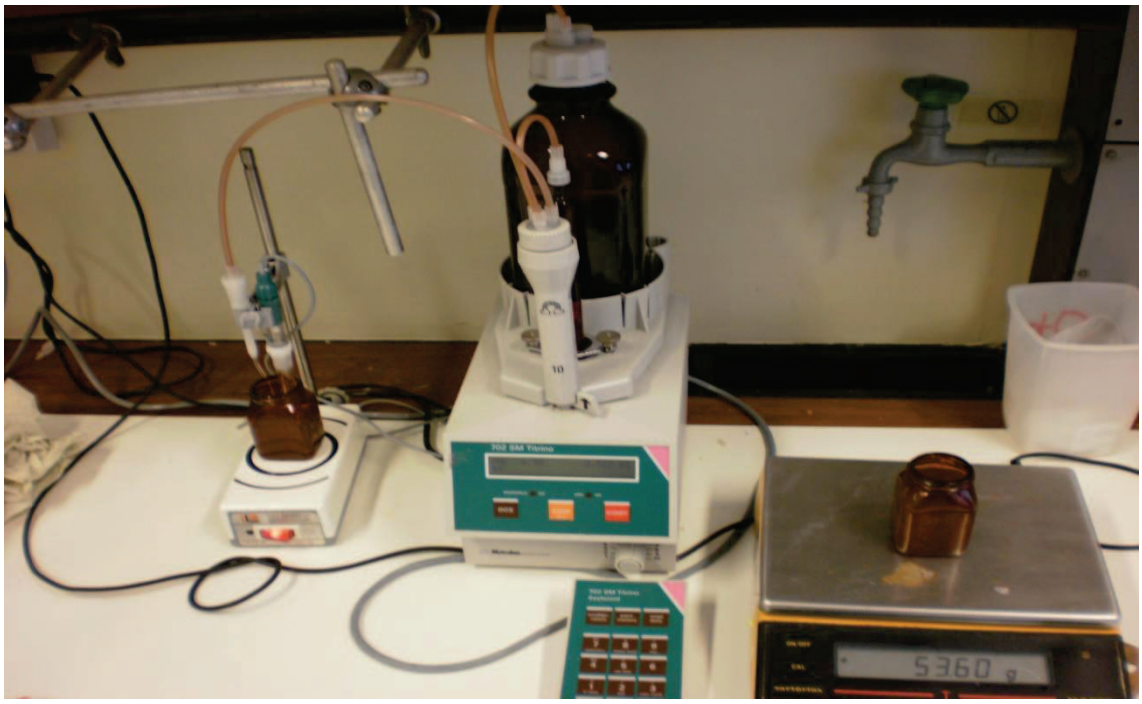
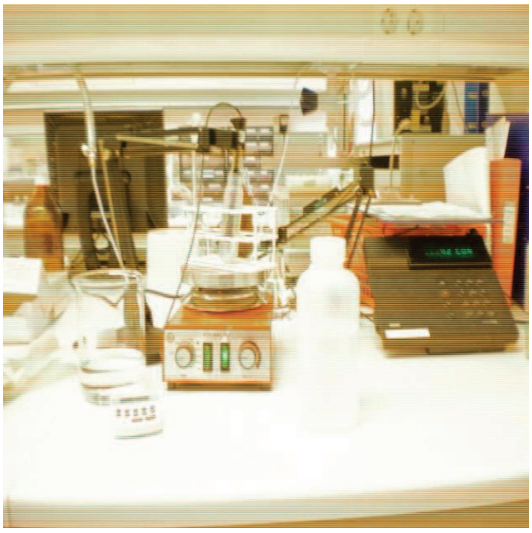


Figure 39. Alkalinity titration device

4.5.6 Bromide concentration

In soil science, bromide ion (Br^-) in various forms (e.g., KBr, NaBr, $SrBr_2$) has been introduced as a non-reactive stable tracer in solute transport studies normally moving freely with the flux of water without substantial chemical or physical interactions with the soil (H. V. Kazemi et al., 1998).

Since the moment that KBr was used as a conservative tracer to identify how water flew through the soil columns, we were really interested in knowing the concentration of bromide in each water sample.



Concentration was measured using a bromide selective electrode. Device was calibrated assuming low concentrations of bromide in the samples. Two standard solutions were prepared in order to obtain a calibration curve. (Standards solutions of 1000 ppm and 10 ppm of bromide)

Figure 40. Bromide concentration measurement

4.5.6.1 Standard solutions preparation

Stock standard 1000 ppm

This standard was prepared using 12.52 ml bromide standard (0.1M; Orion cat. No. 943506), diluting in distilled water to 100 ml.

Note: Plastic volumetric flask was used because bromide is adhering to glass surfaces.

Standard 10 ppm

In this case, standard was prepared using 10 ml of the stock standard 1000 ppm Br, plus 10 ml ISA (Ionic Strength Adjustor) diluted all to 1000 ml in distilled water.

4.5.6.2 Setting up the calibration curve

First 2 ml of ISA were added to 100 ml water in a plastic container of 150 ml. The electrode was rinsed with water and placed inside the continuously stirred solution. Then in the device of measure the calibrate channel was chosen and 5 standards were selected. First standard added to the container was 1.6 ml of 10 ppm Br-standard solution, consequently mores standards were also added according the table.

Step	Standard	Add volume	Concentration (ppm)
Assuming low concentration in the samples:			
1	10 ppm	1.6 ml	0.154
2	10 ppm	3 ml	0.43
3	10 ppm	30 ml	2.53
4	1000 ppm	2 ml	16.9
5	1000 ppm	4 ml	44.5

Table 7. Preparation of the calibration curve by use of Br standards

After all the standards were measured, the calibration coefficient was display in mV/decade, obtaining values inside the range of – (54-60) (This indicates that a liner relationship has been achieved between the standards).

4.5.6.3 Samples measurement

Once we had the device calibrated, the concentration in our water samples was measured; transferring 25 ml of the sample into a plastic beaker and adding ISA in a ration of 50:1, which means 5 ml of it in each 25 ml of water sample. Samples were continuously stirred during all the measurement on a magnetic stirrer. The concentrations in ppm were displaying in the device after 3 min.

4.5.7 Analysis of major cations and anions

In collaboration with this research project, one of my mates in the department of Environmental Chemistry at Oslo University, Alex Engebretsen measured the total content of anions and cations in the filtered water samples.

Cations and anions were measured using Ion Cromatrography. This kind of chromatography is a high-performed version of the ion-exchange one. A mixture of anions is separated by ion exchange and detected by electrical conductivity. The key future of this chromatographic method is removal unwanted electrolyte prior to conductivity measurement.

4.5.8 Total phosphorus and dissolved phosphorus analysis

Phosphorus can be found in different states in water: as orthophosphate, complex phosphates or organically bound phosphorus. Our aim was measured the concentration of orthophosphate (dissolved phosphorus) and Total phosphorus in the water samples that we obtained from the leaching experiment.

Measurements of these two parameters were done using, Norwegian standards, NS 4725 for Total phosphorus and NS 4724 for Dissolved phosphorus.

These methods are based on the color-causing reactions that are specific to ortophophates. Depending on sample preparation, different phosphorus fractions were determined.

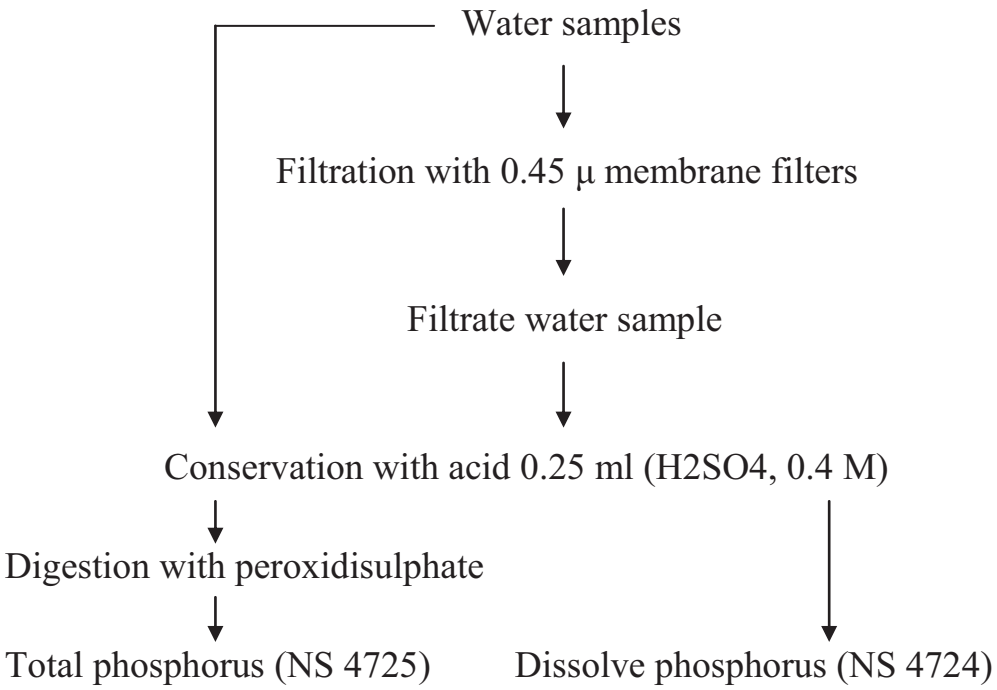


Figure 41. Scheme of sample preparation before analysis

4.5.8.1 Determination of Total phosphorus

Principle

Total phosphorus is determined in non- filtrate samples. Complex, inorganic phosphates and organic complex transfer to orthophosphate by addition of peroxidisulphate under acidic conditions by boiling the samples in an autoclave.

In a sulfuric acid solution orthophosphate reacts with molybdate to a phophorousmolybdate acid, that is reduced with ascorbic acid into a strongly blue colored complex. Absorbance of this color is measured photometically (700nm), in order to obtain the concentration of orthophosphate.

The sample preparation for the absorbance measure of the samples was carried in the following steps:

Note: Our 30 ml samples were conserved since the ending of the leaching experiment by addition of 0.25 ml of H_2SO_4 (4M).

1- Addition of 2 ml of $K_2S_2O_8$ to 10 ml of our water samples
2- $K_2S_2O_8$ solution was prepared diluting 12.50 mg in 250 ml of distilled water. Boiling samples inside autoclave (200 kPa) during 1h.
3- Pipette 5 ml of this new prepared solution and add 0.2 ml of Ascorbic acid solution.
4- In addition add 0.2 ml of molybdate reagent.
5- Samples ready to be measured by colorimetry.

Our solutions were blue due to the complex formed with the ascorbic acid. Absorbance was measured at 700 nm in a spectrophotometer. Three samples of 1ppm phosphate were used as standards to calculate later the concentration.

4.5.8.2 Determination of Dissolved phosphorus

Principle

Dissolved phosphorus (Ortophosphate) is determined in filtered water samples (filtering the samples through 0.45µ membrane filters). Ortophosphate in sulphuric acid solution reacts with molybdate forming a molybdatephophorus complex, which reducing by ascorbic acid form a bluecolored heteropolycomplex. Then this complex is determined spectrophotometrically at 700 nm.

In this case the preparation of the samples varies somewhat in relation to preparation of the TP samples.
Water samples were filtered before using a 0.45µ membrane filters and then were preserved with sulfuric acid (same way as the samples for TP).

Absorbance was measured in samples containing 10 ml of the filtered water sample plus 0.2 ml ascorbic acid plus 0.2 ml of molybdate reagent.
Again three standards of 1 ppm PO_4^{3-} were use to calibrate.

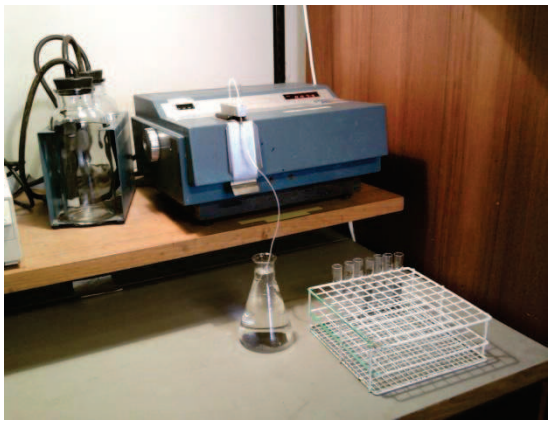


Figure 42. Espectophotometer

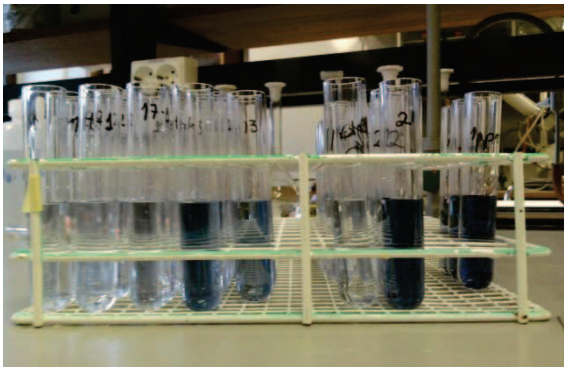


Figure 43. Blue colored solutions

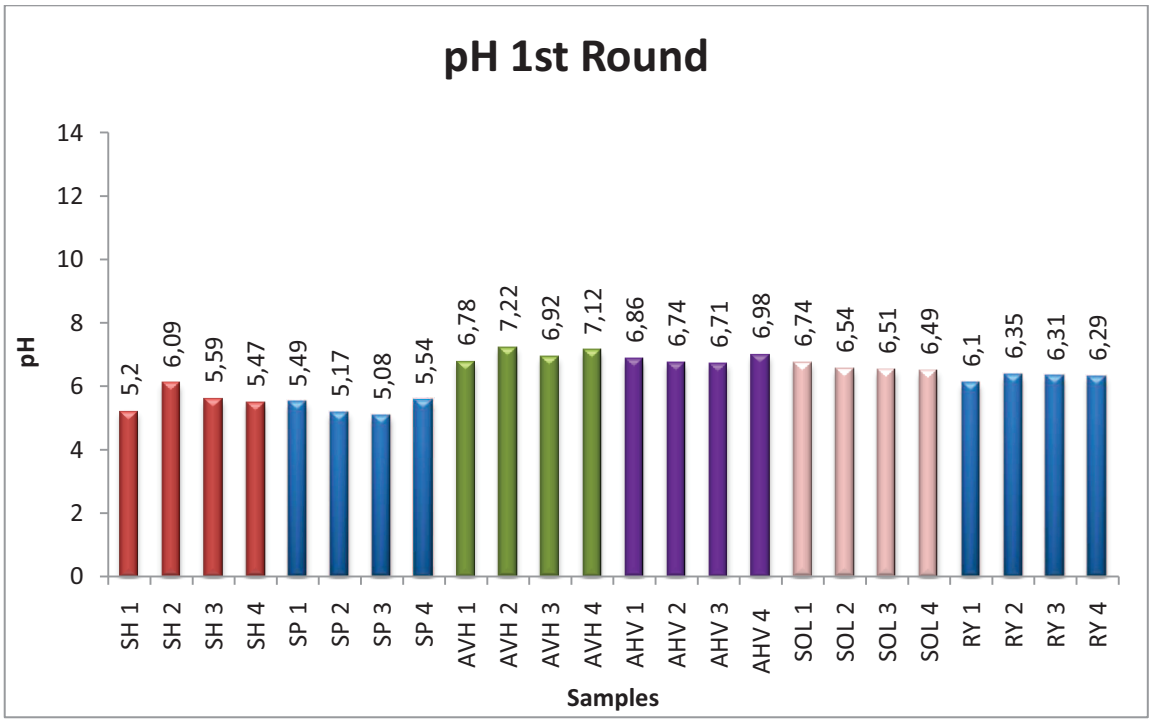
5 Results and discussions

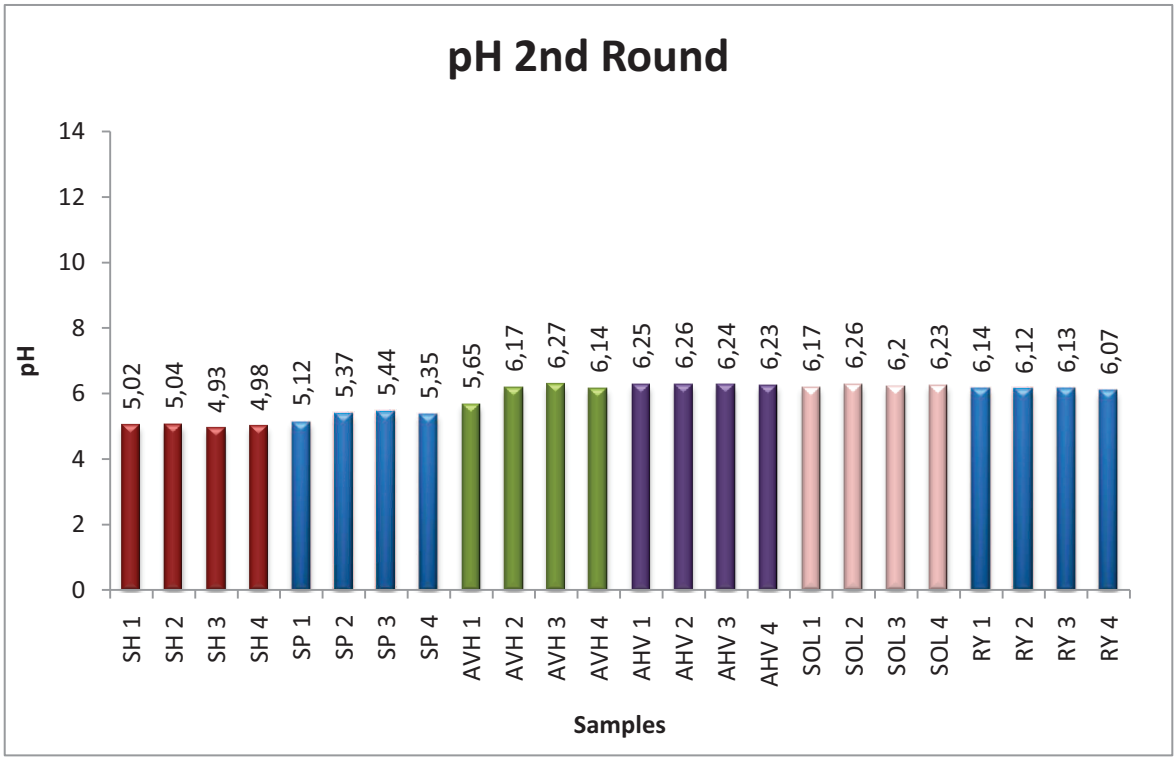
The data result of the differents analysis of the water samples obtained in the leaching experiment are presented and evaluated in this chapter.

5.1 pH

The variation of pH from samples collected in the different fields is shown in figure 42. pH is represented for the three rounds. Data can be found in the APPENDIX

The pH value of a soil is influenced by the kinds of parent materials from which the soil was formed. Soils developed from basic rocks generally have higher pH values than those formed from acid rocks. Is possible to observe that pH for the samples collected in Syverud (SH and SP) are more acidic that the others, this is due to the type of soil, silty clay loam. This lower pH is because this type of soil has a higher metal concentration (El-Klerbemy and Sanders, 1983).





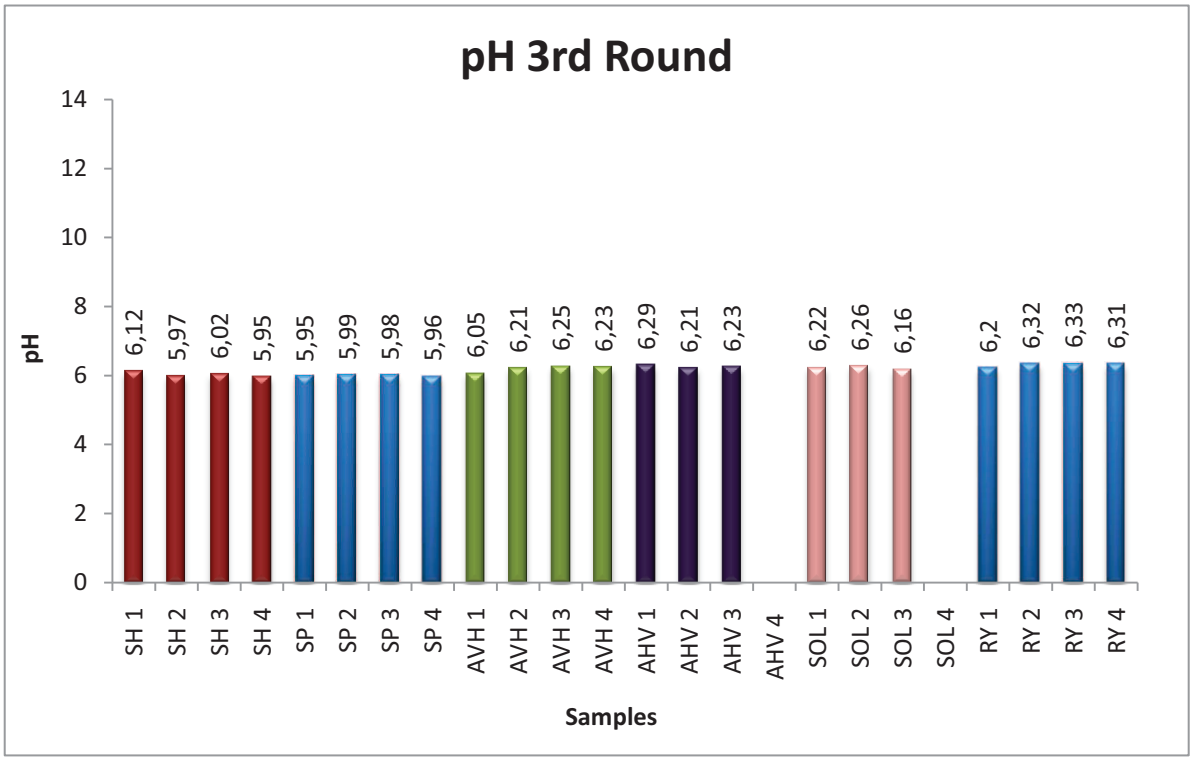


Figure 44. pH along the different rounds of the experiment

As explained above, low pHs are due to the concentration of metals in the soil, this can be check in the APPENDIX D,where is showing the characteristics of the different type of soils collected in the different fields.

Now in this figure the pH obtained through the three rounds is compare in order to analyze the possible effects of the season changes. What most attracts attention is the decrease of pH during the second round and third round. Soil samples during these rounds were stored in an outdoor area, subjected to the weather conditions of winter and spring. This means that were subjected to melting of winter snow and spring rainfalls.

The water that passed through the soil samples leached the basic nutrients such as calcium and magnesium. And then they were replaced by acidic elements such as aluminum and iron. For this reason, soils samples subjected to water melting and rainfall conditions are more acidic (lower pH) than those which were collected during the first round (autumn).

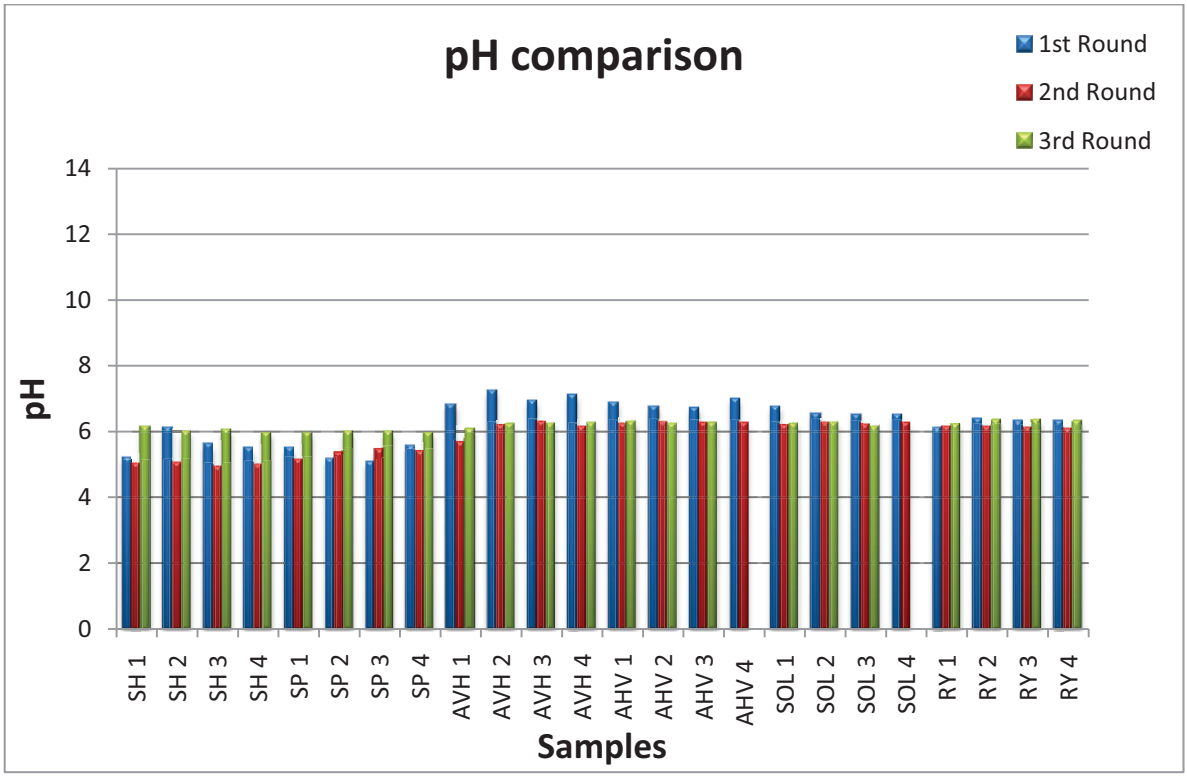


Figure 45. pH comparison through three different rounds

5.2 Conductivity

The electrical conductivity reflects the capacity of water to conduct electrical current, and is directly related to the concentration of salts dissolved in water. Salts dissolve into positively charged ions and negatively charged ions, which conduct electricity. The higher the concentration of ionic (dissolved) constituents, the higher the conductivity is. For example distilled water does not contain dissolved salts and, as a result, it does not conduct electricity and has an electrical conductivity of zero. Elements whose ionic forms contribute the most to these measures include: calcium (Ca_2^+), magnesium (Mg_2^+), sodium (Na^+), potassium (K^+), bicarbonate ($HCO3^-$), sulfate (SO_4^{2-}), and chloride (Cl^-).

As is possible to realized seeing the graphic, our water samples from the first round have a high conductivity comparing with the other two rounds. That can be basically because the soil samples had a high concentration of salts in the first round of the leaching experiment, but as the leaching experiment was repeated, the concentration of salts inside the soil columns decreased, given a lower concentration of salts in the water samples as reflected in the lower conductivity values.

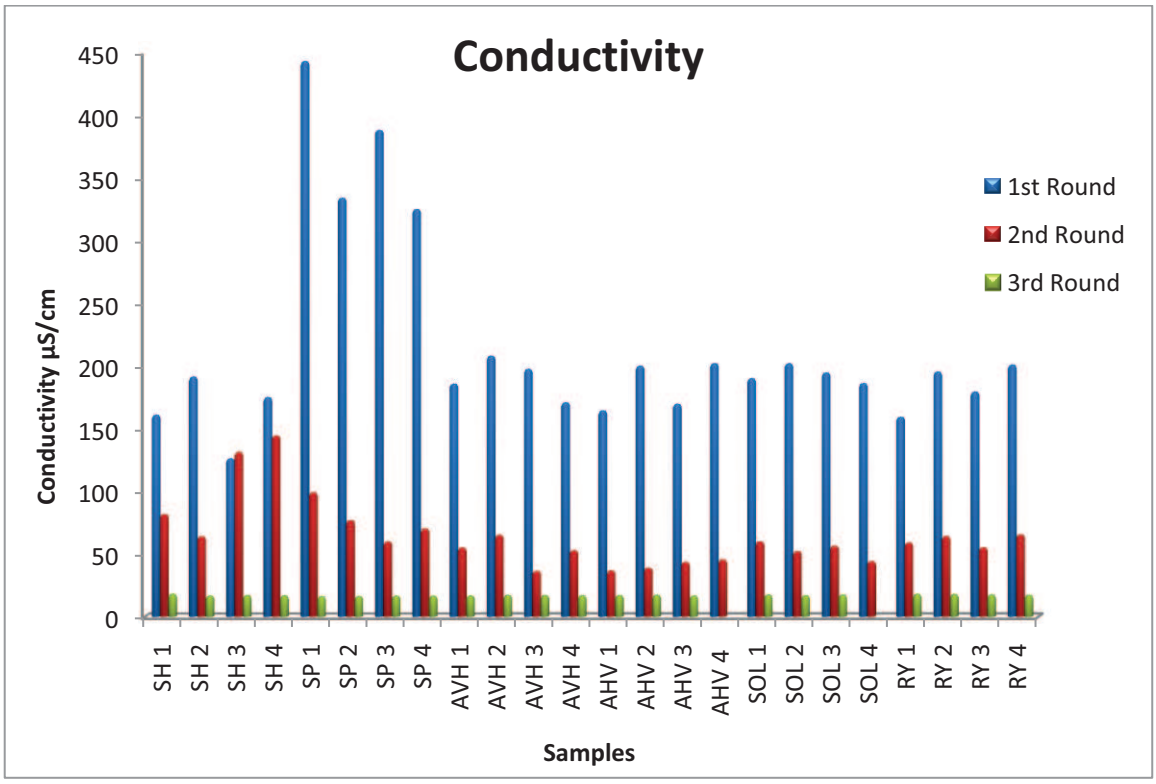


Figure 46. Conductivity water samples

5.3 Absorbance

The importance of measuring absorbance lies in that from the values of absorbance at 254 nm for the different samples is possible calculate the content of DOC.

Dissolved organic carbon (DOC) is a key parameter in environmental studies. DOC is involved in numerous chemical processes: as a reactant in marine photochemical reactions, in the solubilization of hydrocarbons, the chelation of metals, in the formation of particulate matter and in interactions with iron and manganese minerals. Moreover, DOC can act as a substrate for mineralization. The DOC concentration is proportional to the UV absorbance. This hypothesis may not always be true because of the presence of interfering substances, such as nitrate (Ogura and Hanya, 1966), or because the molecular composition of DOC may change rapidly with depth in sediment or from site to site.
Despite the possible variations in UV absorbance for different types of waters, several studies have shown the validity of the basic assumption (Krom and Sholkovitz, 1977).

All wavelengths between 220 and 400 nm can be used for estimating DOC from UV data, but the lower the wavelength is, the higher the sensitivity will be. Wavelengths lower than 230 nm are well known to produce a significant UV absorption by inorganic ions such as nitrate and bromide (Ogura and Hanya, 1966).

We have used the absorbance at 254 nm for DOC. This wavelength shows easily measurable variations in UV absorbance with depth in sediments and is representative of the aromatic moiety present in humic substances that constitute the bulk of natural organic matter composing DOC (Korshin *et al*., 1997).

The UV absorbance of DOC in natural water samples is an integrated spectroscopic signal produced by numerous compounds forming the DOC. The quantification of the UV signal may be difficult in the absence of a universal standard.

We have represented our results using a general rule:

$$\text{mg C/l DOC} = 21 \times \text{UV absorbance 254 nm}$$

The data from the absorbance measurements is available in APPENDIX E

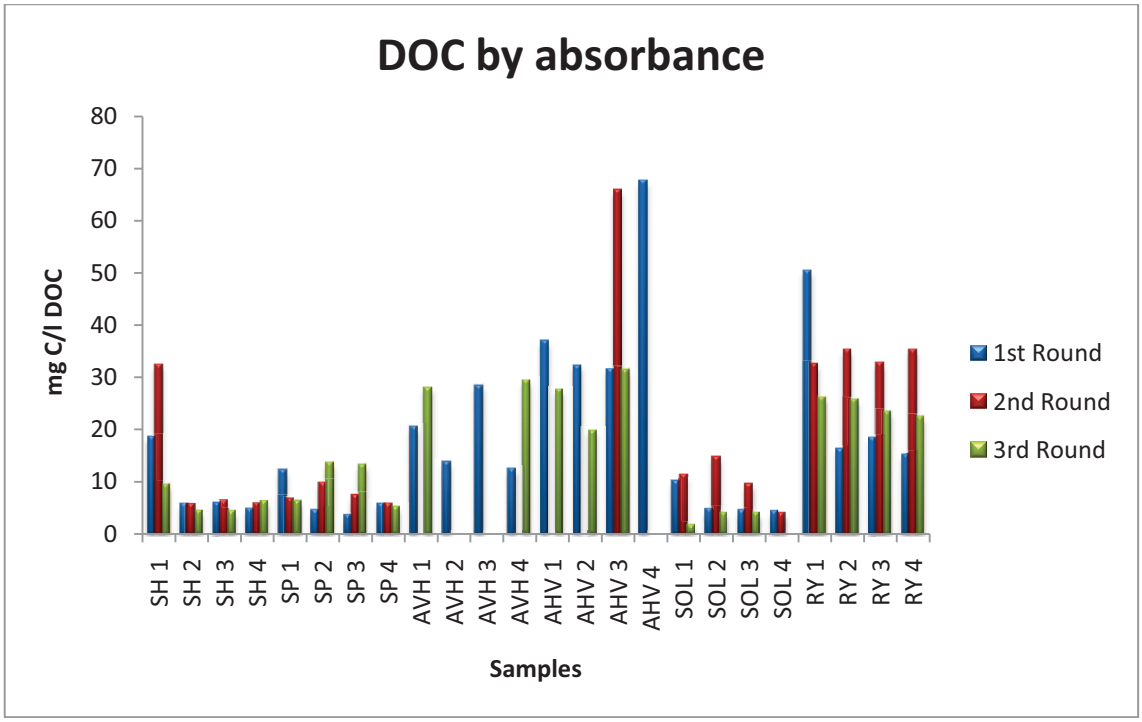


Figure 47. DOC in water samples

Concentrations of DOC in undisturbed watersheds generally range from approximately 1 to 20 mg carbon/L. As is possible to realized seeing the graphic most of our samples have a normal concentration of DOC, however there are some samples that have a strange behavior. This could be due to DOC in soil water is produced by decomposition of both new and old organic matter and by leckage of metabolites from plants and microbial cells (Clark et al., 2005) and is removed largely by adsorption in the mineral soil. Variables that can affect the concentration of DOC include: soil phase properties (litter amount, soil C store, and soil acidity), liquid phase properties (pH, ionic strength), meteorological conditions (temperature, precipitations) and land use factors.

5.4 Alkalinity

Alkalinity titration has only been performed for those water samples which have values of pH higher to 5.5.APPENDIX F

Values has been reported in this case as mg/L as $CaCO_3$. Reporting the alkalinity in this way specifies that the sample has an alkalinity equal to a solution with a certain amount of calcium carbonate ($CaCO_3$) dissolved in water. Alkalinity is measured by adding acid to the sample and figuring out the equivalent alkalinity in water. Then the units for the alkalinity titration are mmol per volume (mmol/L). For converting alkalinity from mmol/L to mg/L as $CaCO_3$ is necessary to consider that one mole of carbonate (CO^{3-}) can neutralize 2 moles of acid (H^+).

$$\text{Alkalinity}\frac{\text{mmoles}}{\text{L}}\times\frac{1\text{ mol}}{1000\text{mmoles}}\times\frac{1\text{mol CaCO3}}{2\text{ moles H}+}\times\frac{100\text{ g CaCO3}}{1\text{ mol}}\times\frac{1000\text{mg}}{1\text{g}}=\text{Alkalinity}\left(\frac{\text{mg}}{\text{L}}\text{as CaCO3}\right)$$

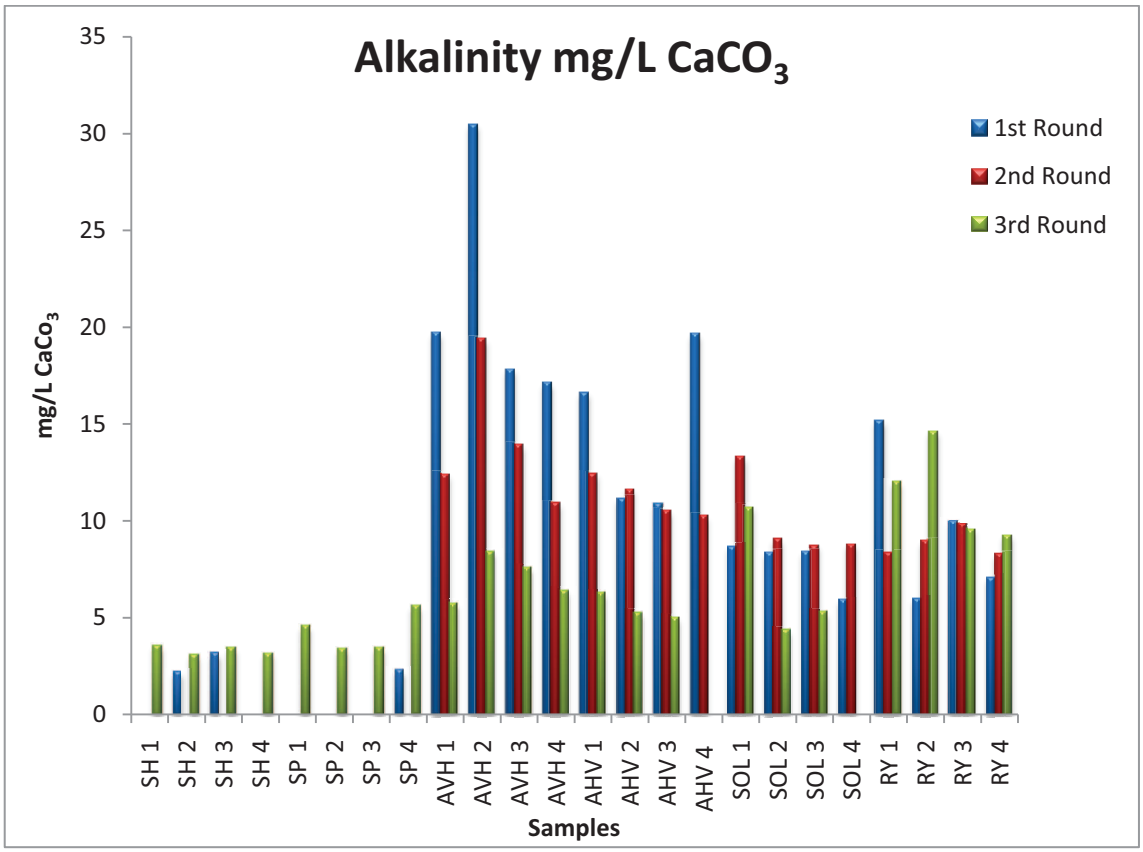


Figure 48. Alkalinity in mg/L $CaCO_3$

	mg/l $CaCO_3$
Rainwater	< 10
Typical surface water	20-200
Surface water in regions with alkaline soils	100-500
Groundwater	50-1000
Seawater	100-500

Table 7. Typical alkalinity ranges expressed in mg/l $CaCO_3$

Observing the table which shows the typical alkalinity ranges for different types of water, our water samples are inside the parameters of normal surface water (20-200 mg/L $CaCO_3$).

Alkalinity can increase the pH (make water more basic), when the alkalinity comes from a mineral source such as calcium carbonate. When CaCO3 dissolves in water the carbonate (CO32-) can react with water to form bicarbonate (HCO3-) which produces hydroxide (OH-):

$$CaCO_3\ (s) \longleftrightarrow Ca^{2+} + CO_3^{2-}$$

$$CO_3^{2-} + H_2O \longleftrightarrow HCO_3^{-} + OH^{-}$$

The hydroxide ion (OH-) is a strong base. An increased then in OH^- concentration, causes then also an increased in the pH. Back to pH values of our samples (see figure 43), we can explain then with a reason why the pH during the first round is higher than during the others. So the less acidic pH from the first round may be due to the high concentration of $CaCO_3$ in the soil columns at the beginning of the leaching experiment.

5.5 Suspended solids

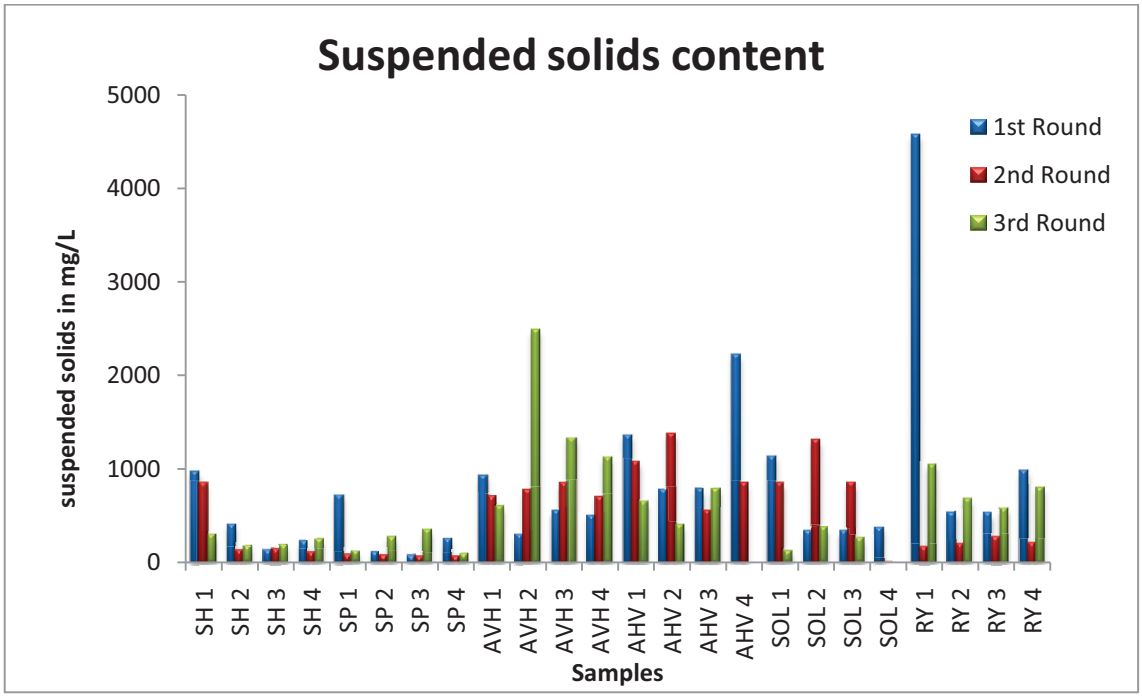


Figure 49. Content of suspended solids

Is not possible make a great interpretation of the graphic due to our water samples content lot of soil particles from the leaching experiment. Water samples are form not only from the leachate, also the soil particles that were on the bottom of the collecting pan were included. That is the reason for what values are so high.

Figure 50. Water samples

Only seeing the picture is possible realize the big amount of particles inside the water sample. If we take out from the characterization the value of the sample from RY 1during the first round is possible realized that the

samples with a highest content in suspended solids are the once collected from Askim. Maybe it is possible to relate the content of suspended solids with the type of soil. Soil samples from Askim were collected from a harrowing field, which means that the surface of the soil was removed using tillage techniques. Then is possible to assume that is a less compacted soil, which has lots of channels inside and that is why after the leaching experiment, we collected that higher amount of particles.

On the other hand, filters were subjected also to ignition in an owen at 500ºC during 4h. Then is possible calculated the percentage of Total organic content by Loss of Ignition (LOI). LOI is reported as:

$$LOI_{500} = ((DW_{105} – DW_{500})/DW_{105})*100$$

Where:

DW105 represents the dry weight of the filter before combustion and DW500 represents the dry weight of the sample after heating to 500ºC (Heiri et al., 1999).

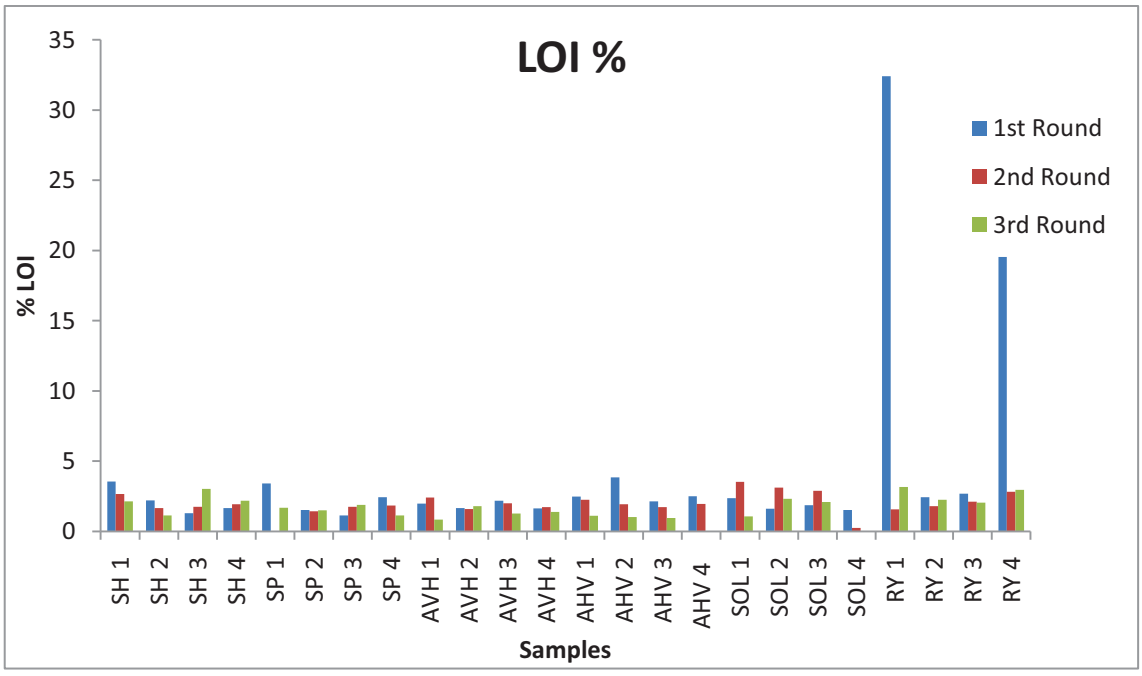


Figure 51. % of LOI

Trying to observe better the behavior of the samples, in the next graphic the outliers from the sample 1 and 4 from Rygge are taken out from the data.

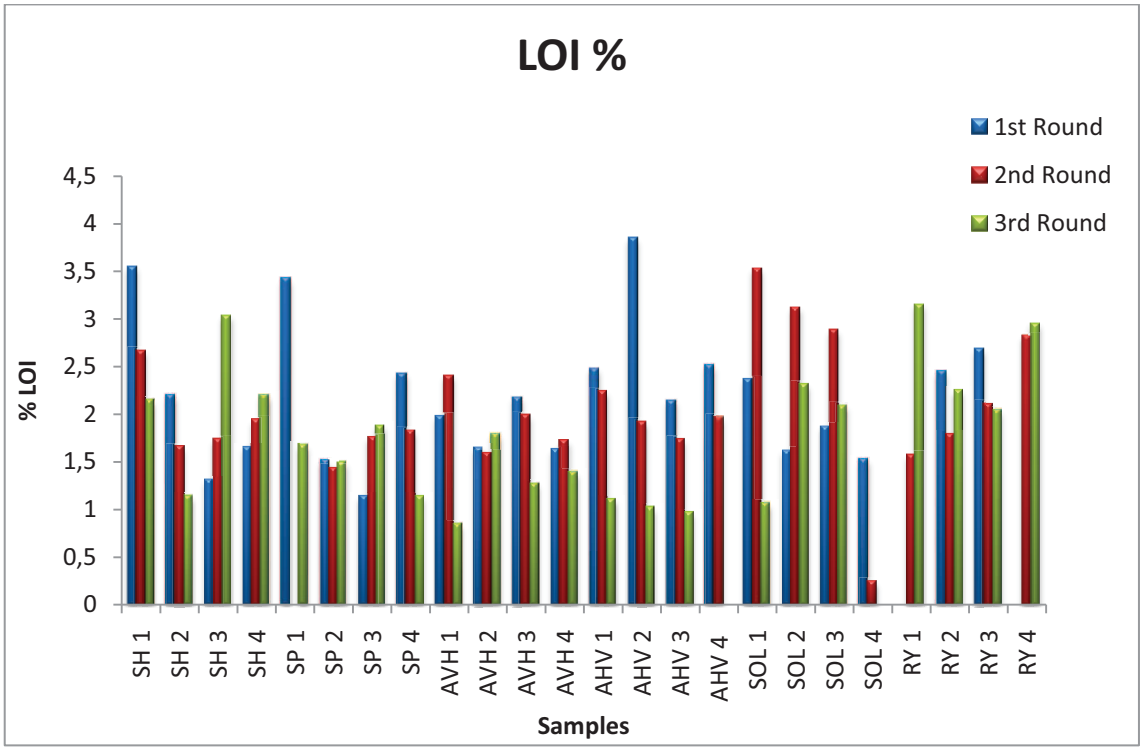
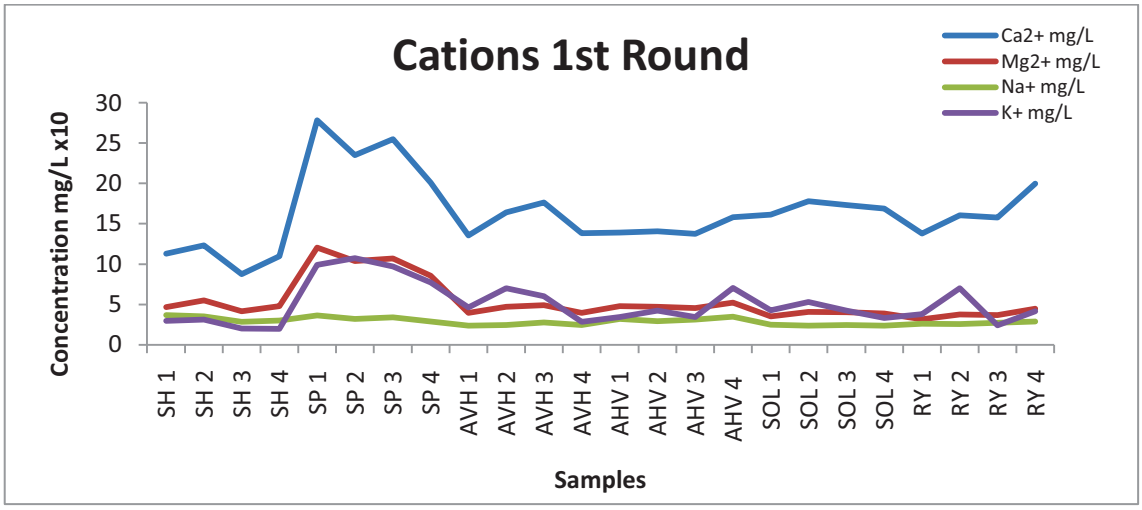
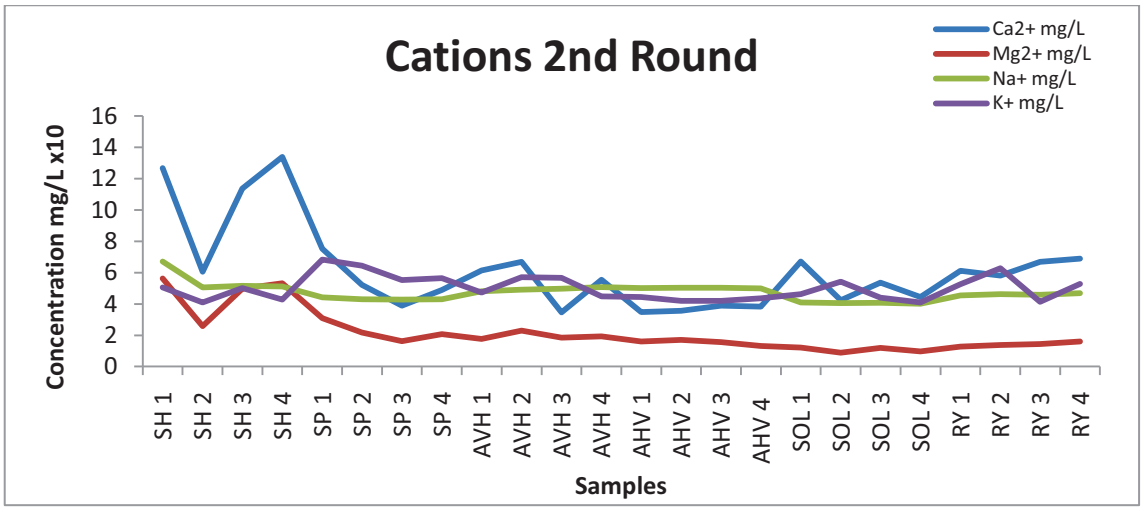


Figure 52. LOI % in samples

The weight loss is proportional to the amount of materials lost, usually "combined water" (hydrates and labile hydroxy-compounds) and carbon dioxide from carbonates. Again it holds that samples from fist round have a higher level of organic matter and carbonate in the sediments, because the percentage of LOI is higher in most of the samples.

5.6 Cations and anions





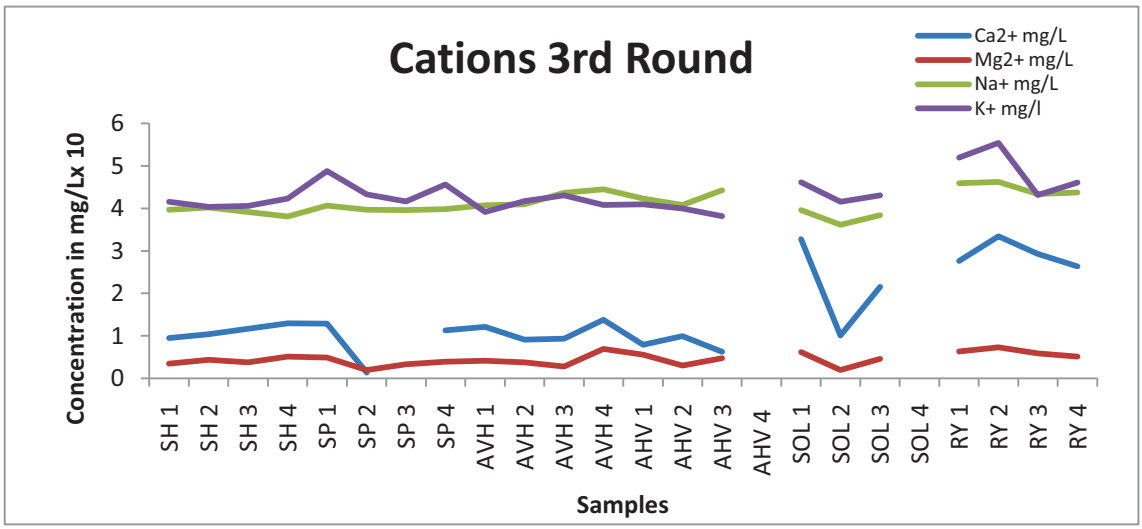


Figure 53. Cation concentrations along the three rounds.

Figure 51 shows the concentration of the major cations presented in the water filtered samples along the different rounds of the leaching experiment. Third graphic is not representative because there are some dates missed, in order to compare then the variation only the first and second round are going to be commented.

The general behavior is a decrease in the concentration of cations from the first round to the second, this may due to, first water that goes through the soil column drags almost all the minerals. Then in consecutive leachates the mineral concentration in the soil columns is lower.

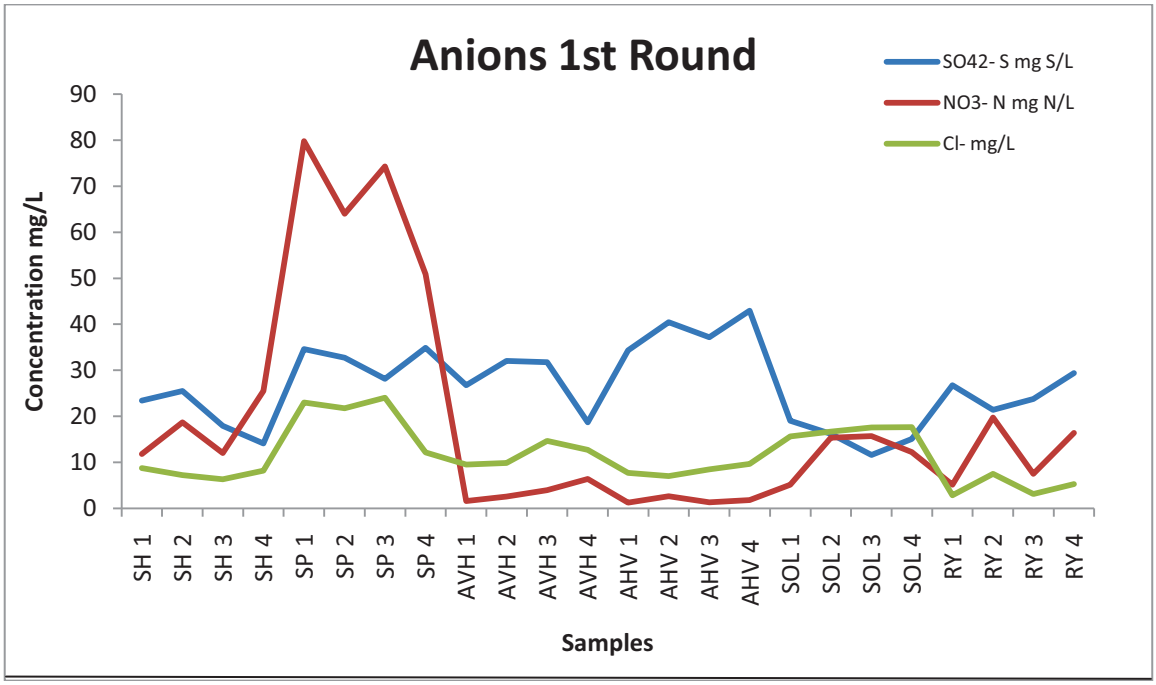


Figure 54. Anions concentration

Concentration of major anions only has been measured for filtered water samples from the first round. Conclusion that can be learned by observing the graph is related with the concentration in the different types of soil. Then is possible to say that soil samples from Syverud, have a higher concentration in NO^{3-}.

5.7 Bromide concentration

Measurement of the concentration of Bromide is really important in order to understand how the flux of the water through our soil columns is.

For that reason and as was explained along the Chapter 4 in paragraph which talk about the leaching experiment procedure, blanks for Bromide were taken from each first column of each sample place. Samples for bromide were taken in different times during the three hours of the leaching experiment in order to obtain a breakthrough curve (concentration of bromide vs time). Only for the first and second round, dates of time were recorded.

First Round

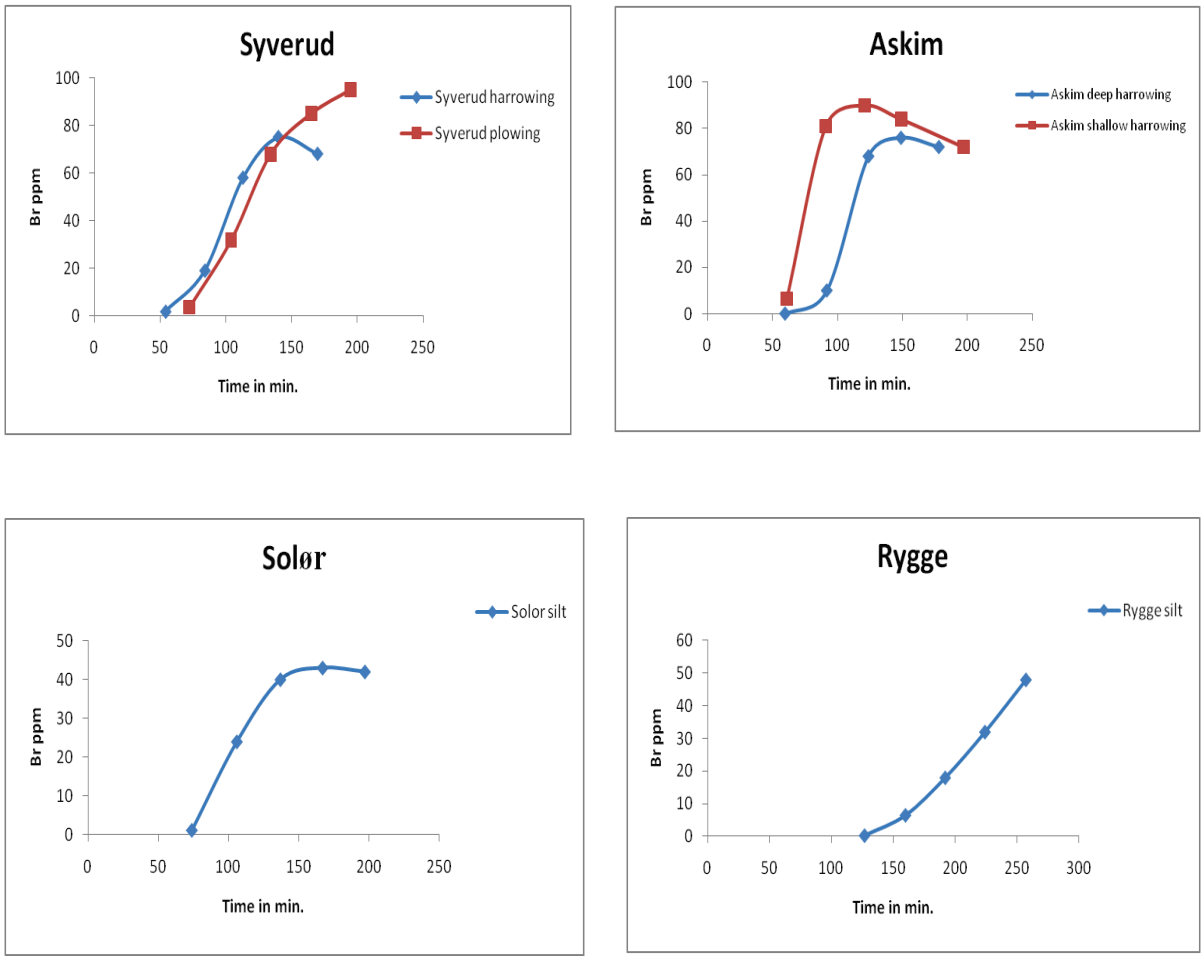


Figure 55. Graphics concentration Br versus Time

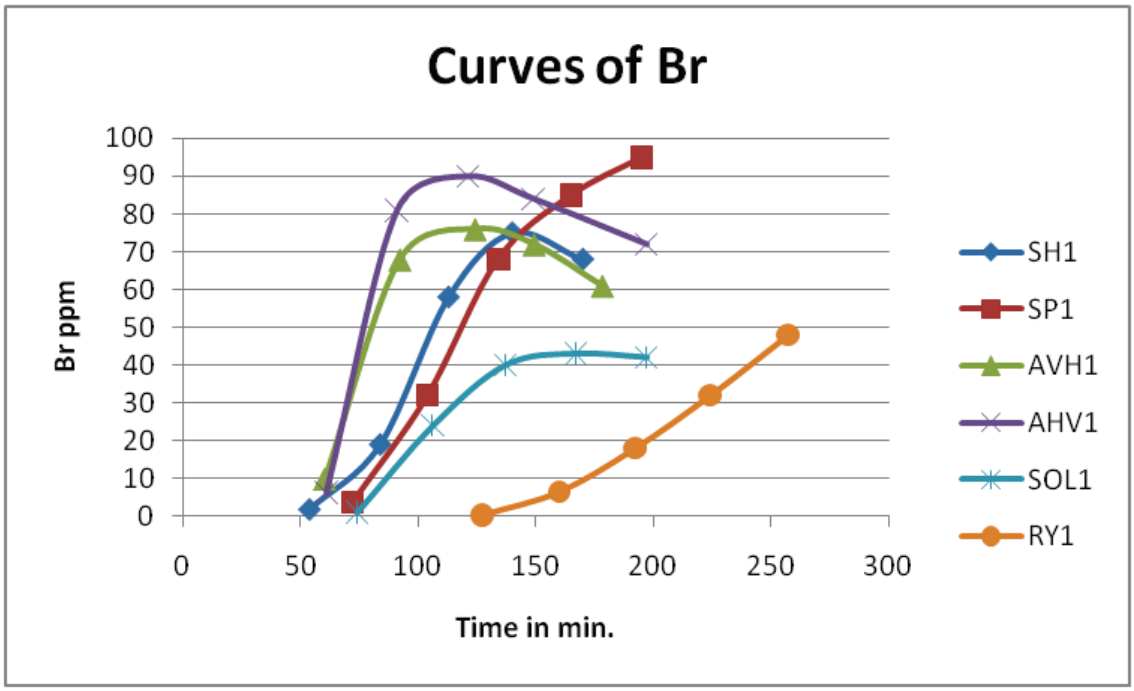


Figure 56. Concentration Br vs Time for all the blanks of the 1st Round

Second round

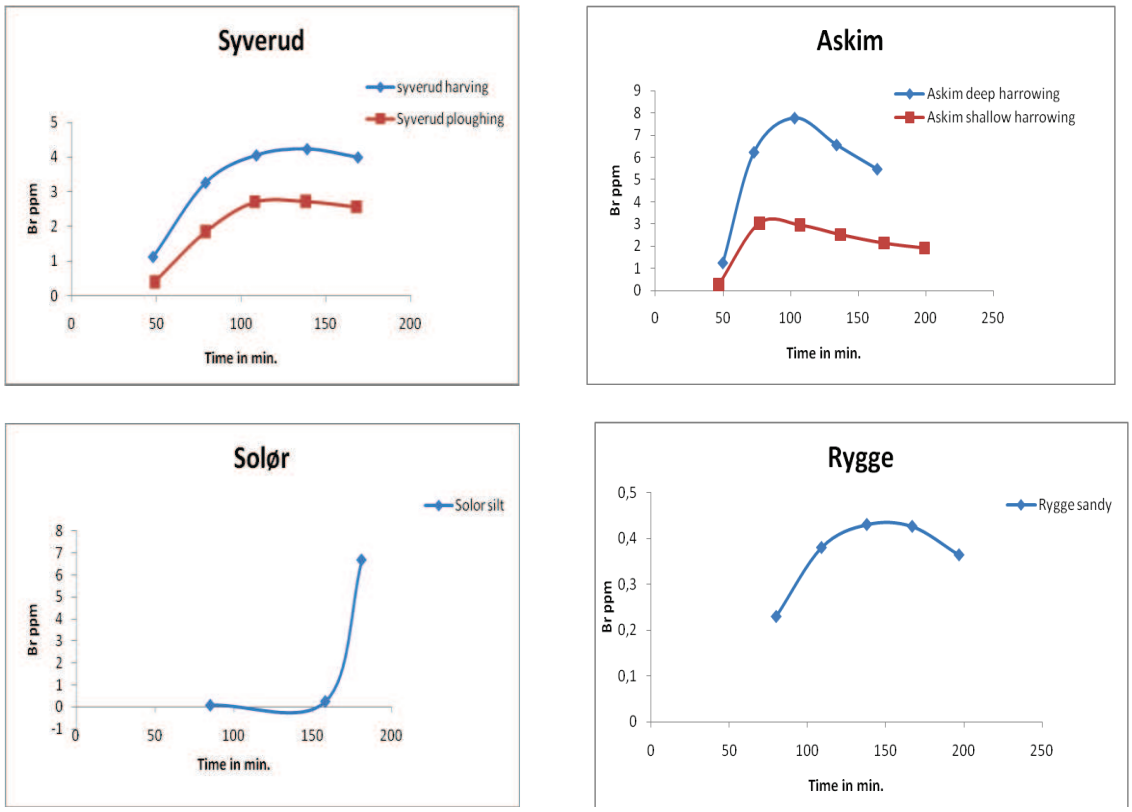


Figure 57. Graphics concentration bromide vs time

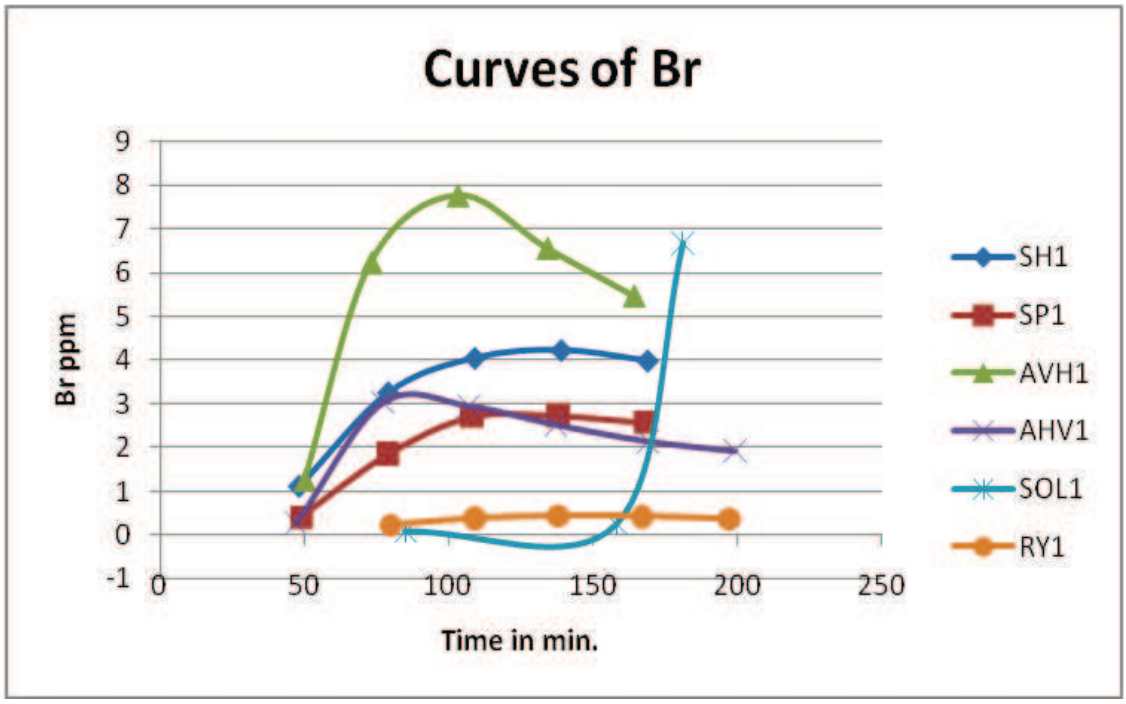


Figure 58. Concetration Br vs Time for all the blanks of the 2nd Round

Syverud soils were subjected to two differents tillage, ploughing and harrowing. This tillage practices can seal-off the larger continuos pores in the soil, this would translate into an increasement in the time it would take the water to flow through the soil column in our experiment.

If we compared the results from the first round, is possible realized that the samples of Syverud needed more time to flow through the soil column comparing with those from Askim, due to the deep tillage techniques applied to this field. But observing the graphic is possible realized that the samples that the water took longer time to go through are the samples from Rygge. This is something strange due to this type of soil is sandy which is translated in having big pores from 0.06-2 mm (see APPENDIX G), through whose the water can flow faster.

No reason has been found for this behavior, but a good explanation for this case can be that maybe soils from Rygge became extremely dry, after a prolonged drought or because had been long periods without any watering then they became what is known as ‘hydrophobic’.

When hydrophobic soils are watered with a hose, or when it rains after a very long spell of dry weather, the water simply flows off and is not absorbed. The condition ‘repels’ water, and this is what maybe has

happened to our soil columns, because sandy soils are particularly susceptible.

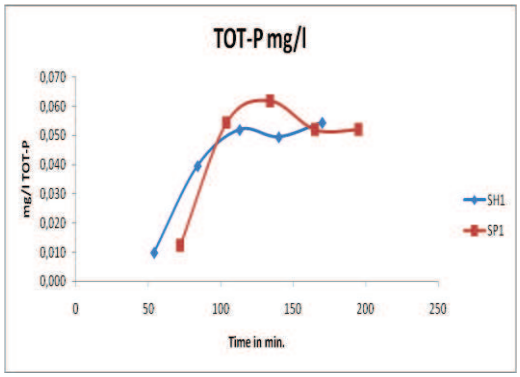
What happens when soils get overly dry is that the organic coating or thin layer of humus on the surface of soil particles dries up causing a waxy surface. Water then just slips by, without actually adhering to the soil particle.

5.8 Total phosphorus and dissolved phosphorus

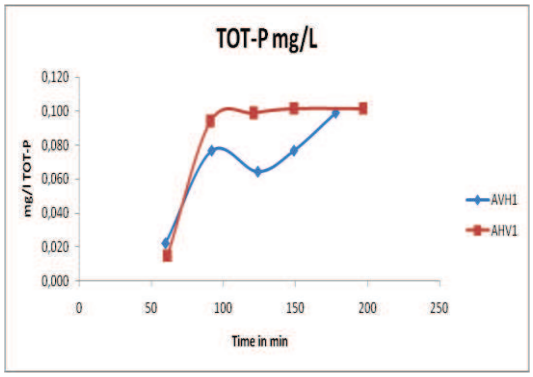
The results for total phosphorus and dissolved phosphorus leachates from the different sample sites along the different rounds of the experiment are summarized in the consequent figures. Other graphics related to the standardization and data can be found in the APPENDIX H .

First round

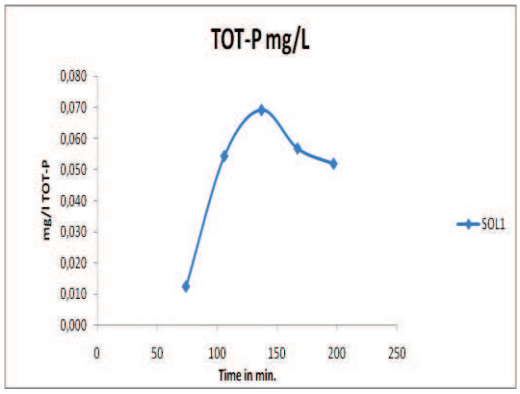
TOT-P



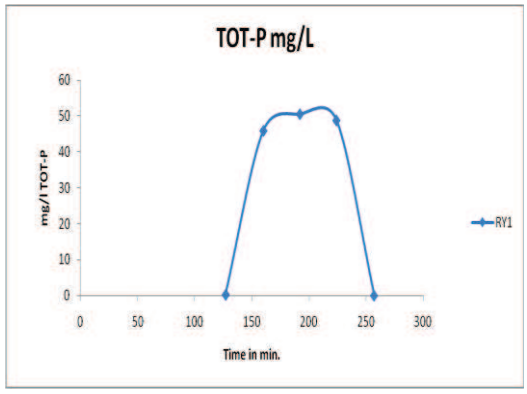
Syverud



Askim



Solør



Rygge

Figure 59. Graphics concentration TOT-P vs time

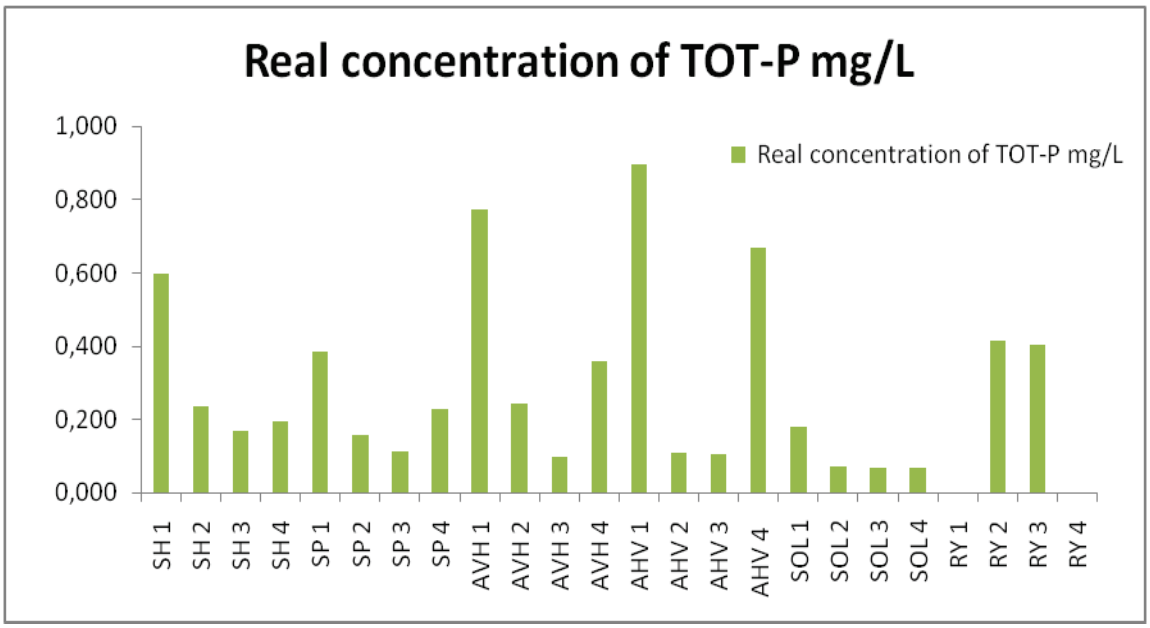
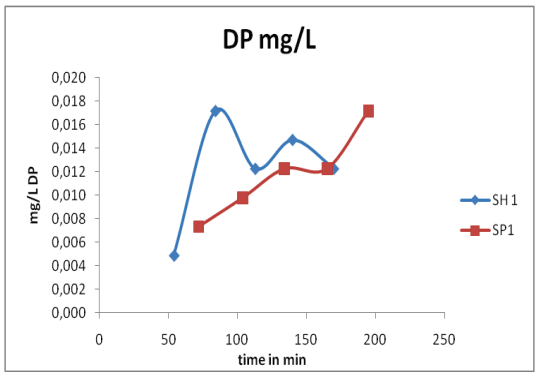
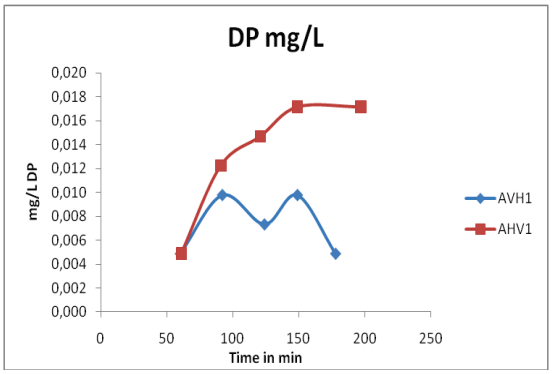


Figure 60. Concentration of TOT-P in water samples from the first round

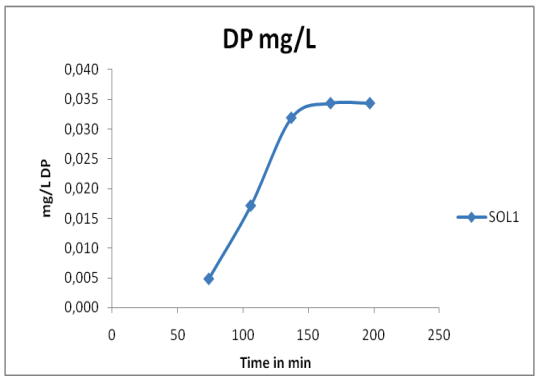
DISSOLVED-P



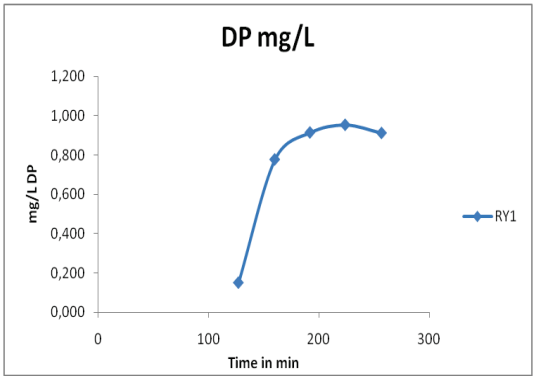
Syverud



Askim



Solør



Rygge

Figure 59. Graphics concentration DP vs time

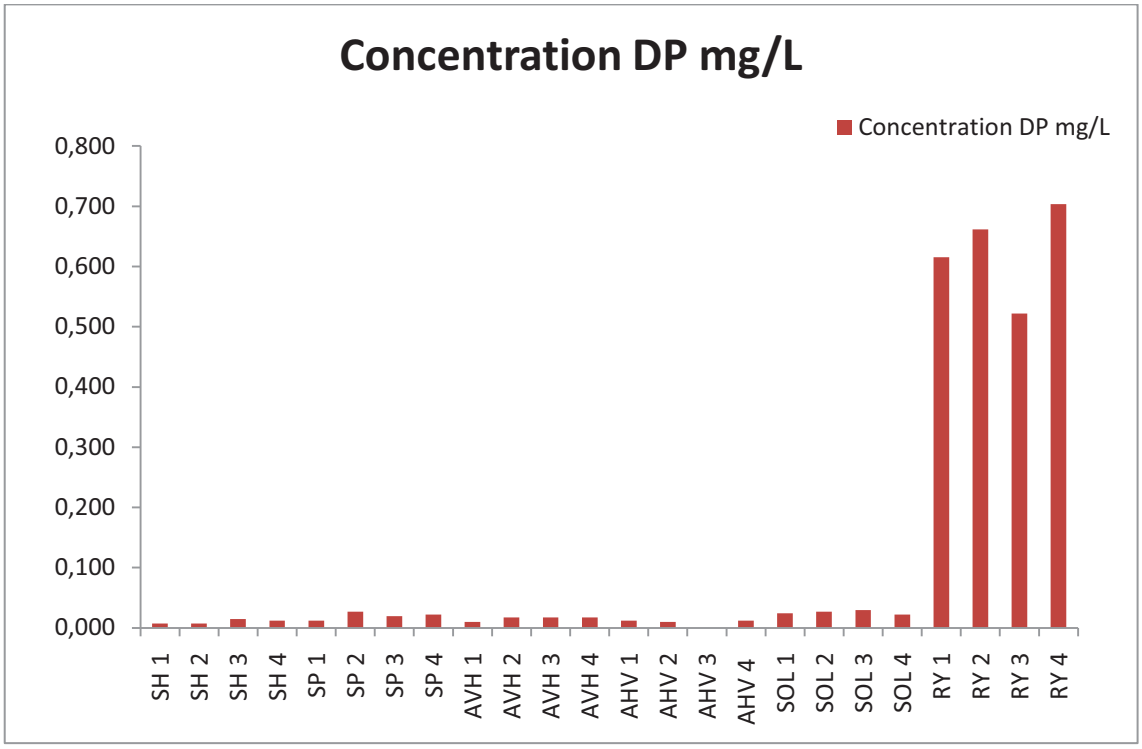
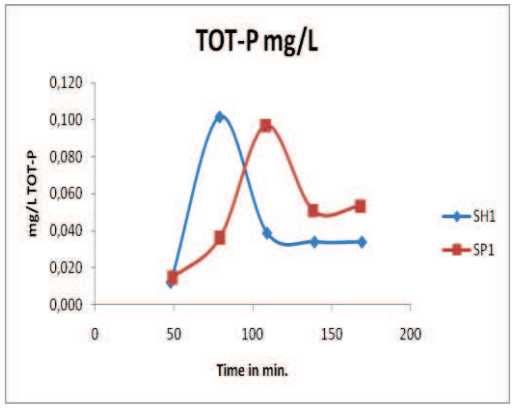


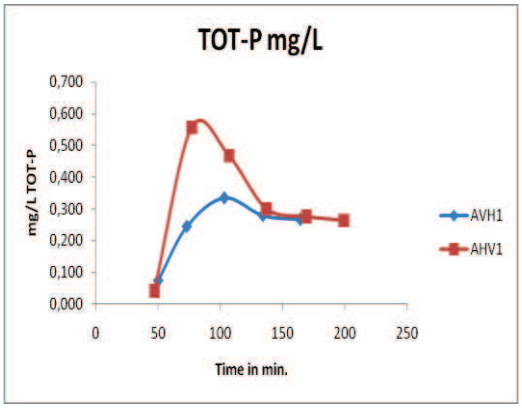
Figure 62. Concentration of DP in water samples from the first round

Second round

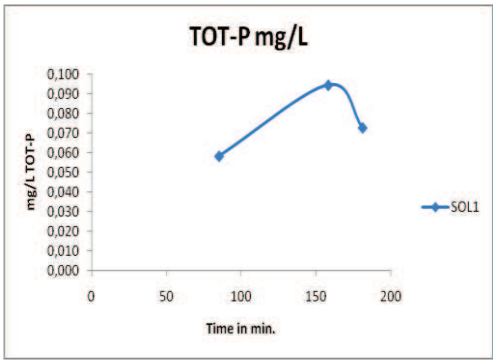
TOT-P



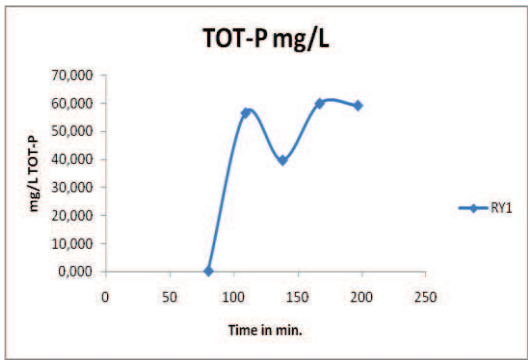
Syverud



Askim

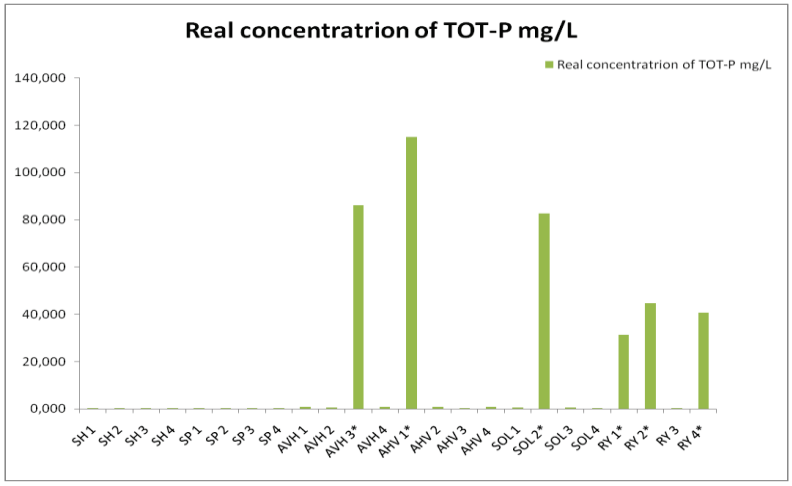


Solør

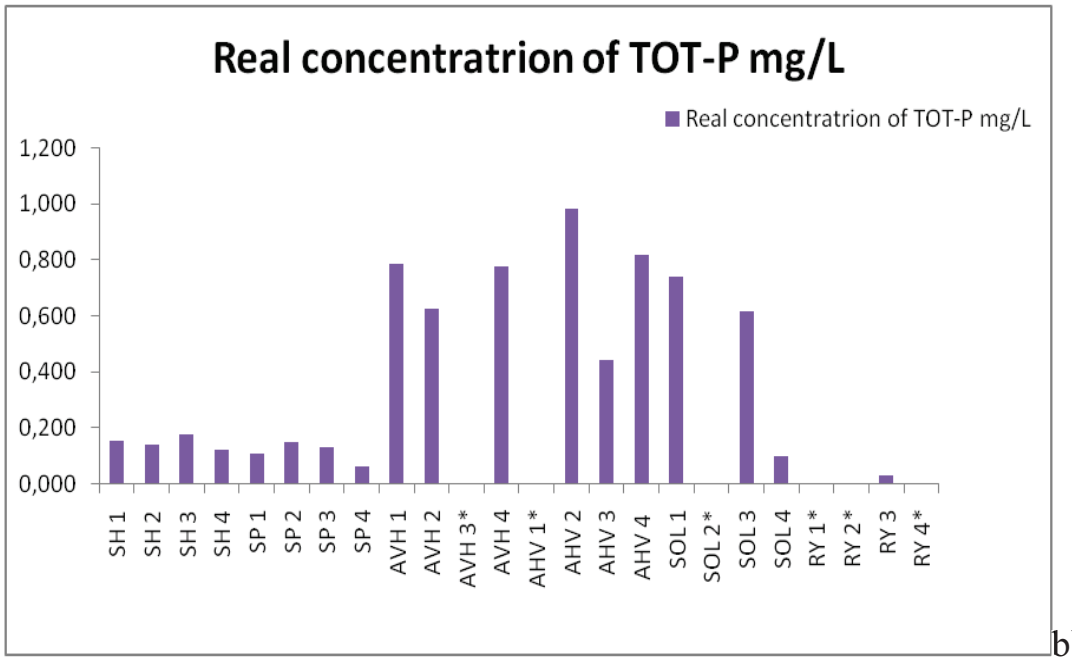


Rygge

Figure 63. Graphics concentration TOT-P vs time



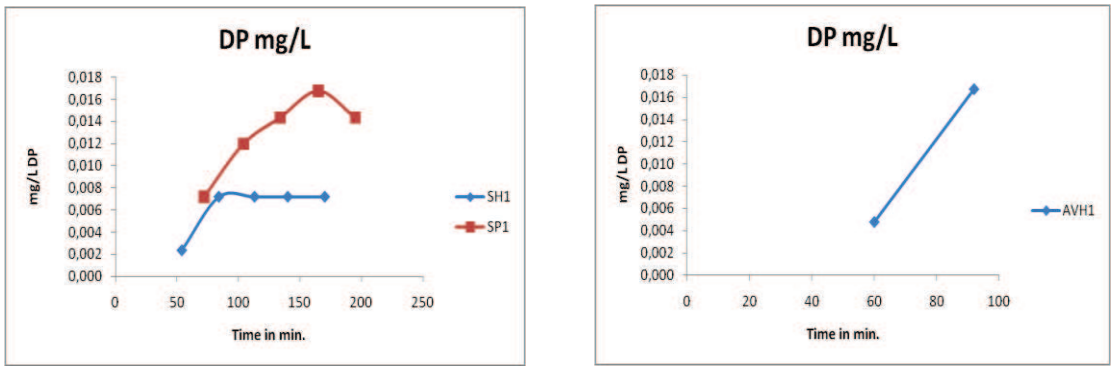
a)



b)

Figure 64. Concentration of TOT-P in water samples during the second round. a) all values in range b)values with high concentration(*) are omitted.

DISSOLVED-P



Syverud Askim

Figure 65. Graphics concentration DP vs time

Only some samples from this round were analyzed to DP content, due to water solution had a high concentration of particles inside and was impossible fitered with the 0.45µm filters.

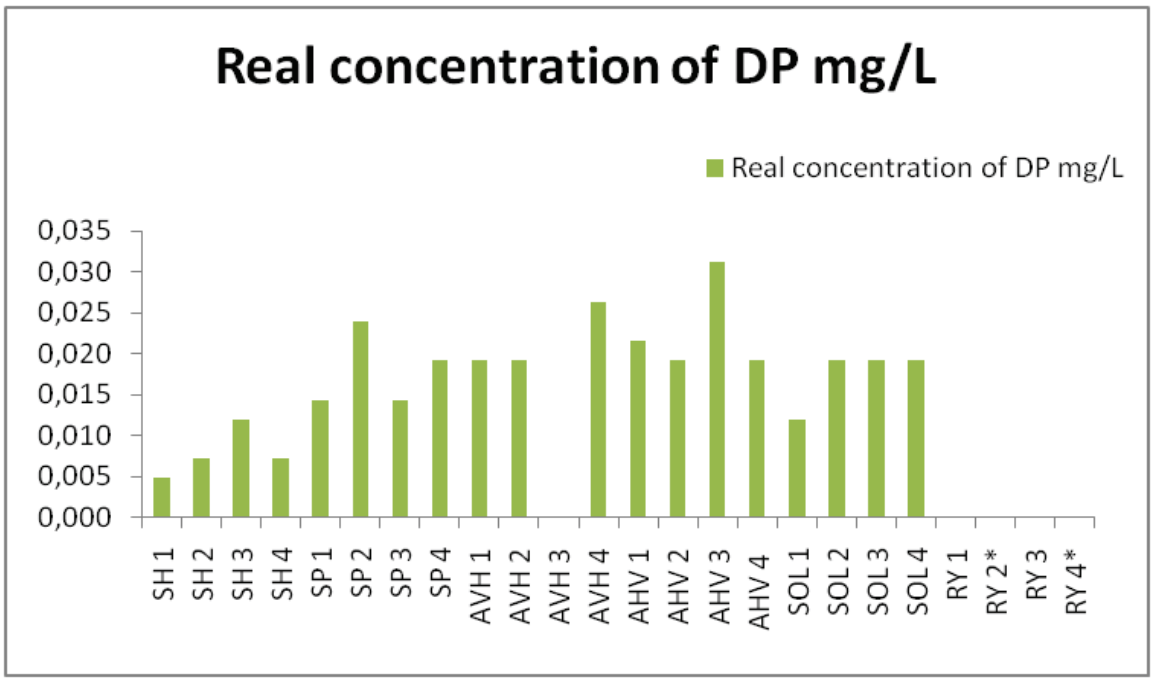
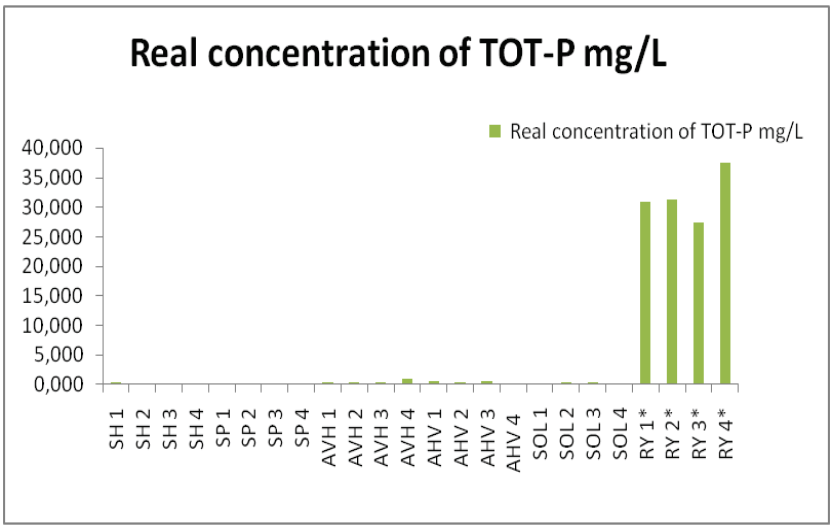


Figure 66. Concentration of DP in water samples during the second round

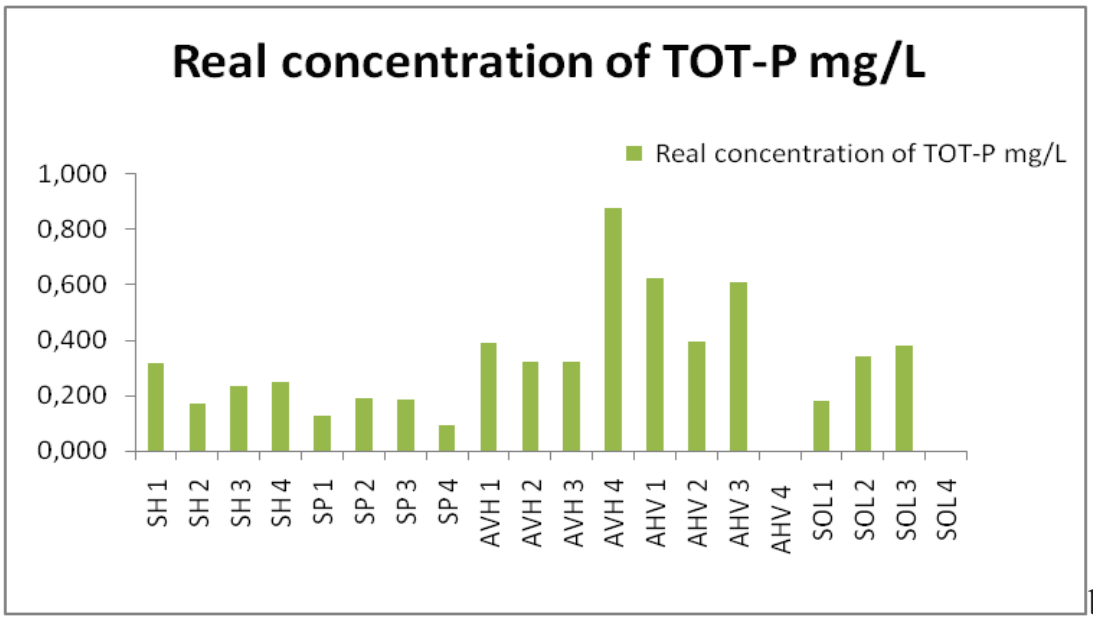
Third round

As was explained along the chapter 4, this round was not performed in the same way as the two predecessors. Changes in the parameters should be interpreted with caution.

TOT-P



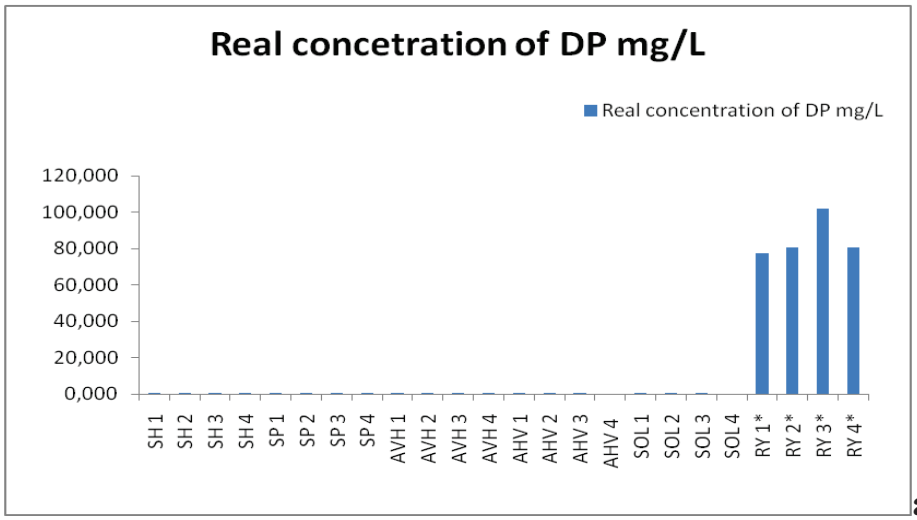
a)



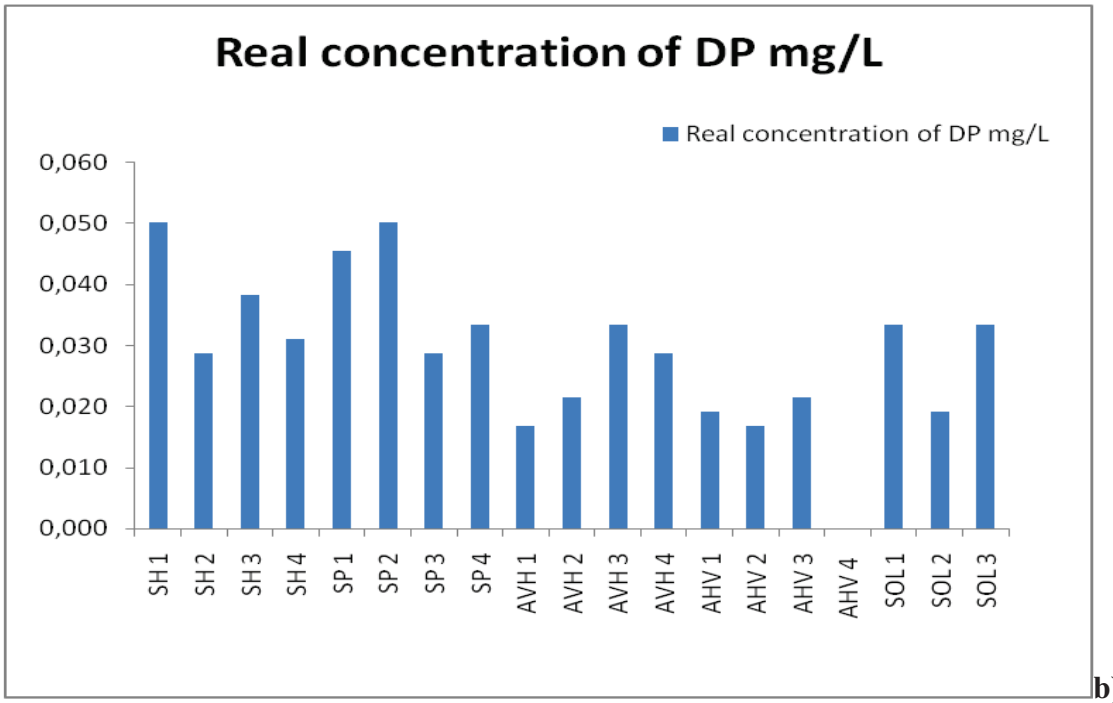
b)

Figure 67. Concentration of TOT-P in water samples during the third round. a) all values in range b)values with high concentration(*) are omitted.

Dissolved-P



a)



b)

Figure 68. Concentration of DP in water samples during the third round. a) all values in range b)values with high concentration(*) are omitted.

Leaching of TOT-P and Disolved phosphorus (PO_4^{3-}) from the control soils from Syverud and Askim was small compared with the samples from Rygge. Large amounts of phosphate and TOT-P were leached from the soil columns of Rygge through the three rounds.

Observing the behavior of leachates TOT-P and dissolved phosphorus from Rygge soil samples is possible determining that sandy soil samples, retained less the flux of water through them. So this results, in a high discharge of phosphorus.

In spite of this, soil under different tillage, as the ones from Syverud or Askim results in low discharges of phosphorus, due to removing the surface and under surface of soil, is reduce the size of the macropores, avoiding then high fluxes of water.

6 Conclusions

Phophorus loss from soils is a phenomenon closely related to soil properties. Results from this study confirmed that accurence and magnitude of P losses from soils depends on edaphatic conditions and tillage practices. Soils with sandy characteristics allowed the transport of phosphorus through them easily, as has been shown in this experiment the higher concentration of phosphorus leachate has occurred in the soil samples from Rygge. Soil type in this collecting sample site has big pores, and this is translated in a faster flux of water through the soil. On the other way, has been showed also that different tillage practice to the soil can reduce the amount of phosphorus leachated. This is what happened with the samples from Syverud. These samples come from to different tillage practices, harrowing and ploughing.

So is possible to conclude, that in order to reduce the losses of phosphorus through soil to underwater, good tillage practices in the fields have to be done. If the amount of phosphorus leaching from the soils is reduced this can benefit in order to reduce the eutrophication problem of many water resources.

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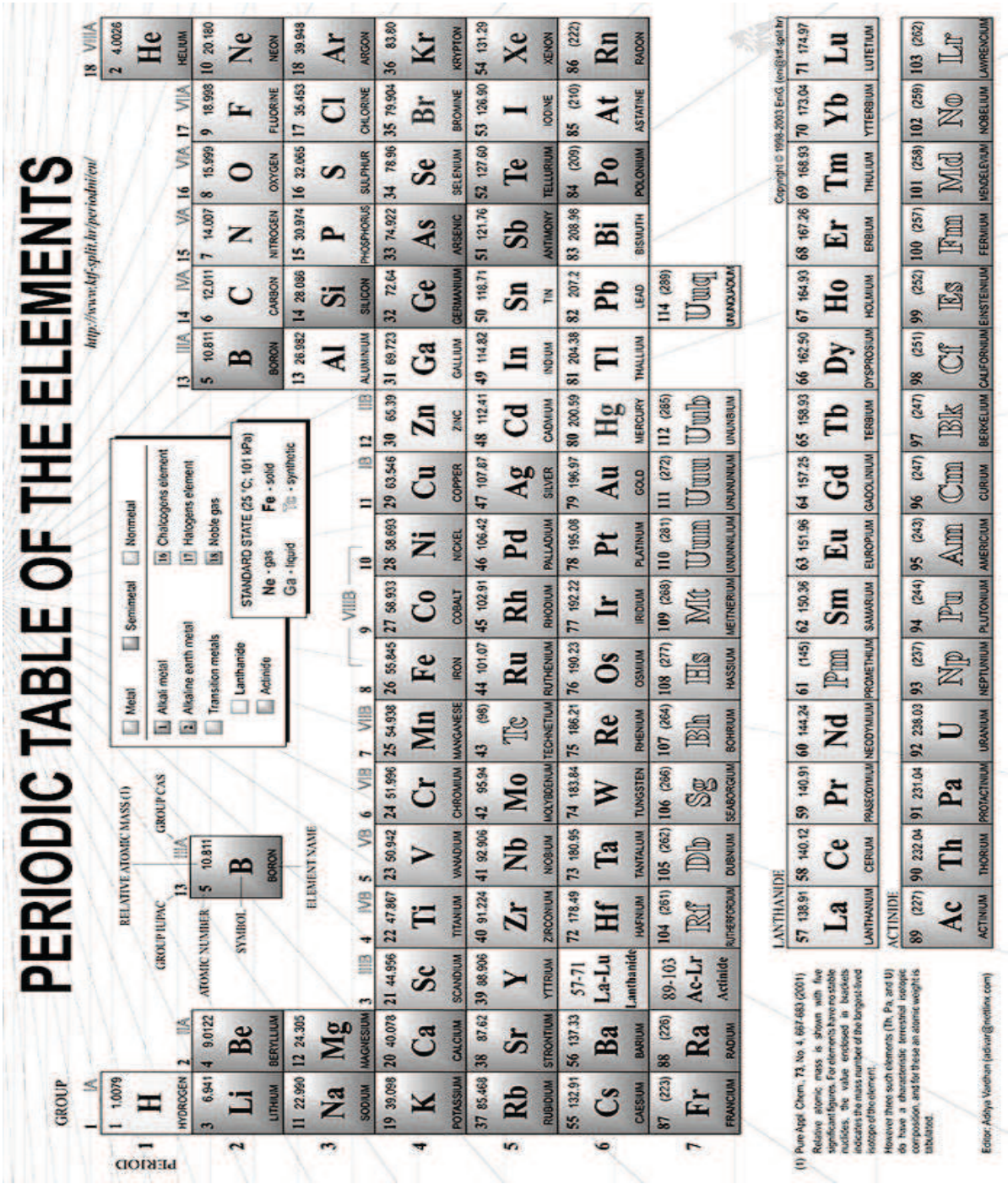
Appendix

Appendix A



Appendix B

Pesticide characteristics and concentration

Glyphosate

Beregning av mengde glyfosat til bruk ved søyleforsøk og nedbrytingsforsøk:

Til nedbrytingsforsøk bør det brukes samme dose glyfosat som ved søyleforsøk.

NAD = 400 ml Roundup Eco/daa. Denne dosen ble sprøytet på Askim i september 2008.

A Roundup Eco inneholder 360 g glyfosat/L og en total tetthet på 1206 g/L.
Mengde glyfosat i 400 ml Roundup Eco/daa: **144 g glyfosat/daa**

B **Beregning av tilsats til sentrifugerør i nedbrytingsforsøk:**

144 g glyfosat/daa tilsvarer 14.4 mg glyfosat/dm^3 når en antar at stoffet fordeler seg i den øverste cm (0.1 dm) i jordlaget.

Dette tilsvarer 14.4 mg/kg jord eller 14.4 µg glyfosat/g jord, dersom jordtettheten antas være lik 1 kg/dm^3.

Til et sentrifugerør med 30 gram jord tilsettes 432 µg glyfosat

C **Beregning av tilsats til søyleforsøk:**

Areal av søyler: 3.14 dm^2 (diameter 20 cm, radius 1 dm))

NAD er 144 g glyfosat/daa = 144 g per 100.000 dm^2.

Per søyle tilsettes: 0.0045216 g glyfosat som tilsvarer **4.5216 mg glyfosat;**

Dersom 1 % av tilsatt stoff lekker ut, tilsvarer det en mengde p 45.216 µg glyfosat

Dersom denne mengden er løst i for eksempel 200 ml utlekkingsvann: 0.226 µg glyfosat/ml

0.2 µg glyfosat/ml er direkte målbart med LC-MS/MS.
Men man kan ikke anta at 1% av tilsatt mengde vil lekke ut i 1 episode, men heller i flere episoder, med mye lavere konsentrasjoner.
Oppkonsentrering av vannprøvene før analyse kan være nødvendig, men det er praktisk å overføre 0.5 ml av hver vannfraksjon til en plastvial for direkte analyse på LC-MS/MS *før* prøvepparbeidelse/oppkonsentrering.

Appendix C

Ionic strength

STASJON	Veide årsmiddelkonsentrasjoner								
	pH	SO4*	NO3	NH4	Ca	K	Mg	Na	Cl
		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Søgne	4,80	0,31	0,43	0,29	0,23	0,29	0,40	3,34	5,71
Birkenes	4,75	0,30	0,33	0,28	0,11	0,06	0,12	0,94	1,57
Vatnedalen	5,31	0,10	0,11	0,13	0,17	0,12	0,10	0,73	1,06
Treungen	4,82	0,23	0,24	0,18	0,08	0,05	0,04	0,27	0,45
Løken	4,92	0,24	0,30	0,28	0,16	0,09	0,06	0,35	0,66
Hurdal	5,13	0,26	0,28	0,36	0,23	0,18	0,05	0,34	0,52
Brekkebygda	4,98	0,18	0,18	0,16	0,13	0,10	0,03	0,14	0,22
Vikedal	5,24	0,14	0,17	0,28	0,22	0,17	0,40	3,31	5,07
Haukeland	5,18	0,09	0,09	0,10	0,12	0,08	0,23	1,63	2,85
Nausta	5,26	0,07	0,08	0,10	0,10	0,07	0,20	1,38	2,54
Kårvatn	5,40	0,05	0,04	0,11	0,11	0,09	0,22	1,52	2,85
Høylandet	5,88	0,08	0,12	0,38	0,25	0,17	0,49	3,58	6,54
Tustervatn	5,28	0,07	0,08	0,14	0,13	0,10	0,26	1,98	3,66
Karasjok	5,15	0,20	0,13	0,18	0,13	0,24	0,06	0,46	0,77
Karpbukt	5,00	0,39	0,10	0,14	0,15	0,11	0,21	1,52	2,68
Ny-Ålesund	5,89	0,19	0,05	0,12	0,79	0,43	1,11	8,18	14,99

Appendix D

Soil data

Syverud		Pløyd		Harva	
		0 - 10 cm	10 - 20 cm	0 - 10 cm	10 - 20 cm
Enhet		1	2	3	4
Volumvekt	kg/L	1,2	1,2	1,1	1,3
pH		5,8	6,0	5,8	5,8
Tot-P	mg/kg	1100	960	1000	810
P-AL	mg/100g	9,6	9,0	11	7,8
K-AL	mg/100g	47	40	23	7,3
Mg-AL	mg/100g	13	20	14	9,0
Ca-AL	mg/100g	63	84	56	36
Na-AL	mg/100g	<5	<5	<5	<5
Glødetap	%	7,2	7,1	6,8	5,1
TOC	g/100g	3	2,7	2,6	2,1

Askim			Vårharva		Høstharva	
			0 - 10 cm	10 - 20 cm	0 - 10 cm	10 - 20 cm
	Enhet		5	6	7	8
Volumvekt		kg/L	1,5	1,7	1,5	1,5
pH			6,7	7,4	6,7	6,7
Tot-P		mg/kg	820	750	740	770
P-AL		mg/100g	3,4	1,5	3,1	5,4
K-AL		mg/100g	17	8,9	17	9,5
Mg-AL		mg/100g	19	26	19	18
Ca-AL		mg/100g	120	200	110	110
Na-AL		mg/100g	<5	<5	<5	<5
Glødetap		%	3,6	3,1	3,8	3,1
TOC		g/100g	1,3	0,83	1,0	0,95

Solør		0 - 10 cm	10 - 20 cm
Enhet		9	10
Volumvekt	kg/L	1,4	1,3
pH		6,5	6,5
Tot-P	mg/kg	1000	1000
P-AL	mg/100g	8,6	8,3
K-AL	mg/100g	8,9	11
Mg-AL	mg/100g	6,2	5,6
Ca-AL	mg/100g	66	62
Na-AL	mg/100g	<5	<5
Glødetap	%	3,5	3,5
TOC	g/100g	1,4	1,5
CEC	meq/100g	9,0	11,9

Rygge		0-10 cm	10 - 20 cm
Enhet		11	12
Volumvekt	kg/L	1,3	1,2
pH		6,5	6,5
Tot-P	mg/kg	1400	1400
P-AL	mg/100g	32	32
K-AL	mg/100g	22	14
Mg-AL	mg/100g	6,0	6,9
Ca-AL	mg/100g	78	85
Na-AL	mg/100g	<5	<5
Glødetap	%	2,7	2,9
TOC	g/100g	1,1	1,0

Appendix E

Absorbance values

Samples	Absorbance					
	1st Round		2nd Round		3rd Round	
	254 nm	400 nm	254 nm	400 nm	254 nm	400nm
SH 1	0,88	0,737	1,536	1,227	0,446	0,617
SH 2	0,275	0,165	0,272	0,137	0,209	0,303
SH 3	0,283	0,135	0,303	0,181	0,2	0,298
SH 4	0,229	0,092	0,279	0,16	0,298	0,386
SP 1	0,578	0,419	0,319	0,0131	0,298	0,463
SP 2	0,211	0,093	0,468	0,203	0,637	0,921
SP 3	0,166	0,061	0,349	0,137	0,623	0,877
SP 4	0,277	0,143	0,275	0,105	0,25	0,48
AVH 1	0,972	0,828		2,223	1,335	2,334
AVH 2	0,648	0,473		2,022		4
AVH 3	1,349	0,993				4
AVH 4	0,585	0,43		2,251	1,396	4
AHV 1	1,755	1,38		2,914	1,305	2,142
AHV 2	1,529	1,17		3,135	0,943	1,658
AHV 3	1,497	1,156	3,135	1,462	1,49	2,683
AHV 4	3,215	2,571		2,057		
SOL 1	0,48	0,351	0,539	0,332	0,079	0,232
SOL 2	0,219	0,105	0,699	0,541	0,188	0,278
SOL 3	0,21	0,098	0,455	0,285	0,188	0,331
SOL 4	0,199	0,09	0,188	0,053		
RY 1	2,395	1,83	1,546	0,722	1,237	2,088
RY 2	0,772	0,337	1,678	0,649	1,22	2,659
RY 3	0,866	0,392	1,557	0,647	1,109	1,969
RY 4	0,72	0,304	1,678	0,667	1,063	1,854

Appendix F

pH values

	pH		
Samples	1st Round	2nd Round	3rd Round
SH 1	5,2	5,02	6,12
SH 2	6,09	5,04	5,97
SH 3	5,59	4,93	6,02
SH 4	5,47	4,98	5,95
SP 1	5,49	5,12	5,95
SP 2	5,17	5,37	5,99
SP 3	5,08	5,44	5,98
SP 4	5,54	5,35	5,96
AVH 1	6,78	5,65	6,05
AVH 2	7,22	6,17	6,21
AVH 3	6,92	6,27	6,25
AVH 4	7,12	6,14	6,23
AHV 1	6,86	6,25	6,29
AHV 2	6,74	6,26	6,21
AHV 3	6,71	6,24	6,23
AHV 4	6,98	6,23	
SOL 1	6,74	6,17	6,22
SOL 2	6,54	6,26	6,26
SOL 3	6,51	6,2	6,16
SOL 4	6,49	6,23	
RY 1	6,1	6,14	6,2
RY 2	6,35	6,12	6,32
RY 3	6,31	6,13	6,33
RY 4	6,29	6,07	6,31

Appendix G

Types of soils

Syverud			**Pløyd**		**Harva**	
			0 - 10 cm	10 - 20 cm	0 - 10 cm	10 - 20 cm
pH			5,8	6,0	5,8	5,8
Tot-P		mg/kg	1100	960	1000	810
P-AL		mg/100g	9,6	9,0	11	7,8
Sand	0,06 - 2 mm	%	25	25	27	29
Silt	0,002 - 0,06	%	45	46	46	45
Leir	< 0,002 mm	%	29	29	26	25

Askim			Vårharva		Høstharva	
			0 - 10 cm	10 - 20 cm	0 - 10 cm	10 - 20 cm
pH			6,7	7,4	6,7	6,7
Tot-P		mg/kg	820	750	740	770
P-AL		mg/100g	3,4	1,5	3,1	5,4
Sand	0,06 - 2 mm	%	10	10	24	21
Silt	0,002 - 0,06	%	63	62	53	53
Leir	< 0,002 mm	%	27	27	24	25

Solør			0 - 10 cm	10 - 20 cm
pH			6,5	6,5
Tot-P		mg/kg	1000	1000
P-AL		mg/100g	8,6	8,3
Sand	0,06 - 2 mm	%	17	17
Silt	0,002 - 0,06	%	73	74
Leir	< 0,002 mm	%	10	9

Rygge			0-10 cm	10 - 20 cm
pH			6,5	6,5
Tot-P		mg/kg	1400	1400
P-AL		mg/100g	32	32
Sand	0,06 - 2 mm	%	65	68
Silt	0,002 - 0,06	%	27	23
Leir	< 0,002 mm	%	9	10

Appendix H

Values for TOT-P and Dissolved P

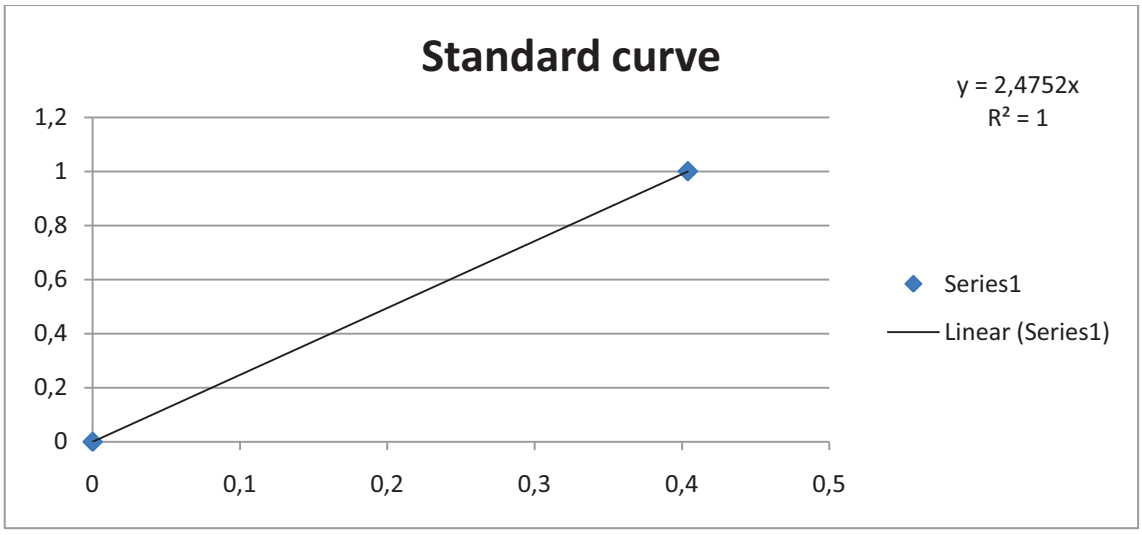
First round

		Absobance	Concentration TOT-P mg/L	Real concentration of TOT-P mg/L	Time in min
	1st extrc.	0,004	0,010	0,010	54
	2nd extrc.	0,016	0,040	0,040	84
SH1	3rd extrc.	0,021	0,052	0,052	113
	4th extrc.	0,02	0,050	0,050	140
	5th extrc.	0,022	0,054	0,054	170
	1st extrc.	0,005	0,012	0,012	72
	2nd extrc.	0,022	0,054	0,054	104
SP1	3rd extrc.	0,025	0,062	0,062	134
	4th extrc.	0,021	0,052	0,052	165
	5th extrc.	0,021	0,052	0,052	195
	1st extrc.	0,009	0,022	0,022	60
	2nd extrc.	0,031	0,077	0,077	92
AVH1	3rd extrc.	0,026	0,064	0,064	124
	4th extrc.	0,031	0,077	0,077	149
	5th extrc.	0,04	0,099	0,099	178
	1st extrc.	0,006	0,015	0,015	61
	2nd extrc.	0,038	0,094	0,094	91
AHV1	3rd extrc.	0,04	0,099	0,099	121
	4th extrc.	0,041	0,101	0,101	149
	5th extrc.	0,041	0,101	0,101	197
	1st extrc.	0,005	0,012	0,012	74
	2nd extrc.	0,022	0,054	0,054	106
SOL1	3rd extrc.	0,028	0,069	0,069	137
	4th extrc.	0,023	0,057	0,057	167
	5th extrc.	0,021	0,052	0,052	197
	1st extrc.	0,114	0,282	0,282	127
	2nd extrc.*	0,088	0,218	45,870	160
RY1	3rd extrc.*	0,08	0,198	50,500	192
	4th extrc.*	0,083	0,205	48,780	224
	5th extrc.	0,015	0,037	0,037	257

Samples with * means that they were diluted, 0.5ml water sample in 4.5ml of distilled water.

	Absorbance	Concentation TOT-P mg/L	Real concentration of TOT-P mg/L
SH 1	0,241	0,597	0,597
SH 2	0,096	0,238	0,238
SH 3	0,068	0,168	0,168
SH 4	0,079	0,196	0,196
SP 1	0,156	0,386	0,386
SP 2	0,063	0,156	0,156
SP 3	0,046	0,114	0,114
SP 4	0,092	0,228	0,228
AVH 1	0,313	0,775	0,775
AVH 2	0,099	0,245	0,245
AVH 3	0,039	0,097	0,097
AVH 4	0,145	0,359	0,359
AHV 1	0,362	0,896	0,896
AHV 2	0,044	0,109	0,109
AHV 3	0,043	0,106	0,106
AHV 4	0,27	0,668	0,668
SOL 1	0,073	0,181	0,181
SOL 2	0,029	0,072	0,072
SOL 3	0,028	0,069	0,069
SOL 4	0,027	0,067	0,067
RY 1	0,242	0,599	16,690
RY 2	0,168	0,416	0,416
RY 3	0,163	0,403	0,403
RY 4	0,08	0,198	50,500

Standard curve

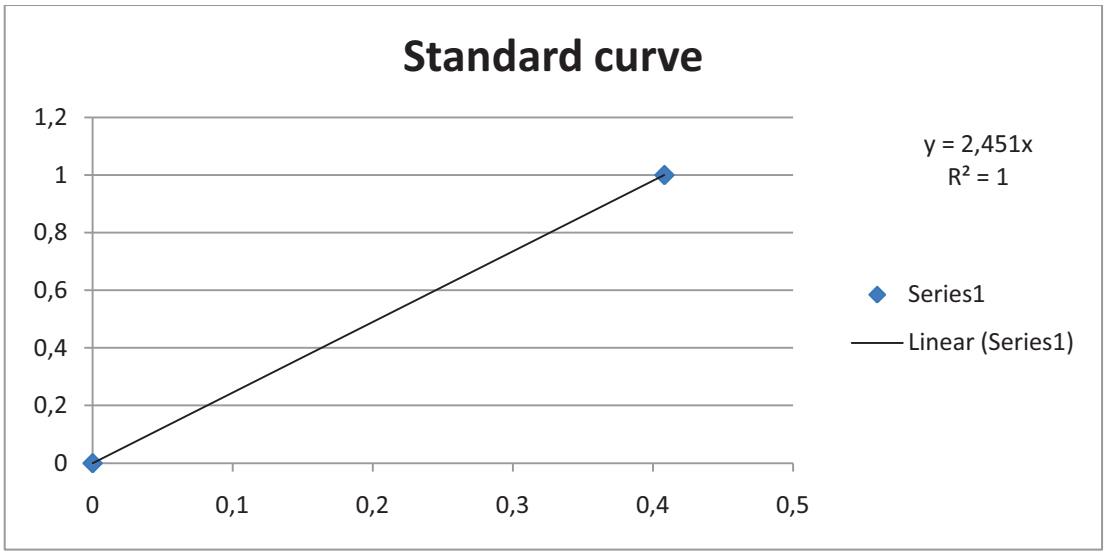


1ppm PO_4^{3-} Absorbance 0.404

	Absobance	Concentration DP mg/L	Time in min
1st extrc.	0,002	0,005	54
2nd extrc.	0,007	0,017	84
3rd extrc.	0,005	0,012	113
4th extrc.	0,006	0,015	140
5th extrc.	0,005	0,012	170
1st extrc.	0,003	0,007	72
2nd extrc.	0,004	0,010	104
3rd extrc.	0,005	0,012	134
4th extrc.	0,005	0,012	165
5th extrc.	0,007	0,017	195
1st extrc.	0,002	0,005	60
2nd extrc.	0,004	0,010	92
3rd extrc.	0,003	0,007	124
4th extrc.	0,004	0,010	149
5th extrc.	0,002	0,005	178
1st extrc.	0,002	0,005	61
2nd extrc.	0,005	0,012	91
3rd extrc.	0,006	0,015	121
4th extrc.	0,007	0,017	149
5th extrc.	0,007	0,017	197
1st extrc.	0,002	0,005	74
2nd extrc.	0,007	0,017	106
3rd extrc.	0,013	0,032	137
4th extrc.	0,014	0,034	167
5th extrc.	0,014	0,034	197
1st extrc.	0,061	0,150	127
2nd extrc.	0,317	0,777	160
3rd extrc.	0,373	0,914	192
4th extrc.	0,389	0,953	224
5th extrc.	0,372	0,912	257

	Absorbance	Concentration DP mg/L
SH 1	0,003	0,007
SH 2	0,003	0,007
SH 3	0,006	0,015
SH 4	0,005	0,012
SP 1	0,005	0,012
SP 2	0,011	0,027
SP 3	0,008	0,020
SP 4	0,009	0,022
AVH 1	0,004	0,010
AVH 2	0,007	0,017
AVH 3	0,007	0,017
AVH 4	0,007	0,017
AHV 1	0,005	0,012
AHV 2	0,004	0,010
AHV 3	0	0,000
AHV 4	0,005	0,012
SOL 1	0,01	0,025
SOL 2	0,011	0,027
SOL 3	0,012	0,029
SOL 4	0,009	0,022
RY 1	0,251	0,615
RY 2	0,27	0,662
RY 3	0,213	0,522
RY 4	0,287	0,703

Standard curve



1ppm PO_4^{3-} Absorbance 0.408

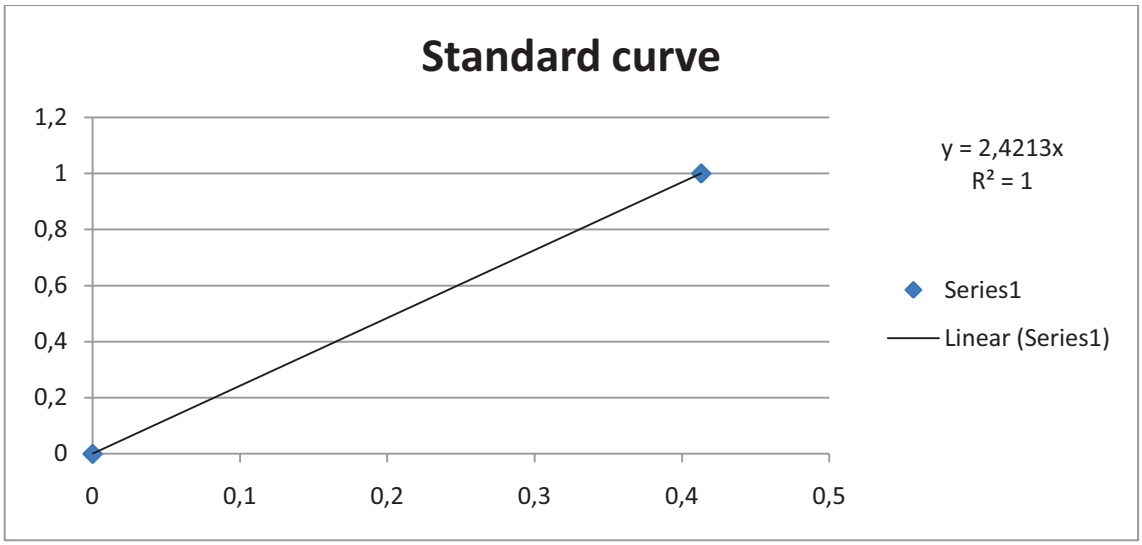
2nd Round

		Absobance	Concentration TOT-P mg/L	Real concentration of TOT-P mg/L	Time in min
	1st extrc.	0,005	0,012	0,012	48
	2nd extrc.	0,042	0,102	0,102	79
SH1	3rd extrc.	0,016	0,039	0,039	109
	4th extrc.	0,014	0,034	0,034	139
	5th extrc.	0,014	0,034	0,034	169
	1st extrc.	0,006	0,015	0,015	49
	2nd extrc.	0,015	0,036	0,036	79
SP1	3rd extrc.	0,04	0,097	0,097	108
	4th extrc.	0,021	0,051	0,051	138
	5th extrc.	0,022	0,053	0,053	168
	1st extrc.	0,031	0,075	0,075	50
	2nd extrc.	0,101	0,245	0,245	73
AVH1	3rd extrc.	0,138	0,334	0,334	103
	4th extrc.	0,115	0,278	0,278	134
	5th extrc.	0,11	0,266	0,266	164
	1st extrc.	0,017	0,041	0,041	47
	2nd extrc.	0,23	0,557	0,557	77
AHV1	3rd extrc.	0,193	0,467	0,467	107
	4th extrc.	0,124	0,300	0,300	137
	5th extrc.	0,114	0,276	0,276	169
	6st extrc.	0,109	0,264	0,264	199
	1st extrc.	0,024	0,058	0,058	85
SOL1	2nd extrc.	0,039	0,094	0,094	158
	3trd extrc.	0,03	0,073	0,073	181
	1st extrc.	0,111	0,269	0,269	80
	2nd extrc.*	0,073	0,177	56,490	109
RY1	3rd extrc.*	0,104	0,252	39,680	138
	4th extrc.*	0,069	0,167	59,880	167
	5th extrc.*	0,07	0,169	59,170	197

Again some samples are diluted *

	Absorbance	Concentation TOT-P mg/L	Real concentratrion of TOT-P mg/L
SH 1	0,064	0,155	0,155
SH 2	0,057	0,138	0,138
SH 3	0,073	0,177	0,177
SH 4	0,051	0,123	0,123
SP 1	0,044	0,107	0,107
SP 2	0,061	0,148	0,148
SP 3	0,053	0,128	0,128
SP 4	0,026	0,063	0,063
AVH 1	0,324	0,785	0,785
AVH 2	0,259	0,627	0,627
AVH 3*	0,048	0,116	86,200
AVH 4	0,321	0,777	0,777
AHV 1*	0,036	0,087	114,940
AHV 2	0,406	0,983	0,983
AHV 3	0,182	0,441	0,441
AHV 4	0,337	0,816	0,816
SOL 1	0,305	0,738	0,738
SOL 2*	0,05	0,121	82,644
SOL 3	0,255	0,617	0,617
SOL 4	0,041	0,099	0,099
RY 1*	0,132	0,320	31,250
RY 2*	0,092	0,223	44,840
RY 3	0,012	0,029	0,029
RY 4*	0,101	0,245	40,810

Standard curve



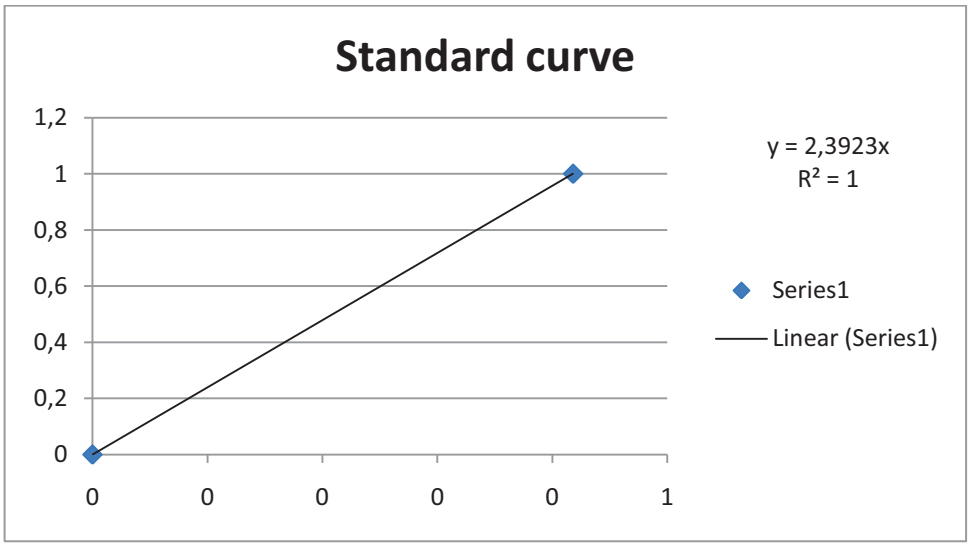
1ppm PO_4^{3-} Absorbance 0.413

		Absobance	Concentration DP mg/L	Time in min
	1st extrc.	0,001	0,002	54
	2nd extrc.	0,003	0,007	84
SH1	3rd extrc.	0,003	0,007	113
	4th extrc.	0,003	0,007	140
	5th extrc.	0,003	0,007	170
	1st extrc.	0,003	0,007	72
	2nd extrc.	0,005	0,012	104
SP1	3rd extrc.	0,006	0,014	134
	4th extrc.	0,007	0,017	165
	5th extrc.	0,006	0,014	195
AVH1	1st extrc.	0,002	0,005	60
	2nd extrc.	0,007	0,017	92

	Absorbance	Concentation DP mg/L	Real concentration of DP mg/L
SH 1	0,002	0,005	0,005
SH 2	0,003	0,007	0,007
SH 3	0,005	0,012	0,012
SH 4	0,003	0,007	0,007
SP 1	0,006	0,014	0,014
SP 2	0,01	0,024	0,024
SP 3	0,006	0,014	0,014
SP 4	0,008	0,019	0,019
AVH 1	0,008	0,019	0,019
AVH 2	0,008	0,019	0,019
AVH 3			
AVH 4	0,011	0,026	0,026
AHV 1	0,009	0,022	0,022
AHV 2	0,008	0,019	0,019
AHV 3	0,013	0,031	0,031
AHV 4	0,008	0,019	0,019
SOL 1	0,005	0,012	0,012
SOL 2	0,008	0,019	0,019
SOL 3	0,008	0,019	0,019
SOL 4	0,008	0,019	0,019
RY 1	0,359	0,859	0,859
RY 2*	0,233	0,557	17,95
RY 3	0,28	0,670	0,67
RY 4*	0,228	0,545	18,34

Some values are missed in this round due to was impossible filter the water samples.

Standard curve

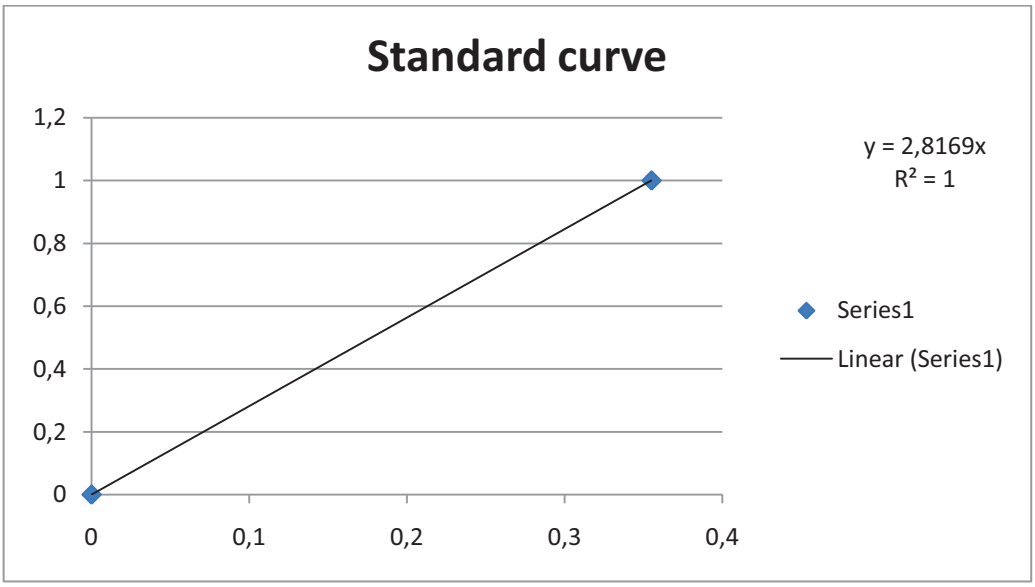


1ppm PO_4^{3-} Absorbance 0.413

Third round

	Absorbance	Concentration TOT-P mg/L	Real concentration of TOT-P mg/L
SH 1	0,112	0,315	0,315
SH 2	0,06	0,169	0,169
SH 3	0,083	0,234	0,234
SH 4	0,089	0,251	0,251
SP 1	0,046	0,130	0,130
SP 2	0,068	0,192	0,192
SP 3	0,066	0,186	0,186
SP 4	0,034	0,096	0,096
AVH 1	0,138	0,389	0,389
AVH 2	0,114	0,321	0,321
AVH 3	0,114	0,321	0,321
AVH 4	0,312	0,879	0,879
AHV 1	0,222	0,625	0,625
AHV 2	0,14	0,394	0,394
AHV 3	0,217	0,611	0,611
AHV 4			
SOL 1	0,064	0,180	0,180
SOL 2	0,121	0,341	0,341
SOL 3	0,135	0,380	0,380
SOL 4			
RY 1*	0,134	0,324	30,860
RY 2*	0,132	0,320	31,250
RY 3*	0,151	0,366	27,322
RY 4*	0,11	0,266	37,590

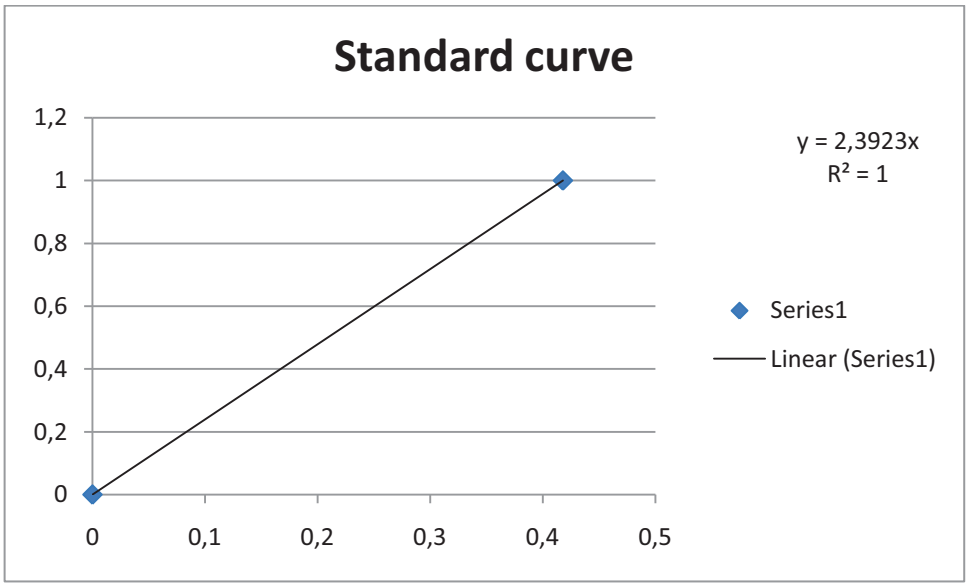
Standard curve



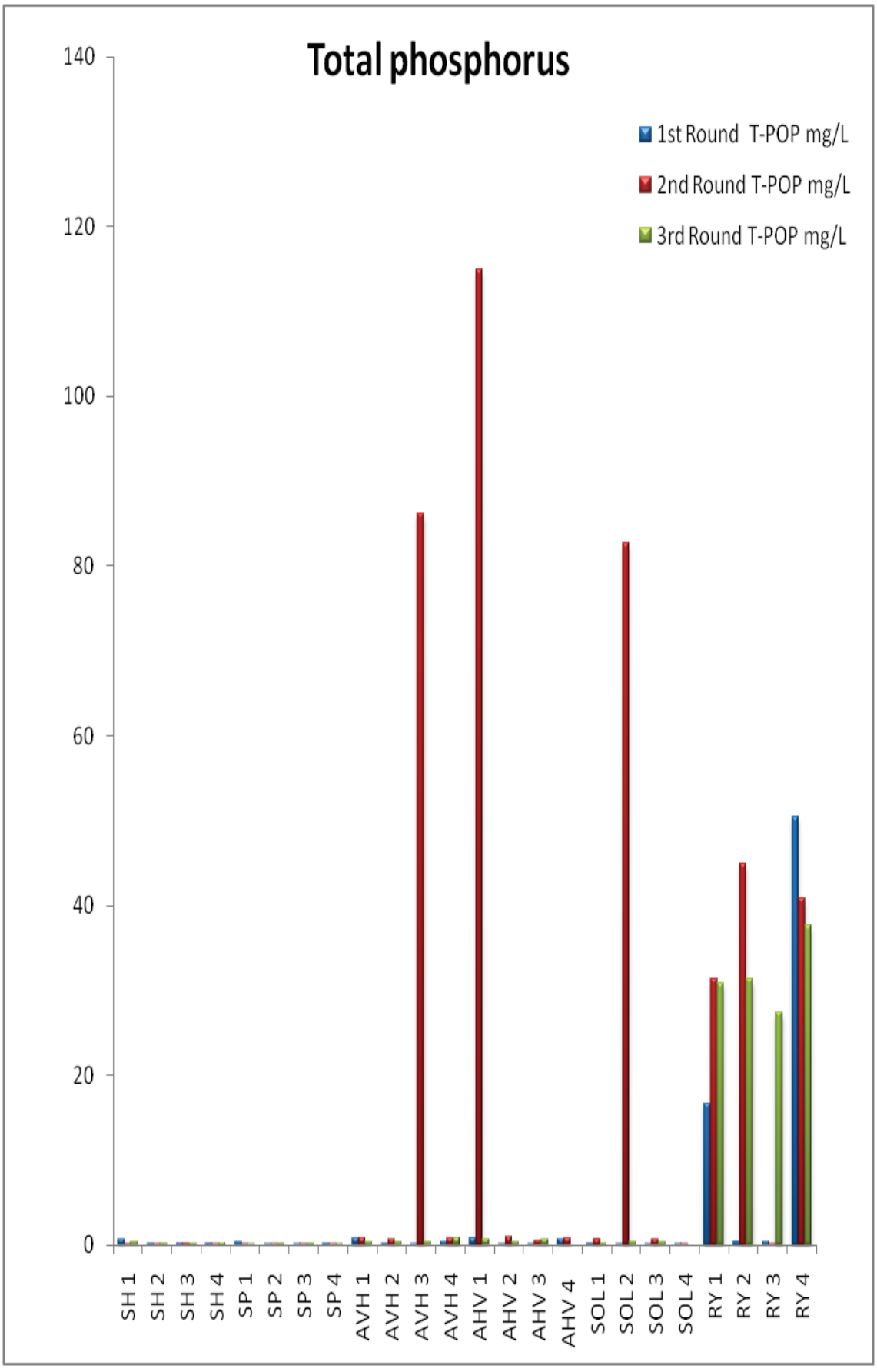
1ppm PO_4^{3-} Absorbance 0.355

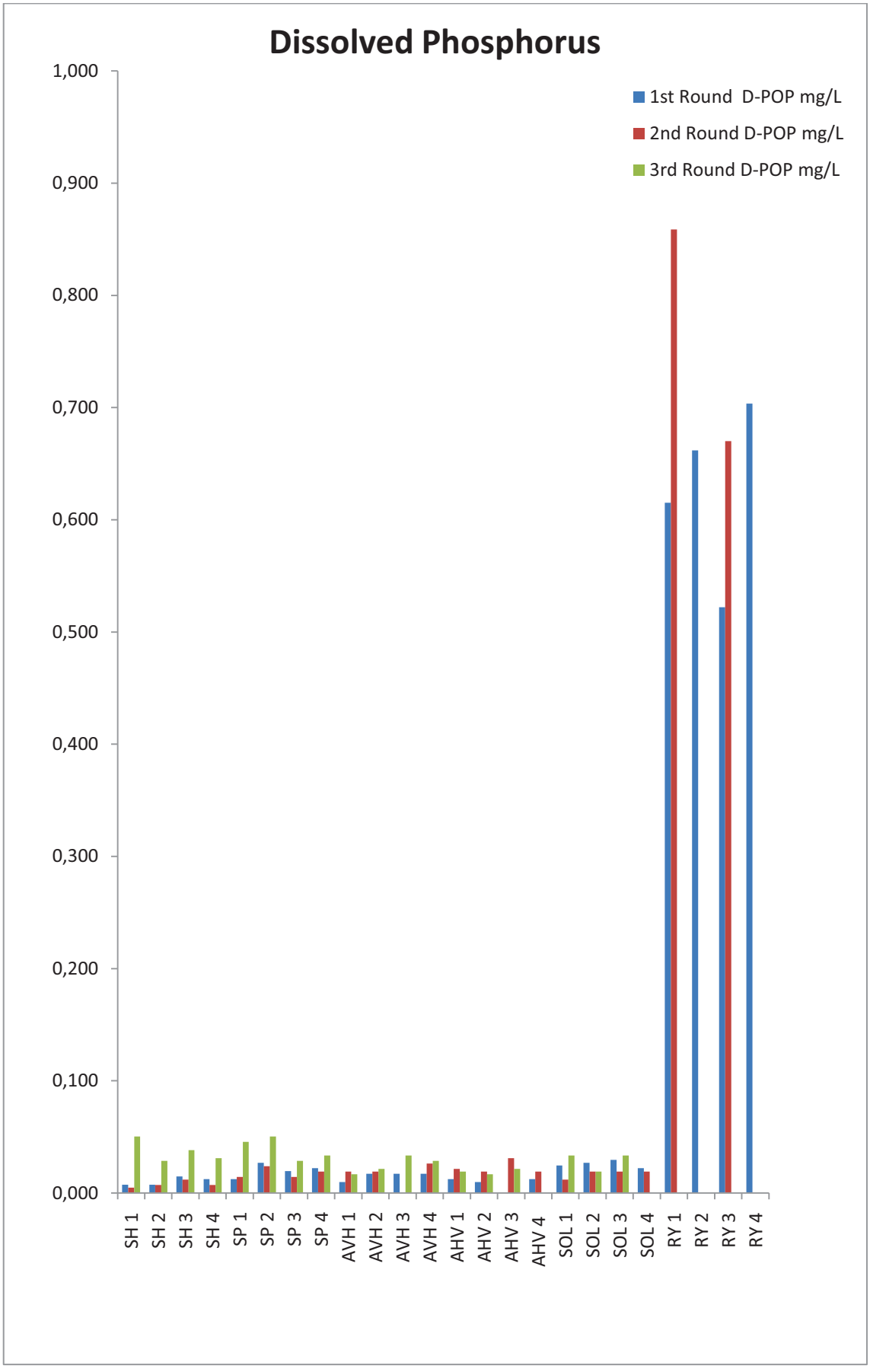
	Absorbance	Concentration DP mg/L	Real concentration of DP mg/L
SH 1	0,021	0,050	0,050
SH 2	0,012	0,029	0,029
SH 3	0,016	0,038	0,038
SH 4	0,013	0,031	0,031
SP 1	0,019	0,045	0,045
SP 2	0,021	0,050	0,050
SP 3	0,012	0,029	0,029
SP 4	0,014	0,033	0,033
AVH 1	0,007	0,017	0,017
AVH 2	0,009	0,022	0,022
AVH 3	0,014	0,033	0,033
AVH 4	0,012	0,029	0,029
AHV 1	0,008	0,019	0,019
AHV 2	0,007	0,017	0,017
AHV 3	0,009	0,022	0,022
AHV 4			
SOL 1	0,014	0,033	0,033
SOL 2	0,008	0,019	0,019
SOL 3	0,014	0,033	0,033
SOL 4			
RY 1*	0,054	0,129	77,510
RY 2*	0,052	0,124	80,64
RY 3*	0,041	0,098	102,04
RY 4*	0,052	0,124	80,64

Standard curve



1ppm PO_4^{3-} Absorbance 0.421


Total phosphorus
1st Round T-POP mg/L
2nd Round T-POP mg/L
3rd Round T-POP mg/L
140
120
100
80
60
40
20
0
SH 1
SH 2
SH 3
SH 4
SP 1
SP 2
SP 3
SP 4
AVH 1
AVH 2
AVH 3
AVH 4
AHV 1
AHV 2
AHV 3
AHV 4
SOL 1
SOL 2
SOL 3
SOL 4
RY 1
RY 2
RY 3
RY 4


Dissolved Phosphorus
1st Round D-POP mg/L
2nd Round D-POP mg/L
3rd Round D-POP mg/L
1,000
0,900
0,800
0,700
0,600
0,500
0,400
0,300
0,200
0,100
0,000
SH 1
SH 2
SH 3
SH 4
SP 1
SP 2
SP 3
SP 4
AVH 1
AVH 2
AVH 3
AVH 4
AHV 1
AHV 2
AHV 3
AHV 4
SOL 1
SOL 2
SOL 3
SOL 4
RY 1
RY 2
RY 3
RY 4

Appendix I

Other analysis values

Concuctivity

	Conductivity		
Samples	1st Round	2nd Round	3rd Round
SH 1	160,9	81,6	18,2
SH 2	191,3	63,9	16,7
SH 3	126,1	131,3	17,1
SH 4	175	144,3	16,8
SP 1	443	99,1	16,2
SP 2	334	76,8	16,2
SP 3	388	59,8	16,6
SP 4	325	70,1	16,6
AVH 1	185,7	55	16,7
AVH 2	208	65	17,2
AVH 3	197,5	36,3	17,1
AVH 4	170,8	52,8	17
AHV 1	164,4	36,7	17,1
AHV 2	200	38,8	17,3
AHV 3	169,6	43,5	16,7
AHV 4	202	45,5	
SOL 1	190,1	59,9	17,5
SOL 2	202	52,1	17
SOL 3	194,6	56,3	17,5
SOL 4	186,2	44,2	
RY 1	159,3	58,9	18,1
RY 2	195,3	64,1	17,9
RY 3	179,4	55,1	17,6
RY 4	201	65,3	17,3

Alkalinity

Samples	1st Round					2nd Round					3rd Round				
	start pH	end pH	sample vol (ml)	HCl vol (ml)	Alkalinity (mmol/L)	start pH	end pH	sample vol (ml)	HCl vol (ml)	Alkalinity(mmol/L)	start pH	end pH	sample vol (ml)	HCl vol (ml)	Alkalinity(mmol/L
SH 1											5,84	4,47	51,13	0,181	0,0708
SH 2	5,1	4,49	51,28	0,112	0,043681747						5,81	4,49	51,14	0,157	0,0614
SH 3	5,45	4,49	50,52	0,159	0,062945368						5,95	4,48	51,95	0,176	0,0678
SH 4											5,76	4,48	52,36	0,164	0,0626
SP 1											6,01	4,44	50,2	0,228	0,0908
SP 2											5,79	4,48	51,48	0,173	0,0672
SP 3											5,84	4,48	50,94	0,173	0,0679
SP 4	5,12	4,5	50,62	0,114	0,0450						5,97	4,47	51,9	0,29	0,1118
AVH 1	6,25	4,45	50,03	0,983	0,3930	6,53	4,49	52,79	0,654	0,2478	6,33	4,49	50,91	0,293	0,1151
AVH 2	6,39	4,48	52,01	1,583	0,6087	6,66	4,46	55,46	1,074	0,3873	6,36	4,49	52,01	0,436	0,1677
AVH 3	6,35	4,46	50,55	0,9	0,3561	6,32	4,47	51,75	0,719	0,2779	6,33	4,49	51,82	0,393	0,1517
AVH 4	6,41	4,46	49,98	0,853	0,3413	6,46	4,49	50,52	0,549	0,2173	6,34	4,5	52,8	0,338	0,1280
AHV 1	6,35	4,45	50,68	0,841	0,3319	6,51	4,49	50,57	0,628	0,2484	6,36	4,5	51,56	0,323	0,1253
AHV 2	6,26	4,48	50,88	0,567	0,2229	6,49	4,49	51,78	0,601	0,2321	6,22	4,49	50,63	0,265	0,1047
AHV 3	6,17	4,43	50,6	0,548	0,2166	6,33	4,48	52,33	0,549	0,2098	6,18	4,49	50,17	0,251	0,1001
AHV 4	6,27	4,45	50,95	0,999	0,3921	6,42	4,47	51,01	0,522	0,2047					
SOL 1	6,12	4,48	50,84	0,441	0,1735	6,52	4,47	50,28	0,666	0,2649	6,53	4,49	51,14	0,548	0,2143
SOL 2	6,15	4,49	51,03	0,426	0,1670	6,29	4,48	50,22	0,454	0,1808	6,2	4,49	50,35	0,218	0,0866
SOL 3	6,13	4,48	51,45	0,43	0,1672	6,25	4,42	50,88	0,444	0,1745	6,24	4,48	51,14	0,27	0,1056
SOL 4	6,03	4,48	51,02	0,299	0,1172	6,35	4,48	50,74	0,445	0,1754					
RY 1	6,08	4,48	51,55	0,781	0,3030	6,23	4,47	51,81	0,431	0,1664	6,48	4,48	51,28	0,614	0,2395
RY 2	5,94	4,48	50,58	0,301	0,1190	6,23	4,49	50,12	0,448	0,1788	6,66	4,49	51,89	0,756	0,2914
RY 3	6,02	4,47	51,46	0,512	0,1990	6,33	4,49	50,57	0,497	0,1966	6,42	4,48	50,05	0,479	0,1914
RY 4	5,87	4,45	50,7	0,357	0,1408	6,19	4,48	50,83	0,42	0,1653	6,45	4,49	52,44	0,484	0,1846