

NORWEGIAN UNIVERSITY OF LIFE SCIENCES



Acknowledgments

This work is a contribution to the PURA-project, and accomplished as my master thesis at the Department of Plant and Environmental Sciences (IPM), Norwegian University of Life Sciences. The work is part of a detailed mapping of the sediments in Lake Årungen. I would like to thank my supervisors at IPM Tore Krogstad, Gunnhild Riise, Ingard Blakar, Ståle Haaland and Aleksandra Romarheim for helpful discussion, advices and corrections through the work with this project. I will further thank Jonny Christensen for carrying out the oxalate extraction and Solfrid Lohne for carrying out the ICP-OES analysis, Irene Dahl and Grete Bloch for indispensable help with the lab work and friends and family for support and patience. A special thanks to Sara, Kristne and Johnson whom I have been working together with in this project and my aunt Eli who has been correcting my English. You have been an indispensable source for creativity, help and good discussions.

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Torgeir Åstveit Reierstad

Abstract

Lake Årungen has since last world war become a highly eutrophic lake because of increased supply of phosphorus from sewage and agriculture. Despite high effort to reduce the phosphorus loading through the last 30 years, the lake is still highly eutrophic, and with frequent algae blooms. The lake is located in Akershus County in southeast Norway. The lake surface area is 1.2km² and drains an area of 52km². The catchment consist of mainly marine clay and some glacial tills. More than 50% of the area is agriculture fields, mainly with cereal production, and agriculture is the main contributor to the phosphorus load today.

In early spring 2009, while the lake still was ice-covered, 122 sediment cores were collected from the lake. The cores were sectioned in to layers, one from 0 to 2.5cm and one from 2.5 to 5cm. This is one of four master these conducted on these sediment samples, and together they gives the most complete mapping of surface sediments ever conducted in Norway. I have in this thesis analysed the sediment samples for tot P, organic- and inorganic P, oxalate extractable Al, Fe and P, and P-AL. In addition the sediment samples were analysed for carbon, nitrogen, sulphur, metals and mineralogy in the three other theses.

All the parameters showed increasing concentrations towards greater water depth. This was also a pattern that was reported for clay, total iron and total aluminium, which is known to be important for the adsorption of phosphorus. There were also a general trend that the phosphorus concentrations was highest in the upper layer, but the storage was highest in the lower, mainly due to higher dry matter content.

The sediment overall contains higher concentrations of all measured fractions of phosphorus compared with agriculture soil in the drainage area. The increase was highest for the inorganic phosphorus fractions, which increased as much as 80% from field to sediment, while P-AL only shows a slightly increase. The phosphorus sorption degree decreased from field to sediment which implies a stronger binding of phosphorus in the sediment than in the soil.

The annual accumulation of sediments in Lake Årungen were estimated to be $1.5*10^{6}$ kg dw, which contains 3000kg phosphorus. The estimated accumulation and measured flux in the outlet gave a total load of $2*10^{6}$ kg dry matter and 5700kg phosphorus. This gives a retention factor of 0.5 for phosphorus and 0.75 for dry matter in the lake.

Sammendrag

Årungen har siden siste verdenskrig blitt en sterkt eutrof innsjø på grunn av økt tilførsel av fosfor fra kloakk og landbruk. Til tross for høy innsats for å redusere fosfor belasting gjennom de siste 30 årene, er innsjøen fortsatt sterkt eutrof, og med hyppige alge oppblomstringer. Årungen ligger i Akershus fylke i sørøst Norge, i et område med høy landbruks aktivitet, hovedsakelig med kornproduksjon. Innsjøen er 1.2km² og har et nedslagsfelt på 52km², som består av hovedsakelig marin leire og noen isbreer kasser. Mer enn 50% av arealet er jordbruksområder, og jordbruk er den største bidragsyteren til fosfor belastningen i dag.

Tidlig våren 2009, mens innsjøen fortsatt var is dekket, ble 122 sedimentkjerner hentet inn fra sjøen. Kjernene ble delt i to lag, fra 0 til 2,5cm og fra 2.5 til 5cm. Dette er en av fire masteroppgaver som er utført på disse sedimentprøvene, og disse oppgaven tilsammen gir den mest komplette kartlegging av overflaten sedimenter som noen sinne er gjennomført i Norge. Jeg har i denne avhandlingen analysert sedimentprøvene for total fosfor, organisk og uorganisk fosfor, oxalate extrherbart Al, Fe og P, og P-AL. I tillegg er sedimentet gjennom de andre masteroppgavene analysert for karbon, nitrogen, svovel, metaller og mineralogi.

Alle analyserte fraksjoner av fosfor viste økende konsentrasjoner ved økende dyp. Dette er et mønster som også er rapportert for leire, total jern og total aluminium, som er kjent for å være viktig for binding av fosfor. Det er også en generell trend at konsentrasjonene av fosfor er høyere i øvre enn i nedre laget, men at lagret mengde er størst i det nedre laget, hovedsakelig som en følge av høyere tørstoff innhold.

Sedimentet inneholder generellt høyere konsentrasjoner av alle mål fraksjoner av fosfor sammenlignet med jordbruksjord i nedslagsfelt. Økningen er størst for uorganisk fosfor som økte så mye som 80% fra jord til sediment, mens P-AL bare viser en svak økning. Fosfor metningsgraden synker fra jorde til sediment, noe som innebærer en sterkere binding av fosfor i sedimentet enn i jorda.

Den årlige akkumulering av sedimenter i innsjøen Årungen er estimert til $1,5 * 10^6$ kg tørrstoff, som inneholder 3000 kg fosfor. Den estimerte akkumulering og målt fluks i utløpet gir en total tilførsel på $2 * 10^6$ kg tørrstoff og 5700 kg fosfor. Dette gir en retensjons faktor på 0,5 for fosfor og 0,75 for tørrstoff i innsjøen.

Table of Contents

A	cknowle	edgments	i
A	bstract		ü
Sa	ammend	drag	iii
T	able of (Contents	iv
A	bbrevia	tions	vi
1	Intro	oduction	1
2	Mat	erial and Method	5
	2.1	Site description	5
	2.1.1	1 Catchment area	6
	2.1.2	2 Lake	7
	2.2	Field work	8
	2.3	Laboratory work	8
	2.3.1	1 Dry matter content	8
	2.3.2	2 Total phosphorus	8
	2.3.3	3 Inorganic and organic phosphorus	8
	2.3.4	4 Oxalate extractable Fe, Al and P	9
	2.3.5	5 P-Al	9
	2.4	Data analysis	10
	2.4.1	1 Statistics	10
	2.4.2	2 Geographical information system	11
3	Resu	ults	12
	3.1	Total phosphorus	12
	3.2	Organic and inorganic phosphorus	16
	3.3	Oxalate extractable Fe, Al and P	20
	3.4	P-AL	25
	3.5	Storage and accumulation	27
4	Disc	cussion	30
	4.1	Distributions	30
	4.1.1	1 Total phosphorus	31
	4.1.2	2 Inorganic and organic phosphorus	31

	4.1.3	PSD and oxalate extractable Fe, Al and P.	32	
	4.1.4	P-AL	32	
	4.2	Changes from fields to sediment	32	
	4.3	Accumulation of phosphorus in sediment	34	
	4.4	Internal loading	35	
5	Con	clusions	36	
6	Refe	erences	37	
7	Figu	ires	40	
8	3 Appendix			

Abbreviations

Bio P	Bioavailable phosphorus
BØ	Bølstabekken
Clay%	Weight percent clay in mineral matter
dw	
ICP-OES	Inductive Coupled Plasma – Optical Emission Spectrometer
inorg P	Inorganic phosphorus
LOI	Loss on ignition
NO	Norderåsbekken
org P	Organic phosphorus
ox Al	Oxalate extractable aluminium
ox Fe	Oxalate extractable iron
ox P	Oxalate extractable phosphorus
PSD	Phosphorus saturation degree
P-AL	Ammoniumlactate extractable phosphorus
SM	Smebølbekken
ST	Storgrava
tot C	
tot N	
tot P	
TRP	
UMB	NorwegianUniversity of Life Sciences
VO	

1 Introduction

Lake Årungen is considered to be one of the most polluted lakes in Norway when considering nutrients in the water and in the sediment. The lake was until around 1950 a mesotrophic lake and it was used for bathing until approximately 1960. From 2^{nd} world war the phosphorus input to the lake increased due to change in farming systems, increased use of fertilizer and considerable amounts of sewage. From 1950 to 1976 the agriculture area with meadow and pasture decreased from 60% to 19% in the county where the lake is, and has since been relatively stable, and is today approximately 17% (SSB 1951; SSB 1977; SSB 2009). This led to a hypereutrophic lake with anoxic conditions, fish death and release of H₂S-gas. Due to increased focus on farming systems and use fertilizer, as well as new systems for handling the sewage, the water quality improved radically in the 80-thies and 90-thies. But there are still frequent episodes with algae bloom, and often with blue green algae (Romarheim & Riise 2009). Total phosphorus (tot P) concentrations in the water are still approximately 30µg/l while the goal for the lake is 15µg/l. The goal is set based on a wish to make the lake suitable for bathing, increase the biodiversity and no blue green algae blooms (Borch *et al.* 2007; Løvstad 2010).

There have been done several studies on the water quality, the ecosystem and sources and sinks for pollutants in Lake Årungen. Some studies have also been done on the sediments, but there is still a need for more detailed information about the distribution and total content of nutrients and other substances like metals and organic matter. In 1977-78 Skogheim (1978) carried out an investigation on the horizontal and vertical distribution of redox potential, pH, los on ignition (LOI), total carbon (tot C), total nitrogen (tot N) and tot P in the sediments in Lake Årungen. He found that tot P in sediment from 0 - 25cm depth in the sediment was positively correlated with tot C, tot N, LOI and pH. In the top sediment (0 - 3cm) he also found that tot P was positively correlated with water depth. The yearly phosphorus load to the lake has been calculated several times through last years, based on models, measurements, or a mixture of these. Ås municipality calculated in 2003 a total load of phosphorus of 4106kg P with main contribution from agriculture (2440kg P) and surface and waste water from urban areas (1110kg P)(Yri 2003). In 2007 Bioforsk made a new report for Ås municipality, where the total load of P to Lake Årungen was calculated to 3121kg/yr (Table 1)(Borch et al. 2007). Calculations done with the LIMNO-SOIL model by Krogstad (2008) indicate that 2763kg phosphorus (1277kg bioavailable P) are lost from agriculture fields in the drainage area of Årungen (excluding Skibekken and Skuterudbekken, who drain through Østensjøvannet, 23% of the total drainage area). There are some variations in the estimate of tot P load, all in the range of 3000 to 4500kg of tot P. Around one half is considered bioavailable. The load differ greatly from year to year, mainly because runoff from agriculture is highly influenced by climatic conditions and farming systems.

Runoff from different sources differ in the total amount of phosphorus and in the distribution between the phosphorus fractions. The runoff will thereby influence the system in dissimilar ways. In a short time scale the bioavailability of the phosphorus is important, while in a longer time perspective the total content of phosphorus also is important. Phosphorus in runoff from forest can have an average bioavailability as low as 11% (measured on glacier mud), while waste water has a relatively high amount of bioavailable phosphorus and sewage as high as 90% (Berge & Källqvist 1990). Runoff from agriculture has a bioavailability that varies between 25% and 75%, depending on the distribution between organic phosphorus (org P) and inorganic phosphorus (inorg P) (Krogstad & Løvstad 1991). Because of the relatively high contributions from agriculture, change in farming systems have a great potential to reduce phosphorus load to the lake (Borch 2009). Through the last several decades there have been used more phosphorus in the soil, and an increase in ammoniumlactate extractable phosphorus (P-AL) concentrations. Krogstad *et al.* (2008) recommended a reduced P-fertilizing of about 50% or more at common P-AL levels.

The phosphorus fractions in the sediments are a central part of the phosphorus metabolism in the lake. The sediment can acts as both a source and sink, and has the possibility to store a considerable amount of phosphorus. The sediment is subject to both processes that remove phosphorus from the water, and the processes that can bring it back to the water phase. The sedimentation and resuspension processes are in most cases difficult to quantify in large scale. This is because different processes can be difficult to distinguish from each other, and phosphorus mobilized from one fraction, can immediately be sedimentated to another fraction (Boström et al. 1988). Transport of phosphorus from water to sediment can be divided into six main processes; i) sedimentation of detrital phosphorus minerals derived from the watershed, ii) adsorption to, or precipitation with, inorganic compounds, iii) sedimentation of phosphorus with allochtonous organic matter, iv) sedimentation of phosphorus with autochthonous organic matter, v) direct uptake by assimilation of phosphorus from the water column by periphyton and other biota in surficial sediments, vi) direct adsorption of lake water dissolved phosphorus onto particles in the sediment. Concerning the release of phosphorus from the sediment this can either be from resuspended sediment particles to the lake water, or from the sediment to the mobile pool, from which it is transported upwards to the lake water. The main release processes are; i) desorption, ii) dissolution of phosphorus containing precipitate, iii) ligand exchange mechanisms, iv) mineralization processes ending up with hydrolysis of phosphate-ester bonds, v) release of phosphorus from living cells as a result of changed cellular metabolism, and vi) autolysis of cells (Boström et al. 1988).

Sediment composition is considered to be the major factor controlling phosphate adsorption. Wang *et al.* (2009) showed that organic matter and metal hydroxides were the main factor controlling P adsorption in sediments. Also sediment particle size and ionic strength are important for the phosphate

sorption (Wang et al. 2006). In a constructed marsh in Korea, amorphous and some poorly crystalline forms of iron and aluminium, organic matter and calcium are shown to be closely related to P sorption of the sediment (Yoo et al. 2006). Ca and precipitations of phosphorous as apatite are important in areas with hard water, and the solubility of apatite decrease with increasing pH (Golterman 1995; Stumm & Morgan 1996). pH is shown to influence both on adsorption and release of phosphorous in the sediment. The effect differ between adsorption and release, and is also dependent on sediment types (Jin et al. 2005; Wang et al. 2005). Another important characteristic of adsorption of phosphorous to the sediment is that it is not fully reversible (Wang et al. 2005). Temperature is also important for the adsorption of phosphate because the adsorption is a endothermic reaction, and hence increase with increasing temperature (Jin et al. 2005). Redox conditions in the sediments are important for adsorption and release of P from the sediments. This was early demonstrated by Einsele (Einsele 1936; 1938) and Mortimer (1941; 1942). Andersen and Ring (1999) found that the release rate of iron and phosphorous was significantly higher under anoxic than under oxic conditions. Løvstad et al.(1992) found increasing concentrations of phosphorus in water just above sediment when the oxygen concentration was reduced towards zero in a investigation in Lake Årungen. Under anoxic conditions, phosphorous from the iron-bound pool dominated phosphorous release from sediment. When changing from oxic to anoxic condition, the iron goes from Fe(III) to Fe(III). Fe(III) form a solid ironhydroxide and has a great affinity for binding phosphorus, while Fe(II) is dissolved. This implies that the adsorbed phosphorus also dissolves (Søndergaard 2007).

With knowledge about the phosphorous fractions, sedimentation and remobilisation processes, and the physical and chemical properties that influence the distribution of among these fractions, it will be possible to evaluate the importance of different processes, and thereby the possibility for internal loading. The fractions considered in this study are the same as those used when analysing Norwegian soil samples. Total phosphorus and inorganic and organic phosphorus are well known. P-AL gives an estimate of easily exchangeable phosphorus that is available to plants directly, or that can be available in a relatively short time. The P-AL fraction explains 83% variation in total reactive phosphorus (TRP), which is shown to be a good measure for bioavailable phosphorus (Bio P), (Blakar & Løvstad 1990; Ogaard 1995). Oxalate extractable compounds are amorphous and poorly crystalline metal-hydroxides, and phosphorus adsorbed to these. In this investigation oxalate extractable iron (ox Fe), oxalate extractable aluminium (ox Al) and oxalate extractable phosphorus (ox P) are measured. The main reason for analysing for oxalate extractable compounds is to calculate the phosphorus sorption degree (PSD), as shown by Sharpley (1995) to be linearly related to dissolved phosphorus in surface runoff.

This is the most complete investigation on sediment in one lake done in Norway, and probably in the entire world. The reason for carrying out a project like this is to get detailed information on how specific substances distribute in the lake sediments in Lake Årungen. The study is part of the PURA

4 Introduction

project, which were established after implementation of EU's Water Framework Directive in Norway. To fulfil the directive, Lake Årungen has to gain good ecological and chemical status within 2015. The water quality of the lake is today classified as very poor. The PURA project shall evaluate the status today, and make recommendations for possible actions to reach good status within the deadline (Løvstad 2010; PURA 2009). In early spring 2009, while the lake still was ice-covered, 122 sediment cores were collected from the lake. The cores were split in two sections, 0 - 2.5cm and 2.5 - 5cm and analysed for mineralogy, grain size distribution, metals organic matter and nutrients.

I will in this thesis describe the distribution, changes from field to sediment and total storage of phosphorus in the top sediment in Lake Årungen. In the discussion the collected data will be used to evaluate the following hypotheses:

- Clay content in sediment controls the concentration of total phosphorus in sediment.
- Concentrations of phosphorus and phosphorus fraction in sediments equal concentrations in cultivated soil in the drainage area.
- The retention of phosphorus in Lake Årungen is higher than the phosphorus flux through the outlet.

2 Material and Method

2.1 Site description

Lake Årungen and its drainage area is located in Ås, Ski and Frogn municipality, approximately 30km south of Oslo, on the east side of the Oslofjord (59° 40'N, 10° 44'E). The lake is located in varied, but highly man influenced landscape, with a mixture of agriculture and forest together with some urban areas (Photo 1). The lake has always been a nutrient rich lake because of the high amount of marine clay in the drainage area. There are also some areas with glacial till, and in the northern parts the lake is dammed up by the Ås-Ski moraine ridge. In addition there is a manmade dam in the outlet.



Photo 1: Air Photo of Årungen and the nearest surroundings. The photo is taken from south east (photo: Mapaid A/S).

2.1.1 Catchment area

The drainage area to Lake Årungen consists mainly of seven sub catchment areas (Figure 1, Table 1). Skuterudbekken and Skibekken has outlet to Østensjøvannet, which is a part of Bølstadbekken (BØ). Brønnerudbekken have outlet thorough Vollebekken (VO), while Storgrava (ST), Smebølbekken (SM), and Norderåsbekken (NO) have direct outlet to the lake. In addition there are some areas around the lake that drain directly to the lake. Ås centre, Ski centre and campus of the Norwegian University of Life Sciences (UMB) have the main concentration of inhabitants. In the rest of the area houses are more scattered, with a mixture of ordinary houses and farms. Except in Ski centre there is minimal industrial activity in the catchment area.



Figure 1	Lake	Årungen	with sub	catchment	areas	(Borch e	t al.	2007).
- igui e i	. Dune	1 in angen	with buo	eutemient	areas	(Doren e	<i>v cvv</i> .	2001).

Table 1: Main sub catchments with area and annuall	ly discharge (Borch et al. 2007).
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Stream/catchment area	Area	Discharge ^(*)	Supply P ^(**)
	(km ²)	(mill m ³ /year)	(kg/year)
Bølstadbekken	25.5	12.6	1403
Storgrava	8.4	4.2	552
Smebølbekken	7.3	3.6	298
Vollebekken	2.1	1	437
Norderåsbekken	2.7	1.3	205
Brønnerudbekken	0.8	0.4	26
Remaining area	4.2	2.1	200
Including Årungen and Østensjøvann 1.6 km ²			
Sum	51,0	25,3	3121

(*) The discharge is based on a yearly average precipitation and evaporation. In the last years the precipitation and then the discharge have been higher than the average.

(**)Based on the theoretical discharge and average phosphorus concentrations in grab samples from the streams. A higher discharge will then also lead to higher P supply.

The former waste disposal site for Ås is located within the Bølstadbekken catchment. There is still considerable leakage of pollutants from this site (Hensel *et al.* 2010).

Årungen catchment area consist of 53% agriculture, 34% forest and outfields, 10% urban areas and 3% water (Borch *et al.* 2007).

2.1.2 Lake

Lake Årungen is considered to be a semi shallow dimictic lake with stratification due to temperature, both summer and winter. Morphometric data for the lake is presented in Table 2. Almost every year there will be a full circulation of the water, both spring and autumn, but the duration of the period varies from a few days to weeks, and maybe months, depending on the climatic conditions (Hexum 1963; Romarheim & Riise 2009; Sanni 1985). The stratifications together with high load of organic matter may in some periods lead to anoxic condition in the hypolimnion (bottom water). Because of the north-south alignment of the lake, it is highly exposed for wind, which contributes to mixing of the water and less stratification. The lake basin has relatively steep sides down to 8 to 10 meters where it flattens out. In the central part of the lake there is a relatively flat area around 12 to 13 meters.



Table 2: Main data for lake Årungen

Lake area [*]	1.2km ²
Maximum depth	13.4m
Medium depth [*]	8.1m
Length [*]	3.04km
Medium width ^{**}	0.45km
Volume [*]	$9.7*10^{6} \text{m}^{3}$
Discharge (theoretical)***	25.3*10 ⁶ m ³
Discharge (2008)****	$29.2*10^{6} \text{m}^{3}$
Discharge (2009)****	$25.5*10^{6} \text{m}^{3}$
Theoretical residence time	4.6 month
Height above sea level ^{**}	33m
Total drainage area ^{***}	51km ²

(*) (Skogheim & Abrahamsen 1979) (**)(Yri 2003) (***)(Borch *et al.* 2007) (****)(Bioforsk 2010)

Figure 2: Depth profile for Lake Årungen. Ekvidistanse 2 m (Skogheim & Abrahamsen 1979).

2.2 Field work

Sediment cores were collected from Årungen in Mars and April 2009. In this period Årungen was covered with ice, and a Rapalla ice drill was used to get through the ice. Cores were collected in a grid of 100m * 100m, totally 122 sampling points (Appendix 7). A GPS (Garmin, Colorado 300) was used to locate the position for sampling. The sediment cores were collected using an Uwitec Corer with a 60cm long acryl tube with an inner diameter of 5.95cm (Photo 2). The sediment cores were immediately sectioned in 0-2.5cm, and 2.5-5cm, and stored in plastic cups at 2-4°C in darkness until further analyses.

2.3 Laboratory work

2.3.1 Dry matter content

In order to calculate the weight percent dry matter, the sediments were homogenized. Subsamples of approximately 13.5g or 15g, from below or above 4m depth respectively, were weighed using a laboratory scale (Sartorius LC 3201D, three digits after comma) and dried at 105°C over night. After cooling for 30 minutes in desiccators, the samples were weighed again with the same weight. In the samples, if possible, surplus water was removed before homogenizing.

2.3.2 Total phosphorus

From freshly homogenized sediment samples, subsamples of 0.3 - 0.5g dry weight (dw) were transferred to 18 ml acid washed Teflon tubes and dried for 24 hours at 75°C. 5ml concentrated 69% HNO₃ and 250µl internal standard (consists of 4mg/l of tellurium, indium, thallium and rhodium in 2% HNO₃) was added, and the samples were decomponated in a MLS-MILESTONE ultraCLAVE III. Under pressure, the samples were heated to 260°C, and the temperature was held for 10 minutes. After cooling, the samples were diluted using deionised water to a total volume of 50ml and sedimentated. After sedimentation, subsamples were diluted 1:10 using deionised water and analysed with Inductive Coupled Plasma – Optical Emission Spectrometer (ICP-OES) (Perkin Elmer, Optima 5300DV).

2.3.3 Inorganic and organic phosphorus

Measurement of the inorganic phosphorus fraction is based on the method described by Møberg and Peterson (1982). 1.00g dried and crushed sample was transferred to a 60ml acid washed snap caps glass, mixed with 5.0ml 6M H₂SO₄ and heated in a water bath at 70°C for 10 min. Further 5.0ml 6M H₂SO₄ was added before cooling for one hour. The sample was diluted to a total volume of 250ml using deionised water in an acid washed 250ml volumetric flask. After dilution the sample was left for sedimentation for at least three days, or until the solution was clear. A subsample was further diluted 1:10, to a total volume of 10ml, and measured using the molybdenum blue method on a Gilford Stasar II at 700nm (Murphy & Riley 1962).

Organic phosphorus was calculated as the difference between tot P and inorg P.

2.3.4 Oxalate extractable Fe, Al and P

Analysis of acid oxalate extractable Fe, Al and P is based on a method described in "Procedures for soil analysis" (van Reeuwijk 1995). A subsample from freshly homogenized sediment, corresponding to 0.8g dry matter, was transferred to NAGLENS Round Centrifuge Tube, PPCO, 50ml. The sample was mixed with 32ml of acid oxalate reagent and shaken for 4 hours in darkness (Edmund Bühler SM-30, 3cm movement and 60 back and forth movements pr. min). After shaking, the sample was immediately centrifugated at 10000rpm for 10min (BECKMAN Model J2-21M with rotor JA-20). 1ml of the centrifugate was transferred to a15 ml sterile PP-test tube and diluted 1:7 using deionised water. The concentration of Fe, Al and P in the centrifugate was determined by ICP-OES (Perkin Elmer, Optima 5300DV).

PSD is calculated on mol basis (Equation 1)

Equation 1:
$$\frac{mol \ ox \ P}{\frac{1}{2}(mol \ Al + mol \ Fe)} * 100 = PSD\%$$

2.3.5 P-Al

The method for analysing P-Al is based on the procedure described by Krogstad (2004), with some modifications. A subsample from freshly homogenized sediment, corresponding to 1.00g dry matter was transferred to 50ml DURAN bottles. In order to avoid problems due to different content of water in the samples, deionised water was added to the sample so that the total content of water in each sample was 10ml. To the sample there were added 10ml AL-solution (diluted 1:5 from stock). The sample was then shaken for 90min (Edmund Bühler SM-30, 3cm movement and 120 back and forth movements pr. min) and filtrated through S&S Faltafilter 100 Ø125mm. Prior to filtration, the filters have been washed with AL solution diluted 1:100 (Photo 2). The filtrate was stored in 50ml VWR centrifuge tubes at 2 - 4°C in darkness, until further analyses. The filtrate was diluted 1:50 (HAMILTON MICROLAB plus 1000) using deionised water to a total volume of 10ml P concentration was measured with the molybdenum blue method on a Gilford Stasar II at 700nm (Murphy & Riley 1962).

2.4 Data analysis

2.4.1 Statistics

All statistical analysis has been conducted with Minitab® 15.1.0.0 from Minitab Inc.

Paired t-test

This test was used to test for mean differences between the layers. All the tests were conducted on a 95% level. To use this test the observation has to be paired, and the paired differences have to be normally distributed. All the tests referred to in this thesis fulfil the prerequisites for this test. The hypothesis tested is

H₀: $\mu_d = \mu_0$ versus H₁: $\mu_d \neq \mu_0$

where μ_d is the population mean of the differences and μ_0 is the hypothesized mean of the differences.

When testing the layers against each other, the data are in some cases divided in groups depending on water depth (0 - 4m, 4 - 8.4m, 8.4 - 11.3m and 11.3 - 13.4m) or percent clay of the mineral matter (clay%) in the sediment (< 50, 50 - 60, 60 - 68 and 68 <)

Stepwise regression

Standard stepwise regression (adds and removes variables), forward selection (adds variables), or backward elimination (removes variables) are used. All three methods are used in order to determine the best subset of variables for predicting a response. For all methods the alpha to remove or enter is set to 0.15. The results from the stepwise regression, together with knowledge about the system are the basis for the multiple linear regression analysis.

Linear regression analysis

The regression analysis is based on the Ordinary least squares model, that determines the equation that minimizes the sum of the squared distances between the samples data points and the values predicted by the equation. The analysis is based on a set of assumptions, and it is important that these are fulfilled in order to get a good result. The main assumptions are that the residuals are normally distributed with mean zero, have constant variance, are not correlated with each other or the predictors and that no predictor is perfectly correlated with another predictor.

Box-and-whisker plots

The box-and-whisker plots are used to assess and compare the sample distribution. The boxes represent the centre 50% of the measurements (from 1st to 3rd quartile), the horizontal line within the

box are the median, while the vertical line is the whisker line, extended to the outer measurement, within 1.5 times the height of the box. The stars represent outlier observations.

2.4.2 Geographical information system

The maps were created with ESRI Ark Gis 9.3 based on all the collected data, and interpolated with the method "Spline with Barrier" (Chou 1997). The interpolation was done in cells with a diameter of 5 meter, and a polyline of the shape of Lake Årungen was used as barrier.

How the interpolation with "spline with barriers" works (from ArcGIS desktop Help)

"This implementation of the minimum curvature method is implemented through a one-directional multi-grid technique that moves from an initial coarse grid, initialized in this case to the average of the input data, through a series of finer grids until an approximation of a minimum curvature surface is produced at the desired row and column spacing. At each grid refinement level the current grid-based surface model is treated as an elastic membrane and a convergent linear iterative deformation operator is applied repeatedly at each node to achieve an approximation to a minimum curvature surface that honours both the input point data and discontinuities encoded in the barriers. The deformation that is applied to each cell is calculated on the basis of a "molecular summation" which compares the weighted summation of 12 neighbouring cells with the current value of a central target cell to calculate a new value for the target cell."



Photo 2: From left: Sediment core from Lake Årungen. Washing of filter prior to filtration of P-AL. Algae bloom in Lake Årungen, late summer 2007.

3 Results

In the result there are used information about tot Fe and tot Al from Zambon (2010), tot C, tot N and LOI from Naas (2010) and mineralogy from Rutsinda (2010). Al can only be used to show the relative differences in the sediment, not the total concentrations, as is the case with the other parameter. Aluminium can't be decomposed properly using HNO₃ decomposing acid as are the case here. When analysing for tot P three reference sediments were used to verify the method. The average concentration for the reference sediments were within the certificate value \pm one st.dev. This means that the accuracy of the method is good. All the data are presented in Appendix 8 and Appendix 9.

3.1 Total phosphorus

Tot P in the two sediment layers in Lake Årungen are presented in Figure 3 and Figure Figure 4. The distribution of tot P in the two layers differ to some degree. This is especially true for the northern part of the lake, where there is a higher concentration of P in the upper than in the lower layer. The concentration of tot P also seems to be highest in the central and deepest part of the lake.





When evaluating the two layers with a paired t-test, the layers significantly differ at 95% confidence level. When evaluating the layers within the four water depth groups, the results showed that from 1-4m and from 8.3-11.3m the layers significantly differ (at 95% confidence level). In both groups the upper layer was found to have a higher concentration of tot P compared to the lower. No such difference was found for the other two depth groups (Appendix 1).

Tot P increases with increasing water depth, but when the data are grouped after clay%, there is no longer a clear effect of the depth within each clay% group. When the data are grouped after depth, there is still a clear effect of the clay% (Figure 5). When tot P are compared with clay content in the box plot, it seems clear that the concentration of phosphorus in the sediment increases with increasing clay content, but that it levels of around 60% clay. In Figure 6 where tot P are plotted against clay% no such levelling off are to be found.



Figure 4: Regional distribution of P in the two sediment layers. The outlet and inlets are marked with arrows.

When evaluating tot P and tot C in the sediment (as a measure for organic matter, the two components show some correlation This is especially true when excluding the results from shallow areas close to the shore, where tot C show greater variation than in the rest of the lake (Figure 7). When comparing these result with tot N, mostly the same results are found



Figure 5: Total phosphorus in the lower sediment layer grouped after clay% and depth. Only observations with data about the grain size distribution are used, 61 point in each layer.

A stepwise regression analysis with tot P as response and tot Fe, tot Al, tot N, tot C, depth and with and without clay% as possible predictors, was used to decide which factors that can contribute to explain the horizontal variation in tot P. Tot Fe, tot Al, depth and tot N are the significant predictors in the upper layer. In addition to the predictors mentions above, clay% is a significant predictor in the lower sediment layer (Appendix 2 and Appendix 3). A regression with tot Fe, tot C and depth as predictors gives an R-sq value of 90.3% and 81.7% for the upper and lower layer respectively.

Generally tot P increases with increasing concentration of tot Fe and Al, ox Fe and ox Al, depth and clay% (Figure 6), but because of high correlations between several of the predictors in this dataset, it is difficult, if not impossible, to tell which factor or factors that are controlling the distribution of tot P in Lake Årungen (Table 3). P is known to bind to metal-hydroxides, and show high significant correlation with both tot Fe, tot Al, ox Fe and ox Al. The correlation is for some reason higher for the total amount of Al and Fe, than for the oxalate extractable fraction of Al and Fe.

	Tot P	Tot Fe	Tot Al	Ox Fe	Ox Al	Clay%	
0 – 2.5cm							
Tot Fe	0.935						
Tot Al	0.913	0.983					
Ox Fe	0.881	0.794	0.777				
Ox Al	0.911	0.873	0.877	0.948			
Depth	0.754	0.718	0.704	0.767	0.789		
2.5 – 5cm							
Tot Fe	0.878						
Tot Al	0.823	0.981					
Ox Fe	0.803	0.776	0.748				
Ox Al	0.753	0.858	0.875	8.871			
Clay%	0.814	0.950	0.961	0.688	0.798		
Depth	0.725	0.687	0.670	0.699	0.727	0.602	

Table 3: Pearson correlations for the two layers. All P-values are <0.000



Figure 6: Total phosphorus in the two layers compared with **a**) tot Fe **b**) ox Fe **c**) tot Al **d**) ox Al **e**) depth and **f**) clay% (only the lower layer)



Figure 7: Total phosphorus compared with tot C in the two layers. In **a**) all the data are presented, while in **b**) the depth groups from 0 to 8.5m are excluded.

3.2 Organic and inorganic phosphorus

The organic and inorganic fraction of tot P is analysed in two transects, and a couple extra samples near the inlet from Storgrava. The results are presented in Figure 8, Figure 9, Figure 10 and Table 4. From Figure 10A it is apparent that when considering the concentration of Inorg P in the sediments the two layers do not differ much. In some locations the top layer contains the highest concentration, and in others the lower.



Figure 8: Frequent distribution of the inorganic phosphorus in the two sediment layers. **a**) absolute values, and **b**) as a fraction of tot P



Figure 9: Frequent distribution of the organic phosphorus in the two sediment layers. **a**) absolute values, and **b**) as a fraction of tot P

Table 4: Summary	of main analysed	data for organic	and inorganic P.
2	2	0	0

	Inorg P (g/kg dw)		Inorg P (% of tot P)		Org P (g/kg dw)		Org P (% of tot P)	
	0 - 2.5 cm	2.5 - 5 cm	0 - 2.5 cm	2.5 - 5 cm	0 - 2.5 cm	2.5 - 5 cm	0 - 2.5 cm	2.5 - 5 cm
average	1.35	1.29	72	75	0.52	0.43	28	25
median	1.38	1.27	78	74	0.54	0.44	27	26
max	1.66	2.18	79	83	0.70	0.56	36	35
min	0.76	0.72	64	65	0.27	0.15	21	17
std. dev.	0.24	0.30	2.99	4.08	0.10	0.09	2.99	4.02
samples	34	34	34	34	33	33	33	33



Figure 10: Organic and inorganic phosphorus in Lake Årungen. **A** absolute values of inorg P, **B** percent inorg P relative to tot P, **C** absolute values of org P, and **D** percent org P relative to tot P.

This is also the result from the paired t-test, where it is not possible to conclude that there are significant differences between the two layers (Appendix 4). When the inorg P is evaluated as a fraction of tot P, the difference between the two layers becomes significant. The fraction is generally higher in the deeper layer, but there are also areas where the fraction is higher in the upper layer. Inorg P, as well as tot P, generally increases with depth (Figure 11a)). From Figure 11b) and Table 4 it is clear that it has to be a strong correlation between tot P and inorg P. When inorg P is presented as a fraction of tot P, the standard deviation is lower than 5% of the average value. Inorg P vs. tot P (Figure 11b)) follows close to a straight line. This is also confirmed by the regression analysis between them. The R-sq value from the analysis is above 95% for both layers.

The organic phosphorus in the sediment shows no significant correlation with organic matter expressed as tot C, but show some correlation with tot P and to some extent tot N and depth (Table 5, Figure 12 and Figure 13).

Organic and inorganic P, as fraction of tot P, shows little variation in the lake. Compared with depth and tot P the inorganic fraction increases slightly towards greater depth and higher tot P concentrations (Figure 14). The increase is highest in the lower layer, while the upper layer is close to constant. The organic P fraction shows the opposite trend.



Figure 11: Inorg P compared to a) depth and b) tot P

Table 5: Correlation between org P and tot C, tot N, tot P and							
	Tot C	Tot N	Tot P	Depth			
Org P	-0.130	0.361	0.857	0.639			
(0 - 2.5cm)	0.465	0.036	0.000	0.000			
Org P	-0.255	0.584	0.685	0.332			
(2.5 - 5cm)	0.146	0.000	0.000	0.059			

Cell Contents: Pearson correlation P-Value



Figure 12: Concentration of org P compared to **a**) tot C and **b**) tot N. The values from sample point 120 are removed because of high concentrations of tot C and tot N



Figure 13: Concentration of org P compared to a) tot C and b) tot P. In a) the result for location 120 is removed because of extremely high tot C content.



Figure 14: Fraction of inorganic and organic P in the two layers compared to a) water depth b) tot P

3.3 Oxalate extractable Fe, Al and P

The oxalate extractable fractions of Fe, Al and P follow mostly the same distribution pattern, which also are concurrent with the pattern of clay and depth. The results are summarised in Table 6 and Figure 15. and graphically presented in Figure 16 and Figure 17. The concentrations of ox Fe and ox Al are significantly higher in the upper than in the lower layer. For ox P there is no such difference. This leads to a higher PSD in the lower layer (Appendix 5). The most visible difference between the layers is the increase ox Fe, ox Al and ox P from the lower to the upper layer in the north end, and, at least for ox P a reduction in the central part of the lake.

	Ox Al	Ox Al	Ox Fe	Ox Fe	Ox P	Ox P	PSD	PSD
	(g/kg dw)	(%)	(%)					
	0 - 2.5cm	2.5 - 5cm						
average	3.58	3.35	13.0	11.7	1.31	1.29	23	25
median	3.66	3.55	13.4	11.8	1.36	1.33	23	25
max	4.91	5.13	18.8	20.6	1.98	2.32	30	34
min	0.68	0.51	3.61	3.35	0.32	0.20	12	12
std.dev	0.88	0.92	3.73	3.73	0.36	0.45	3.07	3.90
samples	121	120	121	120	121	120	121	120
sumples	141	120	121	120	121	120	121	120

Table 6: Summary of the main analysis data for oxalate extractable compounds



Figure 15: Frequent distribution of oxalate extractable compounds. a) Ox Al, b) Ox Fe, c) Ox P and d) PSD





The oxalate extractable P are fractions of the inorg P, but for some reason the concentration of ox P exceed the concentration of inorg P in several samples, and in some cases also the concentration of tot P (Figure 18).

Except for the percentage of PSD being higher in the lower layer, there is no clear pattern for the PSD% (Figure 17B). The value varies mainly between 20 and 30% with only some small areas having higher or lower values. There are a couple of hotspots that are worth noticing. These are mainly located in the lower layer. One is located close to the inlet from Storgrava, one west of the inlet from Vollebekken and one in the deepest part, central in the lake. PSD% is very little influenced by depth and tot P concentrations in the sediment, except in the most shallow areas (<2m) and where tot P are <1.3g/kg dw. In these areas the PSD% are lower than in the rest of the lake where there are no effect of tot P or depth (Figure 19).

Ox Fe increases with increasing depth and clay %, also when tot Fe increases, and further there are a good linear relationship between ox Al and Fe (Figure 20 and Figure 21). Ox Al overall shows the same pattern.



Figure 18: Ox P in the two layers compared to a) tot P, b) inorg P. The small dotted line is a1:1 line



Figure 19: PSD% in the two layers compared to a) depth and b) tot P



Figure 20: Ox Fe in both layers compared to a) depth and b) tot Fe



Figure 21: a) Ox Fe compared to clay% in the lower layer and b) ox Al compared to ox Fe in both layers.

3.4 P-AL

P-AL in the two sediment layers is presented in Figure 22 and Figure 23. In the upper layer the highest concentrations of P-AL are found in the deeper part of the northern half of Lake Årungen. In the 2nd layer the highest concentrations are found in the central part of the lake, where the lake is deepest. In the lake there are several "hot spots". Some of these are found in both layers, other are only found in one of the layers.



Figure 22: Regional distribution of P-AL in the two sediment layers. The outlet and inlets are marked with arrows.





When testing the two layers against each other with a paired t-test, the two layers significantly differ at 95% confidence level. Doing the same test with the data divided into all four depth groups revealed that from 1-4m and from 8.3-11.3m the layers significantly differ (at 95% confidence level). In both depth groups the upper layer were found to have a higher concentration of P-AL than the lower layer. No such difference was found for the other two depth groups (Appendix 6)

P-AL seems to increase with increasing concentrations of tot P, ox P and inorg P, and also to some extent with increasing depth (Figure 24). The fraction counts for approximately 10% of the inorg P and ox P and 7 - 8% of tot P



Figure 24: P-AL in both layers compared to a) tot P, b) inorg P, c) ox P, and d) depth.

2.5 - 510.6
29.3
1.67
0.12
1,29
1.29

3.5 Storage and accumulation

In the top sediment of Lake Årungen, considerable amounts of phosphorus are stored over time. Total amount phosphorus in the two layers is calculated based on results obtained in this thesis.

Storage

The calculations (Equation 2 to Equation 7) are based	Table 7: Average input value calculations of total storage	ues for the
on the values presented in Table 7 and a particle density	Layer (cm)	0-2.5
of 2.7kg/dm ³ for mineral matter (Brady & Weil 2004)	Loss on ignition (%)	11.5
and 1.4kg/dm ³ for the organic matter (Håkanson &	Dry matter content (%)	22
Jansson 1983) from (Kohnke 1968). The sediment	Tot P (g/kg dw)	1.79
particle density is calculated as a weighted average	P-AL (g/kg dw)	0.14
between the particle density for mineral and organic	Ox-P (g/kg dw)	1,31
matter. The measured dry matter content is on	Inorg P (g/kg dw)	1.35
weight/weight basis. In this thesis it is recalculated to		
weight/volume.		

The calculation of total content of phosphorus in one layer is exemplified below with the calculations for tot P in the top layer. All the results for the two layers are presented in Table 8.

With a LOI of 11.5%, the sediment particle density becomes

Equation 2:

Sediment particle density =
$$11.5\% * 1.4 \frac{kg}{dm^3} + (100\% - 11.5\%) * 2.7 \frac{kg}{dm^3} = 2.55 \frac{kg}{dm^3}$$

In order to get the weight/volume-basis, the volume of a known amount of sediment has to be calculated. The total weight of 1kg is here used as illustration of the calculations.

Equation 3:

Wet sediment desity =
$$\frac{1 kg}{\frac{22\% * 1kg}{2.55 \frac{kg}{dm^3}} + \frac{(100\% - 22\%) * 1kg}{1\frac{kg}{dm^3}}} = 1.15 \frac{kg}{dm^3}$$

Equation 4:

Dry bulk density =
$$1.15 \frac{kg}{dm^3} * 22\% = 0.253 \frac{kg}{dm^3} = 253 \frac{kg}{m^3}$$

The dry bulk density can then be used to calculate the total amount of dry sediment within one layer.

Equation 5:

Total amount of sediment within $0 - 2.5cm = 1.2km^2 * 2.5cm = 30000m^3$

Equation 6:

Dry matter within
$$0 - 2.5cm = 30000m^3 * 253 \frac{\text{kg}}{\text{m}^3} = 7.6 * 10^6 \text{kg}$$

The total storage of phosphorus then become

Equation 7:

Tot P in sediment
$$0 - 2.5cm = 7.6 * 10^6 kg * 1.79 \frac{g}{kg} = 13600 kg P$$

1

Table 8: Calculations of total storage of phosphorus.

Layer (cm)	0 - 2.5	2.5 - 5	total
Tot drymat.(kg)	$7.6^{*}10^{6}$	10^{7}	$1.7*10^{7}$
Tot P (kg)	13600	16700	30300
P-AL (kg)	1064	1200	2264
Ox-P (kg)	9956	12900	22856
Inorg P (kg)	10260	12900	23160

The total storage of phosphorus and its fractions show higher storage in the lower, than in the upper layer, despite higher average concentrations in the upper layer. This is mainly due to higher dry matter content

Accumulation

In Lake Årungen there is some uncertainty about the sedimentation rate, and this has not been fully investigated during the last years. In April 1978 sediment cores from 12.8, 9.8 and 5.8m depth were collected and dated. The results are reported by Skogheim (1984) and Augustson *et al.*(1978) and presented in Table 9. Lilleberg *et al.* (2009) found a sedimentation rate of 7mm in the same area(10 clearly visible layers, within the 7cm top sediment). This is 20% lower than what is previous reported.

Table 9: Sedimentation	i rate in Lake Arungen		
Depth	Period	Sedimentation rate	
m		mm/yr	
12.8	1954-1978	$8.4{\pm}0.4$	
9.8	1954-1978	5.9 ± 0.4	
5.8	1963-1978	$1.7{\pm}0.2^*$	

Table 9: Sedimentation rate in Lake Årungen

(*) Some uncertainty because of low refinding of Cs in the core

From this data sedimentation rate at different depth are calculated with three different equations:

Method 1: A linear relationship between depth and sedimentation rate (Equation 8).

Method 2: A power relationship between depth and sedimentation rate (Equation 9).

Method 3: A power relationship between depth and sedimentation rate without the dating from 5.8m because this is more uncertain than the others, and will influence considerably on the regression (Equation 10).

Equation 8:

Sedimentation rate
$$(mm) = 0.96 * depth(m) - 3.8$$

Equation 9

Sedimentation rate $(mm) = 0.0558 * depth (m)^{1.9856}$

Equation 10

Sedimentation rate
$$(mm) = 0.2448 * depth (m)^{1.3868}$$

The yearly accumulation is calculated with sedimentation rates from the dating in 1978 and using a 20% reduction according to the result obtained in 2009. The sedimentation is calculated for each sample point and summed up in the end. It is assumed that all the sample points represent an equal area. The results of the calculations are presented in Table 10. The linear equation for sedimentation rate gives no sedimentation above 3.9 m depth.

As seen from the results the different methods for calculating the yearly sedimentation rate have low influence on the yearly accumulation of dry matter and phosphorus. The linear equation and the two power equations return in practice the same result, all within average \pm 5%.

Table 10: Yearly accumulation of sediment and phosphorus in Lake Årungen using different calculations
methods. Adjusted values are calculated values reduced by 20% based on the sedimentation rate found by
Lilleberget et al. (2009)

	Average	Dry matter	Phosphorus
	sedimentation		
	mm/yr	kg/yr	kg/yr
Calculated *	4.3	$1.5*10^{6}$	2900
Adjusted	3.5	1.2*10 ⁶	2300
Calculated **	4.4	1.5*10 ⁶	3000
Adjusted	3.5	1.2*10 ⁶	2400
Calculated ***	4.8	1.6*10 ⁶	3100
Adjusted	3.8	1.3*10 ⁶	2500

(*) Calculated based on method 1

(**) Calculated based on method 2

(***) Calculated based on method 3 $\,$

4 Discussion

4.1 Distributions

Total phosphorus and all the measured fractions of P generally show the same distribution pattern in sediments in Lake Årungen. They all accumulate in higher concentrations in the deep part, and decreases towards shallower areas. This is the same pattern shown for clay% by Rutsinda (2010), and for tot Fe and tot Al by Zambon (2010) (Figure 25). The covariance for tot P with tot Fe and Al, ox Fe and Al and clay% is in accordance with previously reported distribution patterns (Wang et al. 2006; Wang et al. 2009; Yoo et al. 2006). The distribution also reflects different composition of stream water in the inlet streams. At the inlet from Norderåsbekken, Bølstadbekken and Smebølbekken there are areas that have lower concentrations of tot P and all the phosphorus fractions. No such area is found at the inlet from Storgrava and Vollebekken. These streams are known to have a higher concentration of tot P and Bio P than the other inlet streams. The catchment area for Storgrava consists of 71% agricultural land, while the percentage for Norderåsbekken and Smebølbekken is 55% and Vollebekken 45%. Vollebekken receives considerable amounts of phosphorus from the campus UMB (Borch et al. 2007; Krogstad 2008). Bølstadbekken drains considerable forest areas and receives water from Skuterudbekken and Skibekken through Østensjøvannet, which leads to a lower concentration of phosphorus in the water. Thus, phosphorus concentrations are higher in Storgrava and Vollebekken compared to the other streams, and this is probably the reason for the lack of areas with low concentration of phosphorus at the inlets.



Figure 25: Horizontal distribution in the lower layer of **a**) tot Al (Zambon 2010), **b**) tot Fe (Lilleberg *et al.* 2009) and **c**) clay % (Rutsinda 2010).

4.1.1 Total phosphorus

The pattern for the distribution of tot P in this study is mostly the same as seen in the study by Skogheim (1978), but the concentrations is considerably lower in 2009 (this study) than in 1977 (Skogheim). Skogheim found tot P concentrations above 3.5g/kg dw in large areas of the lake. In this study the highest measured concentration of tot P is 2.68g/kg dw. Concentrations ranging between 2 and 2.5g/kg dw are most common in the deeper part. During the last 30 years, the reduction in P concentrations in the top sediment is around 25 to 50%. In the same time span, the P concentration in the lake water is reduced a lot. In 1962 - 1984 the average P concentration in the lake water during the summer (May to September) was $127 - 400\mu$ g P/l. In 2004 and 2005 this concentration was reduced to 29 and 23μ g P/l respectively (Borch *et al.* 2007). The main reason for this reduction is probably the decrease in the supply of P through new and better systems for handling waste water. In addition, some actions have been taken towards agriculture to reduce autumn ploughing and optimize the use of fertilizer. In 2007 there was some kind of action towards erosion on 60% of the agricultural fields (Krogstad 2008).

The reason for testing the regression for tot P with and without clay% is that information on mineralogy for only 61 samples was available. The correlation between tot Al and tot Fe in the upper layer, and tot Al, tot Fe and clay% in the lower, are so high that using only one of these as predictor will not lead to a critical loss of explanation power with the regression (Table 3). There are also some correlation between these and depth, but not more than that depth are used in the final regression. Depth, tot Fe and tot C are therefore used and R-sq values of 90.3% and 81.7% for the upper and lower layer respectively are obtained.

4.1.2 Inorganic and organic phosphorus

In Lake Årungen approximately 70 - 75% of the phosphorus is inorganic. The distribution between inorganic and organic P shows low variation in the lake sediment, and both fractions increase with increasing depth. Søndergaard (2007) found in an investigation of 32 lakes in Denmark that inorg P counted for 55-60% of tot P on average. This is considerably lower than in Lake Årungen.

The organic phosphorus shows low correlation with tot C, which means that the organic matter in the lake differ greatly in composition when it comes to C:P ratio. This may be connected to the origin and the age of the organic matter. The sediments in Lake Årungen consist of a mixture of autochthonous and allochtonous produced organic matter, and the degree of decomposition varies within the sediment. In contrast to several previously reported analyses of phosphorus sorption, organic matter in the sediments in Lake Årungen show low correlations to tot P (Wang *et al.* 2009; Yoo *et al.* 2006). The relatively low percent of organic bound phosphorus and the lack of correlations between tot C and org P are probably the explanation.

4.1.3 PSD and oxalate extractable Fe, Al and P.

The analysis of PSD gives no clear pattern, only great differences between the sediment layers. PSD is higher in the lower layer than in the top layer. This is probably connected to the oxidised micro layer at the top of the sediment where reduced iron species from the deeper and anoxic part of the sediment are oxidised and precipitated. The ironhydroxides are accumulated, more binding sites are available and PSD are reduced. This is in accordance with finding in river sediments by Mc Callistor & Logan (1978). Since there is no established relationship between the phosphorus content in the water and PSD in the sediment in Lake Årungen, it is difficult to evaluate the PSD compared to the phosphorus content in the water.

4.1.4 P-AL

P-AL show weaker correlation with depth than the other fractions of phosphorus. In the top layer the highest concentrations are found in the northern half of the lake, mainly in the deep part. In the lower layer the highest concentrations are found in the central part of the lake, at the greatest depth. On average the P-AL concentrations are higher in the top layer. The high concentrations in the top layer in the northern part may be due to a different composition of the water from Storgrava. This catchment has the highest average P-AL concentration, and therefore it is highly possible that the water contains more P-AL (Borch *et al.* 2007). This is a result of the high amount of farmland, and high P-AL concentrations in the soil. In the last 50 years the practise for fertilizing the area has lead to an increase in plant available phosphorus in the soil, and thus an increased phosphorus runoff from the catchment. P-AL concentrations between 0.05 and 0.07g/kg dw are considered as optimal for both crop growth and environmental concerns (Krogstad *et al.* 2008). In the sediments in the lake the concentrations of P-AL are close to the double.

4.2 Changes from fields to sediment

The catchment areas consist of 53% agricultural fields and 34% of forest and outfields. The mineral matter in the sediment mainly originates from these areas. In 2006, 21 soil samples were taken in the area around the south end of the lake. Of these, 17 samples originated from agricultural fields and 4 from the forest (Krogstad 2006). The samples were analysed for identical fractions of P and with similar analytic methods as used in this thesis. The concentrations from the two studies are used to evaluate the change in P from field to sediment.

Krogstad found average tot P concentrations of 1.1g/kg dw and 0.85g/kg dw for agriculture and forest respectively. In Lake Årungen the average concentrations were found to be 1.79g/kg dw for the upper layer, and 1.67g/kg dw for the lower layer. The highest concentration of phosphorus in the soil was 1.7g/kg dw (agriculture), which is within range of the average concentration found in the sediments. This gives an increase from field to top sediment of about 63%.

Inorganic P shows the highest increase from field to sediment with an increase of 80% from agricultural soil to top sediment. This also causes an increase in inorg P as a fraction of tot P. Inorg P in the soil is 0.75g/kg dw and 0.55g/kg dw in agriculture and forest respectively, while the concentration in the sediment is 1.35g/kg dw in the upper layer and 1.29g/kg dw in the lower. The average concentration in the agricultural soil is in the same range as the lowest concentration measured in the sediments.

All the oxalate extractable compounds show a clear increase in concentration from field to sediment, but the increase for ox Al and ox Fe are higher than for ox P, which leads to a lower PSD. PSD in sediments are slightly higher than in forest soils, but lower than in cultivated soils. PSD in the soils are on average 29% and 22% in agricultural and forest soil respectively, while the average concentrations in the sediments are 23% in the upper layer and 25% in the lower layer.

P-AL is the fraction from the sediment that shows the lowest increase compared to agricultural soil. In agricultural soil the average was 0.12g/kg dw and in forest soil 0.04g/kg dw. In the sediment the average was 0.14 and 0.124g/kg dw for the upper and lower layer respectively. This gives more or less equal concentrations for the lower sediment layer and the agricultural soil. This seems strange considering the apparent enrichment of tot P as well as other fractions of phosphorus in the sediment. The P-AL fraction is the easily solvable fraction that can be utilized by plants. It is likely that this phosphorus is utilized by algae or dissolved in the water. On the other hand, it would be expected that easily solvable phosphorus, for instance from sewage, would end in this fraction when sedimentated. The fact that P-AL has become a smaller portion of tot P in the sediment, together with the decrease in PSD, implies that the phosphorus is stronger adsorbed in sediments than in the fields. The decrease in PSD may also contribute to a lack of increase in P-AL because there are more binding sites available with metal hydroxides, which to some degree adsorb phosphorus stronger than the phosphorus found in the P-AL fraction.

It is obvious that there has been an enrichment of P in all measured fractions, except P-AL, between soil and sediment. This may be due to several processes both on land and in the water and sediment. One process that can lead to increased concentration of phosphorus is selective erosion (Krogstad & Løvstad 1987). Different particles erode in different ways, and erosion may favour particles high in phosphorus. This is shown by Sharpley (1985) who found that the sediment after erosion was enriched with tot P as well as all other measured P fractions compared to the parental soil, with enrichment ratios up to 3 for some fractions. Tot N, exchangeable K and organic C were also enriched. Bechmann *et al.* (2005) reported an enrichment ratio up to 1.8 for silty clay loam, but around 1 when the soil was frozen, and a decreasing enrichment ratio with increasing transport of suspended soil. The eroded particles may adsorb dissolved phosphorus from water, in streams and in the lake water (Boström *et al.* 1988). This phosphorus may origin from the soil, or from runoff and sewage from urban areas.

4.3 Accumulation of phosphorus in sediment

Augustson *et al.*(1978) reported that the sedimentation at 5.8m might be underestimated. For this reason method three might give the most correct result. The sediment rates calculated are found in the top 7cm in Lilleberg *et al.* (2009), and up to top 25cm in Augustson *et al.*(1978). In the top 2.5cm layer used in this thesis, the sediment is less compacted and counts for fewer years than deeper in the sediment (Photo 2). Therefore, using the sediment rate from the dating in 1978 might be the most correct for the top sediment.

The annual accumulation of phosphorus in the sediment in Lake Årungen was estimated using three different methods. All methods returned approximately the same accumulation. The average of the methods is 3000kg P and 1.5*10⁵kg of dry matter. In 2008 and 2009, 2789 and 2691kg P, and 5.4*10⁵kg and 4.6*10⁵kg of dry matter, respectively were measured in the outlet (Bioforsk 2010). The year 2009 was close to normal when considering discharge. Thus, 2700kg P/yr and 4.6*10⁵kg dry matter/yr as an average discharge from the lake seem to be a good estimate. The sum of the estimated accumulation and measured out flux gives a total load of 5700kg P/yr and a retention factor of 0.5 for the lake, which are higher than what is calculated using the model from Larsen and Mercier (1976). Their model gives a retention factor of 0.4, but the model is known to underestimate for lakes with high loads of particles due to erosion (Løvstad 2010). When considering the dry matter, the total load to the lake is almost 2*10⁶kg, and the retention factor is 0.75. Løvstad (2010) suggested a retention factor of 0.7 for phosphorus in Lake Årungen. This seems to be overestimated based on estimate in my thesis. A retention factor as high as 0.7 also indicates a load of phosphorus of approximately 9000kg/yr, which is up to three times the load reported earlier.

The total load of P calculated in this thesis is higher than previously reported loads during the last ten years. A load of 5700kg P/yr does not seem unrealistic when taking into account measurements from the outlet and knowledge about retention of phosphorus in lakes. The retention of P was calculated to be 0.4, using a model that is known to underestimate for lakes like Årungen (Larsen and Mercier (1976; Løvstad 2010). With a total load of 5700kg P/yr the retention factor is just above 0.5. This is a realistic number considering the known weakness in the model. The reason for the underestimate in other reports is difficult to evaluate because of little information about the background for the estimate and the sampling systems.

If all the annually accumulated phosphorus in Lake Årungen could be utilised by plants, the amount of P would be enough to fertilise a crop of 700 tons of barley (Yara 2009). If the phosphorus that yearly leaves the lake is taken into account, the amount of barley fertilised would be just above 1300 tons. In the top five cm of the sediment there is a considerable amount of phosphorus stored. When compared to the amount stored in the plough layer (top 20cm) of an equal area, the amount in the sediment

equals less than 10% of the amount in the soil. The concentration of P, given as g/m^3 , is twice as large in the soil compared to the sediment, mainly due to a higher density in the soil.

4.4 Internal loading

There have been subjected that Lake Årungen are internal loaded with phosphorus in periods. This are also probably what Løvstad *et al.* (1992) found when measuring increasing phosphorus concentrations in the bottom water in Lake Årungen when the oxygen concentration decreased. Andersen and Ring (1999) found in their study on phosphorus release from sediment in a shallow eutrophic lake, that the release of phosphorus was significantly higher at anoxic then oxic conditions and that under anoxic conditions the iron-bound phosphorus was the most important fraction for loss of phosphorus, while under oxic conditions the org P fraction become more important. In a analysis of shallow Danish lakes, Jensen *et al.* (1992) found that with a Fe:P ratio above 15 (by weight on total measurements) it may be possible to control the internal loading by keeping the surface sediment oxidised. In Lake Årungen the Fe:P ratio is 26 and 27 in the upper and lower layer respectively. Iron are thereby most probably able to control the internal loading as long as the surface sediment are oxidised. When top sediment is reduced, the phosphorus that are adsorbed to iron hydroxides can be remobilized if the iron hydroxide are reduced.

The PSD% in Lake Årungen varies overall between 20-30%. In the Netherlands a PSD of 25% is used as a critical value for phosphorus leaching from cultivated soil. Values above 25% increase the potential for unacceptable amounts of phosphorus leaching from the soil (Sibbesen & Sharpley 1997). If the same criteria is used as for soil in The Netherlands the sediments in Lake Årungen are in a critical range for phosphorus leaching.

Climatic changes are expected to change the weather in the nearest future. The most likely case in the area where Lake Årungen is located is more wind and precipitation, higher temperature and more frequent extreme weather. The phosphorus release from the sediment is shown to be positively correlated with temperature (Jensen & Andersen 1992). With climatic changes this might be more important in the future. A higher summer temperature alone will probably lead to stronger stratification, and thereby no increase in temperature in the deeper part, but combined with more wind it can lead to less or no stratification and thereby higher temperature in the sediment water interface in the lake. On the other hand the lower degree of stratification in the water will lead to fewer episodes with reducing condition in the sediment water interface and thereby less internal loading from reduction of iron hydroxides.

It is difficult to evaluate the potential for internal loading in Lake Årungen. As long as the water sediment interface is well oxygenised the internal loading appears to be limited. If the interface is reduced, the internal loading will most likely be considerably.

5 Conclusions

All the analysed parameters showed increasing concentrations towards higher clay content in the sediment. Because of the high correlations between the possible predictors for phosphorus concentration in the sediment it is not statistically possible to distinguish whether it is the clay content or one of the other possible predictors that has the main influence on concentration of phosphorus in the sediment. It is not possible to either verify or reject the hypothesis "*Clay content in sediment controls the concentrations of total phosphorus in the sediment*"

The sediment overall contains higher concentrations of all measure fractions of phosphorus compared with agriculture soil in the drainage area. The increase is highest for the inorganic phosphorus fractions which increased as much as 80% from field to sediment, while P-AL only shows a slight increase. The phosphorus sorption degree decreases from field to sediment which implies a stronger binding of phosphorus in the sediment than in the soil. The hypothesis *"Concentrations of phosphorus and phosphorus fraction in sediments equal concentrations in cultivated soil in the drainage area"* can be rejected

The yearly accumulation of sediments in Lake Årungen are estimated to $1.5*10^{6}$ kg dw, which contains 3000kg phosphorus. The estimated accumulation and measured flux in the outlet gives a total load of $2*10^{6}$ kg dry matter and 5700kg phosphorus. This gives a retention factor at 0.5 for phosphorus and 0.75 for dry matter in the lake. The estimated value for accumulation is higher than the measured flux in the outlet, but because of the uncertainty in the in the estimated value it is not possible to either verify or reject the hypothesis *"The retention of phosphorus in Lake Årungen is higher than the phosphorus flux through the outlet"*

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7 Figures

Figure 1: Lake Årungen with sub catchment areas (Borch <i>et al.</i> 2007)
Figure 2: Depth profile for Lake Årungen. Ekvidistanse 2 m (Skogheim & Abrahamsen 1979)7
Figure 3: Frequent distribution, and analysis results of tot P for the two layers
Figure 4: Regional distribution of P in the two sediment layers. The outlet and inlets are marked with
arrows
Figure 5: Total phosphorus in the lower sediment layer grouped after clay% and depth. Only
observations with data about the grain size distribution are used, 61 point in each layer14
Figure 6: Total phosphorus in the two layers compared with a) tot Fe b) ox Fe c) tot Al d) ox Al e)
depth and \mathbf{f}) clay% (only the lower layer)
Figure 7: Total phosphorus compared with tot C in the two layers. In a) all the data are presented,
while in b) the depth groups from 0 to 8.5m are excluded
Figure 8: Frequent distribution of the inorganic phosphorus in the two sediment layers. a) absolute
values, and b) as a fraction of tot P16
Figure 9: Frequent distribution of the organic phosphorus in the two sediment layers. a) absolute
values, and b) as a fraction of tot P16
Figure 10: Organic and inorganic phosphorus in Lake Årungen. A absolute values of inorg P, B
percent inorg P relative to tot P, C absolute values of org P, and D percent org P relative to tot P 17
Figure 11: Inorg P compared to a) depth and b) tot P
Figure 12: Concentration of org P compared to a) tot C and b) tot N. The values from sample point
120 are removed because of high concentrations of tot C and tot N
Figure 13: Concentration of org P compared to a) tot C and b) tot P. In a) the result for location 120 is
removed because of extremely high tot C content
Figure 14: Fraction of inorganic and organic P in the two layers compared to a) water depth b) tot P
Figure 15: Frequent distribution of oxalate extractable compounds. a) Ox Al, b) Ox Fe, c) Ox P and
d) PSD
Figure 16: Oxalate extractable compounds in the sediment. A) oxalate extractable Al and B) oxalate
extractable Fe
Figure 17: Oxalate extractable compounds in the sediment. A) oxalate extractable P and B) PSD 22
Figure 18: Ox P in the two layers compared to a) tot P, b) inorg P. The small dotted line is a1:1 line23
Figure 19: PSD% in the two layers compared to a) depth and b) tot P
Figure 20: Ox Fe in both layers compared to a) depth and b) tot Fe
Figure 21: a) Ox Fe compared to clay% in the lower layer and b) ox Al compared to ox Fe in both
layers

Figure 22: Regional distribution of P-AL in the two sediment layers. The outlet and inlets are marked
with arrows
Figure 23: Frequent distribution, and analysis results of P-AL for the two layers
Figure 24: P-AL in both layers compared to a) tot P, b) inorg P, c) ox P, and d) depth
Figure 25: Horizontal distribution in the lower layer of a) tot Al (Zambon 2010), b) tot Fe (Lilleberg
<i>et al.</i> 2009) and c) clay % (Rutsinda 2010)

Appendix 1: Paired t-test of tot P between the two layers

- Appendix 2: Stepwise Regression: Tot P vs depth, Tot C, Tot N, Fe, Al, clay%, and without clay% (0 2.5cm)
- Appendix 3: Stepwise Regression: Tot P vs depth, Tot C, Tot N, Fe, Al, clay%, and without clay% (2.5 5cm)
- Appendix 4: Paired t-test of inorganic P between the two layers.
- Appendix 5: Paired t-test for oxalate extractable compounds between the two layers.
- Appendix 6: Paired t-test of P-AL between the two layers
- Appendix 7: Map with sampling locations.
- Appendix 8: Analyse data from the upper layer (0 2.5 cm)
- Appendix 9: Analyse data from the lower layer (2.5 5cm)

Results for: All Paired T-Test and CI: Tot P; Tot P_1

Paired T for Tot P - Tot P 1

 N
 Mean
 StDev
 SE Mean

 Tot P
 120
 1,7997
 0,3431
 0,0313

 Tot P_1
 120
 1,6697
 0,3915
 0,0357

 Difference
 120
 0,1300
 0,2147
 0,0196

95% CI for mean difference: (0,0912; 0,1688)T-Test of mean difference = 0 (vs not = 0): T-Value = 6,63 P-Value = 0,000

Results for: depth cat1 Paired T-Test and CI: Tot P; Tot P_1

Paired T for Tot P - Tot P 1

	Ν	Mean	StDev	SE Mean
Tot P	25	1,3742	0,3440	0,0688
Tot P_1	25	1,1896	0,3653	0,0731
Difference	25	0,1846	0,1686	0,0337

95% CI for mean difference: (0,1150; 0,2542)T-Test of mean difference = 0 (vs not = 0): T-Value = 5,47 P-Value = 0,000

Results for: depth cat2 Paired T-Test and CI: Tot P; Tot P_1

Paired T for Tot P - Tot P 1

	Ν	Mean	StDev	SE Mean
Tot P	29	1,7255	0,2263	0,0420
Tot P_1	29	1,6811	0,2555	0,0474
Difference	29	0,0445	0,1260	0,0234

95% CI for mean difference: (-0,0035; 0,0924)T-Test of mean difference = 0 (vs not = 0): T-Value = 1,90 P-Value = 0,068

Results for: depth cat3 Paired T-Test and CI: Tot P; Tot P_1

Paired T for Tot P - Tot P 1

	Ν	Mean	StDev	SE Mean
Tot P	29	1,9487	0,2543	0,0472
Tot P 1	29	1,6596	0,1776	0,0330
Difference	29	0,2892	0,1623	0,0301

95% CI for mean difference: (0,2275; 0,3509)T-Test of mean difference = 0 (vs not = 0): T-Value = 9,60 P-Value = 0,000

Results for: depth cat4

Paired T-Test and CI: Tot P; Tot P_1

Paired T for Tot P - Tot P_1

N Mean StDev SE Mean Tot P 37 2,0284 0,1354 0,0223 Tot P_1 37 1,9932 0,2732 0,0449 Difference 37 0,0353 0,2509 0,0413 95% CI for mean difference: (-0,0484; 0,1189) T-Test of mean difference = 0 (vs not = 0): T-Value = 0,86 P-Value = 0,398

Stepwise Regression: Tot P versus depth, tot C, Tot N, Fe, AI, clay Alpha-to-Enter: 0.15 Alpha-to-Remove: 0.15

Response is Tot P on 6 predictors, with N = 61 N(cases with missing observations) = 61 N(all cases) = 122

Step	1	2	-0 36033	4
Constant	0.00925	0.40007	0.30033	0.44091
Fe T-Value P-Value	0.0394 17.32 0.000	0.0428 20.52 0.000	0.0354 14.84 0.000	0.0547 7.06 0.000
tot C T-Value P-Value		0.0054 4.67 0.000	0.0073 6.79 0.000	0.0081 7.58 0.000
depth T-Value P-Value			0.0232 4.70 0.000	0.0232 4.92 0.000
Al T-Value P-Value				-0.0148 -2.61 0.012
S R-Sq R-Sq(adj) Mallows Cp	0.134 83.57 83.29 61.8	0.115 88.06 87.65 31.3	0.0984 91.40 90.95 9.2	0.0937 92.33 91.79 4.4

Stepwise Regression: Tot P versus depth, tot C, Tot N, Fe, AI

Alpha-to-Enter: 0.15 Alpha-to-Remove: 0.15

Response is Tot P on 5 predictors, with N = 122

Step	1	2	3	4
Constant	0.03407	0.14159	-0.01483	-0.07897
Fe	0.0373	0.0324	0.0312	0.0463
T-Value	28.91	18.47	19.03	7.34
P-Value	0.000	0.000	0.000	0.000
depth		0.0151	0.0217	0.0224
T-Value		3.88	5.62	5.90
P-Value		0.000	0.000	0.000
Tot N T-Value P-Value			0.0334 4.65 0.000	0.0377 5.21 0.000
Al T-Value P-Value				-0.0116 -2.48 0.014
S	0.124	0.117	0.108	0.106
R-Sq	87.44	88.85	90.58	91.05
R-Sq(adj)	87.34	88.67	90.34	90.75
Mallows Cp	45.1	28.8	8.3	4.2

Stepwise Regression: Tot P_1 versus depth, tot C_1, tot N_1, Fe_1, Al_1, clay Alpha-to-Enter: 0.15 Alpha-to-Remove: 0.15

Response is Tot P 1 on 6 predictors, with N = 59N(cases with missing observations) = 63 N(all cases) = 122

Step	1	2	3	4	5
Constant	-0.2692	-0.4856	-0.6961	-0.5740	-0.8462
Fe_1	0.0429	0.0417	0.0922	0.0842	0.0923
T-Value	12.75	13.48	8.61	9.49	9.85
P-Value	0.000	0.000	0.000	0.000	0.000
tot C_1		0.0075	0.0095	0.0121	0.0143
T-Value		3.55	5.22	7.74	7.84
P-Value		0.001	0.000	0.000	0.000
Al_1 T-Value P-Value			-0.0384 -4.86 0.000	-0.0403 -6.25 0.000	-0.0327 -4.58 0.000
depth T-Value P-Value				0.0314 5.34 0.000	0.0335 5.81 0.000
clay T-Value P-Value					-0.0112 -2.16 0.035
S	0.196	0.179	0.151	0.123	0.119
R-Sq	74.03	78.80	85.17	90.30	91.09
R-Sq(adj)	73.58	78.05	84.37	89.59	90.25
Mallows Cp	98.4	72.2	36.6	8.3	5.6

Stepwise Regression: Tot P_1 versus depth, tot C_1, tot N_1, Fe_1, Al_1 Alpha-to-Enter: 0.15 Alpha-to-Remove: 0.15

Response is Tot P 1 on 5 predictors, with N = 120 $\,$ N(cases with missing observations) = 2 N(all cases) = 122

Step	1	2	3	4
Constant	-0.09373	-0.25194	-0.12641	-0.26773
Fe_1 T-Value P-Value	0.0390 19.97 0.000	0.0818 8.94 0.000	0.0741 8.52 0.000	0.0824 10.34 0.000
Al_1 T-Value P-Value		-0.0317 -4.77 0.000	-0.0311 -5.02 0.000	-0.0402 -6.92 0.000
depth T-Value P-Value			0.0227 4.34 0.000	0.0322 6.40 0.000
tot N_1 T-Value P-Value				0.0453 5.35 0.000
S R-Sq R-Sq(adj) Mallows Cp	0.188 77.16 76.97 81.7	0.173 80.88 80.55 51.5	0.161 83.55 83.12 30.4	0.145 86.83 86.37 4.0

Paired T-Test and CI: InorgP1; Inorgp2

Paired T for InorgP1 - Inorgp2

	Ν	Mean	StDev	SE Mean
InorgP1	34	1,3456	0,2353	0,0403
Inorgp2	34	1,2971	0,3006	0,0515
Difference	34	0,0485	0,2043	0,0350

95% CI for mean difference: (-0,0227; 0,1198) T-Test of mean difference = 0 (vs not = 0): T-Value = 1,39 P-Value = 0,175

Paired T-Test and CI: InorgP%; InorgP2%

Paired T for InorgP% - InorgP2%

	Ν	Mean	StDev	SE Mean
InorgP%	34	72,147	2,992	0,513
InorgP2%	34	74,718	4,017	0,689
Difference	34	-2,571	5,089	0,873

```
95% CI for mean difference: (-4,347; -0,795)
T-Test of mean difference = 0 (vs not = 0): T-Value = -2,95 P-Value = 0,006
```

Paired T-Test and CI: oxAl1, oxAl2

Paired T for oxAl1 - oxAl2

 N
 Mean
 StDev
 SE Mean

 oxAl1
 119
 3.5954
 0.8746
 0.0802

 oxAl2
 119
 3.3742
 0.8976
 0.0823

 Difference
 119
 0.2211
 0.4790
 0.0439

95% CI for mean difference: (0.1342, 0.3081)T-Test of mean difference = 0 (vs not = 0): T-Value = 5.04 P-Value = 0.000

Paired T-Test and CI: oxFe1, oxFe2

Paired T for oxFe1 - oxFe2

	Ν	Mean	StDev	SE Mean
oxFel	119	13.045	3.706	0.340
oxFe2	119	11.752	3.670	0.336
Difference	119	1.294	2.959	0.271

95% CI for mean difference: (0.757, 1.831)T-Test of mean difference = 0 (vs not = 0): T-Value = 4.77 P-Value = 0.000

Paired T-Test and CI: oxP1, oxP2

Paired T for oxP1 - oxP2

	Ν	Mean	StDev	SE Mean
oxP1	119	1.3202	0.3548	0.0325
oxP2	119	1.3007	0.4412	0.0404
Difference	119	0.0195	0.2823	0.0259

95% CI for mean difference: (-0.0318, 0.0707)T-Test of mean difference = 0 (vs not = 0): T-Value = 0.75 P-Value = 0.453

Paired T-Test and CI: PSD%1, PSD%2

Paired T for PSD%1 - PSD%2

	Ν	Mean	StDev	SE Mean
PSD%1	119	23.297	3.042	0.279
PSD%2	119	24.790	3.872	0.355
Difference	119	-1.494	3.325	0.305

95% CI for mean difference: (-2.097, -0.890)T-Test of mean difference = 0 (vs not = 0): T-Value = -4.90 P-Value = 0.000

Results for: All

Paired T-Test and CI: P-AL; P-AL 1 Paired T for P-AL - P-AL 1

Ν Mean StDev SE Mean
 P-AL
 121
 0,13920
 0,03938
 0,00358

 P-AL_1
 121
 0,12306
 0,04194
 0,00381

 Difference
 121
 0,01614
 0,04269
 0,00388

95% CI for mean difference: (0,00845; 0,02382) T-Test of mean difference = 0 (vs not = 0): T-Value = 4,16 P-Value = 0,000

Results for: depth cat1 Paired T-Test and CI: P-AL; P-AL_1

Paired T for P-AL - P-AL_1

	Ν	Mean	StDev	SE Mean
P-AL	26	0,09755	0,04056	0,00795
P-AL_1	26	0,07513	0,03818	0,00749
Difference	26	0,02242	0,02639	0,00518

95% CI for mean difference: (0,01176; 0,03308) T-Test of mean difference = 0 (vs not = 0): T-Value = 4,33 P-Value = 0,000

Results for: depth cat2 Paired T-Test and CI: P-AL; P-AL 1

Paired T for P-AL - P-AL 1

	Ν	Mean	StDev	SE Mean
P-AL	29	0,12948	0,03413	0,00634
P-AL 1	29	0,13712	0,02767	0,00514
Difference	29	-0,00764	0,03529	0,00655

95% CI for mean difference: (-0,02106; 0,00579) T-Test of mean difference = 0 (vs not = 0): T-Value = -1,17 P-Value = 0,254

Results for: depth cat3 Paired T-Test and CI: P-AL; P-AL_1

Paired T for P-AL - P-AL 1

	Ν	Mean	StDev	SE Mean
P-AL	29	0,17033	0,02625	0,00488
P-AL_1	29	0,11762	0,02336	0,00434
Difference	29	0,05271	0,03692	0,00686

95% CI for mean difference: (0,03867; 0,06675) T-Test of mean difference = 0 (vs not = 0): T-Value = 7,69 P-Value = 0,000

Results for: depth cat4[W5] Paired T-Test and CI: P-AL; P-AL_1

Paired T for P-AL - P-AL 1

StDev SE Mean Ν Mean P-AL 37 0,15169 0,01773 0,00292 37 0,15000 0,03526 0,00580 P-AL 1 Difference 37 0,00169 0,04225 0,00695

95% CI for mean difference: (-0,01239; 0,01578) T-Test of mean difference = 0 (vs not = 0): T-Value = 0,24 P-Value = 0,809

PHOSPHORUS IN EUTROPHIC LAKE SEDIMENTS 49

Appendix 7

Map with sample locations. Numbers equal sample location in and Appendix 8 and Appendix 9.



						0-2.5	ст					
Location	depth	dry matter	Tot P	ох	alate e	xtracta	ble	P-AL	Inorg P	Inorg P	Org P	Org P
				Al	Fe	Р	PSD					
nr	m	%	g/Kg	g/kg	g/kg	g/kg	%	g/kg	g /kg	% of totP	g/kg	% of totP
1	5.64	35	1.07	1.90	5.96	0.70	25.7	0.088	0.79	73.24	0.29	26.76
2	11.90	28	1.91	3.98	15.06	1.48	22.9	0.163				
3	12.73	26	1.98	4.43	15.92	1.54	22.2	0.161				
4	12.73	26	2.06	3.88	12.27	1.57	28.0	0.141				
5	7.68	18	1.83	3.31	9.91	1.35	29.1	0.148	1.34	73.40	0.49	26.60
6	2.54	19	1.43	2.76	9.51	0.93	22.1	0.124				
7	1.10	5	1.13	3.11	9.94	0.61	13.3	0.029				
8	6.29	19	1.66	3.04	9.34	1.18	27.2					
9	11.27	22	2.14	4.46	17.19	1.73	23.6	0.192	1.59	74.08	0.56	25.92
10	12.38	26	1.98	4.61	17.88	1.68	22.0	0.161				
11	12.52	27	1.94	4.28	16.40	1.62	23.1	0.161				
12	9.56	24	1.75	3.57	14.37	1.40	23.2	0.190				
13	2.32	26	1.27	2.37	9.06	0.88	22.7	0.139	1.00	78.75	0.27	21.25
14	3.07	25	0.955	1.49	4.78	0.56	25.7	0.090				
15	12.06	29	1.88	4.28	15.48	1.49	22.0	0.151				
16	12.01	27	2.07	4.54	17.19	1.63	22.1	0.151				
17	11.45	25	2.14	4.73	18.45	1.80	23.0	0.197	1.58	73.75	0.56	26.25
18	10.20	22	1.86	3.84	13.58	1.48	24.8	0.175				
19	3.72	18	1.43	2.57	8.50	1.00	26.0	0.105				
20	5.98	18	1.75	3.68	13.63	1.29	21.9	0.151	1.21	69.05	0.54	30.95
21	8.33	25	1.66	3.23	11.70	1.26	24.8	0.161	1.18	70.93	0.48	29.07
22	9.70	22	1.94	4.18	15.98	1.56	22.8	0.187	1.33	68.58	0.61	31.42
23	11.02	22	2.00	4.43	16.29	1.54	21.8	0.161	1.48	74.13	0.52	25.87
24	12.30	24	2.02	4.37	16.91	1.56	21.7	0.168				
25	9.36	15	1.97	3.96	15.99	1.55	23.1	0.185				
26	2.93	19	1.34	2.44	8.49	0.89	23.6	0.088				
27	5.41	21	1.51	2.86	9.00	1.07	25.9	0.109				
28	11.99	23	2.19	4.10	14.63	1.52	23.7	0.178				
29	9.81	18	2.13	4.37	17.50	1.77	24.1	0.190	1.56	73.31	0.57	26.69
30	6.06	15	1.57	3.32	10.10	1.04	22.0	0.097				
31	3.08	21	1.53	2.86	11.42	1.06	22.0	0.145				
32	4.49	22	1.56	2.69	11.18	1.14	24.5	0.172				
33	1.31	24	1.07	1.73	5.29	0.40	16.3	0.049				
34	11.64	23	2.01	4.41	16.74	1.59	22.2	0.165	1.52	75.72	0.49	24.28
35	10.39	19	2.02	4.05	16.30	1.61	23.5	0.197				
36	1.50	13	1.17	2.80	9.59	0.51	11.9	0.047				
37	8.42	20	1.84	3.31	10.09	1.30	27.8	0.152				
38	12.31	25	2.16	4.62	18.14	1.72	22.4	0.192	1.66	76.81	0.50	23.19
39	1.76	14	1.15	2.75	5.74	0.49	15.6	0.049				
40	7.19	13	2.03	4.31	17.35	1.57	21.5	0.165				
41	11.98	21	2.19	4.57	18.13	1.80	23.5	0.197	1.64	74.89	0.55	25.11

42	7.84	17	1.75	3.66	10.49	1.25	25.0	0.138				
43	7.86	17	1.90	4.05	16.10	1.47	21.7	0.170				
44	10.74	23	2.24	4.60	16.83	1.61	22.0	0.179	1.54	68.73	0.70	31.27
45	9.30	11	2.07	4.39	16.20	1.63	23.3	0.206				
46	10.15	17	2.42	4.47	18.75	1.98	25.4	0.231				
47	9.50	13	2.16	4.46	17.24	1.71	23.3	0.201	1.62	74.77	0.55	25.23
48	7.08	16	1.86	3.44	11.86	1.35	25.7	0.140				
49	5.25	13	1.78	3.66	14.22	1.26	20.9	0.130				
50	8.44	14	2.06	3.86	13.45	1.48	24.9	0.170	1.48	71.67	0.58	28.33
51	10.65	18	2.07	4.84	17.79	1.67	21.7	0.160				
52	7.06	12	1.93	4.07	14.13	1.43	22.8	0.130				
53	7.30	12	1.95	3.54	10.72	1.29	25.7	0.125				
54	8.84	10	2.11	4.31	16.58	1.60	22.7	0.179				
55	6.56	15	1.83	3.51	10.95	1.27	25.2	0.130	1.29	70.51	0.54	29.49
56	3.80	16	1.68	3.02	11.43	1.21	24.6	0.113	1.20	71.12	0.49	28.88
57	5.32	17	1.74	3.77	11.66	1.12	20.7	0.111				
58	5.01	13	1.74	3.14	11.93	1.22	23.8	0.120				
59	4.21	24	1.36	2.14	7.86	0.90	26.4	0.118	1.01	74.32	0.35	25.68
60	12.21	27	1.96	4.64	16.66	1.63	22.4	0.150				
61	12.77	27	2.02	4.91	17.81	1.75	22.5	0.147				
62	11.08	21	2.27	4.46	16.98	1.76	24.2	0.184				
63	3.65	21	1.55	2.57	9.38	1.08	26.5	0.113	1.08	69.66	0.47	30.34
64	9.45	20	2.16	3.86	11.93	1.61	29.1	0.172				
65	12.78	26	2.04	4.46	16.38	1.61	22.6	0.138				
66	12.91	25	2.17	4.72	17.30	1.70	22.7	0.143				
67	11.91	27	1.91	4.60	15.98	1.53	21.6	0.138	1.41	73.80	0.50	26.20
68	10.40	25	1.99	4.10	16.08	1.59	23.4	0.152				
69	1.89	15	1.55	3.15	11.17	1.02	20.9	0.138				
70	7.23	23	1.82	3.67	15.10	1.43	22.7	0.140				
71	12.48	26	2.01	4.61	16.31	1.55	21.7	0.145				
72	12.39	25	2.01	4.01	14.17	1.38	22.1	0.130	1.43	71.07	0.58	28.93
73	13.23	24	2.18	4.76	17.20	1.74	23.2	0.140				
74	12.53	27	2.19	4.77	18.84	1.75	21.9	0.147				
75	4.06	19	1.82	2.95	11.43	1.31	27.0	0.135				
76	9.73	21	2.06	3.69	11.48	1.56	29.4	0.174				
77	13.18	25	2.15	4.52	15.70	1.73	25.0	0.167				
78	13.26	25	2.14	4.85	17.98	1.76	22.6	0.128	1.54	71.67	0.61	28.33
79	12.69	28	2.01	3.68	13.22	1.34	23.1	0.140				
80	11.45	30	1.80	3.49	13.66	1.30	22.4	0.155				
81	10.72	36	1.54	3.08	12.79	1.13	21.2	0.128				
82	13.04	27	2.02	4.46	16.37	1.58	22.2	0.143				
83	13.33	25	2.27	4.82	17.26	1.70	22.4	0.140	1.56	68.91	0.70	31.09
84	12.60	25	2.15	4.30	16.46	1.54	21.9	0.152				
85	2.94	42	0.785	0.68	3.61	0.32	23.2					
86	2.68	22	1.38	2.30	7.14	0.81	24.6	0.111				
87	11.94	26	1.97	4.60	15.93	1.48	20.9	0.138				

88	13.42	26	2.11	4.39	16.84	1.65	23.0	0.135	1.54	72.97	0.57	27.03
89	12.73	33	1.58	3.33	12.26	1.18	22.2	0.140				
90	1.65	28	1.14	2.43	8.06	0.67	18.4	0.091				
91	6.63	21	1.86	3.51	13.33	1.30	22.7	0.131				
92	11.99	26	1.95	4.14	15.56	1.42	21.3	0.123				
93	13.14	28	2.08	4.51	16.03	1.60	22.7	0.158	1.51	72.79	0.56	27.21
94	11.60	24	2.10	3.94	16.18	1.53	22.7	0.148				
95	11.03	23	2.03	4.20	14.61	1.43	22.1	0.150				
96	11.23	26	2.07	3.38	12.84	1.20	21.8	0.145	1.40	67.88	0.66	32.12
97	5.96	19	1.85	3.35	10.86	1.36	27.5	0.140				
98	1.80	19	1.06	2.18	6.06	0.51	17.2	0.057				
99	2.41	20	1.83	4.13	14.20	1.28	20.2	0.116				
100	11.53	30	1.85	3.27	13.60	1.33	23.5	0.135	1.35	72.80	0.50	27.20
101	9.44	22	2.09	3.51	10.80	1.50	30.0	0.177				
102	6.67	19	1.83	3.40	10.57	1.23	25.2	0.126				
103	11.35	29	1.86	3.31	11.63	1.43	27.8	0.150	1.34	71.96	0.52	28.04
104	1.59	19	0.937	2.07	6.84	0.44	14.2	0.057				
105	5.61	21	1.60	2.99	8.86	1.08	25.8	0.113				
106	10.47	30	1.83	3.47	13.29	1.36	24.0	0.167	1.28	70.35	0.54	29.65
107	2.60	24	1.16	2.48	6.83	0.65	19.7	0.108				
108	3.28	21	1.62	2.68	9.38	1.09	26.4	0.131				
109	9.66	29	1.88	3.63	13.75	1.38	23.5		1.28	68.04	0.60	31.96
110	8.65	30	1.73	3.38	12.45	1.29	23.9	0.170				
111	2.98	22	1.48	2.49	8.73	1.05	27.2	0.121				
112	8.89	35	1.51	2.82	11.35	1.14	24.0	0.121				
113	8.60	25	1.62	2.76	8.67	1.21	30.4	0.145	1.22	74.87	0.41	25.13
114	3.98	21	1.67	3.43	14.75	1.28	21.1	0.133				
115	8.79	34	1.41	2.76	10.58	1.02	22.6	0.126	1.05	74.68	0.36	25.32
116	8.51	31	1.46	2.41	7.86	1.04	29.2	0.126				
117	1.95	15	1.44	2.96	10.52	1.10	23.8	0.106				
118	0.93	15	0.983	1.65	4.66	0.41	18.4	0.027				
119	4.81	24	1.67	2.62	8.55	1.15	29.7	0.159				
120	4.85	10	1.18	2.05	9.53	0.77	20.1	0.086	0.76	63.79	0.43	36.21
121	0.75	1	2.21									
122	1.18	10	1.99	3.71	16.09	1.55	23.5	0.125				
average	8.13	22.0	1.79	3.58	12.97	1.31	23.23	0.14	1.35	72.15	0.52	27.85
median	8.87	22.3	1.86	3.66	13.45	1.36	22.97	0.14	1.38	72.80	0.54	27.20
max	13.42	42.2	2.42	4.91	18.84	1.98	30.44	0.23	1.66	78.75	0.70	36.21
min	0.75	1.0	0.78	0.68	3.61	0.32	11.95	0.03	0.76	63.79	0.27	21.25
st.dev	3.92	6.4	0.35	0.88	3.73	0.36	3.07	0.04	0.24	2.99	0.10	2.99
n	122	122.0	122	121	121	121	121	118	34	34	34	34

2.5-5cm												
sample	le depth dry matter Tot		Tot P	oxalate extractable		ole 2	P-AL I		norg P	Org P		
				Al	Fe	Р	PSD					
nr	m	%	g/Kg	g/kg	g/kg	g/kg	%	g/kg	g /kg	% of tot P	g/kg	% of tot P
1	5.64	50.3	0.870	1.46	5.21	0.50	22.11	0.081	0.72	82.45	0.15	17.55
2	11.90	33.3	1.62	3.68	12.13	1.22	22.25	0.113				
3	12.73	29.0	2.24	4.05	14.99	1.94	29.86	0.132				
4	12.73	29.4	2.28	4.03	17.35	1.85	25.96	0.172				
5	7.68	24.4	2.03	3.99	15.18	1.95	30.03	0.176	1.49	73.44	0.54	26.56
6	2.54	45.7	1.01	1.39	4.86	0.53	24.85	0.071				
7	1.10	13.0	1.06	3.28	5.14	0.44	13.19	0.017				
8	6.29	28.0	1.69	3.24	11.23	1.47	29.53	0.132				
9	11.27	32.0	1.80	3.54	12.25	1.16	21.28	0.118	1.33	73.51	0.48	26.49
10	12.38	29.2	2.15	4.61	15.26	2.00	29.07	0.145				
11	12.52	31.2	2.00	3.94	14.96	1.55	24.17	0.147				
12	9.56	32.0	1.74	3.84	13.36	1.87	31.66	0.157				
13	2.32	42.0	1.21	2.39	8.64	0.82	21.70	0.091	0.92	76.16	0.29	23.84
14	3.07	50.2	0.788	0.99	3.38	0.39	25.77	0.088				
15	12.06	29.3	1.75	3.88	12.10	1.50	26.93	0.108				
16	12.01	32.1	1.88	4.22	15.68	1.57	23.15	0.123				
17	11.45	37.6	1.56	2.30	7.36	0.86	25.69	0.113	1.26	80.78	0.30	19.22
18	10.20	28.2	1.84	3.57	12.09	1.33	24.62	0.152				
19	3.72	28.7	1.49	2.46	9.50	1.12	27.73	0.103				
20	5.98	27.9	1.62	3.49	11.74	1.56	29.61	0.127	1.19	73.00	0.44	27.00
21	8.33	31.3	1.83	2.75	10.59	1.44	32.00	0.179	1.36	74.42	0.47	25.58
22	9.70	27.8	1.62	3.62	10.61	1.31	26.19	0.098	1.17	72.52	0.44	27.48
23	11.02	29.8	1.67	4.05	13.88	1.28	20.77	0.088	1.22	73.26	0.45	26.74
24	12.30	32.2	2.05	3.81	15.32	1.57	24.41	0.159				
25	9.36	32.8	1.58	3.25	11.30	1.15	23.06	0.108				
26	2.93	40.3	1.10	2.52	9.83	1.01	24.30	0.078				
27	5.41	28.9	1.58	2.42	9.37	1.18	29.56	0.135				
28	11.99	32.0	1.74	4.25	15.25	1.45	21.70	0.118				
29	9.81	28.7	1.80	3.97	11.90	1.44	25.88	0.103	1.28	71.14	0.52	28.86
30	6.06	24.5	1.53	3.34	9.76	1.09	23.63	0.098				
31	3.08	34.8	1.22	2.21	6.44	0.78	25.64	0.069				
32	4.49	36.5	1.54	2.40	8.84	1.13	29.61	0.150				
33	1.31	70.5	0.799	1.05	3.91	0.49	28.79	0.064				
34	11.64	29.6	1.90	4.34	15.64	1.48	21.63	0.135	1.47	76.96	0.44	23.04
35	10.39	30.0	1.56	3.66	10.76	1.28	25.12	0.083				
36	1.50	14.3	1.04	3.12	7.51	0.49	12.66	0.032				
37	8.42	24.8	1.92	3.15	11.79	1.43	28.14	0.174				
38	12.31	29.1	2.34	4.21	15.14	1.94	29.28	0.186	1.78	75.92	0.56	24.08
39	1.76	15.0	1.06	3.48	6.47	0.47	12.43	0.015				
40	7.19	19.3	1.85	4.06	14.32	1.63	25.91	0.127				
41	11.98	29.3	1.95	4.31	15.25	1.50	22.35	0.127	1.48	76.27	0.46	23.73

42	7.84	24.2	1.74	3.40	11.49	1.39	26.96	0.135				
43	7.86	22.6	1.67	3.97	12.34	1.13	19.87	0.105				
44	10.74	29.3	1.76	4.00	11.81	1.39	25.04	0.115	1.27	72.07	0.49	27.93
45	9.30	23.0	1.64	4.15	12.06	1.06	18.46	0.083				
46	10.15	24.8	1.89	4.23	13.88	1.76	28.01	0.125				
47	9.50	27.3	1.65	3.89	10.72	1.24	23.81	0.103	1.23	74.30	0.42	25.70
48	7.08	21.4	1.81	4.01	20.19	2.08	26.31	0.130				
49	5.25	22.3	1.75	3.25	12.59	1.30	24.34	0.132				
50	8.44	24.3	1.88	3.81	13.13	1.62	27.85	0.130	1.44	76.71	0.44	23.29
51	10.65	27.3	1.71	4.47	13.92	1.21	18.87	0.108				
52	7.06	19.8	2.06	3.89	13.44	1.79	30.00	0.154				
53	7.30	19.8	1.88	3.80	12.61	1.40	24.73	0.164				
54	8.84	23.5	1.67	3.86	11.85	1.32	24.02	0.103				
55	6.56	20.5	1.91	3.50	11.83	1.39	26.19	0.154	1.41	73.46	0.51	26.54
56	3.80	21.4	1.76	3.13	12.97	1.44	26.75	0.147	1.22	69.31	0.54	30.69
57	5.32	25.4	1.54	3.25	8.95	0.97	22.40	0.100				
58	5.01	21.1	1.87	3.27	12.55	1.35	25.22	0.143				
59	4.21	34.2	1.15	1.69	5.26	0.59	24.45	0.114	0.75	65.10	0.40	34.90
60	12.21	29.9	1.90	3.62	11.75	1.36	25.57	0.121				
61	12.77	25.1	2.33	4.42	20.18	2.03	24.91	0.155				
62	11.08	29.4	1.78	4.09	12.31	1.45	25.22	0.117				
63	3.65	26.8	1.30	2.41	7.90	0.85	23.78	0.095	0.98	75.11	0.32	24.89
64	9.45	24.6	1.84	4.02	13.70	1.41	23.07	0.143				
65	12.78	25.2	2.07	3.97	15.32	1.72	26.38	0.124				
65 66	12.78 12.91	25.2 25.7	2.07 2.68	3.97 4.45	15.32 20.61	1.72 2.31	26.38 27.87	0.124 0.228				
65 66 67	12.78 12.91 11.91	25.2 25.7 29.0	2.07 2.68 1.82	3.97 4.45 3.75	15.32 20.61 11.73	1.72 2.31 1.43	26.38 27.87 26.56	0.124 0.228	1.37	75.58	0.44	24.42
65 66 67 68	12.78 12.91 11.91 10.40	25.2 25.7 29.0 32.8	2.07 2.68 1.82 1.59	 3.97 4.45 3.75 2.68 	15.32 20.61 11.73 8.35	1.72 2.31 1.43 0.87	26.38 27.87 26.56 22.64	0.124 0.228	1.37	75.58	0.44	24.42
65 66 67 68 69	12.78 12.91 11.91 10.40 1.89	25.2 25.7 29.0 32.8 18.2	2.07 2.68 1.82 1.59	3.97 4.45 3.75 2.68	15.32 20.61 11.73 8.35	1.72 2.31 1.43 0.87	26.38 27.87 26.56 22.64	0.124 0.228	1.37	75.58	0.44	24.42
65 66 67 68 69 70	12.78 12.91 11.91 10.40 1.89 7.23	25.2 25.7 29.0 32.8 18.2 27.3	2.07 2.68 1.82 1.59	 3.97 4.45 3.75 2.68 3.42 	15.32 20.61 11.73 8.35 12.32	1.72 2.31 1.43 0.87 1.16	26.38 27.87 26.56 22.64 21.62	0.124 0.228	1.37	75.58	0.44	24.42
65 66 67 68 69 70 71	12.78 12.91 11.91 10.40 1.89 7.23 12.48	25.2 25.7 29.0 32.8 18.2 27.3 30.7	2.07 2.68 1.82 1.59 1.62 1.95	 3.97 4.45 3.75 2.68 3.42 3.79 	15.32 20.61 11.73 8.35 12.32 13.39	1.72 2.31 1.43 0.87 1.16 1.60	26.38 27.87 26.56 22.64 21.62 27.20	0.124 0.228 0.160	1.37	75.58	0.44	24.42
65 66 67 68 69 70 71 71	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8	2.07 2.68 1.82 1.59 1.62 1.95 1.93	 3.97 4.45 3.75 2.68 3.42 3.79 4.56 	15.32 20.61 11.73 8.35 12.32 13.39 15.53	1.72 2.31 1.43 0.87 1.16 1.60 1.50	26.38 27.87 26.56 22.64 21.62 27.20 21.60	0.124 0.228 0.160 0.155	1.37	75.58 72.64	0.44	24.42 27.36
65 66 67 68 69 70 71 72 73	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4	2.07 2.68 1.82 1.59 1.62 1.95 1.93 2.37	 3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05	26.38 27.87 26.56 22.64 21.62 27.20 21.60 28.66	0.124 0.228 0.160 0.155 0.170	1.37 1.40	75.58 72.64	0.44 0.53	24.42 27.36
65 66 67 68 69 70 71 72 73 74	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23 12.53	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4 31.0	2.07 2.68 1.82 1.59 1.62 1.95 1.93 2.37 1.96	3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 4.61	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04 17.40	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05 1.63	26.38 27.87 26.56 22.64 21.62 27.20 21.60 28.66 21.76	0.124 0.228 0.160 0.155 0.170 0.167	1.37	75.58 72.64	0.44 0.53	24.42 27.36
65 66 67 68 69 70 71 72 73 74 75	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23 12.53 4.06	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4 31.0 24.6	2.07 2.68 1.82 1.59 1.62 1.95 1.93 2.37 1.96 1.62	3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 4.61 2.89	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04 17.40 11.04	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05 1.63 1.22	26.38 27.87 26.56 22.64 21.62 27.20 21.60 28.66 21.76 25.88	0.124 0.228 0.160 0.155 0.170 0.167 0.153	1.37 1.40	75.58 72.64	0.44 0.53	24.42 27.36
65 66 67 68 69 70 71 72 73 74 75 76	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23 12.53 4.06 9.73	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4 31.0 24.6 25.4	2.07 2.68 1.82 1.59 1.62 1.95 1.93 2.37 1.96 1.62 1.88	3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 4.61 2.89 4.11	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04 17.40 11.04 12.94	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05 1.63 1.22 1.71	26.38 27.87 26.56 22.64 21.62 27.20 21.60 28.66 21.76 25.88 28.71	0.124 0.228 0.160 0.155 0.170 0.167 0.153 0.175	1.37	75.58 72.64	0.44	24.42 27.36
65 66 67 68 69 70 71 72 73 74 75 76 77	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23 12.53 4.06 9.73 13.18	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4 31.0 24.6 25.4 25.4 28.8	2.07 2.68 1.82 1.59 1.62 1.93 2.37 1.96 1.62 1.88 2.08	3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 4.61 2.89 4.11 4.11	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04 17.40 11.04 12.94 16.47	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05 1.63 1.22 1.71 1.69	26.38 27.87 26.56 22.64 21.62 27.20 21.60 28.66 21.76 25.88 28.71 24.32	0.124 0.228 0.160 0.155 0.170 0.167 0.153 0.175 0.160	1.37	75.58 72.64	0.44	24.42 27.36
 65 66 67 68 69 70 71 72 73 74 75 76 77 78 	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23 12.53 4.06 9.73 13.18 13.26	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4 31.0 24.6 25.4 28.8 26.7	2.07 2.68 1.82 1.59 1.62 1.95 1.93 2.37 1.96 1.62 1.88 2.08 2.24	3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 4.61 2.89 4.11 4.11 4.29	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04 17.40 11.04 12.94 16.47 15.52	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05 1.63 1.22 1.71 1.69 1.85	26.38 27.87 26.56 22.64 21.62 27.20 21.60 28.66 21.76 25.88 28.71 24.32 27.28	0.124 0.228 0.160 0.155 0.170 0.167 0.153 0.175 0.160 0.155	1.37 1.40 1.79	75.58 72.64 79.68	0.44 0.53	24.42 27.36 20.32
 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23 12.53 4.06 9.73 13.18 13.26 13.26	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4 31.0 24.6 25.4 25.4 28.8 26.7 28.4	2.07 2.68 1.82 1.59 1.62 1.93 2.37 1.96 1.62 1.88 2.08 2.24 1.77	3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 4.61 2.89 4.11 4.11 4.29 4.03	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04 17.40 11.04 12.94 16.47 15.52 16.46	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05 1.63 1.22 1.71 1.69 1.85 1.55	26.38 27.87 26.56 22.64 21.62 27.20 21.60 28.66 21.76 25.88 28.71 24.32 27.28 22.55	0.124 0.228 0.160 0.155 0.170 0.167 0.153 0.175 0.160 0.155 0.138	1.37 1.40 1.79	75.58 72.64 79.68	0.44 0.53 0.46	24.42 27.36 20.32
 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23 12.53 4.06 9.73 13.18 13.26 12.69 11.45	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4 31.0 24.6 25.4 28.8 26.7 28.4 34.9	2.07 2.68 1.82 1.59 1.62 1.95 1.93 2.37 1.96 1.62 1.88 2.08 2.24 1.77 1.54	3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 4.61 2.89 4.11 4.11 4.29 4.03 3.46	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04 17.40 11.04 12.94 16.47 15.52 16.46 10.80	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05 1.63 1.22 1.71 1.69 1.85 1.55 1.31	26.38 27.87 26.56 22.64 21.62 21.60 28.66 21.76 25.88 28.71 24.32 27.28 22.55 26.37	0.124 0.228 0.160 0.155 0.170 0.153 0.167 0.153 0.160 0.155 0.138 0.121	1.37 1.40 1.79	75.58 72.64 79.68	0.44 0.53 0.46	24.42 27.36 20.32
 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23 12.53 4.06 9.73 13.18 13.26 12.69 11.45 10.72	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4 31.0 24.6 25.4 28.8 26.7 28.4 34.9 41.0	2.07 2.68 1.82 1.59 1.62 1.93 2.37 1.96 1.62 1.88 2.08 2.24 1.77 1.54 1.30	3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 4.61 2.89 4.11 4.29 4.03 3.46 2.53	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04 17.40 11.04 12.94 16.47 15.52 16.46 10.80 8.90	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05 1.63 1.22 1.71 1.69 1.85 1.55 1.31 0.99	26.38 27.87 26.56 22.64 21.62 27.20 21.60 28.66 21.76 25.88 28.71 24.32 27.28 22.55 26.37 25.29	0.124 0.228 0.160 0.155 0.170 0.167 0.153 0.175 0.160 0.155 0.138 0.121 0.107	1.37 1.40 1.79	75.58 72.64 79.68	0.44 0.53 0.46	24.42 27.36 20.32
 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23 12.53 4.06 9.73 13.18 13.26 12.69 11.45 10.72 13.04	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4 31.0 24.6 25.4 28.8 26.7 28.4 34.9 41.0 31.2	2.07 2.68 1.82 1.59 1.62 1.93 2.37 1.96 1.62 1.88 2.08 2.24 1.77 1.54 1.30 2.12	3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 4.61 2.89 4.11 4.29 4.03 3.46 2.53 3.75	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04 17.40 11.04 12.94 16.47 15.52 16.46 10.80 8.90 13.80	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05 1.63 1.22 1.71 1.69 1.85 1.55 1.31 0.99 1.79	26.38 27.87 26.56 22.64 21.62 21.60 21.60 21.76 25.88 28.71 24.32 27.28 22.55 26.37 25.29 29.93	0.124 0.228 0.160 0.155 0.170 0.153 0.167 0.155 0.138 0.121 0.107 0.223	1.37 1.40 1.79	75.58 72.64 79.68	0.44 0.53 0.46	24.42 27.36 20.32
 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23 12.53 4.06 9.73 13.18 13.26 12.69 11.45 10.72 13.04 13.33	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4 31.0 24.6 25.4 28.8 26.7 28.4 34.9 41.0 31.2 29.1	2.07 2.68 1.82 1.59 1.62 1.93 2.37 1.96 1.62 1.88 2.08 2.24 1.77 1.54 1.30 2.12 2.03	3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 4.61 2.89 4.11 4.29 4.03 3.46 2.53 3.75 4.48	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04 17.40 11.04 12.94 16.47 15.52 16.46 10.80 8.90 13.80 19.22	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05 1.63 1.22 1.71 1.69 1.85 1.31 0.99 1.79 2.12	26.38 27.87 26.56 22.64 21.62 27.20 21.60 28.66 21.76 25.88 28.71 24.32 27.28 22.55 26.37 25.29 29.93 20.93	0.124 0.228 0.160 0.155 0.170 0.167 0.153 0.175 0.160 0.155 0.138 0.121 0.121 0.123 0.123	 1.37 1.40 1.79 1.68 	75.58 72.64 79.68 82.89	0.44 0.53 0.46	24.42 27.36 20.32
 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23 12.53 4.06 9.73 13.18 13.26 12.69 11.45 10.72 13.04 13.33 12.60	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4 31.0 24.6 25.4 28.8 26.7 28.4 34.9 41.0 31.2 29.1 28.1	2.07 2.68 1.82 1.59 1.62 1.95 1.93 2.37 1.96 1.62 1.88 2.08 2.24 1.77 1.54 1.30 2.12 2.03 2.09	3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 4.61 2.89 4.11 4.29 4.03 3.46 2.53 3.75 4.48 4.26	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04 17.40 11.04 12.94 16.47 15.52 16.46 10.80 8.90 13.80 19.22 14.75	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05 1.63 1.22 1.71 1.69 1.85 1.55 1.31 0.99 1.79 2.12 1.81	26.38 27.87 26.56 21.62 21.60 21.60 21.76 25.88 28.71 24.32 27.28 22.55 26.37 25.29 29.93 26.80 27.75	0.124 0.228 0.160 0.155 0.170 0.153 0.175 0.160 0.155 0.138 0.121 0.107 0.223 0.189 0.160	 1.37 1.40 1.79 1.68 	75.58 72.64 79.68 82.89	0.44 0.53 0.46 0.35	24.42 27.36 20.32 17.11
 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23 12.53 4.06 9.73 13.18 13.26 12.69 11.45 10.72 13.04 13.33 12.60 2.94	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4 31.0 24.6 25.4 28.8 26.7 28.4 34.9 41.0 31.2 29.1 28.1 59.1	2.07 2.68 1.82 1.59 1.62 1.95 1.93 2.37 1.96 1.62 1.88 2.08 2.24 1.77 1.54 1.30 2.12 2.03 2.09 0.775	3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 4.61 2.89 4.11 4.11 4.29 4.03 3.46 2.53 3.75 4.48 4.26 0.51	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04 17.40 11.04 12.94 16.47 15.52 16.46 10.80 8.90 13.80 13.80 19.22 14.75 3.35	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05 1.63 1.22 1.71 1.69 1.85 1.31 0.99 1.79 2.12 1.81 0.28	26.38 27.87 26.56 22.64 21.62 27.20 21.60 28.66 21.76 25.88 28.71 24.32 27.28 26.37 25.29 29.93 26.80 27.75 23.25	0.124 0.228 0.160 0.155 0.170 0.153 0.167 0.155 0.160 0.155 0.138 0.121 0.107 0.223 0.189 0.160 0.061	1.37 1.40 1.79 1.68	75.58 72.64 79.68 82.89	0.44 0.53 0.46 0.35	24.42 27.36 20.32 17.11
 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 	12.78 12.91 11.91 10.40 1.89 7.23 12.48 12.39 13.23 12.53 4.06 9.73 13.18 13.26 12.69 11.45 10.72 13.04 13.33 12.60 2.94 2.68	25.2 25.7 29.0 32.8 18.2 27.3 30.7 31.8 25.4 31.0 24.6 25.4 28.8 26.7 28.4 34.9 41.0 31.2 29.1 28.1 59.1 26.6	2.07 2.68 1.82 1.59 1.62 1.95 1.93 2.37 1.96 1.62 1.88 2.08 2.24 1.77 1.54 1.30 2.12 2.03 2.09 0.775 1.14	3.97 4.45 3.75 2.68 3.42 3.79 4.56 4.24 4.61 2.89 4.11 4.29 4.03 3.46 2.53 3.46 2.53 3.75 4.48 4.26 0.51 2.37	15.32 20.61 11.73 8.35 12.32 13.39 15.53 17.04 17.40 11.04 12.94 16.47 15.52 16.46 10.80 8.90 13.80 19.22 14.75 3.35 7.36	1.72 2.31 1.43 0.87 1.16 1.60 1.50 2.05 1.63 1.22 1.71 1.69 1.85 1.31 0.99 1.79 2.12 1.81 0.28 0.71	26.38 27.87 26.56 22.64 21.62 21.60 23.66 21.76 25.88 28.71 24.32 27.28 22.55 26.37 25.29 29.93 26.80 27.75 23.25 20.82	0.124 0.228 0.160 0.155 0.170 0.153 0.175 0.160 0.155 0.138 0.121 0.107 0.223 0.189 0.160 0.061 0.075	1.37 1.40 1.79 1.68	75.58 72.64 79.68 82.89	0.44 0.53 0.46 0.35	24.42 27.36 20.32 17.11

88	13.42	30.0	2.62	4.01	16.24	2.32	34.06	0.256	2.18	83.15	0.44	16.85
89	12.73	31.4	1.95	4.19	16.48	1.67	23.93	0.155				
90	1.65	28.4	1.05	2.29	6.12	0.60	19.85	0.074				
91	6.63	23.2	1.79	3.56	11.40	1.30	24.89	0.140				
92	11.99	29.5	1.74	3.79	11.86	1.43	26.10	0.118				
93	13.14	31.7	2.21	3.93	14.76	1.82	28.67	0.201	1.68	76.24	0.53	23.76
94	11.60	30.1	1.72	4.01	11.95	1.39	24.68	0.108				
95	11.03	26.6	1.88	5.13	16.49	1.57	20.91	0.108				
96	11.23	29.6	1.72	4.29	13.05	1.56	25.69	0.118	1.25	72.76	0.47	27.24
97	5.96	22.6	1.75	3.25	10.42	1.29	27.15	0.145				
98	1.80	17.4										
99	2.41	26.3	1.32	3.24	10.05	0.94	20.30	0.064				
100	11.53	32.0	1.72	3.17	12.27	1.23	23.52	0.125	1.28	74.76	0.43	25.24
101	9.44	23.9	2.00	4.16	14.60	1.79	27.77	0.167				
102	6.67	19.8	1.75	3.49	11.54	1.35	25.85	0.138				
103	11.35	33.3	1.72	2.84	9.42	1.20	28.26	0.130	1.30	75.14	0.43	24.86
104	1.59	47.9	0.493	0.83	4.03	0.20	12.42	0.015				
105	5.61	23.8	1.63	3.25	12.38	1.50	28.41	0.123				
106	10.47	35.4	1.58	3.23	10.80	1.20	24.67	0.103	1.14	71.90	0.44	28.10
107	2.60	40.1	0.882	1.56	5.84	0.58	22.94	0.093				
108	3.28	25.0	1.29	2.59	7.41	0.85	23.91	0.091				
109	9.66	37.2	1.48	3.08	9.80	1.13	25.11	0.103	1.06	71.84	0.42	28.16
110	8.65	35.5	1.44	2.91	9.46	1.01	23.58	0.113				
111	2.98	26.2	1.42	2.56	8.51	1.02	26.62	0.130				
112	8.89	38.6	1.33	2.88	8.27	1.08	27.29	0.113				
113	8.60	34.5	1.50	3.21	10.40	1.08	22.80	0.120	1.06	70.57	0.44	29.43
114	3.98	27.4	1.33	2.93	9.82	1.04	23.57	0.103				
115	8.79	40.6	1.43	2.46	8.90	0.98	25.37	0.133	0.98	68.44	0.45	31.56
116	8.51	35.8	1.44	2.62	8.37	1.05	27.41	0.143				
117	1.95	16.6	1.21	3.43	18.02	1.54	22.11	0.093				
118	0.93	15.9	1.03	1.56	6.30	0.48	18.28	0.044				
119	4.81	29.1	1.65	2.34	9.22	1.30	33.31	0.211				
120	4.85	34.9	1.22	2.14	10.86	0.78	18.29		0.96	78.91	0.26	21.09
121	0.75	29.0	2.29	0.99	3.59	0.48	30.99					
122	1.18	9.7	1.68	3.59	13.17	1.13	19.83	0.096				
average	8.13	29.29	1.67	3.35	11.68	1.29	24.84	0.12	1.30	74.72	0.43	25.28
median	8.87	29.01	1.72	3.55	11.85	1.33	25.12	0.12	1.27	74.36	0.44	25.64
max	13.42	70.48	2.68	5.13	20.61	2.32	34.06	0.26	2.18	83.15	0.56	34.90
min	0.75	9.74	0.49	0.51	3.35	0.20	12.42	0.01	0.72	65.10	0.15	16.85
st.dev	3.92	8.34	0.39	0.92	3.73	0.45	3.90	0.04	0.30	4.02	0.09	4.02
n	122	122	120	120	120	120	120	115	34	34	34	34