Fate of Phosphorus and Nitrogen in sediment deposited on two Danish floodplains: laboratory experiments

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Preface

This report describes the experiments realised during my internship, at the National Environmental Research Institute, in Silkeborg, Denmark, from the 7th April 2008 to the 22nd of August 2008, in order to obtain a “Master 2 professionnel Géohydrosystème Continentaux en Europe” from the University of Tours, France.

I am very thankful to Carl Christian Hoffmann for supervising my work and giving me the opportunity to come at NERI. I wish also to thank the director of the stream group, Brian Kronvang for his comments on my work and for finding me a place where to live. I am grateful to Dorthe Nedergaard for her assistance in the laboratory procedure and for answering many of my questions about laboratory analyses. I want to give a special thank to Tommy Silberg, Marlene Skjærbæk and Uffe Mensberg for their help in the lab, and to Tinna Christensen for the design of the cover. Special thank as well to the director of the department, Kurt Nielsen, for his enthusiasm and his permanent good mood.

I want to thank all my colleagues from the freshwater department especially my internationals colleagues and Klaire Houeix. I express my gratitude to Lena Vought for helping me to find this internship.

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Joachim Audet

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Abstract

The release of phosphorus and nitrogen from two contrasting floodplains sediment deposits have been studied during the post-flooding period. The floodplain sediments were collected from the Skjern and Odense Rivers. Two laboratory experiments were performed: In the first study, dry sediment, without bacterial activity, was subjected to repeated cycles of drying and rewetting under aerobic conditions.

In the second study, artificial rainwater was applied on fresh sediment in order to simulate the climatic conditions occurring in April and May (i.e. after the flooding has ceased).

In this report, the release of phosphate from sediment has been quantified: in the first experiment which could be regarded as potential P-release, the Phosphate release was 20 times higher from Odense sediment than from Skjern sediment (22 µg/g DW and 357 µg/g DW respectively). The higher release of phosphate from Odense sediment was caused by lower iron content in the sediment and because the sorption capacity for phosphate was fully exploited. The potential release of Nitrogen in the first laboratory experiment revealed at the end of the experiment, that the total Nitrogen, i.e. NH_4^+, release in the sediment was 11.2 % and 7.4%, for Skjern sediment and Odense sediment respectively.

The second experiment, approaching natural conditions, was carried out only with Odense sediment, and showed a very low release of phosphate (maximum amount: 0.045 %). The amount of Nitrate released compared to the total nitrogen content in the sediment amounted to between 0.06 % and 6.42 % for the sediment collected at 5.6 m and 101 m respectively.

Both experiments demonstrated the role of floodplains as an efficient sink for nutrients especially phosphorus and also brought more evidence on the interest of restoring floodplains and riparian areas in order to decrease the phosphorus and nitrogen transport in rivers, thereby also mitigating the load of these nutrients on downstream recipients. Further it may in particular contribute in reaching the aims required to fulfill the objectives in the Water Framework Directive.

Key words: Phosphorus, phosphate, Nitrogen, Nitrate Desorption, Release, Floodplain, Sediment, Skjern, Odense, River

Résumé

Le relargage du phosphore et de l'azote par des sédiments provenant de deux plaines d'inondation aux caractéristiques contrastées ont étés étudiées pendant la période post-inondation. Les sédiments de plaine d'inondation ont étés collectés pour les rivières Skjern et Odense. Deux expériences en laboratoire ont étés réalisées: dans la première, des sédiments secs, sans activité bactérienne, ont subi des cycles répétés de séchage et de ré-humectation en conditions oxiques.

Dans la seconde, des pluies artificielles ont été appliquées sur des sédiments frais dans le but de reproduire les conditions climatiques présentes en avril et mai (après la période d'inondation).

Dans ce rapport, le relargage du phosphore par les sédiments a été quantifié: dans la 1ère expérience, pouvant être considéré comme le relargage potentiel de Phosphore, le relargage de phosphate était 20 fois plus élevé depuis les sédiments de la rivière Odense que depuis des sédiments de la rivière Skjern (22 µg/g DW and 357 µg/g DW respectivement). Ce relargage plus important pour le sédiment d'Odense est due à une concentration en fer plus faible dans le sédiment et par une capacité d'adsorption pour les phosphates complètement exploitée. Le relargage potentiel d'azote à la fin de l'expérience, comparé a l'azote total dans le sédiment était de 11,2 % et 7,4 %, pour les sédiments de Skjern et les sédiments d'Odense respectivement.

La 2ème expérience, approchant les conditions naturelles, réalisée avec des sédiments d'Odense, a démontré un très faible relargage de phosphate (maximum relargué 0,045 %). La quantité de nitrate relargué comparée à la concentration totale en azote représentait entre 0,06 % et 6,42 % pour le sédiment collecté à 5,6 m et 101 m respectivement.

Ces expériences démontrent le rôle des plaines d'inondation comme un piège à nutriment, particulièrement pour le phosphore, et ainsi apporte des preuves sur l'intérêt de la restauration des plaines d'inondations et des aires ripariennes dans le but de diminuer la concentration en phosphore et en azote dans les rivières et dans les zones situées en aval. Ces aspects contribuent à d'atteindre les objectifs définis par la Directive Cadre sur l'Eau.

Mots-clefs: Phosphore, Phosphate, Azote, Nitrate, Désorption, relargage, plaine d'inondation, Sédiment, Skjern, Odense, Rivière

I. Environmental context in Denmark

With a population of 5,4 million inhabitants and an area of 43 098 km^2 (without Greenland and Faroe islands), the kingdom of Denmark has a population density of 126 inhabitants per km^2, above the European Union (EU) average (115 inh./km^2) (Eurostat, 2008). Therefore it is understandable that, anthropogenic activities, in particular agriculture, have widely shaped the landscape, including watercourses. In 2006, 62% of the land area was used by agriculture, (second in EU after UK) (Eurostat, 2008). Drainage of land for agricultural purpose, intensive culture, increase of live stocks, especially after World War II, has deeply modified the environment. The increasing utilisation of fertilizers and agricultural manure on culture, to enhance productivity, has led to the situation where large quantities of nutrients are not used by the crops and consequently, through some processes, such as erosion, solubilisation or in particular leaching, are delivered to water bodies.

In the late 70's, the loss of nutrients from agricultural land started to spark off some concerns mainly about groundwater supplies (Kronvang et al., 2008). However, it is at the beginning of the 80's, that an event alarmed Danish people. A TV report showed some dead lobsters, in the Kattegat Sea, between Sweden and Denmark. The reason of these deaths was attributed to hypoxia due to an algal bloom provoked by agricultural nutrients. This incident, among others, increased the concern about nutrients and led, in 1985, to the vote, by the Danish parliament, of an action plan to reduce N and P load with a series of measures mostly destined to the agriculture. In 1987, the first Action Plan for the Aquatic Environment (AP-I) was imposed with the ambitious objective to halve Nitrogen losses and to reduce Phosphorus losses by 80%.

As a member of European Union since 1973, Denmark is prone to EU directives and therefore to the Water Framework Directive (WFD). The aim of this directive is to prevent further degradation of water bodies and to enhance status of aquatic ecosystems (European Parliament and of the Council, 2000) The transcription in Danish legislation was realised the 17/12/2003 and the Third Action Plan for the Aquatic Environment (AP-III) was imposed in 2004. This last plan includes the objectives defined by the WFD and the Habitat directive.

Parallel to these policy measures, an effort was made in the sector of environmental research to develop some methods and to have a better understanding of the environmental processes to fulfil the objectives defined by the legislation. These tasks were entrusted notably to the National Environmental Research Institute.

The National Environmental Research Institute (NERI), also called Danmarks Miljøundersøgelser in Danish, was established in 1989 to enhance the coherence and consistency within Danish environmental research. The institute is responsible for providing the technical and scientific foundation for national and some European policy decisions related to nature and environment. NERI is responsible of the nation-wide monitoring programme. It collects processes and assesses information about nature and environment and utilizes this knowledge as the basis for producing independent scientific advices to decision makers and various governmental agencies. NERI also communicates information about nature and environmental issues to the general public. In 2007, NERI became part of University of Aarhus which is the second largest University in Denmark.

The following study was carried out within the Freshwater Ecology Department described below.

The competences of the department of Freshwater Ecology are centred on the structure and function of freshwater ecosystems with a view to determining how they are influenced by anthropogenic pressures. The development of methods for restoring lakes, watercourses, riparian wetlands, floodplains and river valleys and for analysing measures to reduce environmental pressure from agriculture is an integral part of the department's research, as is the development of models for quantifying the effect of eutrophication, climate change, physical pressures and hazardous substances on freshwater ecosystems and for use in river basin management planning. The development of management-related models, restoration methods and measures at river basin level supports both national and international authorities with the implementation of EU directives, aquatic environment plans and action plans.

I.1. General remarks about Phosphorus and Nitrogen in river ecosystem

Nowadays in Denmark, Agriculture is responsible of more than 80 % of Nitrogen (N) and 50 % of Phosphorus (P) delivered to watercourses, lakes and coastal waters (Kronvang et al., 2005). The excess of nutrients can cause degradations such as eutrophication (Meybeck, 1982; European Environment Agency, 2005) and prevents water bodies to reach the good ecological status required by the WFD. N and P are two chemical elements naturally found in the ecosystems. They are nutrients essentials to plant growth.

Phosphorus

In river ecosystems, Phosphorus is dissolved or bound to particles in either organic or inorganic form. Despite its low solubility dissolved phosphorus plays a very important role due to its negative impact on the ecosystem, if it is found in excess, because it is often the limiting nutrient in freshwater systems (e.g. lakes) (Jeppesen et al., 2003).

Under its particulate form, phosphorus is bound to particles by sorption or precipitation.

The main mechanism of binding is however adsorption. Scheidegger and Sparks (1996) defines adsorption by the accumulation of a substance or material at an interface between the solid surface and the bathing solution. Adsorption, in the case of phosphorus, is of major interest because phosphorus can be accumulated in sediment by adsorption onto ferric hydroxide Fe(OOH).

Accumulation of phosphorus can also occurs by precipitation with Ca-ions (Golterman, 1995a) but this process is of minor interest in the case of the two Danish rivers studied because of the low Ca content in the geological substrate and consequently in the water.

The adsorption of orthophosphate $H_2PO_4^-$ onto Fe(OOH) can be described as follow (Golterman, 1995b).

$$Fe(OOH) + H_2PO_4^- \leftrightarrow Fe(OOH) \approx P \text{ (oxic conditions)}$$

The fact that most of P is bound in ferric hydroxides has the consequence that the P-dynamic would be closely link to iron cycle (Baldwin and Mitchell, 2000) which is redox-sensitive.

Under anoxic conditions iron is reduced and Phosphate would be desorbed:

$$Fe \equiv HPO_4 \leftrightarrow Fe^{2+} + HPO_4^{2-}$$

Nitrogen

Nitrogen in sediment is present under,

- Organic form: Compounds from amino acids, amines, protein and humic compounds.
- Inorganic N: Ammonium, nitrate, nitrite.

The nitrogen cycling is described in figure 1.

In this study, the steps of ammonification and of nitrification are of particular interest.

Ammonification

Reddy and Patrick (1984) define ammonification as the conversion of organic N to ammonium N. This conversion is generally realized by heterotrophic bacteria or fungi under aerobic condition. Ammonification is possible under anaerobic conditions but the rate would be slower. The ammonification is part of the process of mineralization which is the degradation of organic matter into mineral compounds. If oxygen is present the ammonium can be transformed to nitrate via Nitrification.

Nitrification

Nitrification is the biological oxidation of ammonium to nitrate (Reddy and Patrick, 1984). The two stage of nitrification are realised by bacteria under aerobic conditions.

1st stage

Nitrosomonas $NH_4^+ + 1/2\ O_2 \rightarrow NO_2- + 2H^+ + H_2O$

2nd stage

Nitrobacter $NO_2^- + 1/2\ O_2 \rightarrow NO_3$

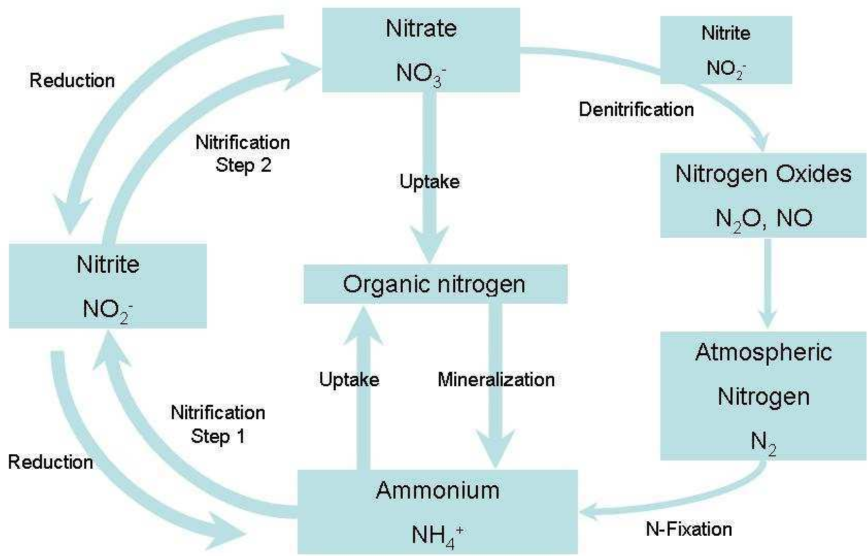


Figure 1: Nitrogen cycle modified from Hoffmann (1998)

I.2. Problematic

To answer to the problems caused by these nutrients and especially P, the NERI launched, in 2006, the project "Best Management of Stream Banks, Bufferzones and Floodplains for reducing Agricultural Phosphorus Losses" (BUFFALO-P). One of the aims was to investigate the P-release kinetics from riparian sediments.

This report will focus on the mobilisation of Nitrogen and Phosphorus, from floodplain sediment subjected to repeated cycles of drying and rewetting by rainwater. This study describes two laboratory experiments carried out to simulate and to determine the effect of the interaction between rainwater and sediment, deposited after a flood, from two Danish River floodplains: The Skjern River and the Odense River.

II. Introduction

In order to reach the good ecological status required by the WFD (European Parliament and of the Council, 2000), special attention must be given to N and P which are responsible of degradation of ecosystems.

River floodplains are considered as an important link of the nutrient cycle and budget, especially for Phosphorus (Mitsch et al., 1979; Brunet and Astin, 1998; Brunet and Astin, 2000; Kronvang et al., 2007). During a flood event, sediment will be deposited on the floodplain. This sediment deposition has been studied regarding to nutrient composition (Kronvang et al., 2007), particle size composition (He and Walling, 1997) but little is known about the fate of deposited sediment on the floodplain, especially subjected to rainfall, in term of nutrient storage efficiency.

Many studies describes the effect of reflooding soil’s (Sharpley, 1996; Turner et al., 2003; Siddique and Robinson, 2004; Styles and Coxon, 2006), lake sediment (Baldwin, 1996; Qiu and McComb, 1996; Mitchell and Baldwin, 1998; Xiangcan et al., 2006) or wetland sediment (Baldwin and Mitchell, 2000; Baldwin et al., 2000; Olde Venterink et al., 2002; Surridge et al., 2007). They have shown a release of N and P from the materials considered. The release of nutrients from floodplain sediment subjected to a flood has been studied by (Baldwin et al., 2005; Olde Venterink et al., 2006; Noe and Hupp, 2007). However, the effect of rainwater on the sediment has barely been studied yet.

In the following study, the effect of rainwater applied on floodplain sediment is described using some laboratory experiments.

The first experiment concerns the release of nutrients from dry sediment placed in a beaker filled with rainwater. A comparison between two contrasting catchments, a sandy one and a clay / moraine catchment will be done.

Experiment and analyses, except grain size analysis, for Odense River sediment, were realised in 2006 by Tommy Silberg, lab-technician at NERI under the supervision of Dr Carl Christian Hoffmann, senior scientist at NERI. Some of the results are discussed as part of a publication by Kronvang and Hoffmann, 2008, in review.

The second experiment consists of studying the effect of rainfall applied to a layer of sediment deposited on the Odense floodplain.

For this purpose, fresh sediment was placed under a rainfall simulator reproducing the alternation of rainy and dry conditions.

The objectives are:

- To study the effect of rainwater applied to floodplain sediment,
- To quantify the release of P and N from the sediment to the water phase,
- To determine the parameters influencing the release of N and P,
- To discuss the potential differences in the results from Skjern and Odense sediments.

The first experiment enables to determine the chemical changes due to the interaction between rainwater and sediment and the impact of drying phases and rewetting.

In the second experiment, sediment will be exposed to temperature and rainfall reproducing the climatic conditions occurring in April and May, i.e. after the flooding period has ceased (winter is the discharge period in DK).

III. Materials and Methods

III.1. Study sites

Sediments used in these experiments came from two Danish rivers, the river Skjern and the river Odense (figure 2). These two rivers were selected because of their differences in soil's texture. Odense catchment is composed of clay/sand whereas Skjern catchment is very sandy. Considering that P and N are mostly stored in the fine grain especially the fraction below 63 µm (Andrieux-Loyer and Aminot, 2001; Owens and Walling, 2003; Kronvang et al., 2007), results between these two rivers should show some differences in term of storage and release of nutrients.

Figure 2: Map of Denmark with the position of the two study sites (source google Earth).

III.1.1. Odense site

The study site is located on the island of Funen, between the cities of Brobyværk and Hillerslev Bro (32 U 058-2137 UTM 61 20156). It is part of the Odense catchment which encompasses an area of 1046 km^2. The river basin include 1100 km of watercourses and 2600 ponds and lakes (>100 m^2). Water from the catchment is drained to the Odense Fjord which is connected to the Baltic Sea. The floodplain was restorated in autumn 2003 and has been transformed from arable land to a permanent grazed meadow. The Odense river basin was one of the fifteen Pilot river basins selected by EU to test the implementation of the WFD.

Geology and pedology

The landscape was shaped during last glacial period (Weichsel) when the area was covered by ice. Consequently the common feature is moraine plain covered by moraine clay.

Clay soil's represents 51 % of the basin whereas 49 % is sandier (Fyns Amt, 2003). These soils are of good quality for the agriculture.

Land use and population

Agricultural activities use 68 % of the territory. The remaining part encompasses forest (10 %), urban area (16 %) and natural or semi-natural site (6 %). The population is 246 000 inhabitants mainly concentrated in the city of Odense (182 000 inh.) situated downstream from the study site.

Climate

The average temperature according to the data collected from Danish Meteorological Institute (DMI) is 9.2°C for the period 1999-2006. Monthly precipitations for the period 1999-2006 are presented in figure 3. The median annual precipitation is 753 mm. The climate is dominated by oceanic influence.

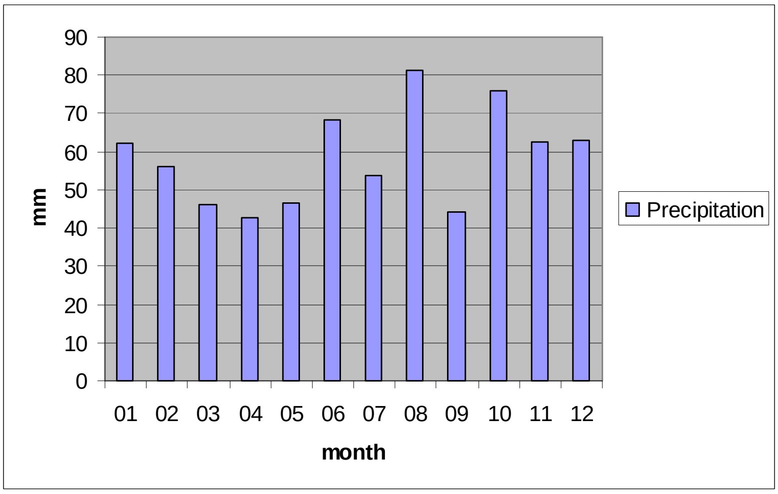


Figure 3: monthly average precipitation for the Odense study site (1999-2006).

Hydrology

The annual mean discharge at Broby monitoring station (≈ 5 km downstream of the study site) is 2.9 m^3/s. The monthly mean discharge for the 1917-2006 period is presented in figure 4.

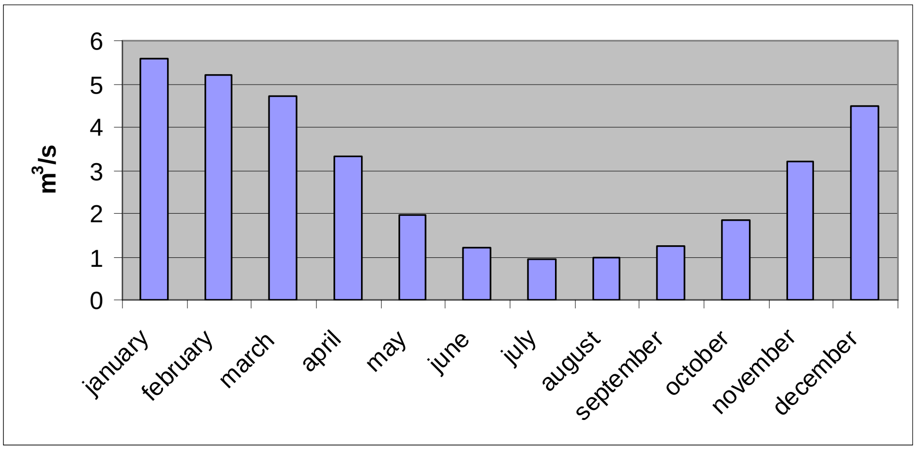


Figure 4: Mean discharge of the Odense River at Broby monitoring station (1917-2006)

The annual mean discharge at the mouth of the river is 6.5 m^3/s (Thodsen, 2007)

III.1.2. Skjern Site

The Skjern River, situated in Jutland, is the river with the highest discharge in Denmark. Its river basin drains 2490 km^2 to the Ringkøbing fjord at the North Sea coast. During the period 1999-2002, the Skjern River was the place of one of the largest restoration project in Europe. The project included the restoration of 22 km^2 of cultivated, drained land by re-meandering the river and re-establishing the natural water levels to enhance biodiversity and water quality in the river and in the estuary (Pedersen et al., 2007). The study site is located near the city of Skjern (32 U 046 8173 UTM 61 97689).

Geology and pedology

During the last glaciation (Weichsel), the glacier did not reach the western part of Jutland where the study site is situated. Nevertheless, it strongly influences the morphology of the landscape, digging the valley at the ice melt and depositing till. This explains the high proportion of sandy soil's which are covering 70 to 80 % of the area. The remainder includes loamy sandy and organic soils.

Land use and population

A large proportion of the watershed is used by agriculture (75 %), (Svendsen and Hansen, 1997). The population numbers about 87 000 inhabitants which represents a relatively low density of 35 inh/km^2.

Climate

The average temperature is 7.6 °C and the median precipitation is 843 mm (Svendsen and Hansen, 1997). The climate is oceanic.

Hydrology

The closest monitoring station from the study site is the station of Ahlergaarde. The monthly mean discharge calculated for the period 1920-2006 is presented below (figure 5):

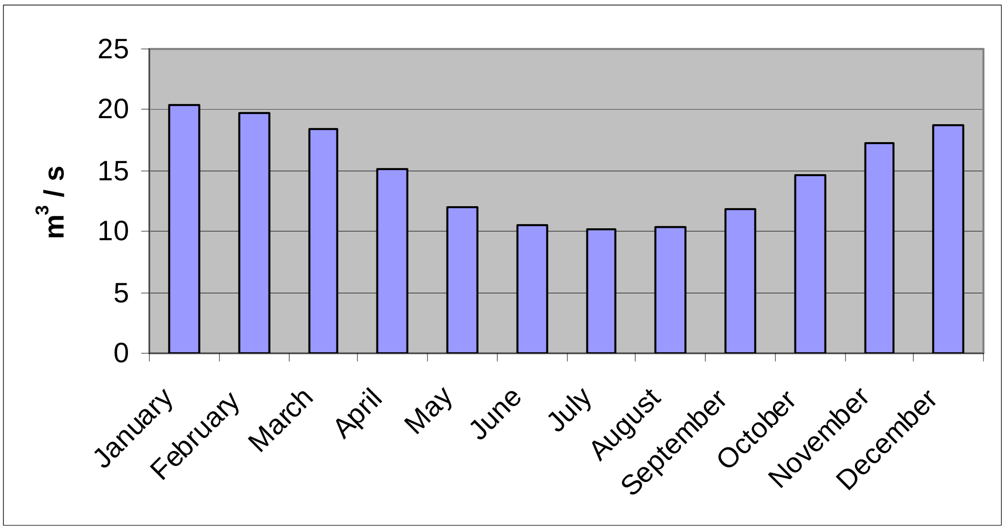


Figure 5: Mean discharge of the Skjern River at Ahlergaarde monitoring station (1920-2006)

The annual mean discharge at the mouth of the river is 35 m^3/s (Pedersen et al., 2007).

Recap of the main characteristics of both catchments

Despite both watersheds are dominated by agriculture, there are some differences especially in term of pedology and population density. The main characteristics of the entire catchments are compiled in the table 1.

	Catchment area (km^2)	Mean Discharge m^3/s	pedology				Land-use				Precipitation (mm)	Average Temp ℃	Population	density inh/km^2
			Sandy %	Loamy sandy %	Clay %	Organic %	Forested area %	Cultivated area %	Urban area %	Natural, semi-natural area %				
Skjern	2490	35	70-80	15-20	-	4-8	13	75	5	7	843	7.6	87150	35
Odense	1046	6.5	49	-	51	-	1	68	16	6	600-850	8.2	246000	235

Table 1: Main features of the Skjern and Odense catchment

III.2. Experiment 1: Phosphate and ammonium release from floodplain sediment under aerobic conditions.

Sediment sampling

Sediment deposited by the river during flood events were trapped on artificial grass mats (Astroturf® 15 x 15 cm) (Figure 6).

Figure 6: Artificial grass mats Astroturf® placed on the Skjern River floodplain

These grass mats were placed at different distances (table 2) on floodplain forming a transect perpendicular to the river channel. For the river Skjern site, the mats were placed on 19/11/2007 and harvested on 27/03/2008 just after a flood event. For the Odense site, grass mats were installed on 03/11/2005 and collected on 29/03/2006. After some few days of storage in cold room at 5 °C, the mats with their layer of sediment were oven dried at 60 °C during 5 days, and then after were weight, removed from the mat and dried for 2 hours at 105 °C, this stage of drying enabling to kill bacteria.

	sampling distances (in meters from the channel)								
Skjern	1	5.6	10.7	16.5	23.8	31.1	40.8	52.3	70.9
Odense	1	8	10.7	16.5	23.8	31.1	40.4		

Table 2: Localisation of the mat on transect on the floodplain for Skjern River and Odense River.

Experiment procedure

Double samples of 5 g dried sediment were placed in beakers. The beakers were filled with 1000.00 g of artificial rainwater representative of the composition of Danish rainwater (composition of the water can be found in appendix 1).

Every day, water was stirred during 1 min with a magnetic beater, then allowed to settle and water samples were taken out from the beaker, filtered at 0.45 µm to avoid particulate-P and placed into cold room before analyses. At day 6 and 12, water from the beakers was gently removed and beakers and the sediment were oven dried at 60 °C during two days. Then 1000.00 g of artificial rainwater were poured into the beaker and stirring and sampling were done every day following the same procedure as described before. In order to consider the influence of stirring in the experiment, water and sediment were left undisturbed between day 19 and 23. The experiment was realised at laboratory temperature (i.e. 20-22 °C).

Analyses realised

Analyses were carried out to determine:

- chemical changes in water composition due to the interaction between water and sediment
- the main characteristics of the sediment.

Ammonium

Water samples were analysed for NH_4-N on flow injection analyser spectrophotometer Lachat QC 8000 according to the method Quickchem 10-107-06-3-A

Ortho-phosphate

Ortho-phosphate (PO_4^{3-}) concentration in the water was determined as PO_4-P on flow injection analyser spectrophotometer Lachat QC 8000 according to the method Quickchem 10-115-01-1-B (equivalent to Murphy-Riley molybdate blue procedure (Murphy and Riley, 1962)).

Total Phosphorus and Iron

Total P and Iron concentration in the sediment before and after incubation were measured on spectrophotometer Shimadzu UV-160 after combustion at 550 °C and boiling in mild hydrochloric acid according to the method described by Andersen (1976).

Sequential extraction of Phosphorus

Non-incubated sediment went trough a sequential extraction according to the method of Psenner and Pucsko (1988) modified by Paludan and Jensen (1995). This fractionation allows determining the different pools phosphorus is sorbed to.

The first step (water fraction) gives the Dissolved Reactive Phosphorus (DRP), the Dissolved Non-Reactive Phosphorus and the loosely adsorbed DRP.

The second step (Bi-Dithionite fraction) makes possible to extract Dissolved Reactive Phosphorus (DRP) adsorbed onto the surfaces of oxidized compounds of Fe and Mn.

The lasts steps give the rest of the phosphorus contained in the sediment.

Organic matter

Organic matter was determined by loss on ignition (LOI) at 550 °C in a muffle furnace.

Grain size analyse

Grain size analyse was performed using wet sieving method with 10 g DW sediment on Fritsch® sieving machine. Five different sieves were used: 2mm, 1mm, 500µm, 250µm, 125µm, 63µm. The sediment was not oxidized before the sieving.

C/N analyse

The Carbon and Nitrogen analyses were done on spectrophotometer Europa Scientific Roboprep CN and Tracer Mass.

Data analyse

The Pearson product moment correlation was used to test for correlations among parameters. Relationships between variables were assessed using linear regression. The significant level used for all tests was $p = 0.05$.

III.3. Experiment 2: Release of phosphorus and nitrogen from floodplain sediment submitted to rainfall.

Sediment sampling

Following the same procedure described in section III.2 sediment was trapped on artificial mats Astroturf® 30 x 30 cm on Odense floodplain during winter 2007/2008. 4 mats were collected at 5.6 m, 16.5 m, 23.8 m, 101 m from the channel.

Experiment procedure

In a climatic chamber, the 4 mats with their layer of fresh sediment were placed under 4 rainfall simulators (figure 7 and 8). This device, designed by Dr Carl Christian Hoffmann (NERI, Silkeborg, Denmark), is constituted by:

- a pump,
- a generator,
- a rain water reservoir,
- an upper part with 180 needles,
- a cylinder (diameter = 30 cm),
- a lower part with a Nytal filter membrane (30µm),
- a sampling bottle.

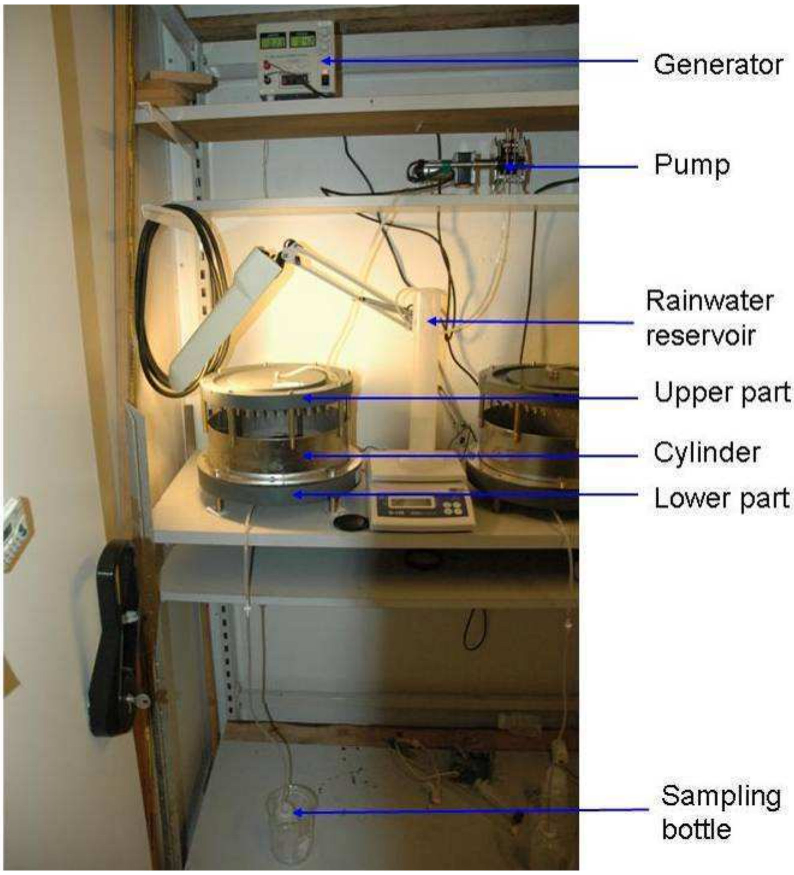


Figure 7: Photo of the experimental device

Figure 8: Cylinder with the sediment (left), upper part of the system with the needles (right)

The generator enables to control the speed of the pump and consequently to manage the intensity of the precipitation. The pump is connected by a pipe to the artificial rainwater reservoir which is placed on a balance to know and to control the amount of the rainfall. The water is pumped up to the upper part where the needles are reproducing rain drops all over the surface of the sediment which is placed in the cylinder. The grass mats and the sediment were previously cut to give the shape of a disk to match with the diameter of the cylinder.

The mats were perforated using an awl to let the water percolate the artificial grass mat. At the bottom of the cylinder was placed a membrane with a grid size of 30 µm in order to prevent loss of sediment. After infiltration trough the membrane, the outflow water was collected by a pipe to a plastic bottle. After collect, samples were placed at 2 °C in darkness.

The sediment was alternatively subjected to rainfall and dry period during 2 months in conditions simulating the temperature and the pluviometry of April and May.

Rainfall

In order to reproduce natural condition, rain data were gathered from the Danish Meteorological Institute (DMI) for the station DMI 10352. Data covered period from 1999 to 2006. Monthly rainfalls for April and May were used. These months were chosen in order to simulate the conditions after flood period. The flood period normally takes place during winter time and ends at spring. A median monthly rainfall of 43 mm for April and 47 mm for May was calculated. As it was not possible to get data of rain intensity, it was decided to apply the monthly amount in 9 days of rain. The choice of 9 days was done as the median number of rainy day for May and April. After conversation with Dr Carl Christian Hoffmann (NERI, Silkeborg, Denmark), a rain intensity of 1.5 mm / hour was chosen. This intensity enables a good infiltration in the sediment. To simulate the alternation of dry and rainy period, it was decided to apply rain on 2 consecutives days and to have 5 days without any precipitation. So for practical reasons, it was decided to have rain on Mondays and Tuesdays.

Temperature

To simulate the temperature condition in April and May, temperature data for the period 1999-2006 were used and the monthly median temperature was calculated. A temperature of 8 °C was determined for April and 12 °C for May.

Evaporation

The mean daily evaporation was determined for April and May with evaporation data from DMI for the period 1999-2006 and the zone concerned. This number was 0.09 mm / hour and 0.13 mm / hour respectively for April and May. It was not possible to control the humidity in the climate chamber and the functioning of the chamber presented the inconvenient of drying the air. To measure the evaporation caused by the climate chamber, a bucket filled with water and weight every week, was used. It was determined that the evaporation was around 0.3 mm / hour which is above the natural conditions.

Analyses

Ammonium, orthophosphate, total phosphorus, Iron were measured following the methods described in III.2. nitrite + nitrate were measured as nitrite at spectrophotometer Lachat QC 8000 according to the method Quickchem 10-107-04-1-B.

Grain size analyse was realised using wet sieving method previously described in III.2. The dry weight deposited on each mats was measured at the end of the experiment.

Data Analyses

Data were analysed following the same procedure mentioned in section III.2

IV. Results and Discussion

IV.1. Experiment 1: Phosphate and ammonium release from floodplain sediment under aerobic conditions

IV.1.1. Phosphorus

IV.1.1.1. Phosphate analyses

The cumulated concentration of phosphate released is presented in the figure 9 for both rivers. The results of the analyses of water samples revealed a general increase in the concentration during the time of the experiment. This corresponds to a release of phosphate from the sediment to the water phase. The term release refers to all the processes (e.g. desorption, dissolution) contributing to a mobilisation of phosphate from the sediment to the water phase. The amount released differs within the two rivers and also between the different sampling points at the two rivers.

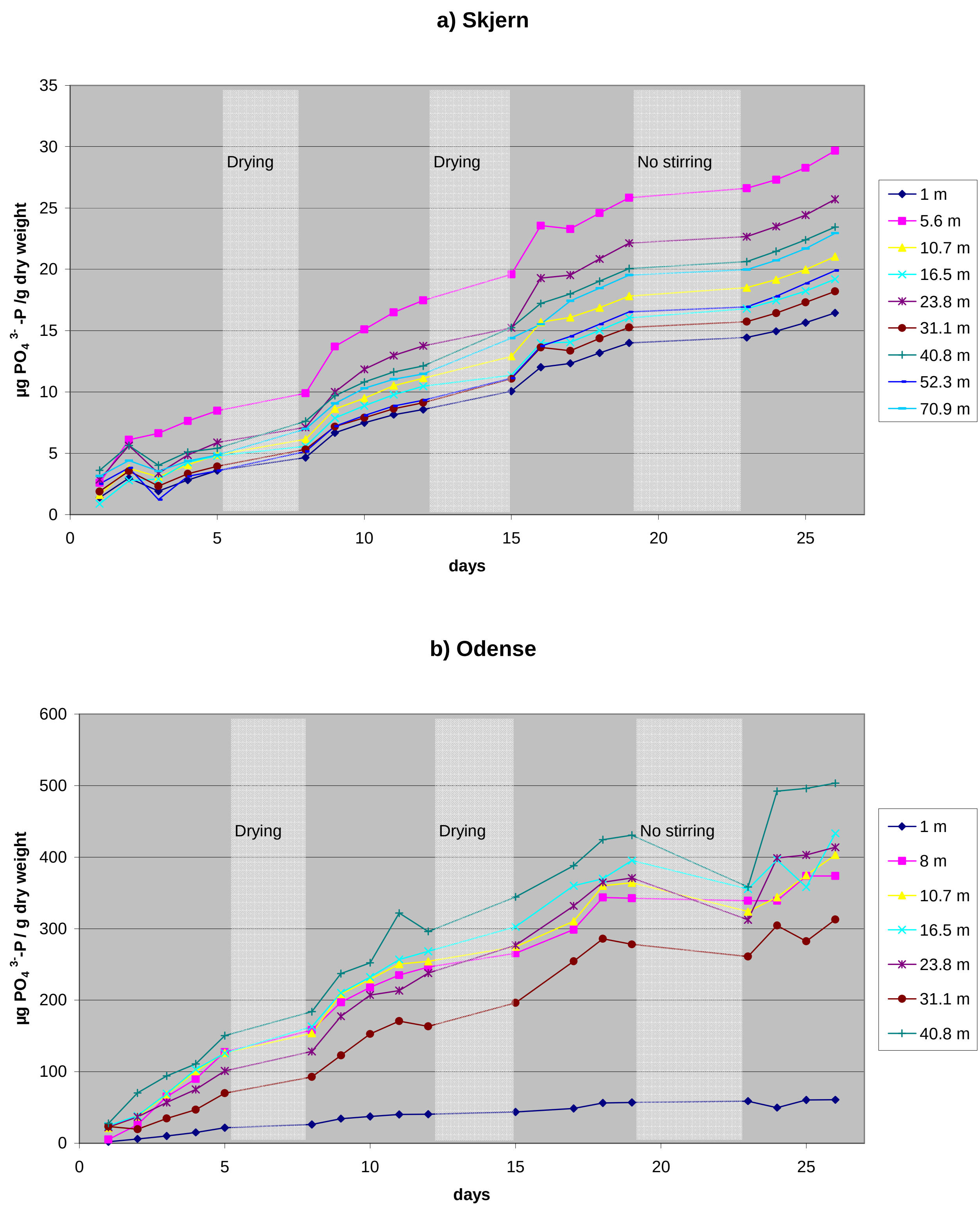


Figure 9: Cumulated concentration of phosphate (PO_4^{3-}-P) in the water during the experiment and at the different distances (m) from the river channel.

(a) for the sediment from the river Skjern; (b) for the sediment from the river Odense. The drying phases lasted 2 days at 60 °C. Note the different scale between the Y- axes.

The P-release for the Skjern sediment samples was relatively low, as are the variations between sampling points. the smallest amount of phosphate released from the sediment at the end of the experiment was 16 µg PO_4^{3-}-P / g dry weigh, at a distance of 1 m, whereas the largest amount, 30 µg PO_4^{3-}-P /g DW, was released at 5.6 m from the channel.

For Odense sediment, the amount of PO_4^{3-}-P released after 26 days ranges between 61µg / g DW and 503 µg /g DW at respectively 1 and 40.8 m from the channel. The curve of release of the sediment harvested at 1 m from the channel shows a clear difference with the other distances. A possible explanation of such a difference is given in section IV.1.1.2

The average amount released at the end of the experiment is 22 µg / g DW for Skjern and 357 µg / g DW for Odense, i.e. almost 20 times more for Odense than for Skjern. The variability within the sample for Odense river is higher with a coefficient of variation of 40 % whereas is 19 % for Skjern River.

In both cases, the procedure of drying the sediment appears to stimulate the release of phosphate to the water phase as a net increase in the release can be observed in the days following the drying. The increase in release following drying is illustrated by figure 10 which shows the release rate in µg PO_4^{3-}-P /g DW per day. Peaks of release can be noticed after each drying period for Skjern. In the case of Odense, after each drying period the release of PO_4^{3-}-P seems to be a more gradual increase as compared to the Skjern sediment. During the period without agitation (day 19 until day 23), there were very low release for Skjern and even some uptake for Odense. This effect can be due to the absence of agitation during these days which would allow some of the phosphate to be re-adsorbed in the sediment.

It can be noticed that even without absence of agitation some uptake seems to appear for some days (e.g Day 3 for Skjern). This might be explained by some effects due to laboratory procedure.
There is not any significant relationship between P-release and the distance from the channel (Skjern: $R^2 < 0.001$ $p = 0.979$ / Odense: $R^2 = 0.39$ $p = 0.135$).

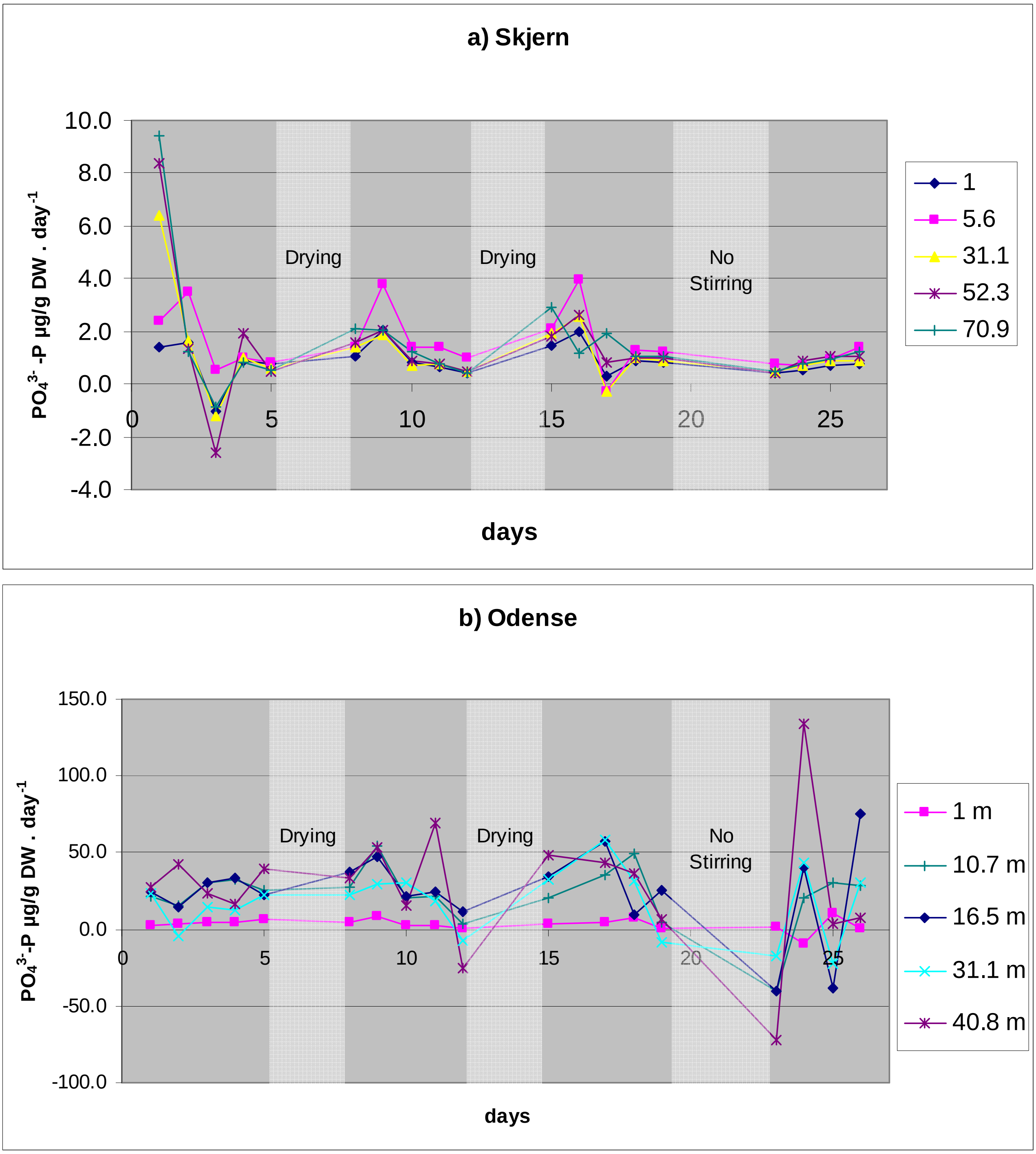


Figure 10: rate of release in µg / g DW . day^{-1} for the sediment from a) Skjern River b) Odense River and at different distances (m) from the channel. For a better reading only few distances are represented. The other distances can be found in appendix 2.

Sources of Phosphate

This release of Phosphate after drying is in accordance with the results of (Qiu and Mccomb, 1994; Qiu and McComb, 1996; Baldwin and Mitchell, 2000; Baldwin et al., 2005; Styles and Coxon, 2006) who described a flush of P after drying phase and reflooding sediment. The main hypotheses of the release are:

1) cell lysis of bacteria due to drying
2) Decomposition of Organic Matter before the first stage of drying
3) Disruption of phosphate bonds during drying and stirring.

1) The potentials contribution of dead cells to phosphorus release has been described by Turner (2003) who explained that some phosphorus come from the lysis of microbial cells provoked by osmotic shock due to rewetting dry sediment. In his study, soils were dried at only 30 °C whereas in the present study, sediment was dried at 60 °C and 105°C. As a consequence, it can be assumed that after such stages of drying, all the bacteria were killed and therefore that the release of phosphorus would occur not because of an osmotic shock but because of the solubilisation of phosphorus contained in dead cells. As no bacterial activity was detected during the experiment, this contribution from bacteria cells should have happened only in the first days of the experiment, after the first drying stage which took place before the first addition of water (i.e. before day 0 in the experiment).

2) During the period when the mats were on the floodplain and before the first stage of drying, mineralization may have occurred and may thus have accumulated some phosphorus (Baldwin and Mitchell, 2000)

3) Van Gestel et al (1991) reported the stabilizing role of clays on soil organic matter and biomass. The procedure of drying, stirring and rewetting could have modified the structure by desiccation of clays, exposure of fresh surfaces of sediment particles, disruption of the weakest bonds and may consequently have increased the availability of phosphorus.

IV.1.1.2. Relationships with sediment characteristics and comparison between the two rivers

Total Phosphorus

An explanation of the higher P-release from the Odense sediment as compared to the Skjern sediment could be higher Total phosphorus (TP) content (table 3). The median TP concentration is 1.2 mg / g DW in Skjern materials and 2.2 mg / g DW in Odense materials. This difference in TP content can not entirely explain that the PO_4^{3-}-P release is almost 20 times higher for Odense than for Skjern. A study realised by Jensen (2006) has already shown a high difference in P-release between Skjern and Odense by placing particles collected at the estuaries into P-free sea water for 24H. The amount released by Odense sediment was 7 times higher than for Skjern particles (23.6 µmol/g DW and 3.4 µmol/g DW respectively).

The ratio PO_4^{3-}-P released / TP expressed as a percentage indicates the proportion of PO_4^{3-}-P released compared to the total P content (table 3 and figure 11). The mean proportion of P released from Odense sediment is 10-fold larger than from Skjern sediment. An average of 1.7 % of the P-content is released for the Skjern sediment whereas for Odense the average is of 17.3 %. There is no significant linear correlation between TP and P released for Skjern materials (R^2 <0.001 p = 0.94). The correlation is significant for Odense (R^2 = 0.65 p = 0.028). It can be deduced from these results that the mechanisms of releasing are not only controlled by the initial TP concentration in the two sediments but should be influenced by other parameters.

Skjern				Odense			
Dist. from the channel (m)	PO4-P released µg/g	Total P µg/g DW	% PO4-P released	Dist. from the channel (m)	PO4-P released µg/g	Total P mg/g DW	% PO4-P released
1	16	935	1.8%	1	61	412	14.7%
5.6	30	737	4.0%	8	374	1516	24.7%
10.7	21	1224	1.7%	10.7	403	1817	22.2%
16.5	19	883	2.2%	16.5	433	2240	19.3%
23.8	26	1157	2.2%	23.8	414	2796	14.8%
31.1	18	1823	1.0%	31.1	313	2755	11.4%
40.8	23	3091	0.8%	40.8	503	3600	14.0%
52.3	20	2123	0.9%				
70.9	23	2761	0.8%				

Table 3: Concentration in Total Phosphorus and PO4-P released for the sediments collected at each distances for both rivers, and percentage of PO4-P released compared to TP.

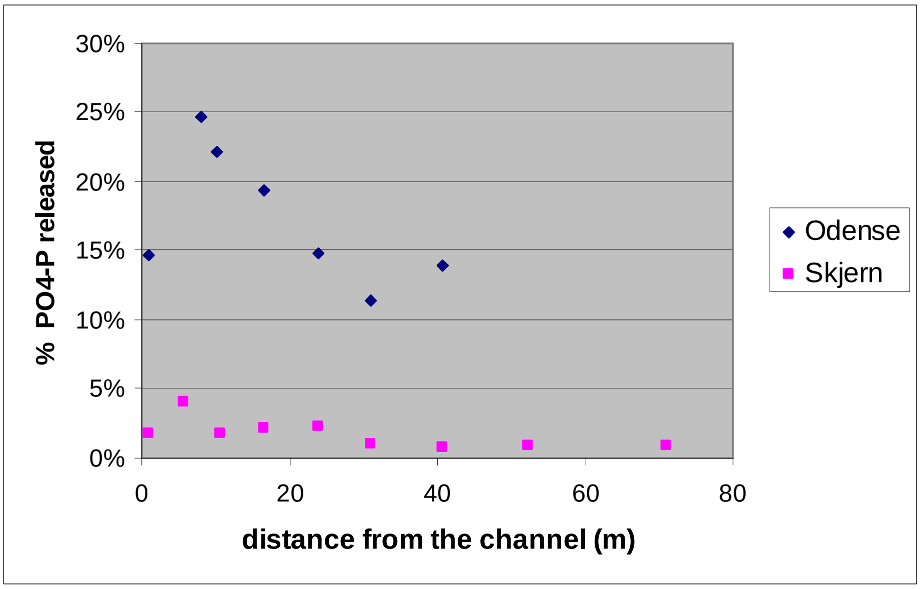


Figure 11: Percentage of PO4-P released during the experiment, by the sediments at the different distances from the channel.

Iron

It was mentioned in the introduction that phosphorus can be linked to iron. The link between iron and phosphorus in sediment is well known as P can be bound onto Iron hydroxides (Mortimer, 1941; Mortimer, 1942; Lijklema, 1980; Golterman, 1995a). Hence, Iron concentration was measured in order to provide an explanation in the difference in P release for the 2 rivers.

With a median concentration of 40 mg Fe / g DW, the Total Iron content in Skjern sediment is higher than for Odense (26 mg Fe / g DW) (table 4). The higher iron content in Skjern sediment is due to the fact that the Skjern catchment naturally contains high amounts of iron, originally under the form of pyrite (FeS_2) and siderite (Fe_2CO_3). The channellisation and the deepening of the river associated to the ditching of riparian areas during the 1960s has provoked oxidation of these minerals and consequently the release of ferrous iron followed by oxidation of ferrous iron and formation of ochre and other ferric iron compounds. The restoration of the area has improved the situation by decreasing iron concentration in water but there is still much left.

There is a strong correlation between Total Iron (TFe) and TP (figure 12) for both rivers. Nevertheless there is no significant correlation between iron content and P released (Skjern R^2 = 0.02 P=0.731 Odense R^2 = 0.42 P= 0.113). This absence of correlation can be explained by the fact that P adsorbed onto iron hydroxides is released under anoxic condition. As this experiment is realised in oxic condition very little of the P bound to iron should be mobilised.

Dist from the channel	TFe mg Fe /g DW	Dist from the channel	TFe mg Fe /g DW
1	35.1	1	4.5
5.6	24.4	8	20.2
10.7	40.5	10.1	20.8
16.5	31.6	16.5	26.3
23.8	34.1	23.8	36.9
31.1	63.8	31.1	47.5
40.8	94.3	40.8	46.4
52.3	72.1		
70.9	82.3		

Table 4: Total iron concentration in each samples collected.

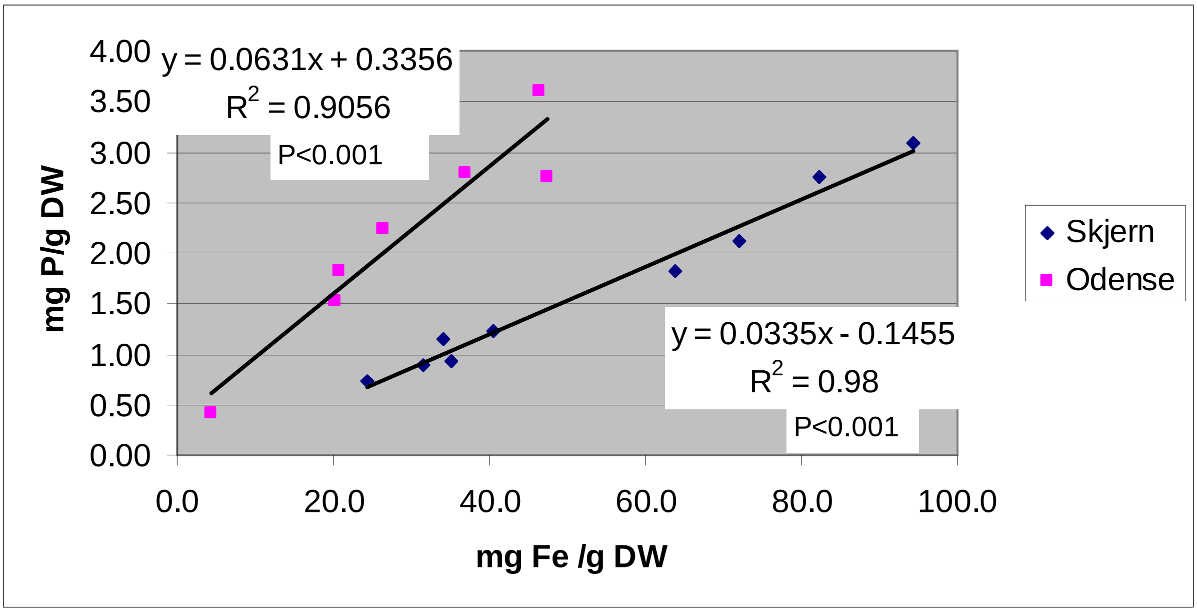


Figure 12: Relationship between total iron concentration (TFe) and Total Phosphorus (TP) in the sediment from Skjern and Odense.

Sequential extraction

The sequential extraction performed enables us to determine which pools phosphorus is sorbed to. In the table 5 the results of the fractionation are presented. It can be noticed that most P is found in the residual fraction which includes Apatite P, humic acid P and refractory P. This fraction is of minor interest in this experiment as the P it contains should not be mobilised. It is interesting to notice the significant correlation between the concentration of PO_4^{3}-P in the water fraction and PO_4^{3-}-P released for the river Skjern (R^2 = 0.753 p = 0.002) (figure 13). For Odense, the correlation is not significant (R^2 = 0.98 p = 0.081) but as the fractionation data only were available for three distances (1 m, 16.5 m, 31 m), these values are mentioned just as indication. Nevertheless, it can be supposed that there is a relationship between the PO_4^{3-}-P released and the PO_4^{3-}-P in water fraction as the water fraction represents the water soluble P.

dist (m)	water fraction mgP/1000g DW	BD fraction mg P/1000g DW	Residual P mg P/1000g DW
1	6.97	278	1248
5.6	10.76	359	510
10.7	4.24	358	883
16.5	3.90	167	250
23.8	13.33	393	1736
31.1	7.28	347	1480
40.8	3.58	308	3090
52.3	7.07	277	2265
70.9	14.15	308	451

Table 5: Results of the sequential extraction for Skjern River.

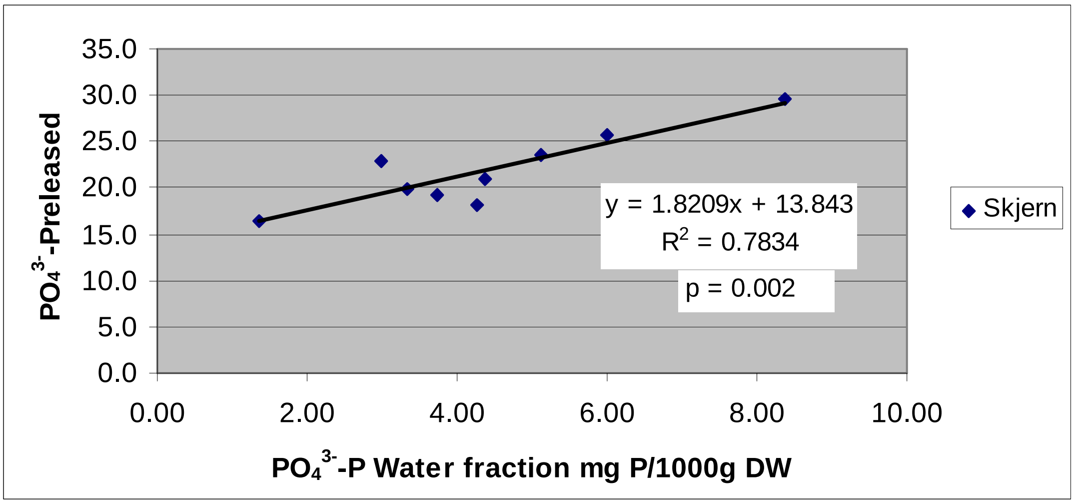


Figure 13: Comparison between PO4 released and water soluble IP

The ratio PO_4^{3-}-P in Water fraction / TP expressed as a percentage, indicated in the table 6, shows that Odense sediment has a larger proportion of Water P than Skjern sediment. This parameter could explain, in some measure, that higher amounts of PO_4^{3-}P are released from Odense sediment as compared to Skjern sediment. The low value of PO_4^{3-}-P in the water fraction at 1 m from the Odense river channel can explain that the lowest value of release was obtained at 1 m.

However water fraction cannot be considered as the only source of P liberated to the water as the amount of PO_4^{3-}-P in water fraction represents less than the amount of the PO_4^{3-}-P released at the end of the experiment.

Skjern		Odense	
Dist (m)	% PO_4^{3-}-P water fraction	Dist (m)	% PO_4^{3-}-P water fraction
1	0.09%	1	12.8%
5.6	0.93%	16	2.8%
10.7	0.34%	31	0.9%
16.5	0.88%		
23.8	0.28%		
31.1	0.23%		
40.8	0.14%		
52.3	0.12%		
70.9	0.06%		

Table 6: percentage of PO_4^{3-}-P in water fraction compared to TP in each sample of sediment.

The molar ratio Fe:PO4, for the Bi-Dithionite (BD) fraction which contains iron hydroxides, presented in the table 7 can provide good indications about the binding capacity of the sediment, that is to say the capacity for iron to provide adsorption site for PO4. It is considered that for one mole of PO4 adsorbed, two moles of Fe are mobilised (Golterman, 1995b; Lehtoranta and Heiskanen, 2003). Thus, The BD fraction of Odense, with a ratio Fe:PO4 around 4.4, is much more loaded in PO4 than the one of Skjern River which shows a ratio ranging between 27.6 and 111.5. The TFe:TP reflects the same trend. The negative correlation between TFe:TP molar ratio in the sediment and the concentration of PO_4^{3-}-P in the water is in accordance with the results of Jensen (1992) who noticed a relationship between this ratio and the P concentration in the Danish lakes included in the study.

	a) Skjern					
	BD fraction			Total		
dist (m)	µmol Fe /g	µmol PO4 / g	Fe:PO4	µmol Fe /g	µmol P / g	TFe:TP
1	583.3	11.3	51.7	629.8	51.6	12.2
5.6	319.7	12.3	26.0	436.8	29.0	15.0
10.7	507.5	12.6	40.4	725.6	41.2	17.6
16.5	151.0	5.5	27.4	566.5	13.7	41.4
23.8	593.2	12.8	46.2	611.5	69.0	8.9
31.1	699.9	12.0	58.3	1142.8	59.9	19.1
40.8	1106.9	14.6	75.7	1690.6	114.5	14.8
52.3	893.4	14.0	63.6	1292.5	87.2	14.8
70.9	1106.6	16.3	67.9	1474.4	154.1	9.6

	b) Odense					
	BD fraction			Total		
dist (m)	µmol Fe /g	µmol PO4 / g	Fe:PO4	µmol Fe /g	µmol P / g	TFe:TP
1	43.9	10.6	4.1	80.1	13.2	6.1
16.5	278.0	62.6	4.4	471.3	72.3	6.5
31.1	355.9	80.0	4.4	851.3	88.7	9.6

Table 7: Results of the sequential extraction and ratio Iron: Phosphorus

Even though no significant correlation between Iron concentration and PO_4^{3-}-P released were found (Skjern R^2 = 0.018 p = 0.73 / Odense R^2 = 0.266 p = 0.235), it may still be assumed that the difference in Iron concentration between Odense and Skjern can explain why the highest amount of PO_4^{3-}-P released was from the Odense sediment. Furthermore the ratio TFe / TP indicates that Odense sediment is more loaded, that its sorption capacity is lower for Odense than for Skjern. This hypothesis of the influence of iron content on P release can be established by comparing the Fe:PO4 ratio with the proportion of PO_4^{3-}-P in the water fraction (figure 14). A significant correlation between these two parameters is found. Accordingly, it can be concluded that the Fe:PO4 ratio influences the proportion of the PO_4^{3-}-P in the water fraction and consequently the availability of PO_4^{3-} for the release.

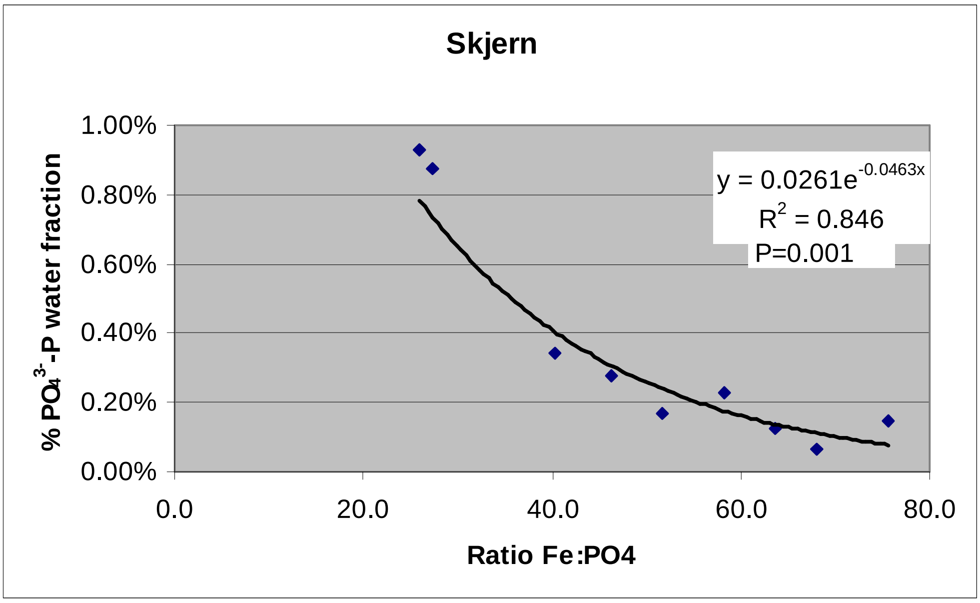


Figure 14: Ratio Fe:PO4 in the BD fraction and Phosphate in the water fraction

Spatial variability

As mentioned before, there is no relationship between the distance from the channel and P released. Nevertheless, the distance seems to explain 73% and 91% of the TP variation for Skjern and Odense respectively (figure 15).

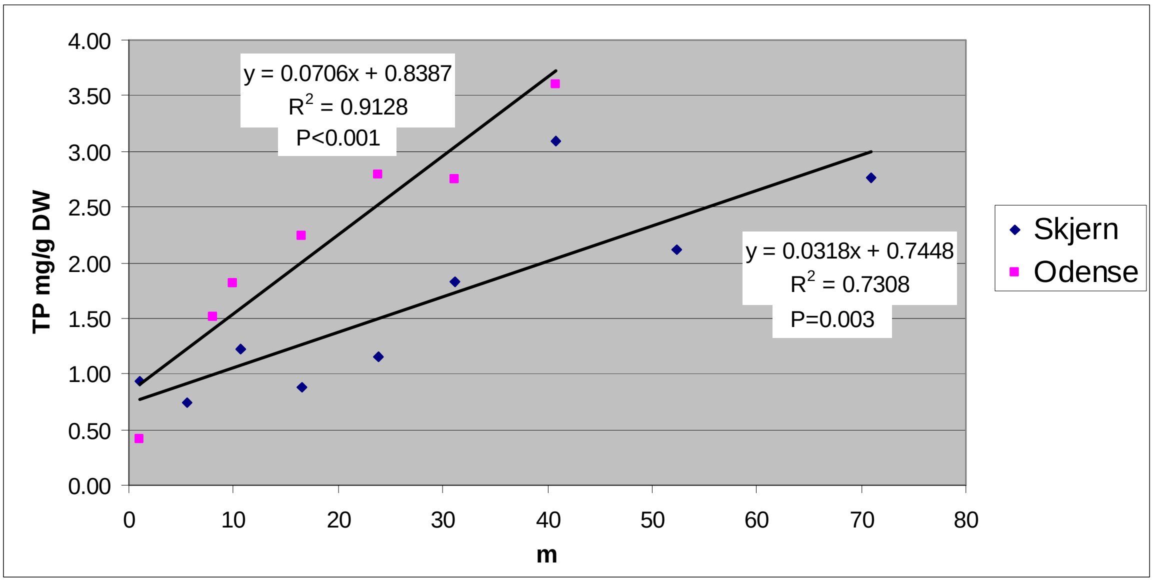


Figure 15: relationship between TP concentration in the sediment and the distance from the channel for river Skjern and river Odense.

Overbank deposition is related to many factors such as floodplain topography and geometry, flood deposition, sediment characteristics, water exchange between river and floodplain and river planform (Kronvang et al., 2007). The link between TP-content and the distance from the channel could be the decrease in grain size as the distance from the channel increase. If the median grain size (D50) is compared with the distance from the channel, a significant negative correlation is found for both rivers (figure 16).

It has to be noticed that, as the average D50 for Skjern (124 µm) is higher than average D50 for Odense (88 µm), the hypothesis formulated in the introduction that the sediment in Skjern catchment is coarser than for Odense catchment is confirmed.

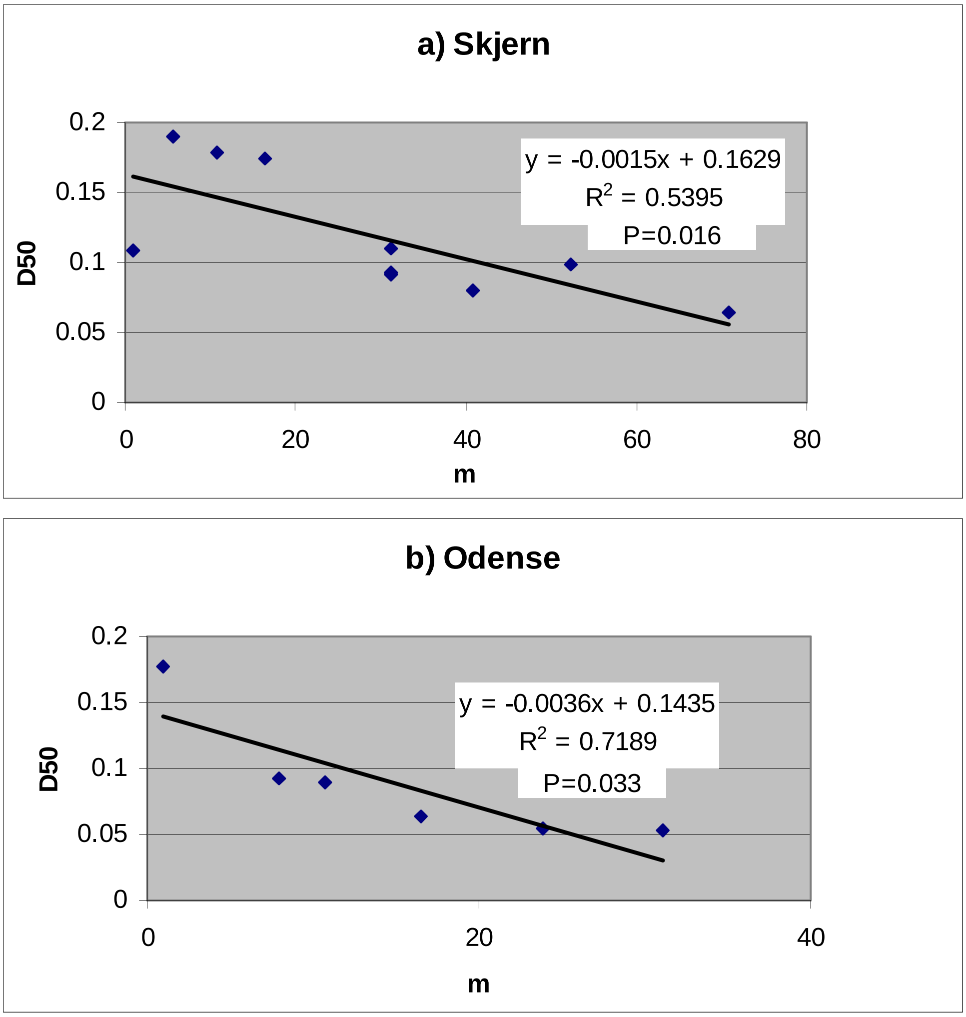
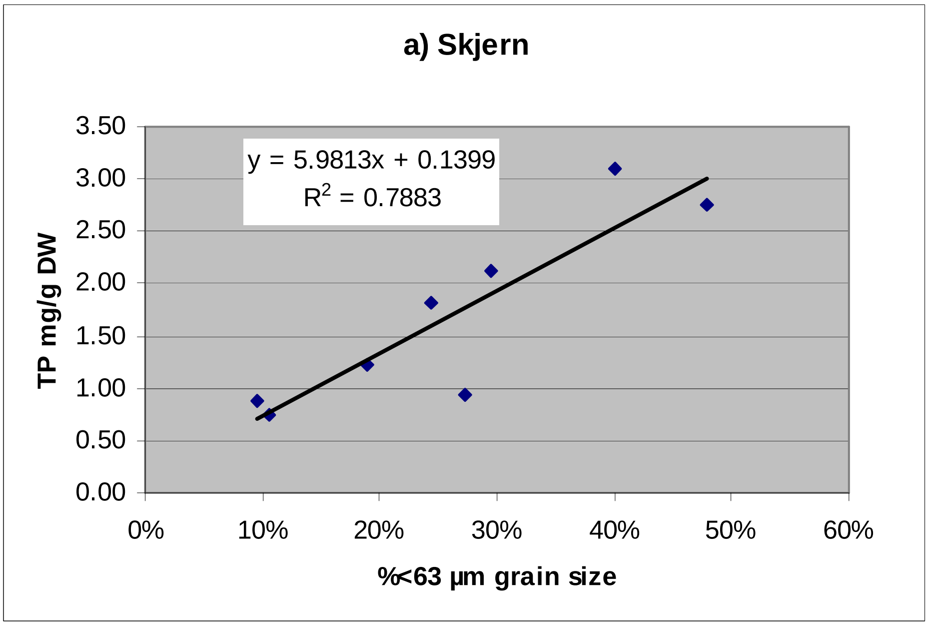


Figure 16: relationship between median grain diameter and distance from the channel for both rivers.

As mentioned before in section III.1, phosphorus is mainly stored in the fine fraction, for that reason a special attention was given to the fraction under 63µm which contains silts and clays. There is a significant relationship between the fraction below 63 µm and TP, (Skjern R^2 = 0,789 p = 0.003 Odense R^2 = 0.96 $p < 0.001$) (figure 17). Some analyses of an even finer fraction could probably give even better correlations, especially analyses of the clay fraction. Furthermore, differences between types of clays (e.g. kaolinite) could as well explain some differences in the retention of P.



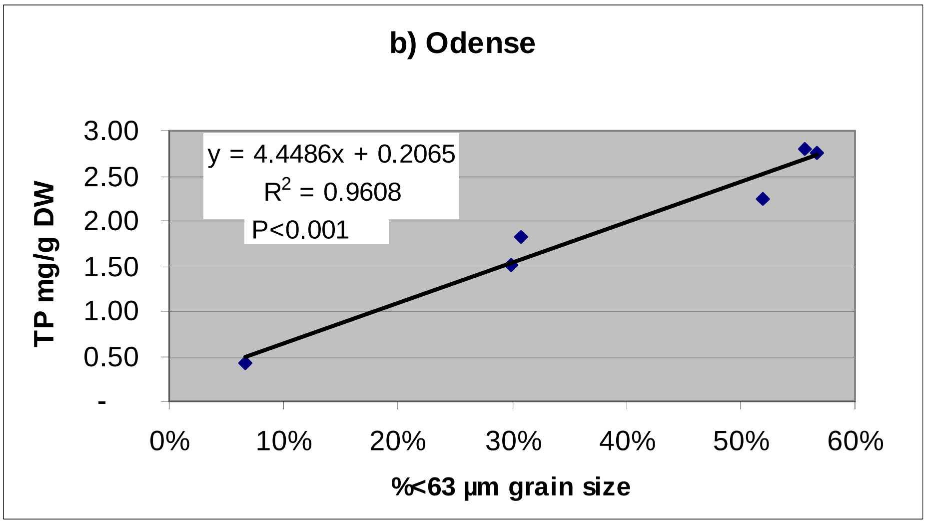


Figure 17: relationship between total phosphorus in the sediment and fraction under 63µm

The figure 18 illustrates the strong correlation between TFe and the percentage of grain size below 63µm. It can be seen that as the percentage of fine fraction in the sediment rises, the TFe content increases. This relationship might reflect the capacity for iron to be stored in clays.

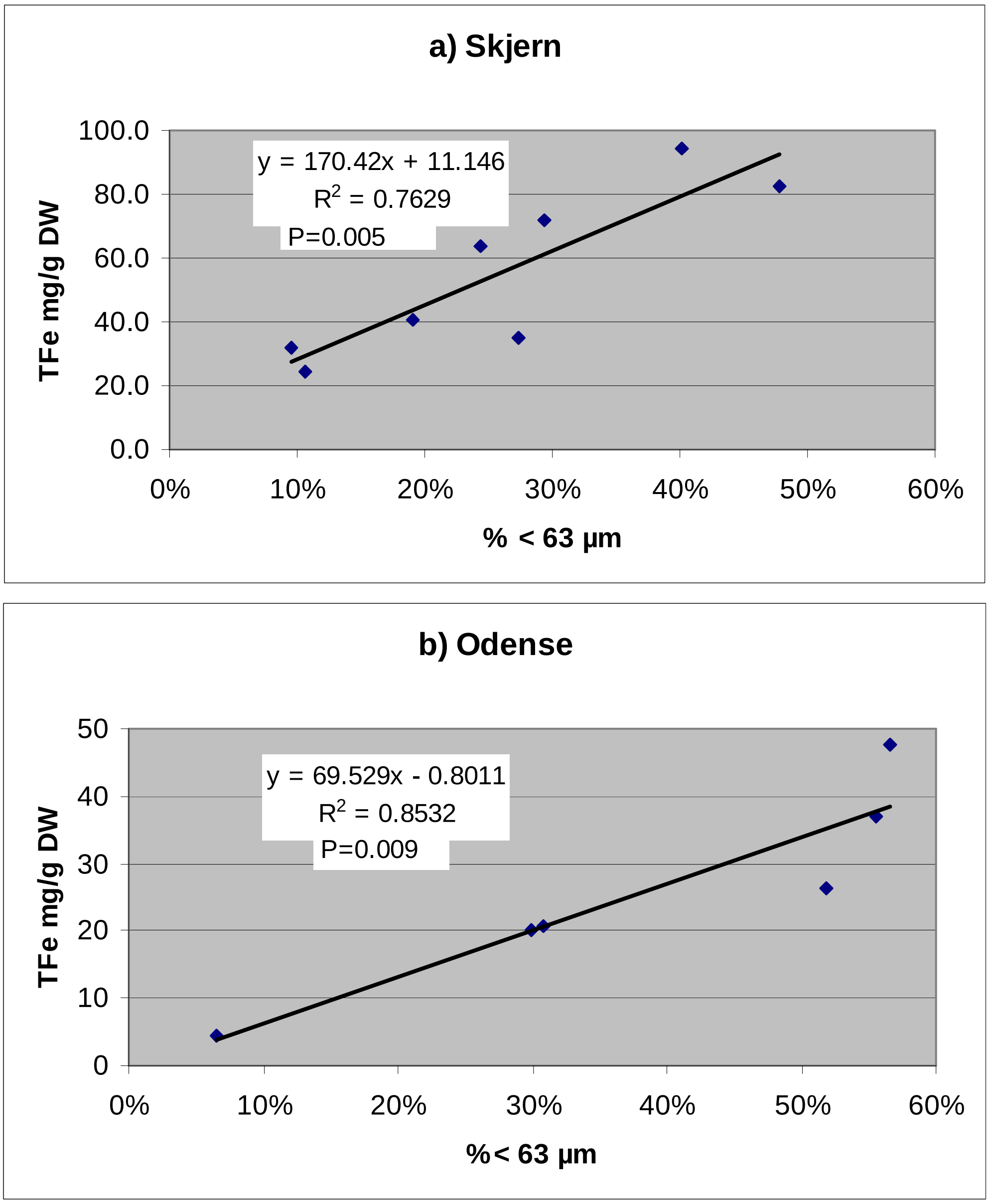


Figure 18: relationship between the percentage of fraction under 63µm and the Total iron content in the sediment.

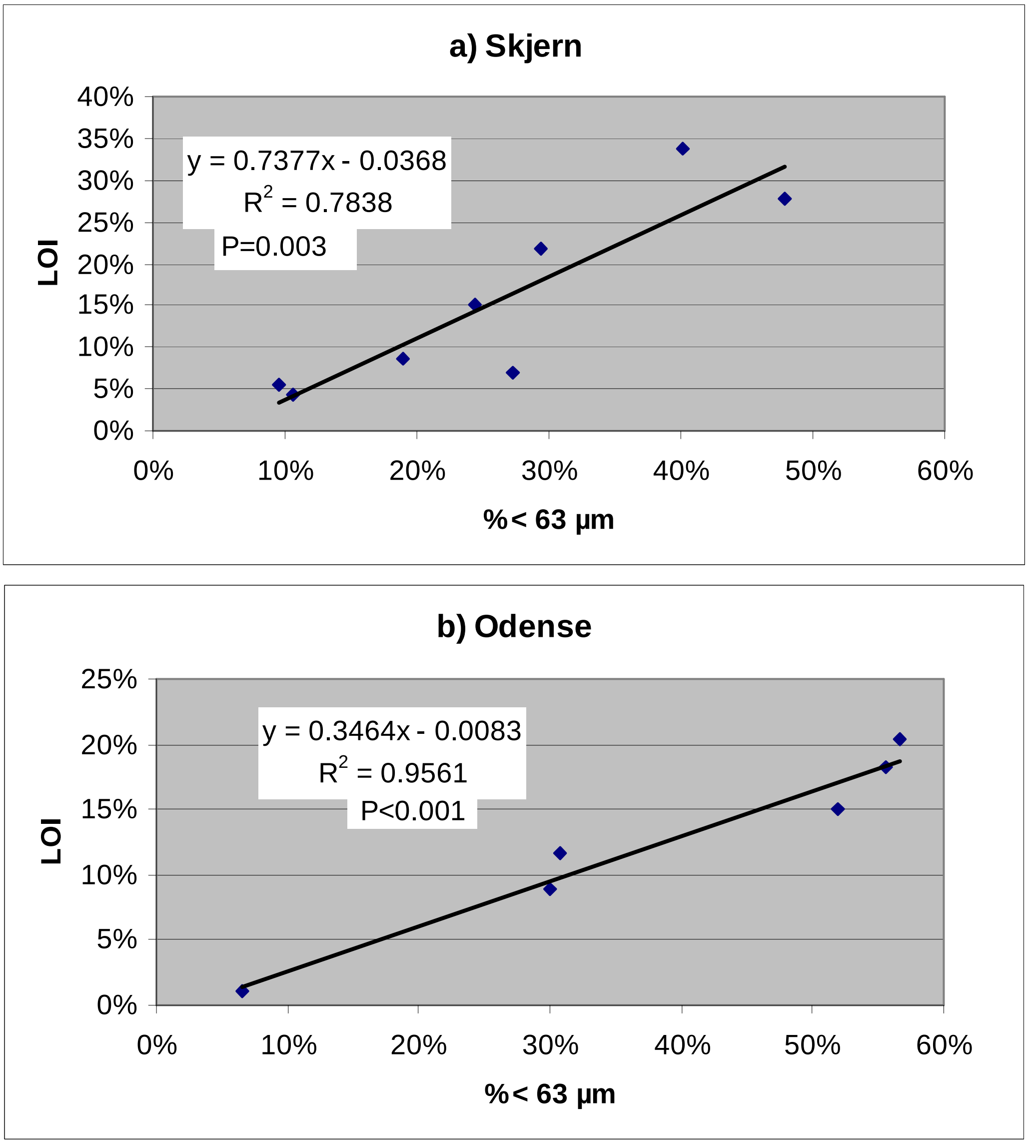


Figure 19 : relationship between the percentage of particles under 63 µm in the sediment (%< 63 µm) and the organic matter content (LOI)

Relationship from the same order than for TFe and are found between LOI and the fraction less than 63 µm as it can be seen in figure 19. The relationship between TFe and LOI in the materials might be explained by a segregation in the sediment due to internal transport and sieving (Danenlouwerse et al., 1993) and /or by some associations between iron and organic matter such as clay-humic complex.

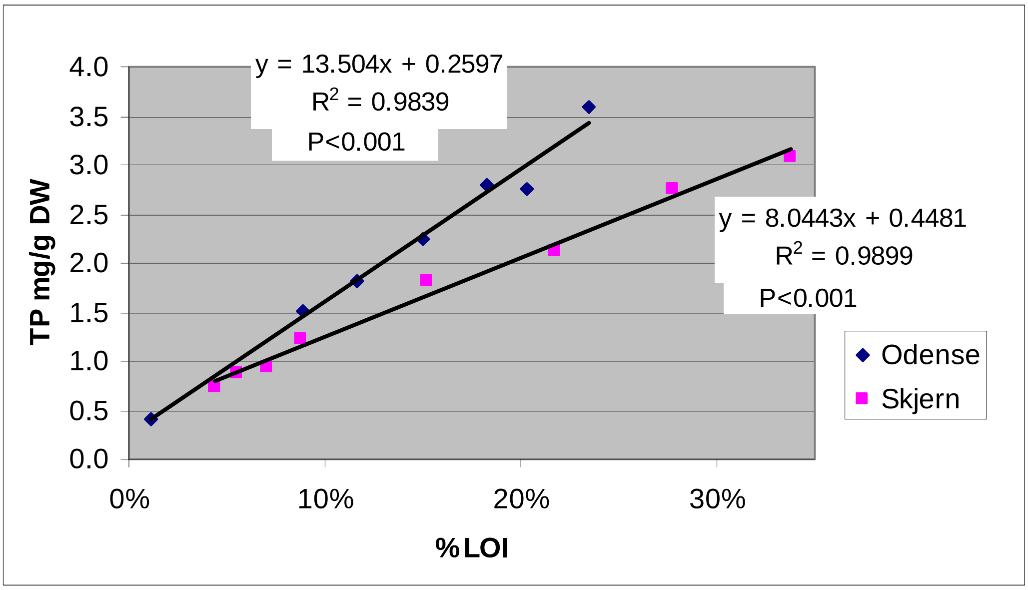


Figure 20: Relationship between Loss on Ignition (LOI) and Total Phosphorus for the sediment from river Skjern and River Odense.

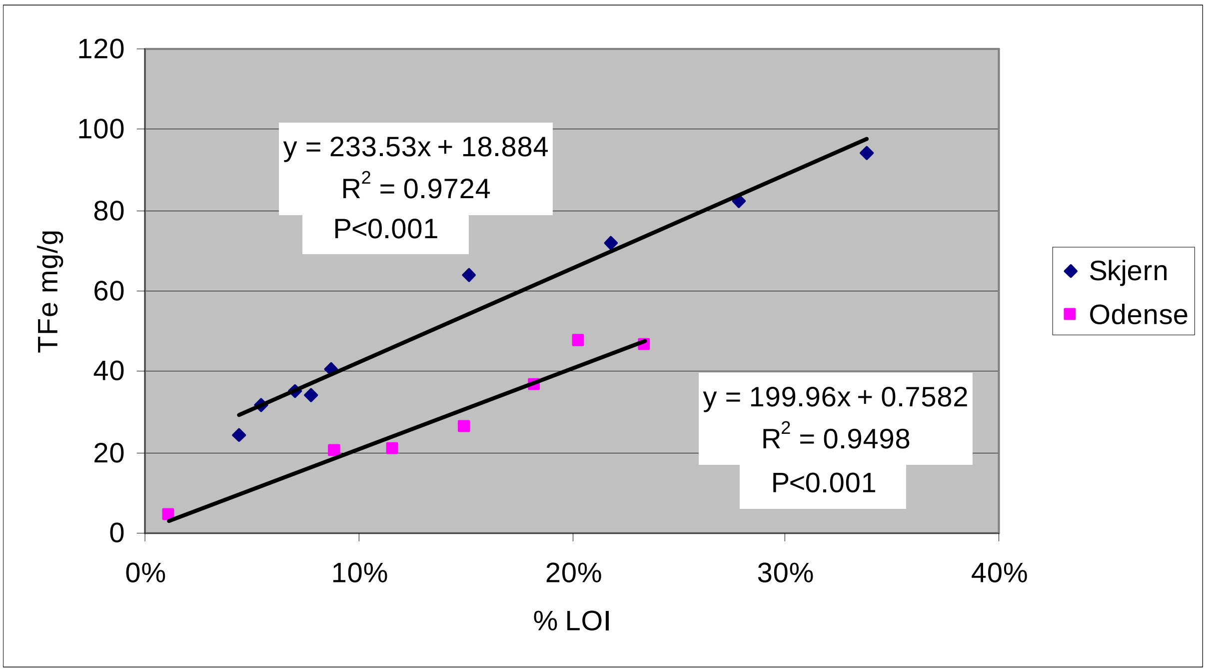


Figure 21: relationship between Loss on Ignition (LOI) and Total Iron (TFe) in the sediment for Skjern River and Odense River.

The figure 20 shows some strong relationships between TP and LOI. These correlations might be explained by the fact that as LOI and TFe are strongly correlated (figure 21) and as TFe and TP are strongly correlated as well, therefore it is not surprising to find some correlations between TP and LOI. In addition, it is known that some of the phosphate comes from the mineralization of organic matter which could strengthen this relationship.

IV.1.2. Nitrogen

IV.1.2.1. Ammonium analyses

As the experiment is realised under aerobic condition and without any bacterial activity, the only Nitrogen specie present in solution should be ammonium. The analyses done to determine ammonium concentration in the water revealed an increase in concentration for the water samples from both rivers (figure 22). For the river Skjern the release of NH_4^+-N increases with the distance from the channel (except for 16.5 m and 40.8 m). The same trend can be noticed for Odense sediment although the samples 8 m - 10.7 m – 16 m do not follow exactly this order.

At the end of the experiment, for Skjern sediment, ammonium reached concentrations, in the water, ranging between 106 and 650 µg/g DW at respectively 16.5 m and 40.8 m while for Odense sediment these concentrations ranged between 45.5 and 930 µg/g DW at respectively 1 m and 40.8 m from the channel. In the case of Skjern River we can distinguish two groups of curves: the five lowest curves with a final released concentration between 178 and 300 µg/g DW and the 3 uppermost curves ranging between 500 and 930 µg/g DW. The cause of these differences will be developed further.

There are significant correlations between NH_4^+-N released and the distance from the channel (Skjern y = 7.0083x + 144.41 R^2 = 0.70 p = 0.005 Odense y = 22.071x - 11.787 R^2 = 0.92 p < 0.001)

In both case it can be noticed that a large amount is released in the first's days of the experiment. At day 5, for Skjern sediment, between 51 and 68 % of the total amount released was already released and between 71 and 121 % for Odense sediment. This pulse can be provoked by the first drying stage which would have engendered lysis of cells. Another possible source of ammonium can be the solubisation of ammonium which was accumulated in the sediment before the first drying stage. A similar pulse of N after drying was established by in the case of Australian lake sediment dried at 20 °C during 40 days (Qiu and McComb, 1996). This pulse is even clearer in our case as there is no bacterial activity. Thus, N released coming from lysis of cells will be delivered at the rewetting after the 1st stage of drying, resulting in a flush of ammonium.

It is difficult to see the influence of the 2nd and 3rd drying steps even if in the case of Skjern the drying phase between day 5 and 7 appears to stimulate the release. For Odense it is not possible to see any effect but it could be explained by a larger amount already released. For the same reason it is not possible to determine any effect of the agitation.

The release is after the first week very slow because almost all the stock of NH_4^+ was already liberated to the water phase and as there is no bacterial activity there is no more mineralization and production of ammonium.

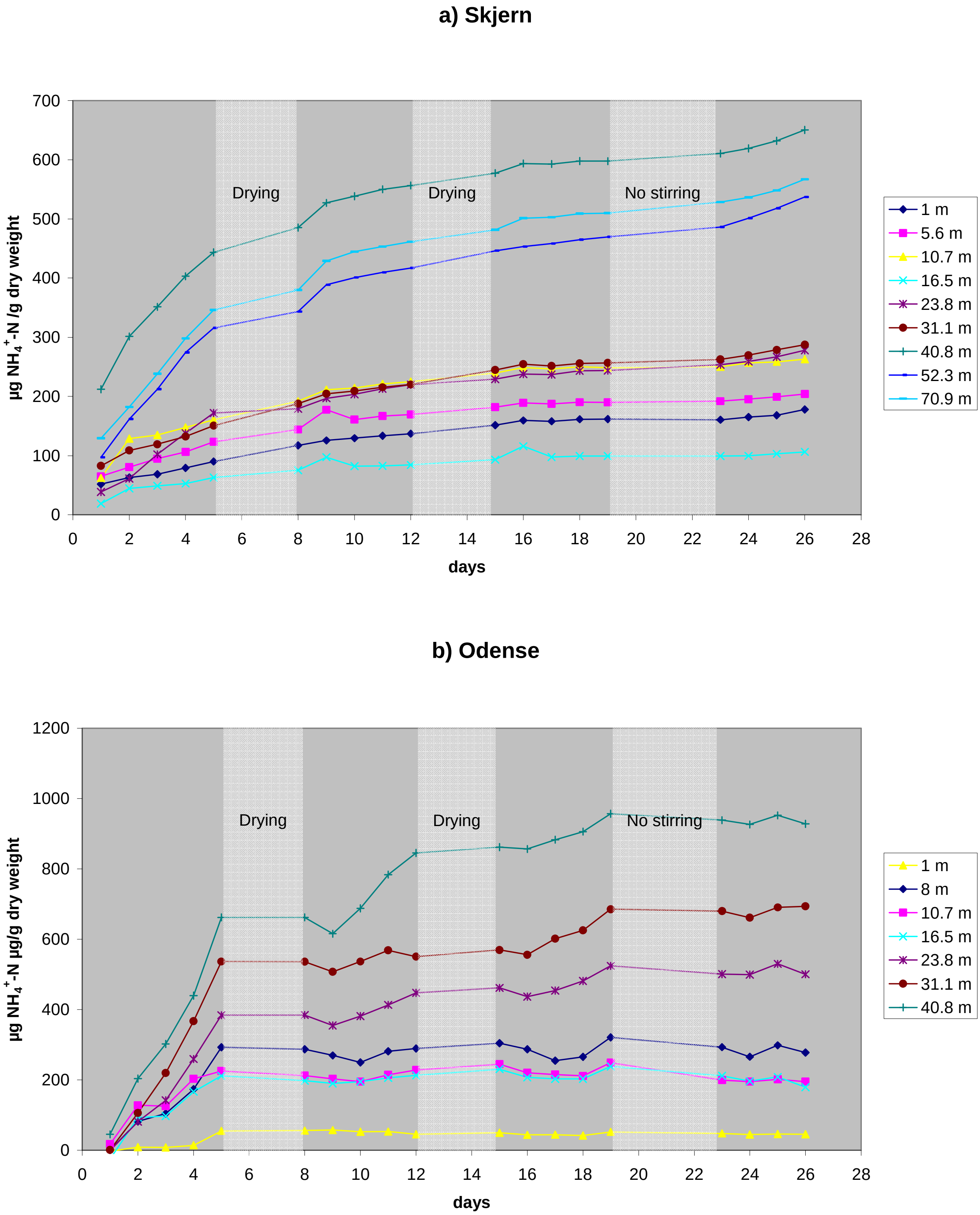


Figure 22: Cumulated concentration of Ammonium (NH_4^+) in the water during the experiment and at the different distances (m) from the river channel. a) for the sediment from the river Skjern; (b) for the sediment from the river Odense. The drying phases were done during 2 days at 60 °C. Note the different scale between the Y-axes.

IV.1.2.2. Relationships with sediment characteristics and comparison between the two rivers.

Total Nitrogen

The values of TN in the sediment before incubation are mentioned in the table 7. The average TN concentration incubation is 3.3 mg/g DW for Skjern and 8.1 mg/g DW for Odense. There is a linear correlation between TN and NH_4-N released (Skjern y = 0.0818x + 70.085 R^2 = 0.75 p = 0.004 Odense y = 0.0565x - 71.436 R^2 = 0.75 p = 0.01).

The percentage of TN that was released was calculated (table7). The average amount released is 11.2 % for Skjern and 7.4 % for Odense. A remarkable value of 23.6 % is reached at 1 m from the Odense river channel.

Skjern				Odense			
Distance (m)	TN µg/g DW	NH4 released µg/g	% released	Distance (m)	TN µg/g DW	NH4 released µg/g	% released
1	2583	178	6.9%	1	193	46	23.6%
5.6	1913	204	10.7%	8.0	4860	278	5.7%
10.7	3412	263	7.7%	10.7	6645	195	2.9%
16.5	757	106	14.1%	16.5	9631	179	1.9%
23.8	1705	278	16.3%	23.8	10471	500	4.8%
31.1	3678	287	7.8%	31.1	12612	694	5.5%
40.8	7121	650	9.1%	40.4	14321	928	6.5%
52.3	2937	537	18.3%				
70.9	5712	567	9.9%				

Table 8: Total Nitrogen (TN) contained in each samples and amount of ammonium (NH_4^+) released to the water.

Organic Matter

As it was explained in part I most of nitrogen is found in organic matter and will be liberated throughout mineralization. As a consequence, the relationships between LOI and TN (fig. 23) and between LOI and NH_4^+ released show some strong correlations (Skjern y = 1734.9x + 86.718 R^2 = 0.92 Odense y = 3675.9x - 115.05 R^2 = 0.77 p < 0.001). Three samples from the river Skjern show some percentage of Organic matter much higher than the other (22 to 34 versus 4 to 15 %) (table 8), these numbers could explain the higher release previously described for the 3 furthest distances from the channel in section. The significant correlations between the distance and the percentage of LOI (Skjern y = 0.0039x + 0.0382 R^2 = p = 0.005 Odense y = 0.0053x + 0.0418 R^2 = 0.91 p < 0.001) demonstrate an increase in the organic matter content in the sediment as the distance from the channel increases.

Skjern		Odense	
Distance (m)	LOI	Distance (m)	LOI
1	7.1%	1	1.1%
5.6	4.4%	8	8.9%
10.7	8.7%	10	11.6%
16.5	5.5%	16.5	15.0%
23.8	7.8%	23.8	18.3%
31.1	15.2%	31.1	20.3%
40.8	33.8%	40.8	23.4%
52.3	21.8%		
70.9	27.8%		

Table 9: Loss on Ignition expressed as a percentage in each sample.

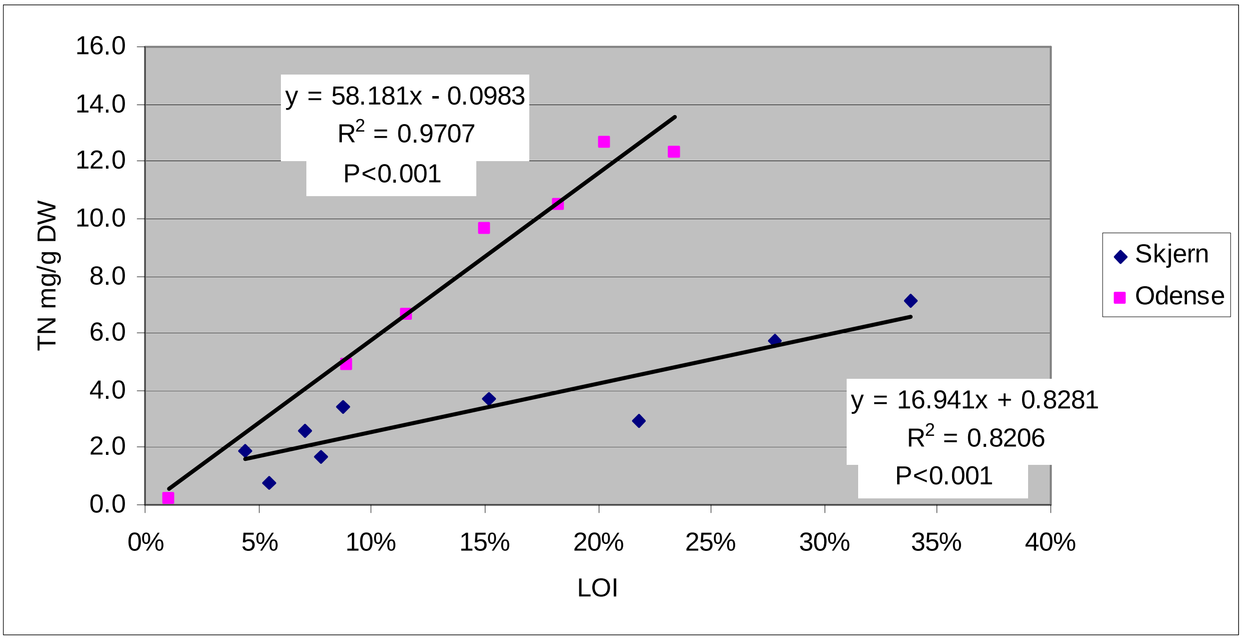


Figure 23: Relationship between Loss on Ignition (LOI) and ammonium released for the sediments from river Skjern and River Odense.

Carbon Nitrogen ratio

The C/N is used as an indicator of the speed of mineralization of organic matter: The higher the ratio, the higher the speed of mineralization. Therefore, it signifies that the production of NH_4^+ is higher and then it could be assumed that a larger proportion of TN would be released if bacteria would be present in the sediment which is not the case here. The C/N ratios are relatively similar within samples from a same river which can be explained by a same origin of the organic matter (table 10).

Skjern				Odense			
Distance (m)	C mg/g DW	N mg/g DW	C/N	Distance (m)	C mg/g DW	N mg/g DW	C/N
1	36.5	2.6	16.5	1.0	3.8	0.2	23.0
5.6	24.0	1.9	14.6	8.0	46.6	4.9	11.2
10.7	44.4	3.4	15.2	10.7	57.2	6.6	10.0
16.5	7.7	0.8	11.9	16.5	86.9	9.6	10.5
23.8	20.4	1.7	14.3	23.8	92.6	10.5	10.3
31.1	46.4	3.7	14.7	31.1	102.9	12.6	9.5
40.8	83.1	7.1	13.6	40.4	102.6	14.3	9.7
52.3	35.9	2.9	11.4				
70.9	71.4	5.7	14.6				

Table 10: Carbon and nitrogen content in the sediment. The ratio C/N is expressed in mol/mol.

Spatial variability

The grain size analysis performed highlight that the TN and OM contents are significantly correlated to the fine fraction of the sediment (figure 24 and 19).

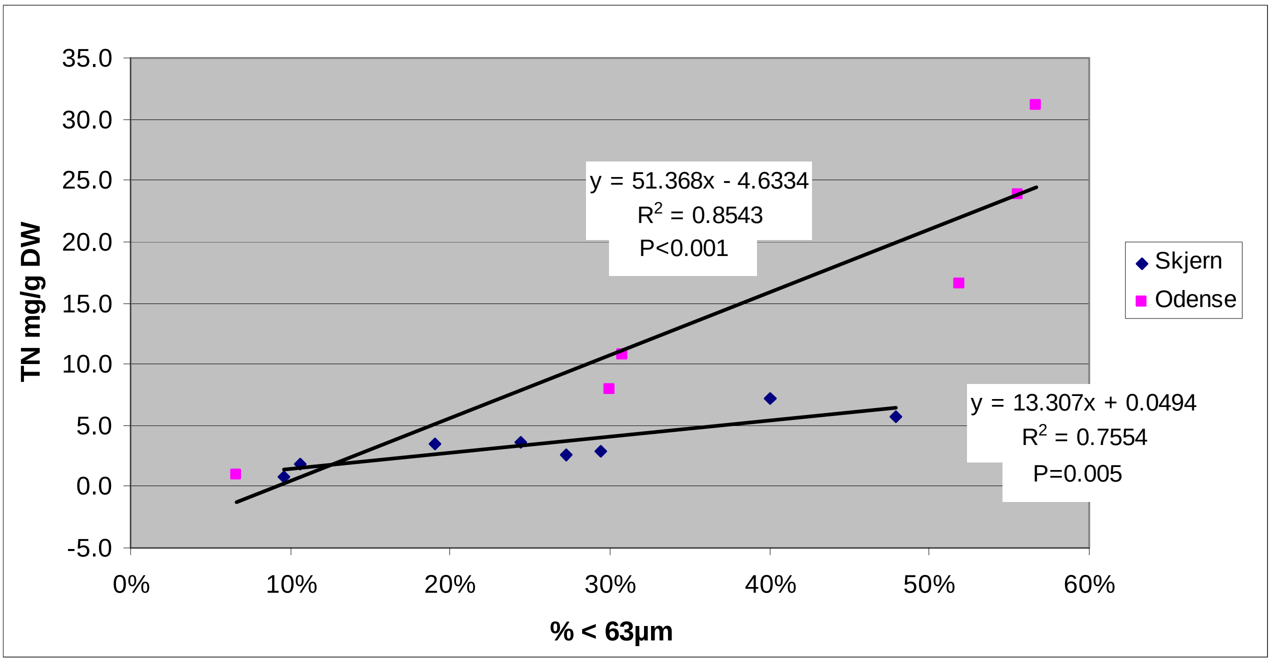


Figure 24: Comparison of the grain fraction under 63µm and the total Nitrogen.

According to these results, it can be hypothesized that the grain size appears to be a factor controlling the OM content which influences TN concentration and consequently the release of NH_4^+. Therefore to know the percentage of LOI could provide good indications of the potential release from the sediment to the water. Indications could be given by the percentage of fine fraction as well but this value is more difficult to obtain than the LOI.

IV.2. Experiment 2: Release of phosphorus and nitrogen from floodplain sediment submitted to rainfall.

After 2 months, the four mats did not show any major changes in visual appearance. Only few seeds germinated and the plants did not grow higher than 3 cm. The absence of plant growth could be attributed to the lack of light which has engendered complicated conditions for photosynthesis or by the absence of an underlying soil which prevents the deepening of the roots. The lack of light was due to the configuration of the system which was creating a lot of shadow above the sediment.

The amount of sediment on each mat was different as it can be read on table 11. The differences are explained by the variation in sediment deposition along the transect on the floodplain.

dist. from the channel	amount of deposited sediment (g)
5.6	634
16.3	322
23.5	169
101	42

Table 11: amount of sediment deposited on each mats. The weight was determined after drying at 60 °C.

The total amount of rainfall precipitated on the sediment is figured on the table 12. It corresponds to 43 mm (precipitation for April) added to 47 mm (precipitation for May) applied on a 30 cm diameter surface. The percentage of water collected ranges between 75 and 81 % which represents an evapotranspiration rate between 0.28 and 0.37 mm / hour. This value is of the same order than the evaporation rate determined by weighing a bucket filled with water every week which was around 0.30 mm / hour.

Distance from the channel (m)	total amount of rainfall (mL)	total amount of water collected (mL)	% of water collected	Evapotranspiration mm / hour
5.6 m	6246	5052	81%	0.28
16.5 m	6246	4774	76%	0.35
23.8 m	6246	4788	77%	0.34
101 m	6246	4689	75%	0.37

Table 12: Quantity of rainfall applied on each sediment, quantity of water collected after percolation in the mats, evapotranspiration rate.

IV.2.1. Phosphorus

IV.2.1.1. Phosphate analyses

A release of PO_4^{3-} to the water phase occurred during the duration of the experiment (figure 25). The release of PO_4^{3-}-P increases with increasing distance from the channel. However, the correlation is not significant ($y = 0.0113\,x + 0.7366$ $R^2 = 0.612$ $p = 0.21$) After 61 days the amount released varied between 0.35 and 1.7 µg / g DW at respectively 5.6 m and 101 m.

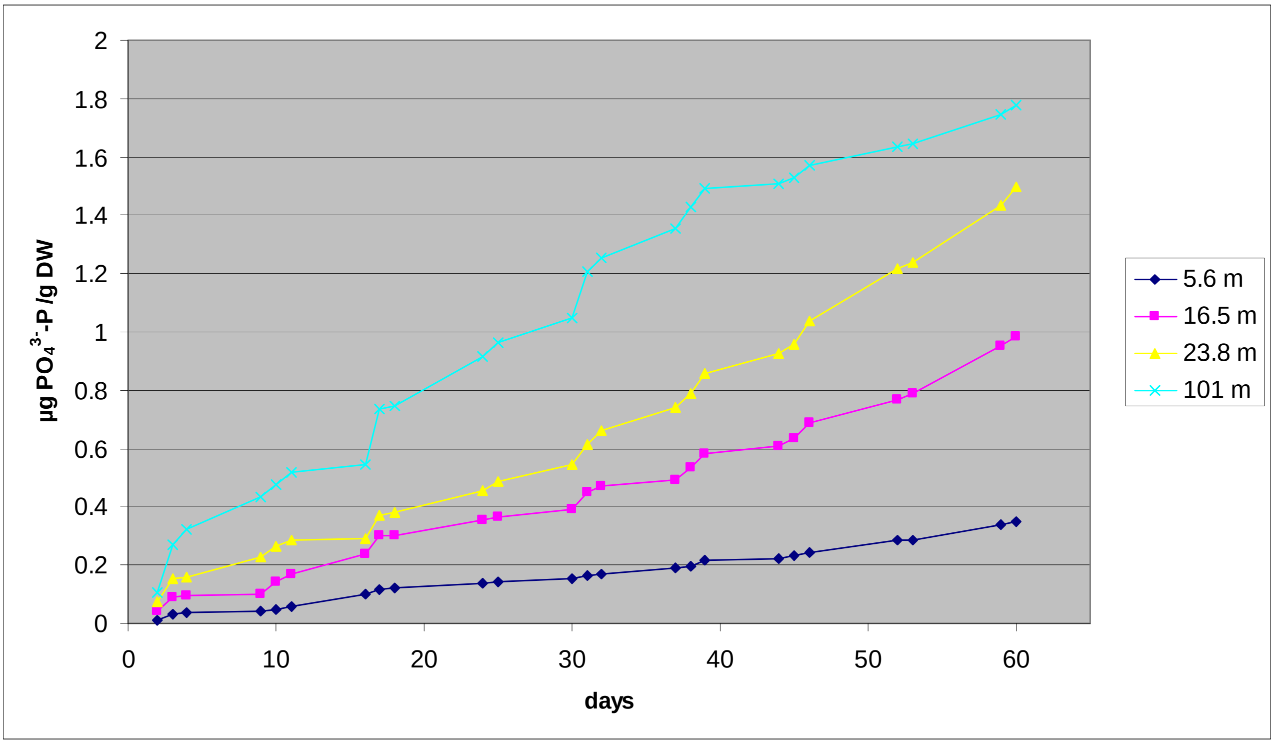


Figure 25 : Cumulated concentration of PO_4^{3-}-P released during the experiment for the different samples of sediment collected at 5.6 m, 16.5 m, 23.8 m and 101 m from the channel on the floodplain of Odense River.

IV.2.1.2. Relationships with sediment characteristics

Total Phosphorus

distance from the channel (m)	TP µg/g DW	PO_4^{3-}-P released µg/g DW	% PO_4^{3-}-P released
5.6	2065	0.35	0.017%
16.5	2997	0.98	0.033%
23.8	3351	1.50	0.045%
101	4830	1.78	0.037%

Table 13 : Content in Total Phosphorus (TP), Phosphate (PO_4^{3-}-P) released to the water phase by the sediment at the end of the experiment and percentage of phosphorus released for each of the samples collected on Odense floodplain.

As it can be seen in table 13, the TP content is increasing with the distance from the channel. TP is significantly correlated with the distance from the channel ($y = 25.057\ x + 2390.05$ $R^2 = 0.90$ $p = 0.05$). PO_4^{3-} released is correlated with TP but the relationship is not significant ($y = 0.0005\ x – 0.5356$ $R^2 = 0.868$ $p = 0.07$). The percentage released is very low, only very little of phosphate are released from the sediment. In natural conditions more plant growth could have been expected and therefore a P-uptake would have presumably reduced the P-release.

Iron

distance from the channel (m)	TFe mg/g DW
5.6	28.6
16.5	32.6
23.8	34.7
101	85.5

Table 14: Total Iron concentration in the sediment at different distances from the Odense River channel.

The material harvested at 101 m is much richer in iron than the three others sampling sites (5.6 m 16.5 m 23.8 m)(table 14). Iron is correlated with the distance from the channel ($y = 0.6161\ x + 22.714$ $R^2 = 0.9938$ $p = 0.003$). This higher iron content might explain the TP concentration in the sediments even if the relationship found is not significant ($y = 0.0216\ x - 26.106$ $R^2 = 0.85$ $p = 0.08$).

Sequential extraction

dist (m)	BD fraction			Total		
	µmol Fe / g	µmol PO4 / g	Fe:PO4	µmol Fe / g	µmol P / g	TFe:TP
5.6	140	15	9.3	340	83	4.1
16	208	21	10.1	522	123	4.3
23	338	23	14.4	777	124	6.2
101	490	31	16.0	1071	236	4.5

Table 15: content in Iron and Phosphorus in the Bidithionite (BD) fraction and in the sediment. The molar ratio between Iron and Phosphate in BD fraction (Fe:PO4) and between Total iron and Total phosphorus in the sediment (TFe:TP).

In the table 15, it can be observed that the ratio Fe:PO4 is increasing with the distance from the channel. It signifies that the sorption capacity is higher for the sediment harvested at 101 m and thus that its particles can bind phosphate more easily and to retain it more strongly. The TFe:TP ratio is really lower for the total sediment than in the BD fraction. The BD fraction contains around 45 % of the Total Iron of the sediment whereas PO4 in BD fraction represents about 17 % of the total Phosphorus. Therefore it means that most of phosphorus is stored in other pools or under organic form. The ratio Fe:PO4 in the BD fraction was lower in the Odense sediment in the previous experiment (cf. table 7). A hypothesis explaining this difference could be that the intensity of the flood event was different and therefore the materials eroded, transported and deposited were of different characteristics.

distance from the channel (m)	% PO_4^{3-}-P Water fraction
5.6	0.053%
16.5	0.036%
23.8	0.030%
101	0.015%

Table 16: Percentage of Phosphate measured in the water fraction compared to TP

The percentage of PO_4^{3-}-P in water fraction is indicated in the table 16, the values are very low which could explain the low percentage of release of PO_4^{3-} from the sediment to the water phase. The relationship between these two parameters is nevertheless not significant (y = -0.5705 x + 0.0005 R^2 = 0.5934 p = 0.22).
The percentage of PO_4^{3-}-P in water fraction seems to be influenced by the Fe:PO4 ratio even if here again the correlation is not significant (y = 4 e^{-05} + 0.0009 R^2 = 0.8384 p = 0.084). The percentage of PO_4^{3-}-P in water fraction and the percentage of PO_4^{3-}-P released are not significantly correlated (y = -0.5705 x + 0.0005 R^2 = 0.22 p =0.22). Although the correlation in sot significant it can be assume that there is a relationship between these two parameters as the percentage of PO_4^{3-}-P in the water fraction represents the Phosphate soluble in water. The absence of correlation might be explained by:

- The bacteria might play a role by retaining some of the phosphate or by delaying the release.

Grain size

The median grain size (D50) decreases for the first 3 distances and then is higher at 101 m (table 17). This can be explained by the composition of the sample. Indeed, contrary to the other samples which are more mineral, the sample collected at 101 m from the river is composed by much of fragment of plants, wood, etc. The density of these matters is under 1, therefore it can float on the water and go further than minerals particles which are subjected to the action of gravity. An oxidation of the organic matter before the wet sieving would have probably given very different results.

Distance from the channel (m)	D50	%<63µm
5.6	0.089	33%
16.5	0.057	54%
23.8	0.046	64%
101	0.148	29%

Table 17: Grain size of the sediment collected: median diameter (D50) and percentage of particles under 63 µm.

Organic matter

The organic matter content confirms that the sample collected at 101 m is much more organic than the sediment the three other grass mats (table 18). .

distance from the channel (m)	LOI
5.6	21%
16.5	24%
23.8	26%
101	64%

Table 18: Percentage of Loss on Ignition (LOI) in the different samples collected on Odense floodplain.

IV.2.2. Nitrogen

IV.2.2.1. Ammonium analyses

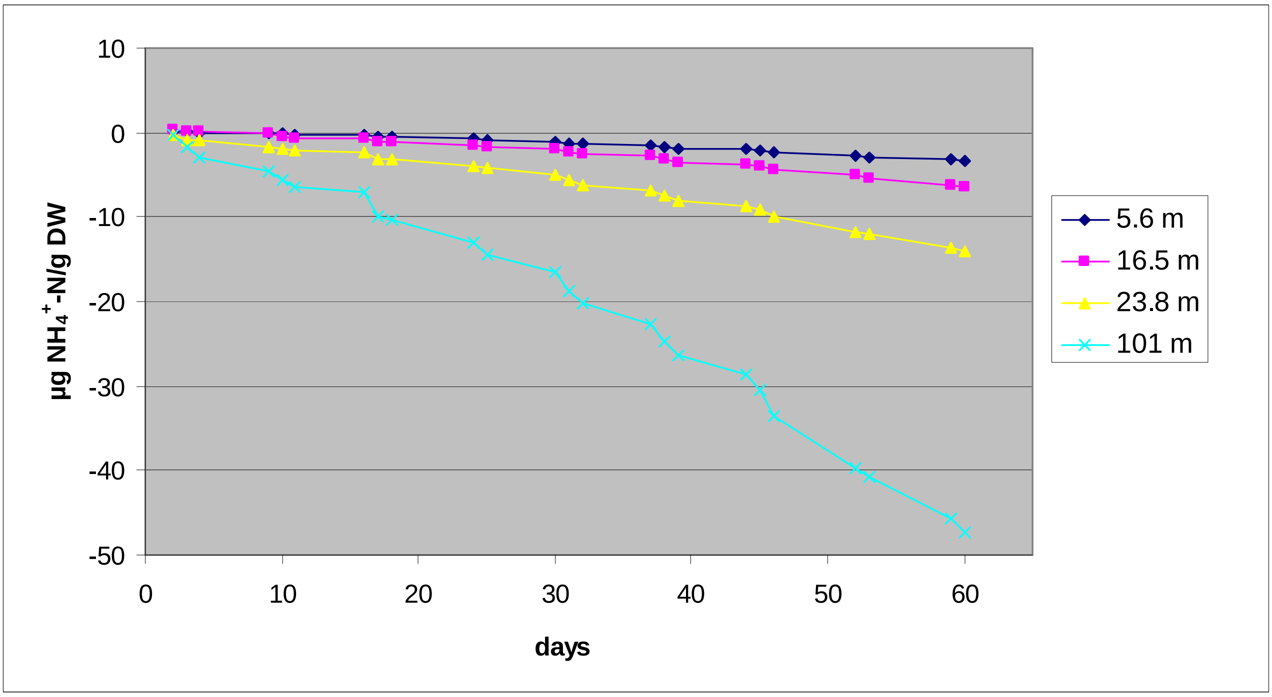


Figure 26: Cumulated concentration of ammonium measured in the water compared to the concentration ammonium in the rainwater during the experiment for the different samples of sediment.

The cumulative concentration of NH_4^+ measured in the outflow water sampled is presented in figure 26. The negative values are explained by the fact that the concentration of NH_4^+ is lower in the samples collected that in the rainwater applied on the sediment. Therefore it means that some of the NH_4^+ has been has been retained, taken up or transformed to another compound in the sediment.

Rainwater is not the only source of ammonium in the sediment. NH_4^+ comes as well from the organic matter by the ammonification process which is performed by bacteria. The “uptake” of NH_4^+ in the sediment can also be explained by the transformation of NH_4^+ into NO_3^- via the process of nitrification done by bacteria.

Thus, this should contribute to an increase in the concentration in NO_3^- concentration in the sediment. There is a strong correlation between TN measured in the sediment before the experiment and NH_4^+ concentration (y = -2.2383 x + 8.8866 R^2 = 0.9933 p = 0.003). It signifies that the higher is the total Nitrogen, the higher is the NH_4^+ consumption. Knowing that TN represents the measurement of Nitrogen in the sediment and that the NH_4^+ consumed is coming from the rainwater it is, at first sight, difficult to conclude about the origin of this correlation.

However it is known that TN and NH_4^+ are not independent values, TN concentration is the sum of organic N (org-N) + NH_4^+ + NO_3^-. More precisely TN = org-N_{asd} + org-N_{sol} + $NH_4^+{}_{ads}$ + $NH_4^+{}_{sol}$ + $NO_3^-{}_{sol}$ (ads: Adsorbed on particles; sol: in solution)

Nitrification processes can take place in the water phase and in the sediment.

Ammonification of org-N occurs in the sediment. Therefore, in the water phase, NH_4^+ and NO_3^- will be found whereas in the sediment NH_4^+, NO_3^- and org-N are present. The only species measured during the experiment are NH_4^+ and NO_3^-. A high TN in the sediment is linked to a high organic matter content (y = 43.579x - 2.7338 R^2 = 0.9678 p = 0.02). Thus it can be assumed that sediment with high organic matter content will have more bacteria to consume NH_4^+ and consequently a linear relationship can be found between the consumption of NH_4^+ and total Nitrogen. This assumption is right if it is assumed that the quality of the sediment is similar for every sample which is not the case as C/N differs within the samples. Nevertheless, as the C/N increases with the distance, our explanation might be still valid except the fact that a linear regression would not be the best tool to correlate the two variables.

IV.2.2.2. Nitrate analyses

According to the conditions of the experiment (aerobia and bacterial activity) and knowing that oxidation of nitrite to nitrate proceeds at a faster rate than the oxidation of ammonium (Reddy and Patrick, 1984), nitrite level should be negligible or very low, thus it was decided to measure both NO_2^- and NO_3^- as NO_2^-. In the figure 27, it can clearly be seen that nitrate concentration increase in the outflow water during the experiment. The amount released at 101m from the channel is much higher than for the others distances.

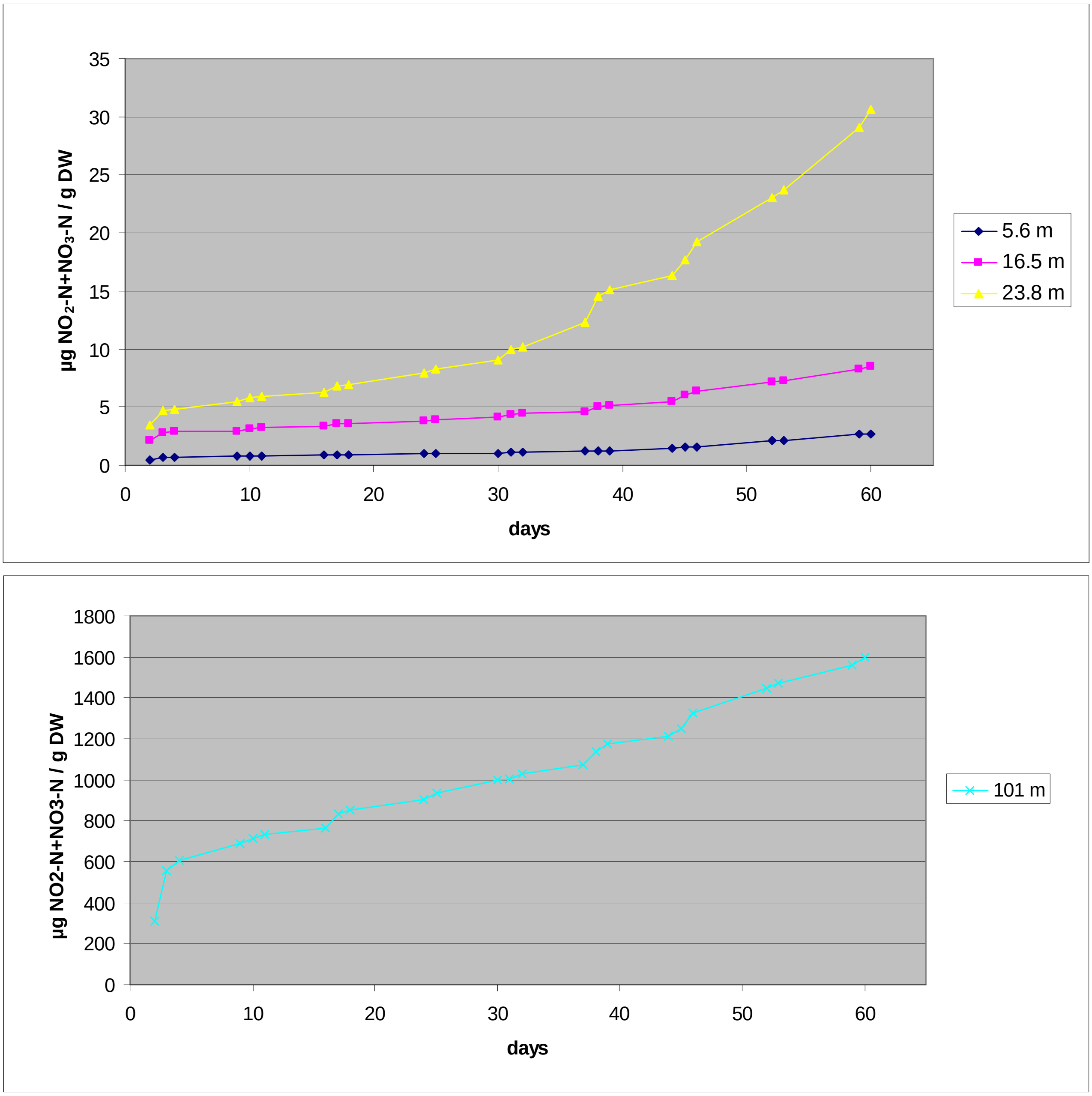


Figure 27: cumulated concentration of nitrite + nitrate measured in the water for the different samples of sediment collected. Due to a higher release, the curve for 101 is shown in another plot with a different scale.

Nitrate probably both comes from the mineralization of organic matter (i.e. ammonification) and the subsequent nitrification of NH_4^+ to NO_3^-. An additional contribution could be the nitrification of the ammonium already present in the sediment. A much higher amount of nitrate is released by the sediment collected at 101 m from the channel. It could be explained by a higher amount of organic matter resulting in a higher bacterial activity. The correlation is significant ($y = 3890.1x - 897.63$ $R^2 = 0.9943$ $p = 0.02$) but must be taken with caution due to the configuration of the data (i.e. 3 values of similar order and one extreme value). This amount is not only from what was "uptaken" from the rainwater because if it is compared with NH_4^+ from rainwater the absolute value is lower than the concentration of NO_3^- for the four distances but the closest from the channel. Consequently, the amount released might be attributed to the mineralization of organic matter. Besides, a look at C/N ratio (table 20) indicates that mineralization and hence ammonification is more intense at 101 m.

An increase of the rate of release seems to happen after day 30 as a breakpoint in the curves can be observed. This effect might be attributed to the rise of temperature from 8 to 12 °C and its possible influence on bacterial activity. A higher temperature can stimulate the activity of bacteria which could degrade organic matter faster and therefore increase the production and the release of NO_3^-. Frederick (1956) has demonstrated that the greatest increase of nitrification in soils is between 7 and 15 °C, therefore even a rise of 4 °C (i.e. from 8 to 12 °C) can make a significant difference in the formation of nitrate.

Total Nitrogen

distance from the channel (m)	N mg/g DW	%N released
5.6	4.6	0.06%
16.5	7.7	0.11%
23.8	10.5	0.29%
101	24.9	6.42%

Table 19: Total Nitrogen in the sediment and Percentage of Nitrogen released compared to the total.

The release of nitrogen is ranging between 0.06 and 6.42 % at respectively 5.6 m and 101 m from the river channel, after 61 days of experiment (table 19). The percentage of release is linked with the total nitrogen in the sediment ($y = 85.207\,x - 605.2$ $R^2 = 0.936$ $p = 0.03$)

C/N

distance from the channel (m)	C mg/g	N mg/g	C/N
5.6	53.7	4.6	13.7
16.5	78.6	7.7	11.9
23.8	90.7	10.5	10.1
101	165.2	24.9	7.7

Table 20: Carbon and Nitrogen content in the sediment.

The observation of the Carbon and Nitrogen content and especially of the C/N ratio shows that the rate of mineralization is increasing with the distance from the river (table 20). Thus the lowest bacterial activity will take place at 5.6 m while the highest one will be at 101 m from the river.

V. Conclusion

V.1. Experiment 1

The study of the drying and rewetting of floodplain sediment placed in beakers filled with rainwater and the subsequent release the two nutrients studied has demonstrated different results for the two rivers.
The main results and conclusions are:

Phosphorus

- After 26 days, the average release of phosphorus was 22 µg/g DW and 357 µg/g DW for the Skjern sediment and the Odense sediment respectively. It means that the release from Odense materials was almost 20 times higher than for Skjern.
- The procedure of drying and rewetting had a stimulating effect for the P-release. Stirring contributed as well to the P-release by breaking the weakest bonds between particles and PO_4^{3-}.
- The P-release to the water phase was attributed to:
    - Cells lysis due to drying,
    - Decomposition of Organic matter (before first drying),
    - Disruption of P binding by drying or stirring.
- Sediment from Odense River had a higher Total Phosphorus (TP) content as compared to the Skjern River (2.2 mg/g DW and 1.2 mg/g DW respectively).
- The mean P-release from the sediment as compared to the total P content is around 10 times lower from Skjern sediment than from Odense sediment with respective value of 1.7 % and 17 %.
- The iron concentration in the sediment is higher for Skjern than for Odense (40 mg /g DW and 26 mg/g DW) respectively. This difference is explained by the fact that the iron content is naturally higher in the River Skjern catchment.
- Phosphorus can be bound onto iron hydroxides which is confirmed by TP concentrations strongly linked with the iron concentration (Skjern R^2 = 0.98 $p<0.001$ Odense R^2 = 0.9056 $p<0.001$).
- The Fe:PO4 ratio in the BD fraction is significantly lower for Odense than for Skjern (4.3 and 51). It means that the sorption capacity is almost fully exploited for Odense sediment. Thus, the retention of Phosphate is weaker for Odense sediment than for Skjern.
- An influence of the Fe:PO4 ratio on the percentage of phosphate in the water soluble fraction has been distinguished. The higher the ratio, the smaller the proportion of phosphate in the water soluble fraction.
- The proportion of phosphate in the water soluble fraction is correlated with the percentage of phosphate released to the water phase. Hence, the Fe:PO4 ratio influences the percentage of PO4 in the water fraction and consequently the release of PO4 to the water phase.

- The LOI and TFe are strongly correlated probably because of the sorting of particles or by association of these two compounds in clay-humic complex.
- The grain size is smaller for Odense than for Skjern which confirm one of the initial hypotheses of a different texture between the two catchments.
- The grain size influences the quantities of Iron, P, OM in the sediment as most of these elements are stored in the fine fraction.

Nitrogen

- Ammonium is released from the sediment to the water phase during the experiment. The release ranged between 106-650µg/g DW and 45.5-950 µg/g DW for Skjern and Odense respectively.
- The release of ammonium was positively correlated with the distance from the river channel.
- The procedure of drying had a stimulating effect on the N-release.
- At day 5 of the experiment the amount of N released compared to the value at the end of the experiment was 51-68 % for Skjern and 71-121 % for Odense. These values characterise the very fast release of ammonium to the water phase after rewetting.
- At the end of the experiment, an average of 11.2 % and 7.4 % of the total nitrogen content in sediment was released from Skjern sediment and Odense sediment respectively.
- The source of N released were identified as:
  - Cell lysis due to drying induced,
  - Solubilisation of ammonium accumulated in the sediment by mineralization (ammonification) of organic matter before 1st stage of drying.
- The release of NH_4^+ is correlated to the initial total Nitrogen and to the Organic matter content in the sediment.

V.2. Experiment 2

The release of P and N from Odense sediment exposed to climatic conditions reproducing the months of April and May has led to the following results and conclusions:

Phosphorus

- The release of phosphate from the sediment to the water phase was very low, being between 0.35 and 1.7 µg/g DW at 5.6 m and 101 m respectively.
- The mean P-release from the sediment compared to the total P content, was also very low as the highest percentage of P released at the end of the experiment (i.e. after 61 days) was 0.045 % from the sediment sample collected at 23.8 m.

- The TP concentration in the sediment was increasing with the distance from the river channel with values ranging between 2.1 and 4.8 mg/g DW.
- The total iron content in the sediment was strongly correlated with the distance with values ranging between 28.6 and 85.5 mg/g DW at 5.6 m and 101 m respectively.
- The Fe:PO4 ratio in the BD fraction varied gradually with the distance being 9.3 in the sediment at 5.6 m and 16.0 at 101 m.
- The percentage of phosphate measured in the water soluble fraction compared to the TP content is decreasing with the distance to the river and appears to be controlled by the Fe:PO4 ratio in the BD fraction.
- The percentage of phosphate in the water fraction was not found to be significantly correlated with the percentage of phosphate released in the water.

Nitrogen

Ammonium

- The analyses of the outflow water, after its transit throw the sediment layer, put into evidence a consumption of the ammonium contained in the rainwater by the sediment. This consumption was the result of retention by the sediment, an uptake by bacteria or a transformation to other compounds (e.g. nitrate by nitrification).
- The consumption was increasing with the distance from the river channel due to a higher bacterial activity.
- The rainwater was not the only source of ammonium. Ammonium was also derived from organic matter via ammonification.

Nitrate

- A release of Nitrate from the sediment to the water phase was measured. The amount released varied increasingly with the distance from the channel. The amount released by the sediment collected at 101 m (1600 µg NO_3^--N /g DW) was much higher than for the three other sediments collected (5.6 m: 2.7 µg NO_3^--N /g DW, 16.5 m: 8.5 µg NO_3^--N /g DW, 23.8 m: 30.6 µg NO_3^--N /g DW).
- The amount of Nitrate released compared to the total nitrogen content represents between 0.06 % and 6.42 % for the sediment collected at 5.6 m and 101 m respectively.
- The amount of nitrate released to the water is correlated with the total concentration in Nitrogen and with the percentage of organic matter.
- The C/N ratio which is an indicator of the speed of mineralization of organic matter is decreasing as the distance from the channel increase. Therefore the highest mineralization rate is found at 101 m from the river (C/N = 7.7 which favours nitrification).

- An increase in the release of NO_3^- to the water phase is noticed after day 30 which corresponds to the increase of temperature from 8 to 12 °C in order to reach the mean temperature of May. This temperature increase is responsible for the stimulation in bacterial activity resulting in higher nitrification rate and consequently increasing the release of NO_3^- to the water phase.

V.3. Conclusion

A non-negligible proportion of phosphorus (1.7 % and 17 % for Skjern and Odense respectively) was released in the first experiment (i.e. after repeated cycles of drying and rewetting), whereas a very low amount of phosphorus was released (0.045 % from Odense sediment) during the second experiment which is closer to natural conditions.
In the case of nitrogen the release varied between 11.2 % and 7.4 % for Skjern and Odense respectively in the first experiment while in the second experiment, it was ranging from 0.06 % to 6.4 % from Odense sediment collected at 5.6 m and 101 m respectively.

Therefore the first experiment could be considered as a potential P-release due to the tough treatment applied to the sediment (i.e. cycles of drying, rewetting and no bacterial activity) while the second experiment was closer to natural conditions
This report has provided some evidences on the utility of floodplain and riparian area restoration, as a very efficient trap for phosphorus and a good way for reducing and delaying the release of Nitrogen which is totally in line in the perspective to fulfil the objectives defined by the WFD.

Prospects and recommendations for future researches:

- The utilisation of the Fe:PO4 ratio in the BD fraction as an indicator of potential P-release could be developed in order to determine the status of sediment in term of nutrient storage capacity.
- It has to be emphasized that the rainfall simulator does not reproduce the kinetic energy raindrops have in natural conditions, therefore the effect of destroying, modifying the structures of the particles: the “splash effect” was not taken into consideration. This effect, by degrading the structure of the soils, could increase the release of phosphorus by exposing new surface to the action of water. Moreover, in this study, the focus was on the solubilisation of phosphorus. In real conditions, erosion, transport of phosphorus bound to particles and colloids might have an impact in the mobilisation of phosphorus. These aspects could be checked in an *in-situ* experiment.
- Furthermore, an *in-situ* experiment would provide some information about what happens during a whole year especially in winter when the release of P is generally higher due to the decomposition of plants. This could lead to the construction and the development of a P-release model.

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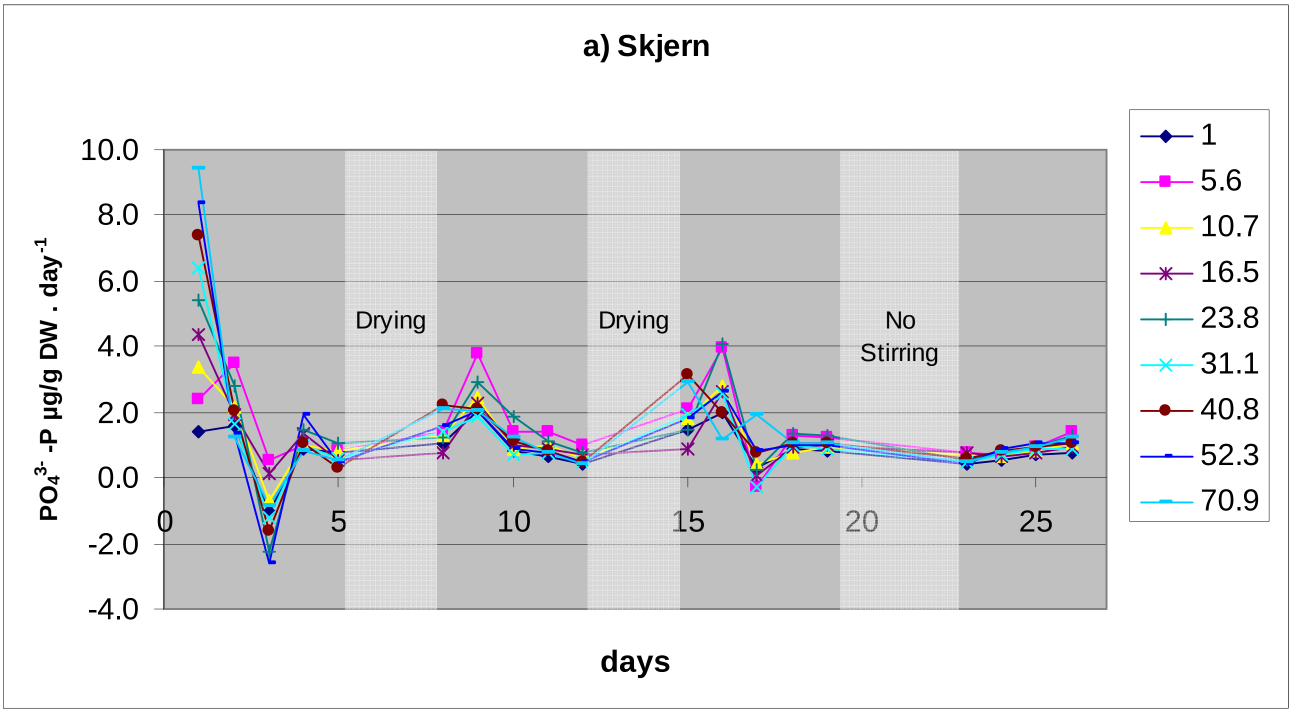
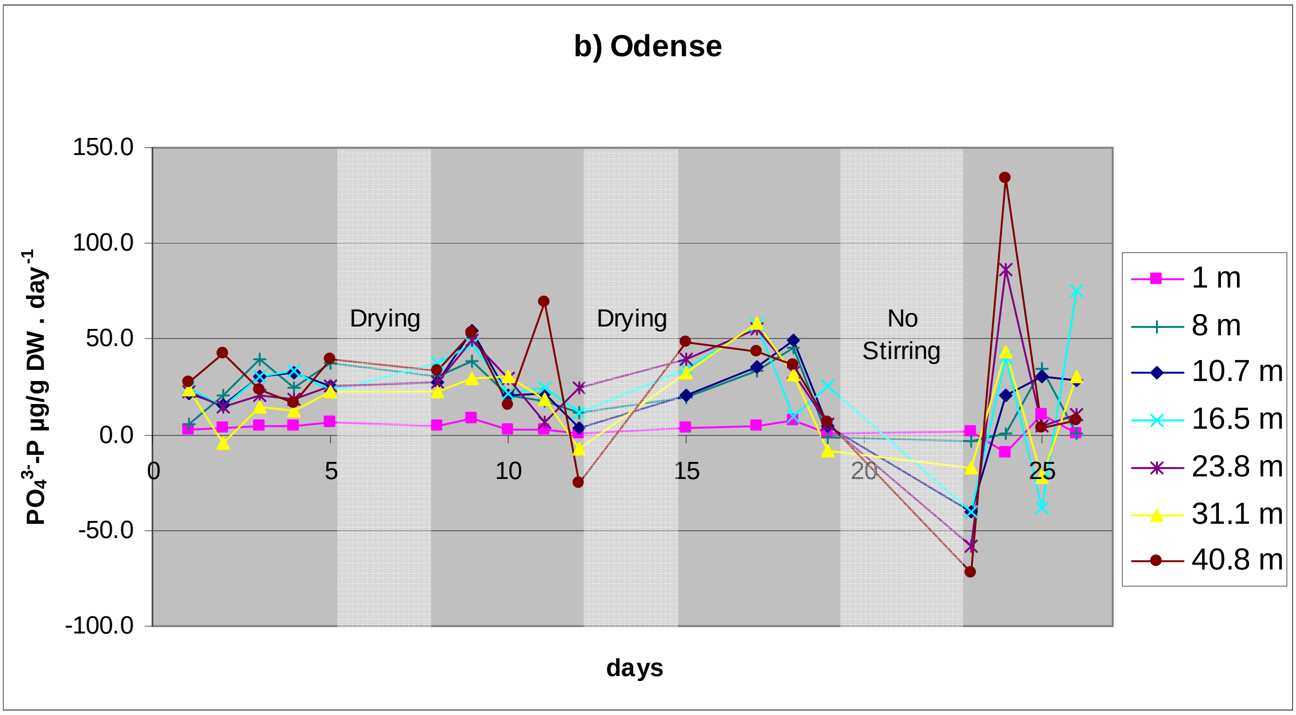
Appendices

Appendix 1: Composition of the artificial rainwater

NH_4-N = 0.50 mg/l
NO_3-N = 0.48 mg/l
Cl = 5.76 mg/l
K = 1.34 mg/l
Na = 2.67 mg/l
Ca = 0.21 mg/l
Mg = 0.069 mg/l
SO_4 = 0.273 mg/l or SO_4-S = 0.091 mg/l

Appendix 2: release rate





Rate of release in µg / g DW . day^{-1} for the sediment from a) Skjern River b) Odense River and at different distances (m) from the channel.

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