National Environmental Research Institute
University of Aarhus · Denmark

Report performed from April to August 2008

for obtaining of Master II

"Géo-Hydrosystèmes Continentaux en Europe"

Klaire HOUEIX

Investigating sources to a gradient in total phosphorus content in buffer strips along the Odense River

Supervised by Brian Kronvang

Recipients

Cécile GROSBOIS
U.F.R. des Sc. et Techniques
Département de Géologie
Parc de Grandmont
37200 Tours

Florentina MOATAR
U.F.R. des Sc. et Techniques
Département de Géologie
Parc de Grandmont
37200 Tours

Olivier COULON
Ag. de l'Eau Loire Bretagne
Avenue de Buffon
BP 6339
45063 Orléans

ACKNOWLEDGEMENTS

I thank all the people who inspired and helped me during this project.

I am especially grateful to Brian Kronvang, my research supervisor, for the advisability he offered me to work at NERI, and his constant encouragement, advices and enthusiasm.

I wish to acknowledge Deputy Director General Kurt Nielsen for his help in my integration at the workplace and in Denmark, and also his wife, for the wonderful day we had at their place.

Thanks to Uffe Mensberg, Henrik Stenholt and Marlene Venø Skjærbæk for field and laboratory work.

Many thanks to Søren Erik Larsen, Mickael Stjernholm, Kjeldgeerd Ane, Jøorgensen Joan, Carl Christian Hoffman, Peter Mejlhede Andersen, Tinna Christensen and Hans Estrup Andersen for their help in statistical analyses, GIS and their helpful advices during my work. I learnt a lot from them and almost became keen on statistical analyses.

Thanks to Anne-Dorte Villumsen, Inge-Lise Madsen, Lilian Mex-Jørgensen, Dorte Nedergaard, Anne-Mette Poulsen, Lars Kjær Møller, and John-Geert Rytter and the PC-supporters for technical design.

I also thank Dr Adrian Collins at ADAS in United Kingdom for performing the trace elements analyses.

Also, a special thank to colleagues at NERI who helped and whose company I have appreciated and all the “foreigners” (Caro, Marcello, Sandra, Pere, Carlos, Natalia, Juanito, David, Lucia, Elsa, Amandine, Franco, Marianna, Idylle, and Khoran) including Thomas of course!!

My stay in Denmark was supported in part by the European Commission and “la Région Centre” within the ERASMUS programme.

TABLE OF CONTENTS

SUMMARY

The origins of phosphorus (P) were investigated in 35 buffer strips in the Pilot Odense River Basin, in Denmark. The investigated 35 x 100 m reaches drain sub-catchments varying in soil type, land use and topography and are located along streams varying in stream order (sensu Strahler 1957) and height of riparian vegetation. The first two horizons (0-5 cm and 5-25 cm) of soil buffer strips and bank material at 60 cm and 20 cm above the stream bed were analysed for total phosphorus (total-P), Olsen-P (Pt), Water extractable P (Pw), carbon (C), and organic nitrogen (oN). Contents of 47 heavy metals were measured in the top horizon of soil buffer strips in a view to be used as tracer elements from agricultural activities (Cu, Ni, and Zn), from deeper groundwater bodies (As, Ba and Mo) and from sewage (Pb).

High gradient of total-P (from 259 to 4094 mg P kg^{-1} DW^{-1}) in soil buffer strips was evidenced and no significant difference was shown compared to contents in bank material. Total-P contents in buffer strips were found to be related to soil types, erosion risk and land use. Higher total-P concentrations were measured in peat soil, and buffer strips draining sub-catchments predominantly used as agricultural land and with low erosion risk. Total-P contents in stream bank were shown to be affected by stream order, indicating the importance of increasing deeper groundwater discharge with increase of stream order in the catchment. P in soil buffer strips was shown to be strongly bond with iron (Fe) and organic C. Moreover, Fe was shown to be strongly correlated respectively with tracer elements from deeper groundwater (As, Mo and especially Ba) and peat soil type. No clear evidence of impact of agricultural activities on P contents in buffer strips was found during the study.

Although we could not reach a final conclusion on the origin of P measured in buffer strips within the Odense River catchment utilising two different methodological approaches, this study evidenced that the binding capacity for P in buffer strips seems to be delivered by groundwater seepage into the hyporheic zone and that this phenomenon seems to occur in peaty areas and with increasing stream order.

Key words: phosphorus, buffer strip, agriculture, trace elements, deeper groundwater, catchment relationships

RESUME

Les sources potentielles de phosphore (P) ont été étudiées sur 35 bandes enherbées expérimentales, au sein du bassin de référence de la rivière Odense au Danemark. Ces 35 bandes de 100 m de long, reçoivent les eaux de ruissellement de sous-bassin variant en termes de nature de sol, occupation des sols et topographie ; elles sont situées le long de cours d'eau de rang (sensu Strahler 1957) différent dont la hauteur de la ripisylve diffère également. Le phosphore total (total-P), P-Olsen (Pt), phosphore dissous (Pw), carbone organique (C) et azote organique (oN) on été analysés pour les 2 horizons superficiels (0-5 cm et 5-25 cm) des bandes enherbées ainsi que dans les sédiments des berges à 60 et 20 cm depuis le fond du lit. Les concentrations de 47 métaux lourds ont été étudiés dans le premier horizon de sol, afin d'en utiliser certains comme traceurs des activités agricoles (Cu, Ni et Zn), des nappes souterraines (As, Ba et Mo) ou encore des eaux usées (Pb).

Un important gradient en total-P (entre 259 et 4094 mg P kg^{-1} MS^{-1}) dans les sols des bandes enherbées a été mis en évidence, ainsi que l'absence de différence significative avec les concentrations mesurées dans les sédiments des berges. La quantité en total-P s'est vue liée à la nature des sols, leur érodabilité ainsi que l'occupation des sols. Des teneurs plus élevées ont été mesurées dans les sols tourbeux ainsi que dans les sites expérimentaux recevant les eaux de ruissellement de sous-bassin à dominance agricole et dont le risque d'érosion est faible. Les concentrations se voient influencées par le rang des cours d'eau, indiquant donc l'importance de la contribution des eaux souterraines augmentant vers l'aval du bassin versant. Le phosphore dans le sol était fortement lié à l'élément fer (Fe) ainsi qu'à la matière organique carbonée. Aussi, le fer a montré d'importantes corrélations avec les éléments traceurs des nappes souterraines (As, Mo et Ba) et les sols tourbeux. Il n'a pas été mis en évidence d'impact de l'agriculture sur les concentrations en P mesurées durant cette étude.

Bien qu'aucune conclusion quant à l'origine du phosphore stocké, dans le sol des bandes enherbées, au sein du bassin versant de la rivière Odense, n'ai été avancée par la méthodologie appliquée, ce travail a permis de mettre en exergue que le potentiel de liaison du P dans ces sols semble être délivré par la présence et la communication avec des nappes souterraines profondes, au sein de la zone hyporhéique ; ce phénomène paraît prendre se produire en milieu tourbeux et s'accentue avec le rang de Strahler des cours d'eau.

Mots clés : phosphore, bandes enherbées, agriculture, éléments traces, nappes souterraines, relation avec les caractéristiques du bassin versant.

INTRODUCTION

Understanding the causes of, and being able to control, Phosphorus (P) concentrations in soils and water bodies is important because of its impact on water quality and associated effects on public health (Bell and Codd, 1996; Corell, 1998). Thus, in many European river basins, P losses from agricultural areas are the main P source to rivers, lakes, reservoirs, and coastal waters. The current intensive agricultural production systems are net consumers of Nitrogen (N) and P of which part is left in arable soils with a risk of later losses to groundwater and/or surface water via different hydrological pathways.

Denmark is a country in the Scandinavian region of northern Europe. Agriculture is today the main driving force for the P pressure on the Danish aquatic environment (Paulsen and Rubæk, 2005; Kronvang et al., 2005). Excess delivery of sediment and phosphorus to streams and lakes can damage spawning ground and high phosphorus concentration can create eutrophication in rivers and lakes (Kronvang et al., 2005).

The adopted European Union Water Framework Directive (EUWFD 2000) transposed in Denmark in 2003, into national legislation via the Environmental Objectives Act, demands that a good ecological condition shall be established in streams before the end of 2015. In Denmark, the objective of reaching a good ecological quality in water bodies will demand that the P-loss from agricultural areas is reduced. Consequently, responses in the form of introduction of general and targeted mitigation measures against agricultural P-losses in source areas and along the different P-pathways are needed. The P loss from agricultural areas in river basin arises from the contribution of dissolved and particulate phosphorus loss to surface water via different pathways (soil erosion and surface runoff, bank erosion, leaching, tile drainage water, Kronvang et al., 2002b).Based on the findings of Laubel et al.,(2003) the breakdown of total-P losses showed that stream bank erosion is the main P source to Danish surface waters. This has also be demonstrated by Kronvang et al.,(2005); they found out that estimated annual loss due to bank erosion was the greater compared to other pathways and draws on 275-645 $mg.yr^{-1}$. Bank erosion as a P source is rarely included when P losses in river basin are modelled. That is so for these reasons why research in Denmark are so interested in measuring bank erosion and P contents in strips and banks.

It is in this context, that the “Best Management of Stream Banks, Buffer zones and Floodplains for reducing Agricultural Phosphorus Losses” (BUFFALO-P) research project uprose: the aim is to develop and test guidelines, methods and tools that can support end users in implementing targeted mitigation measures in streams, buffer zones and floodplains for immediate reduction in the agricultural losses of phosphorus to the aquatic environment (Kronvang and al., 2007). This project consists in a combination of field work and laboratory experiments and field measurement to test and validate different research questions regarding the function of floodplains, buffer zones and river banks as sources and sinks for sediment and phosphorus forms.

The research project conducted during this internship has been titled: "Investigating sources to a gradient in total phosphorus content in buffer strips along the Odense River."

The catchment area of the Odense River covers approximately 1046 km² and represents the most common geomorphologic region in Denmark, that is to say, loamy moraine landscape, on the island of Funen. The main objectives of this project are to measure the total P content of natural and regulated Danish streams buffer strips, in the Odense River catchment and to search for possible reasons for the large gradient found in P content of these buffer strips.

The project hypotheses are:

- The total P content of Danish buffer strips can be explained by fertiliser and manure spills due to neighbouring agricultural arable land.
- The total P content of Danish buffer strips is linked to the erodibility of adjacent agricultural fields and the transport of soil and P via surface runoff from the field to the buffer zone.
- The total P content of Danish buffer strips can be explained by precipitation of iron and phosphate from seepage of deeper and reduced groundwater in the aerobic hyporheic zone.

The main results expected from this project are to qualify the reasons of the gradient found in P content of the buffer strips and supply knowledge on origins of phosphorus stored in the buffer strips along the River Odense. It will also increase our knowledge on the potential sources and sinks of P in Danish buffer zones lying as a corridor between stream channels and adjacent land use. This project is one of the first in that domain, and will supply knowledge which will be useful in term of management of agricultural practises. It is also enable us to understand the trapping effect of existing buffer zones along streams and qualify the origin of phosphorus contained in these soils.

BUFFALO-P project in which this research project is included is managed by a researcher from the Danish National Environmental Research Institute (NERI), the institute where this internship has been done during five months. 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. 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. In 2007, NERI became part of University of Aarhus which is the second largest University in Denmark. The following study has been carried out within the Department of Freshwater Ecology in Silkeborg (Appendix 1: Diagram of the organisation of National Environmental Research Institute). The competencies 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 watercourses, lakes 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 European Directives and National Action Plans on the Aquatic Environment.

This report consists of six chapters. In the report first will be described the studied area of the Odense River Basin and then some general information about phosphorus cycle in buffer strip will be explained. The third part will present methods implemented for analysing P in buffer zones and the results regarding the extraction of stream and catchment characteristics from GIS and their relationship with the phosphorus content in the investigation buffer zones. Finally, it will be presented the outcome of utilising the ‘fingerprinting’ technique to trace the origin of phosphorus utilising a number of trace elements.

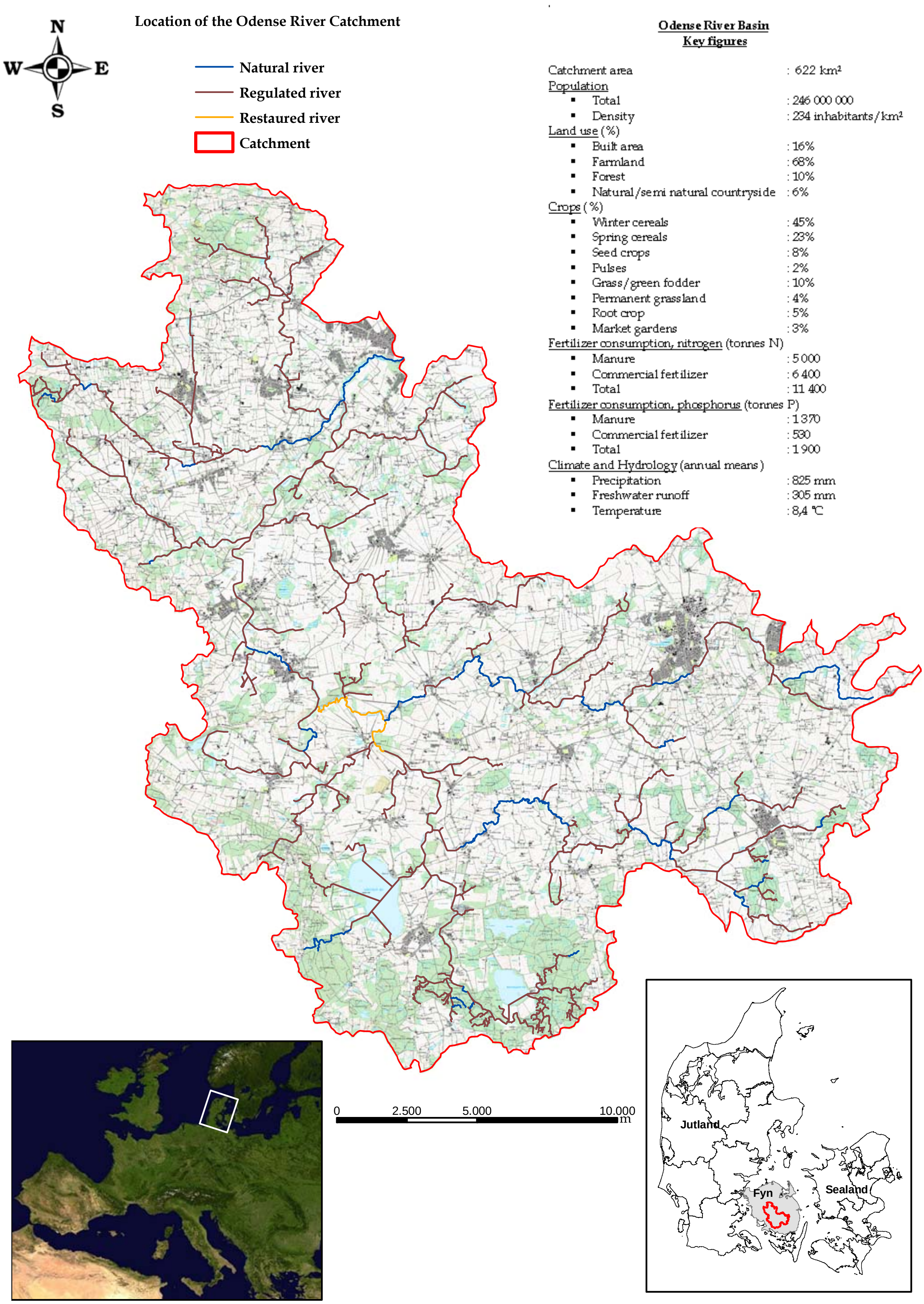


Figure 1. Location of the Odense River Catchment

I Description of the study area: River Odense Catchment

The River Odense catchment has been designated as the Danish pilot river basin on which the local water management authority has tested the implementation of the EU Water Framework Directive ahead of the official timetable. The reason for designating Odense River as a pilot river basin was that it covers a third of Funen, encompasses a broad spectrum of Danish aquatic and terrestrial habitats types, as well as major sources of environmental pressure.

The baseline characterization of Odense River Basin was thus prepared ahead of the official timetable together with a quantitative assessment of the various sources of pollution and the establishment of environmental objectives. The pilot project has also drawn particular attention to the problems concerning agriculture and the aquatic environment. The experience and knowledge gained through the Odense Pilot River Basin project and the other pilot projects are disseminated to water management authorities regionally, nationally and internationally, as well as to the EU Commission.

I.1 General case study characteristics

I.1.1 Location of the case study area

The Odense River Basin is located on the island of Funen in Denmark (Figure 1), the second largest Danish island. The basin comprises an area of 622 km^2 and is part of the Odense Fjord Basin (1046 km^2) and includes approximately 1100 km of open watercourses and 2600 lakes and ponds (>100m^2). The River Odense, which is about 60 km long and up to 30 m wide is the largest river on Funen (Figures 2 and 3).

I.1.2 Geographical characteristics

I.1.2.1 Climate

The annual precipitation and potential evaporation is about, 900 mm and 600 mm, respectively. There is a positive precipitation gradient from the northern coast toward the southern boundary of the catchment. The average monthly precipitation in River Odense catchment varies between approximately 40 mm in April and 90 mm in December/January. The average air temperature in Funen is 8.2˚C.

Figure 2. Odense River in Borreby

Figure 3. Moraine landscape in Borreby

I.1.2.2 Landscape and soil type

The present landscape of Funen was primarily created during the last Glacial Period (Figure 3). The most common landscape feature is moraine plains covered by moraine clay that was deposited by the base of the ice during its advance.

The clayey soils are the dominant soil types and encompass approximately 51% of the river basin, while the sandy soil types cover approximately 49%. The moraine soils of Funen are particularly well suited for the cultivation of agricultural crops.

I.1.2.3 Land use

Just as elsewhere in Denmark, land use in Odense River Basin is dominated by agricultural exploitation of the soil (Figure 4).

Farmland thus accounts for 68% of the river basin. Of the remainder, approximately 16% is accounted for by urban area/roads, 10% by forest and 6% by natural/semi natural countryside (i.e. meadows, mires, dry grassland, lakes and wetland).

The corresponding figures for Denmark as a whole are farmland 62%, forest 11%, and natural/semi natural countryside just over 9%.

The population of Odense River Basin numbers 246 000 000, of which approximately 182 000 inhabit in the city of Odense which is Denmark's third largest city.

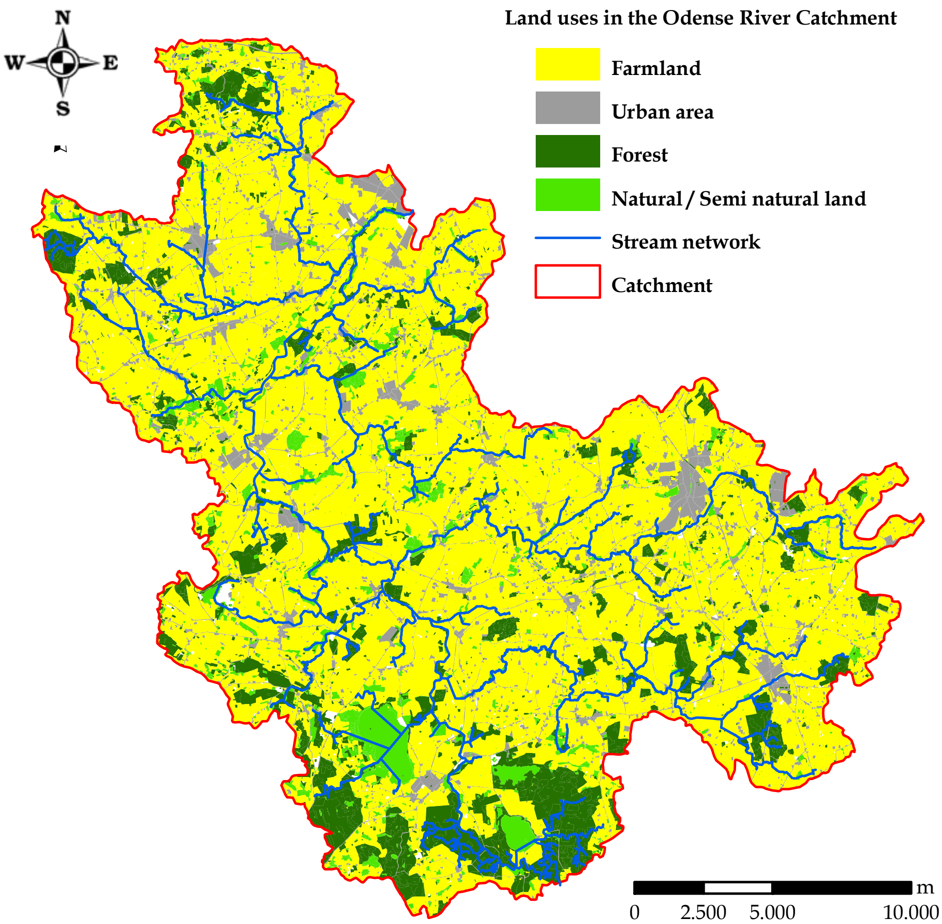


Figure 4. Map of the land uses in the Odense River Catchment in 2000 (Corine land Cover)

- **The main land use: agriculture**

The livestock herd in the river basin numbers approximately 60 000 livestock units, of which 59% is accounted for by pigs, 37% by cattle and 4% by other livestock. Livestock density average 0.9 livestock unit/ha farmland, corresponding to the national average. Nevertheless, it varies somewhat in the individual sub catchments of Odense River Basin.

The predominant crop type in the river basin is cereals (approximately 2/3 winter cereals), encompassing 63% of the arable land, while 10% is permanent grassland.

It is estimated that artificial drainage has been established on at least 55% of the arable land in Odense River Basin over the past 50-100 years. From around the 13^{th} century some of the watercourses in the Odense River Basin were dammed for mill operation. The appearance of the watercourses has also been changed through other forms of regulation. Many naturally meandering or sinuous watercourses have been straightened and the beds excavated, and in places the slope has been neutralized by the construction of falls. These activities really started in the 18^{th} century and accelerated up through the 19^{th} century until the last major regulation project in 1960, which encompassed a considerable part of the Odense River (Riis et al., 1999). The aim of such regulation was to ensure improved drainage and thereby to increase the possibilities to use the adjoining land for agricultural production. At the same time, rapid removal of the water was further accelerated in many places through intensive maintenance in the form of clearance of all aquatic vegetation as well as vegetation along the banks and borders of the watercourses and dredging of the bed substratum.

This disrupted the continuity of the watercourses, thereby hindering fish such as trout and eel from their natural migration between fresh water and sea water. The environmental state of 96% of the water bodies are not expected to meet the "good ecological state" objectives in 2015 due to physical conditions and/or wastewater discharges.

County of Funen estimates that 1/3 of the land area is nitrate sensitive with respect to groundwater quality.

I.1.3 Water system characteristics

I.1.3.1 Groundwater

Within the Odense River Basin there are 31 aquifers of which some are overlapping each other as they are situated in different depths and some transgress the borders of the watershed and are thus situated in more than one river catchment (County of Funen, 2005). The water bodies in the Odense River catchment have been given individual European Union Water Framework Directive objectives which should be reached but it is important to take into account that a water body is not a closed but an open and dynamic system which affects its surrounding and is affected by the surrounding in return.

I.1.3.2 Characterisation of water use

The water cycle in Odense River Basin is affected by a number of human activities. Each year, in the County of Funen, approximately 38 million m^3 of groundwater are abstracted for the drinking water supply. In addition, approximately 11 million m^3 are abstracted for industrials purposes, crop irrigation, etc. The total amount of water abstracted corresponds to approximately 25% of the mean summer runoff in the watercourses of Funen County. Drinking water is "returned" to the watercourses in the form of treated wastewater, but not necessarily in the area from where it was abstracted.

I.1.3.3 Protected areas

The water bodies in Odense River Basin are to varying extents encompassed by international conventions, national legislation and regional regulations.

There are seven Natura 2000 sites located in Odense River Basin. The sites have been designated in order to protect habitat types and species. Three of them have also been designated as Special Protection Areas (SPA) pursuant to the Birds Directive in order to protect selected bird species.

The Natura 2000 sites cover a total area of approximately 8 000 ha, of which half is accounted for by marine areas. Other international protected areas are groundwater bodies used for the water supply.

The wet habitat type mires, freshwater meadows and coastal meadows are protected under section 3 of the Protection of Nature Act along with lakes and watercourses. These three wetland habitat types account for 5.2% of the river basin.

Within Odense River Basin there are large areas that have been designated as national protected areas. The largest of these is the River Odense river valley.

The Funen County Regional Plan for 2005-2013 designates areas of special scientific interest and specifies quality objectives for coastal watercourses, lakes and watercourses, and for the terrestrial natural habitat types. Following the recent reform of Danish municipal and county administrative structure the Regional Plan has been accorded legal status through a National Planning Directive.

I.1.3.4 Odense Fjord

The Odense Fjord holds some unique physical qualities which support a large range of species. It constitutes an important habitat for birds and is as such subject to extensive environmental legislation independent of the European Union Water Framework Directive.

Odense Fjord is by far the largest surface water body in the river basin.

I.2 Institutional aspects

Funen County was the water district authority for the water district of Funen, until 1st of January 2007, according to the Danish national transposition of the EU WFD. After the 1st of January, the water district authority has been transferred to the national level due to the ongoing structural reformation in Denmark.

II Phosphorus cycling in Danish agriculture

A very extensive literature deals with nature of soil P and abiotic and biotic reactions that govern the fate of P in soils (e.g., van Riemsdijk et al., 1984, Sanyal and De Datta, 1991, Frossard et al., 1995, Sharpley, 1995, Robert, 1996 and Morel et al., 2000). The intention, in this part of the report, is not to present a review of phosphorus soil chemistry, but to highlight processes and factors that can be of prime importance for a buffer zone soil receiving various forms of P from upland sources. These processes govern the mobility of P across the buffer zone soils and consequently influence the dynamics of dissolved-P (sorption and desorption; sedimentation and erosion).

Several authors have shown that P accumulates in the surface of agricultural soils because of the net input of P from agricultural production (European Environment Agency, 1995). P application with manure can give rise to excess P loss in surface runoff as documented by Smith et al. (1998). In contrast to nitrogen, no simple relationship exists between the consumption of P in fertilizer and animal manure and the riverine concentration and transport of P (e.g. Kronvang, 1996). As reported by Kronvang et al., (2002), the reason for this is presumable the many sources and pathways of importance for P loss to surface waters (urban wastewater, scattered dwellings, erosional sources and leaching from arable land).

II.1 Nature of phosphorus and key processes of transformation

P is found in organic and inorganic form, which are distributed throughout the solid and aqueous media and living tissue that comprises the soil. Inorganic P is sorbed at the surface of soil particles (e.g., clay, minerals, $CaCO^3$ particles), or is precipitated, mainly with Ca, Al, or Fe. P is also associated with primary minerals in the fine and coarse fractions of the soil.

The overall distribution of P is a result of a series of physico-chemical and biological processes that determine the exchange dynamics among the pools (Sanyal and De Datta, 1991 and Frossard et al., 2000). Sorption–desorption and dissolution–precipitation are the main processes influencing soil and sediment inorganic P. Once adsorbed, P can diffuse into the matrix of the adsorbent substrates, leading to stronger chemical bonds.

Non-living organic P in soils originates from plant and microbial uptake. Interactions of organic P with soil minerals and stabilized organic matter, lead to P associated with organo-mineral complexes resistant to hydrolysis, and thus long-term persistence of organic P in soils. This slower dynamic is governed by immobilization–mineralization processes (Sanyal and De Datta, 1991). Microbial biomass plays an important role in soil P cycling because of its high assimilation rate and turn over rate.

II.2 Variables influencing phosphorus dynamics

When a form of P is added to a system (e.g., runoff into a buffer strip), the solid–solution P equilibrium is altered. The equilibration dynamics depend on time, the concentrations of the various P forms in the solution, and the particular properties of the soil. The ability of the soil to regulate this equilibration process is characterized as its P binding capacity. The P binding capacity expresses the availability of solid phase sites to sorb P. Soil particles are also transported with surface runoff from sloping fields towards buffer zones.

A sedimentation of coarser and finer soil particles will take place in buffer zones due to their lower slopes and their vegetative cover which acts as a barrier for the water and hence decreases the velocity.

The higher the soil binding capacity is, the greater the efficiency of P uptake and the greater the amount of incoming P stored in the soil are. Organic matter tends to decrease the binding capacity. In the long term, high levels of P input can saturate the soils when the P binding capacity is used, leading to greater P mobility and a higher risk of soluble P transfer (Sharpley, 1995).

II.3 Environmental reactivity of phosphorus

Phosphorus is rather rare in nature when compared with its requirements by terrestrial and aquatic plants. Because of this, P is efficiently taken up into biomass and thus plays a key role in the control of ecosystems productivity. In aquatic ecosystems, excessive P results in pollution due to overproduction of macrophytes and algae, leading to eutrophication. Most of the total-P stored within ecosystems is found associated with particles (particulate-P) because of its strong affinity for the solid phase. As a result, P accumulates in biomass, at the soil surface, and in the sediment compartment of aquatic ecosystems. Only the dissolved forms (dissolved-P), and particularly orthophosphate are taken up by algae, micro-organisms, or higher plants (Figure 5).

The consumption of P in chemical and animal fertilizer in Danish agriculture is at a medium to low level in relation to the rest of Europe (European Environment Agency, 1995). The total P input to Danish arable land reached a maximum in the 1970s and the consumption of P in chemical fertilizer has decreased in Denmark since the late 1980s. At that time, evidence of the possible P loss from arable fields was, for the first time, presented in Denmark, contradicting the traditionally held agronomic view that all P is strongly fixed by most soils. An increase was seen in the consumption of P in animal manure due to increased pig production during the 1990s in Denmark.

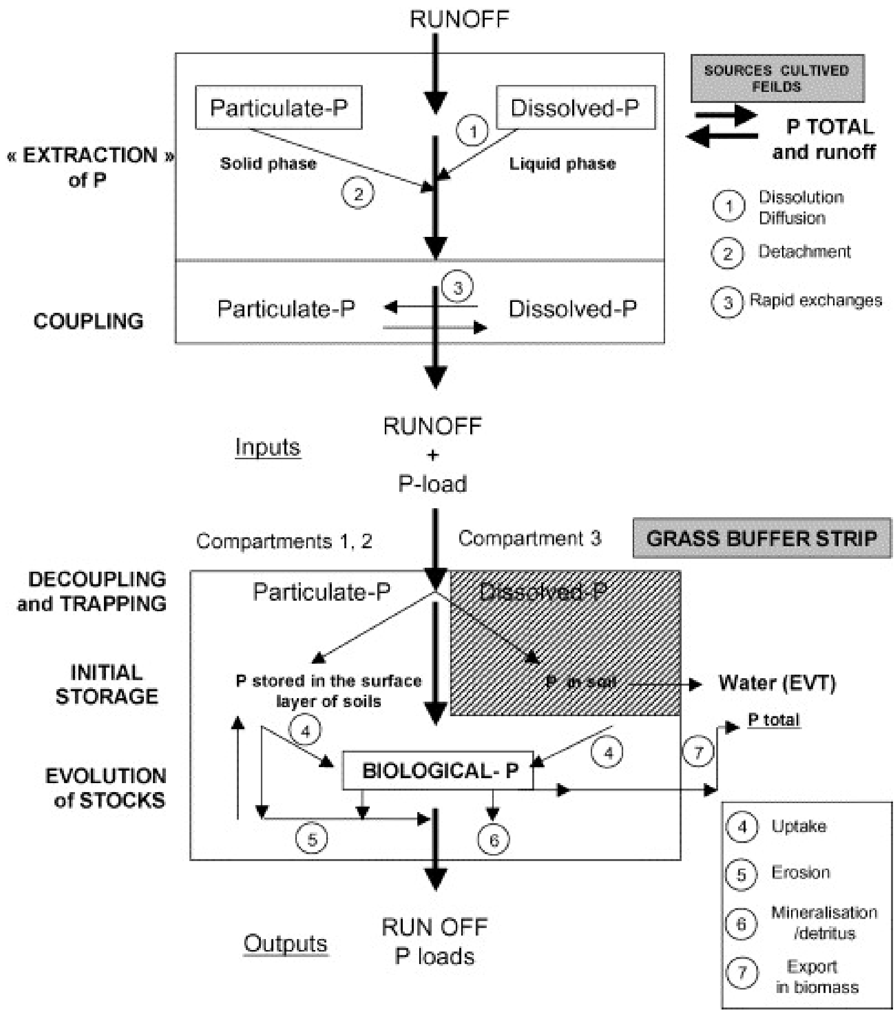


Figure 5. Scheme of the Phosphorus dynamics from cultivated fields through a grass buffer strip (Source: J.M. Dorioz et al., 2006, adapted from Lee et al., 1989)

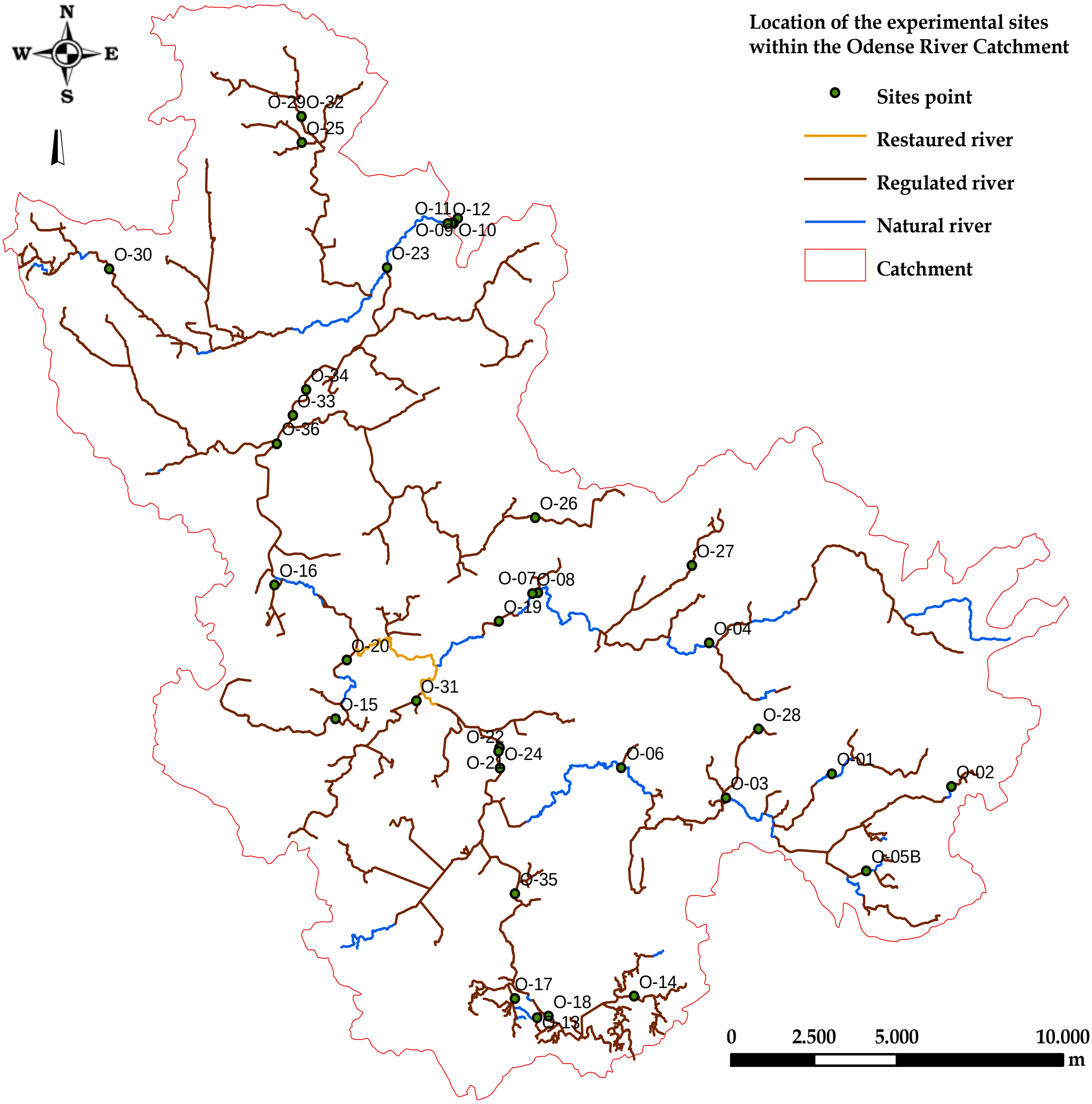


Figure 6. Map of location of the experimental sites

III Stream and catchment characteristics on Phosphorus contents

III.1 Methods

III.1.1 Site selection

This research project was started in 2006, with first of all the selection of the experimental sites within the Odense River catchment which was conducted utilising a random stratified method. For this project were needed locations with a combination of the following characteristics (Table 1):

Table 1. Criteria for choosing the experimental sites

Natural or Regulated streams	Strahler order	Vegetation
Natural	1-2	High (trees, shrubs)
Regulated with large buffer zone (>10 m)	3-4	Low (grass, herbes)
Regulated with small buffer zone (<2 m)	5	

Combining these criteria gave 3x3x2 = 18 different categories. For each category, two locations per river were required, as a replicate.

- Criteria for including water in the river system:

  The 'blue line' or channel network should be connected to the river system,

  The channel network should be shown on the new (2000) and on the old (1880) map,

  The channel network should not clearly be part of a man-made water system (ditches and canals),

- Criteria for selecting natural part of the river:

  The river should be meandering (sinuosity >1.2),

  The river should be more or less the same in the new and the old map,

  If in doubt, check whether the area next to the river is protected by the conservation act, or if the county indicates the river as natural.

As much as possible, locations of the experimental sites have been chosen from all over the catchment area (Figure 6). Each channel reach and buffer strip selected is 100 m long.

During summer 2007, the landscape around the point site O-35 has been modified (restored), so consequently this experimental buffer strip has been deleted from the monitoring program.

III.1.2 Sampling

III.1.2.1 Buffer strip

Soil samples have been taken in five spots (0 m; 25 m; 50 m; 75 m; 100 m) along each buffer strip at the edge of the river, in three replicates and regrouped in order to constitute one composite sample for each buffer strip. On the field, these five spots are symbolized by wood stakes put into the soil and a white plastic stick longer and clearly visible from a large distance. The core samples must be taken into the 50 cm surrounding the wood stake, and vegetation at the sample location is removed by scraping it away. Then the auger is advanced to the chosen depth and afterward removed from the hole. The sample is put into a bucket and the procedure is carried on.

Soil samples have been taken from the surface at two different depths: 0-5 cm which is called horizon 1 (H1) and 5-25 cm, also identified as horizon 2 (H2).

III.1.2.2 Bank material

The same procedure as mentioned above has been implemented. The difference in that case is that the reference is the bottom of the stream instead of the top of the soil. Samples have been taken at the same five spots at two different depths: 20 cm and 60 cm above the stream bed. They correspond to the first 5 cm of bank material. With the aim to draw the gradient of total-P content between depths in the buffer strip, the idea was to project those measurements taken from above the stream bed in the bank into a vertical bank. Computation for the projection of those 20 cm and 60 cm took into account the average angle, the average height and the total length of the bank with bend. Thales theorem has been used. The results will show the depth of sampling in the bank with surface of the soil as reference.

III.1.3 Observations on field

During the sampling period in 2006, data from direct observations on the field was noted. The observations dealt with:

- Dominant land use of the neighbouring land of each buffer strip,
- Distance from the buffer strip to the nearest arable land measured in meters with the help of a tape measure,
- Top soil types at two different depths (0-5 cm and 5-25 cm respectively called H1 and H2). Determination of the soil type was based on estimation of proportion of sand, clay and peat.

III.1.4 Laboratory analyses

The composite samples have been analysed in the laboratory to measure contents in total-P (TP), Olsen-P (Pt), Water extractable P (Pw), Carbon (C) and organic Nitrogen (oN). Experiments took place at NERI and have been done following the below mentioned protocols:

Total-P concentrations in the soils were measured on spectrophotometer Shimadzu UV-160, after combustion at 550ºC, and boiling in mild hydrochloric acid according to the method described by Andersen (Andersen, 1956). The Olsen P analysis has followed the method developed by Sterling R. Olsen and co-workers in 1954 (Olsen et al., 1954). The method is based on the use of HCO_3^-, CO_3^- and OH^- in the pH 8.5, 0.5 M $NaHCO_3$ solution to decrease the solution concentrations of soluble Ca^{2+} by precipitation of $CaCO^3$ and soluble Al^{3+} and Fe^{3+} by formation of Al and Fe oxyhydroxides, thus increasing P solubility. The increased surface negative charges and/or decreased number of sorption sites on Fe and Al oxide surfaces at high pH levels also enhance desorption of available P into solution. Water extractable P contents were determined following the method built up by Olsen and Sommers in 1982. Carbon and organic Nitrogen analyses were done on on spectrophotometer Europe Scientific Roboprep CN and Tracer Mass.

III.1.5 Geographic Information System extraction

Also, one part of the task in this project has been to extract data from GIS layers, using ArcGis 9.2. Were available on the Odense River catchment, GIS layers concerning:

- Stream network, separated into natural, restored and regulated rivers.
- Odense boundary catchment
- Experimental site point location (upstream limit)
- Location of pasture and peat lake from 1880
- Map from 1880 and 1999
- Aerial photography from 1950 and 1999
- Land use from 2000, based on Corine Land Cover
- Soil types in 20 cm depth (top soil)
- Soil types in 1 m depth (subsoil)
- Arable land polygons from 2005
- Erosion risk value
- Elevation model

The first step has been to digitize the 35 x 100 m long buffer strips. From the upstream limit and following the polyline of the stream network, polylines representing each buffer strip, located on the right or left side of the river.

For both of the following GIS layers data have been extracted concerning the neighbouring land of the buffer strip.

III.1.5.1 Land use

Data about the dominant land use neighbouring the buffer strip has been extracted from 1880, 1950 and 2000. The dataset from 1880 contained a topographic map on the 1: 100 000 scale completed with pasture and peat lake polygons. The one from 1950 were aerial photography and for 2000 the dataset contains land use polygons on the 1: 25 000 scale. The polygon features contained a code and boundary representing the land use type.

As the aim of that task was to determine the dominant land use taking place in the land next to each buffer strip a rule has been defined and enforced, in order to implement the same methodology for each buffer strip thus comparison will be possible. The rule said that the dominant land use neighbouring the buffer strip is the one which cover at least 65% of the total length of the buffer strip. There were different legends for each map used so a common legend based on Corine Land Cover thematic classification has been chosen.

All the studied area was not covered by the aerial photography from 1950 so some data were missing for that time.

III.1.5.2 Soil types

Denmark has available two soil maps on the 1: 25 000 scale from 1985. The first one is related to the texture of the plough layer and subsoil (12 classes). It is based on texture analyses (e.g. grain size) and measurement of organic carbon and lime contained in the soil. 36 000 top soil samples (0-20 cm) and 6 000 subsoil samples (35-55 cm) were taken all over the country. Nevertheless it remains some not classified areas as urban zone, forest and coastal dune sands, small arable land, lakes, etc. Dominant top soil is shown in a 25 ha grid.

The drawing of the borderlines was based on the texture analyses, landscape analyses, the surface geology map and the local knowledge from the agronomists involved.

The second map shows the dominant surface geology in a 25 ha grid and is based on the Danish geological survey maps which cover 75% of the country (approximately 50 classes).

As before, the aim being to determine the dominant top soil and the geological types of the land next to each buffer strip, a rule has been defined and enforced, in order to implement the same methodology for each buffer strip thus comparison will be possible. The rule said that the dominant top soil type and the dominant geological type of the land neighbouring the buffer strip is the one which cover at least more than 51% of the total length of the buffer strip.

III.1.5.3 Distance to the nearest arable land

The available GIS layer was from 2005 and it was a specific one representing polygons of arable land all over Denmark. For each buffer strip, measurement of the distance has been taken in five spots (0 m, 25 m, 50 m, 75 m and 100 m) along the buffer strip by using the "Measure" tool in ArcGIS 9.2 to the nearest polygon on the GIS layer as explained in the figure 7.

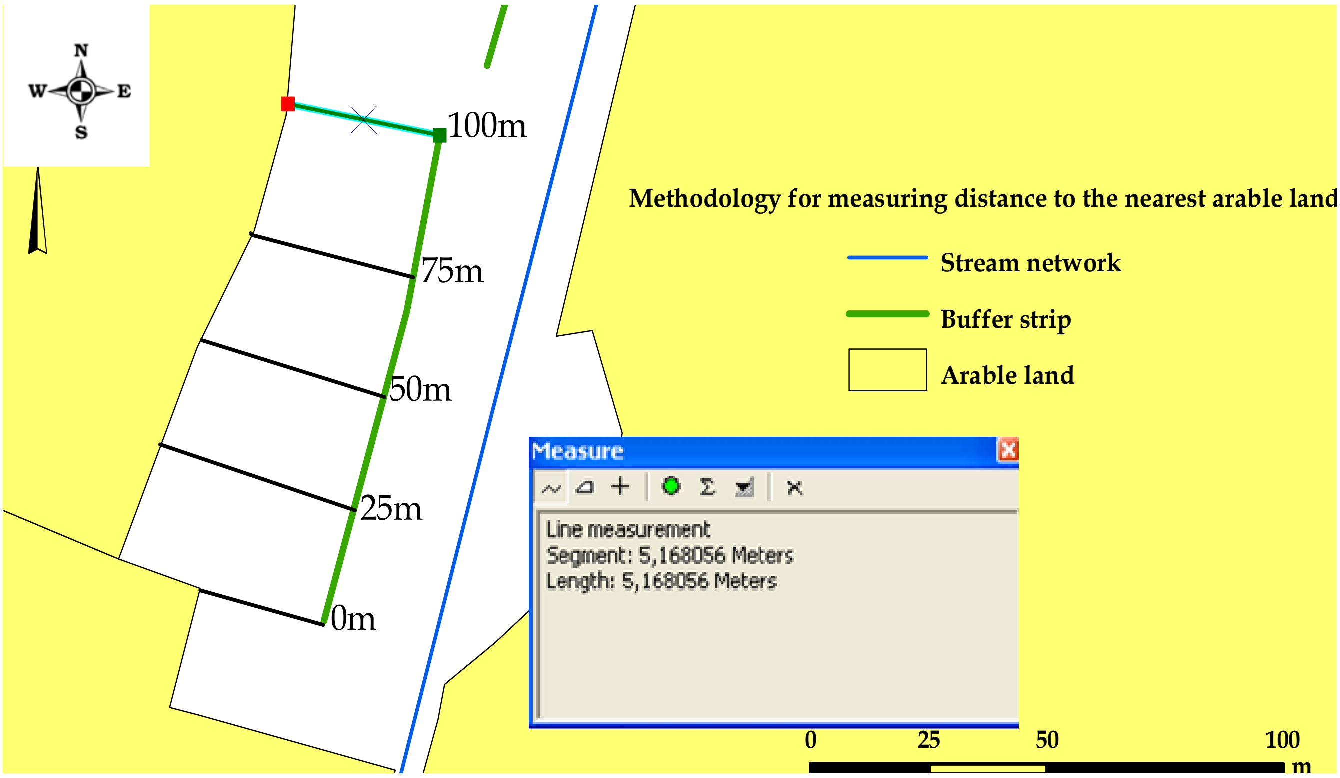


Figure 7. Methodology implemented for measuring distance to the nearest field

Then calculations were performed to determine the median value for each buffer strip in order, later, to compute statistical test. With a view to watch the historical evolution, the same measurement and computation as described above have been made using the aerial photography from 1950. All the distances have been measured in meter. An important point must be mentioned and taken into account for the results and discussion is that the GIS layer includes both the arable land and the permanent grassland.

III.1.5.4 Erosion risk value

Erosion risk layer, available, shows cells with surface of 10 x 10 with an erosion risk value from -1 to 3. Determination of the erosion risk is based on the WaTEM (Water and Tillage Erosion Model) developed by Van Oost et al., 2000. WaTEM is spatially distributed model to simulate erosion and deposition by water and tillage processes in a two-dimensional landscape. WaTEM focuses on the spatial, and less the temporal, variability of relevant parameters. The WaTEM calculates the mean annual soil erosion rate and the mean annual sediment transport capacity for each grid cell in the GIS. Where sediment inflow into a cell exceeds the sediment transport capacity, deposition occurs.

The water component of WaTEM uses an adapted version of the Revised Universal Soil loss Equation (RUSLE) since (approximate) parameter values are readily available for many areas. The tillage component of WaTEM uses a diffusion-type equation whereby the intensity of the tillage process is described by one parameter (tillage transport coefficient).

For each pixel of the catchment, the mean annual transport capacity is calculated using the following equation:

$$\boxed{TC = K_{TC} \times R \times K\ (LS - 5,3\ Sg^{0,8})}$$

where R, K, L, S = USLE parameters

Sg = slope gradient

K_{TC} = transport capacity coefficient

The erosion model is not calibrated to Danish conditions, so it will not be possible to get data dealing with amount of sediment eroded/surface area.

Therefore, the calculated erosion rate values are classified into risk classes:

- -1: Deposition areas (no net erosion)
- 1: Low erosion risk (calculated rates = 0 - 0.5 t soil/ha)
- 2: Medium erosion risk (calculated rates = 0.5 - 3.0 t soil/ha)
- 3: High erosion risk (calculated rates = > 3.0 t soil/ha)

A digital elevation model (DEM) map was already existing for the whole island of Funen. DEM map has first been converted to raster 10 m. The DEM has been used as basis to overplay other thematic layer.

The aim of the study of the erosion risk was to extract a unique and average erosion risk value for land drained and leaching to each of the buffer strip. Erosion value calculated will give a hint to whether the phenomenon can take place and to which extent in the contributing area to the different buffer strip. The first method suggested to determine the contributing area of each buffer strip was to draw a rectangle having a 100 m width, based on the buffer strip and the length being dependant on the distance from the stream to the highest contour line. The rectangle was supposed to be drawn perpendicularly to the buffer strip or perpendicularly to the contour lines. This method was based on the topographic map. Even if a high accuracy is not required, this method despite that it is easy to implement but nevertheless bothersome, seemed be too huge generalization. The drawn contributing area did not take into consideration the potential runoff coming from the left or right side, and the one that can occur in this area but flow out from that one. The final way chosen has been to use the GIS software in order to calculate and draw the theoretical contributing area of each buffer strip.

For this purpose, buffer zones have been created around the studied buffer strips on the correct side of the stream and those buffer zones have been defined as the pour points. Pour points are the cells above which the contributing area will be determined. In the same time, using the DEM 10 x 10 as base of the work, different functions ("fill", "flow direction", "flow accumulation", and "watershed") have been computed in ArcGIS 9.2 for creating the drainage basin of each buffer strip. Afterward, the result showed that the theoretical stream network and the one digitized were not consistent (e.g. some watersheds were not in the right side of the stream). To avoid this phenomenon, the initial DEM has been corrected using trigonometric functions on ArcGIS 9.2 and the previous functions ("fill", "flow direction", "flow accumulation", "watershed") have been computed based on the corrected DEM. At last, results were accurate, and an example can be seen in figure 8, following.

At that step, 35 polygons represented the theoretical contributing area of the 35 experimental sites. The "tabulate area" function on ArcGIS 9.2 was then used to calculate cross tabulated areas between two datasets. To that end, the contributing areas were defined as the zones and the erosion risk layer will have its area summarized within each zone. It adds up the number of cells constituting the contributing area which have the same erosion risk value and saves it in a new table exportable into Microsoft Excel. Data were then disposed to statistical analyses.
Nevertheless, the weakest link of this computation is that some cells have no erosion risk value fill in, so when there was no data for the whole contributing area, the buffer strips concerned did not appear in the table; it happened in some cases that only a part of the contributing area had no erosion risk value, so the calculation was done but the missing data were not taken into account. The sum of all the cells constituting the contributing area has been estimated and then all the cells have been transformed into a contributing area, as the size of each cell (10 m x 10 m) was known.

III.1.5.5 The contributing area

Utilising the contributing area polygons computed in the previous step, it was therefore possible to extract data for land use, and soil types for the contributing area to each buffer zone following the same method used previously for the erosion risk value.

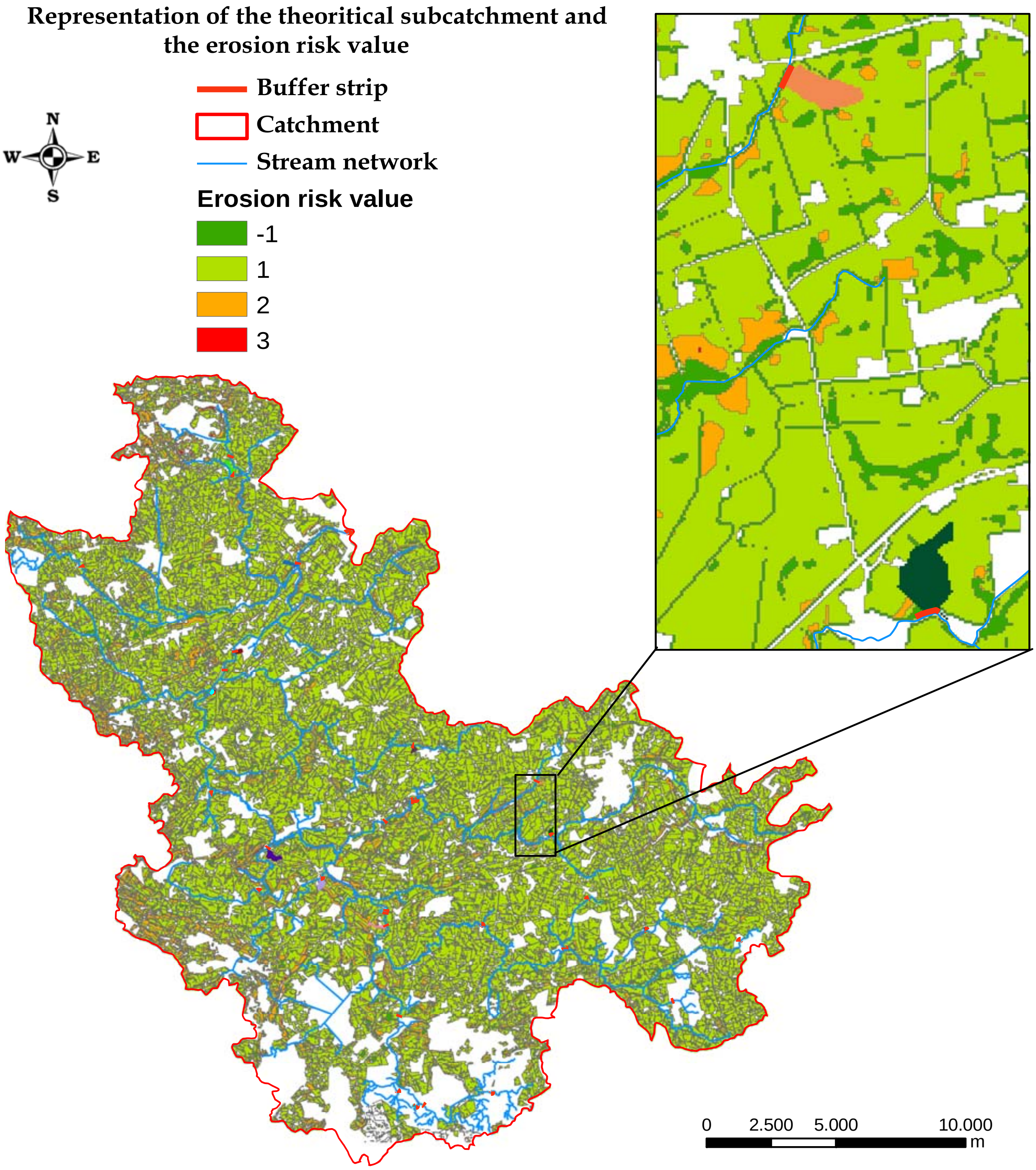


Figure 8. Representation of the theoretical subcatchment and the erosion risk value

III.1.6 Statistical analysis

Data were statistically analysed using Analyse-it, trial version. Parametric and non parametric statistics were used. The statistical tests were carried out on soil data normalised on concentrations in ppm. Student-t tests for paired samples were used to test for differences between contents in the different horizons. Linear regression test R^2 and plots were performed to test for relationship between the different contents in total-P, P(t), P(w), C and oN. Chi-square test has been calculated to compare data extracted for different times or at different depths. It helped also to test for difference between data extracted from the neighbouring land of the buffers strip and those from the whole contributing area.

One-way ANOVA test allows testing out if there were any relationships between the total-P content and the different dataset extracted from GIS both for the neighbouring land and the whole sub-catchment. It makes it possible to test the relationship between top soil and subsurface soil types.

Two-way ANOVA tests were used to test for relationship between total-P contents/ Strahler order and the height of the vegetation growing on the buffer strip. Multivariate Principal Components (ACP) and Linear and stepwise multiple regression were applied to examine relationship among landscape factors and the buffer strip soil P concentrations.

III.2 Results

III.2.1 Raw data and comparison with Danish values

The total-P contents (Table 2) found in horizon 1 ranged from 259.02 to 1546.46 ppm (mg P kg^{-1} DW^{-1}), and in horizon 2 from 266.36 to 4094.66 ppm. The total-P contents found in bank material at 60 cm and 20 cm above the stream bed ranged from 314.17 to 1386.57 ppm and from 333.54 to 1560.07 ppm, respectively. They were all in the same interval, but nevertheless it is noteworthy that the standard deviation and variance values of total-P contents in horizon 2 were higher than in horizon 1 and the bank material. Variance and standard deviation are measures of statistical dispersion, averaging the squared distance of its possible value from the mean. Those results show that the total-P contents in H2 are highly variable. The P(t) contents found in horizon 1 ranged from 3.44 to 117.60 ppm, and in horizon 2 from 2.28 to 105.75 ppm. The P(w) contents found in horizon 1 ranged from 2.78 to 26.03 ppm, and in horizon 2 from 1.26 to 15.95 ppm. It was almost the half of the concentration found in H1.

Table 2. Statistical analysis of the raw data for P contents

Basic statistical analysis of the raw data (mg P kg^{-1} DW^{-1})	TP soil buffer strip H1	TP soil buffer strip H2	TP bank material 60 cm	TP bank material 20cm	P(t) H1	P(t) H2	P(w) H1	P(w) H2
Average	753,67	797,72	722,90	711,86	43,26	34,06	12,14	7,83
Median	689,13	664,35	678,35	640,63	38,55	30,90	12,26	7,03
Standard Deviation	294,40	636,38	280,75	345,96	27,57	23,43	5,90	4,31
Variance	86669,16	404980,32	78822,00	119684,96	760,09	548,92	34,86	18,58
Minimum	259,02	266,36	314,17	333,54	3,44	2,28	2,78	1,26
Maximum	1546,46	4094,66	1386,57	1560,07	117,60	105,75	26,03	15,95

The C concentration (Table 3) in horizon 1 ranged from 17714.32 to 91675.72 ppm, and in horizon 2 from 15892.35 to 75482.08 ppm. The C contents found in bank material at 60 cm and 20 cm above the stream bed ranged from 11182.06 to 132361.43 ppm and from 10159.94 to 87032.31 ppm, respectively. Dispersion of values in bank material at 60 cm above the stream bed was higher than the others at 20 cm and in soil buffer strip.

Table 3. Statistical analysis of the raw data for C contents

Basic statistical analysis of the raw data (mg P kg^{-1} DW^{-1})	C soil buffer strip H1	C soil buffer strip H2	C bank material 60cm	C bank material 20 cm
Average	38776,89	31780,70	33100,12	32251,47
Median	34286,30	29653,71	29020,07	32106,24
Standard Deviation	15913,76	14709,29	21437,24	15285,71
Variance	253247622,90	216363109,32	459555470,19	233652959,18
Minimum	17814,32	15892,35	11182,06	10159,94
Maximum	91675,72	75482,08	132361,43	87032,31

The ranges of oN contents (Table 4) for horizon 1 ranges were from 1611.16 to 9336.34 ppm, and for horizon 2 from 1517.77 to 7745.71 ppm. In bank material at 60 cm and 20 cm above the stream bed they were from 469.81 to 5750.17 ppm and from 522.49 to 8046.08 ppm, respectively. Inversely as before, the dispersion of values in bank material at 60 cm was smaller than the others.

Table 4. Statistical analysis of the raw data for oN contents

Basic statistical analysis of the raw data (mg P kg^{-1} DW^{-1})	oN soil buffer strip H1	oN soil buffer strip H2	oN bank material 60cm	oN bank material 20cm
Average	3641,56	3078,31	2977,66	2768,87
Median	3324,84	2731,31	2984,08	2702,24
Standard Deviation	1498,54	1447,78	1242,84	1461,34
Variance	2245636,17	2096052,47	1544649,47	2135517,16
Minimum	1611,16	1517,77	469,81	522,49
Maximum	9336,34	7745,71	5750,17	8046,08

The C/N ratio (Table 5) calculated in horizon 1 ranged from 9.13 to 16.83, and in horizon 2 from 9.13 to 16.79 ppm. The one found in bank material at 60 cm and 20 cm above the stream bed ranged from 4.45 to 46.93 ppm and from 4.39 to 34.96 ppm, respectively. Maximum values found in bank material were two times higher than in soil buffer strip.

Table 5. Statistical analysis of the raw data for C/N ratio

Basic statistical analysis of the raw data (mg P kg^{-1} DW^{-1})	C/N ratio soil buffer strip H1	C/N ratio soil buffer strip H2	C/N ratio bank material 60cm	C/N ratio bank material 20cm
Average	10,72	10,43	12,97	13,37
Median	10,54	10,10	10,22	11,93
Standard Deviation	1,36	1,46	9,68	7,07
Variance	1,85	2,12	93,73	49,92
Minimum	9,13	9,13	4,45	4,39
Maximum	16,83	16,79	46,93	34,96

As shown by the graph (Figure 9), there was a wide range of total-P content among some of the buffer strip, with the highest concentration in the buffer strip O-10 in H2. The lowest total-P contents were found in the buffer strip O-18. Differences in total-P contents in the 35 buffer strip were not only a result of sporadic P fertilizer and/or manure applications, but also the result of a continuous build-up.

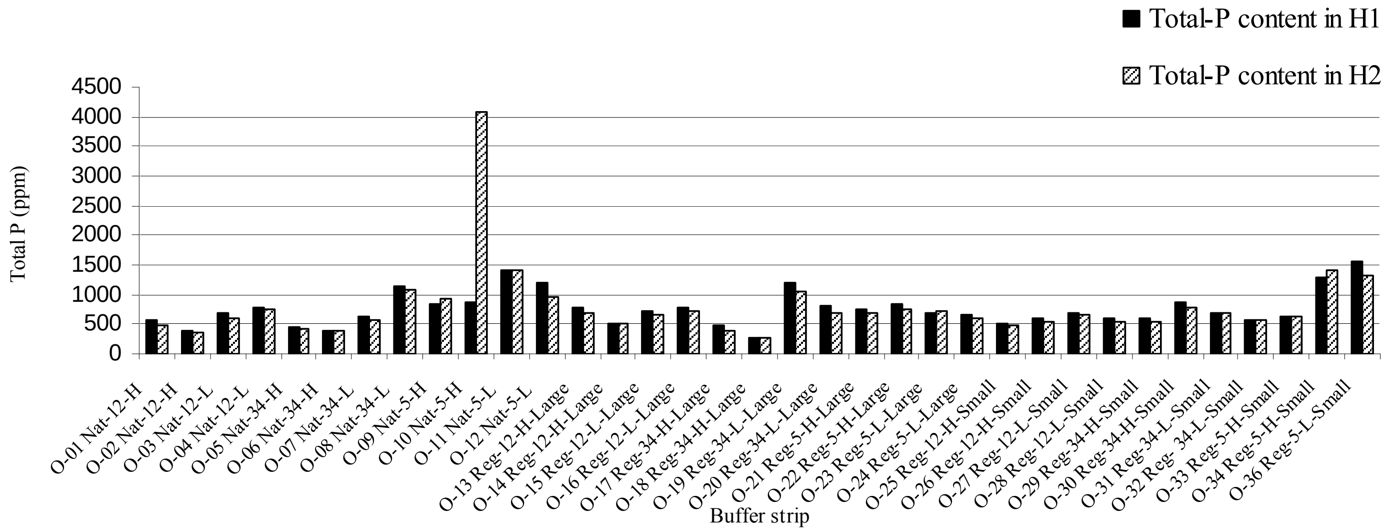


Figure 9. Average total-P contents in the experimental buffer strips along the Odense River

The distribution of the buffer strips in P(t) classes (Figure 10) shows that 36% and 33% of them, respectively, for H1 and H2 are in the range from 3 to 5 which are the normal values found in Danish arable fields. As expected there were less buffer strips with high P(t) value in H2 than H1 (17 and 31% respectively), because it is a deeper soil layer and there is no direct contact with external sources of P (add of fertilizer or manure, faeces of animals or organic matter decomposition). An P(t) value greater than 5 means that there is too much dissolved P in soils so it is saturated. In H1 10 experimental sites present P(t) value greater than 5 and six in H2. Risks of leaching are so increased.

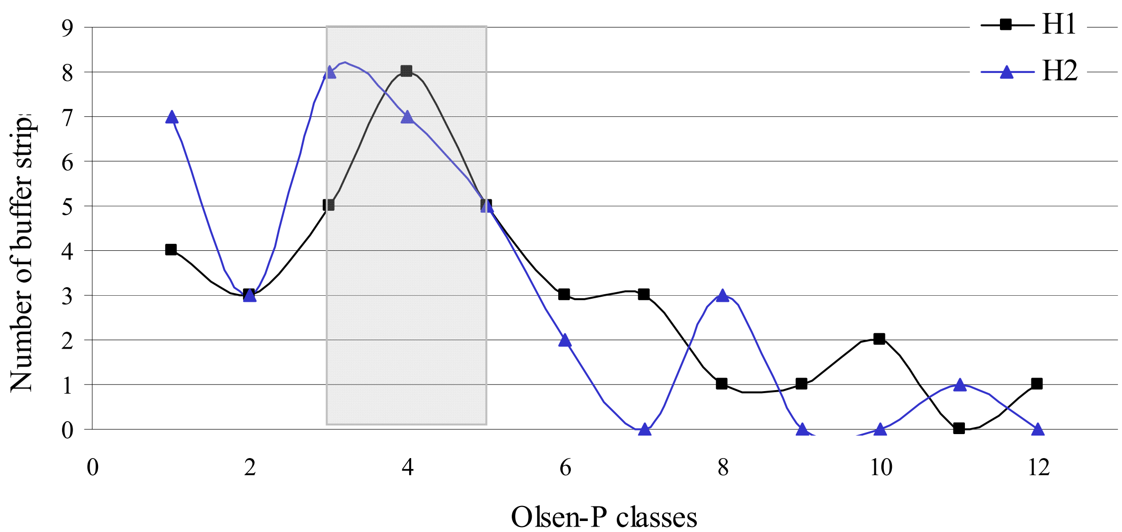


Figure 10. Distribution of the buffer strip according to the Olsen-P classes

Amount of P spread in Danish arable land were until 2002 constituted as shown in the following graph (Figure 11):

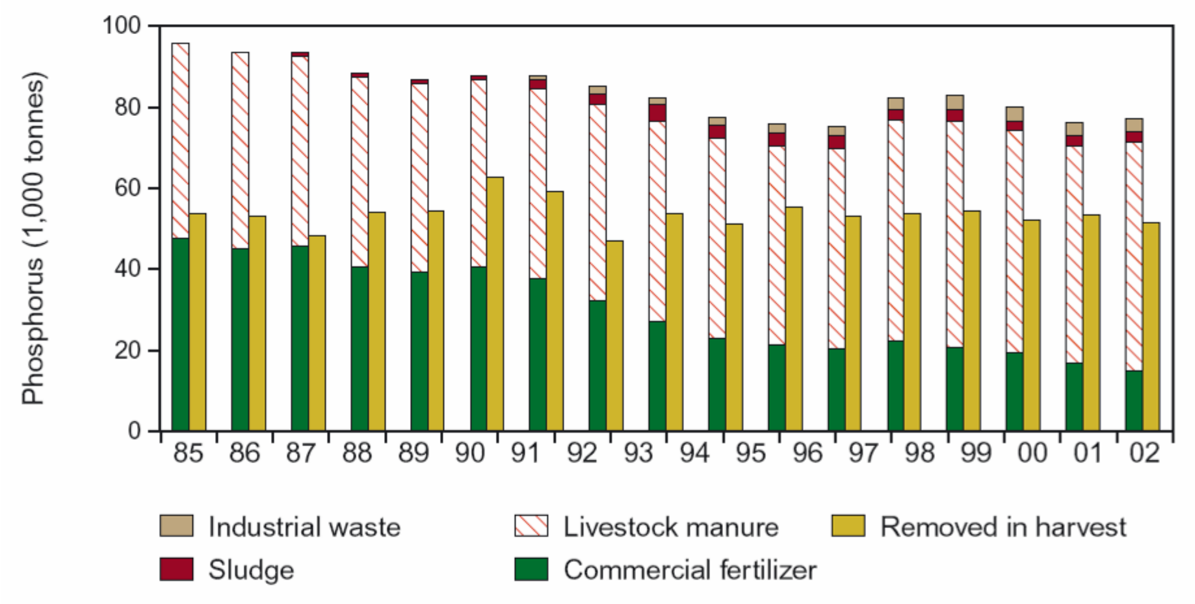


Figure 11. P balances in Danish agriculture from 1985 to 2002 (Source: Aquatic Environment 2003, State and trends-Technical summary, NERI)

Phosphorus in commercial fertilizer was reduced from 47.800 tonnes in 1985 to 13.800 tonnes in 2002, and livestock manure is today the predominant type of phosphorus fertilizer in Denmark. The phosphorus input from fertilizer and manure still exceeds the amount removed from the fields with the crops resulting in an average surplus of around 10 kg P ha^{-1} yr^{-1}.

Table 6. Total-P content (ppm) in Danish agricultural soils and soils under forest and for the studied buffer strips in 2007 (Source: Tab af fosfor fra landbrugsjord til vanmiljoet by Ole Horbye Jacobsen and Brian Kronvang).

	Agricultural land				Soils under forests			
	H1		H2		H1		H2	
Soil types	Buffer strip	Denmark	Buffer strip	Denmark	Buffer strip	Denmark	Buffer strip	Denmark
Sandy soil	753	450	701	290	609	205	611	160
Clayey soil	523	584	527	425		300	4095	230
Peat soil	1279	562		457		416		309

Moreover, comparison of average values of total-P concentrations between the studied buffer strips in the Odense River catchment and data from the whole Denmark (Table 6) shows that concentrations in agricultural land measured in buffer strips are higher than the average values from the country as a whole, except for the clayey soils in H1. In soils under forests comparison showed that average total-P contents in buffer strips were higher than in Denmark in general. To summarise, it is possible to say that total-P contents found in the studied buffer strips within the Odense River catchment are higher than average conditions in Denmark for both arable and forested soils. These results shows that the P-content of Danish buffer strips seems to be very high and that buffer strips are enriched with P even compared to arable fields having an annual average P-surplus. That the P input from fertilizer and manure exceeds the amount removed from the fields with the harvest was proved by the degree of phosphorus saturation in agricultural soils in 1997 and soils under forest in 1986 (Table 7).

Table 7. Degree of P saturation (%) in agricultural soils in 1997 and soils under forest in 1986 (Source: Tab af fosfor fra landbrugsjord til vanmiljoet by Ole Horbye Jacobsen and Brian Kronvang)

	Agricultural land		Soils under forest	
Soil types	H1	H2	H1	H2
Sandy soil	36,70	23,83	16,00	9,00
Clayey soil	31,40	24,23	12,57	8,17
Peat soil	23,60	12,80	12,80	7,90

Those values showed that soils were saturated on total-P; it might be an explanation on why higher concentrations of total-P were measured in 2007 than in 1997 or 1986. It is also noteworthy that H1 was more saturated than H2; like explained previously, it could be linked to the fact that H1 was directly in contact with external sources of P.

III.2.2 Compound contents relationships

Study of relationships between the different compounds measured and analysed in the soil buffer strip at the same depth showed that there was a significant strong relationship between C and oN contents (Figures 12 and 13).

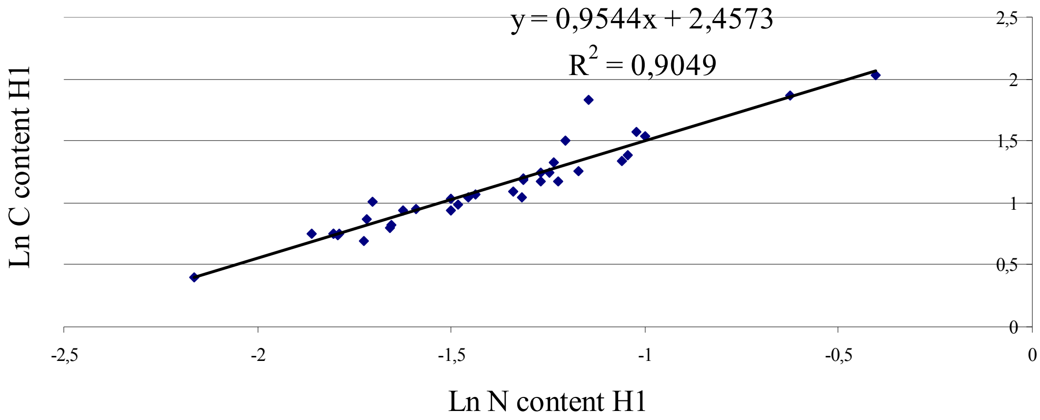


Figure 12. Relationship between C and oN content in H1 (p-value< 0.001)

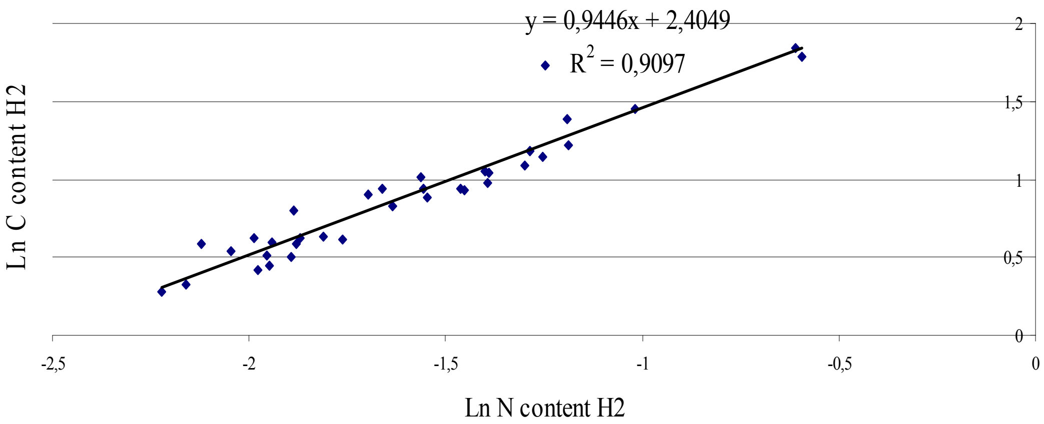


Figure 13. Relationship between C and oN content in H2 (p-value< 0.001)

Table 8. C/N ratio in the 2 horizons of soil buffer strip according to land use

C/N ratio	Farmland		Grassland		Forest	
	H1	H2	H1	H2	H1	H2
	10,67	10,39	10,78	10,52	11,04	10,97

The C/N ratio means the amount of carbon relative to the amount of nitrogen existing in organic matter. As shown by the equation of the regression line there was always more carbon than nitrogen in organic matter.

The C/N ratio measured in soil buffer strips (Table 8) are maybe a bit lower than the normal C/N contents of soils, as comparison with Danish arable soils, etc from basic literature (Brian Kronvang, NERI, Personal communication). Whatever the horizon, the C/N ratio in soils under forest was significantly higher (alpha=0.05) than in farmland and grassland, which both were not significantly different. Soils which had been enriched in fertilizers and/or manures (farmland and grassland) had a lower C/N ratio than soils under forest, which had not been enriched or even impoverished. In soils under forests there was more organic matter and so more assimilation by plants: P contained in organic matter is taken up and incorporated in the period of growth of vegetation. There is then in autumn return of P into the soil by decomposition of falling leaves.

A strong relationship between Olsen-P and Water-P content ($R^2 = 0.83$ and 0.87 for H1 and H2) is also established. These two soil P-fractions are mainly dealing with the same form of P (inorganic P) but analysed in the laboratory with two different extraction agents. All the computed R^2 value between total P and the other P compounds are in the range from 0.29 to 0.52.

III.2.3 Contents in depths

Table 9. Results of Student-t tests dealing with difference on contents between depths for each compound measured

Total-P	H1	H2	60 cm	20 cm
H1	—			
H2	Means are equals	—		
60 cm	Means are equals	Means are equals	—	
20 cm	Means are equals	Means are equals	Means are equals	—

Olsen-P	H1	H2
H1	—	
H2	Means are not equals	—

Water-P	H1	H2
H1	—	
H2	Means are not equals	—

C	H1	H2	60 cm	20 cm
H1	—			
H2	Means are not equals	—		
60 cm	Means are equals	Means are equals	—	
20 cm	Means are not equals	Means are equals	Means are equals	—

N	H1	H2	60 cm	20 cm
H1	—			
H2	Means are not equals	—		
60 cm	Means are not equals	Means are equals	—	
20 cm	Means are not equals	Means are equals	Means are equals	—

Means are equals / Means are not equals

No significant (alpha=0. 05) differences have been established on total-P contents between the different soil or bank horizons sampled neither in buffer strip nor in bank material (Table 9). This result was a surprise as were expected highest values in H1.

The lack of significant differences between the to sampling depths on the surface of the buffer strips may be due to the continuous agriculture activities on these sites over the last 50-100 years that has led to high accumulations of total-P even at deeper depths. Overall, soil-P can increase rapidly by fertilizer and manure applications and feces deposition but will take a significant time to decrease even if all P additions are stopped (Sharpley et al., 2003). P(t) and P(w) values were significantly different ($p < 0.0001$) between H1 and H2.

C contents were significantly different ($p < 0.0001$) between the two horizons in soil buffer strip but not in the bank material ($p = 0.733$). Moreover, C contents found in H1 and H2 were not significantly different ($p=0.0620$ and 0.6532) from the content in bank material at 60 cm above the stream bed; lastly, C contents in H2 were not significantly different from the contents in bank material at 20 cm above the stream bed.

N contents in H1 were significantly different ($p < 0.0001$) from the other measurement either in H2 or in bank material ($p = 4.02 \times 10^{-9}$, 0.0035 and 0.0002, respectively for H2, 60 cm and 20 cm). N contents in the bank material were not significantly different between themselves ($p = 0.221$) and neither from contents found in H2.

In most soils, surface horizons have greater P concentrations than the lower horizons because of the sorption of the added P from fertilizers, manure or livestock feces, greater biological activity, cycling of P from roots to aboveground plant biomass, and more organic material in the surface horizons (Sharpley et al., 2003). Results regarding the distribution of total-P contents in depth are totally different than what was expected (Figure 14).

It was highly interesting that they showed that bank material independent of depth had as much total-P as the soil buffer strip – although great differences in total-P content between individual buffer strips and hence bank material was found.

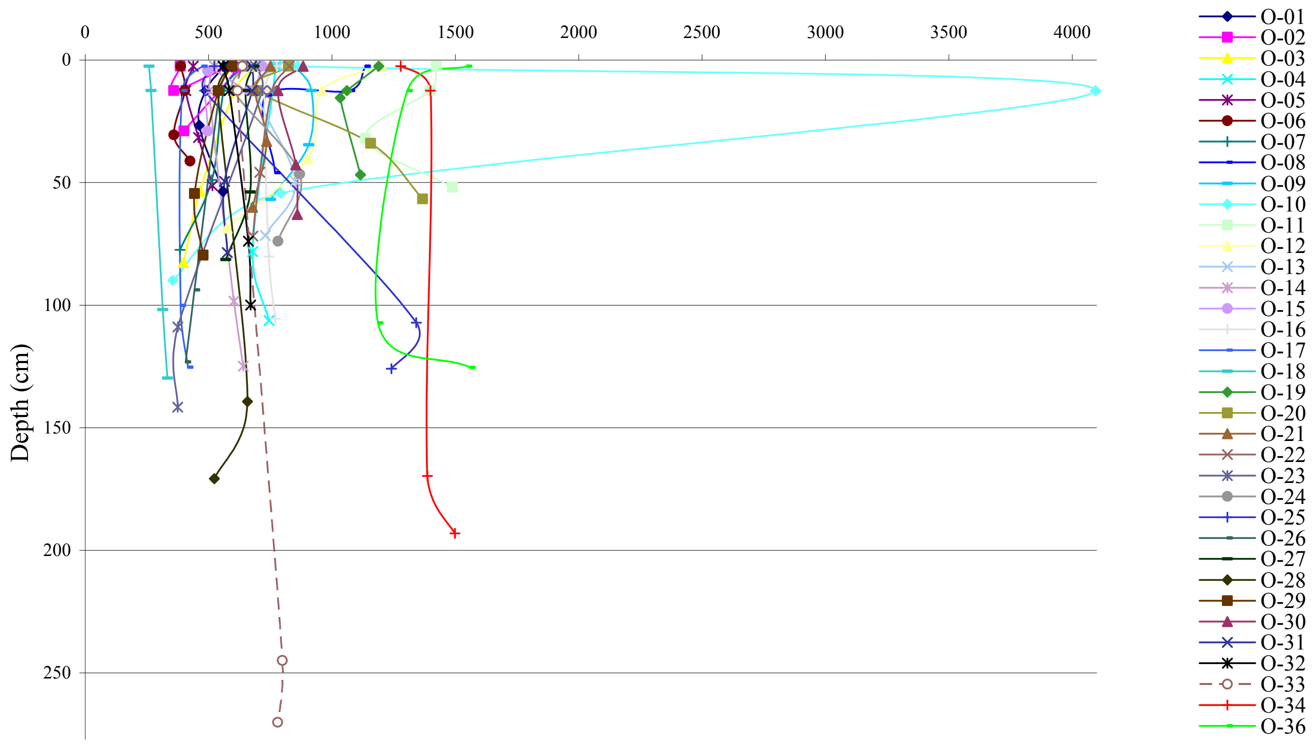


Figure 14. Total-P content distribution in depths (soil buffer strips and stream bank)

The buffer strips which showed a decrease of total-P content in depths from soil buffer strip to bank material are all characterized by:

- Land use as grassland for at least the last fifty years
- Sandy topsoil type
- Peaty subsoil type

An explanation could be that the soils are naturally rich in P, but it did not seem likely; an other possible explanation can be that there was enrichment of bank material in P due to P contents in water of the Odense River. P concentration in water might be partly "adsorbed" to fresh bank material. This hypothesis sounds more likely especially because samples in bank material have been taken only into a depth of 5 cm in the banks.

But some questions remained, as:

- Is the source of total-P in both buffer strips and banks of the same origin?
- Is there different mechanisms working for total-P in buffer strip and total-P in bank material?
- Is the textural composition the same in bank material and buffer strip?

III.2.4 Stream relationships developed for phosphorus

Statistical analysis showed that the height of vegetation had an effect on:

Total-P, C and oN content, both in soil buffer strips and bank material,

It seemed that the higher the vegetation was, the lower total-P contents were. This was significantly true only in horizon 1 ($p= 0.0024$).

The results are probably due to the uptake of soil-P by vegetation. As well, presence of high vegetation (trees) indicates that the buffer zone has been uncultivated for many years, resulting in a lower risk for P input from farming operations into the buffer zone. The higher the vegetation is, the greater amounts of nutrients will be needed for growing and this will lower the N and P contents in the buffer strip. However, C content would be supposed to increase.

It also showed (Figure 15) that Strahler order had an effect on:

Total-P, C and N contents found in bank material

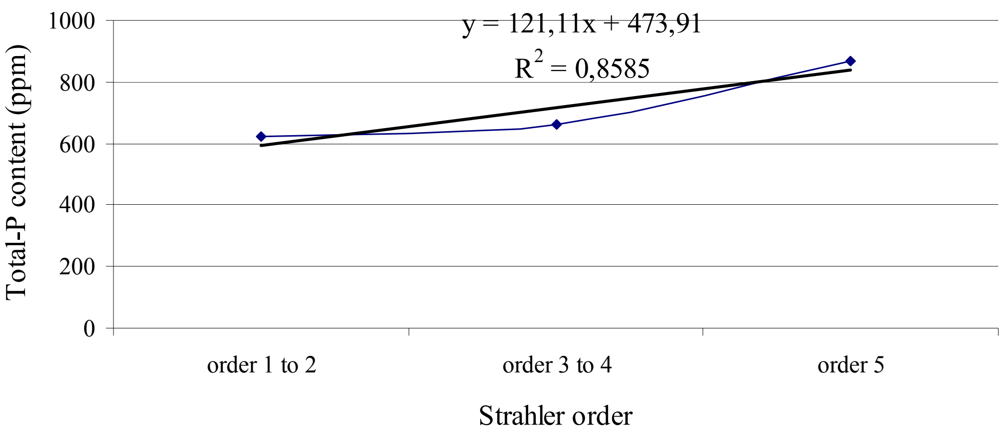


Figure 15. Relationship between the Strahler order and distribution of total-P contents in bank material

Tests showed that total-P, C and oN contents in bank material along streams with a value of 5 in Strahler order were significantly higher (p= 0.0388 and 0.0158, respectively for order 1-2 and order 3-4 in horizon 60 cm above the stream bed) than those in lower ranks. It meant that the larger the stream was (the higher is the Strahler order), the greater were the P, C and oN contents in the bank. In accordance with the River continuum concept, proposed by Vannote et al., (1980) it is known that dense riparian vegetation is mainly found in headwater (1-3 order) so the uptake of soil-P by vegetation for growing is greater. Moreover, stream order also influenced nutrient concentrations according to the River continuum concept in which nutrient concentrations increase with stream order. As shown by the results of the study of the total-P content between depths, it was possible to say that there might probably have been an adsorption of P in bank material from surface water. Furthermore, according to the Groundwater-Surface water Interaction (GSI) concept, deeper groundwater contribution to stream channels also increases with stream order. It indicates that more P will be given by discharge areas in the GSI areas, the further downstream in the river system where there is formation of groundwater..

This correlation between the Strahler order and height of vegetation established in the River continuum concept was significant is the case studied (all p> 0.1312).

III.2.5 Historical evolution

III.2.5.1 Land uses (from 1880 to 2006)

Data on land use dealt with the land neighbouring the buffer strips so this information gave indications on changes in land use historically and today (Figure 16).

Nevertheless, the important point was to know what changes had taken place and from this highlight if in some places there were no changes in the land uses from the past century.

Proportion of forests did not change that much. It increased from 30% in 1880 to 44% in 2006, but especially since 2000. Results showed that 44% of the 35 buffer strips were today, edged by forests. Coniferous tree species were predominantly planted after the Second World War, but since the 1980s plantation of broadleaves has been encouraged through subsidies in several European countries in order to provide forests of higher values for recreation and greater biodiversity (Stanturf and Madsen, 2002).

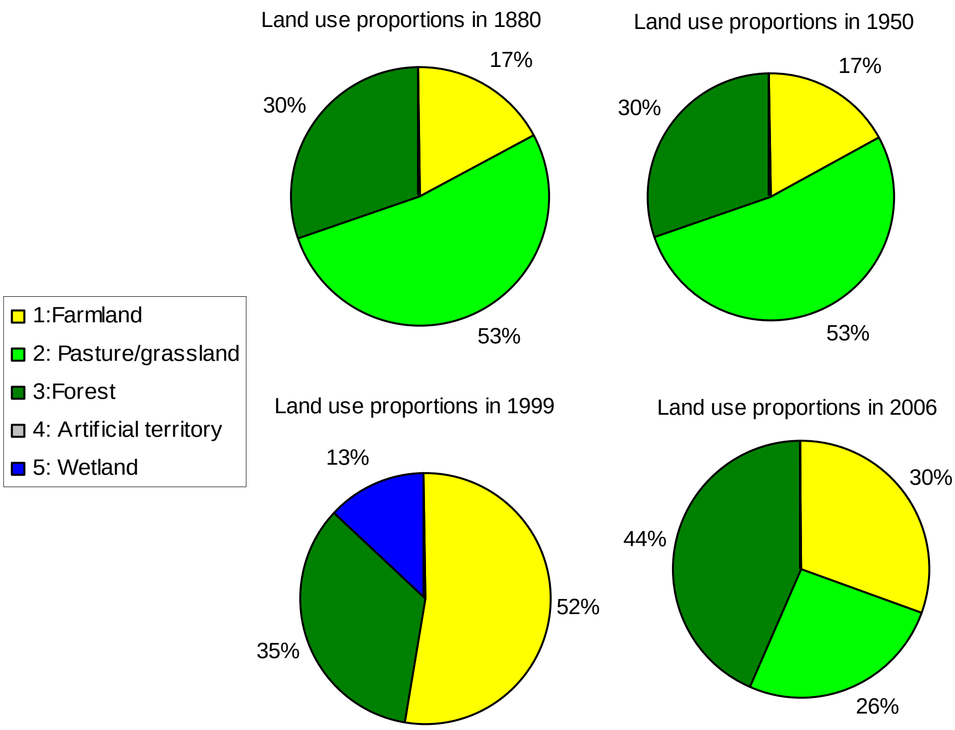


Figure 16. Evolution of land uses neighbouring the buffer strip from 1880 to 2006

Proportion of farmland had considerably increased. There was no difference from 1880 to 1950 but after this, the proportion of farmland neighbouring the buffer strip has increased and has been multiplied threefold (from 17% in 1950 to 52% in 2000). It means that until at least 2000, fields have been cultivated close to the streams. Nevertheless, the figures showed that this trend decreased after 2000, and proportion of farmland next to the buffer strip decreased until 30% in 2006; so a recent decrease of farmland edging the buffer strips in the Odense River catchment has occurred.

Proportion of grassland decreased from 1880 to 2006, exactly in the opposite way of proportion of farmland. There were no grassland neighbouring the buffer strips mentioned on the GIS layer built in 2000, but it could be due to the scale of the map (1: 25 000) that did not permit to show small areas (< 25 ha) of grassland neighbouring the streams. Corine Land Cover map was drawn in a European or national level; it is just an average picture of the main landscape units, so it is difficult to work with such a map as we had to extract data and search out phenomenon taking place in a 100 m reach. In 2006, only the half of the buffer strips edged by grassland in 1950 remained (26%).

The total-P input to Danish arable land reached a maximum in the 1970s. The consumption of P in chemical fertilizer has decreased in Denmark since the late 1880 (Kronvang et al., 2002). An increase in the consumption of P in animal manure was seen due to increased pig production during the 1990s in Denmark (Kronvang et al., 2002). However, it remained difficult to compare those data because they did not come from the same kind of GIS layers. Some were from aerial photography, others from map and also from observations collected on the field. The scales of observation were different.

In an other hand, the study of the changes in land uses during times showed that 61% of the 35 buffer strips did not change in term of dominant land uses neighbouring: 21 of them had been used as agricultural land (arable or grass land) since 1880 and five of them had been forest areas. Consequently, only nine buffer strips showed changes in their neighbouring land uses: among them, seven have changed from agricultural land to forest since 1950 (Table of changes appendix 2) and two from soils under forest to agricultural land since 1950. It was important to take those results into account because several authors have shown that P accumulates in the surface of agricultural soils because of the net input from agricultural production. It means that the past land use of a land could nowadays influenced the total-P content distribution.

III.2.5.2 Distance to the nearest arable land (from1950 to 2006)

First of all, it is important to be aware of that the GIS layer from 2005 included the grassland, so the distance extracted from it could be both between buffer strips and arable lands or pastures. It was not comparable to the two others dataset available because they were dealing only with arable land. As shown in the figure 17, there was a huge difference between dataset from 2005 and 2006. It might be linked with the fact that in 2005, dataset includes also grassland which where not taken into account in 2006. The fact that the GIS layer included grassland explained why such differences had been found between 2005 and 2006- distances decreased a lot in 2005 because of pasture which were installed closer to buffer strips than arable lands. So, for much more strictness, only comparison between values from 1950 and 2006 has been done.

Results showed that distance between buffer strips and the nearest arable land increased from 1950 to 2006. It so means that farmlands are nowadays cultivated further from the streams than in 1950. It proved the evolution of land uses.

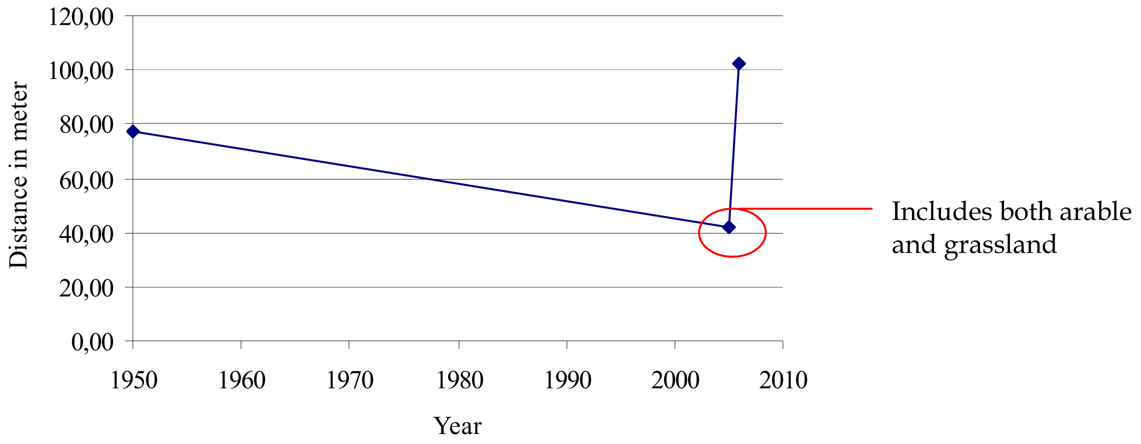


Figure 17. Average distance to the nearest arable land (and grassland in 2005) from 1950 to 2006

This increase of the distance between streams and arable lands means in fact that there was an increase of the width of the buffer strips, according to the European Union Water Framework Directive (EU-WFD). It is interesting results because it shows that there was no buffer strip less than 2 m width, which is the minimal width allowed for buffer strip, in agreement with the national regulations in Denmark; and it was especially noticeable because it was within one of the Pilot River Basin for the implementation of the EU WFD in Denmark.

As there were many missing data in dataset from 1950, the one from 2006 coming from measurements made on the field has been used for statistical analysis. Besides, it was interesting nevertheless to include dataset from 2005 in the final computation in order to search out if there was any effect of cattle grazing on grassland.

It was nevertheless important to mention, as for the dominant land use, that use of the more recent values of distance was maybe not pertinent because changes could have occurred during the last years. In that case, long distance to the arable land in 2006, does not necessarily reflect the land use edging the buffer strip for the last fifty years. It has been previously demonstrated that P can accumulated in soil, so results could perhaps not show the relationship expected Moreover, those values were difficult to construed because when the distance was greater than 100 m it has not been measured exactly. As well a few of them were lower than 100 m, so it has been impossible to extract information from a regression plot.

III.2.6 Neighbouring characteristics relationships developed for phosphorus content

III.2.6.1 Land use

Statistical tests for determining if there was any relationship between dominant neighbouring land uses and the total-P content were computed utilising data from 2000 and 2006 for the neighbouring land and from 2000 for the contributing area.

First of all, it is important to mention that the dominant neighbouring land use and the one for the sub-catchment were significantly different in 2000 and 2006 ($p < 0.0001$and 0.0029, respectively).

As seen before, dominant land use from 2000 and 2006 were significantly different so tests have been performed with both datasets in order to know which data could have an effect on total-P contents measured in samples taken in 2007. As expected and corroborated by literature, tests showed that dominant land uses from 2006 did not have any significant effect (p value from 0.2752 to 0.6073) on total-P contents neither in soil buffer strip nor in bank material. This is possibly due to the accumulation of P in soils over times and changes in land uses from 2000 to 2006 were too recent already for 2007 samples for having an influence on the concentrations found in the soil samples. Consequently, and as expected, neighbouring land uses in 2000 had an effect on the total-P content in soil buffer strip but not in the bank material. Land use effect had influence only on the first centimetres of soil (H1 and H2). The dominant land use for the whole contributing area of each buffer strip did not have significant effect (p= 0.4734) on the total-P contents in soil buffer strips. Those results allowed concluding that P concentrations measured in soil buffer strip might be influenced partly by runoff from the neighbouring land edging the buffer strip. A statistical analysis gave as result that both in H1 and H2, buffer strip neighbouring agricultural land had significant higher (p= 0.0013) total-P concentration than those edged by forested land (Figure 18).

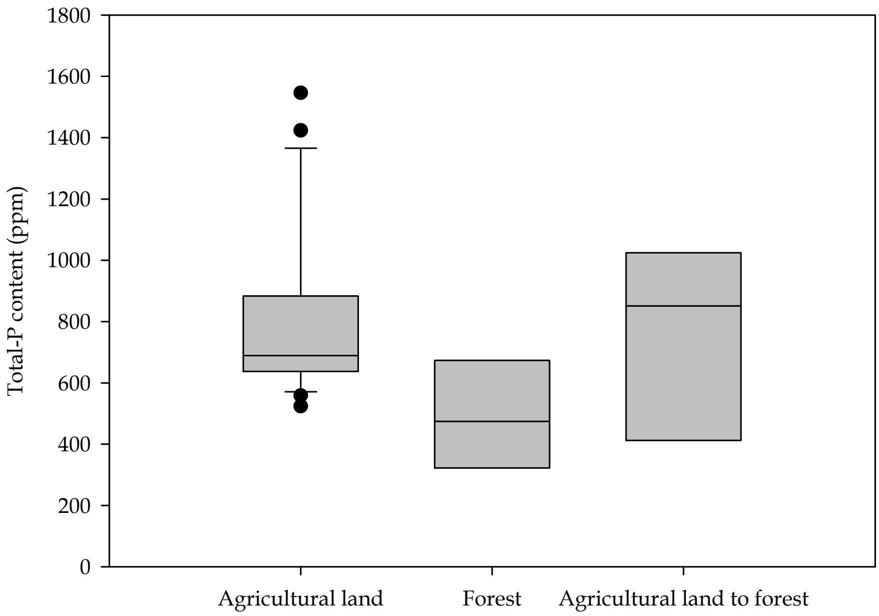


Figure 18. Distribution of Total-P content between the different land uses

The historical land use practise as agricultural land seems to have led to high buffer strip soil total-P concentrations which in turn are difficult to decrease once elevated even if land use is changed to forest for a longer period. No else significant differences were found in total-P distribution between the different land uses. Intensive row-crop agriculture produces a surplus of P from fertilizer and animal waste inputs, and in pasture soils P can increase because of animal fecal deposition. In agricultural land, P import substantially exceeding export had led to local accumulation of P in the soil profile. This caused locally elevated concentrations of P in buffer strips soils, and the accumulated P will indefinitely be a long-term source of environmental problems even if the land uses change. In forest areas, P is up taken by vegetation during the growth period and can be released during decomposition of the falling leaves.

III.2.6.2 Soil types

Chi square tests showed that all the data from the different ways of mapping soils – GIS layers and directly on the field- dealing with the top soil types were significantly different (p value from < 0.0001 to 0.0028).

So it meant that it was not possible to use data from observations made on the field for filling out the dataset from GIS layer in 1999, where many data were missing in forested and urban areas. Another way of filling in the dataset from GIS layer could have been to establish a relationship between the topsoil types and the subsoil types. Unfortunately, statistical analyses showed as result that there was no significant relationship (p= 0, 8685) between the two soil types (topsoil and subsoil).

The significant differences highlighted in top soil types between the different datasets (map and observations) and the absence of relationship between topsoil and subsoil types might be due to the scales of observations which were quite differents. On the field, observations focused on the 100 m long of the buffer strip while the soil type map was drawn in a 1: 25 000 scale (25 ha). Furthermore, an other reason why it had not been found any relationship between topsoil and subsoil types may be that there were mismatches between the two maps because soil samples from 20 cm and 1 m depth had not been taken at the same place.

So, as there were many missing data, the dataset extracted from the GIS software could not be used in the statistical analysis and so neither the dataset for the sub-catchment.

To analyse the relationship between topsoil types and total-P content have been used datasets from observations made on the field. The two datasets corresponded to the two soil horizons (H1 and H2) that have been sampled in soils buffer strip. One-way ANOVA test showed that there was no significant effect (p= 0.5333) of the neighbouring topsoil type on the total-P contents in the first horizon (H1) but there was one (p= 0.0490) in the second horizon (H2). As expected, there was no relationship between total-P contents in bank material and topsoil types. It was possible that the nature of topsoil did not have effect on P concentration in the first horizon because of the introduction of fertilizers, manure and or organic matter from vegetation and microbial activities.

Statistical analyses showed that the total-P contents in H2 were higher in peat topsoil, than in clayey, where concentrations were also greater than in sandy topsoil (Figure 19).

These results were influenced by the sorption capacity of the different soil types. Soils have a finite P sorption capacity which varies widely as a function of clay content, clay type, organic matter content, the concentration of exchangeable Al, Fe, and Ca, and soil pH (Tisdale et al. 1985).

Phosphorus sorption capacity increases with clay content, while sandy soils have the lowest P sorption capacity. Soils, as clay, high in Al, Fe, or Ca also have a high P sorption capacity. Also, Djodjic et al., (2003) found that in soils with slow water transport and prolonged contact time between soil particles and percolating water, P leaching is usually low which is the case in peat subsoil.

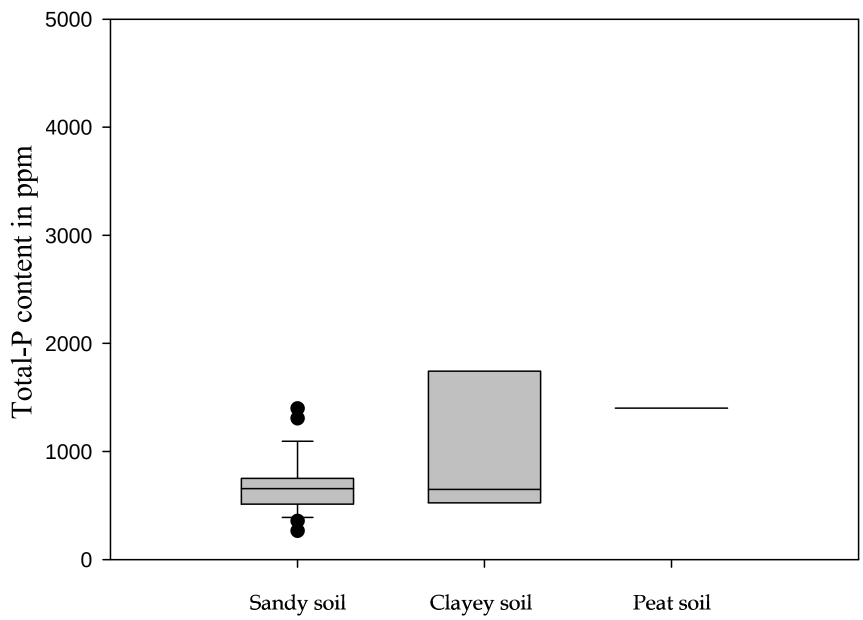


Figure 19. Distribution of total-P content between the different topsoil types in H2

On the other hand, mineralization of peat releases large amount of P and literature has found higher P content in peat soils than in sandy or clayey soils. It therefore corroborates with our results.

Dominant neighbouring subsoil types and dominant subsoil types for the sub-catchment have been tested for any differences and as a result it was possible to say that datasets were significantly different ($p=0.0116$). So, it was necessary to test both for relationship with total-P contents in soil buffer strips. Those statistical tests showed that there was significant relationship ($p= 0, 0376$) between the dominant neighbouring subsoil types and the Total-P content measured in soil buffer strips and also bank material.

Significant differences between total-P contents in buffer strip on peat and sandy subsoil have been found ($p< 0, 005$) but not with concentrations on clayey subsoil. The results should be analyzed cautiously because there were more peat subsoil than clayey ones and only a few number of buffer strips were edged by sandy subsoil.

In some cases subsoil can be a source of P and lead to increase total-P concentrations. Water is moving vertically and quickly from the soil surface down to the water table within the subsoil. Then, the subsequent slow and lateral movement of that water to a subsurface drain tile allows P-deficient subsoil to adsorb or precipitate that P before the water reaches and is released by the drain tile.

The dominant subsoil type from the contributing area of each buffer strip seems to have no significant effect ($p> 0, 0535$ for bank material) on total-P content neither in bank material nor in soil buffer strips..

It allowed to conclude that the total-P contents in soil buffer strips were not influenced by the subsoil type dominating the whole contributing area but concentrations of total-P in bank material could be influenced by the soil properties of the contributing area, as the p-value is not consequently higher than the significant level.

III.2.6.3 Erosion risk value

From the table extracted from GIS computation, a weighted erosion risk value has been computed, for each contributing area. The weighted value has been performed following this equation:

$$\text{Weighted Erosion Risk Value} = \frac{(-1 \times \text{nr of cells}) + (1 \times \text{nr of cells}) + (2 \times \text{nr of cells}) + (3 \times \text{nr of cells})}{(\text{Nr of cells in the contributing area}) - (\text{nr of cells with missing data in the contributing area})}$$

Results from this calculation did not give entire value so they have been rounded up to the nearest entire value.

Then, an expert adjustment with help of the GIS layers has been implemented in order to define an approximate erosion risk value for the contributing area where data were missing. The expert adjustment was based on observations of the slope, land uses and topsoil types in 3D with Arc Scene 9.2.

When this has been done no value of -1 were found but some of 0 that did not appear in the classification on the WaTEM model. It had so been defined four classes as described following:

[-1; 0] : Deposition area

]0; 1] : Low Erosion Risk

]1; 2] : Moderate Erosion Risk

]2; 3] : High Erosion Risk

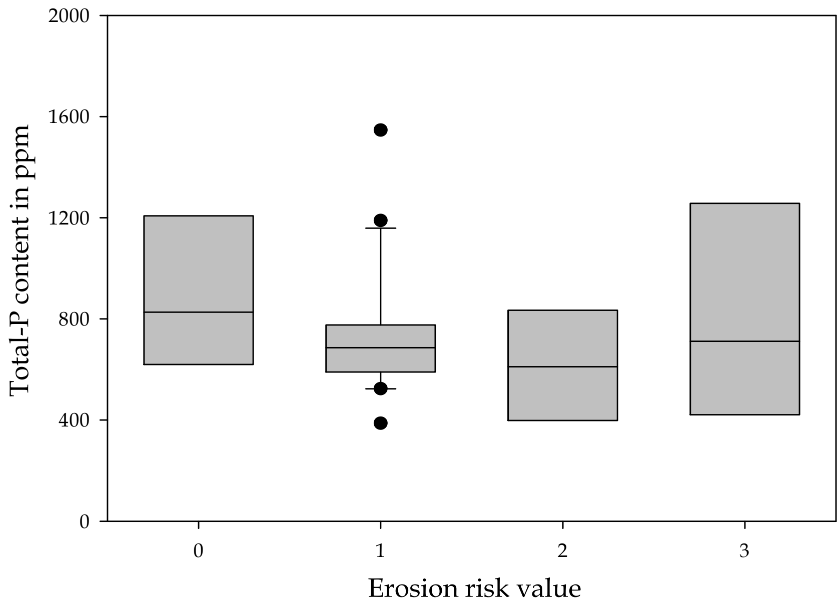


Figure 20. Distribution of the total-P content between the erosion risk values of neighbouring land in H2

Results on figure 20, showed that 57% of the buffer strips got runoff from contributing areas with low erosion risk value. Respectively, 17% and 11% of the sub-catchments had a high and moderate erosion risk value. 15% of them were considered as deposition areas, so it meant that from those ones, small amount of sediments were coming to the buffer strips and that total-P contents found there, were not mainly influenced by neighbouring land use, use of fertilizers and/or manure. Experimental sites edged by contributing areas with erosion risk value of 0 showed the highest total-P contents. It was not proper with what was expected.

The erosion risk value of the contributing areas in itself did not give much information related to total-P contents. It should be connected with data from land use and/or soil types.

It is known that erosion risk value depends partly on the slope of the land: the greater is the slope, the higher the erosion risk is. Within the Odense River catchment which is predominantly agricultural lands, forests were mainly located in the steepest areas. The erosion risk value computed with WaTEM does not take into consideration the plant cover, nevertheless it is well known that vegetation can decrease considerably the erosion phenomena. It is therefore possible to say that high erosion risk and arable land use is very high risk whereas high erosion risk and forest is very low erosion risk, as vegetation will act as a trap of eroded sediments. Then it was not possible to conclude anything about the soil types because they were all distributed between the four erosion risk classes.

III.2.7 Explanatory variables for the total-P contents (Multivariate Principal Component Analysis).

Independently of one another, analysis had shown that total-P contents measured in soil buffer strips along the Odense River catchment can be influenced by the land use, the topsoil type and the subsoil type of the neighbouring land.

The last step was so to compute a Multivariate Principale Component Analysis in order to find out the weight of these explanatory variables on the total-P contents distribution. It is possible that statistical analyses do not reflect significant relationship between total-P and a variable but the later can have an important weight on its distribution.

The Multivariate Principle Component analysis gave the following figures, where:

TPH1 or TPH2 means total-P content in horizon 1 or 2

NLu is the dominant neighbouring land use

CLu is the dominant land use in the contributing area

NTt means dominant neighbouring topsoil types

NSt means Dominant neighbouring subsoil types

CSt means dominant subsoil types in the contributing area

Dist_2005 is for the distance to the nearest arable land or grassland in 2005

Dist_2006 is for the distance to the nearest arable land in 2006

WERV is for weighted erosion risk value

In H1, the correlation matrix Pearson (Appendix 3) between the total-P contents and the different explanatory variables was significant at a significance level alpha=0.05 for NSt, Clu, and NTt. In H2, it was significant at a significance level alpha=0.05 for NTt, NSt, and WERV.

The multivariate analysis in both horizons (Figure 21) of soil buffer strips showed that the total-P contents were not influenced by the same variables. Nature of the topsoil and the subsoil were in both cases some of the main explanatory factors but in H1, the total-P concentrations were more influenced by the land use and especially the one from the contributing area whereas in H2 it was the erosion risk value.

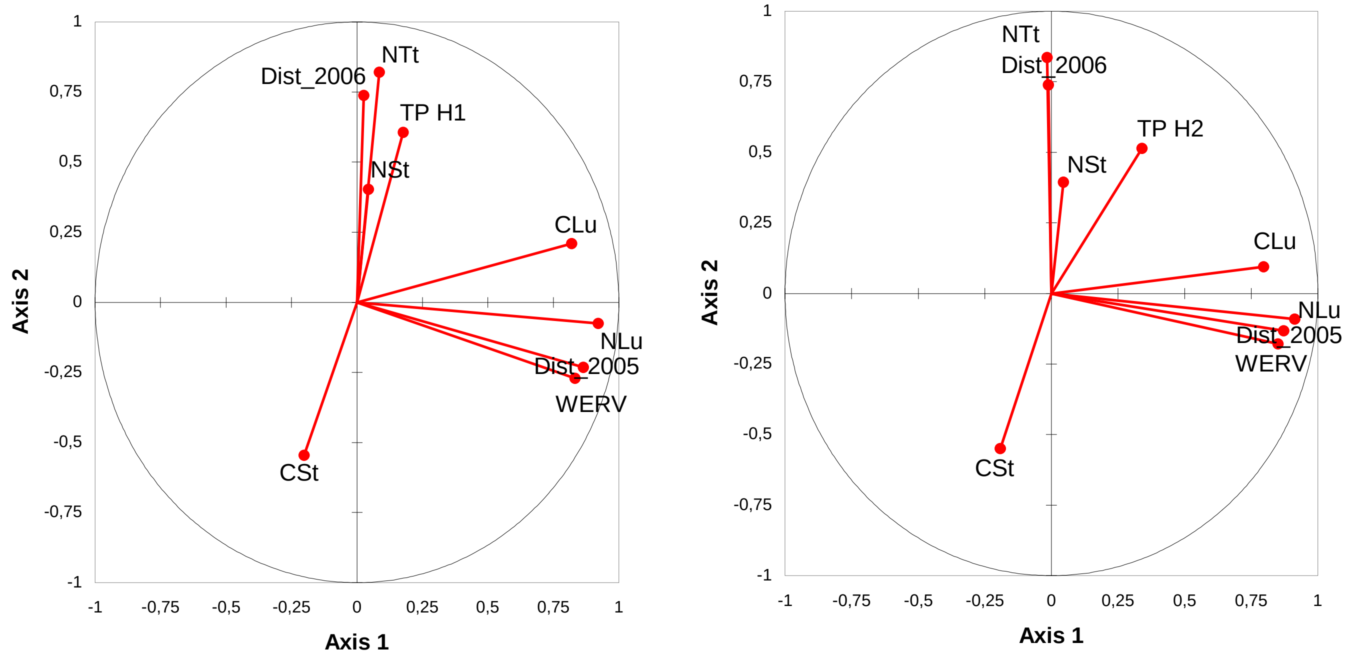


Figure 21. Results of Multivariate Principle Component Analysis in H1 and H2

Buffer strips where total-P contents were above 1000 ppm in H1 and/or H2 hold interest; they were named O-08, O-10, O-11, O-12, O-19, O-34 and O-36.

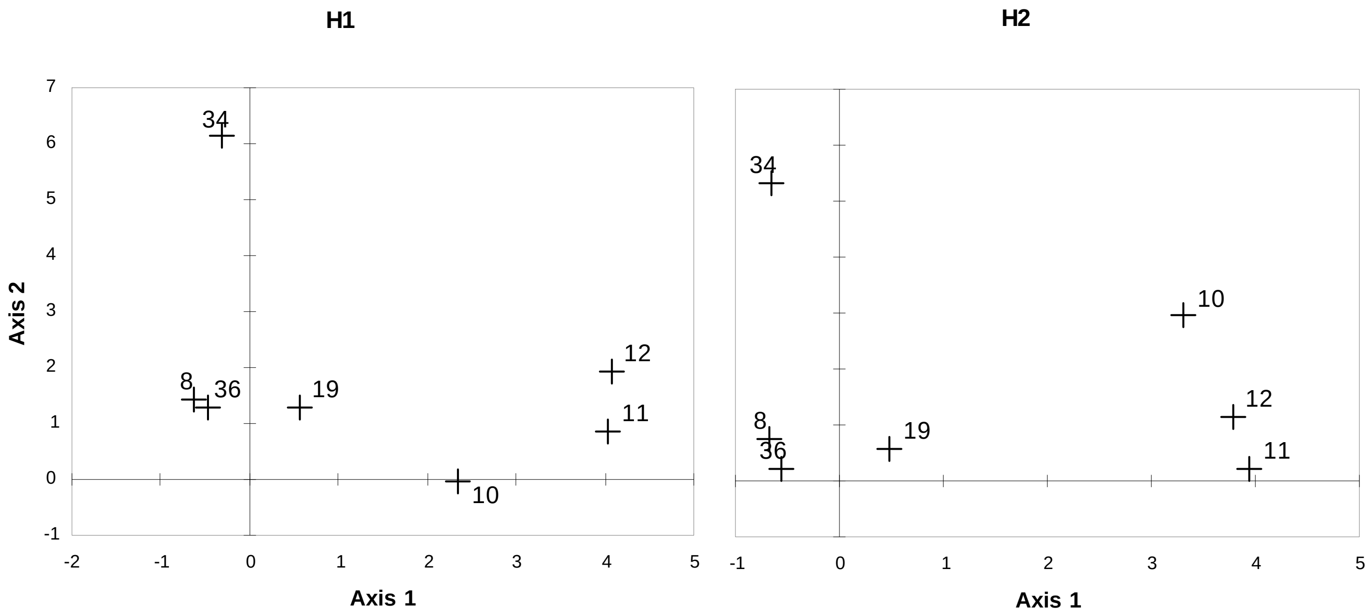


Figure 22. Multivariate Principal Component Analysis plots of observations in H1 and H2

Analysis of the plots of observation (Figure 22) showed that the total-P contents found in buffer strips named O-11 and O-12 are linked to the land use in the contributing area, which was wetland. Actually, it is known and still studied that wetland are traps and sink of P but they can also when they become saturated, release P to soil and water. The contents measured in these two buffers strips, were above 1000 ppm only in H1. Corroborating with the results commented previously, land use could be the major reason of such concentration found at these locations. The P concentration in O-34 in H2 is linked to the neighbouring topsoil type which is peat.

This buffer strip is the only one among all studied which is edged by peat topsoil. Thus, the nature of the topsoil and particularly peat seemed to show higher total-P contents. Regarding the others experimental sites, no variables tested seemed to explain why such high concentrations were found in soil buffer strips. Importance

III.3 Discussion

Results showed that total-P contents within the Odense River catchment were mostly higher than those measured in Denmark on arable land and forested areas.

There was no, as hypothesized, decrease of total-P content in depth. Total-P contents were not significantly different from soil buffer strips to bank material. This phenomenon needs to be analyzed more in details and if more soil samples will be done it should be an important subject of a following study. Regarding these results, two hypotheses can be put forward:

- Soils are naturally rich in P, or
- There is enrichment of bank material in P due to adsorption of P dissolved in surface water by fresh bank material.

P in surface water could come from upstream but also originates from deeper groundwater discharge within the aerobic hyporheic zone.

Height of vegetation and Strahler order of the streams can influence the total-P contents found in soil buffer strips and stream bank: increase of total-P concentrations with high Strahler order is maybe due to increase in discharge of deeper and reduced groundwater and decrease of P with higher riparian vegetation could be explained by a high biological uptake or low input of P due to a large distance to agricultural activities.

The landscape within the Odense River catchment changed since 1880: farmland neighbouring the buffer strips had decreased and are nowadays cultivated further than the streams. One hypothesis could have been that longer is the distance, lower could be the total-P concentration in soil buffer strip, because the time transportation of the eroded material could be longer so there is more chance for material deposition before it reaches the buffer strip. Nevertheless, available dataset from measurement on the field did not permit to conclude on it or not. Further and more precise measurement would have been necessary for illustrating the influence of distance between buffer strip and arable land. Grassland had decreased also and forest areas did not change. Land use has an effect only on the first horizons of the buffer strips. Its effects are not reflected in the bank material. The highest total-P contents were found in experimental sites edged by agricultural land, which have been cultivated since the last century. It therefore reinforces our hypothesis of a potential strong impact of agricultural practises on gradient of total-P in buffer strips. In agricultural land, there occurs enrichment of soils in P whereas in forested soils P is exported by vegetation during the growth period.

Regarding the topsoil type, it had an effect only on the horizon from 5 to 25 cm, where the highest total-P concentrations were measured in peat soils, then in clay soils and the lowest in sandy soils. Mineralization of peat releases large amount of P and it is also known that clay soils have a higher sorption capacity than sandy soils. Concerning the subsoil type (1 m depth), it had an effect on the horizon from 5 to 25 cm and on the bank material and the highest total-P concentrations were found in peat and sandy soils.

Within the Odense River catchment, the highest erosion risk values were found in forested areas which are located mainly on the steepest areas. With soil erosion there is detachment and movement of soil particles by the erosive forces of wind or water. Particles are detached and transported away from one location and are then deposited at some other place. Eroded soils can contain nutrients, fertilizers and pesticides.

Nevertheless, plant cover can reduce transport of particles. It functions as a trap for sediment. It is therefore worst to have high erosion risk in agricultural land than in forested area.

To conclude, it was possible to say that the functioning of the buffer strips did not cease between runoff events, and that there were a set of complex processes and feedbacks among the sediments, P and the plant-soil system that occurred on seasonal and annual time scales. Since the last fifty years, agricultural practices have changed within the Odense River catchment and management of the catchment has followed the European union Water Framework Directive. Nevertheless, total-P contents higher than the national mean were found in the soil buffer strips. Study has shown that there was an anthropogenic effect of the land uses (application of fertilizers and manures) because of accumulation of P in soils but also natural characteristics which were the topsoil and subsoil types which can be naturally rich in P. Nevertheless they did not seem to be the only factors influencing total-P contents distribution, as they have not permit to conclude on the variables influencing the contents measured in buffer strips O-08, O-10, O-19, or O-36 for example.

The second part of this study, dealing with the trace elements would probably help to search out the origins of P found in soil buffer strips at these places.

IV Fingerprinting method

The second part of this study deals with the so-called "fingerprinting" technique. It has been tested as a mean to explain the origins of the total-P contents found in the experimental buffer strips. It has been seen before that the main factors influencing the concentrations of total-P in soil buffer strips are the topsoil type, the subsoil type, the erosion risk and the land use of the whole contributing area. The "fingerprinting" technique is based on the study of the content of forty seven trace elements in the soil buffer strip and then it was tried to be link the trace elements found to elements (tracers) derived from either agriculture, deeper groundwater or maybe sewage.

36 groundwater bodies have been identified within Odense River Basin: together these cover an area of 722 km^2, corresponding to 69% of the total area of the river catchment. Nearly all the groundwater bodies are located in sand aquifers (Odense Pilot River Basin, 2007). The majority of the groundwater bodies (29) are in contact with surface water, typically with lakes and watercourses. As a consequence, the quality and quantity of the groundwater can influence the quality and the environmental status of the surface water bodies. Of the groundwater bodies that are in contact with surface waters, 26 are in contact all year round, and the remaining 3 are only in contact during the winter period.

Trace elements, to a large extent, are derived from soil parent material and partially from anthropogenic activities, such as agricultural application of fertilisers. Heavy metals are not biodegradable; they can accumulate in the food chain and present a threat to crop quality as well as human and animal health (Underwood, 1971; Adriano, 1986; Tiller, 1989; Fergusson, 1990).

Chromium (Cr), Nikkel (Ni), Copper (Cu) and Uranium (U) are known to be present in considerable amounts in phosphate fertilisers (Mermut et al., 1996), and it is highly probable that their presence in soil stemmed from phosphate fertiliser application. In addition, sludge and compost (for Cr, Ni and Cu) and pesticides (Cu) could be the main sources of these elements in agricultural soils, if these materials have been applied for a long time.

According to Danish previous studies and literature (Stockmarr et al., 2000), it was shown that trace elements which can be used as tracers elements from agricultural activities are Cadmium (Cd), Copper (Cu), and Zinc (Zn) as they are the ones present in the highest amount in pig manures. It is well know that Cd, Cu and Zn are frequently added at high concentrations to pig diets as growth promoters, so livestock grazing pasture contaminated with pig slurry may, therefore, be at risk from excessive intake of these elements; almost all slurry is spread on agricultural land. Also, Schwærter, R.C. & Grant, R. showed that the trace elements found in highest concentrations in Danish groundwater bodies, were Barium (Ba), Arsenic (As) and Molybdenum (Mo). These three elements were so used as tracers from deep groundwater bodies. Table from Jensen, 2000, showed that Lead (Pb) could also be a tracer element from sewage sludge.

This study will focus on those seven trace elements considered as tracers from agriculture, sewage sludge and deep groundwater bodies, but also on Aluminium (Al), Magnesium (Mg), Manganese (Mn) and Iron (Fe) with the aim to reveal the elements bound to total-P.

IV.1 Methods

IV.1.1 Soil samples

Samples of soil buffer strips were taken only from the first horizon (H1= from 0 to 5 cm) and following the same procedure as previously (five sampling spots along each of the 100 m long buffer strip). Samples were taken at two times: six of the experimental sites (O-05, O-14, O-28, O-27, O-31 and O-16) were sampled on the 22nd of April 2008 and the rest during the last week of April 2008. On return to the laboratory, each sediment composite sample from each buffer strip was wet sieved through a 63 µm sieve in an automatic machine named "Fritsh Laborgeräteban". Amplitude of vibration was set 4 and in low interval between vibrations. The < 63 µm portion was allowed to settle, the supernatant decanted off and 5 g of the settled material was collected, stored in 20 ml poly-ethylene bottles and then sent to United Kingdom for analysis of the trace elements.

Due to a conflict with the land owner, buffer strip number O-29 could not be sampled.

IV.1.2 Laboratory analysis

Chemical preparation and analyses of < 63 µm samples were made using a direct acid digestion with nitric and hydrochloric acid. Trace elements were analyzed using inductively coupled plasma mass spectrometry (ICP-MS).

IV.1.3 Statistical methods

Descriptive statistical analyses (mean, median value, 90-pct, standard deviation, minimum and maximum) were computed. The contents of trace elements in soil buffer strips within the Odense River catchment were compared to the typical Danish values in agricultural and forest soils (values from Jensen, 2000), especially As, Cd, Cu, Cr, Ni, Pb and Zn.

Simple and multiple linear regression tests and plots were computed in order to find out relationships between the total-P contents and the tracers elements from either agricultural activities, deep groundwater bodies or sewage sludge and also to highlight binds of total-P with other compounds.

Pearson correlation matrix were calculated with the aim to find out the degree of correlation between the forty seven trace elements analysed and especially if one of them was correlated with most of the others.

Canonical correspondence Analysis (CCA) was used to analyse the effect on trace elements composition of the set of characteristics of buffer strip and contributing catchment found at the first step of this study as the main explanatory variables. CCA is designated to detect the patterns of variations in trace elements data that can be explained by the extracted characteristics of neighbouring and contributing land from GIS previously.

IV.2 Results

A complete list of all elements and their concentrations in the 34 buffer strips is in appendix 4.

IV.2.1 Tracer elements in soil buffer strips

The range (median value (min-max)) of tracers elements chosen found in soil buffer strips within the Odense River catchment were in order of increasing median concentration: Cd: 0.58 ppm (0.25-1.38), Mo: 0.71 ppm (0.33-6.44), As: 8.32 ppm (2.79-26.31), Cu: 14.46 ppm (7.22-39.84), Pb: 20.31 ppm (12.56-98.91), Zn: 65.54 ppm (37.24-145.99) and Ba: 106.40 ppm (41.25-174.36).

IV.2.2 Comparison with Danish median values

Results on table 10 showed that generally in Denmark, heavy metals contents were higher in agricultural land than in forested areas, except for Pb.

Table 10. Typical heavy metals values in rocks, soils and fertiliser (A. Laubel modified: Danish values from Jensen, 2000 and world wide numbers from Alloway, 1995), modified.

Trace elements content (ppm)	As	Cd	Cu	Cr	Hg	Ni	Pb	Zn
Sandstone*	0,25	0,05	30	35	0,29	9	10	30
Granite*	0,04	0,09	13	4	0,08	0,5	24	52
Shales and clays*	13	0,22	39	90	0,18	68	23	120
Earth's crust*	0,07	0,1	50	100	0,05	80	14	75
Agricultural soils, Britain*	-	0,7	18	39	-	23	40	82
Agricultural soils, USA*	-	0,2	19	-	-	18	11	53
Agricultural soils, Denmark	3,6	0,18	7,8	10,7	0,04	5,7	11,3	29,1
Reference soils, Denmark	1,3	0,07	0,9	3,8	0,01	1,5	8,7	7,7
Forest soils, Denmark	2,3	0,09	2,8	7	0,04	2,9	12,1	18,9
Sewage sludge, Denmark	5,1	1,5	298	34	1,4	26	72	878
Animal manure, Denmark	0,3	0,66	636	3,6	<0,1	10	2	897
Animal manure*	3-25	0,1-0,8	2-272	1,1-55	0,01-0,36	2,1-30	1,1-27	15-666
Nitrate fertilisers*	2-120	0,05-8,5	-	3,2-19	0,3-2,9	7-34	2-27	1-42
Phosphate fertilisers*	2-1200	0,1-170	1-300	66-245	0,01-1,2	7-38	7-225	50-1450
Agricutural soils, buffer strips (n=22)	9,72	0,6	16,2	9,56	/	9,57	20,31	67,39
Forest soils, buffer strips (n=12)	4,52	0,49	12,78	8,52	/	10,1	21,11	57,82

Results for the experimental buffer strips within the Odense River catchment did not follow exactly the same trend: Ni median value was higher in soil buffer strips edged by forest soils than agricultural land (both farmland and grassland). Whatever the land use of the neighbouring land, the contents of trace elements measured in soil buffer strips were significantly greater than median values in Denmark, except for Cr concentration in buffer strips edged by agricultural land. This result seems to evidence that the buffer strips are enriched with a large range of trace elements.

In buffer strips neighbouring agricultural land, As and Cd contents were three-fold greater than the Danish median values and two times higher for Cu, Ni, Pb and Zn. In those neighbouring forested areas, differences were more important: As and Pb contents were multiplied by two, Zn by three, and Cu, Cd and Ni concentrations were all more than four-fold greater than the Danish median values.

Over-all, this comparison allowed to say that concentrations of the studied trace elements (As, Cd, Cu, Cr, Ni, Pb and Zn) were greater within the Odense River catchment than on average in Denmark. Some of those heavy metals are the chosen tracers elements from agricultural activities or from groundwater bodies, so it means that phenomenon occurring within Odense catchment, regarding origins of total-P, are most important than on the Danish average.

IV.2.3 Relationship with Total-P

Results from linear regression tests established between total-P contents, the tracer elements and also Fe, Mg, Mn and Al are shown in the following table 11.

Table 11. Results from linear regression tests of Total-P and the tracer elements chosen, Fe, Al, Mn and Mg.

	Trend line equation	R2 value	p-value
Fe	**y= 11,585x + 7084,6**	**0,4021**	**$5{,}66.10^{-5}$**
Mg	y= 0,055x + 1622,7	0,0015	0,826
Mn	**y= 1,4991x + 285,05**	**0,2442**	**0,003**
Cu	y= 0,0083x + 9,7705	0,1042	0,063
Cd	y= 0,0001x + 0,4884	0,0277	0,347
Zn	**y= 0,0323x + 48,7**	**0,1319**	**0,034**
Ba	**y= 0,0987x + 31,796**	**0,5189**	**$1{,}56.10^{-6}$**
As	**y= 0,0104x + 1,8988**	**0,2639**	**0,002**
Al	y= 0,0848x + 4840,8	0,004	0,912
Mo	y= 0,0004x + 40,6684	0,0149	0,492
Pb	y= 0,0085x + 30,497	0,031	0,319

Values in bold are significant with a significant level alpha= 0,05

It showed that Total-P contents were not only, as shown before, linked to carbon contents, but they were also bound to Fe (Figure 23). P is bound to Fe and not significantly to Al. Phosphate has a strong tendency to interact with ferric iron to form a "mixed" ferric hydroxo-phosphate precipitate (Stumm and Morgan, 1970). Several investigators have emphasized the significance of Fe and its hydrous oxides to the precipitation and sorption of P (Mortimer, 1941; MacPherson and al., 1958; Jitts, 1959). Jarie et al., 2007 have shown that Fe oxyhydroxides have a high P-sorption capacity. Total-P was also linked with Zn, which is one of the tracer elements from agricultural activities. Nevertheless it could be qualified as a low to moderate relationship. Relationship between total-P and Pb, which was chosen as sewage sludge tracer element was not significant. It is more nicely related with As and especially Ba (Figure 24), which are both tracer elements from deeper groundwater. Linear regression (Figure 25) established between Fe and Ba showed a strong relationship between these two elements, and a moderate one between Fe and As.

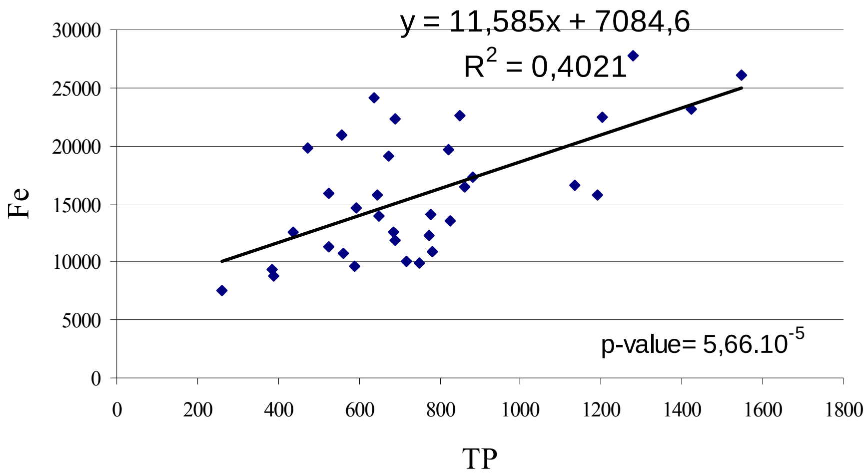


Figure 23. Relationship between Fe and Total-P contents in horizon 1

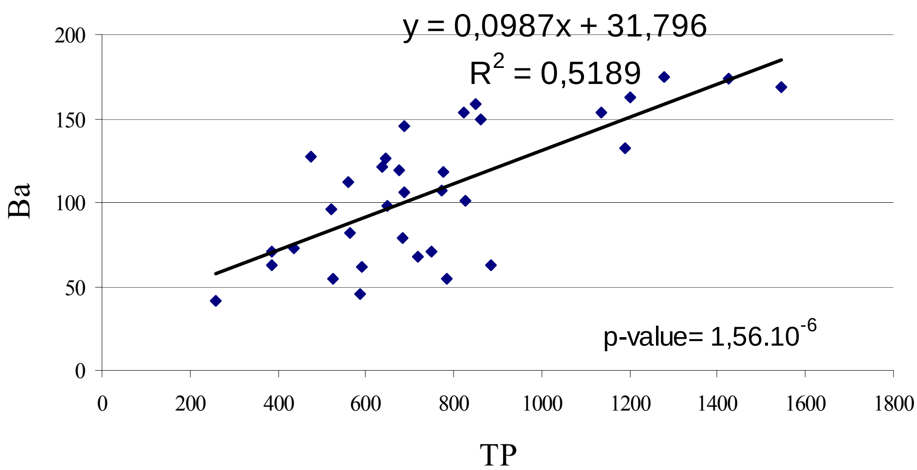


Figure 24. Relationship between Ba and Total-P contents in horizon 1

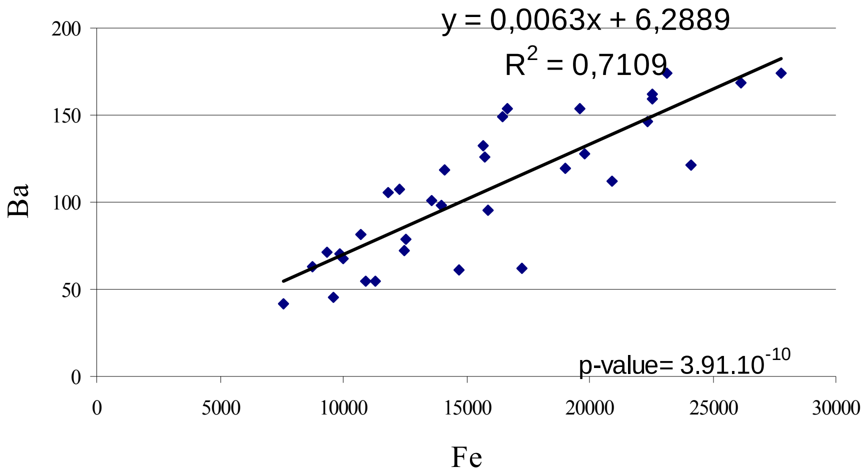


Figure 25. Relationship between Ba and Fe contents in horizon 1

These relationships seemed to evidence that Ba and Fe have the same origin: the deeper groundwater bodies .Total-P is strongly bond to Fe. As Fe and total-P are strongly correlated, they can not come from the same point source (Henning Jensen, Institute of Biology, Personal communication).

IV.2.4 Catchment relationships developed for tracer elements and total-P in soil buffer strips

A CCA analysis between tracer elements concentrations in soil buffer strips, Fe, Mn, and Al and the four main explanatory variables of total-P distribution (neighbouring topsoil type, neighbouring subsoil type, erosion risk value and dominant land use of the contributing area), highlighted in the first part of this work and the total area of the contributing catchment was conducted for the two soil horizons (Figures 26 and 27).

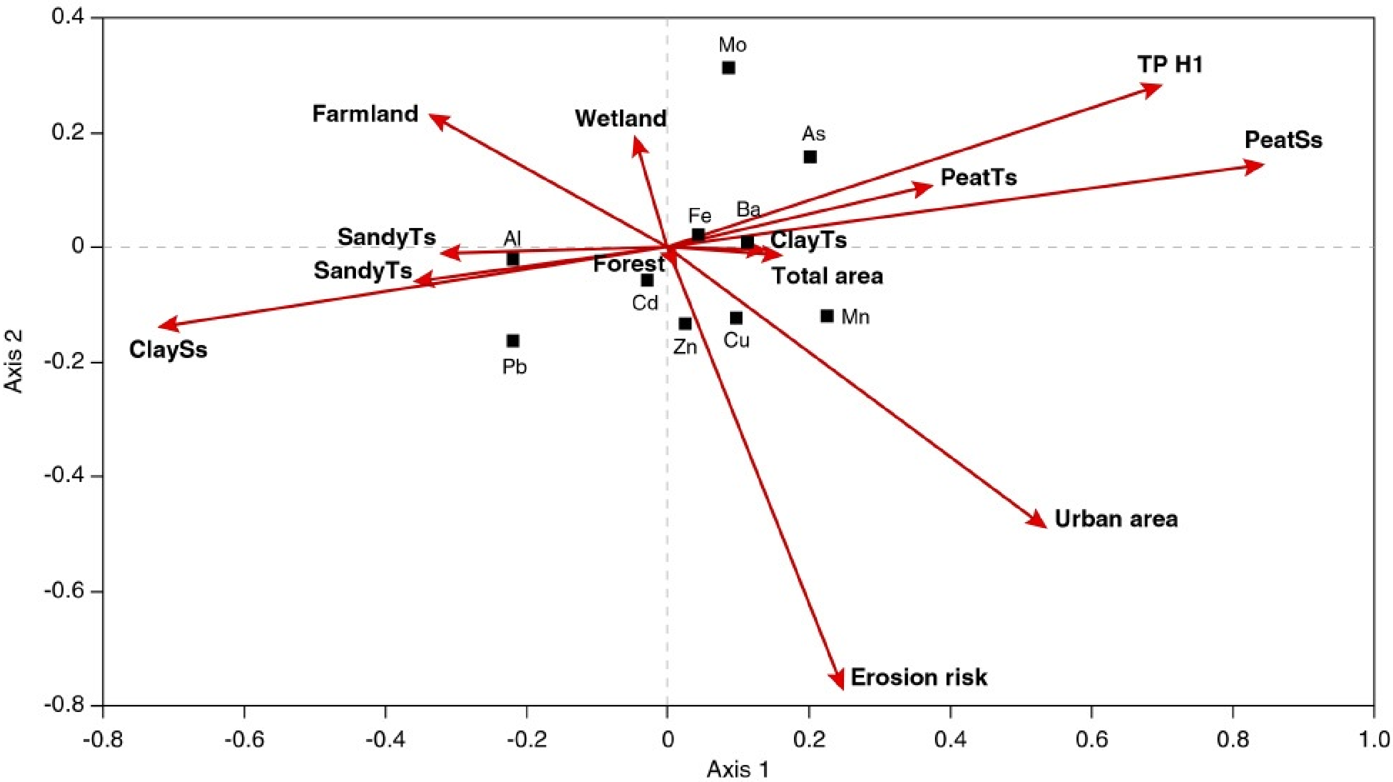


Figure 26. Canonical correspondence analysis (CCA) of the concentration of tracers elements against descriptive variables for the neighbouring land and contributing area (dominant land use within contributing area, neighbouring soil types (topsoil and subsoil), erosion risk value, and area of contributing catchment) in horizon 1

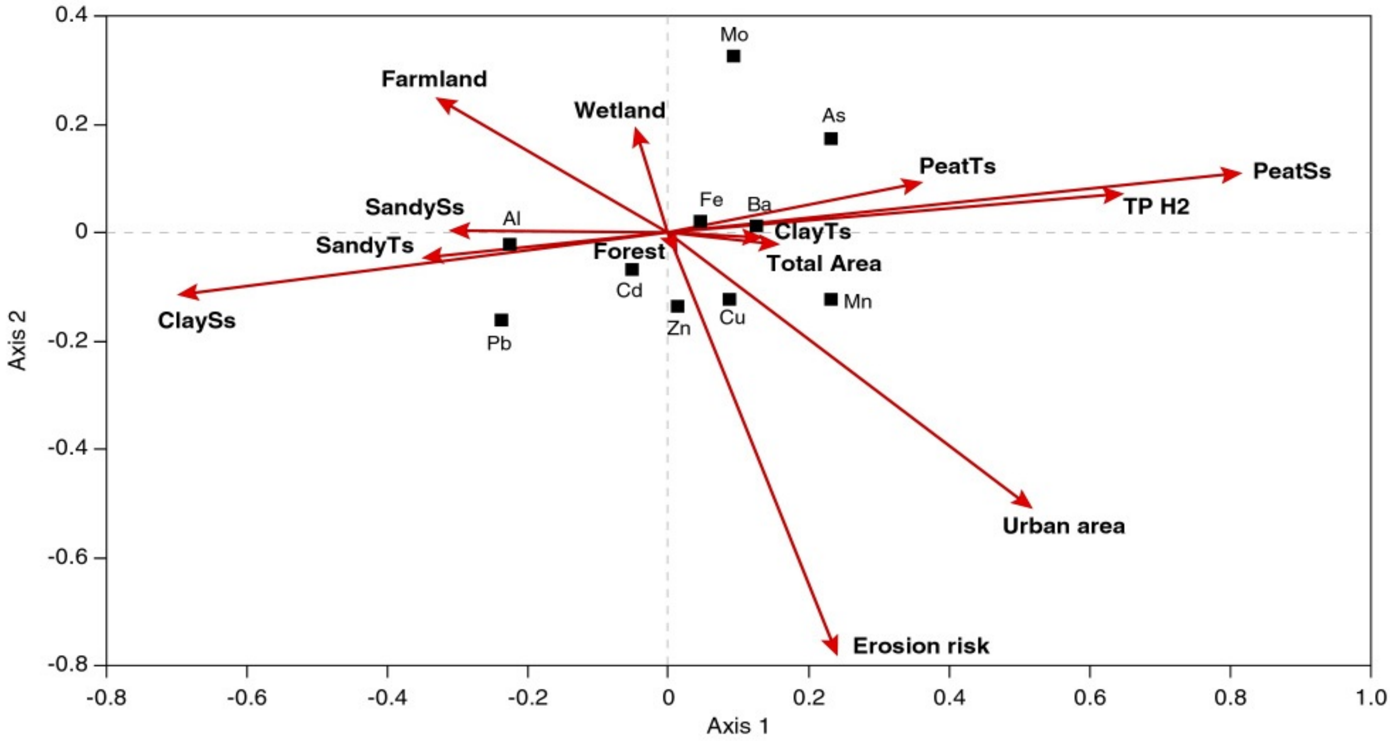


Figure 27. Canonical correspondence analysis (CCA) of the concentration of tracers elements against descriptive variables for the neighbouring land and contributing area (dominant land use within contributing area, neighbouring soil types (topsoil and subsoil), erosion risk value, and area of contributing catchment) in horizon 2

The CCA analyses explained respectively in H1 and H2, 48% and 45% of the variance and revealed a clear tendency of total-P to be correlated with one group of trace elements, which are the ones tracers from deep groundwater bodies: As, Ba and Mo were highest with high proportion of total-P, especially in the more peat contributing area (particularly in H2).

The concentrations of Zn, Cu and Mn on the other hand were highest in more urbanized contributing areas and related to the erosion risk value. Contents were highest with high erosion risk value. Regarding Sansalone and Buchberger study in 1997, Zn and Cu contents could come from storm water runoff from urban roadways. Zn, Cu and Mn contents were inversely related to proportion of farmland within the contribution area, whereas they were chosen as tracer elements from agricultural activities. As demonstrated previously, Fe was in the figure in the same quarter as As, Ba and Mo so it corroborated with the finding saying that Fe was linked to deeper groundwater bodies. It also fitted with the arrow of total-P contents so supporting the previous results about the strong bond between those two compounds.

The Al concentration was previously not significantly correlated with total-P contents and these figures showed that they were highest in sandy contributing area. It confirmed the results that total-P was not bound to Al particles. Pb contents were not obviously link with any of the variables or others trace elements. It showed that, as expected, there was no clear impact of sewage on the total-P contents as there is no big city within the catchment area.

Total-P contents were not correlated with any land uses. Explanation of the total-P distribution seemed to be much more influenced by axis 1 which corresponded to soil types. Figures showed that total-P contents were highest with increasing of peat proportion in topsoil and/or subsoil. In addition, the total-P concentrations were partly linked to the amount of clay into topsoil, but inversely correlated with clay content in subsoil.

It also illustrated that increase in particles grain size to sandy soils was inversely proportional to high total-P contents. Total area, expressed in hectare (ha) did not show any correlation with the total-P contents.

There was no increase of total-P contents with increase of contributing area. It was also noteworthy, that forest land use and highest erosion risk value were correlated as it was shown in the first part of this report that forested areas within the Odense River catchment are mainly located in area with high erosion risk value.

When inter-comparing trace elements concentration with Pearson matrix correlation, no trace element showed any positive relationship with all the others. Otherwise, in this case, trace elements concentration could have been normalised to the common trace element concentration in order to investigate the out come of an additional CCA analysis using trace elements ratios rather than concentrations.

IV.3 Discussion

In this study, the trace elements concentrations in soil buffer strips were considerably higher than those of Danish soils being monitored and reported by Jensen, 2000. It can be explained by the fact that it was a median value from thirty four experimental buffer strips compared to the Danish median value which was calculated on more than 900 soil samples taken all over the country. For this comparison, significance of agricultural land was not totally clear concerning data for Denmark. It has been compared with data from the buffer strips, including in agricultural land both farmland and grassland. Moreover, not only related to land use, concentration in trace elements can vary widely because of differences in particle size distribution and organic matter. This comparison was established only regarding the land uses and did not take into consideration the soil types.

This study confirm that relationships can be developed between the presence of total-P and trace elements in Odense River catchment and explanatory variables such as soil types, erosion risk, land use, but also hydrological pathways, especially from deep groundwater bodies.

Dissolving into groundwater of sedimentary rocks is the primary source of naturally occurring Ba, so it proves its representativeness when it was used as tracer element from deep groundwater bodies.

A number of authors have investigated the influence of catchment land use characteristics on heavy metals concentrations in streambed sediments, especially the influence of urban and industrial activities (e.g. Rees et al, 1999, Rice, 1999). A number of heavy metals (Cd, Cu, Cr, Hg, Pb and Zn) correlated with urban activity across the USA (Rice, 1999) and Danish streambed (Kronvang et al, 2003). Two trace elements (Cu and Zn) were based on the CCA analysis in this study. They indicated to derive from urban activity even if at the beginning they were chosen as tracer elements from agricultural activities. This is in accordance with what was concluded from the investigations of Kronvang and al., (2003), on pesticides and heavy metals in Danish streambed sediments. Fe and Mn on the other hand seemed related to natural sources.

The fact that total-P contents were inversely related to sand proportion into soils was due to the leaching of P through the soil profile in coarse texture as sand particles. This finding corroborated with those found by Candron et al., 2006. Previous studies on peat soils have shown that accumulation of Al and/ or Fe in organic soils increases the capacity of phosphate-sorption (Cuttle, 1983; Richardson, 1985; Nieminen and Jarvo, 1996).

An explanation of the weak relationship between clay in subsoil and total-P contents could be, as it has already been demonstrated by Bortlesson, 1971, that in clay subsoil, Fe is probably associated primarily with clay minerals particles which would provide little opportunity for P precipitation with iron compounds.

Fe oxides are the major sorbent of P in peat soils and this was also shown in this study by the strong correlation found between the two compounds in buffer strip soils.

The combined results allow hypothesizing that groundwater discharge areas may be important sink for iron P compounds. Results suggested that accumulation of Al and Fe in peat soils has a large impact on the phosphate sorption capacity despite the presence of large amount of soil organic matter.

There was no clear influence of the total contributing sub-catchment area whereas works from Kronvang et al., (2003) on pesticides and heavy metals in Danish streambed sediment confirmed that relationships can be developed between the presence of currently applied pesticides in Danish streambed sediments and explanatory variables such as catchment size.

It is remarkable afterward that buffer strips O-08, O-10, O-19 and O-36, which showed high total-P contents are characterised by neighbouring peat subsoil. The phenomenon highlighted in this study regarding discharge of groundwater into peat soil, enhancing sorption capacity of total-P bond with Fe, is supposed to take place in the surrounding of these buffer strips and could be the justification of the gradient of total-P concentration in soil buffer strips studied within the Odense River catchment.

V Conclusion

Our investigations of the total phosphorus content of Danish buffer strips and stream banks in the Pilot River Odense Basin has made us reach the following mains conclusions:

A huge gradient in total phosphorus content was found in Danish soil buffer strips ranging from 259 ppm (mg P kg^{-1} DW^{-1}) to 1546 ppm in the first horizon, and from 266 to 4094 ppm in the second horizon. In bank material, total phosphorus contents varied from 314.17 to 1386.57 ppm at 60 cm above the stream bed and from 334to1560 ppm, at 20 cm.

Nearly a third of the experimental sites showed Olsen-phosphorus concentrations in buffer strip greater than the normal recommend value for agricultural production in Denmark, meaning that risk of dissolved-phosphorus leaching are increased and that soils are saturated.

Comparison with Danish average contents in agricultural soils showed that total-phosphorus contents in buffer strips in the Pilot Odense River catchment was higher in most 70% of the cases.

The total- phosphorus contents of the two buffer strips horizons and the two stream bank depths showed no statistical significant differences, maybe indicating that the binding capacity and source of total-phosphorus in both buffer strips and banks is the same, or maybe different mechanisms are regulating total-phosphorus content in buffer strips and in bank material.

Height of vegetation growing on the top of the buffer strips showed a statistical significant negative relationship with total-phosphorus contents. Decrease of phosphorus concentration with higher riparian vegetation may be an indicator of a higher uptake of phosphorus with high riparian plant cover possibly combined with low input of phosphorus to the buffer strip due to a large distance to agricultural activities.

The total-phosphorus content in the stream banks showed a significant relationship to stream order (sensu Strahler 1957), maybe indicating the importance of increasing deeper groundwater discharge with increasing of stream order in the catchment.

The total-phosphorus content in buffer strips and stream banks showed a significant positive relationship to stream order (sensu Strahler 1957), maybe indicating the importance of increasing deeper groundwater discharge with increasing stream order in the catchment.

Concentrations of total phosphorus were higher in peat soils and in buffer strips draining contributing areas predominantly covered by agricultural land and with low erosion risk.

Results evidenced that the experimental buffer strips were enriched with high concentrations of trace elements as compared to Danish average contents in agricultural and forested soils.

Significant statistical relationship was established between phosphorus contents in the buffer strips top soil (0-5 cm) and respectively total iron (Fe) and organic carbon contents. Furthermore, multiple linear regressions including both variables improved the relationships found.

Iron is shown to be strongly correlated respectively with tracer elements from deeper groundwater bodies (As, Ba and Mo) and peat topsoil and subsoil.

No clear impact of agricultural activities was found on total phosphorus content in buffer strips the only indication being the inverse relationship with height of vegetation and positive relationship to agricultural activities in the contributing area to the 100 m channel reach with its buffer strip.

The single statistical results have not permitted us to reach a firm conclusion on the origin of phosphorus measured in buffer strips and stream banks within the Pilot Odense River Basin. However, the combined results of applying two methodologies for investigating the buffer strips gave strong indications for phosphorus content in the buffer strips to be related to the origin of the binding capacity (iron content) which is again linked to deeper groundwater seepage into the riparian area as shown by the enrichment of trace elements from groundwater (Ba, Ar). The established positive relationship between total phosphorus content in buffer strips and stream order reinforced the hypothesis of deeper groundwater seepage to be responsible for the enrichment in phosphorus sorption capacity (Fe). Thus, whatever the sources of phosphorus (agriculture, groundwater and/or stream water), the binding capacity in the investigated buffer strips seems to be delivered by deeper groundwater seepage during thousands of years also giving rise to the formation of peat soil. The origin of phosphorus is, however, still uncertain whether it is delivered from agriculture, coming with deeper groundwater seepage or from stream water. More investigations are needed for clarifying this issue further.

VI Perspectives

Based on my investigations, I can recommend that further research should be conducted regarding phosphorus content of buffer strips and stream banks:

More detailed knowledge of fertilizer and manure application at the field level (e.g. amount, substances, and time) are needed for study of agricultural activities impact.

More measurement of distance to the arable land could also provide information regarding the effect of application of fertilizer and manure.

Investigation of phosphorus gradients with depth in buffer strips and stream banks and in transects towards agricultural fields are required to answer the remaining questions, such as:

- Is the source of total phosphorus in both buffer strips and bank material of the same origin?
- Is there different mechanisms working for total phosphorus in buffer strips and total phosphorus in stream bank?
- Is the textural composition the same in bank material and soil buffer strip?

A survey of the amount of water discharging along the 100 m reach could be made. It might be done by measuring the flow in two sites located respectively 100 m upstream and 100 m downstream to the buffer strip and comparing if there is afterthought of water or not.

Analyses of trace elements contents in subsoil layers may also indicate location where deeper groundwater seepage takes place.

Regarding the most harmful heavy metals, comparison with Danish thresholds (qualitative levels) could be established with a view to qualify the degree of contamination of soil buffer strips in the Pilot Odense River Basin.

Field experiments and research projects concerning bank erosion and its contribution to phosphorus losses will follow through.

Study of possible toxicological effects of phosphorus and heavy metals in stream biota could be implemented.

At a larger scale, all over Denmark but also in the others European countries, research projects must continue to be accomplished, with the aim, in the coming years, to achieve significant reduction in phosphorus losses to the aquatic environment.

REFERENCES

Andersen H.E., & Svendsen L.M. 1996. Suspended sediment and total phosphorus transport in a major Danish river: Methods and estimation of the effects of coming major restoration. Aquatic conservation: marine and freshwater ecosystems, **Vol 7**: (1997) 265-276.

Andersen, J.M., Boutrup, S., Svendsen, L.M., Bøgestrand, J., Grant, R., Jensen, J.P., Ellermann, T., Rasmussen, M.B., Jørgensen, L.F. & Laursen, K.D. 2004: Aquatic Environment 2003. State and trends – technical summary. National Environmental Research Institute. 52 pp. – Technical Report **No. 500**.

Andersson, L., Arheimer, B., Larsson, M., Olsson, J., Pers, C., Rosberg, J., Tonderski, K., & Ulén, B. 2003. Integrated modelling of phosphorus fluxes at the catchment scale. Diffuse Pollution conference, Dublin 2003.

Baldwin D. S. 1996. Effects of Exposure to Air and Subsequent Drying on the Phosphate Sorption Characteristics of Sediments from a Eutrophic Reservoir. Limnology and Oceanography, **Vol. 41**, No. 8, (1996), 1725-1732.

Bedrock C. N., Cheshire M.V., & Shand C.A. 1997. The involvement of iron and aluminium in the bonding of phosphorus to soil humic acid. Commun.soil sci. plant anal., **28** (11&12), 961-971 (1997).

Benbi D.K., & Brar S.P.S. 1992. The interpretation of Olsen extractable P values in relation to recommendations for the fertilizer requirements of crops. Fertilizer Research **32**: (1992) 223-227.

Bernet Catch. 2006. Regional report- Odense fjord, water management plan- Provisional Management Plan pursuant the EU water Framework Directive. Published by Fyn County, Nature Management and Water Environment Division (2006): 46 pp.

Boggs G., Devonport C., Evans K., & Puig P. 2001. GIS-based rapid assessment of erosion risk in a small catchment in the wet/dry tropics of Australia. Land Degrad. Develop. **12**: (2001) 417-434.

Bradford, G. R., Chang, A. C., Page, A. L., Bakthar, D., Frampton, J. A., & Wrigth, H. (1996). Background concentrations of trace and major elements in California soils, Technical Report, Karney Foundation Spec. Rep,Univ. of California, Riverside.

Carlyle G.C., Hill A.R. 2001. Groundwater phosphate dynamics in a river riparian zone: effects of hydrologic flowpaths, lithology and redox chemistry. Journal of hydrology **247** (2001) 151-168.

Chardon W.J., & Schoumans O.F. 2007. Soil texture effects on the transport of phosphorus from agricultural land in river deltas of Northern Belgium, The Netherlands and North-West Germany. British Society of Soil Science **23 (**Suppl. 1): (2007) 16-24.

Cooper J.R., & Gilliam J.W. 1987. Phosphorus redistribution from cultivated fields into riparian areas. Soil Sci. Am. J. **51**, 1600- 1604.

Dahl M., Nilsson B., Lanhoff J.H., & Refsgaard J.C. 2007. Review of classification systems and new multi-scale typology of groundwater-surface water interaction. Journal of Hydrology **344**: (2007) 1-16.

Deacon J.R & Driver N.E. 1999. Distribution of Trace Elements in Streambed Sediment Associated with Mining Activities in the Upper Colorado River Basin, Colorado, USA, 1995-96. Arch. Environ. Contam. Toxicol. **37**: (1999) 7-18.

De Carlo E.H, Beltran V. L. & Tomlinson M.S. 2004. Composition of water and suspended sediment in streams of urbanized subtropical watersheds in Hawaii. Applied Geochemistry **19** (2004) 1011-1037.

De Temmerman L., Vanongeval L., Boon W., Hoenig M., & Geypens M. 2003. Heavy metals content of arable soils in Northern Belgium. Water, Air, and Soil Pollution **148**: (2003) 61-76.

Dillaha T.A., Reneau R.B., Mostagnimi S., & Lee D. 1989. Vegetation filter strips for agricultural non-point source pollution control. Trans. Am. Soc. Agr. Eng. **32**, 513- 519.

Djodjic F., Börling K., & Bergström L. 2004. Phosphorus leaching in relation to soil type and soil phosphorus content. J. Environ. Qual. **33**: (2004) 678-684.

Dorioz J.M., Wang D., Poulenard J., & Trévisan D. 2006. The effect of grass buffer strip on phosphorus dynamics- A critical review and synthesis as a basis for application in agricultural landscapes in France. Agriculture, Ecosystems and Environment **117**: (2006) 4-21.

Dubgaard A., Hasler B., Andersen K.S., & Nygaard-Pedersen J. 2007. Case study status report- Odense river basin, Denmark. AquaMoney **D25- D34**.

Environment Centre Odense (2007). Odense Pilot River Basin. Pilot project for river basin management planning. Water Framework Directive Article 13. Danish Ministry of the Environment- Environment Centre Odense, 126 pp.

Falkengren-Grerup U., Brink D.J., & Brunet J. 2005. Land use effects on soil N, P, C and pH persist over 40-80 years of forest growth on agricultural soils. Forest Ecology and Management **225**: (2006) 74-81.

Fu B.J., Zhao W.W., Chen L.D., Liu Z.F., & Lü Y.H. 2005. Eco-hydrological effects of landscape pattern change. Landscape Ecol. Eng. **1**: (2005) 25-32.

Fergusson J.E. 1990. The heavy elements: Chemistry, environmental impact, and health effects. Pergamon Press, New York.

Franklin R.E & al. 2005. Trace Element Content of Selected Fertilizers and Micronutrient Source Materials. Soil Sc. and Plant Analysis. **36**: (2005) 1591-1609.

Graetz D.A., Nair V.D., Portier K.M., & Voss R.L. 1999. Phosphorus accumulation in manure-impacted Spodosols of Florida. Agriculture, ecosystems and Environment. **75**: (1999) 31-40.

Haygarth P.M., & Jarvis S.C. 1999. Transfer of phosphorus from agricultural soils. Adv. Agr. **66**, 195- 249.

Heckrath G., Rubæk G.H., & Kronvang B. 2007. The 5th International Phosphorus Workshop 3-7 September 2007 in Silkeborg, Denmark. Diffuse phosphorus loss- Risk assessment, mitigation Options and Ecological Effects in River Basin. DJF Plant Science No **130**.

Hodgkinson R.A., Chambers B.J., Withers P.J.A., & Cross R. 2002. Phosphorus losses to surface waters following organic manure applications to a drained clay soil. Agricultural Water Management. **57**: (2002) 155-173.

Holmgren G.G.S., Meyer M.W., Chaney R.L., & Daniels R.B. 1993. Cadmium, Lead, Zinc, Copper, and Nickel in agricultural soils of the United States of America. J. Environ. Qual. **22**: (1993) 335-348.

He Q., & Walling D.E. 1997. Spatial variability of the particle size composition of overbank floodplain deposits. Water, Air and Soil Pollution **99**: (1997) 71-80.

Jacobsen O.H., & Kronvang B. 2000. Phosphorus loss from agricultural areas to the aquatic environment. DJF rapport Markbrug **No 34** (2000) (in Danish).

Jain M.K., & Kothyari U.C. 2000. Estimation of soil erosion and sediment yield using GIS. Hydrological Sciences- J. des Sciences Hydrologiques **45**: (2000) 5-11.

Jensen, J. 2000. Heavy metals in the environment. In: A Helweg (Ed.), Kemiske stoffer I miljøet, Gad Forlag (in Danish).

Jensen, J. 2000. Heavy metals in the environment. In: A. Helweg (Ed.), Kemiske stoffer I miljøet, Gad Forlag (In Danish).

Jiang X., Jin X., Yao Y., Li L., & Wu F. (2008). Effects of biological activity, light, temperature and oxygen on phosphorus release processes at the sediment and water interface of Taihu Lake, China. Water Research, **42** (2008) 2251-2259.

Kronvang B., Laubel A., Larsen S. E., & Friberg N. 2003. Pesticides and heavy metal in Danish streambed sediment. Hydrobiologia **494**: (2003) 93-101.

Kronvang B., Grant R., Laubel A., & Pedersen M.L. 2002. Quantifying sediment and nutrient pathways within Danish agricultural catchments. Agriculture, Ecology and Water Quality (eds P.M. Haygarth and S.C.Jarvis).

Kronvang B., & al. 2008. Effects of policy measures implemented in Denmark on nitrogen pollution of the aquatic environment. Environmental Science & Policy **11**: (2008) 144-152.

Kronvang B., Laubel A., Andersen H.E., & Djurhuus J. 2005. Buffer zones as a sink for sediment and phosphorus between field and stream: Danish field experiences. Water Science & Technology **Vol 51** No 3-4 pp 55-62.

Kronvang B., Hoffman C.C., Dröge R., & Andersen H.E. 2003. Sediment deposition and net phosphorus retention in a hydraulically restored lowland river-floodplain in Denmark: combining field and laboratory experiments. Not published.

Kronvang B., et al. 2005. Phosphorus losses from agricultural areas in river basins: Effects and uncertainties of Targeted mitigation measures. j. Environ. Qual. **34**: (2005) 2129-2144.

Laubel, A., Kronvang B., Hald A.B., & Jensen C. 2003. Hydromorphological and biological factor influencing sediment and phosphorus loss via bank erosion in small lowland rural streams in Denmark. Hydrol. Process. **17**: (2003) 3443-3463.

Laubel A., Kronvang B., Svendsen L.M., Pedersen M.L., & Larsen S.E. 2000. Danish buffer strips as sediment and phosphorus traps. Verh. Internat. Verein. Limnol. **27**: (2000) 1536-1540.

McBride M.B., & Spiers G. 2001. Trace element content of selected fertilizers and dairy manures as determined by ICP-MS. Communic. Soil Sci. Plant Anal., **32** (1&2): (2001) 139-156.

Mermut A.R., Jain J.C., Song L., Kerrich R., Kozak L., & Jana S. 1996. Trace element concentrations of selected soils and fertilizers in Saskatchewan, Canada. J. Environ. Qual. **25**: (1996) 845-853.

Mitchell A. & Baldwin D. S. 1998. Effects of Desiccation/Oxidation on the Potential for Bacterially Mediated P Release from Sediments. Limnology and Oceanography, **Vol. 43**, No. 3, (1998), 481-487.

Owens P.N., Deeks L.K., Wood G.A., Betson M.J., Lord E.I., & Davison P.S. 2007. Variations in the depth distribution of phosphorus in soil profiles and implications for model- based catchment – scale predictions of phosphorus delivery to surface waters. Journal of Hydrology **350**: (2008) 317-328.

Owens P.N., & Walling D.E. 2003. Temporal changes in the metal and phosphorus content of suspended sediment transported by Yorkshire Rivers, U.K. over the last 100 years, as recorded by overbank floodplain deposits. Hydrobiologia **494**: (2003) 185-191.

Pautler M.C., & Thomas Sims J. 2000. Relationships between Soil Test Phosphorus, Soluble Phosphorus, and Phosphorus Saturation in Delaware Soils. Soil Sci. Soc. Am. J. 64: (2000) 765–773.

Peter van der Keur & Jens Christian Refsgaard. The Odense River Basin Case Study in HarmoniRiB – Strategy and Methodology. Geological Survey of Denmark and Greenland, Copenhagen, November 2006 (www.harmonirib.com).

Pilot River Basins, European Commission, DG Environment, & the joint Research Centre. 2007. Pilot river Basin Activity Report- Phase II: 2005-2006- Water Framework Directive implementation pilot activities- key challenges and recommendations from the Pilot River Basin.

Pote D.H., Daniel T.C., Sharpley A.N., Moore Jr., P.A., Edwards D.R., & Nichols D.J. 1996. Relating extractable soil phosphorus to phosphorus losses in runoff. Soil Sci. Am. J. **60**, 855- 859.

Refsgaard J.C., Van Der Keur P., Nilson B., Müller- Wohlfeil D.I., & Brown J. 2006. Uncertainties in river basin data at various support scales- Example from Odense Pilot River Basin. Hydrol. Earth Syst. Sci. Discuss. **3**: (2006) 1943- 1985.

Riisgård H.U., Jensen M.H., & Rask N. 2007. Odense fjord and Kerteminde fjord/ Kertinge Nor- Chapter 16. U.Schiewer (ed.), Ecology of Baltic Coastal waters. Ecological Studies, 197.

Schwærter, R.C. & Grant, R. (2003): Undersøgelse af miljøfremmede stoffer i gylle. Danmarks Miljøundersøgelser. - Faglig rapport fra DMU 430: 62 s.

Smith J.W.N. 2005. Groundwater-surface water interaction in the hyporheic zone. Science report SC030155/SR1.

Snowdon P., Ryan P., & Raison J. 2005. Review of C:N ratios in vegetation, litter and soil under Australian native forests and plantations. National Carbon Accounting System Technical Report; **No.45**.

Stockmarr, J.(ed.), Juhler, R.K., Nyegaard, P., Larsen, C.L., Felding, G., Brüsch, W., Rasmussen, P., Christensen, B., Hansen, M. & Laier, T. 2000: Grundvandsovervågning 2000. Særudgivelse København: GEUS, 137 pp.

Styles D., & Coxon C. 2006. Laboratory drying of organic-matter rich soils: Phosphorus solubility effects, influence of soil characteristics, and consequences for environmental interpretation. Geoderma **136**: (2006) 120-135.

Takeda A., Kimura K., & Yamakasi S. 2003. Analysis of 57 elements in Japanese soils, with special reference to soil group and agricultural use. Geoderma **119**: (2004) 291-307.

Thian J.R., & Zhou P.J. 2007. Phosphorus fraction of floodplain sediments and phosphorus exchange on the sediment-water interface in the lower reaches of the Han River in China. Ecological Engineering. **30** (2007) 264-270.

Thodsen H., Hasholt B., & Kjærsgaard J.H. 2008. The influence of climate change on suspended sediment transport in Danish rivers. Hydrol. Process. **22** (2008), 764-774.

Tiller K.G. 1989: Heavy metals in soils and their environmental significance. p. 113- 142. In B.A. Stewart (ed) Advances in soil science. **Vol 9**. Spinger Verlag New York, New York.

Underwood E.J. 1971. Trace elements in human and animal nutrition. 3rd ed. Academic Press, New York.

Van Oost K., Govers G., & Desmet P. 1999. Evaluating the effects of changes in landscape structure on soil erosion by water and tillage. Landscape Ecology **15**: (2000) 577-589.

Van Der Keur P., Hansen J.R., Hansen S., & Refsgaard J.C. 2008. Uncertainties in simulation of nitrate leaching at field and catchment scale within the Odense River Basin. Vadose Zone Journal. **Vol 7,** No1 (2008) 10-21.

Van Der Paauw F. 1971. An effective water extraction method for the determination of plant-available soil phosphorus. Plant and Soil **34**: (1971) 467-481.

Vezina K., & Bonn F. 2006. Modélisation et analyse de la dynamique spatio-temporelle des relations société-érosion et pollution diffuse en milieu agricole: Etudes de cas au Viêtnam et au Québec. Interactions Nature-Société, analyse et modèles. **UMR6554 LETG**, La Baule, 2006.

Vought L., Pinay G., Fuglsang A., & Ruffinoni C. 1995. Structure and function of buffer strips from a water quality perspective in agricultural landscapes. Landscape and Urban Planning **31**: (1995) 323-331.

Watson C.J., Smith R.V., & Matthews D.I. 2007. Increase in phosphorus losses from grassland in response to Olsen-P accumulation. J. Environ. Qual. **36**: (2007) 1452-1460.

Watts C.J. 2000. The effects of organic matter on sedimentary phosphorus release in an Australian reservoir. Hydrobiologia **431**: (2000) 13-25.

William J. Mitsch, Carol L. Dorage, & John R. Wiemhoff. 1979. Ecosystem Dynamics and a Phosphorus Budget of an Alluvial Cypress Swamp in Southern Illinois. Ecological Society of America, Ecology, **Vol. 60**, No. 6 (1979) 1116-1124.

Young E.O., & Briggs R.D. 2008. Phosphorus concentrations in soil and subsurface water: A field study among cropland and riparian buffers. J. Environ. Qual. **37**: (2008) 69-78.

Zaimes G.N., & al. 2008. Total phosphorus concentrations and compaction in riparian areas under different riparian land-uses of Iowa. Agric. Ecosyst. Environ. (2008), doi 10.1016/j.agee.2008.02.008.

LISTE OF TABLE

LISTE OF FIGURES

Photos : K.HOUEIX

APPENDICES

Appendix 1. Diagram of the organisation of National Environmental Research Institute

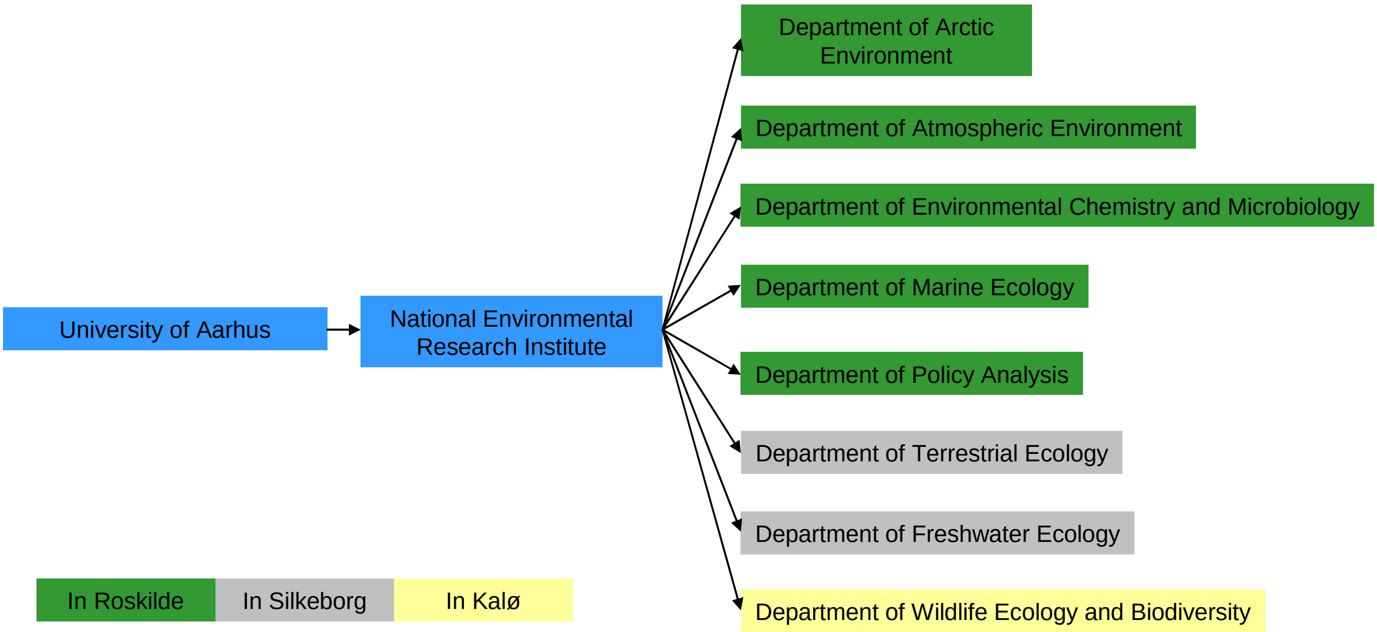
Appendix 2. Table of changes in land uses from 1880 to 2006

Appendix 3. Tables of correlation matrix Pearson in H1 and H2

Appendix 4. Complete list of all elements and their concentrations (in ppm) in the 34 buffer strips within the Odense River catchment

Appendix 1. Diagram of the organisation of National Environmental Research Institute

NERI's scientific work is organised in 8 departments located in 3 places.



Around 450 employees are working at the Institute whereof 220 research scientists.

Appendix 2. Table of changes in land uses from 1880 to 2006

	No changes		**Changes**			
Buffer strip	Soils under forest	Agricultural land	From soils under forest to agricultural land	From agricultural land to soils under forest	From pasture to farmland	From farmland to pasture
O-01 Nat-12-H	**X**					
O-02 Nat-12-H	**X**					
O-03 Nat-12-L					**X** (2000)	
O-04 Nat-12-L		**X** (pasture)				
O-05 Nat-34-H				**X** (2000)		
O-06 Nat-34-H				**X** (2000)		
O-07 Nat-34-L		**X** (pasture)				
O-08 Nat-34-L		**X** (pasture)				
O-09 Nat-5-H				**X** (2000)		
O-10 Nat-5-H				**X** (2000)		
O-11 Nat-5-L					**X** (2000)	
O-12 Nat-5-L					**X** (2000)	
O-13 Reg-12-H-Large	**X**					
O-14 Reg-12-H-Large				**X** (1950)		
O-15 Reg-12-L-Large				**X** (2006)		
O-16 Reg-12-L-Large						**X** (2000)
O-17 Reg-34-H-Large	**X**					
O-18 Reg-34-H-Large	**X**					
O-19 Reg-34-L-Large				**X** (1950)		
O-20 Reg-34-L-Large					**X** (2000)	
O-21 Reg-5-H-Large			**X** (1950)			
O-22 Reg-5-H-Large			**X** (1950)			
O-23 Reg-5-L-Large						**X** (2000)
O-24 Reg-5-L-Large					**X** (2000)	
O-25 Reg-12-H-Small		**X** (farmland)				
O-26 Reg-12-H-Small		**X** (farmland)				
O-27 Reg-12-L-Small		**X** (farmland)				
O-28 Reg-12-L-Small		**X** (farmland)				
O-29 Reg-34-H-Small		**X** (farmland)				
O-30 Reg-34-H-Small					**X** (2000)	
O-31 Reg-34-L-Small					**X** (2000)	
O-32 Reg- 34-L-Small		**X** (farmland)				
O-33 Reg-5-H-Small					**X** (2000)	
O-34 Reg-5-H-Small					**X** (2000)	
O-36 Reg-5-L-Small					**X** (2000)	

Agricultural land = farmland and grassland

X (time of change)

X (nature of agricultural land)

Appendix 3. Tables of correlation matrix Pearson in H1 and H2

Correlation matrix (Pearson (n)):

Variables	TP H1	NLu	CLu	NTt	NSt	CSt	Dist_2005	Dist_2006	WERV
TP H1	**1**	0,172	**0,344**	**0,313**	**0,403**	-0,249	-0,129	0,102	-0,079
NLu	0,172	**1**	**0,729**	0,032	0,059	-0,023	**0,714**	-0,056	**0,755**
CLu	**0,344**	**0,729**	**1**	0,123	0,139	-0,288	**0,580**	0,058	**0,440**
NTt	**0,313**	0,032	0,123	**1**	0,092	-0,252	-0,071	**0,800**	-0,029
NSt	**0,403**	0,059	0,139	0,092	**1**	-0,177	-0,058	-0,011	-0,171
CSt	-0,249	-0,023	-0,288	-0,252	-0,177	**1**	-0,090	-0,269	0,003
Dist_2005	-0,129	**0,714**	**0,580**	-0,071	-0,058	-0,090	**1**	-0,039	**0,778**
Dist_2006	0,102	-0,056	0,058	**0,800**	-0,011	-0,269	-0,039	**1**	-0,060
WERV	-0,079	**0,755**	**0,440**	-0,029	-0,171	0,003	**0,778**	-0,060	**1**

Values in bold are significantly different from 0 with a significance level alpha=0,05

Correlation matrix (Pearson (n)):

Variables	TP H2	NLu	CLu	NTt	NSt	CSt	Dist_2005	Dist_2006	WERV
TP H2	**1**	0,204	0,208	**0,357**	**0,280**	-0,225	0,130	0,076	**0,236**
NLu	0,204	**1**	**0,729**	-0,039	0,059	-0,023	**0,714**	-0,056	**0,755**
CLu	0,208	**0,729**	**1**	-0,051	0,139	-0,288	**0,580**	0,058	**0,440**
NTt	**0,357**	-0,039	-0,051	**1**	0,151	-0,201	-0,062	**0,661**	-0,075
NSt	**0,280**	0,059	0,139	0,151	**1**	-0,177	-0,058	-0,011	-0,171
CSt	-0,225	-0,023	-0,288	-0,201	-0,177	**1**	-0,090	-0,269	0,003
Dist_2005	0,130	**0,714**	**0,580**	-0,062	-0,058	-0,090	**1**	-0,039	**0,778**
Dist_2006	0,076	-0,056	0,058	**0,661**	-0,011	-0,269	-0,039	**1**	-0,060
WERV	**0,236**	**0,755**	**0,440**	-0,075	-0,171	0,003	**0,778**	-0,060	**1**

Values in bold are significantly different from 0 with a significance level alpha=0,05

Appendix 4. Complete list of all elements and their concentrations (in ppm) in the 34 buffer strips within the Odense River catchment

Sample	Al	As	Ba	Bi	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu	Fe	Ga	Gd	Ge	Hf	Ho	K	La	Li	Ln
0-01	3931,50	5,18	81,40	1,34	0,65	22,59	5,67	7,78	0,74	13,79	2,34	1,31	0,54	10720,00	7,15	4,06	1,36	0,14	0,47	572,50	7,60	2,15	1,10
0-02	4649,12	3,22	71,05	0,29	0,60	25,22	5,54	7,86	0,58	11,26	2,87	1,68	0,64	9342,11	5,85	4,72	1,08	0,16	0,57	517,98	8,59	3,10	0,10
0-03	5122,55	7,16	105,59	0,47	0,82	24,47	5,20	9,60	0,57	16,05	2,54	1,42	0,60	11818,63	7,84	4,27	0,73	0,15	0,51	570,59	8,31	2,64	0,07
0-04	5731,13	6,11	107,22	0,40	0,76	24,42	5,25	10,17	0,65	17,42	2,54	1,46	0,61	12287,74	7,82	4,09	0,63	0,12	0,51	569,81	8,38	3,98	0,03
0-05	5782,61	5,33	72,23	0,24	0,38	28,29	4,81	9,18	0,69	11,90	3,22	1,79	0,71	12500,00	6,35	5,36	0,85	0,19	0,63	542,07	10,48	2,71	0,03
0-06	3337,50	3,87	62,59	0,13	0,41	17,81	3,83	6,05	0,40	11,14	1,90	1,15	0,42	8763,89	4,80	3,23	0,79	0,12	0,38	374,31	6,17	2,00	0,01
0-07	4173,33	8,46	125,78	0,19	0,66	19,49	5,91	9,52	0,53	16,96	2,16	1,29	0,49	15772,22	8,49	3,62	1,33	0,14	0,43	600,00	7,05	1,46	0,01
0-08	4301,04	8,80	153,65	0,16	0,61	19,32	5,11	9,08	0,44	13,21	2,27	1,37	0,53	16661,46	10,71	3,86	1,21	0,12	0,47	476,82	7,18	2,42	0,01
0-09	4715,00	15,97	159,00	0,22	0,66	23,57	7,85	26,64	0,54	38,64	2,38	1,35	0,58	22577,78	10,65	4,06	2,25	0,15	0,48	728,33	8,28	1,78	0,01
0-10	2515,63	16,22	149,01	0,12	0,46	10,38	6,16	13,93	-0,05	13,66	1,18	0,66	0,28	16463,54	10,62	1,87	1,50	0,07	0,24	347,76	3,71	1,91	0,01
0-11	4694,27	16,65	173,70	0,18	0,81	19,80	7,20	25,28	0,40	27,88	2,25	1,33	0,52	23119,79	12,09	3,69	2,49	0,15	0,47	728,65	7,06	1,77	0,01
0-12	5133,72	15,26	162,33	0,21	0,76	20,27	7,32	28,70	0,46	23,30	2,25	1,32	0,52	22523,26	11,28	3,76	2,23	0,16	0,46	600,00	7,22	1,63	0,01
0-13	4580,36	2,79	54,33	0,12	0,25	24,96	5,12	6,55	0,53	7,39	2,10	1,20	0,45	10937,50	4,78	3,62	0,72	0,09	0,42	654,46	8,21	2,02	0,01
0-14	4758,85	3,00	54,64	0,13	0,26	26,31	5,31	6,35	0,38	7,22	2,24	1,26	0,49	11291,67	4,82	3,84	0,73	0,07	0,45	567,71	8,63	2,17	0,01
0-15	4085,27	3,51	67,28	0,11	0,40	16,40	3,20	5,91	0,38	7,33	1,56	0,91	0,36	10031,25	5,25	2,63	0,64	0,12	0,32	425,45	5,39	1,14	0,01
0-16	5153,65	18,23	118,18	0,15	0,59	18,86	4,82	7,78	0,39	17,91	1,67	0,98	0,40	14145,83	8,38	2,87	1,04	0,08	0,34	525,00	6,16	2,17	0,01
0-17	6432,29	6,99	127,71	0,23	0,94	38,61	8,74	15,36	0,79	19,59	3,70	2,13	0,84	19791,67	9,55	6,24	1,48	0,20	0,76	1002,60	13,68	3,29	0,03
0-18	3444,90	3,02	41,25	0,17	0,53	19,97	3,69	10,68	0,22	15,49	2,01	1,13	0,44	7591,84	3,82	3,38	0,60	0,13	0,40	661,22	7,20	1,97	0,01
0-19	4454,02	8,19	132,01	0,16	0,63	19,60	5,75	12,10	0,36	15,14	2,33	1,33	0,52	15714,29	8,99	3,80	1,22	0,16	0,47	572,77	7,17	1,38	0,01
0-20	5345,65	8,55	153,26	0,19	0,89	20,57	6,27	10,77	0,55	21,96	2,20	1,25	0,48	19625,00	10,53	3,56	1,73	0,18	0,44	891,85	7,12	2,97	0,01
0-21	2883,64	11,52	70,45	0,09	0,36	14,78	3,39	15,08	0,20	10,30	1,61	0,93	0,35	9886,36	4,89	2,57	0,73	0,12	0,32	389,50	5,20	1,60	0,00
0-22	4530,10	26,31	100,56	0,12	0,41	19,67	3,15	10,55	0,29	11,85	2,19	1,26	0,48	13586,73	7,24	3,65	0,61	0,18	0,44	813,78	7,33	3,78	0,01
0-23	4077,00	15,18	145,95	0,14	0,57	16,85	6,34	18,47	0,27	16,35	1,88	1,09	0,43	22370,00	9,77	3,03	1,82	0,13	0,37	568,50	5,98	2,51	0,01
0-24	4625,00	17,99	98,10	0,12	0,46	21,09	4,98	15,16	0,38	12,08	2,25	1,32	0,52	14008,62	7,10	3,67	0,89	0,18	0,45	726,29	7,24	1,56	0,01
0-25	5192,31	8,98	95,54	0,13	0,41	21,35	4,75	7,85	0,27	10,67	2,64	1,56	0,61	15911,54	7,02	4,39	0,88	0,17	0,53	820,00	8,05	1,99	0,01
0-26	4409,84	4,23	45,45	0,11	0,44	14,91	3,64	6,08	0,30	9,05	1,49	0,85	0,33	9610,66	3,60	2,40	0,50	0,12	0,30	843,85	5,05	0,99	0,01
0-27	5585,00	5,66	78,70	0,12	0,78	16,72	3,92	7,10	0,38	10,38	1,79	1,05	0,44	12540,00	5,88	2,97	0,53	0,17	0,37	851,00	5,75	0,96	0,00
0-28	7105,26	3,39	61,40	0,15	0,40	19,67	5,04	8,91	0,52	15,16	1,97	1,12	0,44	14706,14	5,40	3,21	0,59	0,22	0,39	1360,09	6,52	1,43	0,01
0-30	8905,00	4,59	62,35	0,17	0,36	20,08	6,37	11,27	0,69	12,31	1,77	1,00	0,39	17245,00	6,04	2,89	0,95	0,24	0,35	1601,50	6,23	1,84	0,01
0-31	7071,43	8,10	119,23	0,16	0,71	24,62	5,97	9,46	0,47	17,62	2,46	1,43	0,56	19051,02	8,49	3,94	0,98	0,21	0,50	1410,20	8,26	2,24	0,01
0-32	6723,40	10,46	112,13	0,12	0,46	26,57	5,63	8,84	0,33	11,52	2,71	1,55	0,60	20920,21	8,13	4,44	1,30	0,24	0,55	1027,66	8,80	1,67	0,01
0-33	3374,00	16,70	121,35	0,14	1,38	15,60	7,14	6,17	0,31	39,84	1,71	0,97	0,40	24105,00	7,93	2,79	2,17	0,12	0,34	1107,00	5,36	3,52	0,01
0-34	4945,45	15,00	174,36	0,13	0,38	14,68	4,38	6,94	0,13	24,16	1,94	1,06	0,42	27809,09	11,17	3,02	1,99	0,12	0,38	827,73	5,56	5,40	0,01
0-36	5004,26	17,95	168,72	0,16	0,78	18,74	5,04	15,76	0,19	16,86	2,16	1,25	0,50	26132,98	10,89	3,41	1,38	0,13	0,44	1210,11	7,06	4,94	0,01

Sample	Mg	Mn	Mo	Na	Nd	Ni	Pb	Pd	Pr	Rb	Sb	Sc	Sm	Sn	Sr	Tb	Ti	Tl	U	V	Y	Yb	Zn	Zr
0-01	1418,00	1584,00	0,36	79,35	12,32	10,24	22,98	1,58	3,17	7,02	0,14	1,38	2,34	0,00	22,69	0,45	12,18	0,29	1,77	11,64	4,93	1,27	59,10	2,61
0-02	1337,72	1117,11	0,54	38,60	14,38	9,97	25,59	1,82	3,71	5,41	0,21	2,04	2,90	0,00	17,20	0,52	10,61	0,14	1,79	11,36	5,96	1,54	56,54	2,88
0-03	1425,00	479,36	0,61	90,44	13,33	9,30	33,42	1,63	3,46	5,60	0,24	2,44	2,49	0,00	13,45	0,46	16,25	0,14	1,03	11,85	5,33	1,32	95,74	3,21
0-04	1509,43	471,70	0,41	43,21	13,15	9,66	32,43	1,68	3,45	6,67	0,14	2,24	2,50	0,00	13,36	0,47	15,30	0,12	0,96	11,27	5,33	1,36	97,22	2,66
0-05	1785,87	580,43	0,83	66,41	17,00	9,17	98,91	2,07	4,41	7,03	0,28	3,10	3,18	0,00	11,37	0,60	13,95	0,11	1,24	12,95	6,72	1,68	73,48	4,15
0-06	1310,65	727,31	0,35	42,94	10,00	7,50	14,35	1,25	2,60	4,79	0,11	1,64	1,90	0,00	22,77	0,36	13,28	0,08	0,57	8,06	4,05	1,04	49,68	3,00
0-07	1334,44	1496,67	0,60	55,07	11,33	10,11	20,11	1,55	2,89	5,47	0,20	2,46	2,25	0,00	26,64	0,40	20,87	0,10	0,79	10,13	4,79	1,19	98,44	3,69
0-08	1212,50	1213,02	0,59	44,19	11,49	9,13	20,09	1,54	2,98	4,11	0,14	3,33	2,20	0,00	19,50	0,43	18,93	0,08	0,82	9,77	5,07	1,24	67,14	3,41
0-09	2076,11	2816,11	1,23	70,44	12,56	13,41	23,30	1,59	3,34	7,31	0,20	2,03	2,29	0,00	65,11	0,46	27,78	0,15	0,98	13,87	5,22	1,26	113,06	3,45
0-10	1325,00	2025,52	1,13	82,66	5,84	11,15	19,24	0,80	1,51	2,74	0,17	1,07	1,17	0,00	92,29	0,21	14,41	0,11	0,56	9,53	2,71	0,61	69,64	1,82
0-11	1978,13	3256,25	1,09	232,14	11,40	13,87	23,58	1,53	2,94	6,55	0,21	1,91	2,17	0,00	56,20	0,41	25,19	0,12	0,77	11,97	5,09	1,25	145,99	3,81
0-12	1930,23	2713,95	0,93	62,27	11,47	13,18	22,42	1,57	2,97	6,01	0,18	2,16	2,09	0,00	49,84	0,41	23,51	0,12	0,80	11,87	5,04	1,24	119,77	3,91
0-13	1484,38	664,73	0,38	73,35	12,35	6,49	18,47	1,27	3,31	8,58	0,09	1,34	2,22	0,00	6,25	0,39	16,68	0,12	0,76	10,86	4,32	1,17	51,96	1,83
0-14	1517,19	688,02	0,45	26,49	13,03	6,45	18,76	1,24	3,50	8,82	0,12	1,42	2,35	0,00	6,29	0,41	22,60	0,13	0,79	11,85	4,54	1,17	50,06	1,71
0-15	1049,55	682,14	0,35	45,58	8,18	6,13	18,18	0,99	2,17	3,36	0,12	2,36	1,56	0,00	11,21	0,29	15,96	0,06	0,72	8,18	3,27	0,84	43,15	2,92
0-16	1413,02	1231,25	2,16	22,65	8,88	7,81	26,76	0,99	2,37	6,94	0,23	1,62	1,61	0,00	21,35	0,31	27,30	0,10	0,91	9,92	3,71	0,86	72,29	1,63
0-17	2782,81	1656,25	0,73	51,96	20,97	15,37	37,31	2,31	5,55	10,52	0,20	2,61	3,75	0,00	21,67	0,69	17,55	0,18	1,52	18,76	7,93	2,04	108,80	4,31
0-18	1511,73	622,45	0,72	173,11	10,98	17,27	27,62	1,29	2,85	5,42	0,25	1,54	1,99	0,00	16,20	0,37	20,58	0,09	0,68	9,04	4,28	1,03	48,54	3,02
0-19	1449,55	1527,68	0,71	40,72	11,42	11,74	18,91	1,48	2,95	4,51	0,17	1,79	2,15	0,00	32,24	0,42	15,73	0,09	0,79	9,46	5,19	1,23	87,90	3,75
0-20	1632,61	2283,15	0,90	185,92	11,07	12,63	23,04	1,40	2,80	7,41	0,19	1,78	2,05	0,00	35,84	0,41	22,87	0,11	1,00	11,64	4,90	1,17	101,63	3,84
0-21	1223,64	965,45	2,23	35,85	8,31	6,34	12,56	0,96	2,18	3,07	0,11	1,18	1,53	0,00	37,27	0,30	12,51	0,05	0,56	7,03	3,57	0,89	44,81	2,79
0-22	1465,82	540,31	6,44	75,20	11,42	7,78	20,51	1,36	3,00	5,14	0,19	1,70	2,16	0,00	47,68	0,40	15,47	0,07	0,93	10,93	4,70	1,20	47,07	3,98
0-23	1781,50	2842,00	1,18	23,65	9,49	9,71	17,42	1,22	2,47	4,49	0,14	1,70	1,80	0,00	42,99	0,34	20,44	0,09	0,65	10,02	4,25	1,02	90,90	3,13
0-24	1734,05	1109,05	2,23	18,16	11,67	8,67	15,34	1,31	3,02	5,35	0,12	1,49	2,22	0,00	36,27	0,42	13,19	0,08	0,68	8,63	4,84	1,19	59,27	3,93
0-25	1864,62	1070,77	0,58	31,49	13,36	10,04	17,32	1,55	3,40	4,94	0,18	1,90	2,59	0,00	21,15	0,49	9,94	0,07	0,70	10,18	5,75	1,44	56,08	4,30
0-26	1267,62	536,89	0,64	167,79	7,56	6,86	16,63	0,93	2,01	4,99	0,16	1,96	1,41	0,00	13,91	0,28	13,97	0,06	0,79	9,82	3,22	0,80	37,24	3,04
0-27	1191,00	519,00	0,33	76,70	9,18	6,53	18,08	1,06	2,39	4,39	0,13	3,86	1,67	0,00	16,31	0,34	12,96	0,07	0,69	8,47	3,94	0,96	49,65	3,35
0-28	2256,14	633,77	0,44	131,32	10,14	9,49	17,89	1,14	2,67	8,93	0,15	2,10	1,95	0,00	23,62	0,37	13,06	0,10	0,52	9,66	4,22	1,02	56,93	4,35
0-30	2791,00	1093,50	0,51	67,20	9,28	11,47	21,73	1,02	2,45	11,95	0,19	2,45	1,69	0,00	15,02	0,31	29,83	0,13	0,84	15,34	3,69	0,91	67,65	4,84
0-31	1793,37	1104,08	0,94	74,29	12,80	9,80	29,29	1,45	3,35	5,09	0,25	2,23	2,34	0,00	20,26	0,46	20,93	0,08	1,42	14,17	5,28	1,34	76,38	4,70
0-32	2218,62	1586,70	0,75	39,84	13,95	10,07	15,74	1,48	3,69	6,68	0,10	5,45	2,72	0,00	16,97	0,50	27,32	0,09	0,83	14,77	5,61	1,43	60,21	5,07
0-33	2101,00	3564,00	1,03	110,10	8,64	10,75	24,36	0,99	2,19	11,38	0,19	1,31	1,65	0,00	43,47	0,31	18,29	0,29	0,55	11,09	3,80	0,93	112,25	2,42
0-34	1641,36	3095,91	0,62	44,64	9,10	6,92	19,75	1,14	2,38	3,28	0,14	1,32	1,72	0,00	24,18	0,34	9,55	0,08	0,73	7,10	4,22	1,05	56,68	2,16
0-36	1775,00	1844,15	1,22	134,47	10,95	9,44	25,74	1,33	2,87	4,05	0,15	1,41	2,08	0,00	48,31	0,40	22,50	0,09	0,98	12,77	4,76	1,15	63,94	2,74

DETAILED TABLE OF CONTENTS