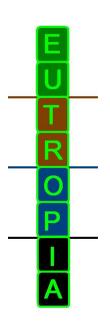
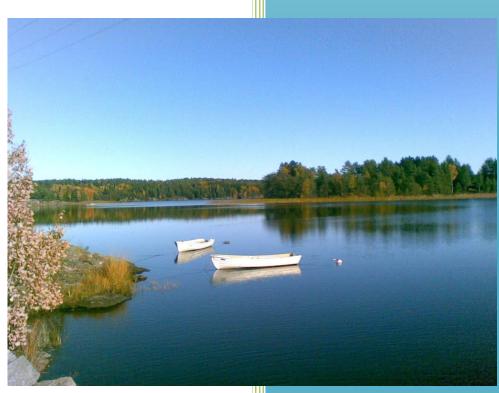
The role of particles and phosphorus bound to particles in eutrophication





Picture: Rolf David VOGT



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Abbreviations

DOC: Dissolved Organic Carbon

DOM: Dissolved Organic Matter

DOM-P: Phosphorus bound to Dissolved Organic Matter

DOP: Dissolved Organic Phosphorus

DRP: Dissolved Reactive Phosphorus

EUTROPIA: Watershed EUTROphication management through system oriented process modeling of

Pressures, Impacts and Abatement actions

IP: Inorganic Phosphorus

MBM: Molybdenum Blue Method

OP: Organic Phosphorus

PP: Particulate Bound Phosphorus

sUVA: Specific UV Absorbency

SAR: Specific Absorbency Ratio

TDP: Total Dissolved Phosphorus

TP: Total Phosphorus

UiO: Universite tet I Oslo (University of Oslo)

WFD: Water Framework Directive

Introducing the University of Oslo (UiO)

The University of Oslo (UiO) is Norway's leading institution of research and higher education. The University was founded in 1811 and is the oldest and largest Norwegian university. UiO is divided into eight faculties. There are 27 000 students and 7000 employees. About 4500 students are graduated each year, including more than 400 doctorates. Four scientific Nobel Prize winners (one in chemistry, one in physics, two in economics) and one Nobel Peace Prize have been affiliated with the UiO. (UiO, 2013a)

The Research group of Environmental analysis

This research group is part of the Department of Chemistry (Faculty of Mathematics and Natural Sciences) and combines expertise in analytical chemistry with challenges within specific environmental issues. The group studies the hydro-, bio- and geo-chemical processes that control the leaching and transport of chemicals between pools in biogeochemical cycles. The focus is on mechanisms governing the transport from soil to fresh water. More specifically, they are conducting research on eutrophication, the effects of climate change on water quality, heavy metals (especially Hg), and the properties and the role of natural dissolved organic matter (humus). (UiO, 2013b)

I - Introduction

This study is focused on the transport of phosphorus (P) with particles, in a watershed comprising a eutrophic lake. The study site is Vansjø (Fig. 1), situated near Moss, a city about 60km south of Oslo. Particles are the main transport (by absorption + adsorption) carrier for phosphorus into the lake. The fate and thus impact of the P associated with the particles is not clear.

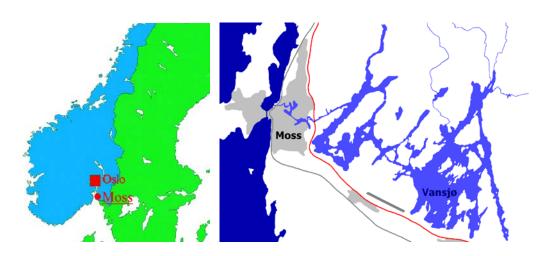


Figure 1: Map showing the location of studied site

The following two hypotheses were tested:

- In streams with high concentrations of free phosphate, the particles eroded from the soil may sorb more P from the water.
- The particle bound P can be released as free phosphate when the particles are exposed to the lake water with lower phosphate concentration.

Sampling was done in three different places around the lake Vansjø. All water samples and two sediments samples were characterized but only one (Hobøl) was used for the experiments. The three samples will be studied in the master project of Frøydis Meen Wærsted.

II - Bibliographic synthesis

1-Eutrophication and degradation of lakes

a) **Eutrophication**

Eutrophication is usually referring to water bodies with an increased loading of nutrients such as nitrogen or phosphorus. This increase leads to algae blooms, due to an increased growth of phytoplankton biomass.

Two types of eutrophication can be distinguished: natural eutrophication and cultural eutrophication. Eutrophication is a natural phenomenon in which all lake bodies accumulate nutrients, sediments, and plant materials, which eventually will slowly fill the lake basin. Cultural eutrophication, on the other hand, is a rapid anthropogenic-induced process resulting from enhanced nutrients inputs from diffuse sources such as agricultural fields and point sources, such as partially treated sewage (Lake Scientist, 2013).

b) Degradation of lakes

A subsequent impact of increased algal growth is a pH change and a loss of available oxygen (anoxia) below the photic zone (zone where there is enough light to produce the photosynthesis) where the dead alga biomass is mineralized by bacteria (Salameh and Harahsheh, 2011; Sharpley et al., 1994). These anoxic conditions render the water uninhabitable for fish and other aquatic organisms (Lake Scientist, 2013). The growth of algae and aquatic weeds induced with eutrophication, involves a reduction of the clarity of the water and of the light penetration.

<u>2-Phosphorus</u>

a) The phosphorus cycle

The P cycle (Fig. 2) differs from the other biogeochemical cycles because it does not include a gas phase and thus does not constitute a real cycle. The largest reservoir of phosphorus is in sedimentary rock. Weathering releases the P in the sedimentary rock to the soil and water. Plants assimilate the phosphate ions and the phosphorus can be transferred up through the food chain. Phosphate returns to the soil through decomposition and mineralization of dead biomass and faeces, including especially the excretion of urine. Released phosphate is efficiency re-assimilated or adsorbed to the soil, creating a very rapid internal cycling of P between the soil and the vegetation. Since phosphate is not a mobile anion, there is little free phosphate leaked out of the soils and into surface waters. Instead some phosphate bound to particles and incorporated into dissolved natural organic matter is transported to aquatic ecosystems.

Humans can alter the phosphorus cycle in several ways. An important pressure is through the use of fertilizers and poor agricultural management practices causing enhanced soil erosion. (Environmental Literacy Council, 2008)

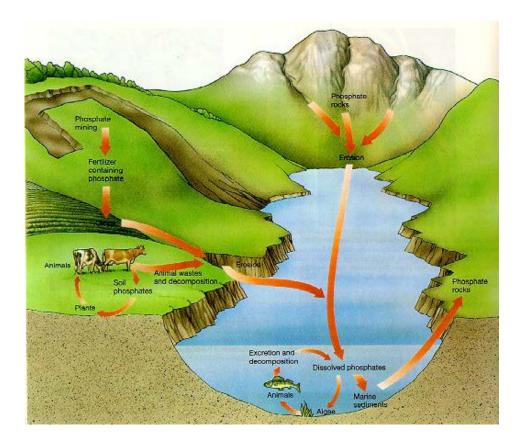


Figure 2: The phosphorus cycle

b) The role of particle transport of Phosphorus

Eroded sediment particles, especially from agricultural fields, are important in the transport of P to aqueous environments since the P load is mainly associated with the suspended sediments in rivers and streams (Stone and English, 1993). With increased runoff there is an increase in erosion and P transport, mainly as P bound to suspended particles P (Shigaki et al., 2007).

Increase transport of P is therefore mainly governed by factors that control the transport of particles. These factors influence the mechanisms causing the movement of particles within the catchment (Bechmann, 2005). Runoff is the main driver of transfer processes for nutrients and soil particles to water.

Runoff from forests and non-cultivated soils carries little sediment and TP. This is mainly due to that the plant cover of perennial species efficiently limits the soil erosion. The runoff is therefore generally dominated by dissolved organically bound P, released with the humic substances from the soil and plant material (Sharpley et al., 2003). Particle transport of P is mainly from tilled agricultural fields. This erosion is imposed by the soil texture and thus the particle size distribution of the soil. The small size soil particles (clay and silt) are more easily transported with the flowing water. Moreover, the small particles have larger surface areas with higher holding capacity of nutrients such as P. The eroded sediments contain therefore more fine particles (clay and silt) and higher total P (TP) content compared to the original surface soil (Øygarden, 2000) (Zhang et al., 2011).

c) Fractions of Phosphorus

In soils and sediments, phosphorus is a component of some primary minerals, occluded within the amorphous hydrous oxides of Fe and AI, and linked with organic component of the

sediment (VanLoon and Duffy, 2005). The term "orthophosphates" refers to the sum of H_3PO_4 , H_2PO_4 , H_2PO_4 , H_2PO_4 and PO_4 . They are reactive, bioavailable and easily sorbed onto particulate surfaces such as soil and sediments. (Sims & Sharply, 2005)

Three different fractions of phosphorus are measured in water samples during the experiments (Fig. 3 on the left): total phosphorus (TP), total dissolved phosphorus (TDP) and dissolved reactive phosphorus (DRP).

TP takes into account all the Phosphorus present in the water, either in dissolved or particulate form. Dissolved forms are determined after a filtration with nitrocellulose 0,45µm filters.

Other important P fractions are determined (Fig. 3 on the right) by difference between these measured parameters:

Particle bound phosphate PP = TP - TDP

Phosphate bound to dissolved organic matter DOM-P = TDP - DRP

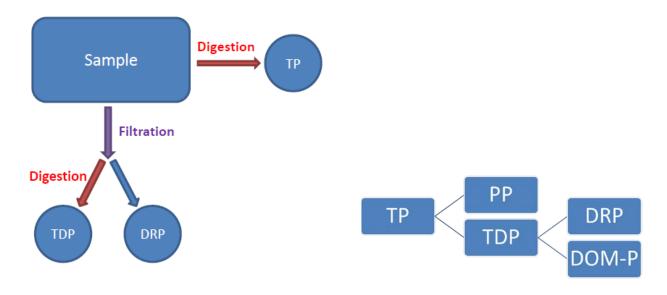


Figure 3: Phosphorus fractions measured (on the left) and different P fractions measured or determined by difference between measured parameters (on the right)

The pools of total phosphorus and inorganic phosphorus were determined in the soil and sediment samples used in the experiments. The P pools were extracted from the soils and sediments using 12M sulphuric acid according to the method of Møberg and Petersen (1982). Total phosphorus is extracted from a pre-ignited sample while inorganic phosphorus is extracted directly from the raw sample. The method of Møberg and Petersen (1982) is explained in the appendix n°2.

Organic phosphorus was deducted by difference between the total and inorganic pool of P:

Organic P = Total P - Inorganic P

3-Study area: the Lake Vansjø

Vansjøis the main lake (36km²) in the Morsa catchment (690km²) situated in the South-East of Norway. The Morsa watershed is used as a pilot case study for the implementation of the Water Framework Directive (WFD) in Norway. Only 3-4% of the land area in Norway is used for agriculture (Hauken and Kværnø, 2013). In Morsa, about 15% of the catchment area is agricultural land and is consequently one of the most cultivated watersheds in Norway. The remaining 85% of the catchment area is comprised mainly of forest. The lake is divided into two main basins: Storefjorden (the largest part) and Western Vansjø (Vanemfjorden, the smallest part). The anthropogenic input of total phosphorus (of which 76% is from agriculture) to Lake Vansjø from the entire catchment is estimated to account for 75 % of the total loading. (Solheim et al. 2001). Vanemfjorden has had serious problems with blooms of toxic blue-green algae. (Bjørndalen et. al 2007).

Samples of stream water and sediments were collected in Dalen, Støa and Hobøl (Fig.4) on April 18th, 2013, a day with a relatively high discharge flow.

Dalen (North-West) and Støa (South-East) are two small sub-catchments of Vanemfjorden (Western Vansjø).

Dalen is a small forested catchment, located in the north-western part of Vanemfjorden, with an environment believed to be generally representative for most of the forested area of the Hobøl-Vansjø catchment (Mohr, 2010; Desta, 2013). The small catchment above the stream water sampling point is approximately 556000m². Of this area 89% is forested area and the remaining 11% are bogs in the valley bottom. At the time of sampling there was still ice bellow the water in the Dalen stream. Dalen is generic of an Al rich and acidic low order stream draining forested subcatchments with shallow acid sensitive soil (Shekobe, 2012).

Støa is a 100% agricultural catchment, while Hobøl drains a large catchment comprised of a mix of forest and agricultural land. (Parekh, 2012)

Støa represents a P-loaded and pH neutral agricultural stream. (Shekobe, 2012)

Hobøl (Hobølelva) is the largest river in the catchment area and contributes about 40% of the total discharge into the lake Vansjø, draining into Storefjorden (Skarbøvik & Bechmann, 2010).

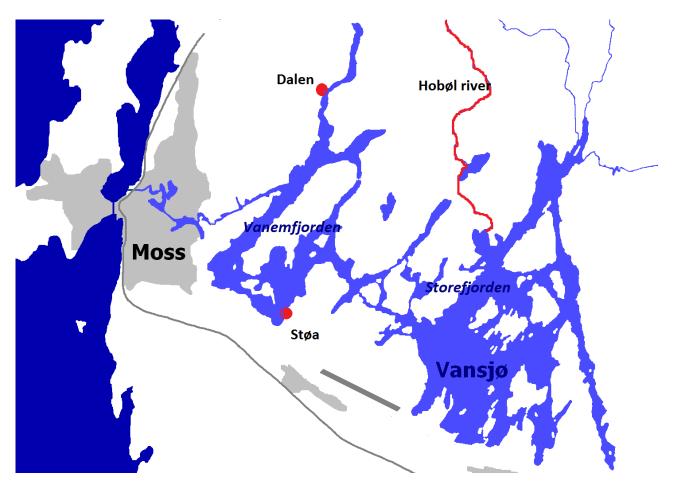


Figure 4: Map showing the different places of sampling: Hobøl, Dalen and Støa

4-Eutropia project

The European Union Water Framework Directive (WFD) has been adopted by the Norwegian government. This directive demands a good surface water status and that the condition of all water reserves should not have large deviations from their natural condition. This requires that scientists have to assess the original and the present state of the environment and be able to predict the future changes. The EUTROPIA project (Watershed EUTROphication management through system oriented process modelling of Pressures, Impacts and Abatement actions) was an interdisciplinary research project funded by the Research Council of Norway (project no. 19028/S30) in 2009, with the aim to address the following knowledge needs. The development of sampling and laboratory methods for P, the catchment processes-(influence of land-use and hydrology on nutrient fluxes into aquatic systems), the modelling of catchment and lake processes, the integrated uncertainty analysis of cost-effectiveness of measures using Bayesian belief network methodology and the Societal response are studied. (UiO, 2009)

III - Material and methods

1 - Separation of water and sediments

Two 25L containers were filled with samples of stream water mixed with sediments vacuumed up (from each of the three sites Dalen, Støa and Hobøl). These samples were let to rest in a dark cooling room allowing the particles to sediments. The water was subsequently carefully pumped into a 50L container without disturbing the sediments. The sediments were rinsed out and put in plastic boxes. Sodium azide was added as a biocide to the different samples (water and sediments) to avoid the development of bacteria, which would change the distribution of P fractions in the sample.

2 - Characterization of the samples

The three different samples were characterized to have an idea about their composition and their characteristics. Only Hobøl water and sediments were used for the experiments.

Characterization of water

Parameter	Standard/Method		
Total suspended solids	ISO 11923 (1997)		
Proxy for DOM	UV-Vis 254, 400 and 600nm		
DOC	NS-EN-1484(1997)		
рН	ISO 10523 (2008)		
Conductivity	ISO 7888 (1985)		
P fractions	UV-Vis spectrophotometry		
	ISO 6878 (2004)		

Table 1
Chemical and physical parameters and references to methods used to characterize the water samples used in the experiments

Characterization of soil and sediments

Parameter	Standard/Method
P fractions (Total, Inorganic and Organic)	Møberg and Petersen's method (1982)
Loss on ignition	Krogstad's method (1992)

Table 2
Chemical and physical parameters and references to methods used to characterize the soil and sediments samples used in the experiments

4- Determination of the orthophosphates concentration by the Molybdate Blue Method

Analysis procedure:

The concentration of orthophosphate in water and soil extract was determined according to the ISO standard ISO6878.

This method is generally used for the determination of phosphate at low concentrations. It is based on that the orthophosphate reacts with ammonium molybdate in acid solution, producing a yellow heteropolyacid. This complex changes into a blue complex in the presence of a reductant (ascorbic acid). The molybdate solution contains antimony, which participates in the formation of the P-Mo complex, retards the reduction and stabilizes the colour of complex. (Denigès, 1920)

The procedure is described in the Appendix n°1.

<u>5 - Study of sorption and desorption of phosphorus onto particles</u>

To modelize a natural aquatic process with sediments going from a water with high phosphorus concentration to a water with a lower concentration of phosphorus, the following experiment was done:

Procedure:



Figure 5: Procedure used to do the experiments

Sediment samples (corresponding to 200mg dry weight, taking into account the water content) were mixed with 2L of water and added increments of orthophosphate. The slurry was then mixed (see appendix n°3).

12 to 14 hours shaking: The shaking table turned out to not produce sufficient mixing of the sample. A magnetic stirrer was therefore applied for the remaining experiments. In the mix of Hobøl water and sediment with $50\mu gP/L$, the stirring system caused the temperature in the sample to increase to $33^{\circ}C$. To avoid this increase of temperature, the Erlenmeyer containing the water and the sediments was isolated from the magnetic stirrer with a piece of Polystyrene, and the shaking time was reduced to 8 hours for practical reasons for the last experiment (Hobøl + $100\mu gP/L$). After mixing, the samples were to set to rest for at least 8 hours so that the particles could sediment.

The water was separated from the sediments using a pipette, to avoid disturbing the sediments at the bottom of the Erlenmeyer flask.

To produce a Hobøl water sample with low concentration of phosphorus, 10mL of a solution of aluminium (2g/L KAl(SO_4)₂) was added to the 2L of water. At the sample pH, the aluminium precipitated as oxy-hydroxides and co-precipitated the phosphate. The precipitates were removed by filtration with $0.45\mu m$ nitrocellulose filters.

The sediments enriched in phosphate were mixed with the water depleted of phosphate and stirred for 12 to 14 hours.

Aliquots of 100mL were taken each time (t=0;1;2;4;8;16;24;48 hours) for measurements of conductivity, pH, TP, DRP and TDP. The samples of water for phosphorus measurements (TP, TDP and DRP) were preserved prior to the MBM analysis by adding 0,20mL 4M H_2SO_4 .

Combinations of water and sediments types studied:

Particles	Water
Hobøl	Hobøl
Illite	Type I water
Kaolinite	Type I water

Table 3: Particles and types of water used for the experiments

Illite and kaolinite are used as standard materials. Illite is found in the Hobøl-Vansjø catchment, and kaolinite is common clay that is found many places in the world. These two clays differ in that illite is a 1:2 layer clay while kaolinite is a 1:1 layer clay. The numbers denote the relative number of tetrahedral silicate layers relative to the octahedral aluminium hydroxide layers.

IV - Results

1 - Characterization of samples

a) Characterization of waters samples

Here are the results obtained for the characterization of the three water samples.

	Hobøl	Støa	Dalen
рН	6,8	7,2	4,9
Conductivity (μS/cm)	81	124	31,70
Alkalinity (mg/L)	0,23	0,83	-
TP (μgP/L)	80	171	5,2
DRP (µgP/L)	48	126	2,2
TDP (µgP/L)	66	160	3,7
DOC (mg/L)	10,1	11,9	16,8
Total Suspended solids (mg/L)	4,0	4,0	0,4
UV 254	0,519	0,452	0,623
UV 400	0,052	0,064	0,070
UV 600	0,007	0,007	0,006

Table 4: Chemical and Physical parameters measured for the three samples (*approximations)

The three water and sediment samples are different, both in their origin (forest, a mixed land-use and agricultural land) and their physiochemical characteristics. The P concentrations in Dalen, Hobøl and Støa are low, intermediate and high, respectively.

Dalen sample is acid with pH lower than 5,5. This acidity is produced by the high concentration of weak humic acids associated with a high DOC. The water from Hobøl and Støa has higher pH due to more readily weatherable minerals along with liming of the agricultural fields. This provides the soils with higher base saturation (Desta, 2013). At pH below 5,5, the alkalinity is assumed below detection limit while there may be significant concentrations of aluminium. The level of alkalinity was therefore only measured in the water from Hobøl and Støa, and aluminium fractions would have been determined in Dalen water.

Dalen DOC is the highest of all the samples. Organic Carbon is the result of decomposition of plants and animal material. Dissolved Organic Carbon can be defined as the organic matter that is able to pass through a filter (0,45 μ m here). Dalen is a forested area, consequently DOC is higher.

The Total Suspended Solids concentration is lower in the Dalen sample. That could be explained by low erosion. Støa and Hobøl have a lot of particles due to high erosion. The soil in Dalen is covered by forest and is not easily eroded away, giving low particle concentrations in the water.

The absorbencies measurements at $\lambda(254, 400 \text{ and } 600 \text{nm} \text{ along with the concentration of DOC})$ allow to determine the specific UV Absorbency (sUVA = A_{254}/DOC), Specific Absorbency Ratio SAR (= A_{254}/A_{400}) and the ratio E4:E6 (= A_{400}/A_{600}).

These parameters provide information about the physicochemical characteristics of the Dissolved Organic Matter (DOM) in the water. Conjugated double bonds are the chromophore responsible for the absorbency. These bonds are omnipresent in DOM as they are inherent in the aromatic rings, constituting the framework of the humic substances. Larger and longer chains of conjugated double bonds absorb at higher wavelengths such as 400 and 600nm.

	Hobøl	Støa	Dalen
sUVA	51	38	37
SAR	10,0	7,1	8,9
E4:E6	7,4	9,1	11,7

Table 5: Characterization of the Dissolved Organic Matter in the three samples

sUVA shows the degree of aromaticity of DOM and varies commonly between 20 and 30. The sUVA values are in the range of what has been measured previously in the streams, though the value for Dalen is relatively low compared to previous measurements. The sUVA values indicate that the DOM material is rather aromatic, especially the material from the Hobøl river.

SAR reflects average molecular weight. The higher is SAR value, the lower the Mw is, implying that average molecular weight of the DOM in the Hobøl river is smaller than in Dalen and Støa.

E4:E6 is a simple indicator of differences in DOM type and is usually between 3 and 15. This value indicates the relative amounts of humic and fulvic acids in the DOM. Fulvic acids have generally ratio between 8 and 10 (Vogt). This implies that the DOM from Støa contains mainly fulvic acids. As humic acids have low ratios (<5) the data indicate that none of samples contain mainly humic acid. DOM from Hobøl contains a mixture of the two types of acids. Summing up the DOM quality parameters indicate that the DOM from Hobøl is relatively aromatic, low Mw mixture of humic and fulvic acids. The Støa material is of relatively large size and the Dalen DOM consists mainly of fulvic acids which are less aromatic.

The water chemistry in these three streams is found to span most of the variation found in the tributaries to Vansjø (Parekh, 2012). This was the aim of the selection of sampling sites, which thus was deemed successful. The experiments were designed to see if the adsorption and desorption of phosphorus to particles are different between these sites. If no difference is observed one can conclude that the processes are uniform throughout the watershed. If there are differences then this factorial design may facilitate an identification of important governing factors.

b) Characterization of soils samples

Here are the results obtained for the characterization of Hobøl and Støa sediments samples.

	Hobøl	Støa
TP (mg/g)	3,84	4,11
IP (mg/g)	2,93	3,11
OP (mg/g)	0,91	1,00
Loss on ignition (%)	5,36	5,93

Støa sediments contain more phosphorus than Hobøl sediments. The inorganic and organic fractions are also more important. However, Hobøl and Støa have almost the same distribution of phosphorus: 76% of inorganic phosphorus and 24% of organic phosphorus. These sediments have the same origin. The differences obtained for phosphorus concentrations are perhaps an adsorbed part.

Loss on ignition reflects the organic matter in the sediments then, there is less organic matter in Hobøl sample. The value of this parameter is higher for Støa sample, which also has higher concentrations of phosphorus.

3 – Adsorption/Desorption experiments

The experiment design was illustrated in Figure 5. For the adsorption experiment, Hobøl water samples were spiked with 0, 50 and $100\mu gP/L$ of free phosphate and mixed with 100mg/L of sediments from Hobøl. The samples were left on a stirrer for 12 to 14 hours in order to ensure adsorption equilibrium. Then, the particles were allowed to sediment for at least 8 hours.

For the desorption experiment, water from Hobøl was depleted of DRP by precipitation with aluminium, and PP was removed by filtration through a 0,45µm membrane filter (Part III-5). The sediments from the adsorption experiment (enriched in adsorbed phosphate) were mixed with the depleted water in an Erlenmeyer flask set on a magnetic stirrer. Desorption of phosphorus was followed over time by measuring P fractions in the water at increasing time intervals. Time zero corresponds to the time when the water depleted of DRP is added to the particles.

Desorption experiments

Note: The water depleted of DRP with aluminium has a DRP concentration between 10 and $14\mu gP/L$. "Aluminium water" was prepared adding 10mL of the solution 2g/L KAI(SO_4)₂.

Hobøl sediment spiked with 0μgP/L mixed with depleted Hobøl water (Hobøl + 0μgP/L)

TDP looks stable around $17\mu gP/L$. DRP looks stable too, around $10\mu gP/L$, that corresponds to the DRP concentration in the water depleted of DRP (after the aluminium treatment). Looking at just these results, it could be concluded that no phosphorus is desorbed of the sediments when they are exposed to a similar water chemistry. But, if distributions of TP and TDP (see fig15 and fig16 in the appendix n°4) are compared, it is found that the PP concentration increased from 17,5% of the TP in the original Hobøl water to 65-70% in the experiment Hobøl water, and the DOM-P concentration from 27% of TDP to 35-40%.

The concentrations of phosphorus fractions (TP, TDP and DRP) remain constant over time in a mixture of only water from the Hobøl stream and its sediments. The exception is at one point (t=1h) with TP and DRP outliers. An increase in TP must be due to a contamination during the sampling. These data are therefore omitted from the further discussion.

This implies that the PP being transported to the lake is a potential source of TDP. An increase of PP in the solution is likely due to suspended fine sediment particles that have not settled within 2-3 hours. This sedimentation time (after the time of adsorption) was therefore increased from 3 to 12 hours, for the two following experiments. The very high fraction of PP supports the theory of that not all of the clay and silt fraction was allowed to sediment before samples were taken for analysis. It can be concluded from this experiment that the phosphorus originally on the particles is desorbed when exposed to water depleted of DRP. The desorption looks instant, that was showed with constant concentrations measured over time. Phosphorus that has been bound to particles is possible to desorb.

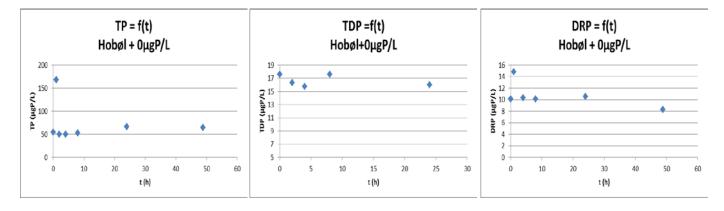


Figure 6: Results obtained for the experiment Hobøl + 0µgP/L

Hobøl sediment spiked with 50µgP/L mixed with depleted Hobøl water (Hobøl + 50µgP/L)

The TP concentration remained rather constant, though the TDP and DRP concentration may appear to be increasing with the time (if one ignores points at t=8; t=24 and t=48). The TDP increases from around $20\mu gP/L$ to about $25\mu gP/L$ after 20 hours. This is basically recaptured in the DRP fraction as an increase from approximately $8\mu gP/L$ to around $16\mu gP/L$.

The increase in TDP from 17 to $25\mu gP/L$, shows an increase compared to the un-spiked sediments (concentration stable around $17\mu gP/L$). The increasing concentration of phosphorus measured is likely phosphorus desorbed after to be adsorbed to the sediments in the solution which was added $50\mu gP/L$.

Assuming a constant TP, the average value is around $110\mu gP/L$. This is more than a doubling compared with the background level of $50\mu gP/L$ found in the previous experiment. This increase is not accounted for by any similar increase in TDP and must therefore be due to an increase in PP. Then, the particles in suspension in the solution during the experiment are more loaded with P, due to the spiking with $50\mu gP/L$ in the preceding adsorption step.

Considering the distribution of TP (Fig. 17 appendix n°4), PP constitutes about 80%, a little higher than the PP fraction in the previous experiment. The distribution of TDP is completely different, with much more DOM-P: this concentration decreases from 80% to 60% of TDP, compared to a stable concentration around 40% of TDP for the first experiment. It is probably due to the mixing (magnetic stirring for this experiment, a shaking table was used for the first experiment) and the bigger time of sedimentation before the addition of water depleted of DRP.

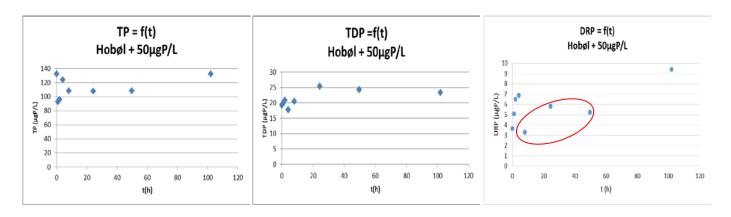


Figure 7: Results obtained for the experiment Hobøl + 50µgP/L

Hobøl sediment spiked with 100μgP/L mixed with depleted Hobøl water (Hobøl + 100μgP/L)

The two last points in all fractions are too high as it is reasonable that the TP increases. The reason for this is likely P contamination from the filter paper. For these samples, filter paper from a new box of nitrocellulose filters was used. (This is implied by that the blank samples using these new filters were found to give ten times higher P concentration than what was found in previous measurements) More explanations about this contamination can be found in the appendix n°5.

The TP increased from about $110\mu gP/L$ using sediments spiked with $50\mu gP/L$ to $125\mu gP/L$ in this experiment where the sediments were spiked with $100\mu gP/L$. Assuming the same amount of suspended material as in the previous experiment, this increase in TP must be due to increase P adsorption by the higher P concentration during the adsorption step. That the increase is only $15\mu gP/L$, and about $5\mu gP/L$ of this increase is accounted for by TDP, implies that there is not a large additional increase in the

amount of P adsorbed to the particles when doubling the concentration of labile phosphate from 50 to 100µg P/L. This may be due to a saturation of available sites for phosphorus adsorbed on the particles. Additional adsorption experiment with a higher addition of phosphorus would be necessary in order to produce a sorption isotherm.

TDP concentration increased from 25 to a stable concentration of $30\mu gP/L$, and DRP concentration from 15 to a stable concentration of $20\mu gP/L$. TDP and DRP concentrations have about the same growth. That is normal because DRP is a part of TDP. Then, the DOM-P concentration calculated from TDP and DRP looks constant around 8 and $10\mu gP/L$. Thus, the phosphorus added is not adsorbed into the Organic Matter. Compared to the background of $17\mu gP/L$ the TDP increased by only $13\mu gP/L$. This is about a doubling of the increase found for the sediments spiked with $50\mu gP/L$, yet still rather low considering the amount of phosphorus the sediments were spiked with. This demonstrates that phosphorous sorbed to the particles due to mixing with elevated P concentrations are only partly remobilized when exposed to water with low phosphate concentrations.

DRP represents about 60-70% of TDP, that is closer than the distribution obtained in the first experiment.

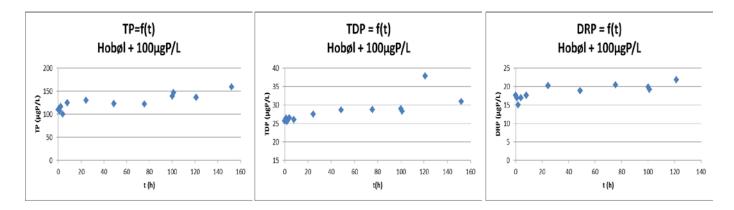


Figure 8: Results obtained for the experiment Hobøl + 100µgP/L

Illite + 0µgP/L

Formula illite: $K_{0,65}Al_{2,0}[Al_{0,65}Si_{3,35}O_{10}](OH)_2$

Results obtained look very strange. No phosphorus was added and there is normally no phosphorus bound to illite and inside illite, but the TP measured is between 31 and 33 μ gP/L. Perhaps the material used is not pure and contains apatite, which contains phosphate [formula: Ca₅(PO₄)₃(OH,Cl,F)].

It can be considered a DRP concentration stable around 4µgP/L. No desorption is observed.

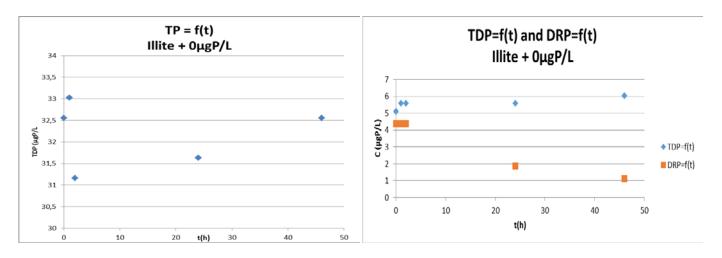


Figure 9: Results obtained for the experiment Illite + 0µgP/L

Kaolinite + 0μgP/L

Formula kaolinite: Al₂(Si₂O₅)(OH)₄

Results obtained for this experiment look strange too. The TP measurement is even higher. Perhaps the kaolinite used for the experiment is not pure and contains apatite. DRP is zero concentration (except for one point), that seems to be normal because no phosphorus was added. No phosphorus is contained in the kaolinite then no desorption has to be observed.

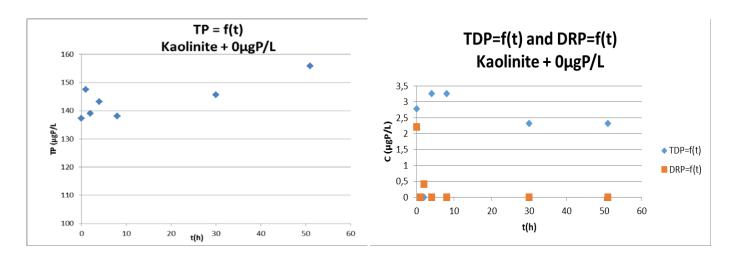


Figure 10: Results obtained for the experiment Kaolinite+0µgP/L

Conclusion

These experiments were intended to assess changes in phosphorus fractionation when a stream with a high concentration of phosphorus and containing particles drains into an aquatic environment with a lower concentration of phosphorus. It is difficult to interpret exactly what happens in reality as the experimental conditions, such as temperature, pressure etc., and the mixture cannot reflect the real in-situ conditions.

It would seem that free phosphate in a stream with high free phosphate concentration is adsorbed onto the particles and desorbed when the water arrives in an aquatic area with a lower concentration of free phosphate. Then, transport of phosphorus contributes to eutrophication on this way.

The results indicate that already with a spiking of 100µg P/L, there is less adsorption to the particles than at lower spiking concentrations. This implies that the phosphate adsorption at these concentrations is not linear and that we therefore are approaching or have reached the limit of adsorption, at which the particles are saturated with phosphorus. More experiments, with higher concentrations of added phosphorus, will be necessary to construct a sorption isotherm enabling a clarification of this issue.

More experiments will also be necessary to compare different types of water and with higher (Støa) or lower concentration (Dalen) of phosphorus.

Since it is difficult to determine concentrations of phosphorus lower than 2µgP/L with the molybdenum blue method, other analytical technique, such as liquid scintillation counting, would be needed to be employed in order to study the mechanisms in samples with lower concentrations (Dalen).

Appendix n°1: The Molybdenum Blue Method

a) Preparation of the calibration solutions

Mother solutions:

S1: 250 mg P /L

<u>Preparation:</u> Weigh 0,573g of Na₂HPO₄. Put in a 500mL volumetric flask and complete until the mark with type I water 8ultrapure water).

S2: 10 mg P/L

<u>Preparation:</u> Take 20,0mL of S1 with a volumetric pipette. Put in a 500mL volumetric flask. Complete the flask until the mark with ultrapure water.

S3: 100 mg P/L

<u>Preparation:</u> Take 200,0mL of S1 with a volumetric flask. Put in a 500mL volumetric flask. Complete the flask until the mark with ultrapure water.

S4: 250μgP/L

<u>Preparation:</u> Take 1,00mL of S1 with a micropipette. Put in a 1L volumetric flask. Complete the flask until the mark with ultrapure water.

Preparation of the Orthophosphate solutions (acidified)

- Take a volume V_m of mother solution (see the following tables) in a 1000mL volumetric flask.
- Add 10mL of H₂SO₄ 4M and complete the flask until the mark with Type I water.

Range 1:

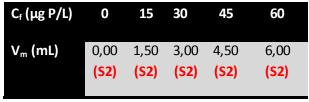


Table 6: Preparation of the calibration solutions (range 1)

Range 2:

C _f (µg P/L)	60	150	300	400	500
V _m (mL)	6,00 (S2)	1,50 (S3)	3,00 (S3)	4,00 (S3)	5,00 (S3)
	(32)	(33)	(33)	(33)	(33)

Table 7: Preparation of the calibration solutions (range 2)

Range 3:

Cf (µg P/L)	0	2	4	7,5	10
Vm (mL)	0,00	8,00	16,00	30,00	40,00
	(S4)	(S4)	(S4)	(S4)	(S4)

Table 8: Preparation of the calibration solutions (range 3)

For each series of analyzes, the adequate calibration solutions are measured. The following table shows some results obtained, but the equations were not exactly the same each time.

Range	Equation	R²	Detection Limit (µgP/L)	Quantification Limit (μgP/L)
1	A = 0,00305C+0,00280	0,99730	6,4	21,3
1 digested	A = 0,00302C+0,01528	0,99849	5	15
2	A = 0,00332C-0,01606	0,99996	64	73
2 digested	A = 0,00309C+0,00982	0,99982	72	100
3	A = 0,00215C+0,00638	0,98811	1,5	5
3 digested	A = 0,00294C+0,00604	0,99622	0,7	2,3

Table 9: Calibration curves equations and limits (of detection and of quantification) determined statistically

b) Preparation of the reagents

<u>Ascorbic acid solution:</u> Dissolve 10±0,5g of ascorbic acid in 100mL of Type I water.

Molybdenum solution:

 $6,5\pm0,25g$ of ammonium heptamolybdate tetrahydrate are dissolved in a 50mL volumetric flask. (Mo)

0,175±0,025g of antimony potassium tartrate hemihydrate are dissolved in a 50mL volumetric flask. (Sb)

The solution (Mo) is added to 150mL of sulfuric acid 9M with a continuous stirring (magnetic stirring). The solution (Sb) is added and the solution is mixed well.

c) <u>Procedures to determine the orthophosphate concentrations: the Molybdate Blue Method (according the ISO6878)</u>

Reminder: Filtration necessary with nitrate cellulose filter 0,45μm for DRP and TDP samples.

• Without oxidation/digestion (determination of DRP)



Figure 11: MBM procedure to determine DRP

With oxidation/digestion (determination of TP and TDP)

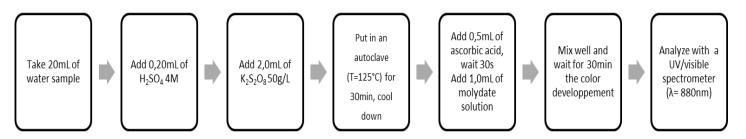


Figure 12: MBM procedure to determine TP and TDP

The UV/visible analysis is done using a 5cm long cuvette.

Appendix n°2: The Møberg and Petersen 's method (1982)

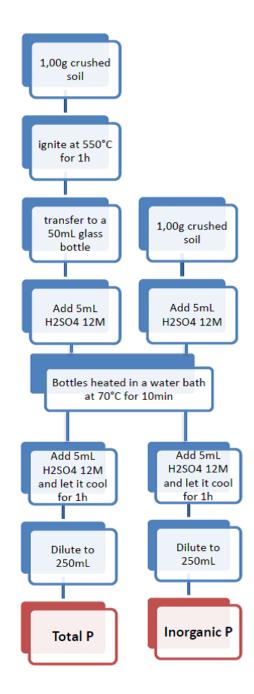


Figure 13: Method of Møberg and Petersen for the determination of P fractions in the soils and the sediments

Once this procedure done, the solutions obtained are filtrated and diluted by 25. The MBM is used to determine the phosphorus concentrations.

Appendix n°3: Determination of water content of the sediments

Method:

Weigh an empty and dry container. Add sediments. Weigh again to know the amount of wet sediments in the container (mass m_1). Put in the oven for duration of 5 hours. Wait until the sample cools down. Weigh again to know the amount of dried sediments (mass m_2). Then, the amount of water in the sediments is the difference between m_1 and m_2 .

Results:

	Hobøl	Støa
Water content	64%-66%	50%-68%

Table 10: Water content determined for Hobøl and Støa samples (2 determinations)

This determination allows knowing how much wet sediments take to have 200mg of sediments for the experiment. Then, for Hobøl, 555mg are necessary and 400mg for Støa.

<u>Appendix n°4: distributions of fractions of TP and TDP for Hobøl experiments</u>

TP	TDP	DRP	PP	DOM-P
80	66	48	14	18

Table 11: P fractions of Hobøl water (µgP/L)

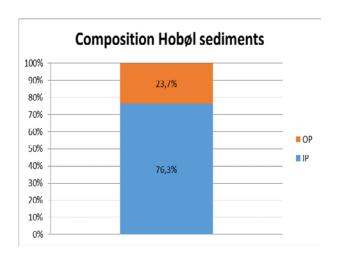


Figure 14: Distribution of phosphorus in the Hobøl sediments



Figure 15: Distributions for the Hobøl water

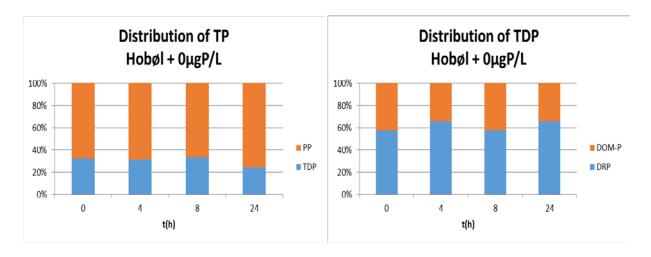


Figure 16: Distributions for the experiment Hobøl + 0μgP/L

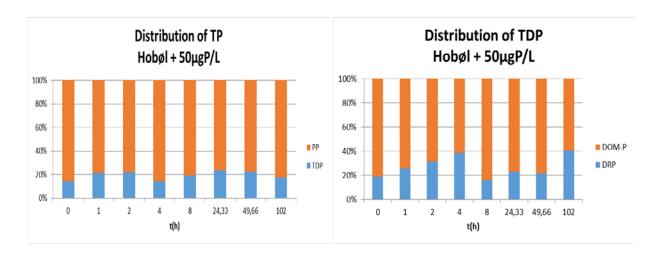


Figure 17 : Distributions for the experiment Hobøl + $50\mu gP/L$

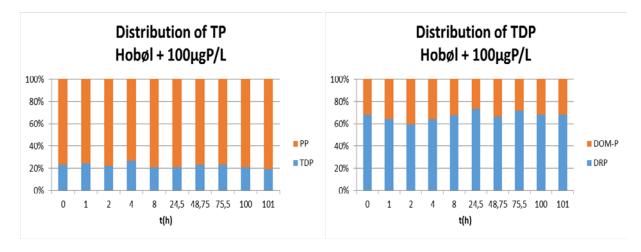


Figure 18: Distributions for the experiment Hobøl+100 μ gP/L

Appendix n°5: Test of contamination with different filter papers

Samples	Absorbance measurement sample n°1	Absorbance measurement sample n°2
Type I Water not filtrated	0,0036	0,0043
Type I water passed through the filter equipment without filter paper	0,0077	0,0063
Type I water filtrated with nitrocellulose filters with reagents	0,0216	0,0525
Type I water filtrated with nitrocellulose filters without reagents	-0,0007	
Type I water filtrated with acetate cellulose filters	0,0059	0,0043
Type I water filtrated with glass microfiber filters	0,0038	0,0029

Table 12
Results tests of contaminations with several types of paper filters.

Conclusions of these measurements:

These data indicate clearly that the contamination does not come from the filter equipment (the absorbance measured is the same "magnitude" (A#10⁻³) or the reagents (zero absorbance).

The absorbance measured on the water filtrated with nitrocellulose filters has a magnitude ($A#10^{-2}$) ten times higher than the absorbance measured ($A#10^{-3}$) with the other filters (acetate cellulose and glass microfiber).

These data allow concluding there is a contamination with the nitrocellulose filters. The contamination is random (the values measured [0,0216 and 0,0525] have the same magnitude but are very different). Another measurement [A=0,034] can confirm that hypothesis.

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