Phosphorus Leaching from Swedish Arable Organic Soils

Quantification and Mitigation Using Biochar

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Phosphorus Leaching from Swedish Arable Organic Soils. Quantification and Mitigation using Biochar

Abstract

Organic soils account for 9% or ~225,000 ha of Sweden's 2.5 million ha of agricultural land, with around half being intensively cultivated. This thesis examines the role of chemical and physical properties of arable organic soils in leaching of phosphorus (P) and whether these losses can be reduced by employing a metal-oxide coated biochar mitigation strategy. These issues were investigated by analysing two organic soils (organic 1 and organic 2) and two P-rich mineral soils (sand and loam) using laboratory and field-based methods.

In a rainfall simulation study using short soil columns from four 20-cm soil layers to 80-cm depth, the main location of P release and the concentrations of P leached from the selected organic and mineral soils were identified. The highest concentrations of P were found to be released from the 0- to 20-cm layer in both organic and mineral soils, with 70-90% in phosphate-P form. The highest losses occurred from organic 2, followed by the sand. Soil test total-P correlated well with total-P and phosphate-P in leachate from the rainfall simulation study.

A 17-month follow-up study using 90-cm long lysimeters with intact soil revealed that losses were highest from the organic soils, while the sand, known for its high P leaching, had relatively low leaching losses. The amount of total-P leached during the 17-month period decreased in the order: organic 2 (1.2 kg ha^{-1}) > organic 1 (1.0 kg ha^{-1}) > sand (0.3 kg ha^{-1}) > loam (0.2 kg ha^{-1}). Higher P losses from the organic soils were attributed to fewer sorption sites, humic matter competition with phosphate for those same sites and presence of preferential flow pathways (organic 1).

Evaluation of 'Skogens kol', a wood biochar coated with iron (Fe_3O_4; magnetite) and 'Ecoera', an agricultural residue biochar coated with magnesium ($MgO/Mg(OH)_2$; periclase/brucite) under laboratory conditions revealed a maximum sorption capacity of 3.38 and 65.4 mg P g^{-1}, respectively. Results from the 90-cm lysimeter study also showed greater reductions in P leaching using Mg-coated biochar, with phosphate concentration in leachate being reduced by up to 74% in one organic soil. Magnesium-coated biochar performance was worse in the mineral soils, probably due to greater numbers of sorption sites already being present in those soils. Efficiency of P removal in relation to Fe applied on the biochar was shown to be good in laboratory studies, but poor at field scale.

The two organic soils studied leached sufficiently high P concentrations and potential loads to contribute to eutrophication of surface waters. However, due to complex chemical and redox interactions with P, larger field-scale monitoring is required to identify whether the P losses measured in lysimeters are representative of those reaching surface drains.

Keywords: phosphorus leaching, organic soil, lysimeter, soil column, biochar, magnetite, periclase, brucite.

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Dedication

To my girls….

Well, we knocked the bastard off!
Sir Ed. Hillary

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List of publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Riddle, M., L. Bergström, F. Schmieder, H. Kirchmann, L. Condron and H. Aronsson. 2018a. Phosphorus leaching from an organic and a mineral arable soil in a rainfall simulation study. *Journal of Environmental Quality*, 47(3): 487-495.

II Riddle, M., H. Cederlund, F. Schmieder, and L. Bergström. 2018b. Magnetite-coated biochar as a soil phosphate filter: From laboratory to field lysimeter. *Geoderma* 327: 45-54.

III Riddle, M., L. Bergström, F. Schmieder, D. Lundberg, L. Condron and H. Cederlund. Impact of biochar coated with magnesium (hydr)oxide on phosphorus leaching from organic and mineral soils (submitted)

Papers I and II are reproduced with the permission of the publishers.

The contribution of Matthew Riddle to the papers included in this thesis was as follows:

I Planned the study together with the first and third co-authors. Performed all experimental work, data analysis and interpretation. Wrote the paper with frequent help from the co-authors.

II Took part in planning the study with the first and third co-authors. Performed most of the experimental work. Performed biochar data analyses and interpretation with frequent assistance from the first co-author. The XANES spectroscopy and analysis were carried out by the second co-author. The SEM-EDS and XPD were carried out and analysed by other researchers. Carried out the rest of the experimental work, data analysis and writing, with assistance from all authors.

III Planned the study together with the first and last co-authors. The XANES spectroscopy and XPD and their analyses were carried out by co-authors two and three, respectively. The SEM-EDS was carried out by another researcher. Carried out the rest of the experimental work, data analysis and interpretation. Writing was carried out with assistance from all co-authors.

Abbreviations

Al_{ox}	Oxalate-extractable aluminium
DOC	Dissolved organic carbon
DPS	Degree of phosphorus saturation
DRP	Dissolved reactive phosphorus
Fe_{ox}	Oxalate-extractable iron
ICP-OES	Inductively coupled plasma optical emission spectroscopy
P-AL	Ammonium lactate-extractable phosphorus
P_{ox}	Oxalate-extractable phosphorus
pH_{pzc}	The pH at the point of zero charge
PP	Particulate phosphorus
PVC	Polyvinyl chloride
Q_{max}	Langmuir maximum adsorption capacity
SEM-EDS	Scanning electron microscopy with energy dispersive spectroscopy
SMHI	Swedish meteorological and hydrological institute
Total-P	Total phosphorus
XANES	X-ray adsorption near edge structure spectroscopy
XPD	X-ray powder diffraction

1 Background

Until the 18th century, organic soils, typically peatlands, were of little or no use to farmers in Sweden. As the population increased, more land was required for food production and the interest in developing these organic matter-rich soils was sparked. In the 1840s, the Swedish economy was gaining ground and subsidies for draining peatlands were introduced by the Swedish government. In 1886, the Swedish Moss Culture Association was created. The main goal of this association was to spread research-based knowledge on the use of peatlands as soil conditioners and for growing crops using improved management practices, including fertiliser use (Runefelt, 2008). Drainage of peat soils was at its peak from 1870s until the 1930s. In the early 1900s the area of cultivated peatlands was around 600,000 ha (Löfroth, 1991) and it peaked at around 700,000 ha in the mid-1900s (Berglund, 2008), owing mainly to increasing knowledge of agricultural management practices and intensive fertilisation. However, many of these peat soils, mainly lower-productivity sphagnum peats, were eventually abandoned due to drainage problems and poorer productivity compared with fen peats and mineral soils, leaving around one-third of the area still in agricultural production today.

Now in the 21st century, a great deal of environmental knowledge and understanding has been gained internationally regarding issues arising from the cultivation of organic soils. These include: carbon dioxide, a well-documented greenhouse gas that is constantly emitted when organic soils are aerated (Berglund, 2011); subsidence, also resulting from aeration, which causes the soil to basically vanish (Rojstaczer and Deverel, 1995); application of fertilisers, which on these soils can cause losses of nitrogen (N); and, most relevant for this thesis, phosphorus (P) losses to drainage systems and subsequently surface waters.

In Sweden, there has been almost no recent evaluation of the amount of P leaching from the organic soils that are still in agricultural production. Investigating whether these soils pose a significant environmental threat was the main focus of this thesis.

2 Aims and Objectives

The overall aim of this thesis work was to gain a better understanding of how chemical and physical properties relate to the P leaching potential of arable organic soils and whether biochar can be used to reduce these losses.
Specific objectives were to:

- Identify the source/s of P leaching losses in an arable organic soil profile, the load potentially lost from the soil profile layers and the mechanisms behind these losses (Paper I)

  - Identifying the layers from which P can be lost and the potential load originating from these layers can help ascertain the role of the topsoil/subsoil in P leaching. Suitable mitigation measures can be used more efficiently and effectively when the source area and P form are known.

- Quantify and compare leaching from organic soils with that from intensively farmed mineral soils with known high P leaching risk (Papers I and III)

  - Quantification of concentrations and loads of P leached from organic soils at different scales and over longer periods allows for accurate determination of the potential threat to surface water quality. Utilisation of longer soil columns allows the complex P interactions within soil to be accounted for and soil processes important for accelerating P losses to be identified. Measuring P leaching from mineral soils, including known high-risk P leaching soils, under the same conditions allows for more accurate soil comparisons.

- Compare laboratory adsorption of P using metal-oxide coated and uncoated biochar (Papers II and III)

  -Initial evaluation of biochar coating in the laboratory enables assessment of potential P adsorption by the biochar, without

interference from environmental factors. It also allows adsorption potential to be compared with values from other studies.

- Evaluate effects of biochar with metal-oxide coatings on P leaching in a field lysimeter study (Papers II and III)

  - On introducing variables, e.g. *climate, soil characteristics and microbial activity, the maximum P adsorption potential of biochar may be considerably different. Using a more field-like scenario gives a better understanding of its potential in the environment in which it will be used.*

- Compare the effectiveness and efficiency of phosphate-P adsorption on biochar in laboratory and field lysimeter studies (Paper II)

  -*By understanding how well a biochar functions in terms of resources used to adsorb P, a judgement can be made on whether it is resource-efficient, which can help in future economic comparisons against other mitigation measures.*

3 Introduction

Phosphorus (P) is a vital macronutrient found in cells of all living organisms, both animals and plants. Without P, life as we know it would cease to exist. It is important in crop production for reliable and high yield returns. Manure or fertiliser P is often applied to meet crop demands, but also in excess as a P banking strategy by farmers. A mismatch between P supply and plant demand, rainfall soon after application or even natural soil processes can cause P leaching. Even relatively low concentrations in water bodies, *e.g*. 0.01 mg P L^{-1} (Daniel *et al.*, 1994), can lead to eutrophication. Eutrophication (from the Greek, meaning ‘well nourished’) can result in enhanced growth and subsequent death and decomposition of detrimental algae and aquatic weeds, followed by microbial decomposition and an associated decrease in water oxygen content. Although nitrogen (N) and carbon (C) are also required for algal growth, P is the main concern, as it is regarded as the limiting factor in fresh and brackish water systems for organisms such as blue-green algae, which can fix their own nitrogen from atmospheric nitrogen gas (Sharpley *et al.*, 1994). This has follow-on implications, including reducing drinking water quality for both humans and animals and endangering a healthy environment for aquatic species or those using it for recreational purposes, *e.g*. fishing and boating (Sharpley *et al.*, 1994).

Eutrophication-related problems are a worldwide phenomenon, with cases reported in *e.g*. Belgium (Brookes et al., 1997), Ireland (Lennox *et al.*, 1997) the USA (Sharpley *et al.*, 1994), Sweden and Finland (Rekolainen *et al.*, 1997).

In Sweden, P losses from agricultural soils contribute approximately 40% of the nation’s total anthropogenic P loads to the Baltic Sea (Brandt *et al.*, 2009). The Baltic Sea, in northern Europe, is a brackish water body receiving eutrophication-causing P from many point and diffuse sources from countries around the coastline. In order to attain good ecological status as outlined in the European Union Water Framework Directive (WFD) and meet Country Allocated Reduction Targets (CART) specified in the HELCOM declaration (HELCOM, 2013), all potential diffuse P sources to the Baltic Sea need to be identified.

3.1 Phosphorus losses from Swedish agricultural soils

Agricultural mineral soils in Sweden have been studied intensively to identify their role in contributing P to eutrophication. At a small scale, such studies have included topsoil columns with applied manure, exposed to simulated rainfall (Liu *et al.*, 2012b) and effects of catch crops on P leaching (Riddle and Bergström, 2013). At a larger scale, field lysimeters have been used (Djodjic *et al.*, 2004; Andersson *et al.*, 2013; Svanbäck *et al.*, 2013). In one lysimeter study on mineral soils, total phosphorus (total-P) losses of between 0.65 and 7.4 kg ha^{-1} were recorded over a 21-month period (Andersson *et al.*, 2013). Djodjic *et al.* (2004) reported P losses of between 0.03 and 1.09 kg ha^{-1} yr^{-1} in a lysimeter study on mineral soils. In a separate field plot experiment, Svanbäck *et al.* (2014) identified losses of on average 0.86 kg P ha^{-1} yr^{-1} from a heavy clay soil. Furthermore, a Swedish agricultural monitoring programme that has been recording drainage flows and P concentrations from 16 fields since the early 1970s has reported losses of on average 0.37 kg P ha^{-1} yr^{-1} from agricultural fields (Data Hosting Agricultural Land, 2017). Only one organic soil was monitored in that programme and, over a 19-year period, it had shown concentrations of up to 0.15 mg P L^{-1} and a mean annual load of 0.49 kg P ha^{-1}. To my knowledge, only one study involving organic topsoil P leaching concentrations and loads has been published in recent times, a rainfall simulator study by Parvage *et al.* (2015). Phosphorus concentrations of 3.4 mg L^{-1} and loads of up to 8 kg P ha^{-1} were measured after 300 mm of applied rainfall in that study, which indicates that organic soils have the potential to contribute significant concentrations and loads of P to surface waters.

3.2 Organic soils

Organic soils are classified as Histosols according to the World Reference Base (WRB) and account for between 325 and 375 million ha throughout the world (Driessen and Deckers, 2001). They are generally found in boreal, sub-arctic and low arctic regions, with most located in temperate lowland areas. A small percentage are also found in the tropics. They are internationally known as ‘peat soils’, ‘muck soils’, ‘bog soils’ and ‘organic soils’ (Driessen and Deckers, 2001). In short, to be classified as a Histosol according to the World Reference Base, soils need to have an organic layer (20% or more organic carbon in the fine earth by mass) of 10-cm thickness or more, down to ice or bedrock material.

Alternatively, if the organic material starts less than 40 cm from the soil surface and falls within 100 cm of the soil surface, to be classified as a Histosol it has to have a combined thickness of either: a) greater than 60 cm, if more than 75%

(by volume) of the material consists of moss fibres; or b) more than 40 cm in other materials (FAO, 2015).

Organic soils are quite unlike any other soil type in that they are derived primarily from organic parent material (Wilding, 1983). As a consequence, their physical, chemical and mechanical properties differ from those of mineral soils. Mineral topsoils usually have around 1.5% organic matter content, which is relatively low in comparison with organic soils, with more than 35% organic matter by weight (~20% organic carbon). These organic matter accumulations occur in an anaerobic environment that makes organic matter degradation unfavourable. Such conditions are typically caused by a high rainfall climate, high watertable, low temperatures, extreme acidity or extreme mineral deficiencies.

The anaerobic conditions produced in the underwater environment are conducive to preservation of organic matter through reduced oxygen availability (Brady and Weil, 2007). These soils are poorly drained and to be used for agriculture require installation of subsurface tile drains or open ditches, often including pumping systems to help remove excess water (Cogger and Duxbury, 1984). This is the case for most of the cultivated organic soils in Sweden.

Organic soils found in temperate climates can be classified into two main types, due to their location and formation. Soils referred to as ‘low moor peats’, ‘topogenous peats’ or ‘fen peats’ are formed in the presence of permanent groundwater in lowland areas. In Sweden, they begin with small depressions carved out during glaciation periods. Over many years, accumulation of nutrient-rich material from inflowing waters occurs in the depressions. These materials produce an environment suitable for algae, zooplankton, bacteria and diatoms, which die and sink to the bottom. Eventually the depth of the water decreases enough to allow sunlight to penetrate to the bottom of the depression, allowing growth of submerged water weeds. This biomass, combined with other organic materials, settles to the bottom. Microbial respiration increases, which generates an anoxic environment, thereby stopping any production of organic matter. At this stage other plants, *e.g.* rushes (*Scirpus* spp.) and sedges (*Carex* spp.) colonise the water’s edge. Organic matter from these plants then accumulates in the depression, slowly filling it to the surface. The organic matter is oxygen-deprived and almost all nutrients are removed by the plants, leaving a nutrient-poor substrate. Eventually larger plants colonise the surrounding area, including alder (*Alnus* spp.), late spruce (*Picea* spp.) and willow (*Salix* spp.) (Wilding, 1983). Evapotranspiration causes water removal from the organic-rich soils, leaving habitats suitable for shade-tolerant mosses, lichens and ferns. Little additional organic matter is added to the system from the trees, in comparison with the rushes and sedges. These soils stay in such a state until disturbed either naturally or via human interference.

Organic soils referred to as 'high moor peats', 'bog peats' or 'ombrotrophic peats' are typically found in upland areas. They are formed from acidic *Sphagnum* spp. moss that only obtains water from precipitation. Microbial activity is retarded due to severe acidity or organic toxins present in the soil. These nutrient-poor soils have very limited agricultural significance in most parts of the world today, and most have been abandoned for agricultural use in Sweden (Berglund, 2011).

3.3 Cultivated organic soils

Organic soils are very porous, with low bulk density of between 0.15 and 0.4 g cm^{-3} (Brady and Weil, 2007), in comparison with typical sand-textured soils (1.3-1.4 g cm^{-3}) or clay soils (1.2-1.4 g cm^{-3}) (Andersson *et al.*, 2013). This low bulk density results in an often favourable high water-holding capacity. While mineral soils can hold 20-40% of their dry weight in water, a cultivated organic soil can hold a mass of water equal to 2-3 times its dry weight. Organic soils are easily cultivated and, together with the ease of harvesting root crops, this makes them desirable for growers of *e.g.* potatoes (*Solanum tuberosum* L.) and carrots (*Daucus carota* L.). However, in their untouched state soils developed from organic matter are typically low in P in comparison with mineral soils (Cogger and Duxbury, 1984). Therefore, once drained, large quantities of manure and mineral fertilisers are typically applied. Liming is also common on these acidic soils, to increase the pH to a more agronomically optimal level. Increasing soil pH and use of an intensive cultivation regime stimulate soil micro-organisms due to increased oxygen levels (Snyder and Morace, 1997), which leads to organic matter oxidation. Together with high fertiliser applications, this can potentially release problematic concentrations of P to surface waters (Chardon and Schoumans, 2007).

Organic soils account for 9% (~225,000 ha) of Sweden's 2.5 million ha of agricultural land (Berglund and Berglund, 2008; Lundblad, 2015). This includes a mixture of arable land, pasture and wetlands. Around 60%, or 133,000 ha, of the agricultural organic soils in Sweden are currently in arable use (Lundblad, 2015). International research has identified that organic arable soils have the potential to contribute significantly to eutrophication (Hortenstine and Forbes, 1972; Reddy, 1983; Martin *et al.*, 1997; Chardon and Schoumans, 2007; Simmonds *et al.*, 2015).

3.4 Soil phosphorus

The natural P content in soil is initially related to the parent material. In mineral soils, for example, weathering of apatite is one of the most common sources of phosphate. However, in the case of organic soils, decomposed plant material can be relatively low in P, which is why cultivated organic soils tend to require heavy fertilisation rates in order to be productive.

Phosphorus applied as a mineral fertiliser or manure is initially plant-available to a high degree, *e.g.* as orthophosphoric acid in the form $H_2PO_4^-$ or HPO_4^{2-} (at pH 4.5-6.2). In this thesis the plant available/leachable P form is referred to as phosphate-P. If not taken up by plants as soluble P, it can be sorbed to aluminium (Al) or iron (Fe) (hydr)oxides, clay surfaces or to organic matter. Alternatively, it can be precipitated as secondary P minerals such as iron (Fe), aluminium (Al) or calcium (Ca) phosphates, immobilised through uptake by soil microorganisms or leached through the soil profile (Fig 1). These processes are dependent on the soil physicochemical processes of sorption-desorption, precipitation-dissolution and immobilisation-mineralisation (Bünemann *et al.*, 2012) (Fig. 1). Desorption, dissolution and mineralisation processes typically control mobilisation of P and are dependent on soil P content, general climate conditions, soil water content, soil pH, concentrations of Fe, Al oxides and hydroxides, Ca (Cui and Weng, 2013; Fink *et al.*, 2016; Gérard, 2016; Bulmer *et al.*, 2018), clay minerals (Holford, 1997) and organic matter content.

Organic matter has been found to compete with P for sorption sites, although not through direct sorption with phosphorus itself (McDowell and Condron, 2001). This has also been noted in organic-rich soils with non-crystalline or organically bound Al and Fe (Kang *et al.*, 2009). Instead, formation of metal-organic matter complexes is proposed to provide P sorption sites (McDowell and Condron, 2001). Moreover, Gerke and Hermann (1992) found that phosphate sorption in Fe-humic mixtures is up to seven-fold greater than in amorphous Fe oxide, and suggested that this may be due to the formation of complexes between the Fe-humic substances and phosphate. A reduction in P sorption in the presence of dissolved organic carbon (DOC) has also been found in the presence of a low ionic strength medium (Giesler *et al.*, 2005), again suggesting competition between P and organic matter substances.

Phosphorus release in soils and especially organic soils is possible through reductive dissolution of Fe (III) (hydr)oxides, resulting in release of Fe (II) and adsorbed P into solution P (Schoumans and Groenendijk, 2000; Shenker *et al.*, 2005; Kjaergaard *et al.*, 2012). Drained organic soils often require constant water removal via a system of installed artificial drains and pumps. Farmers may opt to turn off pumps during the non-cropping winter period to save on electricity costs. This results in a water-saturated soil, with a flush of P in drainage water when the pumps are switched on again in the following spring. Flooding of organic soils has been shown to increase P concentrations in drainage water by between 4- and 8-fold the level in continuously drained conditions (Reddy, 1983).

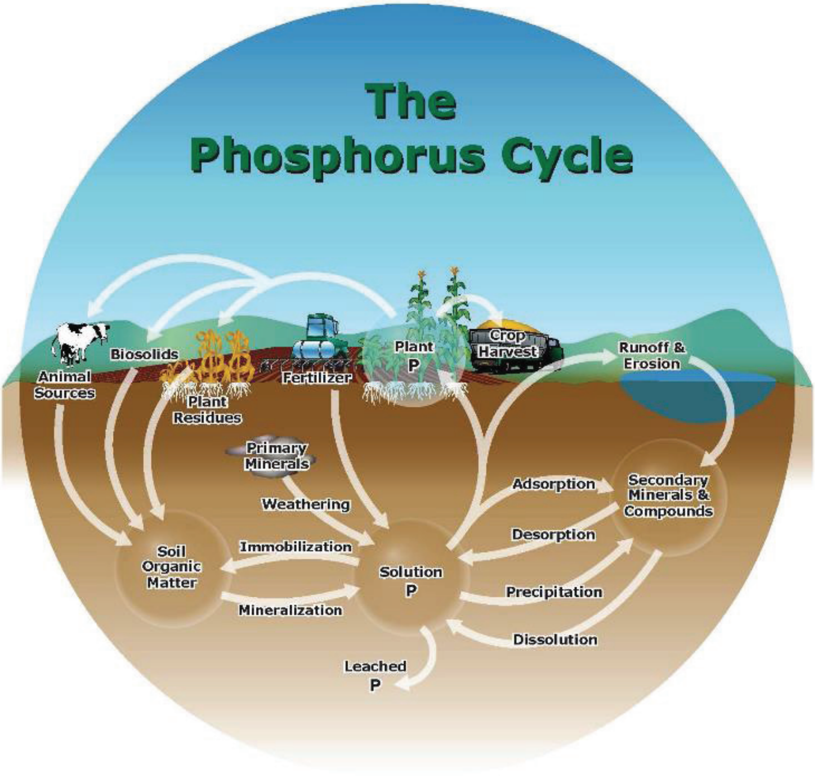


Figure 1. The phosphorus cycle (courtesy of the International Plant Nutrition Institute, IPNI)

3.5 Dynamics of phosphorus leaching in soil

A comparison of raised-bog peat soils and mineral soils by Kuntze and Scheffer (1979) revealed that P losses through leaching were 10- to 20-fold higher from the peat soils, which those authors attributed to fast movement of water-soluble phosphates through the profile. Hortenstine and Forbes (1972) concluded from studies of several organic soils in Florida that soils under natural water-saturated (*i.e.* swampy) conditions were low in orthophosphate, with values of 0.04 and 0.1 mg P L^{-1} at 30 and 90 cm depths, respectively. In comparison, 60-cm soil solution samples from newly drained swamps showed 10-fold more orthophosphate than the natural conditions. Hortenstine and Forbes (1972) also found that losses of P from cultivated organic soils over a 15-year period were highest from 30-cm deep soil solution samples, and considerably lower from 60- and 110-cm samples. However, leachate from 60-cm samples that had been fertilised at twice the normal rate was found to have a noticeably higher P concentration (Hortenstine & Forbes, 1972). In another indoor study using 40-cm lysimeters, Larsen *et al.* (1958) found that labelled P moved 4 cm down the profile of 40 cm indoor mineral soil lysimeters after application of 40 cm of water, while it moved 33 cm down the profile of two different organic soils. This was related to the amount of sesquioxides (*e.g.* Al_2O_3, Fe_2O_3) present in the soils, with considerably less being found in the peat soils, suggesting greater potential losses of P from organic soils. Cogger and Duxbury (1984) compared annual P drainage losses from eight different organic soils and found that they ranged from 1 to 30 kg ha^{-1} yr^{-1}. Several other authors have also found that cultivated organic soils contribute to eutrophication of surface and subsurface waters (Sims *et al.*, 1998), *e.g.* in the case of the Florida Everglades (Porter and Sanchez, 1992) and Lake Ontario (Longabucco and Rafferty, 1989).

Phosphorus flow pathways are also crucial in determining P losses from a soil. One recognised and well-researched pathway is leaching of P through the soil profile. Leaching events occur when mobile P in the soil solution is relocated by water moving down past the root zone, rendering the P unusable by plants (Downie, 2011). Once past this zone, nutrients are free to be leached out of the soil system completely and subsequently into surface water bodies, often via artificial sub-surface drains. This leaching process can be affected by the presence or absence of preferential flow pathways, commonly caused by plant roots, worm channels and soil fissures, which often occur in clay-textured soils (Jarvis, 2007).

Critical soil moisture content was used by Hewelke *et al.* (2016) to predict preferential flow in peat and degraded peat (muck) soils. The degradation of peat improves its wettability and, conversely, the undegraded peat is much more hydrophobic. Hewelke *et al.* (2016) concluded that extended periods of dry weather followed by heavy rain are conducive to preferential flow of water in these soils. A potassium bromide tracer experiment carried out on a peat soil in Somerset, UK, provided indications that preferential flow was occurring (Baird and Gaffney, 2000). In organic soils, preferential flow can occur when the soil dries, resulting in hydrophobicity and shrinkage cracks (Schwärzel *et al.*, 2002). Faster transport by-passing the soil matrix (Bergström and Shirmohammadi, 1999; Edwards *et al.*, 1992) also reduces contact with potential P sorption sites (Heckrath *et al.*, 1995; Simard *et al.*, 2000), resulting in increased leaching of P.

Organic soils typically have a low anion sorption capacity due to a lower abundance of mineral material containing P-sorbing metal oxides (Zak *et al.*, 2004). This sorption capacity is potentially decreased by the presence of organic anions, produced during the mineralisation of added organic matter (Casson *et al.*, 2006), which may compete with phosphate-P for sorption sites (Gu *et al.*, 1994; Hinsinger, 2001). This occurs due to organic acids, typically carboxyl and hydroxyl functional groups of humic and fulvic acids, that form very stable complexes with many metal cations or hydroxy metal cations, with the complexation strength declining in the order: $Fe^{3+} > Al^{3+} > Pb^{2+} > Ca^{2+} > Mn^{2+} > Mg^{2+}$ (Gu *et al.*, 1994).

Cultivated organic soils have been recognised as a potential environmental problem due to their release of carbon dioxide (CO_2) from organic matter oxidation and P release after fertilisation over many years. However, in some cases, organic soils have now been reverted back to their natural flooded state (Snyder *et al.*, 1999). The process whereby P is released is generally understood to be due to reductive dissolution of Fe bound to P. Oxidation-reduction reactions in soils are mainly controlled by microbial activity, where during the respiration process, organoheterotrophic organisms use organic substances as both carbon sources and electron donors (Craft, 2001). The preferred electron acceptor is oxygen, but once it is consumed other electron acceptors can be used: NO_3^-, MnO_2, $Fe(OH)_3$, SO_4^{2-} and CO_2, in that order (Borch *et al.*, 2010). As a consequence, under anoxic conditions Fe(III) is reduced by microorganisms to Fe(II), which is more mobile and less likely to adsorb phosphate. Kjaergaard *et al.* (2012) found that anoxic conditions increased total-P release from a peat soil and that the rate of release increased substantially more with increased water flow rate. Meissner *et al.* (2008) found that the P concentration doubled, from 0.33 to 0.72 mg P L^{-1}, after one month of an incubation/water saturation experiment using fen peat soils. In a similar study using 128-cm long soil columns in a 200-day incubation experiment, Meissner *et al.* (2008) also found that soluble reactive-P losses increased from 0.23 to 0.51 mg L^{-1} under different temperature treatments of 6 and 20 °C, respectively. During this time, those authors noted the P increase started concurrently with the reduction in redox potential and the increase in Fe(II) concentration in solution.

3.6 Predicting phosphorus leaching from soil

Soil P tests are generally used as indicators of plant-available P, which is essential information for targeting optimum crop yields. Depending on the country of residence, different soil analysis methods are used to estimate plant-available P. The calcium-acetate-lactate (CAL) extractant (Schüller, 1969) is used in routine soil testing in Austria and Germany, while Mehlich 3 (Mehlich, 1984) is used in the Czech Republic and in most of Canada and the USA. Denmark, some states in the USA, the UK and New Zealand use the Olsen extract test (Olsen *et al*., 1954). In Sweden, it is common to use the ammonium acetate-lactate test (P-AL), which is more suited to acidic soils, with an extraction pH of 3.75. Six P-AL classes are defined in Sweden; I: <21, II: 21-40, III: 41-80, IVa: 80-120, IVb: 120-160, V: >160 mg kg^{-1}, with III being an agronomic optimum and IV and V being at risk of P losses.

In an attempt to predict the ability of a soil to leach P, soil P tests have been correlated to leachate losses. However, relationships between soil test P values and leachate P concentrations or losses are often poor, since test values do not account for information on flow pathways through the soil and sorption characteristics (Börling *et al.*, 2004; Djodjic *et al.*, 2004). The saturation of potential P binding sites in a soil is calculated as the degree of P saturation (DPS). Van der Zee and van Riemsdijk (1988) used oxalate-extractable Fe (Fe_{ox}), Al (Al_{ox}), and P (P_{ox}) from acid sandy soils to identify the proportion of binding sites occupied by P, which indicates potential soil P desorbability (Beauchemin *et al.*, 1998). This approach has also been tested in organic soils, with some success (Litaor *et al.*, 2003). A soil with low DPS is usually less likely to suffer large P leaching losses than a soil with high DPS. In more acidic soils, the interaction of P with available sorption sites, *e.g*. Al and Fe (hydr)oxides, is important. In neutral and alkaline soils, reactions with Ca are more common (Breeuwsma and Silva, 1992). In non-calcareous sandy soils, several variants of the P saturation capacity index have been suggested to determine P leaching potential (van der Zee and van Riemsdijk, 1988; Schoumans and Chardon, 2015). When a DPS value is calculated, it is then compared against a DPS threshold value above which leaching is substantially (and non-linearly) increased. This threshold value can be determined based on sorption/desorption experiments. In a table complied by Beauchemin and Simard (1999) of threshold values published between 1988 to 1998, several studies utilising the same DPS calculation with acidic soils report values between 25 and 30 %.

3.7 Biochar as a strategy to mitigate phosphorus losses

If cultivated organic soils have the potential to leach large amounts of P to surface waters, causing eutrophication, mitigation measures to reduce such losses are necessary. To be effective, a mitigation strategy must be matched to the specific characteristics of the soil and form of P released.

Most current mitigation measures employed in agricultural fields are based on removing P after it has left the soil system, through *e.g.* two-stage ditches reducing drainage water velocity and therefore increasing sediment settling time (Mahl *et al.*, 2015); constructed wetlands which function in a similar manner (Kynkaanniemi *et al.*, 2013); buffer strips which reduce overland sediment flow (Osborne and Kovacic, 1993) *etc*. Structural liming using calcium oxide (CaO) has been indicated to be effective in reducing particulate phosphorus (PP) losses from clay fields by 44%, by reducing clay dispersion (Svanbäck *et al.*, 2014). Liming can also reduce surface water ponding, by improving water infiltration into the soil matrix, and therefore reduce macropore flow of water and solutes (Jarvis, 2007). However, incorporation of lime into the topsoil can also decrease phosphate-P availability to plants by causing available P to precipitate with, or be co-sorbed to calcium (Murphy and Stevens, 2010).

Once it has entered the soil, due to over-application of mineral or manure fertiliser, excess P not utilised by plants is at the mercy of the soil system as to whether it is leached out or bound within the soil. In Sweden, the former generally entails leachate passing via artificial drainage systems into surface waters. By intercepting phosphate in leachate from fields through use of a filter placed in between the P source and drainage system, these losses can potentially be reduced. Therefore, one suggestion is to place a layer of adsorptive material (*e.g.* biochar) below the topsoil in order to intercept P in leachate before it is lost to the drainage system.

When the feedstock used in biochar production is wood, the biochar produced is in fact barbeque charcoal. However, any organic feedstock material can be used to make biochar, *e.g.* wheat straw, maize leaves or manure. When pyrolysed, *i.e.* incompletely combusted in the absence of oxygen (Chen *et al.*, 2008), this organic material becomes biochar.

The soil-related benefits of biochar were discovered thousands of years ago in the Amazon by farmers creating soils known today as *terra preta*, meaning 'black soil' (Glaser *et al.*, 2014). A recent revival has re-discovered these benefits. Addition of biochar to poor agricultural soils, *e.g.* Oxisols, has been found to improve cation exchange capacity (CEC), nutrient retention and availability (Liang *et al.*, 2006). Addition of biochar also increases soil water-holding capacity (Karhu *et al.*, 2011) due to its large amount of microscopic pores (Lehmann and Joseph, 2012) and large surface area. Incorporating biochar into the soil can also act as a mitigation method against climate change, through sequestering carbon (Liu *et al.*, 2011), thereby offsetting the effects of anthropogenic CO_2 losses. As biochar is recalcitrant, it is less likely to be affected by weathering or microbial decomposition than a raw feedstock, and is therefore more stable in soil.

The use of biochar as an adsorbent is a relatively new idea, with the effectiveness often linked to the feedstock and production temperature (Kizito *et al.*, 2017). It has been used in mostly aqueous applications for removal of pesticides (Cederlund *et al.*, 2016), organic compounds like polychlorinated biphenyls (PCBs) (Wang *et al.*, 2013), heavy metals *e.g.* arsenic (Wang *et al.*, 2015), cadmium and copper (Regmi *et al.*, 2012) and also P (Yao *et al.*, 2011a; Hollister *et al.*, 2013). The majority of this research has been undertaken in a laboratory environment.

Phosphorus removal results for biochar in the literature are varied. Laird *et al.* (2010) found that adding biochar to soil columns amended with swine manure reduced dissolved P in leachate by 69% and noted a correlation between increasing rates of biochar and decreasing rates of P leaching. Pecan shell biochar added to a loamy soil reduced the concentration of phosphate-P in leachate by up to 40% (Novak *et al.*, 2009). Others have reported results to the contrary, with losses of P from biochar. For example, Parvage *et al.* (2013) found that water-soluble P concentrations increased by 11-253% after application of agricultural residue biochar to 11 Swedish soils. In a column experiment, Yao *et al.* (2012) found that Brazilian pepperwood and peanut hull pyrolysed at 600 °C caused a 39% increase in leachate phosphate, compared with the control. This increase in P release is often linked to the feedstock itself containing relatively high concentrations of P, with one review paper listing biochar P concentrations ranging between 0.06 and 3.21 % (Xie *et al.*, 2015).

One reason for poor adsorptive performance of many biochars is the dominance of negatively charged surfaces. Trying to combine biochar with a negatively charged anion such as phosphate can be likened to two magnets repelling one other, which results in poor electrostatic attraction. One possibility to improve the sorption capacity is to coat the biochar with a positively charged mineral oxide, *e.g.* Fe or Mg oxide, which increases the initial electrostatic attraction and introduces surfaces to which the phosphate ions can adsorb. Anaerobically digested sugarbeet tailings have been found to be very effective in removing P from aqueous solutions, due to large concentrations of naturally occurring magnesium oxide (MgO) on the biochar surface (Yao *et al.*, 2011b). Follow-up research by Yao *et al*. (2011a, 2011b, 2012, 2013) using biochar with an increased magnesium concentration resulted in increased adsorption potential of the biochar compared with regular biochar. This was due to the magnesium oxide present on the biochar surface, identified as the main adsorption sites for the aqueous P. Chen et al. (2011) discovered that magnetised biochar (using Fe) was very successful in removing phosphate from water, more so than untreated biochars. In contrast, Takaya *et al.* (2016) found that Fe-coated biochar was inferior to Mg-coated biochar, with less than 5% of phosphate removed from solution. Moreover, the Mg-coated biochar removed up to 70% of phosphate from an aqueous solution, compared with 3.6% removal using uncoated biochar (Takaya *et al.*, 2016).

When used in a controlled laboratory environment, coated biochar can be a very effective adsorbent, but when used in the field there are other factors to be considered. Climate, plant interaction, soil physicochemical properties and soil microorganisms can all potentially affect the P removal efficiency of biochar. The important step of verification of performance under field conditions is often overlooked when evaluating biochar adsorbents and was therefore an important component of this thesis.

4 Soil description and study methods

4.1 Soils used in rainfall simulation and lysimeter studies

Two organic soils (organic 1 and organic 2) were used in the studies included in this thesis. These soils were chosen based originally on the depth to the underlying clay (70-90 cm), agricultural use and pH. However, both soils ended up having similar pH levels and had medium to high soil P values, but differed in selected soil properties, as shown in Table 1. Both organic soils originate from the Örebro region of central Sweden (Fig. 2) and had medium to high soil P values. Organic 1 was drained in the 1980s and organic 2 in the 1940s. Both soils were identified as being fen peats, containing sedges, trees from the *Alnus* genus as well as reeds from the *Phragmites* genus. For comparison, two mineral soils (a sand and a loam) were taken at around 300 m from one another on the same farm outside Kristianstad (Fig. 2). These mineral soils had different textures, but had received the same 45 t ha^{-1} yr^{-1} amount of cow manure over the previous 40 years, which led to high soil P contents. The sand soil was collected from a site that is part of a long-term field drainage water monitoring programme and is reported to return mean annual losses of 1.5 kg P ha^{-1} yr^{-1} (1979-2010) and maximum loads of up to 2.8 kg P ha^{-1} yr^{-1} (Data Hosting Agricultural Land, 2017).

Table 1. *Selected physio-chemical properties of the four soils.*

Soil	Depth	pH[a]	Total-C	Bulk Density	Decomp.[b]	Fe_{ox}[c]	Al_{ox}[c]	Tot-Ca	Tot-Mg	Tot-P	P-AL[d]	Olsen-P	P_{ox}[c]	DPS[e]
	cm		%	g cm^3	H1-H10	mg kg^{-1}								%
Organic 1	0-20	5.4	44.9	0.25	Earthyfied	6587.2	1924.1	34539.3	891.8	970.5	74.5	21.0	437.1	15
	20-40	5.7	36.6	0.32	Undefined	5480.4	9415.5	28650.8	1010.7	975.7	33.8	10.0	790.5	11.3
	40-60	6.0	25.5	0.34	H3-4	4892.3	10037.1	18170.1	3880.9	788.3	18.7	34.0	432.4	6
	60-80	5.1	34.1	0.17	H4-5	7171.4	6202.7	16515.6	2599.8	454.7	4.9	<4	160.1	2.9
Organic 2	0-20	5.1	42.9	0.30	Earthyfied	3635.9	1854.4	21144.8	939.4	1285.4	152.3	61.0	577.5	27.9
	20-40	5.1	30.8	0.20	H4	2707.6	1958.6	16206.5	2526.8	1199.8	279.1	110.0	393.6	21.2
	40-60	5.8	30.3	0.22	H2-3	6448.7	3243.0	19126.5	1622.0	498.4	17.5	5.8	273.7	7.5
	60-80	5.5	36.5	0.42	Mineral	5719.2	2645.0	21737.2	3521.3	587.8	75.6	25.0	321.2	7.5
Sand	0-20	7.3	2.0	1.20		1787.9	1077.4	4982.6	798.3	1194.0	609.1	120.0	1026.7	92.1
	20-40	7.5	1.0	1.20		1231.0	641.9	3776.4	600.2	881.5	439.4	80.0	652.8	77.3
	40-60	7.7	0.2	1.20		2168.3	267.8	2150.4	536.3	530.4	200.8	12.5	199.8	26.6
	60-80	7.9	0.1	1.30		528.7	142.5	2055.9	525.2	472.7	248.4	8.1	95.1	49.3
Loam	0-20	7.3	2.3	1.45		2766.1	1268.3	7521.2	3493.1	590.7	111.9	30.0	436.6	21.6
	20-40	7.5	1.3	1.45		2779.4	1202.3	7009.6	3595.3	557.3	99.0	26.5	403.3	20.3
	40-60	8.0	0.1	1.5		1414.9	1231.1	9423.5	5560.4	473.0	68.9	4.0	365.6	27.8
	60-80	8.2	0.1	1.5		1167.1	956.6	9437.9	4885.1	636.8	138.0	4.0	517.3	52.8

[a] Extracted in water

[b] Von Post method of determining degree of humification. Earthyfied refers to anthropogenic induced secondary soil development. Undefined indicates two horizons

[c] Oxalate extractable

[d] Extractable in ammonium acetate lactate (AL) solution

[e] Degree of phosphorus saturation calculated as $P_{ox}/[0.5(Fe_{ox} + Al_{ox})] \times 100$, where P_{ox}, Fe_{ox} and Al_{ox} are oxalate-extractable P Fe, and Al, respectively.

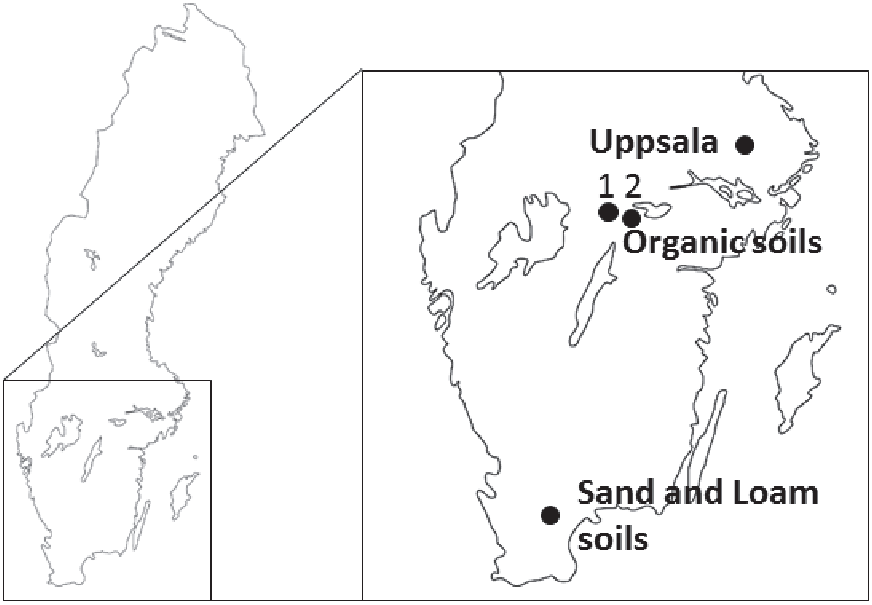


Figure 2. Map of southern Sweden showing the location of the four soils used in Papers I-III.

4.2 Soil column sampling and rainfall simulations

Intact soil columns (each 20-cm deep) were taken from four layers (0- to 20, 20- to 40, 40- to 60 and 60- to 80-cm) at all four sites in November 2014. The columns were collected in 25-cm long polyvinyl chloride (PVC) sewer pipes with 20-cm external diameter (18.8-cm inner diameter). These pipes were placed at the required depth and pressed down 20 cm using a hydraulic press mounted on the rear of a tractor (Fig. 3). Three replicates were collected from each depth at all sites.

Figure 3. The rear mounted hydraulic soil column collection device in action. Photos: Mats Larsbo

A rain simulator was used to impose a ‘worst case’ high P loss scenario. In the simulator (Fig. 4), rainfall amounts were applied at a high intensity of 50 mm over 10 hours on four application occasions. In total, this supplied 200 mm at a rate of 5 mm h^{-1} over 10 to 14 days. On exiting the simulator, the artificial rainwater contained 278 mg Ca L^{-1}, 6.85 mg Fe L^{-1}, <400 mg potassium (K) L^{-1}, <90 mg Mg L^{-1}, 352 mg sodium (Na) L^{-1} and <1 mg total-P L^{-1}, had pH 5.8 and had an electrical conductivity of 0.008 mS m^{-1} (0.1047 mmol L^{-1}). Leachate was sampled after each of the four simulated rainfall occasions and analysed according to the ammonium molybdate spectrometric method (European Committee for Standardization, 1996) for total-P, total dissolved P (TDP) and dissolved reactive P (DRP), also known as phosphate-P. Total-P was analysed on unfiltered samples and TDP and phosphate-P on filtered samples (0.2 µm pore size; Schleicher and Schüll GmbH). The difference between total-P and TDP was defined as particulate-P (PP), while total-P minus phosphate-P and PP was classified as dissolved unreactive-P or residual-P. The residual-P fraction was assumed to represent organic-P.

Figure 4. The rainfall simulator used in Paper I.

4.3 Lysimeters

Intact 80-cm soil columns from the organic 1 and organic 2 soils were used in Papers II and III to determine P leaching under field conditions from these organic soils and to determine the effectiveness of different biochars. In addition, 80-cm columns from the mineral soils (sand and loam) were included in Paper III, to compare P leaching concentrations and loads with those from the organic soils.

All intact lysimeters were collected in October 2013 (organic soils) and November 2014 (mineral soils) in 90-cm long PVC pipes (29.5 cm internal diameter) using the method described by Persson and Bergström (1991), whereby a tractor-mounted drill was used to slowly push the pipes into the soil and then extract the lysimeters (Fig. 5B and C).

Preparation of each lysimeter included inverting the lysimeter and placing a stainless steel mesh (0.5 mm) under the soil and a 4-cm layer of washed gravel (2- to 5-mm), followed by another stainless steel mesh (0.5 mm) and finally a perforated fibreglass lid. The lysimeters were then placed in the upright position and the top was prepared by removing the upper 27 cm of soil, discarding the next 3 cm (27 to 30 cm depth) and replacing it with either 3 cm of iron chloride-coated (671.5 g), or magnesium chloride-coated (679 g) biochar, or alternatively with 3 cm of 2-5 mm washed gravel (control) (Fig 5D-G). The soil was then replaced at a bulk density similar to that before removal. As the lysimeters were shorter than the standard type used in the lysimeter station (118 cm), a 28-cm pipe extension was glued onto the lysimeter bottom (Fig. 5A).

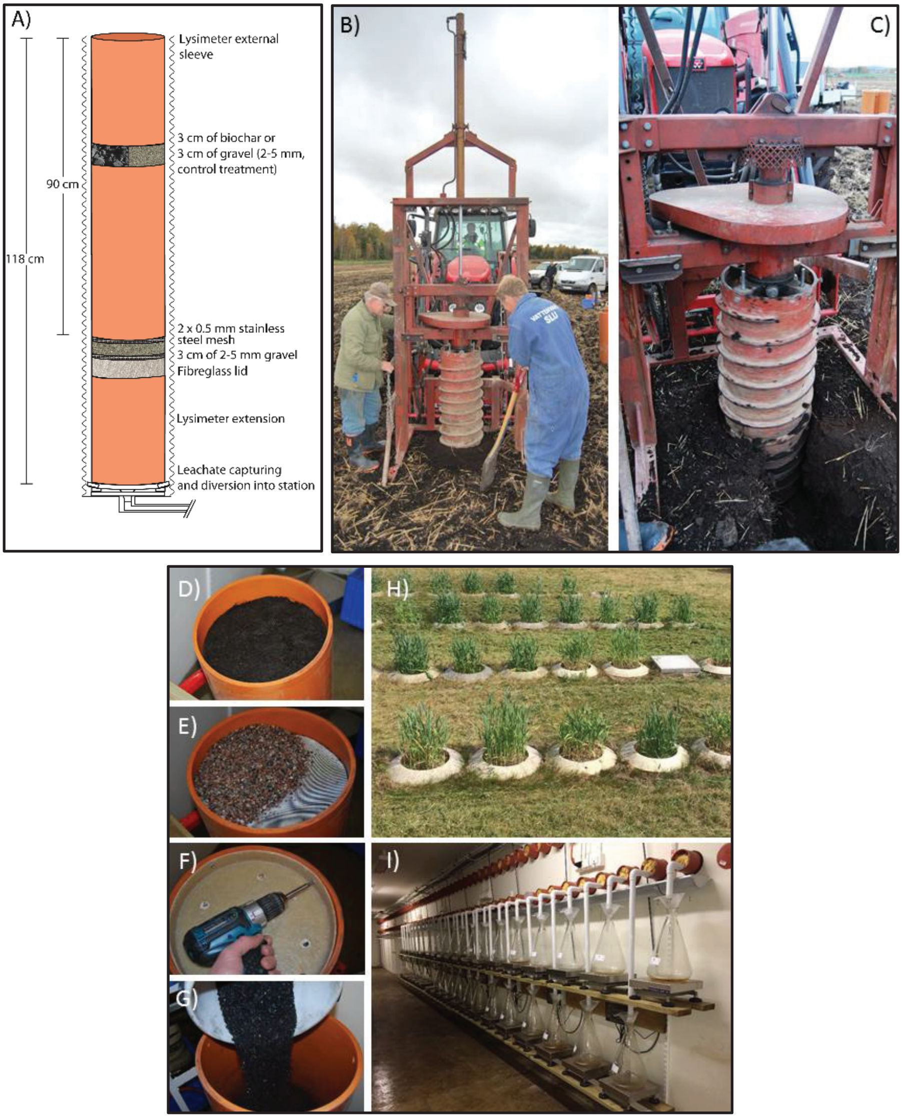


Figure 5. Lysimeter design with preparation steps. A) Lysimeter design; B and C), lysimeter excavation; D), bottom of lysimeter with gyttja clay removed; E), addition of stainless steel mesh and 2-5 mm washed gravel; F), attaching the fiberglass lid; G), addition of biochar to the top of a lysimeter; H), lysimeters installed with wheat crop; I) leachate collection bottles in the lysimeter station.

The Fe-coated biochar layer was installed in March 2014 and was followed by three years of leachate sampling (Paper II), whereas the Mg-coated biochar was installed in September 2015 and underwent only 17-months of leachate sampling (Paper III). Each lysimeter was connected to an individual balance (Fig 5I), which continuously weighed the leachate collection bottle and any incoming leachate. This was connected to a datalogger which logged drainage data every 30 seconds. Leachate was sampled when ~700 mL of leachate had collected in the bottles. This resulted in nine, nine and eight sampling occasions per year, for the three consecutive years between March 2014 and March 2017 (Paper II) and 14 sampling occasions between October 2015 and March 2017 (Paper III). Samples were analysed for P as in the rain simulator experiment.

4.4 Biochar laboratory studies

Due to lack of suitable equipment for producing biochar in the quantities required, the main biochar products used in this thesis were two off-the-shelf products from commercial producers, and thus coated post-pyrolysis. 'Skogens kol' charcoal was chosen as it had been used in several previous studies and therefore an understanding existed of its general characteristics and performance. Furthermore, as it is produced from wood, the P content was relatively low in comparison with that in other feedstocks (Table 2), which was necessary for the purposes of the adsorption/leaching studies. The Skogens kol biochar came from a commercial charcoal production facility in southern Sweden and had a size fraction of < 4 mm. Selected results of biochar analyses are presented in Table 2. The biochar was produced by slow pyrolysis at temperatures between 380-430 °C. The biochar was then coated with $FeCl_2$ with an iron (III):iron (II) ratio of 2:1 to allow surface magnetite (Fe_3O_4) formation.

The second variety of biochar chosen was 'Ecoera', a pelleted biochar produced from agricultural residues at 600 °C at a commercial facility in southern Sweden. This biochar was crushed and sieved to < 4 mm and then coated with Mg by preparation of a $MgCl_2$ solution and further heat-treatment at 600 °C in a muffle furnace.

Detailed descriptions of the analytical methods used can be found in Papers II and III. However, a brief description is presented here:

- Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) were used to take images of the biochar, in order to identify any potential crystalline structures and to analyse the elemental composition on the surface.
- X-ray powder diffraction (XRD) was also used to identify crystalline structures on the biochar surfaces, which helped with characterisation of the biochar coatings.
- X-ray tomography (XRT) (Paper II only) was used to examine the extent of Fe penetration through the biochar, which helped in determining the effectiveness of the coating procedure.
- X-ray adsorption near edge structure (XANES) spectroscopy was used to determine whether phosphate in solution had adsorbed to the biochar itself, to the coating of Fe (Paper II) or to MgO (periclase) or $Mg(OH)_2$ (brucite) (Paper III). Both uncoated and coated samples were analysed.
- The maximum P adsorption capacity of the biochar was determined through batch adsorption studies by shaking biochar samples in a buffer solution with phosphate concentrations of between 0 and 750 mg P L^{-1} (n=5 replicates). Analysis for phosphate-P in supernatants was carried out using Flow Injection Analysis (FIA) (Fiastar 5000, AN 5246, FOSS, Hilleroed, Denmark), according to the Foss Tecator AN 5240 ammonium molybdate method. This allowed the amount of phosphate-P adsorbed to biochar to be calculated. A Langmuir isotherm was fitted to the measured data to calculate the maximum adsorption capacity of the biochar:

  $$q_e = \frac{K \times Q_{max} \times C_e}{1 + C_e} \qquad [1]$$

  where q_e is the adsorbed amount (mg P g^{-1}), C_e is the equilibrium concentration (mg P L^{-1}), K is a constant related to the binding energy (L mg^{-1}) and Q_{max} is the Langmuir maximum adsorption capacity (mg P g^{-1}).

- A pre-study was conducted to determine whether the biochar feedstock or metal coating is most important for phosphate adsorption. The three biochars tested were: Betfor, a sugarbeet by-product used as a stock feed, pyrolysed at 600 °C; SWP 700, a softwood biochar pyrolysed at 700 °C; and Ecoera as introduced earlier. The three treatments included: no coating and 0.25 and 1 g $MgCl_2$ g^{-1} biochar. Samples of 0.5 g of each biochar (n=5) were shaken in a single 500 mg P L^{-1} solution for 24 hours and analysed as in the maximum P adsorption capacity study presented above.
- A laboratory column study was carried out to determine the effectiveness of Fe-coated biochar under high water flow conditions. Six glass columns (37 cm long by 4.2 cm inner diameter) were filled with sand up to 6 cm from the column rim and then 3 cm Fe-coated biochar was applied, corresponding to 83.7 t ha^{-1}. The remainder was then filled with sand (Fig. 6, left). Another six columns were filled with sand only (Fig. 6, right). Each column was filled from the bottom with deionised water 12 hours previously and then drained prior to the start of the experiment, resulting in approximate field capacity conditions. A solution of one of three phosphate ($NH_4H_2PO_4$) concentrations was applied to each column, corresponding to 22, 285 or 570 kg P ha^{-1}. Each concentration was applied to four columns, two with and two without biochar. Deionised was then applied onto individual columns at 14.4 mm h^{-1} for 10 hours, using a peristaltic pump. Samples were collected every 40 minutes and analysed for phosphate following the same method as in the batch adsorption study.

Cumulate phosphate-P loads were then plotted against cumulative drainage for each phosphate concentration and these were fitted to the Gompertz equation:

$$y = ae^{-e^{-\left(\frac{x-x_0}{b}\right)}} \quad [2]$$

where y is the cumulative amount leached (mg P) after x mm of cumulative drainage, a is the cumulative amount (mg P) leached at x_{max} (*i.e.* at the theoretical maximum drainage), x_0 is the inflection point of the curve and b is a parameter that describes the slope of the curve. This allowed comparison of leaching at equivalent drainage volumes.

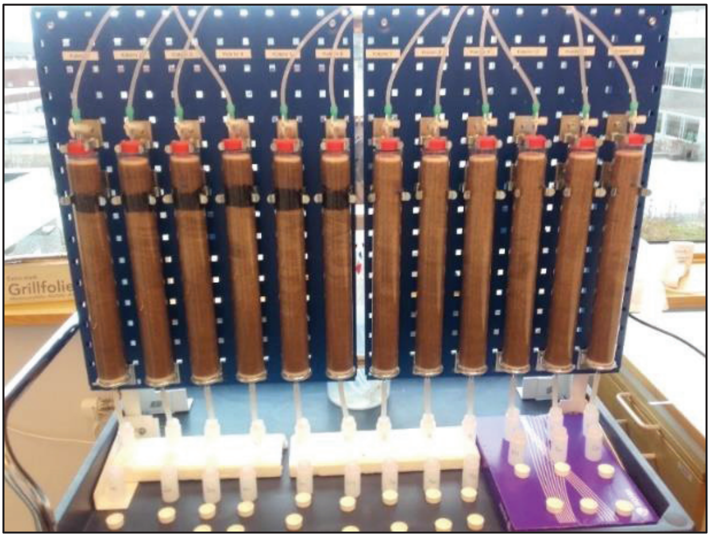


Figure 6. The column leaching apparatus. Photo: Robert Almqvist.

Table 2. *Results of analysis of both biochar types, with and without coating, used in Papers II and III*

Analysis		Uncoated Ecoera [b]	Mg-coated [c]	Uncoated Skogens kol [d]	Fe-coated [e]
Specific surface (BET)	m^2 g^{-1}	80.2	66.1	161.3	99.9
True density	g cm^3	1.7	1.9	1.5	2.0
pH ($CaCl_2$)		8.5	9.7	7.9	8.9
Ash content (550 °C)	% (w/w)	28.3	28.4	9.8	45
Total inorganic carbon	% (w/w)	0.9	0.5	0.1	0.3
Carbon	% (w/w)	59.1	60	83.5	48.4
Hydrogen	% (w/w)	1.6	1.2	2.7	1.5
Total nitrogen	% (w/w)	2.3	1.5	0.6	0.5
Total sulphur	% (w/w)	0.2	0.2	0.00	<0.03
Oxygen	% (w/w)	0.8	9.7	4.1	5.1
H/C ratio		0.3	0.3	0.03	0.03
O/C ratio		0.2	0.1	0.05	0.1
C/N ratio		26.2	40.3	146.5	103.0
H/O ratio		0.1	0.1	0.7	0.30
Total phosphorus [a]	mg kg^{-1}	8809	8798	429.1	170.0
Total calcium [a]	mg kg^{-1}	34978	5522	3468.7	2998.0
Total magnesium [a]	mg kg^{-1}	5421	77931	558.7	470.0
Total iron [a]	mg kg^{-1}	909	8513	1076.1	15 3130
Total potassium [a]	mg kg^{-1}	23988	3174	1595.3	372.2
Total sodium [a]	mg kg^{-1}	256	240	103.5	11 088.0
Total aluminum [a]	mg kg^{-1}	656	3872	398.0	401.8

[a] Biochar sample extracted with HNO_3 and analysed in an accredited laboratory in Uppsala, Sweden. The remainder at a specialist biochar laboratory, Eurofins, Halsbrücke, Germany.

[b] ’Ecoera’ agricultural residue biochar.

[c] Periclase (MgO)-coated ‘Ecoera’ biochar, *i.e.* not hydrated to $Mg(OH)_2$.

[d] ‘Skogens kol’ ~80% hardwood, mainly birchwood (*Betula* sp.) and ~20% Norway spruce (*Picea abies*).

[e] ‘Skogens kol’ Fe-coated biochar.

5 Results and Discussion

5.1 Short column study

Both the sand and loam soils were originally used in the rainfall simulator, for comparison with the organic soils. However, the loam soil showed poor infiltration capacity and was eventually excluded from the study, leaving the sand as the only mineral soil. Organic 1 was also not included in Paper I, due to ponding that occurred on the surface of two of three replicates after rainfall simulations 2 and 3, which potentially resulted in anaerobic conditions and were therefore not comparable to the other soils, as discussed later.

In all three soils examined using the rainfall simulator technique, total-P and phosphate-P losses were highest from the 0- to 20-cm layer (Table 3). The proportion of phosphate-P to total-P was large (*i.e.* 80-100%) in the 0- to 20-cm layer of all three soils (Fig. 7A, E, I). Total-P leaching losses from the one organic 1 replicate in which ponding did not occur (2.1 kg ha^{-1}) were much lower than from organic 2 (15 kg ha^{-1}) (Table 3). Average total-P concentration in leachate was 1.04 mg L^{-1} (n=1) for organic 1 and (± standard deviation) 7.66 ± 2.05 mg L^{-1} (n=3) for organic 2, 0- to 20-cm layer. The average concentration in leachate from the 20-40 cm layer was considerably lower for organic 1 (0.08 ± 0.01 mg L^{-1}; n=3) than for organic 2 (1.16 ± 0.73 mg L^{-1}; n=3). The remaining layers were similar in both organic soils, in that leachate P concentrations became progressively smaller with depth. Parvage *et al.* (2015) also used 20 cm (0- to 20 cm layer only) soil columns from the organic 1 site and detected a mean phosphate-P load of 8 kg ha^{-1} after 300 mm of artificial rainfall, *i.e.* nearly four-fold more than in this thesis but with only one-third more rainwater applied. This may have been a result of higher rainfall intensity combined with use of a low ionic strength rainwater in their study, as discussed later.

The average total-P concentration in leachate from the 0- to 20-cm layer in the sand soil was 5.25 ± 2.25 mg L^{-1}; n=3, which was similar to that in leachate from the same layer in organic 2. From the four rainfall simulations, a combined total of 9.6 kg ha^{-1} total-P was leached from the 0- to 20-cm layer in the sand (Table 3). The lower sand layers also released considerable amounts of P, although these losses were likely an experimental artefact resulting from the low ionic strength rainwater. Solutions with low ionic strength have previously been found to cause dispersion of soil colloids, with this dispersion effect increasing with high flow rates (Ryan and Gschwend, 1994). The presence of large amounts of humus in the organic soils most likely increased the stability of any clay colloids in the organic soil (Tisdall and Oades, 1982) compared with the mineral soil, resulting in lower PP losses.

Dividing the soil profile into separate 20-cm layers is a novel approach, to my knowledge, which makes comparisons with other studies difficult. However, studies of P leaching from 20-cm topsoil columns exposed to rainfall simulations are common and losses are often greater than those measured from full-length lysimeters or field studies. For example, Liu *et al*. (2012b) concluded that they had overestimated P leaching from 20-cm deep topsoil columns exposed to artificial rainfall simulations due to not including the influence of subsoil Fe and Al oxides with low DPS values (between 8-11%). They also concluded that the subsoil interaction may act as a P filter to reduce overall leaching if a whole soil profile is used. They verified this by comparing their topsoil column results with total-P leaching in a field study measuring the P concentration in drainage water from a sand soil (Mellby) at 0.9-m depth, which was 5-9 times less than in leachate from their topsoil-only columns (Liu *et al.*, 2012a). Furthermore, based on comparisons between outdoor lysimeters with and without subsoil, Andersson *et al.* (2013) concluded that P leaching is greatly affected by subsoil properties and that, in general, topsoil studies alone are not sufficient for determining P leaching in soils.

To determine potential concentrations and loads from the entire soil profile, which was not possible with the 20-cm columns, a full-length lysimeter study was also carried out in this thesis.

Table 3. *Cumulative phosphorus loads leached from 20-cm soil columns after addition of 200 mm rainfall in the rain simulator.*

Soil	Depth	Total-P [a]	DPS [b]
	(cm)	kg ha^{-1}	%
Organic 1	0-20	2.1[c] (4.7) [d]	15 [c]
	20-40	0.2 [c]	11.3 [c]
	40-60	0.2 [c]	6 [c]
	60-80	0.2 [c]	2.9 [c]
Organic 2	0-20	15.0	27.9
	20-40	1.8	21.2
	40-60	0.2	7.5
	60-80	0.2	7.5
Sand	0-20	9.6	92.1
	20-40	4.6	77.3
	40-60	4.7	26.6
	60-80	5.0	49.3
Loam	0-20	[e]	21.6 [c]
	20-40	[e]	20.3 [c]
	40-60	[e]	27.8 [c]
	60-80	[e]	52.8 [c]

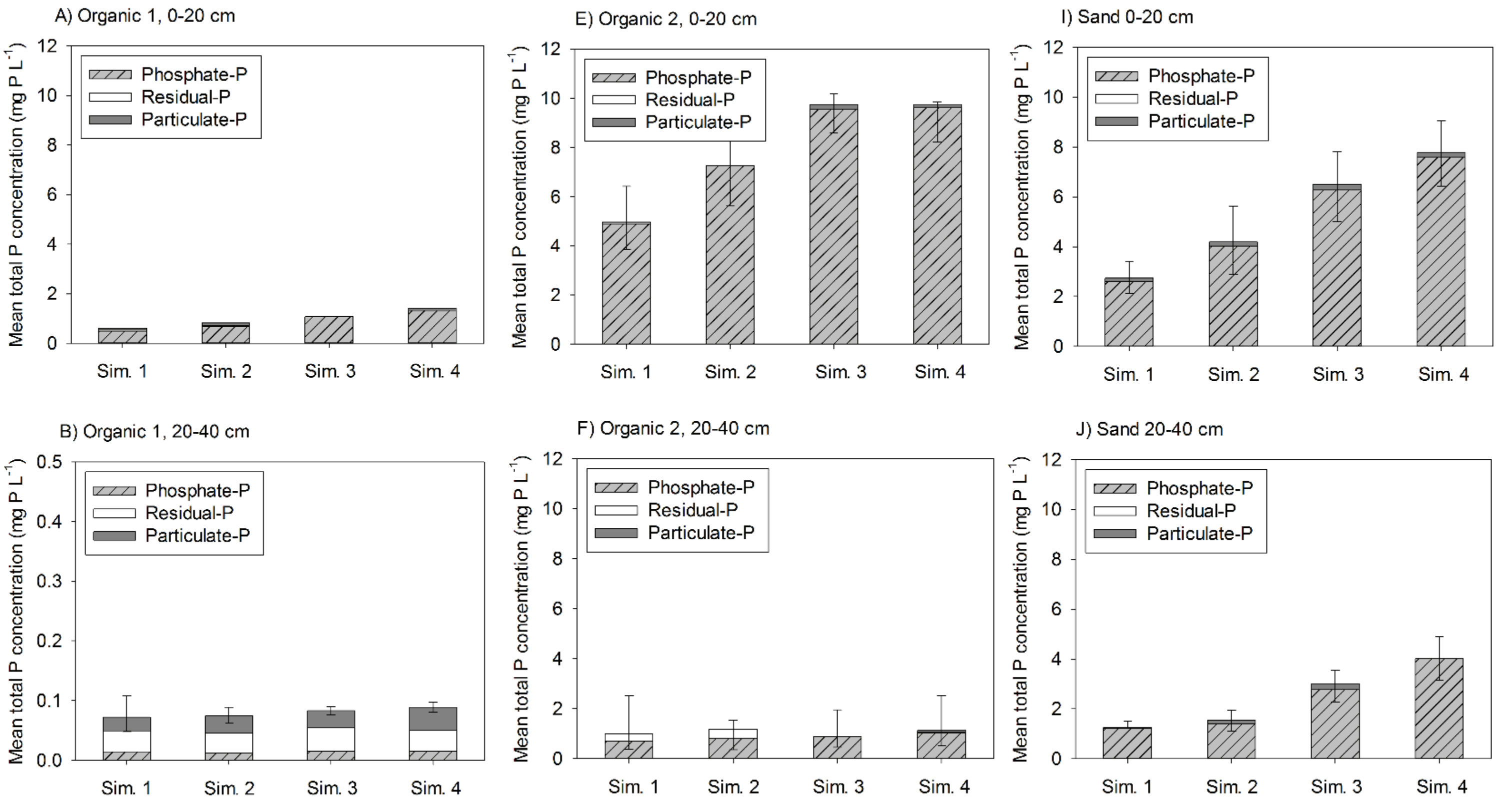
[a] Geometric mean

[b] DPS= Degree of phosphorus saturation $P_{ox}/(0.5\ (Fe_{ox} + Al_{ox})$ x 100 where Pox, Fe_{ox} and Al_{ox} are oxalate-extractable P, Fe and Al, respectively.

[c] Data not presented in Paper I

[d] Includes ponded replicates

[e] Data not collected


A) Organic 1, 0-20 cm
E) Organic 2, 0-20 cm
I) Sand 0-20 cm
B) Organic 1, 20-40 cm
F) Organic 2, 20-40 cm
J) Sand 20-40 cm
Mean total P concentration (mg P L-1)
Phosphate-P
Residual-P
Particulate-P
Sim. 1
Sim. 2
Sim. 3
Sim. 4
0
2
4
6
8
10
12
0.0
0.1
0.2
0.3
0.4
0.5

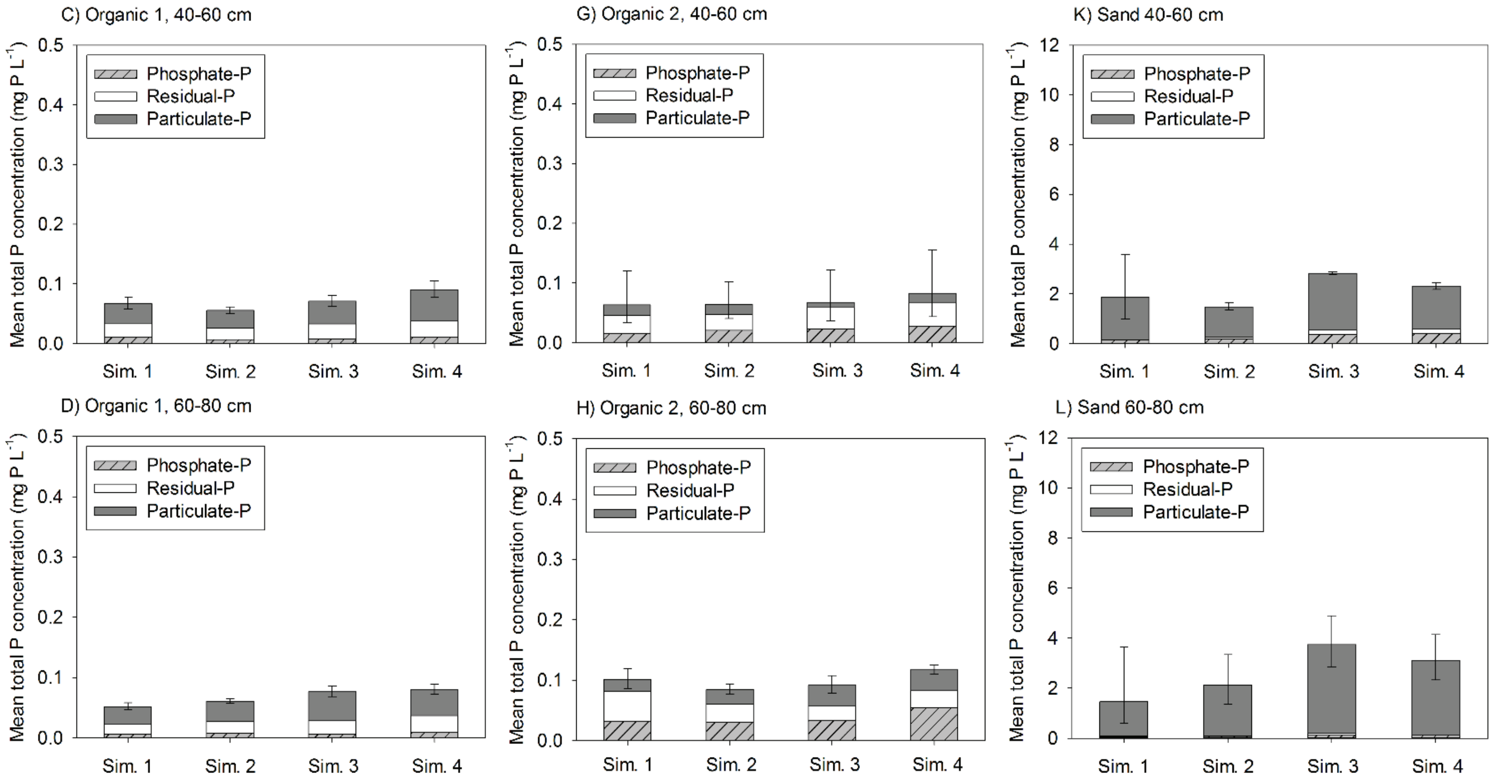


Figure 7. Mean total phosphorus (total-P) concentration in leachate from four layers (0-20, 20-40, 40-60, 60-to 80-cm) in three soils: organic 1 (A-D), organic 2 (E-H) and sand (I-L). Columns are separated into phosphate-, residual- and PP fractions. Note different y-axis scales.

5.2 Field-scale phosphorus leaching from organic soils

The average total-P concentration in leachate reported in Papers II and III consisted of 71% and 76% phosphate-P for organic 1 and 2 lysimeters, respectively. Over the three years of study, the mean phosphate-P concentration was 0.28 ± 0.74 mg L^{-1} for organic 1 lysimeters and 0.71 ± 1.64 mg L^{-1} for organic 2 lysimeters. Geometric mean total-P load (geometric s.d.) was 1.88 (1.33 kg ha^{-1}; n=3) and 2.30 (1.35 kg ha^{-1}; n=3) for organic 1 and 2 lysimeters, respectively, over the three years, values which were not significantly different. This was equivalent to a yearly mean load of 0.63 and 0.77 kg P ha^{-1} from the organic 1 and organic 2 soils, respectively. Studies reporting P leaching from lysimeter studies involving organic soil columns are quite uncommon in the literature. However, one rare exception, a study reported by Reddy (1983), recorded 54-89% phosphate-P and loads between 16 and 168 kg P ha^{-1} yr^{-1} in leachate from 70-cm soil columns taken from organic soils in Florida. Several researchers have presented results from suction lysimeters and field-scale studies, *e.g*. Pahkakangas (2015) found mean phosphate-P concentrations of 78-83% of total-P in drainage ditches beside peatland soils in Finland. Izuno *et al.* (1991) found a higher variation in values from field drainage sampling in the Florida Everglades (40-80% phosphate-P). In Ontario, Canada, Miller (1979) reported loads of up to 37 kg P ha^{-1} yr^{-1} from organic soils. Total filtered-P loads of up to 87 kg ha^{-1} during a one-year period were measured in soil solution samples from 35 cm depth in an organic soil under dairy cow grazing in New Zealand (McDowell and Monaghan, 2015), which was considered extremely high in comparison with 1.9 and 9.0 kg ha^{-1} from two adjacent control soils.

In comparison with these international studies, considerably lower phosphorus concentrations and loads were detected in this thesis. As there are many differences in fertiliser use and scale between different studies, direct comparisons are not often reliable. Thus to determine how the P losses from organic soil lysimeters detected in this thesis related to losses from Swedish mineral soils, a second study was carried out over a 17-month period (Table 4).

5.3 Comparison between organic and mineral soils

As the sand soil was taken from a Swedish national drainage monitoring site with average measured P loads of 1.5 kg ha^{-1} yr $^{-1}$, initial expectations were that the sand soil lysimeters would leach considerable amounts of P. On the contrary, the actual geometric mean total-P load from the sand over the 17-month study was 0.3 kg ha^{-1}, in comparison with 1.0, 1.2 and 0.2 kg ha^{-1} from organic 1, organic 2 and loam, respectively. However, there was considerable variation between all soil replicates, which produced large geometric standard deviations, resulting in fewer statistically significant differences between the soils (Table 4). The actual load lost from the sand drainage monitoring site over the same 17-month period as when the lysimeter study was conducted was very similar to that found in the lysimeter study (0.34 kg ha^{-1}; Data Hosting Agricultural Land, 2017). However, the amount of drainage water recorded at the site was 445 mm, compared with an average of 180.5 mm for the lysimeters at the station in Uppsala. Thus if the drainage volumes had been similar, the losses from the lysimeters would likely have been considerably higher. This may be at least partly due to the fact that the entire volume of drainage water is collected from lysimeters, whereas a reduced volume is collected in the field, caused by a proportion of leachate by-passing drainage pipes. This suggests that caution is needed when comparing the data obtained using these two study techniques, lysimeters and field monitoring.

Variations in drainage volumes can be an issue when comparing P leaching from lysimeter treatments within the same study, as well as between studies. One method is to calculate the volume-weighted average, or geometric average (calculated from total transport (kg ha^{-1}) over the 17-month study, divided by total leachate volumes) total-P (and phosphate-P) concentrations from the 17-months. These were 0.07 (0.05), 0.14 (0.11), 0.03 (0.02) and 0.01 (0.005) mg L^{-1} from the organic 1, organic 2, sand and loam soils. The highest volume-weighted total-P concentration reported by Djodjic *et al.* (2004) was for loamy sand lysimeters (0.11 mg L^{-1}) followed by a silty clay loam (0.07 mg L^{-1}) and loam (0.06 mg L^{-1}). These were all less than the total-P concentrations from organic 2, but greater than the concentrations from the sand and loam soils and similar to those from organic 1 in this thesis. Andersson *et al.* (2013) recorded much higher total-P concentrations (1.05 mg P L^{-1}) from one of their studied sand soils (Nåntuna), which they attributed to high amounts of extractable P (P-AL and Olsen-P) combined with low sorption capacity in the subsoil. However, they also reported lower mean total-P concentrations in leachate from another sand soil (Mellby; 0.12 mg L^{-1}) and from two clay soils (Lanna, 0.19 mg L^{-1}; Bornsjön, 0.16 mg L^{-1}), which they also related to higher sorption capacity of the respective soils.

These results also suggest that leaching loads from all the soils included in this thesis were relatively low in comparison with those observed in previous lysimeter studies and in field monitoring of Swedish agricultural soils.

Individually, both the rainfall simulation study and lysimeter study provide important information. Together, they provide a more thorough understanding of the complex nature of P sorption/desorption in these soils and ultimately how likely they are to leach problematic concentrations and loads of P. The factors that affect leaching losses from these soils are discussed in the following sections.

Table 4. *P loads leached from the 17-month lysimeter study*

	Control				Fe-biochar		Mg-biochar	
Soil	Tot-P kg ha^{-1}	(s.d)	Phosphate-P kg ha^{-1}	(s.d)		(s.d)		(s.d)
Organic 1	1.0ab	(1.37)	0.73ab	(1.42)	0.29ns	(1.81)	0.19*	(1.12)
Organic 2	1.2a	(1.44)	1.01a	(1.54)	0.74ns	(2.28)	0.49ns	(1.26)
Sand	0.3bc	(1.91)	0.21bc	(2.29)	†	†	0.15ns	(2.0)
Loam	0.2c	(1.83)	0.09c	(1.48)	†	†	0.29ns	(2.30)

†Data unavailable

Note. Data presented are geometric mean/geometric standard deviation (s.d.). Geometric s.d cannot be added/subtracted from the geometric mean.

Different letters within columns indicate significant difference ($p < 0.05$). ns = not significantly different between treatment and control.

*Indicates statistically significant difference between treatment and control.

5.4 Factors affecting phosphorus leaching from organic soils

5.4.1 Soil P test values

The P-AL extraction method has been found to potentially overestimate plant-available P by dissolving calcium-phosphate(s) in alkaline soils due to the low extraction pH (Eriksson *et al.*, 2013), which indicates a higher plant-available P and also higher potential to leach P. This was likely the case for both mineral soils included in this thesis, as the sand soil has been identified to contain Ca bound P (Schmieder *et al.*, 2018) and, due to the high pH, this is likely to apply for the loam too. The P-AL concentration from the 0- to 20-cm layers were 609 and 112 mg kg^{-1} for the sand and loam soil, respectively. However, Olsen P values of 120 mg kg^{-1} for the 0- to 20-cm layer of the sand soil were still regarded as high, and much higher than for the other soils (Table 1), which suggests that the soil was saturated with plant-available P irrespective of the test used.

Different studies have found varying degrees of correlation between soil P test results and P leaching losses from soils. Djodjic *et al.* (2004) found no correlation between topsoil plant-available P (P-AL and Olsen-P) and P concentration in leachate from 1-m deep columns of five different agricultural soils in Sweden. Moreover, Eriksson *et al*. (2013) found that none of the soil P tests they used with different extraction agents (calcium chloride, water, Olsen P or P-AL) correlated with the mean annual flow-weighted concentration (1999-2010) of dissolved reactive phosphorus (DRP) in drainage water. Rainfall simulation data from all four rainfall simulations and depths for organic 2 and sand (Paper I) and for organic 1 (the non-ponded replicate only, results not included in Paper 1) were used in a regression analysis of results from different soil P methods and total or phosphate-P concentration measured in leachate from the 20-cm soil columns. The best correlation ($R^2 = 0.69$, $p<0.05$) was between soil total-P and leachate total-P concentration for the two organic soils. There was a similar degree of correlation with phosphate-P in leachate ($R^2 = 0.65$, $p<0.05$). Ammonium acetate lactate extraction (P-AL) resulted in R^2 values of between 0.50 and 0.55 for both total-P and phosphate-P. These lower P-AL values were likely due to the higher P-AL concentrations in the 20- to 40 and 60- to 80-cm layers than in the layer above (Table 1). However, the soil total-P values decreased with each decreasing soil layer, which also corresponded to a reduced amount of P in leachate, resulting in a stronger correlation.

Regression analysis of the volume-weighted average concentration of both total-P and phosphate-P in leachate from the 80-cm long intact soil columns (90-cm lysimeters) revealed no correlation for any of the soil test approaches (total-P, P-AL, Olsen P, P_{ox}) with standard and logged leachate data. However, as only four soils, both organic and mineral, were plotted, caution is needed when interpreting the results.

5.4.2 Degree of phosphorus saturation (DPS)

Although none of the studies in this thesis sought to determine the P saturation capacity of the soils and therefore assist in determining a suitable DPS threshold value, organic 2 gave some insights, at least for the organic soils. The 0-20 layer released 15 kg P ha^{-1} with a DPS of 27.9%, whereas the 20-40 layer released 1.8 kg ha^{-1} but had a slightly lower DPS value of 21.2% (Table 3). This suggests that a threshold value may lie between these two values. There was a statistically significant correlation between the rain simulator leachate total-P values for the organic soils and DPS ($R^2 = 0.90$). Using phosphate-P instead of total-P in the regression gave $R^2 = 0.89$. When the sand soil was included in the regression analysis, the R^2 value dropped to 0.53 and 0.46 for total-P and phosphate-P, respectively, suggesting that DPS is more suitable for organic soils. Both mineral soils were non-calcareous, but neutral to alkaline in pH. This likely caused an overestimation of the P_{ox} values from these soils (Koopmans *et al.*, 2007) (Table 1). For this reason, more suitable extraction methods for P, Ca, Fe and Al at higher pH would most likely give a more realistic value.

5.4.3 Flow pathways

Visual vertical cracks in the organic 1 profile were evident during an initial soil examination, but were not present in the organic 2 profile (Fig.1 in Paper III). These cracks likely resulted in bypass flow, past a proportion of the potentially available P sorption sites (30- to 70-cm region). The cracks probably occurred due to shrinkage of the soil (Schwärzel *et al.*, 2002) caused by moisture loss or, alternatively, decomposition of vertically deposited organic matter during soil development. Drainage data collected daily from each lysimeter (Fig. 2 in Paper III) showed characteristic preferential flow drainage losses, whereby drainage occurred immediately after all rainfall events between August and November 2016, but only from the organic 1 soil. This also indicates that even with a good regression between the 20-cm soil column P leachate losses and DPS, the presence of preferential flow can be an overriding factor when it comes to predicting P leaching from organic soils.

5.4.4 Organic matter competition with potential P sorption sites

Although organic acids were not directly measured in this thesis, it can be hypothesised that the presence of organic acids and subsequent competition with P for sorption sites could explain the high P losses from organic 2 in the lysimeter study. This soil had available sorption sites (low DPS) in lower soil layers (Table 3) and no indication of preferential flow as in organic 1. Although not measured in the lysimeter study, DOC, a measure of the dissolved organic fraction of the total organic carbon present in the leachate, was likely to be higher in the two organic soils (Fig. 8A and B) and also slightly higher in the sand soil (Fig. 8C) than in the loam (Fig. 8D). This assumption can be made based on comparison of the colour of the leachates from the lysimeter and rainfall simulation studies (compare Fig. 8 with Fig. 9), with DOC values measured in the latter (Table 5). These high DOC concentrations could lead to the above-mentioned competition with phosphate anions for sorption sites, increasing P concentrations in leachate.

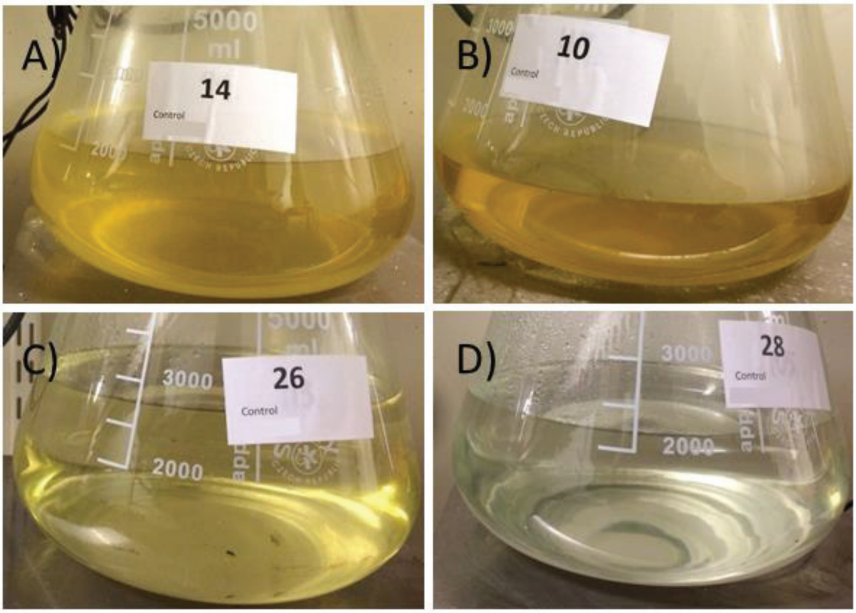


Figure 8. Colour of leachate from the control lysimeters containing: A) organic 1; B) organic 2; C) sand; D) loam

5.4.5 Dissolved organic carbon release under high rainfall intensity

A non-statistically significant, but visually apparent, increase in P concentration and load from the organic 2 and sand soils was noted at successive rainfall simulations (Fig. 7). At the same time, a distinct change in leachate colour occurred for all soils from simulation 1 to 4 (Fig. 9). An initial explanation of the increase in P concentration was as an effect of reducing (anaerobic) conditions causing reductive dissolution of Fe bound to P. However, as Table 5 shows, there was a progressive increase in solution of non-reduction/oxidation (redox) sensitive Al, from simulation 1 to 4, which suggests the presence of an additional, or a completely different, mechanism. An alternative hypothesis is that P dissolution increased over time due to the low ionic strength of the artificial rainwater, applied in both large amounts and at high intensity (200 mm over 10-14 days applied at 5 mm h^{-1}), in the rainfall simulator study. In a study by Chow *et al.* (2003), who subjected surface layers of peat soil to a range of different saline concentrations in a laboratory experiment, it was found that distilled water (low ionic strength) released the highest amount of DOC. That study also showed that at higher saline conditions (in principle, higher ionic strength), DOC flocculated with metal cations. Following this flocculation, cation bridging between the metal and phosphate could potentially occur.

Events supplying high rainfall (which has a low ionic strength), as in the rain simulator study, could destabilise and release into solution DOC, along with the bound Fe and Al and associated phosphate. This was verified in additional analysis of leachate from the rain simulation study, which showed a general increase in Fe, Al, manganese (Mn), DOC and phosphate-P after each subsequent rainfall simulation event (Table 5). One element that contradicted this increasing release trend was calcium (Ca), for which a decrease in concentration was observed after each subsequent rainfall simulation for both organic 2 and the sand. Calcium can also be involved in cation bridging and in lowering the surface charge density of organic molecules, which has been found to reduce the solubility of dissolved organic matter (Tipping and Woof, 1991; Kalbitz *et al.*, 2000). A potential scenario is that when large amounts of rainwater are applied, the soil attempts to maintain equilibrium following a large reduction in the ionic strength of the soil solution. As easily soluble Ca is quickly lost, and replenishment is not fast enough, this may have caused a reduction in solution ionic strength, thereby mobilising DOC and attached Fe, Al and P. However, it is not clear why organic 1 (replicates 1 and 2) showed a slight increase in Ca concentration after subsequent simulations. It may be related to the ponding/waterlogging effect that occurred only on these two replicates, although this is uncertain.

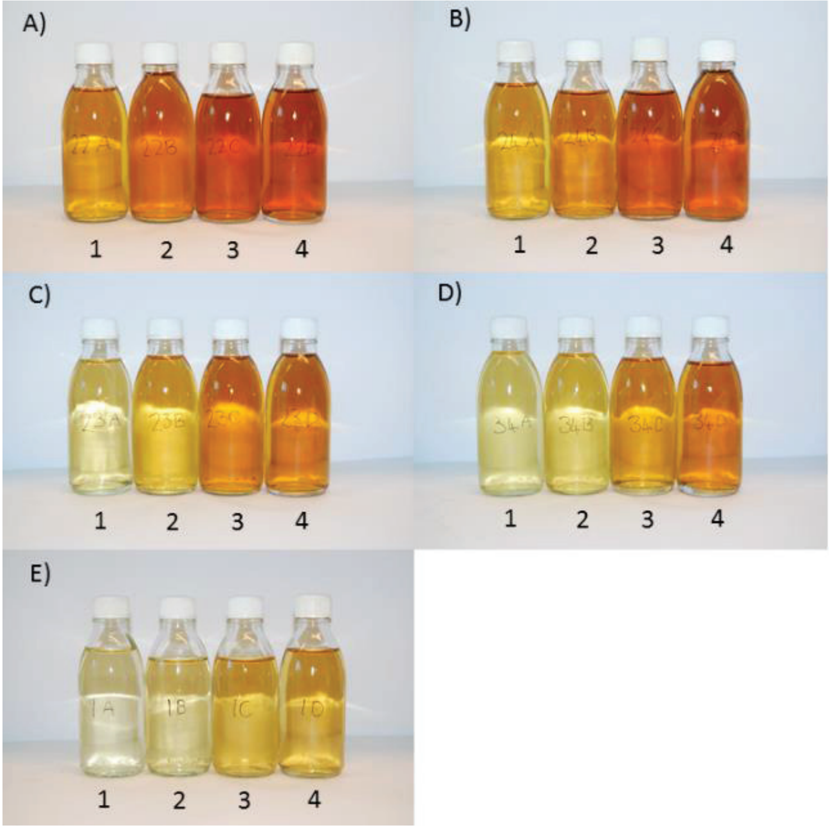


Figure 9. Leachate from organic 1 (3 replicates, A-C), organic 2 (1 replicate, D) and sand (1 replicate, E) following rainfall simulations 1-4. Ponding occurred on replicates 1 and 2 of organic 1 (A, B) for simulations 3 and 4.

Table 5. Results of leachate analysis from the rainfall simulation study (Paper I) and unpublished data

Soil	Rep.	Sim.	Tot-P Conc.	DOC	Ca	Fe	Al	Mn
			mg L^{-1}					
Organic 1	1	1	1.19	182	59	1.1	1	0.04
		2	1.92	241	59	1.7	1.5	0.03
		3†	5.57	290	65	2.4	2	0.06
		4†	13.5	330	73	3.0	2.3	0.13
Organic 1	2	1	0.47	174	63	0.91	0.99	0.02
		2	0.53	225	70	1.3	1.4	0.02
		3†	0.97	267	74	2	2	0.03
		4†	3.5	319	72	2.5	1.2	0.06
Organic 1	3	1	0.62	81	110	0.38	0.44	0.05
		2	0.83	118	92	0.71	0.7	0.03
		3	1.24	196	55	1.4	1.1	0.02
		4	1.25	180	46	1.5	1.2	0.02
Organic 2	1	1	3.74	126	210	0.22	0.71	0.54
		2	6.44	142	220	0.34	0.9	0.87
		3	10.3	212	120	0.65	1.4	0.52
		4	9.58	241	62	0.9	1.7	0.36
Organic 2	2	1	6.13	109	160	0.23	0.71	0.67
		2	9.05	139	120	0.32	0.92	0.6
		3	8.82	200	59	0.69	1.4	0.39
		4	8.12	194	43	0.76	1.5	0.31
Sand	1	1	2.82	27	210	0.07	0.01	0.003
		2	3.73	38	180	0.12	0.1	0.002
		3	6.3	59	58	0.18	0.13	0.002
		4	7.94	54	40	0.22	0.17	0.002
Sand	2	1	2.1	32	180	0.06	0.01	0.005
		2	3.03	47	120	0.13	0.13	0.006
		3	4.98	56	46	0.24	0.17	0.005
		4	6.33	47	36	0.15	0.11	0.002

† ponding occurred.

5.4.6 Effects of reducing conditions on P leaching

In the rainfall simulation experiment, organic 1 experienced ponding conditions on the surface of two of three replicates during the second and third simulation events. Although this was only a visual observation, and there was no investigation of whether anaerobic conditions occurred, the P concentration in leachate did increase substantially (Table 5). For the ponded replicates 1 and 2 of organic 1, the P concentration increased from 1.19 to 13.5 mg L^{-1} and 0.47 to 3.5 mg L^{-1}, compared with an increase from 0.62 to 1.25 mg P L^{-1} for the unponded replicate 3 (Table 5), which suggests the presence of an additional P release mechanism. The increase in Fe and Mn, which are both redox-sensitive, from rainfall simulations 1 to 4 (Table 5) suggests reductive dissolution of Fe-bound P. In contrast, a large increase in P from the sand also occurred, but a resulting decrease in Mn in solution between simulations 1 and 4 suggests this was not due to reductive dissolution. In the case of the rainfall simulation study, the high amount of organic carbon or DOC, as an energy source for organic matter mineralisation, and warm temperature (~20°C) suggest that soil oxygen levels could be depleted relatively quickly, producing anaerobic conditions and potentially the ability to reduce Fe and therefore release associated P into solution.

5.5 Biochar to mitigate phosphorus leaching losses

5.5.1 Metal oxide coating of biochar

The uncoated and metal-coated biochars were compared in a batch adsorption study (Paper II). The Langmuir model for determining maximum adsorption capacity was applied to the Fe-coated batch adsorption data and resulting in a Q_{max} = 3.38 mg P g^{-1}. Although the model was not applied to the uncoated data, Paper II Fig. 4 showed a phosphate-P adsorption of close to 0 mg g^{-1}. An improvement in adsorption is commonly found with Fe-coating of biochar, *e.g.* 0.012 and 0.65 mg P g^{-1} for uncoated and coated maize cobs, 0.04 and 0.90 mg P g^{-1} for uncoated and coated garden wood residues, 0.09 and 1.04 mg P g^{-1} for uncoated and coated wood chips (Micháleková-Richveisová *et al.*, 2017) and 0 and 0.31 mg P g^{-1} for uncoated and coated cotton stalks (Ren *et al.*, 2015). In all untreated cases, the raw biochar functioned poorly as a P filter, but the Fe-coating greatly improved the effectiveness. The cause of the higher adsorption capacity of the biochar in this thesis compared with biochars examined in previous studies is uncertain, but the phosphate concentration and pH of the solution when conducting adsorption studies (discussed below) are likely reasons.

The Q_{max} of the Mg-coated biochar (65.4 mg P g^{-1}) showed nearly 20-fold higher adsorption compared with the Fe-coated biochar. A coating of Mg on biochar surfaces has been tested in several previous studies, which reported Langmuir maximum P adsorption capacity results of 272.21 mg g^{-1} (Zhang *et al.*, 2012) 8.7 mg g^{-1} (Park *et al.*, 2015), 15.1 mg g^{-1} (Cui *et al.*, 2016) and 117 mg g^{-1} (Xu *et al.*, 2017). There is thus a wide variation, but in general, biochars coated with Mg seem to adsorb more phosphate than the Fe coated biochars presented above. However, without direct comparisons between coatings within the same experiment, it is difficult to know whether it is the coating itself or another factor that is responsible for the differences in adsorption capacity. To examine this, Xu *et al*. (2017) compared Mg, Ca, Al and Fe coated waste wood biochars and concluded that the Mg-coated biochar had by far the highest P removal efficiency (97% compared with below 15% for the rest). This was influenced by the $MgCl_2$ concentration used in coating the biochar, with P removal rate increasing from 2.1 to 97% as the concentration increased from 0.4 to 1.4 M.

Although not investigated in this thesis, removal of phosphate by Mg-coated biochar has been found to occur via two mechanisms, precipitation of phosphate through the reaction with Mg oxides (Yao *et al.*, 2013; Cui *et al.*, 2016) and surface adsorption, with the latter seen as the dominant method (Yao *et al.*, 2013).

The reason for the general increase in adsorption when using Mg rather than Fe was not investigated in this thesis. However, there was one hypothesis for the noticed increase in effectiveness when adding a coating containing Mg vs. one with Fe, which may or may not contribute to the general trend seen. The hypothesis is based on the pH level at which the coating surface (on average) becomes neutral, the so-called point of zero charge, pH_{pzc}. For a magnetite sample, $pH_{pzc} = 6.5$, which is contrasted by the one for magnesium (hydr)oxides at pH_{pzc} greater than 10 (Kosmulski, 2016). All measured pH levels in the lysimeters and likely most in the laboratory were below the likely pH_{pzc} for the Mg-coated biochar, meaning that the surface will be positively charged, thus able to form an electrostatic attraction which significantly increases the chances for binding any of the anionic forms of phosphate. In addition, all phosphate ions have the ability to form inner-sphere complexes, which are much more strongly bound than outer-sphere ones, which in turn are much more strongly bound than those loosely bound (adsorbed) diffuse ions (Stumm, 1992).

This difference in maximum adsorption between the two metals may not be solely explained by the actual coating, as the pyrolysation temperature and feedstock were also different between the biochars used in this thesis. However, based on results from a Mg-coated batch adsorption pre-study, the difference in feedstock is unlikely to have a significant effect. This pre-study was initially used to determine which of the potential biochars available would function best for removing phosphate from aqueous solution and also to determine the most effective Mg concentration. The results clearly suggested that the feedstock choice was irrelevant and that the highest concentration of metal oxide (also used in all follow-up experiments) was the most important for effective phosphate removal (Fig. 10). These results also confirm findings for the Fe-coated biochar (Paper II) and the view of Sizmur *et al.* (2017:41) that biochar is only a "porous carbon scaffold upon which metal oxides are precipitated to increase the surface area of the metal oxide".

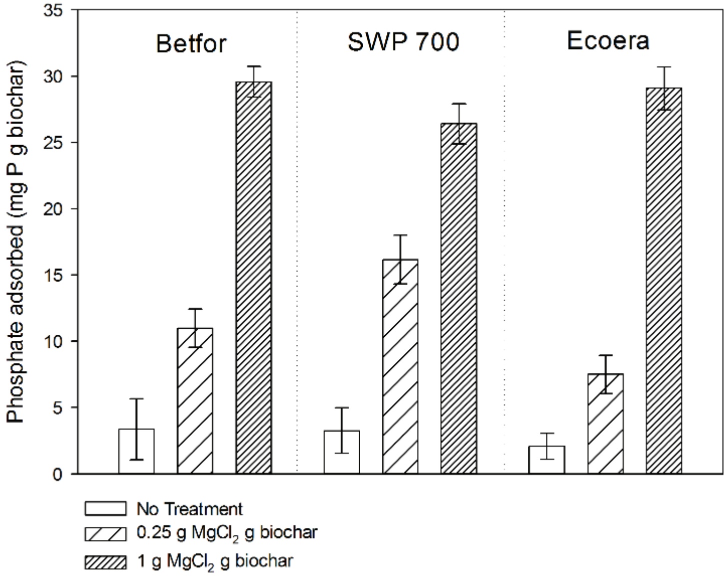


Figure 10. Batch comparison of three biochar feedstocks with Mg coating at two concentrations, with or without coating, in a 500 mg P L^{-1} buffer solution. Betfor is a sugarbeet product pyrolysed at 600 °C, SWP 700 is a softwood biochar produced by the UK Biochar Research Centre, pyrolysed at 700 °C, and 'Ecoera' is comprised of agricultural residues pyrolysed at 600 °C. Error bars indicate standard deviation (n=5).

5.5.2 Pyrolysis temperature

The coated Skogens kol biochar used in this thesis was not further heat-treated past the original pyrolysis temperature range of 380-430 °C. However, the Ecoera was re-pyrolysed at 600 °C, although the effect, either positive or negative for phosphate adsorption, was not tested. Park *et al*. (2015) found that phosphate adsorption increased with pyrolysis temperature of sesame seed straw biochar in the order 600 °C > 500 °C > 400 °C > 300 °C. As the temperature increased, the yield of biochar decreased, from 42.5 at 300 °C to 23% at 600 °C, due to the loss of volatile matter and the gases carbon dioxide, carbon monoxide (CO), hydrogen (H_2) and methane (CH_4) (Park *et al*., 2015), a result also found with maize straw by Chen *et al*. (2012). Park *et al*. (2015) also noted an increase in surface area from 22.1 to 290 m^2 g^{-1} and in total pore volume with a temperature increase from 300 °C to 600 °C. This coincided with an increase in phosphate adsorption to their biochar. Another possible explanation could be that when pyrolysis temperature increases, it reduces organic matter content, but the mineral content (per unit weight) increases and, since phosphate generally adsorbs to this fraction, this may lead to an increase in phosphate adsorption on a per gram basis. Comparing the two uncoated biochar in this thesis (Table 2), the uncoated Skogens kol had twice the surface area of the uncoated Ecoera (160 compared with 80 m^2 g^{-1}). After coating, the biochar surface area decreased to a point where Skogens kol had only 30 m^2 g^{-1} more than Ecoera. In spite of this, the Mg-coated Ecoera still adsorbed more phosphate than the Fe-coated Skogens kol biochar. This suggests that surface area, which is often a direct result of pyrolysation temperature, is important, but that the type of coating is even more important

5.5.3 Solution pH

The P adsorption in the batch pre-study was 29.7 mg g^{-1} biochar (Fig. 10), which was half the measured P adsorption of the Mg-coated biochar in Paper III (65.4 mg P g^{-1} biochar) at the same maximum solution concentration of around 500 mg P L^{-1}. This was likely due to the lower pH (6.5) used in Paper III, compared with that (pH 10) used in the pre-study, a common finding in phosphate adsorption experiments (Micháleková-Richveisová *et al.*, 2017). Nguyen *et al.* (2013) found that, on increasing the pH from 3 to 10, phosphate adsorption decreased from 96 to 91% in soyabean milk by-products treated with Fe(III). This was explained by an increase in OH^- ions at higher pH, causing an increase in negative charge and therefore competition with the negatively charged phosphate ions. As indicated previously, the pH_{pzc} of both MgO and $Mg(OH)_2$ is greater than 10. Therefore MgO and $Mg(OH)_2$ surfaces should be positively charged at naturally occurring soil pH values and should therefore adsorb P through electrostatic attraction (Zhang *et al.*, 2012). On testing a range of pH values (2-10), Krishnan and Haridas (2008) found that pH 3 was the most effective for adsorbing phosphate from aqueous solution. A pre-experiment carried out in Paper II (see Supplementary Figure S2 in Paper II) identified a distinct relationship between pH and phosphate adsorption to Fe-coated biochar whereby P adsorption decreased from 3.7 to 0.06 mg g^{-1} biochar as the pH increased from 3 to 10. A similar experiment was attempted in Paper III, which used brucite-coated biochar in a P buffer solution with a pH range from 2-9. However, the pH of the buffer solution constantly returned to around pH 8-9 during testing in the more acid buffer solutions, due to the strong buffering capacity of the OH^- ions from the Mg-coating, increasing the solution pH. Consequently, the experimental results were unusable and therefore unable to confirm that pH is important for phosphate adsorption, as found in the study using Fe-coated biochar. However, if the surface coating is affected by acid conditions, this may suggest an issue with using this Mg-coated biochar product in acid soils, as it could potentially dissolve the Mg-coating under these conditions, resulting in a product with a reduced effect.

5.5.4 Metal use efficiency

The efficiency of Fe applied relative to the amount of phosphate bound was studied only in Paper II, using Fe-coated biochar, and therefore no comparisons between the two biochar coatings were possible. Laboratory losses of Fe from that biochar were as high as 50%, but three-year lysimeter losses were only 30%, which suggests that harsher physical abrasion from laboratory shaking methods was likely responsible for the increased laboratory losses. The loss of surface coating has been found to be a significant issue in coating biochar (Shin *et al.*, 2005). As the main adsorption mechanism of the biochar is through the metal oxide coating, any significant losses will have a substantial effect on the effectiveness of P removal. This was confirmed by Nguyen *et al.* (2013), who noted that as Fe (III) concentration increased from 1 to 20 g L^{-1} biochar, phosphate adsorption increased from 2 to 90 %, which was suggested to be due to more available binding sites.

The actual molar ratio of Fe used to phosphate bound (Fe:P) was calculated to be 500:1 (lowest amount of P bound per amount of Fe used) post Fe coating and 25:1 (highest) after the batch adsorption studies. The post three-year lysimeter study ratio of 261:1 was very low and illustrates the poor field efficiency of this coated biochar. As the Fe concentration on the biochar was reduced from 0.818 to 0.618 mmol cm^{-3} at the end of the three-year study, it was concluded that the persistence of Fe was not the main issue, but instead its ability to adsorb and/or retain phosphate. The effect of field conditions in reducing the phosphate removal efficiency was likely due to the lower phosphate concentration in the soil solution, which ranged from 0.002 to 7.4 mg P L^{-1} in the three-year study, compared with a maximum of 500 mg P L^{-1} in the batch adsorption study. Competition for sorption sites from organic acids released from the organic soils, as discussed in section 5.4.4 of this thesis, was also a likely reason for the reduced phosphate removal efficiency. Another explanation is the particle size of 0.5-1 mm used in the batch adsorption studies, compared with <4 mm in the lysimeters. A smaller particle size would give an overall larger surface area and therefore more potential adsorption sites, giving a greater adsorption potential.

5.5.5 Field lysimeter performance

For a mitigation strategy to be successful, it needs to perform well in the laboratory and then its end use needs to be tested at larger scale under more field-like conditions to give a full evaluation of its function. A unique component of this thesis work, in comparison with other studies on biochar, is that biochar performance was tested in both the laboratory and in field lysimeters. Phosphate-P was the only P species examined in the laboratory studies and was therefore the only P species described in relation to the biochars. Furthermore, phosphate-P was the most common species of P found in the leachate from the organic soils (Papers I-III). The phosphate concentration and load were often found to be lower with use of either biochar, on each leachate sampling occasion. However, the effects were seldom statistically different from those of the respective controls for any of the soils studied. After three years, significantly lower cumulative phosphate loads were only found to be leached from the organic 1 soil/ Fe-coated biochar treatment compared with the control. This was surprising, as the phosphate concentration was often higher in leachate from organic 2 than organic 1 and as biochar adsorbs more phosphate at higher P concentrations, as shown by the batch adsorption studies in Papers II and III and commonly found in similar biochar articles, *e.g*. Cui *et al.* (2016) and Xu *et al.* (2017). A statistically significant difference between the Mg-coated biochar and control treatment was also found only for organic 1 (Paper III). However, the organic 2 Mg-coated biochar treatment compared to the control had a p-value of 0.06 (Paper III, Fig. 7B), which suggests it was close to being significant ($p<0.05$) and that variation between the replicates due to low number of replicates ($n=3$) was likely an issue.

In order to compare the two biochars and their respective performance as a P filter, the Fe-coated biochar dataset was restricted to the same 17-month duration as the Mg-coated biochar study. Over the 17-months of the study, the Mg-coated biochar treatment tended to result in lower cumulative phosphate loads from both organic soils than the Fe-coated biochar, though the values were not significantly different (Table 4). The cumulative 17-month phosphate loads from the Fe-coated biochar were not significantly different to the controls, from any of the organic soils (Table 4). This contrasted the 3 year cumulative phosphate load from the organic 1 Fe biochar mentioned above. Magnesium-coated biochar was the only biochar evaluated in the mineral soils. The effect on reducing phosphate loads from the sand was very small and not significant (Table 4). The large release of phosphate from the biochar treatment in the loam soil (+230%) was unexpected and, as it was not significantly different from the control, the result should be interpreted with caution. This high increase in leachate P concentration was not thought to be due to release from the biochar itself, since no similar losses occurred from the other soils studied. Instead, both mineral soils were likely strongly influenced by P sorption/desorption from the large amount of other Al, Mg, Ca and Fe hydr(oxides) present in these soils below the 30 cm depth of the biochar (Table 6). Therefore, the relatively small amount of $MgO/Mg(OH)_2$ surfaces introduced by the biochar would have had a minimal impact in reducing the phosphate load compared with the sorption sites already present in the mineral soils.

The impact of solution pH, as discussed above, is one possible reason for the greater reduction in phosphate with biochar in the organic soils (pH 4-6) than the mineral soils (pH 7-8). The increased presence of OH^- increases the negative surface charge at higher pH and therefore increases competition with phosphate for the sorption sites. The overall impression from the biochar studies is that biochar works relatively well in the organic soils, although longer periods of evaluation, especially for the Fe-coated biochar, are required to confirm this finding.

Table 6. Selected soil chemical properties presented on a volume basis. Total profile amounts are presented based on the volume of an 80-cm long soil filled lysimeter, adjusted for variations in bulk density.

Site	Depth	Tot-Al [a]	Tot-Ca [a]	Tot-Mg [a]	Tot-Fe [a]	Al-ox [b]	Fe-ox [b]	P-ox [b]	P-AL [c]	Olsen P [d]	Tot-P [a]
						g cm^3					
Org. 1	0-20	0.98	8.63	0.22	2.07	0.48	1.65	0.11	0.02	0.01	0.24
Org. 1	20-40	5.87	9.17	0.32	2.69	3.01	1.75	0.25	0.01	0.00	0.31
Org. 1	40-60	5.27	6.18	1.32	4.85	3.41	1.66	0.15	0.01	0.01	0.27
Org. 1	60-80	2.50	2.81	0.44	1.74	1.05	1.22	0.03	0.00	0.00	0.08
kg lysim.		199.84	366.20	31.55	155.14	108.83	85.89	7.33	0.50	0.27	12.31
Org. 2	0-20	1.12	6.34	0.28	1.42	0.56	1.09	0.17	0.05	0.02	0.39
Org. 2	20-40	2.20	3.24	0.51	1.83	0.39	0.54	0.08	0.06	0.02	0.24
Org. 2	40-60	5.26	4.21	0.36	1.63	0.71	1.42	0.06	0.00	0.00	0.11
Org. 2	60-80	4.20	9.13	1.48	4.93	1.11	2.40	0.13	0.03	0.01	0.25
kg lysim.		174.65	313.35	35.86	134.18	37.90	74.54	6.11	1.87	0.71	13.43
Sand	0-20	5.95	5.98	0.96	7.16	1.29	2.15	1.23	0.73	0.14	1.43
Sand	20-40	4.47	4.53	0.72	5.81	0.77	1.48	0.78	0.53	0.10	1.06
Sand	40-60	3.23	2.58	0.64	9.86	0.32	2.60	0.24	0.24	0.02	0.64
Sand	60-80	3.16	2.67	0.68	5.62	0.19	0.69	0.12	0.32	0.01	0.61
kg lysim.		229.88	215.49	41.07	388.73	35.13	94.49	32.52	24.91	3.56	51.15
Loam	0-20	29.49	10.91	5.07	24.19	1.84	4.01	0.63	0.16	0.04	0.86
Loam	20-40	30.35	10.16	5.21	24.36	1.74	4.03	0.58	0.14	0.04	0.81
Loam	40-60	46.64	14.14	8.34	33.87	1.85	2.12	0.55	0.10	0.00	0.71
Loam	60-80	33.14	14.63	7.50	28.29	1.43	1.75	0.78	0.21	0.00	0.96
kg lysim.		1908.61	681.22	357	1513.50	93.83	162.86	34.75	8.42	1.12	45.51

[a] Extracted with HNO_3 [b] Oxalate extraction [c] Ammonium acetate lactate (AL) extraction [d] Extracted with $NaHCO_3$

6 Evaluation of study methods

The hypothesis or aim of a study dictates the particular method employed in the investigations. The use of one method cannot answer questions at different scales and this is important to remember when planning and interpreting data from an experiment. Within this thesis there were several different scales: laboratory, soil column and field lysimeter. Each is useful for covering a different subset of P leaching conditions and the results are often only applicable at that scale. In some situations, simplifications made can create artificial conditions. These limitations need to be borne in mind when interpreting results from these different studies.

6.1 Laboratory-scale studies

Many laboratory experiments are based on a set of standards used by researchers to enable repeatability and comparability of results. This was the case for the biochar, including the batch adsorption studies, which were carried out to a similar set of standards to allow comparison of results with those of other experiments. These conditions are highly controlled and often optimised for maximum adsorption and therefore may lead to higher adsorption estimates than in field experiments, which are exposed to many other uncontrollable biotic and abiotic factors.

One interesting point that was noted on several occasions was the variability in chemical analysis between biochar samples within the same batch. This was clearly related to the mixture of agricultural residues used in making the Ecoera biochar and variability in the Skogens kol feedstock. Furthermore, the coating of metal oxides on the biochar surfaces also presented variability for the biochar samples, as shown by the unevenness of the Fe coating in Fig.11. This was confirmed by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) of the various biochar samples, whereby different samples in the same treatment showed varying results. This can be an issue at smaller scales, *e.g.* when taking a sample of <0.1 g, analysing it using X-ray powder diffraction (XPD) and suggesting this result is valid for the whole biochar batch. This is also likely an issue for adsorption capacity testing, where a sample of 0.1 g accurate estimation of whole profile total-P load. This was a known limitation of this study type and therefore the results were not extrapolated to give a whole-profile P loss amount.

6.3 Lysimeter study

The use of field lysimeters was the closest reproduction of a ‘field-like’ situation provided in this thesis. This gave close to field conditions, with the benefit of still controlling important climate variables when comparing soils from different locations for P leaching. The use of lysimeters has its own set of limitations, including possible disruption of macropores that are not only present in a vertical direction, but also in many horizontal directions, which may be artificially cut during lysimeter collection. There is also no possibility for horizontal water movement or vertical movement upwards of water from a watertable, which occurs in field situations. This process is especially important with organic soils, where wetting and drying cycles in the field and can lead to an increase in P leaching due to release of Fe bound P between the growing seasons.

Another limitation that is not normally discussed with lysimeter usage, but emerged in the lysimeter studies presented in this thesis, is the number of replicates used for each treatment. Typical practice by the Water Quality group at SLU is to use three replicates in lysimeter studies (Bergström & Shirmohammadi, 1999; Djodjic *et al.*, 2004; Andersson *et al.*, 2013), mainly to balance the requirements for statistical analysis against costs. The use of three replicates in this thesis often led to non-significant results, mainly due to the large variation between replicates. By adding more replicates, the variation would likely decrease, potentially giving more significant results.

7 Conclusions, recommendations and future work

As only two intensively farmed organic soils were studied in this thesis, it is not possible to draw conclusions for all similar organic soils in Sweden, as large variability can be found within the same field, let alone within an entire country. However, direct comparison of leachate concentrations and loads from the four soil lysimeters suggested that the organic soils have sufficiently high potential to release P at concentrations that pose a risk of polluting surface waters.

At the 20-cm soil column scale, degree of phosphorus saturation (DPS) correlated well with P losses from the organic soils in the rainfall simulator study. However, as there were only two organic soils and two sets of soil analyses for the 90-cm lysimeters, this provided too small a dataset to perform a meaningful regression analysis of DPS and P leachate losses, to ascertain whether DPS is a good method for predicting P leaching losses at a larger scale in organic soils.

As often found in mineral soils, the occurrence of preferential water flow through the soil has a large impact on the amount of P reaching surface waters. This by-passing of important P sorption sites can increase the risk of P losses, as seen in this thesis. However, preferential flow can also potentially reduce losses by reducing contact with the soil matrix, where P is located and potentially desorbed. Although not specifically investigated in this thesis, the presence of high P losses, even with a low subsoil DPS, suggests that preferential flow increased P losses greatly in at least organic 1. This needs to be considered when identifying any potential P leaching index for these organic soils.

Important information regarding P sorption/desorption between the start and the end of the subsurface drainage system used in organic soils is still missing and could help understand P losses from this system. The importance of the complex chemical interaction of phosphate with Fe, under the redox conditions that occur in the drainage system serving organic arable soils throughout a typical farming season was not examined in this thesis, and potentially requires further field-scale investigation.

Although beyond the immediate scope of the research presented in this thesis, it can be speculated that the predicted increase in rainfall intensity and the frequency of rainfall events in the near future, as a result of climate change, has the potential to increase P losses from organic soils. Oxidation of organic soils, thereby reducing the actual soil depth, combined with a reduction in sorption sites due to DOC-Al-P or DOC-Fe-P being leached, may also cause an increase in P leaching in the future if P fertilisers are continually added, especially at rates above plant requirements.

The use of metal oxide-coated biochar as a mitigation strategy has potential, but still requires refinement. The production cost of metal oxide-coated biochar needs to be investigated by comparing both the effectiveness and efficiency of P removal with that of other products. In this thesis, use of Fe as a coating material appeared to be very inefficient, as indicated by poor Fe:P ratios. The efficiency factor is economically important to ascertain for production at larger scale, where ~90-100 t biochar ha^{-1} may potentially be required.

Paper I identified that most P losses came from the topsoil. However, placement of biochar under the topsoil was not effective in reducing P losses from the two mineral soils studied. This was likely due adsorption by biochar of P leached from the topsoil being outweighed by desorption of P from larger quantities of Fe and Al hydr(oxides) in the subsoil, suggesting the need for further refinement of depth of the biochar layer.

Use of biochar as a blanket placement under the topsoil may also be economically unfeasible. Backfilling drainage trenches with biochar or directing drainage flow through replaceable sacks filled with biochar are potential options that could be investigated in the future. Furthermore, once the P adsorption capacity of the biochar is saturated, recycling the biochar as a potential fertiliser/soil conditioner is a future possibility worth exploring.

The Mg-coating for biochar used for analysis and adsorption capacity testing in the laboratory studies reported in this thesis was $Mg(OH)_2$ (brucite), as this was exposed to moisture and low temperature. However, the biochar applied in the lysimeters was not brucite, but MgO (periclase). It would be interesting to test the latter biochar to see whether in fact it was still periclase at the end of the lysimeter study or whether it had hydrated to brucite during the study period, and whether this was important for the effectiveness of the biochar.

The final question is probably the most difficult, but also the most relevant for organic soils, namely what to do with intensively managed organic soils in the future. Returning them to their natural waterlogged conditions by flooding them would reduce carbon dioxide losses, but at the cost of a large flush of P and potential seasonal cycling of P losses if the water becomes anaerobic and then aerobic. Alternatively, pumping drainage water from these fields year round would reduce the likelihood of reductive dissolution of Fe bound P, but at the cost of increased carbon dioxide losses.

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