PHOSPHORUS AND ORGANIC SOILS UNDER GRASSLAND PRODUCTION

Assessment of phosphorus losses for a more sustainable agriculture

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Declaration

This dissertation is the result of my own work, except where explicit reference is made to the work of others, and has not been submitted for another qualification to this or any other university.

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José L. González Jiménez

</div>

Speak the truth… Operate from love

Donella Meadows - The Limits to Growth

Man is too small faced with the vastness of nature

Vladimir Arsenyev – Dersu Uzala

I would like to dedicate this work to Francisco Cambronero, *in memoriam*.

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Abstract

The intensification of agriculture in Ireland aims to increase the exports of dairy and beef products considerably in the coming years, which inevitably implies the expansion of grassland systems to areas that were previously uncultivated. This reclamation of new land is generally made on peats and other related soils rich in organic matter (OM) that typically are located in upland areas, within catchments defined as High Status Waterbodies (HSW) in the European Water Framework Directive (WFD). Previous Irish studies at laboratory scale have shown organic soils to have low phosphorus (P) sorption ability compared to mineral soils. However, the optimum fertiliser P management for these soils is as yet unknown. This is especially important when P fertilisers are applied to these soils to improve grass productivity under land reclamation and expansion. This thesis derived an improved management strategy that accounts for rates, timing and frequency of P additions to minimise P losses to waterbodies from this soil type. Soil samples with contrasting OM content from different HSW catchments across the country were collected and subjected to a series of agronomic, soil chemistry, rainfall and leaching experiments.

Compared to mineral soils, organic soils exhibited an immediate yield response to P applications due to the absence of a build-up phase resulting in a higher proportion of added P available for plant. The limited ability of these soils to adsorb added P into the soil matrix was further evidenced by the diminished ability of organic soils to accumulate added P when soil P fractions were examined following P additions. The low pH of some of the organic soils immobilised freshly applied P, rendering it unavailable for plant uptake. There was a small turnover in recalcitrant soil P pools in organic soils in the short term, and the ability to supply P from non-labile to labile pools was limited. Single fertiliser applications exhibited significantly higher P loads in surface runoff compared to split applications, although the decay rate and time at which P loads in overland flow returned to basal concentrations were similar across the different P treatments. Leachate P losses were very small and did not follow a clear pattern from the different P rates and timing regime treatments. However, nitrification was the main process dominating nitrogen (N) losses in the leached water in organic soils.

This study established the management criteria to minimise losses from organic soils and demonstrated the risk of P transfer from these soils to water due to an inability to build-up their P reserves, suggesting that great care should be taken when they are bought into agricultural production. Optimum management strategies were proposed to mitigate potential P losses, such as liming prior any P fertilisation program or the adoption of a "little and often" approach when P fertilisers are to be applied to newly reclaimed areas under this soil type. Sustainability of these systems will require careful use of P in terms of rate, timing and frequency to protect the quality of waters in catchments with organic soils.

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Abbreviations

AIC	Akaike's Information Criterion
Al	Aluminium
ASC	Anion Storage Capacity
ATP	Adenosine triphosphate
Ca	Calcium
CAN	Calcium Ammonium Nitrate
CAP	Common Agriculture Policy
CEC	Cation Exchange Capacity
CFI	Comparative Fit Index
DIC	Dissolved Inorganic Carbon
DM	Dry Matter
DNA	Deoxyribonucleic Acid
DOC	Dissolved Organic Carbon
DRP	Dissolved Reactive Phosphorus
DUP	Dissolved Unreactive Phosphorus
ECVI	Expected Cross Validation Index
EPA	Environmental Protection Agency
EU	European Union
Fe	Iron
FA	Fulvic Acids
FAO	United Nations Food and Agriculture Organization
FWMC	Flow Weighted Mean Concentration
FH2020	Food Harvest 2020
FW2025	Food Wise 2025
GFI	Goodness of Fit Index

HA	Humic Acids
ha	Hectare
HSW	High status water bodies
K	Potassium
LOA	Low Molecular Weight Organic Acids
M	Million
Mg	Magnesium
Mn	Manganese
N	Nitrogen
NAP	Nitrates Action Programme
OM	Organic Matter
P	Phosphorus
PP	Particulate Phosphorus
P_i	Inorganic Phosphorus
P_o	Organic Phosphorus
PSR	Phosphorus Saturation Ratio
P_t	Total Phosphorus
PAR	Photosynthetically Active Radiation
PP	Particulate Phosphorus
POM	Programme of Measures
PUE	Phosphorus Use Efficiency
PVC	Polyvinyl Chloride
RNA	Ribonucleic Acid
t	Tonne
TDN	Total Dissolved Nitrogen
TDP	Total Dissolved Phosphorus
TIC	Total Inorganic Carbon

TDP	Total Dissolved Phosphorus
TN	Total Nitrogen
TOC	Total Organic Carbon
TON	Total Organic Nitrogen
TP	Total Phosphorus
TPN	Total Particulate Nitrogen
WEP	Water Extractable Phosphorus
WFD	Water Framework Directive

Chapter 1
Introduction

1.1   Overview

The European Union (EU) Water Framework Directive (WFD) 2000/60/EC seeks to establish common ground among member states for water quality monitoring and management towards the protection and improvement of Europe's water bodies. The principal objectives of the WFD are to maintain 'high' and 'good' water quality status, where it exists, and to achieve at least 'good' status for all waters by 2015 (the first reporting period). High Status Water bodies (HSW) are surface water bodies whose measured values reflect undisturbed conditions. In Ireland, trends show that there has been a steady and substantial loss in the number HSW over the last number of years. Diffuse, non-point sources of phosphorus (P) transfers originating to a great extent from agricultural practices, remain as the main cause impacting in the decline of the number of HSW in Ireland (EPA, 2018; Ni Chathain et al., 2013; Carpenter, 2008).

Whilst agricultural nutrients are a pressure on water quality, a catchment's response to this pressure is driven by the mosaic of soil types that characterise the source and hydrology in a catchment. Melland et al. (2012) reported that despite similar farming intensities in two catchments, mean winter P export from one catchment was four times (0.16 mg L^{-1} TP) higher than the other (0.04 mg L^{-1} TP), largely owing to variations in catchment characteristics such as soil drainage and hydrology. In another catchment study in Ireland, Schulte et al. (2009) found that the predominant peat (organic) and gley soils in the catchment contributed to P transfers from land to water due to poor P retention of peats and the impeded drainage characteristics of gleyed soils. Ni Chathain et al. (2013) hypothesised that 'relatively low intensity activities' can become a significant pressure and have a disproportionate impact on high status sites relative to the same pressure on an already degraded system. Therefore, there is an urgent need to stem the degradation of high status sites due to the unique ecosystem services these areas deliver and their significance in supporting aquatic species (e.g. freshwater pearl mussel) and overall catchment biodiversity.

The highest rates of decline in the number of HSW in Ireland have been located in the western seaboard of the country (Ni Chathain et al., 2013). It is generally accepted that most of these

sites are located in upland areas with low population density, and predominantly characterised by extensively farmed land. The predominant soils in these areas are peat soils and soils classed as peaty gleys and peaty podzols. Peat soils are mostly composed of organic materials in which the particle–size distribution of the mineral fraction usually has little textural significance. These soils are often derived from partially decomposed wetland vegetation where plant debris accumulated over long periods of time in flooded conditions, before the land was drained for agricultural production (Okruszko and Ilnicki, 2003). These soils are generally moderately acidic with a low content of clay minerals and aluminium (Al)/iron (Fe) oxides, and are characterised by poor P sorption and buffering capacities. Significant differences in the P sorption mechanisms in soils are due to the content of organic matter (OM), as there are competitive sorption reactions between P and the organic acids (humic and fulvic acids, low molecular weight acids) derived from partial decomposition of this OM for soil sorption sites (Guppy et al., 2005; Daly et al., 2001). Hence, soil OM content plays an important role regarding P dynamics.

The intensification of agricultural production, promoted by a series of national policies, has led farmers to reclaim and expand their farming enterprises to land on peats and other related marginal soils that were otherwise previously undisturbed. This new strategy has implications for sustainable use of fertiliser and slurry on these organic soils. Nutrient application to these soils requires a different management strategy compared to mineral soils due to the high potential for P transfer to water. As Ireland seeks to implement the schedule of the WFD, the maintenance of HSW is now accepted as being of paramount importance, especially in light of the steady decline reported by the EPA.

1.2   Objectives

The main objective of this thesis was to derive a soil-specific P management strategy to optimise the use of P-containing fertiliser on soils with an elevated concentration of OM with-a-view to minimising the risk of P loss to surrounding waters. The specific aims undertaken to achieve this objective were to:

- Characterise and quantify P uptake and growth yield of high OM soils and to compare with mineral soils of similar P status (Chapter 3).

- Develop a model of the P cycle in organic soils that will help to better understand P assimilation, transformation and potential transfers to surrounding waters (Chapter 4).

- Assess different mitigation practices, such as P application rates and timing and frequency regimes, on incidental losses of P, both in runoff (Chapter 5) and leachate (Chapter 6) pathways, arising from soils rich in OM content.

1.3   Structure of the thesis

Chapter 2 comprises a literature review in which the use of P fertilisers on organic soils with an inherently low ability to sorb and retain this nutrient and the subsequent risk of P losses to the surrounding water bodies, is discussed.

Chapter 3 focuses on the quantification of the grass response to increasing P fertiliser applications in six soils with different amounts of OM in a pot experiment. These responses are evaluated using the Mitscherlich equation with-a-view to developing appropriate strategies for P applications that optimise biomass and herbage P content and reduce the potential risk to water quality.

Chapter 4 assesses, using the same six soils of Chapter 3, the changes in the different soil P fractions receiving increasing amounts of P fertiliser, and examines which pools acted as sinks or sources for P so as to gain a better understanding of the soil P cycle.

Chapter 5 evaluates P concentrations in runoff from a rainfall simulation experiment, where P was applied as single and "split" applications and at different P doses. Additionally, the decay rate and persistence of P losses in overland flow derived from the different P applications in this rainfall experiment is assessed.

Chapter 6 compares leaching losses of P and nitrogen (N) from two soils of contrasting OM content receiving different doses of dairy slurry in one single application or split in two, and determines the potential risk of nutrient loss arising from these slurry applications on the leached water.

Finally, Chapter 7 presents the overall conclusions of the previous chapters, in addition to recommendations for further research in this topic.

1.4   Contribution to existing knowledge

1.4.1   Peer-reviewed publications (published)

To date, two international peer review papers have been published from this work, based on Chapters 3, 4 and 5:

- **González Jiménez, J.L.,** Healy, M. G., Roberts, W. M., Daly, K., 2018. Contrasting yield responses to phosphorus applications on mineral and organic soils from extensively managed grasslands: Implications for P management in high ecological status catchments. *Journal of Plant Nutrition and Soil Science*, 181, 861–869. doi:10.1002/jpln.201800201.

- **González Jiménez, J.L.**, Healy, M. G., Daly, K., 2019. Effects of fertiliser on phosphorus pools in soils with contrasting organic matter content: A fractionation and path analysis study. *Geoderma,* 338, 128-135. https://doi.org/10.1016/j.geoderma.2018.11.049Get

- **González Jiménez, J.L.**, Daly, K., Roberts, W. M., Healy, M. G., (2019). Split phosphorus fertiliser applications as a strategy to reduce incidental losses in surface runoff. *Journal of Environmental Management*, 242, 114-120. http://doi.org/10.1016/j.jenvman.2019.04.046

Additionally, a third paper has been published as part of the project HARMONY of which this thesis is encompassed:

- Roberts, W. M., González Jiménez, J.L., Doody, D. G., Jordan, P., Daly, K., 2017. Assessing the risk of phosphorus transfer to high ecological status rivers: Integration of nutrient management with soil geochemical and hydrological conditions. Science of the Total Environment, 589, 25-35. https://doi.org/10.1016/j.scitotenv.2017.02.201

1.4.2   Peer-reviewed publications (under review)

The following paper based on Chapter 6 has been submitted to the Journal of Environmental Management and is currently under review:

González Jiménez, J.L., Daly, K., Roberts, W. M., Healy, M. G., (2019). Impacts of single and split dairy slurry applications on the column leachate of two soils with contrasting organic matter content. (Sumbitted to *Pedosphere*).

1.4.3 Conference papers (in proceedings)

- **González-Jiménez, J.L.,** Healy, M.G., Roberts, W.M., Daly, K. 2016. Grass yield and phosphorus fractions in organic soils. Organic Phosphorus in the Environment: Solutions for Phosphorus Security Conference. Oral presentation. September 5-9, Lake District, England.

As a result of this conference, a peer-reviewed paper with all the presenters has been published:

- George, T. S., Giles, C. D., Menezes-Blackburn, D., Condron, L. M., Gama-Rodrigues, A. C., Jaisi, D., Lang, F., Neal, A. L., Stutter M. I., Almeida, D. S., Bol, R., Cabugao, K. G., Celi, L., Cotner, J. B., Feng, G., Goll, D. S., Hallama, M., Krueger, J., Plassard, C., Rosling, A., Darch, T., Fraser, T., Giesler, R., Richardson, A. E., Tamburini, F., Shand, C. A., Lumsdon, D. G., Zhang, H., Blackwell, M. S. A., Wearing, C., Mezeli, M. M., Almås, Å. R., Audette, Y., Bertrand, I., Beyhaut, E., Boitt, G., Bradshaw, N., Brearley, C. A., Bruulsema, T. W., Ciais, P., Cozzolino, V., Duran, P. C., Mora, M. L,. de Menezes, A. B., Dodd, R. J., Dunfield, K., Engl, C., Frazão, J. J., Garland, G., **González Jiménez, J. L.**, Graca, J., Granger, S. J., Harrison, A. F., Heuck, C., Hou, E. Q., Johnes, P. J., Kaiser, K., Kjær, H. A., Klumpp, E., Lamb, A. L., Macintosh, K. A., Mackay, E. B., McGrath, J., McIntyre, C., McLaren, T., Mészáros, E., Missong, A., Mooshammer, M., Negrón, C. P., Nelson, L. A., Pfahler, V., Poblete-Grant, P., Randall, M., Seguel, A., Seth, K., Smith, A. C., Smits, M. M., Sobarzo, J. A., Spohn, M., Tawaraya, K., Tibbett, M., Voroney, P., Wallander, H., Wang, L., Wasaki, J., Haygarth, P. M., 2018. Organic phosphorus in the terrestrial environment: a perspective on the state of the art and future priorities. *Plant and Soil*, 427, 191-208.

The published journal papers are provided in Appendix A

Chapter 2
Literature review

2.1   Overview

Phosphorus is one of the most important elements for grass and animal health, and is typically applied as fertiliser to replace P exported in products (meat, milk, grass) in either chemical or organic (manure and/or slurry) forms. When applied in excess of crop requirements, it may transfer to surrounding water bodies via leaching and overland flow, causing eutrophication. With the intensification of agriculture, more marginal soils which may have a high content of OM are being brought into production. Organic soils, comprising mainly histosols and other related OM-rich soils such as histic and humic top horizons, typically have a high OM content, low pH and low Al and Fe content, and are therefore associated with a low P sorption capacity.

In this chapter, the use of P fertilisers on organic soils with an inherently low ability to sorb and retain this nutrient and the subsequent elevated risk of P losses to the surrounding water bodies are discussed. Current water quality legislation and agricultural practices, the use of P fertilisers, the P cycle in soils and organic soils in particular, and potential losses of P from organic soils are introduced, with-a-view to determining the main knowledge gaps concerning the efficient use of P in organic soils.

2.2   Background

The growth of the world's population has increased exponentially since the beginning of the industrial revolution and, despite dropping birth rates, is expected to increase to 8.6 billion by 2030, at an average growth rate of 1.1 % per year (UN, 2017; Pimentel, 2012). Predictions estimate that the world's population could stabilise or even begin to decrease before 2100 (Figure 2.1).

Population of the world
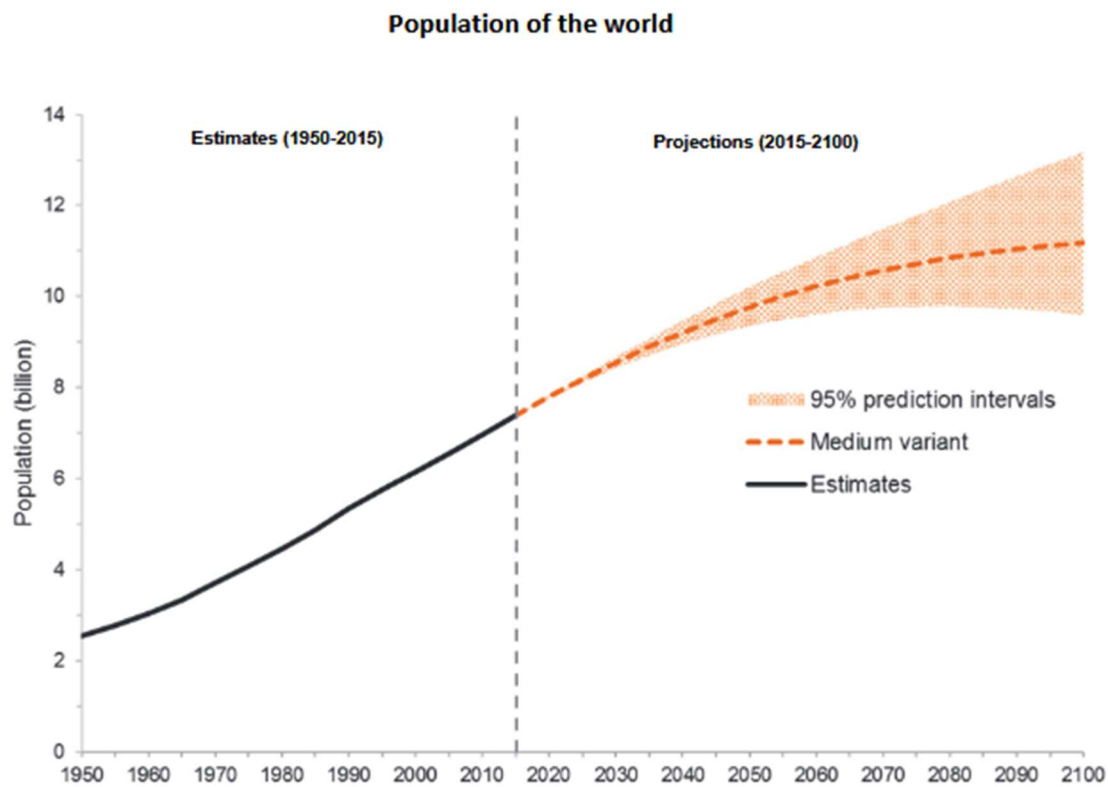
Figure 2.1. World's population prospects for the XXI century. Adapted from: UN (2017).

Food production has increased markedly since the Word War II, doubling or tripling in many places (FAO, 1996). Despite enhanced net agricultural production, per capita food production peaked in the mid-1980s and has remained practically constant since then (FAO, 2015). Currently, there are about 1.5 billion hectares under agricultural production, which has remained largely unchanged for the last three decades (Scherr, 1999). This means that food production increases are mainly due to the intensification of land use, and to lesser extent to the use of pesticides, irrigation and technological development, not from a net expansion of land. This increase in food and agricultural productivity has been achieved primarily due to the use of chemical fertilisers, mainly N and P compounds, which help to maintain and increase soil fertility after continuous cropping cycles. World fertiliser use has increased by approximately 700 % over the last 40 years (Foley et al., 2005), but has stabilised over the last decade in developed countries (Figure 2.2). For example, in the EU, the use of N for agriculture per year was approximately 11 Mt from 2011 to 2016, whereas the use of P for the same period was approximately 1.1 Mt (Eurostat, 2017).
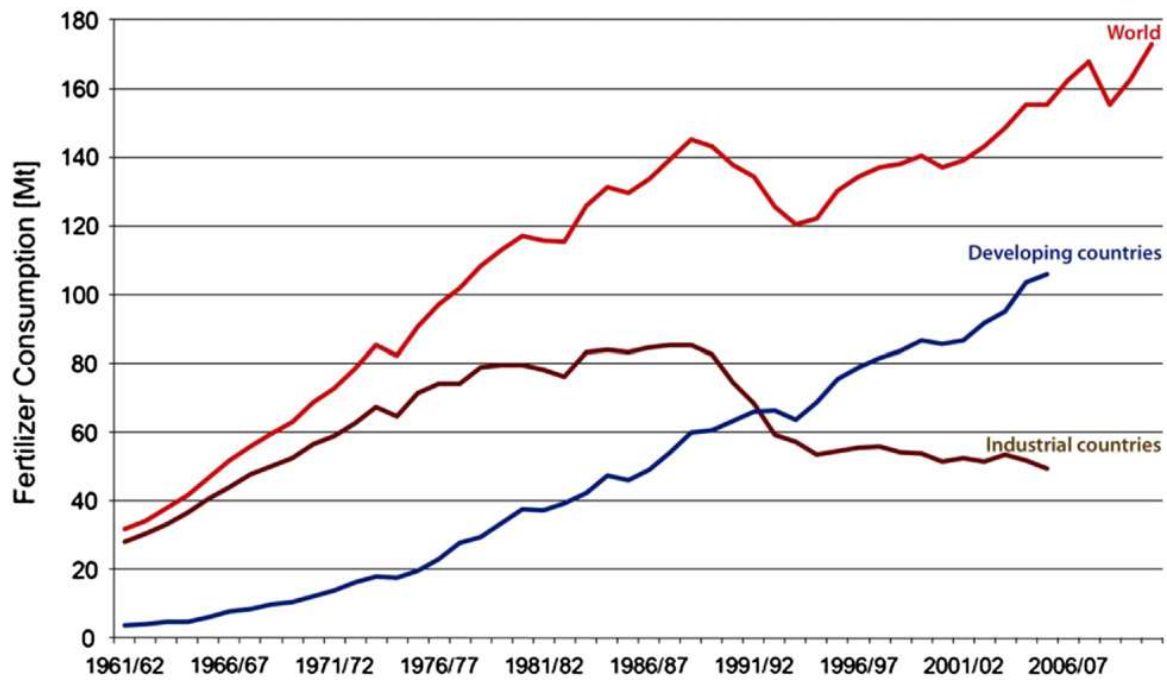
Figure 2.2. Trends of fertilizer consumption in the world, developing countries and industrial countries. Source: Scholz et al. (2013).

In Ireland, the average consumption of N and P mineral fertilisers was approximately 330,000 and 32,500 t, respectively, for the period 2011 to 2016 (Eurostat, 2017). With nearly 5 M ha of land under agriculture production (62 % of total land), managed grassland for dairy and beef cattle production is the predominant type of farming practiced, with more than 4 M ha used (CSO, 2016; DAFM, 2015). In line with the general intensification of agriculture in Europe (EEA, 2013), the Irish Government has enacted Food Harvest 2020 (FH2020; DAFF, 2010) and Food Wise 2025 (FW2025; DAFM, 2015), which aim to increase the agri-food industry's export value by 85% through the expansion of beef, dairy and seafood sectors.

2.3   Phosphorus in soils

Phosphorus is an essential nutrient for plant and animal growth. It plays a key role in fundamental biochemical processes such as the formation of genetic material [deoxyribonucleic acid (DNA), ribonucleic acid (RNA)], energy transfer (adenosine triphosphate, ATP) and the formation of biological structures (phospholipids and

hydroxyapatite) (Tiessen, 2008). Biological productivity depends on an adequate supply of P to the photosynthetic organisms, which incorporates P (in the form of dissolved, mineral orthophosphate) into their tissues, with a subsequent transfer to the rest of the trophic networks. Orthophosphate can exist in three forms in the soil solution, depending on the soil pH, namely, $H_2PO_4^-$, HPO_4^{-2} and PO_4^{3-} (Figure 2.3). These anions are highly reactive with cations and/or positively charged soil surfaces, such as Al and Fe (hydro) oxides, clays or calcium (Ca^{2+})-bearing compounds (Ruttenberg, 2003).
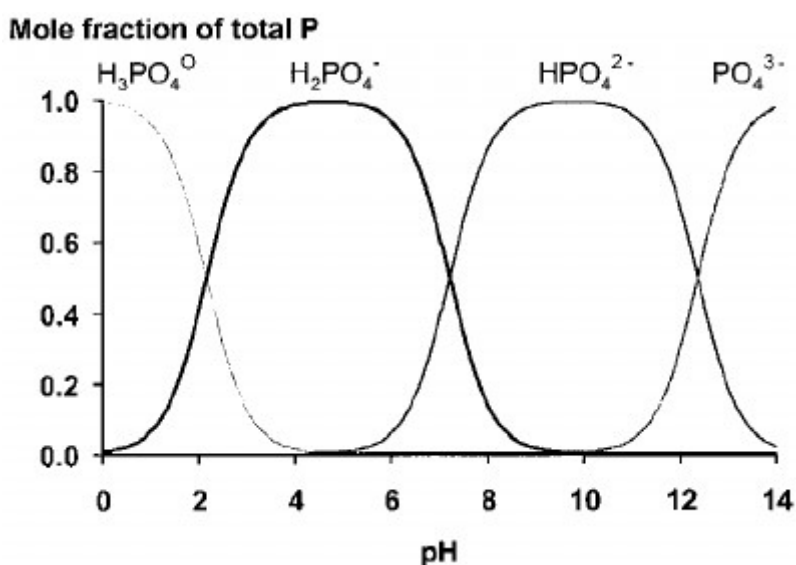
Figure 2.3. Speciation of orthophosphate ions (expressed as mole fraction of total P) in solution as a function of pH. Source: Hinsinger (2001).

The natural source of P in soils comes from the weathering of P-containing minerals [mainly apatite, $Ca_{10}(PO_4)_6(OH,F,Cl)_2$] during soil formation from the continental bedrock, whereby unavailable P is physically eroded and weathered through a series of biochemical reactions that eventually convert it to dissolved orthophosphate, available for plant and microbial uptake, returning to the soil by the decay of living organisms (Ruttenberg, 2003). These processes involved in the terrestrial P cycling can be inorganic or biological. Inorganic processes include physico-chemical reactions such as precipitation/disolution and sorption/reactions, whilst biological processes include active solubilisation of soil P minerals, followed by mineralisation and immobilisation reactions.

Briefly, dissolution-precipitaton processes require a source of H^+ to dissolve P-containing primary minerals (apatite), which can originate from the soil itself or from biological sources

(microbes or plant roots exhudates). The dissolution output releases orthophosphate ions that can precipitate with cations. Depending on the soil pH, the most common are Ca^{2+} (in alkaline soils), and Fe^{3+} and Al^{3+} (in acidic soils). Sorption and desorption reactions control the equilibrium of the orthophosphate ions between the soil surface and the soil solution. Orthophosphate ions adsorb to the surfaces and edges of clay minerals, hydrous oxides, and carbonates by replacing OH^- groups. Adsorption of orthophosphate in the soil is usually enhanced by the presence of metal oxides of Fe or Al, clay minerals, organic ligands or tertiary complexes of humic compounds with metal cations (Sims and Pierzynski, 2005; Frossard et al., 1995).

These processes leave concentrations of orthophosphate in the soil solution to be typically very low (as low as 10 μg L^{-1}) (Johnston et al., 2014), and therefore can severely limit crop productivity if inputs of P are not applied to replace the P exported in the crops (Hedley and McLaughlin, 2005). Bioavailable P needs to be added using soluble P-containing mineral and/or organic (slurry, manures) fertilisers to maintain an adequate supply of P to the crops. Pierzynski et al. (2005) presented a well-established soil P cycle (Figure 2.4), which includes external inputs of P (fertilisers), outputs (losses), as well as the internal cycling of P within the soil.
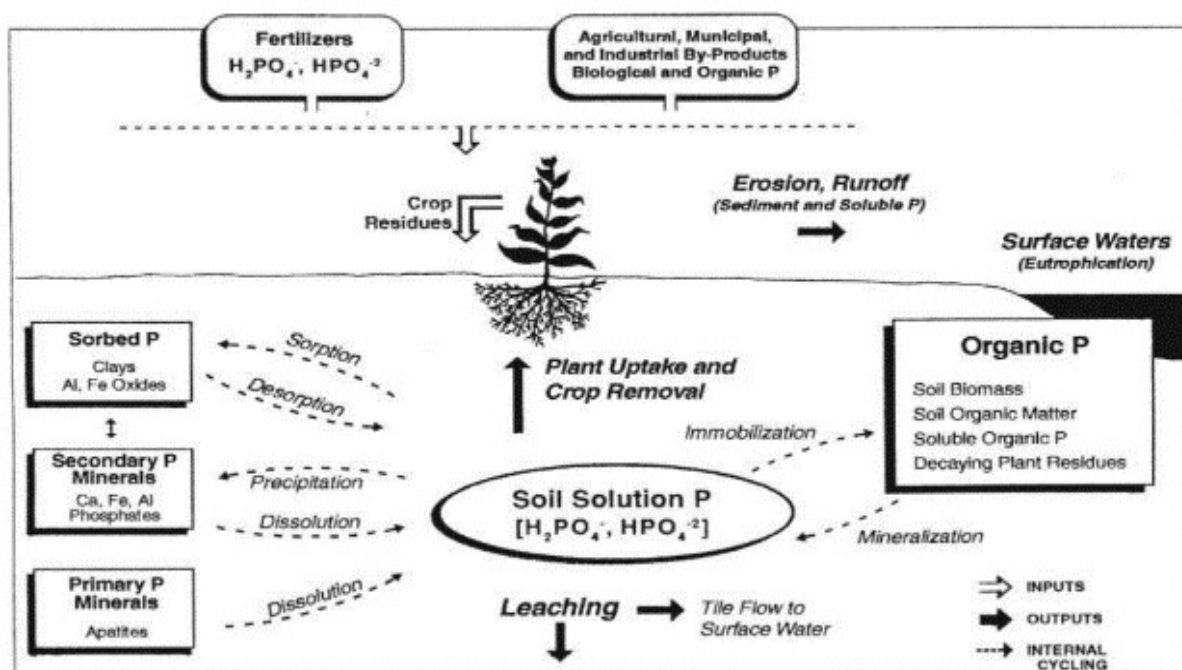
Figure 2.4. The soil P cycle. Source: Pierzynski et al. (2005).

This internal cycling encompasses the different dissolution-precipiation (mineral equilibria), sorption-desorption (interaction between P in solution and soil solid phase) and mineralization-inmmobilization (biologically-mediated conversion of P between inorganic and organic forms) processes discussed above.

The different forms of P in the soil change dramatically with time, soil development and land use management. The simplest classification of P in soils can be grouped into labile (readily available) and non-labile (not readily bioavailable) forms. The labile forms include P dissolved in the soil pore spaces, P adsorbed onto soil particle surfaces (termed *non-occluded P*), as well as P incorporated in the soil OM. The non-labile P forms include P in the primary minerals (such as apatite) and P co-precipitated with and/or adsorbed onto Fe, Al and, to a lesser extent, manganese oxyhydroxides (termed *occluded P*). With time, and depending on the soil development and the land use, the different soil P forms are released from the most recalcitrant, non-labile forms to more labile forms (Figure 2.5). The total amount of P in the soil reduces with time due to the loss of P from the soil profile to the surrounding environment. At the late stage of soil development, soil P is dominated by organic P and occluded P (Cross and Schlesinger, 1995; Yang and Post, 2011).
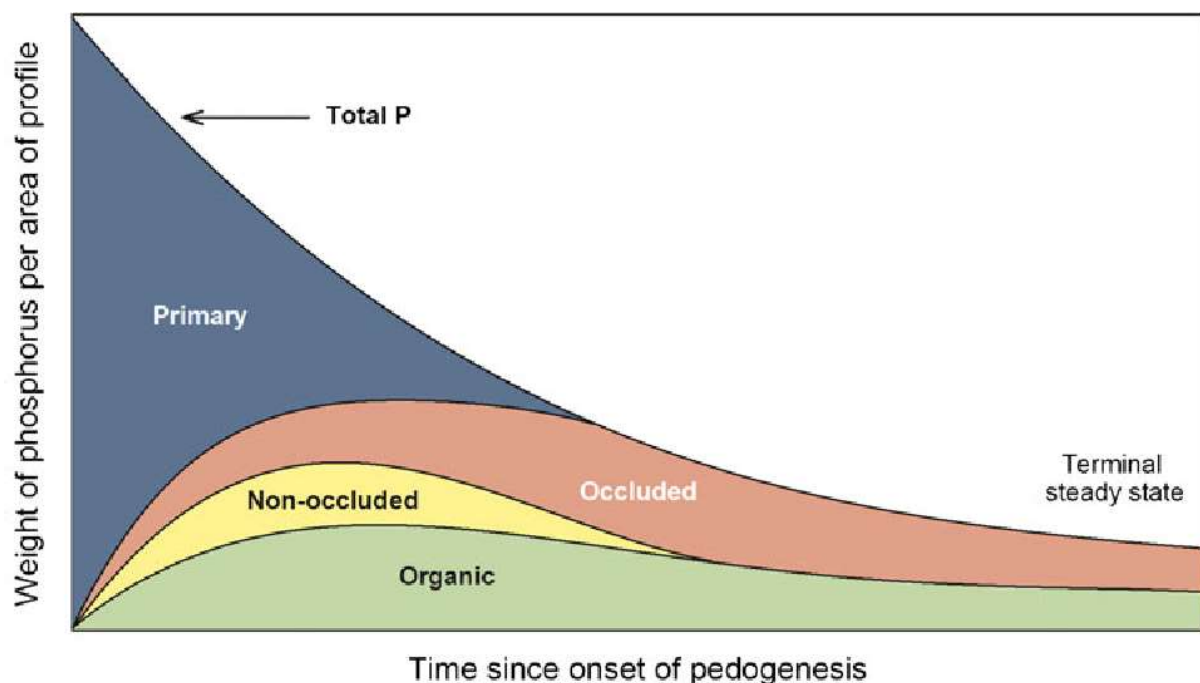
Figure 2.5. Walker and Syers (1976) conceptual model of soil P changes over time. Source: Turner and Condron (2013).

2.4 Phosphorus transport from soil to the surrounding environment

The mobilisation of P from the soil profile to waters includes different processes (erosion, point and non-point sources) and pathways, and may be in different forms (dissolved P, particulate P). The two main pathways of P transfer are overland flow (runoff) and subsurface flow (leaching), and include different chemical, biological and physical mechanisms that are conceptualised as the "transfer continuum model" by Haygarth et al. (2005) (Figure 2.6). In brief, this model includes a *source* of P (mineral and organic fertilisers, or native soil P) susceptible to be *mobilised* from the source by geochemical, biological and/or physical processes, *delivering* P through aquatic vectors that eventually will *impact* on the water quality, adversely affecting surface and groundwater quality.
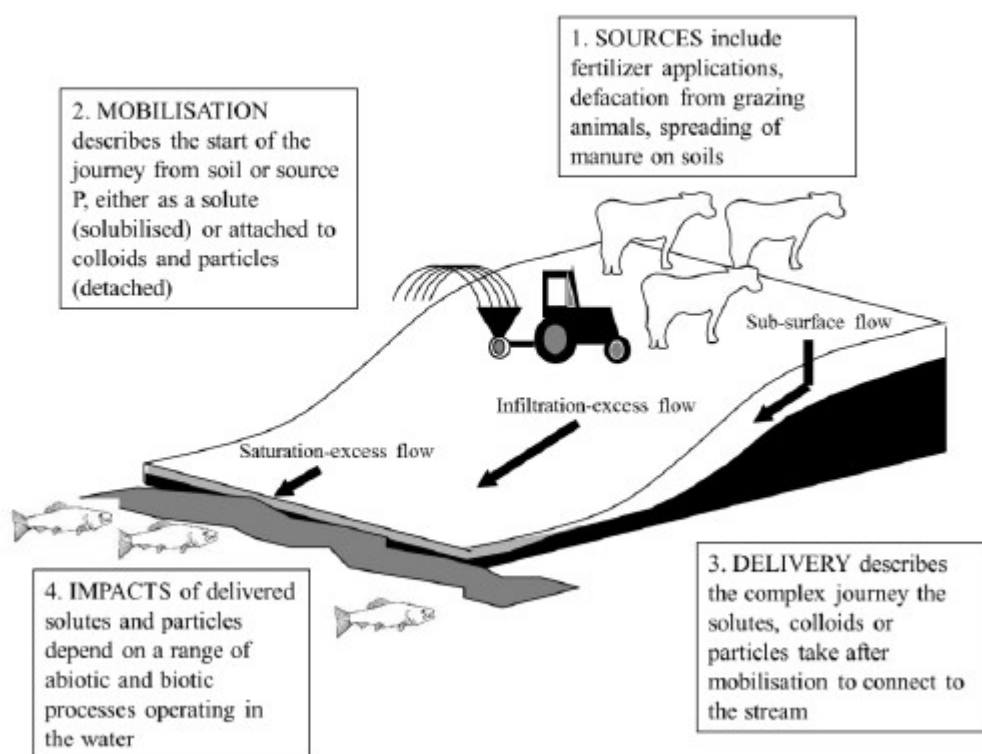
Figure 2.6. The phosphorus transfer continuum. Source: Withers and Haygarth (2007).

Atmospheric deposition is considered to be a minor pathway (Mcdowell et al., 2009). Runoff transport occurs in soils whose moisture storage capacity is saturated and/or when the rainfall

rate exceeds the hydraulic conductivity of the soil, resulting in an accumulation of water on the surface (Kollet and Maxwell, 2006). Although erosion is linked to surface flow of water, which is associated with the transfer of P sorbed onto the soil particles (Kleinman et al., 2009; Hart et al., 2004), dissolved P can be a significant form of P in the runoff water, especially in pastoral land (Hart et al., 2004).

Phosphorus exports in leaching processes are more difficult to quantify and considered to be less relevant when compared to surface flow (Sharpley et al., 1999). However, due to the higher periods of contact between the water and soil matrix, subsurface flow can be a significant path of P loss, especially if the soils have low P sorption capacities (McDowell and Condron, 2004). On the other hand, soils that tend to have cracks and large macropore networks can show significant losses of P in water due to the formation of preferential flow pathways where large amounts of water flow (Litaor et al., 2006; Hart et al., 2004).

2.5 Impacts of agriculture on water quality

Phosphorus fertiliser applications were initially regarded to be immobilised in agricultural soils, so that additions of P in excess of the crop requirements would not pose a threat to the environment due to losses (Haygarth and Jarvis, 1999). However, it is now accepted that P accumulated in the soil from previous fertiliser applications and freshly applied P from organic or mineral fertiliser can be lost from the soil and reach surrounding water bodies (Hart et al., 2004). Phosphorus can enter streams from point and nonpoint sources. Point sources, such as effluent from sewage treatment plants and industrial factories, are easy to detect and therefore have been reduced considerably over the last decades (Haygarth and Jarvis, 1997; Sharpley and Rekolainen, 1997). Nonpoint sources are much more difficult to identify and control, and constitute significant P transfers to waters thorough surface and subsurface pathways, as well as in eroded sediments (Kleinman et al., 2009; Preedy et al., 2001).

Phosphorus (and N) derived from excess fertilisation is the main cause of water quality degradation caused by a well-known process called *cultural eutrophication*. Under natural conditions, lakes and streams typically have very low levels of P, resulting in clear waters, limited growth of algae and other aquatic plants, allowing a diverse community of organisms to thrive. When P arising from agricultural activities reaches these pristine waters, either dissolved or sorbed onto the soil particles, it stimulates excessive growth of algae and other

plants which eventually die, deposit at the bottom of the water body, and are decomposed by microorganisms that consume and deplete the oxygen dissolved in the water, jeopardising the growth of the fish community and other aquatic organisms. Additionally, some of these algal blooms are caused by the *Cyanobacter* group, which produce toxins and therefore render the water unsuitable for human consumption (Weil and Brady, 2016).

In Ireland, eutrophication is still the main problem causing quality degradation of Irish water bodies. In a recent report from the Environmental Protection Agency (EPA), it is stated that "the number of river sites with phosphorus concentrations needed to support high-quality rivers dropped from 58% in 2014–2016 to just over 48% in 2015–2017" (Figure 2.7). There is also an increase in the percentage of sites with higher P concentrations that could lead to pollution, from 26.6% to 37.2% over the respective time periods (EPA, 2018).

2.6   Legislation

To protect water quality, the EU WFD 2000/60/EC came into force in December 2000 with the intention of establishing commonality among member states for water quality monitoring and management toward the protection and improvement of Europe's water bodies (OJEC, 2000). The principal objectives of the WFD are to maintain 'high' and 'good' water quality status, where it exists, and to achieve at least 'good' status for all waters by 2015. High status water bodies are those reflecting minimally disturbed ecological conditions (called *reference conditions*; Pardo et al., 2012), and are sensitive even to small anthropogenic activities such as extensively managed grasslands with low P inputs (Roberts et al., 2016; Ni Chathain et al., 2013).

The WFD incorporates previous policies such as the Nitrates Directive (OJEC, 1991), aimed to protect water quality by implementing sustainable farming practices to minimize nutrient losses from agricultural sources. Each member state implemented a series of Programmes of Measures (POMs) through a Nitrates Action Program (NAP). In Ireland, the "closed period" has been imposed under the NAP, during which landspreading of slurry and fertilisers from the 15th October to 12th/15th/31st January is prohibited, the exact dates and duration of the closed period depends of which part of the country in which a farm is located. Fertiliser applications are also prohibited within a 48-h period when heavy rainfall is forecast to prevent excessive nutrient losses in runoff to water bodies.
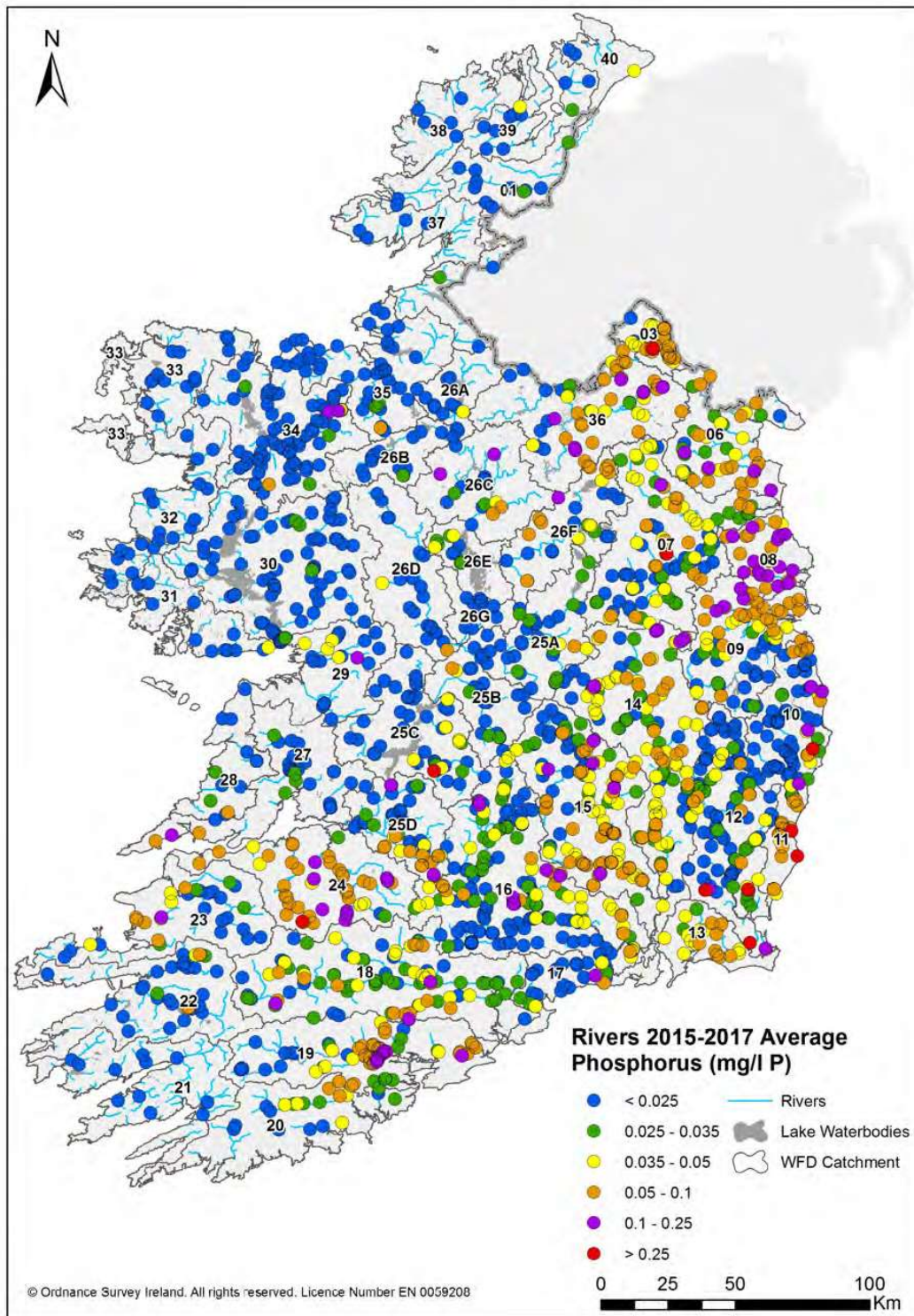
Figure 2.7. Average phosphate concentrations at river sites for the period 2015-2017. Source: EPA (2018).

Phosphorus fertiliser recommendations in Ireland are based on (1) a national P index that classifies mineral soils into *deficient, low*, *optimum* and *excessive* in available P using Morgan's

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P extractant as a soil P test and reflect how likely a crop will respond to fertilisations, and (2) minimum herbage P concentration of 3 g kg^{-1} that ensures dietary requirements for ruminants. The ranges of the P index system for grassland are shown in Table 2.1 (Coulter and Lalor, 2008; Schulte and Herlihy, 2007). Additionally, there is a positive relationship between soil Morgan's P levels and the risk of P loss to waters, so that soils classified as *deficient/low* in the national P index system are deemed to have low risk of P losses to the environment, whereas soils classified as *optimum/excessive* may pose an elevated risk of P transfer. This measurement is aimed at maintaining a zero farm-gate P balance (imports and exports of P are equal to zero on a farm-scale) and to optimise P levels in soils to within agronomic level (SI No 31 of 2014). The Morgan's P test is the national soil test for bioavailable P in Ireland, and is carried out routinely using a volume of dried and sieved soil, rather than on a weight basis, which is the normal procedure for other soil P tests such as Mehlich-3, Olsen P, etc. Therefore, Morgan's P test results are expressed in mg L^{-1}, and can be easily converted to mg kg^{-1} using bulk densities.

Table 2.1. Soil P index system for grassland in Ireland.

Soil P Index	Category	Soil P values[1]	Response to fertiliser	Determination of P fertiliser application rate
1	deficient	0 - 3	Definite	Build-up[2] + maintenance[3]
2	low	3.1 - 5	Likely	Build-up[2] + maintenance[3]
3	optimum	5.1 - 8	Unlikely/tenuous	Maintenance
4	excessive	> 8	None	P application not recommended

[1] Morgan's P test (mg l^{-1}).

[2] Build-up fertiliser rates for grassland are 20 kg ha^{-1} y^{-1}, at index 1, and 10 kg ha^{-1} y^{-1} at index 2.

[3] Maintenance depends on stocking rates, farming systems and grassland usage.

2.6.1   High status water bodies in Ireland

Article 8 of the WFD requires Member States to ensure the establishment of monitoring programme networks to establish a comprehensive overview of the water quality status of the different water bodies. Due to logistics and other considerations, not all the Irish surface water bodies are included in that network, and currently only 1937 river water bodies and 222 lake water bodies are directly monitored by the EPA. This monitoring network establishment has allowed the assessment of Irish rivers over a long period and it enables trends in the quality of river waters to be viewed over the last two decades. The analysis of these trends shows that there has been a substantial loss in the number of sites where the highest quality river sites are

found (i.e. *Q-value* of 5). In the most recent monitoring period (2013-2015), only 21 sites were classified as the highest quality rivers (0.7% of sites) compared with 575 between 1987 and 1990 and 82 between 2001 and 2003 (Figure 2.8).
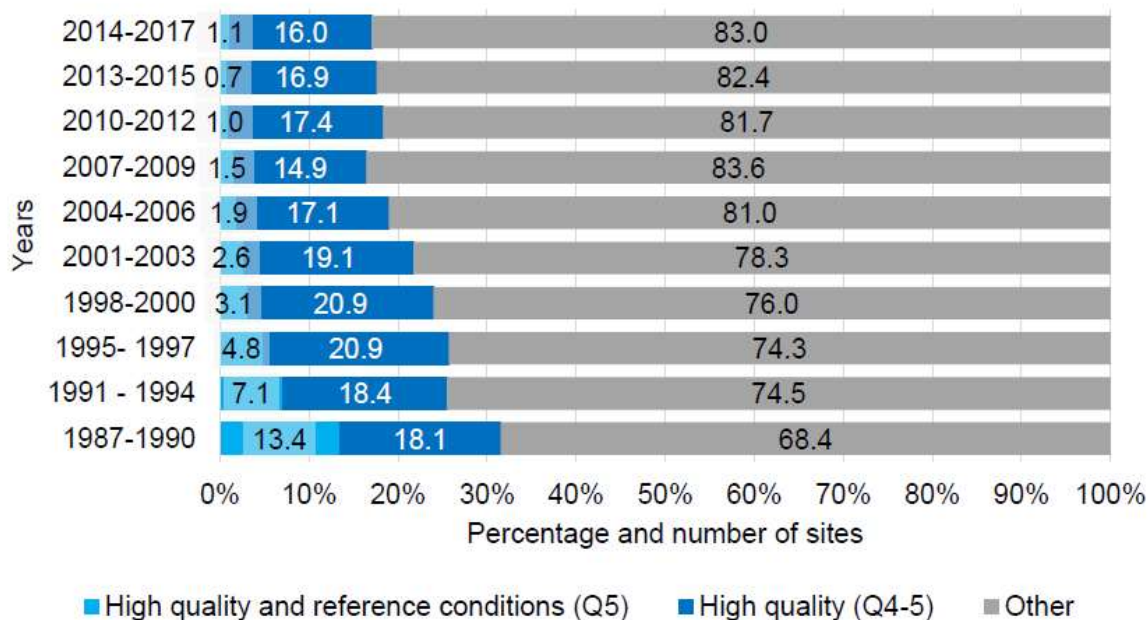
Figure 2.8. Long term trends (1987-2017) in the percentage number of High Ecological Quality River sites (Q5 and Q4-5) in each survey period. Source: EPA (2018).

Similarly, Roberts et al. (2016) reported that, from a total of 508 sites classified as "high ecological status" by the EPA during a period from 2001 to 2012, 337 had reduced to "good status" or below, and only 171 sites maintained "high status". Figure 2.9 shows the distributions of these sites. In a recent report by the EPA, it is stated that, despite a slight decrease in P concentrations observed in Irish rivers over the period 2007-2017, "these improvements in phosphate concentration have not been sufficient to lead to a discernible improvement in the ecological quality of the associated rivers" (EPA, 2018).

Ni Chathain et al. (2013) reported that the highest rates of decline (between 1998 and 2006) occurred from counties Cavan, Clare, Cork, Donegal, Galway, Mayo and Sligo. Most of these sites are located in upland areas characterised by extensively farmed land. The EPA report (EPA, 2018) also supports this observation, stating that the largest number of high-quality sites continues to be in the less densely populated and less intensively farmed regions in the west and south west.

Figure 2.9. Distribution of the 508 river sites for the monitoring period 2001- 2012. Transparent circles indicate sites that have varied in status and opaque circles indicate sites that have maintained high status. Adapted from Roberts et al. (2016).

Ni Chathain et al. (2013) hypothesised that "relatively low intensity activities" can become a significant pressure and have a disproportionate impact on high status sites relative to the same pressure on an already degraded system. Whilst agricultural nutrients are a pressure on water quality, a catchment's response to this pressure is driven by the mosaic of soil types that characterise the source and hydrology in a catchment. For example, Melland et al. (2012) report that despite similar farming intensities in two catchments in Ireland, winter P export from one catchment was four times higher, largely owing to variations in catchment characteristics such

as soil drainage and hydrology.In another catchment study in Ireland, Schulte et al. (2009) found that the predominant peat and clay soils in the catchment contributed as source and transport factor to P transfers from land to water due to poor P retention of peats and the impeded drainage characteristics of clay soils.

More recent reports have documented that it is in these upland areas where HSW under extensive grassland enterprises are more vulnerable to loss of high ecological status (Roberts et al., 2016; White et al., 2014). It is generally accepted that the predominant soils of these upland areas are peat soils, peaty gleys and peaty podzols. These organic soils, comprising mainly histosols and other related OM-rich soils such as histic and humic top horizons (Creamer et al., 2014), typically have a high OM content, low pH and low Al and Fe content, and are therefore associated with a low P sorption capacity (Gerke, 2010; Kang et al., 2009; Guppy et al., 2005; Daly et al., 2001).

2.7 Peat soils, Organic soils and Histosols

These soils are predominantly composed of organic material, ranging from pure organic-rich soils, namely peat soils, to other transitional or organo-mineral soils where the content of OM is less than peats but still high, for instance, peaty loams and peaty sands (Figure 2.10). Organic soils are often derived from partially decomposed wetland vegetation where plant debris accumulated over long periods of time in flooded conditions, before the land was drained for agricultural production (Okruszko and Ilnicki, 2003). These soils are generally moderately acidic with low content of clay minerals and Al and Fe oxides, and are characterised by poor P sorption and buffering capacities (Guppy et al., 2005; Daly et al., 2001).
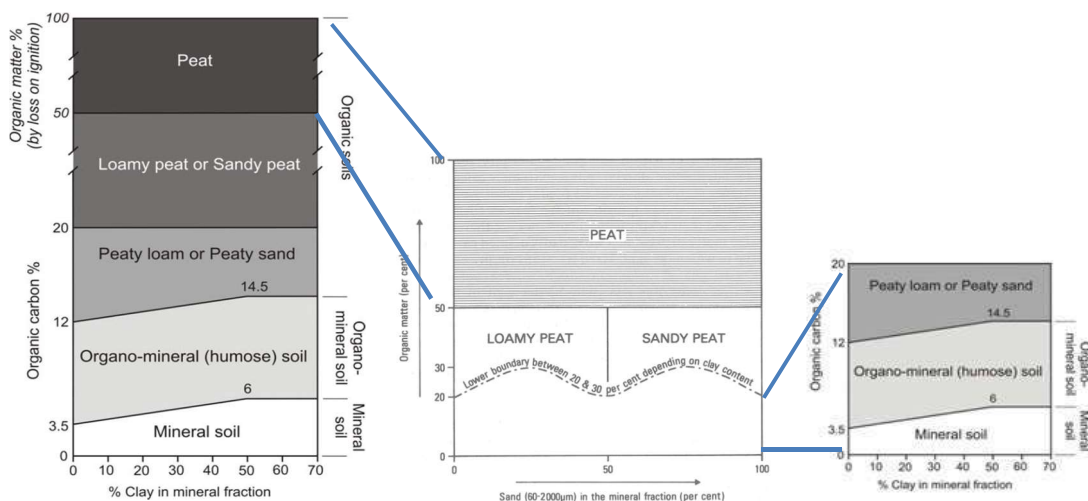
Figure 2.10. Limiting proportions of organic matter (or organic carbon) and clay content in organic and organo-mineral (humose) soils. Adapted from Creamer et al. (2014).

The definition of peat as a soil differs from one soil classification system to another. For example, the Soil Survey of England and Wales define peat soils as predominantly organic soils derived from partially decomposed plant remains that accumulated under waterlogged conditions. Only two groups are distinguished (blanket bog and fens). They are subdivided into oligo- (moist pH<4.0); eutro- or Eu- (pH>4.0 in some part); fibrous (mainly fibrous or semi-fibrous); -amorphous (mainly humified) and sulphuric (sulphuric subsoil within 80 cm depth) subgroups (Avery, 1980). The World Reference Base (formerly FAO–UNESCO scheme) refers to peat soils as Histosols and defines them as soils with a H horizon (well decomposed litter, often mixed with mineral matter, in which the original plant structures cannot be seen) of 40 cm or more (60 cm or more if the organic material consists mainly of sphagnum or moss, or has a bulk density of less than 0.1) either extending down from the surface or taken cumulatively within the upper 80 cm of the soil. The thickness of the H horizon may be less when it rests on rocks or on fragmental material of which the interstices are filled with OM (IUSS Working Group WRB, 2014). The definition of peat soil from the Irish EPA is as "organic soil materials which have sedentarily accumulated and have at least 30% (dry mass) OM over a depth of at least 45 cm on undrained land and 30 cm deep on drained land; the depth requirement does not apply in the event that the peat layer is over bedrock" (Renou-Wilson et al., 2011).

Peatlands cover approximately 4 million km^2 of the world's surface and represent a third of the global wetland resources. They are found predominantly in the boreal, subarctic and tropical zones (Eurasia and North America), although they can be also found in places such as Patagonia, Ethiopia, Table Mountain in South Africa, Mongolia and Iran (Parish et al., 2007). In Europe, they represent about 7 % of the total land area, with Finland (9.84 M ha), Sweden (9.08 M ha), United Kingdom (4.45 M ha) and the Republic of Ireland (1.27 M ha) among the countries with the largest areas covered by this soil type (Montanarella et al., 2006). Under natural, undisturbed conditions, these soils deliver important ecological services such as acting as net carbon store and sinks, flood mitigation and supplying clean water, as well as being major contributors of biological diversity. However, peat soils have been degraded at different degrees all over the world by human activities to provide new resources such as agricultural

land use, cattle ranching, forestry and peat extraction, among others (Renou-Wilson et al., 2011).

2.7.1 Organic soils in Ireland

Peat soils comprise 1.46 M ha (20.6 % of the total area) of land in the Republic of Ireland (Renou-Wilson et al., 2015). Peatlands are typically classified in two different categories, depending on the topography at which they are formed and the availability of nutrients in the water supplying plant growth (Renou-Wilson et al., 2018, 2015, 2011; Hammond, 1981). These are:

- Basin peats: formed at low altitudes (close to sea level) and comprising two types – fen peats (approximately 20,120 ha) and raised bogs (approximately 311,000 ha). Agriculture has been typically the predominant land use for the former and peat cut and extraction for the latter.
- Blanket peats: formed at higher altitudes (around 200 above sea level) under conditions of high rainfall and humidity, and accounts for approximately 774,000 ha (66 % of the total peat area). Forestry is the traditional use of this type of peat due to its poor nutrient status.

Ireland has a mild climate with relatively high rainfall and number of rain days per year that have been important in promoting peatland formation and development. Raised bogs form where rainfall is between 700 mm and 1000 mm and the number of rain days is between 150 and 175 per year (Bord na Mona, 2001). Blanket bogs form where rainfall is greater than 1250 mm and the number of rain days is greater than 200 per year. Additionally, the country generally has poor draining soils, which had a major influence in the formation of peatlands. After the last Ice Age, many of the hollows or basins, particularly in the central plain, had poorly draining soil which were mainly composed of silty clays. These soils led to waterlogging of the soil surface and the formation of lakes where a variety of plants grew annually. As the cycle of growth of vegetation and partial decay continued, peat formed at the bottom of the lakes each year and this led to the development of extensive peatlands (Bord na Mona, 2001).

2.7.2 Management of organic soils in Ireland

The vast majority of peat soils in Ireland have been altered by anthropogenic activities. Among them, drainage for agricultural use is one of the predominant activities (Table 2.2), and

reclamation of organic soils for grassland land use has increased in the last century as a consequence of the intensification of agriculture through the European Common Agriculture Policy (CAP). Organic soils under grassland are predominantly used for grazing, with different levels of improvement. Improved grasslands are artificially drained, fertilised, occasionally reseeded, and heavily grazed. They are by far the most widespread type in Ireland and are typically abundant in the Midlands, often over previously exploited raised bogs. Unimproved grassland is extensively managed, with limited inputs of fertiliser, usually not reseeded and richer in species, and tends to be located in the west of Ireland and in upland areas where HSW are likely to occur (Renou-Wilson et al., 2015).

Table 2.2. Estimated areas of main peatland land use in Ireland. Adapted from Renou-Wilson et al. (2018).

Land Use	Area (ha)
Agriculture	
Grassland	300000 - 374690
Arable	1235
Forestry	321927
Peat extraction	
Industrial	67715-100000
Domestic	260000-600000
Abandoned	> 20000

While FH2020 and FW2025 promote agricultural intensification in a sustainable manner, they inevitably require reclamation of more marginal land in sensitive catchments, such as new semi-natural organic soils and the intensification of unimproved grasslands through the increase of fertiliser inputs on these soils.

Phosphorus fertiliser recommendations for peats and organic soils are not the same as for mineral soils due to the diminished P adsorption ability of these soils (Section 2.7). Inputs of P fertiliser cannot exceed the amounts permitted for index 3 for the mineral soils, irrespective of whether the organic soil has been classified as index 1 or 2 (Table 2.1) (Coulter and Lalor, 2008). Additionally, it has recently been reported that Morgan's extractant, the soil test used to

assess the amount of available P in Ireland, overestimates P availability in organic soils and therefore is not a suitable indicator of P status in these soil types (Roberts et al., 2017).

2.8   Phosphorus losses from organic soils

Once drained for agricultural production, organic soils undergo a series of transformations directly linked to the change in the redox condition. These transformations include morphological and structural changes, enrichment in humic substances, changes in mineral composition, and microbial and mesofauna changes (Ilnicki and Zeitz, 2003).

Organic soils are generally acidic as a consequence of the polycarboxylic acids derived from the OM. The degree of acidification depends on the degree of decomposition and botanical composition of the OM. For example, humic and fulvic acids predominate in sapric peats (low proportion of recognizable plant fibres), whereas long-chain uronic acids and rich carboxyls are more common in fibric peats (high proportion of recognizable plant fibres) (Parent and Tremblay, 2003). The reported low inherent fertility in organic soils (Zheng et al., 2015; Zak et al., 2004) is directly linked to the acidity of these soils that immobilise some of the main macronutrients (N, P, K) for plant uptake (Figure 2.11).
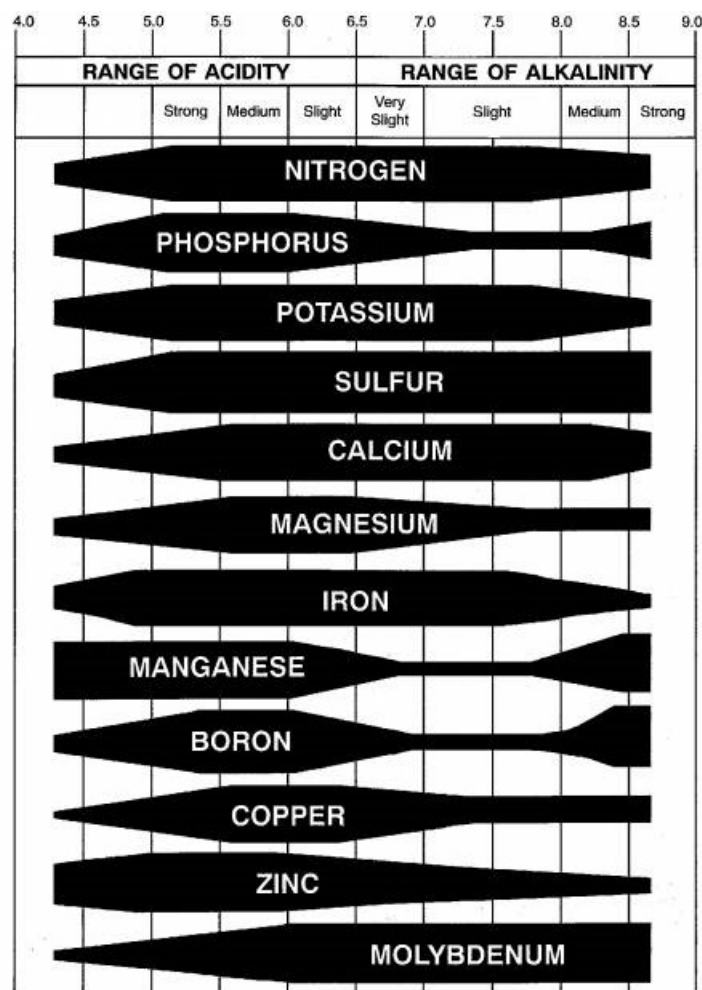
Figure 2.11. Nutrient availability in organic soils. Adapted from Lucas (1982).

As a pH-dependant, the cation exchange capacity (CEC) can be elevated in these soil types and thus they generally require high application rates of lime to reach soil optimum pH (5.5) for crop production (Coulter and Lalor, 2008; Rivière and Rivière, 2003). Other properties of organic soils include high hydrophobicity, low bulk density, high C/N ratio and high total water capacity (Rivière and Rivière, 2003).

From all the properties of the organic soils mentioned, the most relevant for understanding added P behaviour in these soil types is the P retention ability. Phosphorus-bearing fertilisers contain water-soluble P that is available for plant uptake. This soluble P is in the form of orthophosphate (PO_4^{-3}) which interacts with the soil constituents.

In organic soils there is an elevated proportion of humic and fulvic acids (HA and FA, respectively) and low molecular weight aliphatic organic acids (LOA) derived from the partial

decomposition of the soil OM. As a consequence, competitive sorption reactions between HA, FA, LOA, and the added orthophosphate anions for the inherent scarce anion sorption sites occurs (Guppy et al., 2005; Zak et al., 2004; Daly et al., 2001). The main processes affecting the ability of soils to sorb P by these organic acids are represented in Figure 2.12.

Consequently, the commonly applied concept of "build-up and maintenance" for mineral soils (Voss, 1998; Olson et al., 1987), where a soil deficient in available P has first to increase its reserves before it becomes plant available, may increase the likelihood of P losses via leaching and/or runoff when applied to organic soils. Whilst some preliminary work suggests that organic soils under P fertilisation show similar herbage production than mineral soils (O'Connor et al., 2001), the relevance of the concept of build-up of soil P under P fertiliser applications in organic soils is poorly understood (Roberts et al., 2017; Daly et al., 2015, 2001).

Previous studies have shown that HA often possess a high content of aromatic carbon that can strongly complex metals, mainly by carboxylic and phenolic groups (Gerke, 2010). From a quantitative point of view, Al and Fe usually are the most dominant metals in soils. These metals can form stable and strong complexes with humic substances that, in turn, react with soluble orthophosphate, thereby forming tertiary P-metal-organic acid complexes that may enhance the ability to sorb and retain P in soils rich in OM (Gerke, 2010; Kang et al., 2009; Antelo et al., 2007; Giesler et al., 2005; Guppy et al., 2005;).

Therefore, there is a gap in our knowledge on the efficient use of P fertilisers for peats under the present soil P index system and the appropriate management of P mineral fertiliser and organic manures with regard to rates and timing of applications if over-applications are to be avoided. There is a paucity of data on these soils describing the mechanism of P cycling for plant uptake and the incorporation of applied P (slurry and fertiliser P) for crop growth in these soils.

Clearly, the rate of P fertiliser applications is among the main factors influencing P losses from agricultural land to waters (Sharpley et al., 2001). Thus, P inputs applied judiciously to match the crop P requirements should be considered a key step in reducing P losses. However, the concept of build-up that traditionally has been applied for mineral soils may not apply for organic soils. Therefore, the well-established relationship between increasing values of any soil P test (Olsen, Mehlich, etc.) and amounts of P lost from the agricultural land in mineral soils remains poorly understood for organic soils.
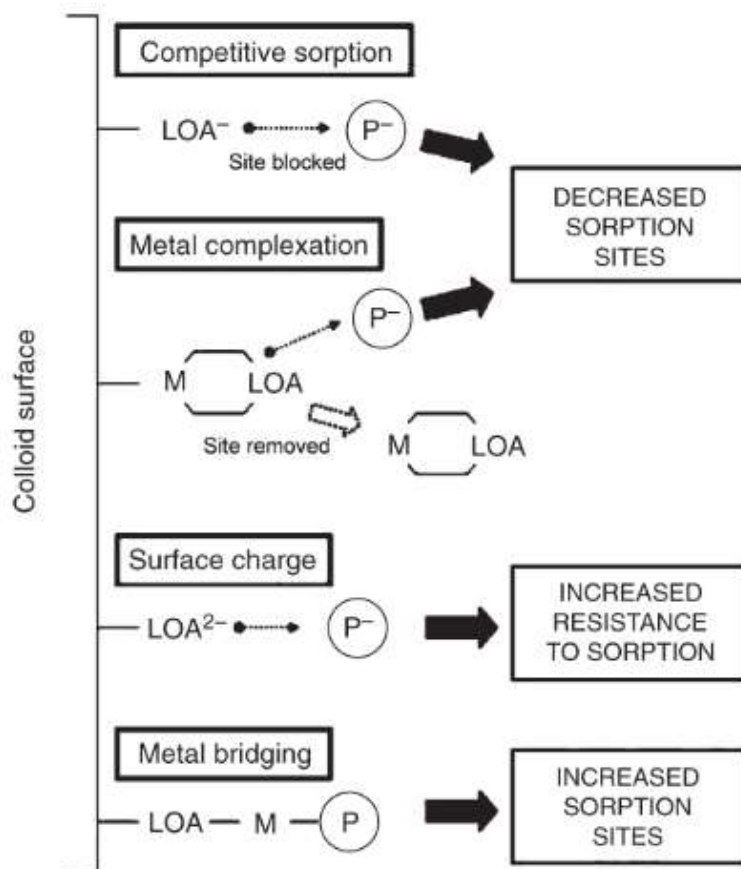
Figure 2.12. Direct effects of organic compounds on P availability. M, Metal (i.e. Fe or Al); LOA, low molecular weight organic acids. Source: Guppy et al. (2005).

The relationships between crop responses (yield) and P applications or soil P tests, whereby a critical value for yield is established beyond which no improvement in production is achieved whilst the risk of P losses increases exponentially (Figure 2.13), are not well understood in organic soils, and warrants further investigation in order to establish optimum P inputs for a more economic use and diminished environmental threat.
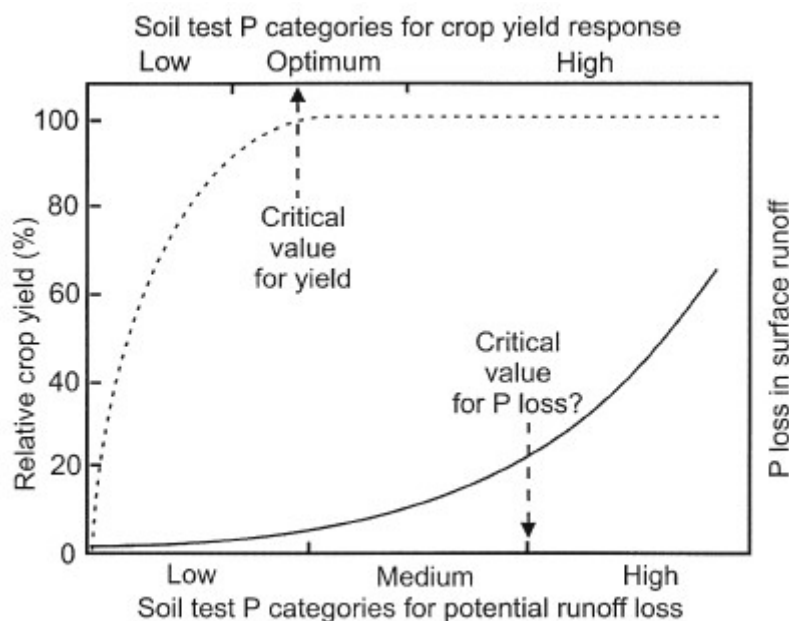
Figure 2.13. Relationships between crop yield, surface P losses relationship and soil P status. Source: McDowell et al. (2002).

Another important strategy proposed to mitigate P losses is the timing of P applications, by which multiple, but smaller, P applications with the same total P amount allocated for one single year are undertaken, in contrast to one single application. Previous research showed that single P application rates of 40 kg ha^{-1} resulted in disproportionally greater runoff P concentrations than three split applications of 13.3 kg ha^{-1} (Burkitt et al., 2011).

However, the authors determined that when the rainfall patterns were incorporated in the risk assessment (they used rainfall records from Australia, a country with defined and well-established rainfall seasons), the overall risk of P losses was greater for the split P applications in comparison to one single P application. Nonetheless, in temperate countries such as Ireland, frequent rainfall events occur across the whole year, with April, May, June and July being the months of least rainfall (national average of 80 mm per month). This increases to 100 mm in February, March, August and September (Walsh, 2012). The coincidence of rainfall events with P applications is therefore likely to occur in Ireland, so that smaller applications compared to one but big application could be regarded as a plausible mitigation for P losses.

2.9   Conclusions and knowledge gaps

In this chapter, an introduction to the terrestrial P cycle and the main processes controlling its mobility in soils was presented, alongside potential impacts on water quality caused by P losses from agricultural practices. The current legislation in Europe (primarily the WFD), and particularly in Ireland, indicates that the reclamation and use of marginal organic soils in agriculture are among the main sources causing impairment in HSW. This is due to their unique soil chemistry and the fact that they are frequently managed as mineral soils. The processes of P assimilation and transport of applied P fertilisers are poorly understood and merits further investigation in order to develop better management strategies if P losses are to be avoided.

The following knowledge gaps have been identified and will be addressed in the thesis:

- While P response experiments have typically been conducted on mineral soils for intensive grassland, little is known about the response of organic soils to P fertilisers. There is a knowledge gap on the efficient use of P for peats and other peat-derived soils under the current P index system.
- There is a paucity of data on these organic soils describing the mechanism of P cycling (assimilation) for plant uptake and the incorporation of applied P (slurry and mineral P fertiliser) for crop growth.
- There are deficiencies in our knowledge on the appropriate management of slurry and mineral P fertilisers with regard to rates and timing of applications in organic soils if over-fertilisation is to be avoided.

Chapter 3

Contrasting yield responses to phosphorus applications on mineral and organic soils from extensively managed grasslands: implications for P management in high ecological status catchments

3.1   Overview

The aim of this chapter is to examine and quantify grass responses to P fertiliser in soils with contrasting amounts in OM using the Mitscherlich equation, and to evaluate these responses with-a-view to developing appropriate strategies for P applications that optimise biomass and herbage P content and reduce the potential risk to water quality, especially in organic soils.

This study has been published in Journal of Plant Nutrition and Soil Science: González Jiménez, J.L., Healy, M. G., Roberts, W. M., Daly, K., 2018. Contrasting yield responses to phosphorus applications on mineral and organic soils from extensively managed grasslands: Implications for P management in high ecological status catchments. *Journal of Plant Nutrition and Soil Science*, 181, 861–869. doi:10.1002/jpln.201800201.

3.2   Introduction

Phosphorus is one of the most important elements for grass and animal health, and is typically applied as fertiliser to replace P exported in products (meat, milk, grass) in either chemical or organic (manure and/or slurry) forms. When applied in excess of crop requirements, it may transfer to the surrounding water bodies via leaching and overland flow, causing eutrophication (Carpenter, 2008).

Histosols account for soils with an elevated proportion of partially decomposed organic material derived from plants. In Ireland, approximately 66 % of this area is located in upper parts of mountain ranges (Renou-Wilson et al., 2011). It is in these upland areas where HSW under extensive grassland enterprises are more vulnerable to loss of high ecological status (Roberts et al., 2016; White et al., 2014). Organic soils, comprising mainly histosols and other related OM-rich soils such as histic and humic top horizons (Creamer et al., 2014), typically

have a high percentage of OM content, low pH and low Al and Fe content, and are therefore associated with a low P sorption capacity (Daly et al., 2001; Guppy et al., 2005; Kang et al., 2009). Consequently, the commonly applied concept of "build-up and maintenance" for mineral soils (Olson et al., 1987; Voss, 1998), where a soil deficient in P has first to increase its reserves before it becomes plant available, may increase the likelihood of P losses via leaching and/or runoff when applied to organic soils. Whilst some preliminary work suggests that organic soils under P fertilisation show similar herbage production to mineral soils (O'Connor et al., 2001), the relevance of the concept of build-up of soil P under P fertiliser applications in organic soils is poorly understood (Daly et al., 2015, 2001; Roberts et al., 2017).

Historically, crop production is based on the law of the diminishing returns, in which the yield response of a crop to incrementally increasing amounts of an applied nutrient asymptotically declines (Black, 1993). Among the different models used to explain these yield response curves, the Mitscherlich equation is one of the best available due to its inherent nature to represent biological concepts such as the maximum yield attainable and the efficiency of the added nutrient in increasing the yield or the initial fertility of the soil (Black, 1993).

This chapter evaluates grass response to increasing amounts of P fertiliser for better management in organic soils. A pot experiment under controlled conditions, in which six soils ranging in OM content received incrementally increasing P application rates, was conducted. Cumulative dry matter (DM) yield and herbage P concentration data were measured and evaluated to assess the use efficiency of P on organic soils.

3.3   Materials and methods

3.3.1   Soil Sampling

Soil samples were collected from six sites, representing predominant grassland soils in high status catchments in the Republic of Ireland. The sites selected included two sites at the River Black catchment in Co. Galway, two sites at the River Allow catchment in Co. Cork, and two sites at the River Urrin catchment in Co. Wexford (Figure 3.1) (Roberts et al., 2017). Using data from the farm survey conducted by Roberts et al. (2017), soils were selected based on their OM content and deemed to be deficient in P as no P fertiliser applications were made in the

years before soil collection, with the exception of Galway peaty mineral, which received an average of 32 kg P ha^{-1} the year before soil collection.
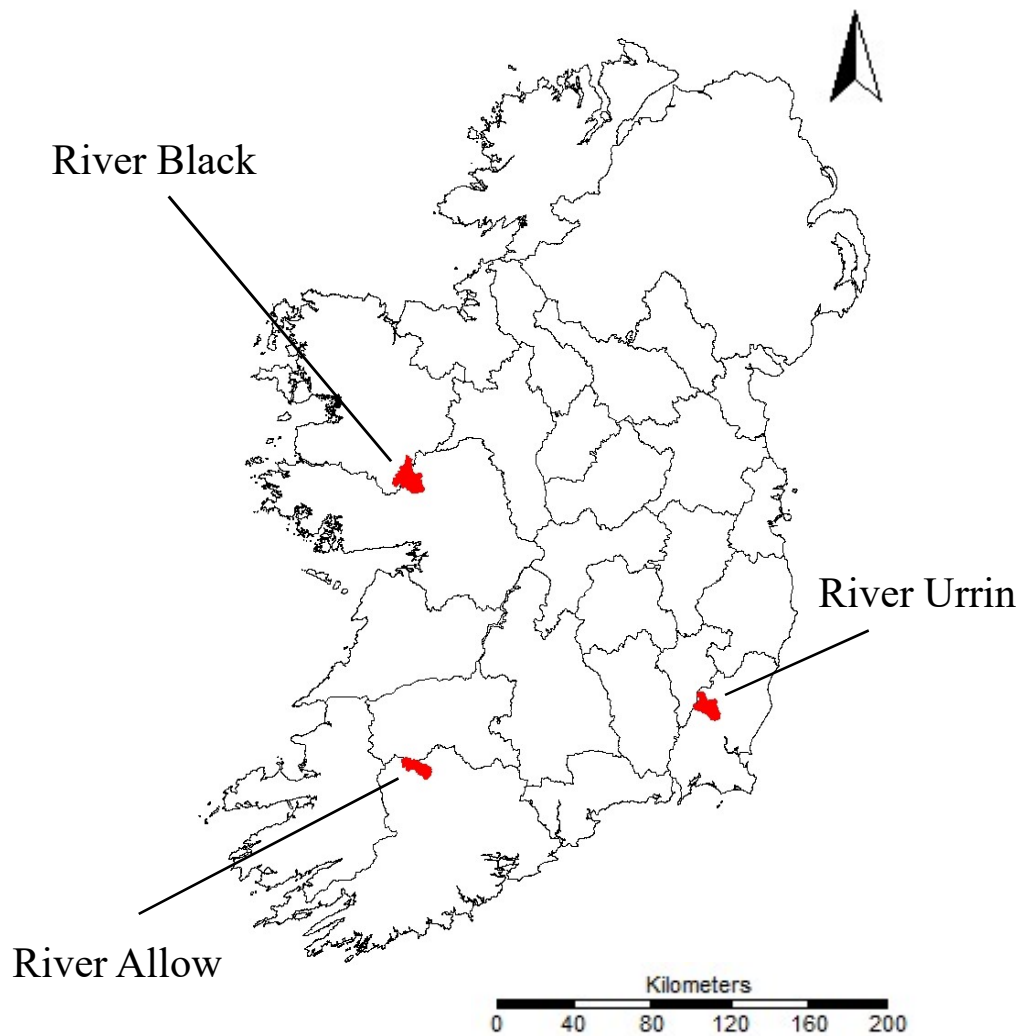
Figure 3.1. Location of the three catchments where the soils were collected for this experiment.

At each site, three bulk samples were randomly selected to a depth of 20 cm below the soil surface, air dried and manually sieved through a 1.2 cm sieve. They were then thoroughly mixed to get a homogenised sample. Fresh bulk density was determined at each site at the time

of sampling and gravimetric water content (on a wet basis) was calculated to recreate field conditions when packing the soil in the pots.

A subsample from each homogenised soil sample was oven-dried at 40° C for three days, sieved through a 0.2 cm sieve and analysed for physico-chemical characteristics. Soil pH (v/v, 1:2) in water was measured according to van Reeuwijk (2002). The soil OM content was determined using loss-on-ignition at 550° C for 16 h (Storer, 1984), which is the standard procedure implemented in the accredited labs in which the soil samples were analysed. Particle size was determined by the hydrometer method (Day, 1965). The core method (Wilke, 2005) was used for the determination of both fresh and dry bulk density. Analysis for total carbon and total nitrogen were carried out on a LECO Truspec C-N analyser (LECO Corporation, Michigan, USA). The plant available P was determined using Morgan's extractant. Total P was determined using the U.S. EPA method 3052 (USEPA, 1996), in which a 0.5 g sample was suspended in 2 ml of deionized water, followed by a combination of 7.5 ml nitric acid (15.5 M) and 2.5 ml concentrated hydrochloric acid. The mixture was then digested at 180° C in a microwave over a ramping time period of 20 min and held for another 20 min at the same temperature. The digestate was analysed using ICP-OES. The Mehlich-3 soil test was used to determine the concentration of Al, Ca, Fe and magnesium (Mg) for each soil (Mehlich, 1984).

3.3.2   Pot experiment

Before starting the experiments, soils were rewetted to bring them to the gravimetric water content at the time of sampling and packed in 18.5 L-capacity pots (30 cm upper diameter x 30 cm height) up to 3 to 4 cm below the rim. This large size of the pots maximized the growth potential of the grass, in addition to ensuring that the water status of the containers remained more stable in comparison to smaller pots (Spomer et al., 1997). A 3 cm-deep layer of gravel/coarse sand mix was placed over the drainage holes in the pots. The pots were left outdoors under natural conditions for two weeks to equilibrate before application of the P treatments. Fourteen P fertiliser treatments, with two replications per treatment, in the form of single superphosphate (16 % P content) were applied uniformly to the surface of each soil at rates equivalent to 0, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 70, 100 and 145 kg P ha^{-1} (0, 70, 110, 140, 180, 210, 250, 280, 320, 350, 390, 490, 710 and 1030 mg P pot^{-1}, respectively). One week prior to the application of superphosphate, all pots received an initial application of N as calcium ammonium nitrate and K as potassium chloride, at a rate equivalent to 55 kg ha^{-1} (389

mg N pot^{-1}) and 245 kg ha^{-1} (1.73 g K pot^{-1}), respectively. Maintenance applications of N at the same rate as the initial one were applied after each harvest to ensure no N limitation to ryegrass growth during the experiment. After nutrient applications, all pots were left to incubate for two weeks (Figure 3.2). Pots were sown with perennial ryegrass (*Lolium perenne* L.) at a rate equivalent to 28 g m^{-2} and maintained in environment-controlled chambers (Figure 3.3) according to a randomized complete block design under conditions similar to those that occur in the growing months in Ireland (Walsh, 2012): (1) photoperiod of 16 h light, (2) day and night temperatures of 14° C and 8° C (± 2° C), (3) relative humidity of 85 ± 10 % during the day and 75 ± 10 % during the night, and (4) photosynthetically active radiation (PAR) of 450 ± 50 µmol m^{-2}s^{-1}. Pots were held between 60 to 90 % field capacity by weighting them regularly and watering three times per week using tap water with a maximum dissolved reactive P (DRP) concentration of 0.0025 mg L^{-1}. Aphids were treated with insecticide every time they were detected. The grass was cut manually when it attained a length of 22 to 26 cm above the soil surface. A total of six harvests were taken. The total duration of the experiment, from the planting of ryegrass seeds to the last grass harvest, was eight months.

3.3.3   Herbage yield, herbage P content, P uptake, P balance and P Use Efficiency

All grass collected at each harvest was oven-dried at 70 °C for 72 h and weighed. This combination of temperature and drying time ensured complete drying of the ryegrass blades while minimizing potential losses due to partial combustion of the plant tissues. Cumulative DM yield for each soil type and P fertiliser treatment was calculated by summing the harvests of the six cuts. Total P uptake was calculated by multiplying the cumulative DM yield at each P rate by the average herbage P content. The P balance was calculated as the difference between the total P uptake and the P fertiliser applied. The Phosphorus Use Efficiency (PUE) was estimated using (Johnston et al., 2014):

$$PUE = \frac{(U_p - U_0)}{F_p} \qquad\qquad [3.1]$$

where U_p is the P uptake (kg ha^{-1}) by ryegrass at a given P rate, U_0 is the P uptake (kg ha^{-1}) by ryegrass at a zero P rate, and F_p is the applied P rate (in kg ha^{-1}).

Figure 3.2. Pots layout when incubating.

Figure 3.3. Pots layout in the growth chambers.

3.3.4 Mitscherlich model

The Mitscherlich model was used to describe the yield response to applied P. The Mitscherlich equation (Black, 1993) is defined by:

$$Y = A[1 - e^{-c(x+b)}]$$
[3.2]

where Y is the cumulative dry matter yield (kg DM ha^{-1}), x is the amount of P fertiliser added (kg P ha^{-1}), b is the initial plant available P in the soil determined by the Morgan's P soil test (kg P ha^{-1}), A is the maximum yield obtained as x increases indefinitely (kg DM ha^{-1}), and c is a proportionality constant related to how quickly Y reaches A.

The coefficient of determination (R^2) was computed using:

$$R^2 = (sst - sse)/sst$$
[3.3]

where sst is the total sum of squares (total variation) and sse is the variation not explained by the regression. Optimum rates of P fertiliser values were considered to be at 95 % of the theoretical maximum yields from each response equation. The choice of this proportion is arbitrary, but choosing an optimum P value of 95 % of the maximum yield ensures that the estimates of the maximum theoretical yield are likely to be within a relatively broad 5 % of the standard error of the estimate and near-maximum grass production.

3.3.5 Statistical Analysis

Data sets were tested prior to analysis for normality (Shapiro-Wilk test) and homogeneity (Bartlett's test) of variance. For each soil type, the total DM yield was subjected to a one-way analysis of variance. Regression analyses were carried out using R statistical software, version 3.4.2 (R Core Team, 2017).

3.4   Results and discussion

3.4.1 Soil physico-chemical properties

Table 3.1 shows the main properties of the soils used in this study. Organic matter content showed a broad spectrum, ranging from 8.7 % (Wexford Mineral) to 76.4 % (Galway Peat).

Cork peaty mineral had a strongly acidic pH (4.5), followed by Cork mineral and Galway Peat (5.1 and 5.3, respectively), with soils from Wexford and Galway peaty mineral having the largest values. Cork mineral and Wexford mineral had the highest values in clay content, with approximately 297 and 182 g kg^{-1}, respectively, followed by Wexford peaty mineral with 101 g kg^{-1}. Mehlich-3 extractable Al and Fe ranged from 2.6 to 991.44 mg kg^{-1} and from 116.99 to 507.39 mg kg^{-1}, respectively, with the highest values of Al for the soils from the Wexford site. Mehlich-3 extractable Al contains crystalline (e.g., gibbsite) and amorphous Al (Kuo, 1996) and does not necessarily imply phytotoxicity as the soluble, plant available Al may only be a small fraction. This is in line with Fay et al. (2007), who reported the highest concentration of Al in the south east of the country. Extractable Ca was lowest for the more acidic soils, and increased at more neutral pH values, except for Galway peat, which had the second highest value (7812 mg kg^{-1}) of the soils examined, and an acidic pH (5.3).

3.4.2   Herbage yield

There was no statistically significant response to P treatments ($p > 0.05$) for both soils from Cork. In contrast, both soils from Galway and Wexford peaty mineral had a significant total DM response to P fertiliser applications ($p < 0.0001$). The response of Wexford mineral soil was weaker but still statistically significant ($p < 0.04$). Cork peaty mineral was moderately acidic (4.5), leading to immobilization and sorption reactions between applied P and Al and Fe oxides. Soil pH has a direct impact on the availability of added P, as adsorption and precipitation reactions with Al and Fe oxides make it plant unavailable (McLaughlin et al., 2011; Oburger et al., 2011). Previous studies showed that P applications can have a limited effect on grass yield in organic soils deficient in P, so that liming should be a priority to increase the yield in these soils (Valkama et al., 2016). The content of clay in Cork mineral soil was approximately 300 g kg^{-1} which, along with the slightly acidic pH (5.1), implies a significant interaction with freshly applied P. In addition to the inmobilisation and co-precipitation of P with these metals, the low pH of both soils from Cork may have promoted solubilisation of Al and manganese (Mn) that can become toxic for plant uptake as they restrict plants root system development, consequently decreasing soil exploration and P uptake (Edwards, 1991). Clay content and extractable Al and Fe have been correlated with P sorption capacity of soils elsewhere (Bolland et al., 2003; Gérard, 2016).

Table 3.1. Soils classification and main parameters of the soils used.

Site	Soil Classification[1]	pH	OM[2]	Particle Size			Texture[3]	Fresh bulk density	Dry bulk density	Total C	Total N	Morgan's P	Total P	Mehlich-3			
				Sand	Silt	Clay								Al	Ca	Fe	Mg
			(g kg^{-1})		(g kg^{-1})			(g cm^{-3})		%		(mg l^{-1})		(mg kg^{-1})			
Galway Peat	Drained Ombrotrophic Peat	5.3	764	174	20	42	Sandy Loam	0.9	0.2	40.3	1.6	6.2	96.3	2.63	7812.6	222.1	422.3
Galway Peaty Mineral	Humic Surface-water Gley	6.6	358	360	184	98	Sandy Loam	1.3	0.6	17.0	1.4	0.9	609.6	61.5	8216.0	238.5	109.8
Cork Mineral	Typical Surface-Water Gley	5.1	91	266	345	297	Clay Loam	1.2	0.6	4.2	0.3	1.7	145.2	884.9	656.1	262.4	137.6
Cork Peaty Mineral	Humic Surface-water Gley	4.5	668	203	58	71	Sandy Clay Loam	0.9	0.2	34.7	2.2	5.9	182.7	605.0	2114.0	507.4	193.6
Wexford Mineral	Typical Brown Earth	6.0	87	366	365	182	Loam	1.5	1.2	3.1	0.3	1.2	1065.2	947.0	1103.1	117.0	199.8
Wexford Peaty Mineral	Typical Brown Podzolic	6.2	141	572	186	101	Sandy Loam	1.0	0.7	7.0	0.4	0.5	290.0	991.4	2405.6	256.4	517.0

According to the concept of build-up and maintenance, added P was rapidly sequestered in Cork mineral and, to a lesser extent, in Wexford mineral soils via sorption and fixation reactions with mineral and clay components into unavailable P forms to fill sorption sites and redress the P deficiency. In this scenario, soil P is largely unavailable for plant uptake until it can reach a threshold or critical point over several fertilization sessions at which time it is soluble and available for uptake. Daly et al. (2015) demonstrated this concept across a range of mineral acid and neutral soils, where the relationship between the ratio of extractable Al:P and plant available, soluble P indicated that P in soils with low amounts of physico-chemically sorbed P relative to amounts of Al (high Al:P) was fixed and insoluble. However, as more P is added to soil and sorbed to mineral components, the Al:P is lowered and P is released as plant available and soluble forms. Under the concept of build-up, mineral soils can sorb P after P fertilizations and make it slowly available in succeeding harvests, when the P in soil solution becomes depleted by plant uptake. The poor response of sites deficient and low in soil P has been observed in previous studies (Herlihy et al., 2004; Valkama et al., 2016).

Galway peat had the strongest yield response to P fertilisations, followed by Galway peaty mineral and Wexford peaty mineral. All these soils had a considerable percentage of OM (Table 3.1). Organic soils typically have a low P retention due to the small mineral fraction present in the soil (Daly et al., 2001; Guppy et al., 2005). Moreover, humic acids derived from the partial decomposition of the OM are mostly negatively charged, and therefore compete with orthophosphates for sorption sites in mineral particles (McDowell and Condron, 2001). On the other hand, humic acids can form complexes with metals such as Al^{+3} and Fe^{+3} and, in turn, adsorb P, thereby contributing to the sorption capacities of the soils (Gerke, 2010). The determination of organically bound Al/Fe through the sodium pyrophosphate extraction method (van Reeuwijk, 2002) and the development of phosphate saturation indices (PSI) that relate the oxalate-extractable P, Al and Fe (Janardhanan and Daroub, 2010) can be a good way to evaluate the potential of OM to sorb P in organic soils. In the current study, the results indicate that the negative relationship between OM and yield response was the predominant event taking place in the organic soils studied, likely due to the low "labile" or organically bound Al/Fe concentrations. Under this scenario, the build-up concept is then limited by the amount of OM present in the soils, and freshly applied P will remain in the soil solution, supplying P directly to the plant. Considering the particular climatology of Ireland with frequent rainfall events over the year, the presence of P in the soil solution increases the risk of losses via leaching and runoff to water bodies. Therefore, organic soils that have been

drained and brought into agricultural production should be fertilised only in the growing period (March-April), when the grass requirements for P are highest, to minimize the risk of P losses due to their inability to sorb and retain applied P in the soil matrix.

Additionally, the national P index, where soils are classified from deficient to excessive in available P based on Morgan's soil test, should not be applied to organic soils, as it has been suggested that the acidic Morgan's extractant may overestimate available P in these soils, probably due to the hydrolysis of part of the organic P forms (Roberts et al., 2017). Other soil tests such as water-extractable P (WEP) have been used in organic soils as a proxy for the plant-available P (Castillo and Wright, 2008) and may be more suitable for describing the P status of these type of soils.

3.4.3   Mitscherlich model

The Mitscherlich response curves for each soil type and the equation parameter values, along with the R^2 values, are shown in Figure 3.4 and Table 3.2, respectively. Values of A (the maximum yield attainable under unlimited P supply) ranged between 7,300 and 11,000 kg DM ha^{-1}. Galway peat and Galway peaty mineral had the highest values of A (11,000 and 10,100 kg DM ha^{-1}, respectively), whereas Wexford mineral soil was the least productive. The greater response in organic soils compared to mineral soils under similar soil P status is in agreement with other studies (Valkama et al., 2016). The reason for this is likely due to diminished P sorption capacity in organic soils, leaving applied P in the soil solution and readily available for plant uptake. There was a large range in values for c (the proportionality constant, i.e., how fast the yield approaches A), which ranged from 0.04 for soils with high R^2 to 1.1 for the soil with lower R^2 values. The proportionality constant c has been correlated with the buffering capacity of soils in previous studies (Brennan and Bolland, 2003). The c parameter in Cork Mineral, Wexford mineral and, to a lesser extent, Cork peaty mineral had the highest values, supporting the concept of P build-up in these soils. The main strength of the Mitscherlich model to describe yield response curves lies in its ability to give a good description of the yield when the range of P applications is large and a maximum yield is achieved at high P rates (Colwell et al., 1988).

Figure 3.4. Cumulative DM yield response to increasing P fertiliser rates for each soil. Dots represent average observed values and lines the fit regression curves from the Mitscherlich equation.

Table 3.2. Parameters of the fit Mitscherlich equation for each soil site. Parameter A is in kg DM ha^{-1}. Standard errors in brackets.

Site	Max yield attainable under unlimited P-supply, A	Optimum P rate	Proportionality constant, c	R^2
	kg ha^{-1}			
Galway Peat	11020 (476)	82	0.04 (4.3×10^{-3})	0.93
Galway Peaty Mineral	10100 (831)	78	0.04 (8.5×10^{-3})	0.67
Cork Mineral	8482 (277)	5	0.64 (2.0×10^{-1})	0.43
Cork Peaty Mineral	8415 (223)	14	0.21 (5.3×10^{-2})	0.39
Wexford Mineral	7348 (227)	3	1.10 (3.6×10^{-1})	0.31
Wexford Peaty Mineral	8415 (499)	79	0.04 (6.0×10^{-3})	0.88

This is the case for the soils from Galway and for Wexford peaty mineral, where the response to P fertiliser was well described along the whole set of P rates (high R^2). However, the Mitscherlich model becomes less accurate when an asymptote is not reached at higher P rates. Both soils from Cork and Wexford mineral did not reach maximum yields at maximum or near maximum P rates, so the accuracy of the Mitscherlich model was relatively poor.

3.4.4 Herbage P content

The average herbage P concentration across the fourteen P applications declined in all the sites over the timeline of the pot trial. The second cut at each soil had the highest herbage P concentrations for all the soils, with values above the threshold limit of 3 g kg^{-1}, followed by a steady decline in each subsequent cut and remaining stable around 1.5-2 g kg^{-1} after the fifth cut for all the soils (Figure 3.5). The decline on herbage P concentration observed in this experiment agrees with other studies (Bailey et al., 1997 and references within), although this pattern is not consistent in the literature (Burkitt et al., 2010). The decline of herbage P throughout the year after one single P application at the start of the grazing period can have negative implications in the health of ruminants if the P requirements are not met for the intermediate to late grazing period (Sheil et al., 2016). Under this scenario, a "little and often" approach, where P fertiliser applications allocated for the whole year are split in two or more smaller rates, would be more suitable to maintain herbage P concentrations within the critical range of 3 to 3.5 g kg^{-1}.

Figure 3.6 shows the cumulative DM yield plotted against the average P concentration in the herbage. Galway peat and Cork peaty mineral soils reached the threshold herbage P concentration of 3 g kg^{-1} at near-maximum yield, around the 50 to 55 kg ha^{-1} P fertiliser application rate, whereas the other soils reached it when the P fertiliser applications were at 100 to 145 kg ha^{-1}. Herbage P concentration continued to increase in Galway peat, Cork peaty mineral and, to a lesser extent, Wexford peaty mineral beyond the critical concentration, although the yield remained the same, thus reflecting a luxurious consumption of P in these soils. Results showed that the P fertiliser requirements to reach a critical P level Mitscherlich model. This is also in agreement with previous findings (Morton et al., 1999; Schulte and Herlihy, 2007). As a result, the fertiliser P required to obtain a critical herbage P concentration around 3 g kg^{-1} would satisfy the P fertiliser requirements to obtain near-to-maximum yields, maximizing grass production. However, these high fertiliser rates can pose an elevated risk of

P losses for organic soils due to their poor P retention capacities as it has been shown above, and hence P fertilizer recommendations derived from plant analysis may not seem suitable for these soils.

of 3 g kg^{-1} were higher than those required to reach 95 % of the maximum yields from the
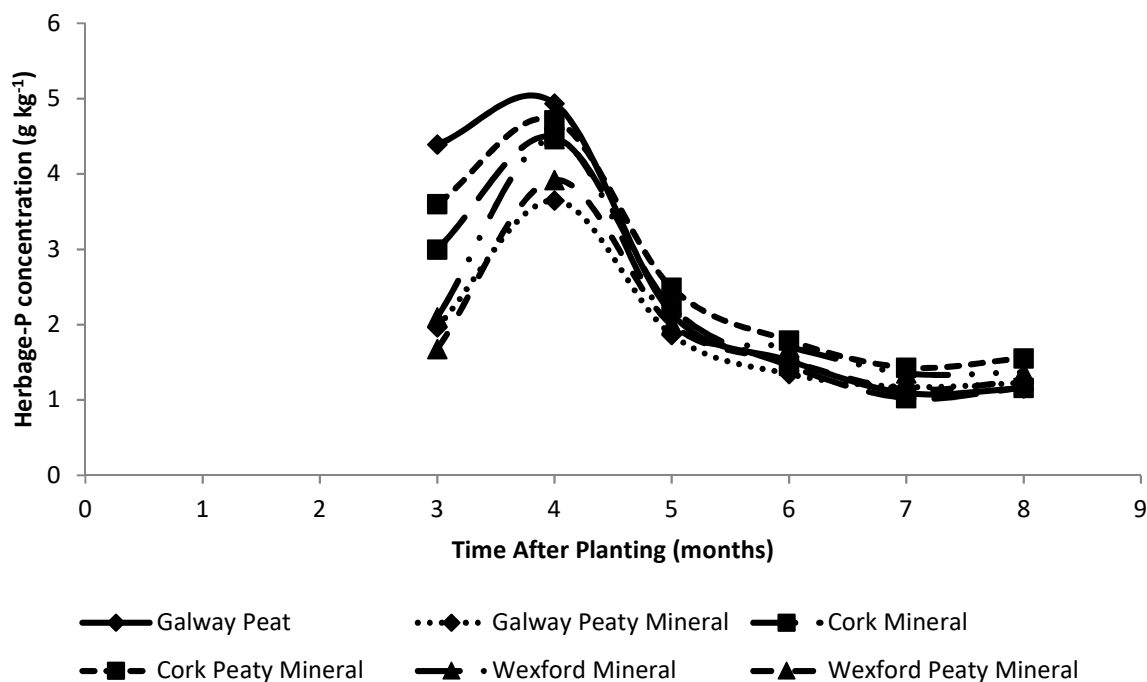
Figure 3.5. Average (n=14) herbage P concentration over 6 months.

3.4.5   P uptake, P balance and P Use Efficiency (PUE)

The P uptake, P balance and PUE at each P fertiliser rate and site are shown in Figure 3.7. Phosphorus uptake increased in all sites as the P fertiliser rates increased. Galway peat had the highest P uptakes at the maximum P fertiliser rates. This increase in P uptake with increased P application rates is in line with the fact that uptake is a function of the DM yield and the herbage P content, which in turn increased with P fertilisations. The P balance was negative at zero P fertiliser rate for all soils and at 10 kg P ha^{-1} for Galway peat, Cork mineral, Cork peaty mineral and Wexford mineral, which indicated a depletion of any stable P reserves in the soil. The P balance became positive for the rest of treatments in all soils, indicating an accumulation of P in the soils.

Figure 3.6. Cumulative grass DM yield versus herbage P content for each soil.
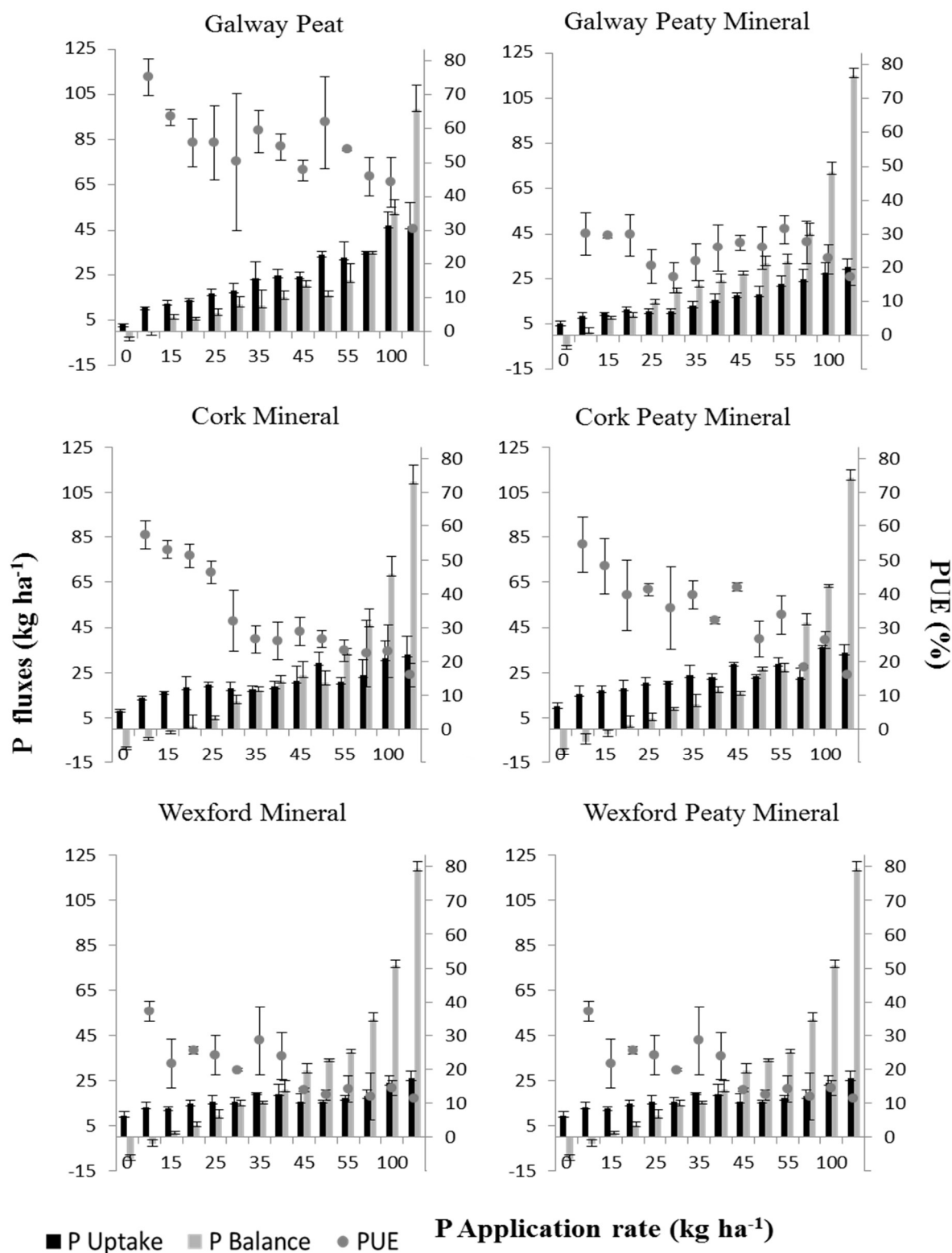
Figure 3.7. Phosphorus (P) uptake and P balance (kg ha^{-1}) and P use efficiency (PUE) (%) for each P fertiliser rate and soil site. Error bars represent standard deviations.

The positive P balance obtained in all soils and almost all P treatments reflected that inputs (P fertiliser) exceeded offtakes (P uptake by the grass), so the surplus of P applied to the soil was either retained in the soil or lost via leaching throughout the duration of the experiment, or a combination of both. The greatest PUE were at low P rates, decreasing in all soils as P rates increased. Galway peat soil had the highest P efficiency, with an average PUE of 54 % across P treatments. Cork mineral and Cork peaty mineral had moderate-to-high PUE at low P rates, but decreased markedly as P application rates raised, attaining an average efficiency of 33 % and 35 %, respectively. Wexford mineral, Wexford peaty mineral and Galway peaty mineral had a low P efficiency over all P application rates, with averages efficiencies of 20 %, 28 % and 25 %, respectively. With the exception of Galway peat, the mean PUE of the other soils were similar to those reported in other studies with ryegrass for low soil P status (Herlihy et al., 2004) and agrees with the tendency for there to be a low PUE in the same year of P application (Johnston et al., 2014). The overall P efficiency of Galway peat, with a high OM content (76 %) was considerably higher than the other soils, indicating that interactions between P fertiliser and the soil mineralogy were minimal and hence applied P was readily available in the soil solution for plant uptake throughout the duration of the experiment.

3.5   Conclusions

Grass response to P fertiliser varied between organic and mineral soils with P deficiencies. When grass yield was modelled using the Mitscherlich equation, mineral soils had a weak response to P applications due to the need to first build up their soil P reserves, whereas more organic soils showed a large response to P applications, which indicated no requirement to build up P reserves. This illustrates the potential risk of P losses to waters if P fertilisers are applied to organic soils even when they are deficient in P. Additionally, the high fertiliser P requirements derived from plant analysis to meet the critical herbage P concentration may not be suitable for organic soils if environmental aspects have to be considered. Losses from these soils can be minimized if P is applied during the growing season only, and under a "little and often" approach rather than one single application, as P will be taken up by the plants shortly after its application. However, these implications might not be feasible in reality, as fields with organic soils may be located far from the farmyard and therefore may be fertilised in one single application to reduce costs and time. In this scenario, bringing new organic soils into

agricultural production may be less desirable than intensification of existing agricultural land if they are within high status or sensitive catchments.

3.6   Summary

This chapter has shown the faster response of organic soils to P applications, in comparison to mineral soils, due to the diminished ability of these soils to react and immobilise soluble P. Therefore, organic soils also have a higher risk of P loss to waters if the added P is in excess of crop requirements. Based on this experiment, Chapter 4 investigates how the different soil P fractions and pools changed after the pot experiment and which transformation pathways of the different P pools were predominant for each soil type in the experiment.

Chapter 4

Effects of fertiliser on phosphorus pools in soils with contrasting organic matter content: A fractionation and path analysis study

4.1   Overview

The objectives of this study were (1) to assess the changes in the different soil P fractions receiving increasing amounts of P fertiliser, and (2) to examine which pools acted as sinks or sources for P so as to gain a better understanding of the soil P cycle.

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4.2   Introduction

Phosphorus applied to soils undergoes a series of physico-chemical (dissolution-precipitation and desorption-adsorption) transformations regulated by soil characteristics such as mineralogy composition, surface area, pH, extractable Fe-Al hydroxides and OM content (Guérin et al., 2011; Janardhanan and Daroub, 2010; Frossard et al., 2000; Porter and Sanchez, 1992). Phosphorus fertiliser recommendations on mineral soils are based on their ability to sorb and gradually build-up P over time until a critical level is reached, followed by the maintenance of that level by replacing the P removed by consecutive harvests (Voss, 1998; Olson et al., 1987). However, the ability of organic soils to sorb and retain P applied is impeded by the inherent large amounts of OM that compete for sorption sites (Guppy et al., 2005; Daly et al., 2001), so that the approach of build-up of P and maintenance on these soils for fertiliser recommendations has been questioned (Roberts et al., 2017; Daly et al., 2015).

The sequential P fractionation procedure, developed by Hedley et al. (1982), extracts P bound from diverse inorganic and organic compounds of different lability using solutions of

increasing extracting strength (Cross and Schlesinger, 1995). Despite its limitations when providing P speciation at the P fraction level and the likelihood to overestimate organic P (Turner et al., 2005), the Hedley method is one of the most comprehensive methodologies used to evaluate the soil P cycle and dynamics into "operationally-defined fractions" of different availability and nature (Condron and Newman, 2011; Negassa and Leinweber, 2009). However, only a few studies have applied this technique in OM-rich soils (Schlichting et al., 2002; Cross and Schlesinger, 1995) and, to our knowledge, none exists in organic soils where the effect of P applied in the different soil P pools has been evaluated using this technique. Therefore, there is a lack of knowledge about the interaction of freshly applied P with the different soil P fractions when organic acids are in direct competition for the same reaction sites as the P applied. Phosphorus assimilation and turnover in agricultural organics soils is poorly understood and needs further research in order to improve their management and minimise potential P loses to the environment.

Sequential P fractionation techniques alone do not provide insight on the relationships and transformations between the soil P pools under different treatments, nor behavioural comparison of soils of different pedogenesis receiving the same treatments (Gama-Rodrigues et al., 2014; Zheng et al., 2004). Path analysis has been shown to be a valuable tool to evaluate the cause-and-effect interrelations between P pools in different soil types and under a variety of management regimes (Tiecher et al., 2018; Zheng et al., 2004; Beck and Sanchez, 1994; Tiessen et al., 1984).

To address these research questions, the same six soils used in Chapter 3 were subjected to P fractionation analysis before and after the experiment to ascertain how the different soil P pools changed. Additionally, the P pools at the end of the experiment were subjected to a path analysis to evaluate the interrelations of the different P pools.

4.3   Materials and methods

4.3.1   Pot experiment

Six grassland soils deficient in P and representing a range of OM content, were selected from three high status catchments in the Republic of Ireland (Table 4.1). All soils were under a low intensity grazing system and received no P applications in the years prior to soil collection,

with the exception of Galway peaty mineral, which received P applications of approximately 32 kg P ha^{-1}y^{-1} in the years prior to the soil collection. The soils were collected from the surface horizon (0-20 cm), air dried, and sieved through a 12 mm sieve. A subsample was taken from each soil and analysed for selected physico-chemical properties and to determine initial P concentrations in the different P pools, defined in the following section (Table 4.1).

Soils were rewetted to their field gravimetric water content and placed in 18.5 L pots (0.3 m upper diameter, 0.3 deep). Each soil received fourteen P fertiliser applications (n=2) as single superphosphate (16 % P content) at rates equivalent to 0, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 70, 100 and 145 kg P ha^{-1} (0, 70, 110, 140, 180, 210, 250, 280, 320, 350, 390, 490, 710 and 1030 mg P pot^{-1}, respectively). Each pot received an initial application of N as calcium ammonium nitrate and K as potassium chloride, at a rate equivalent to 55 kg ha^{-1} (389 mg N pot^{-1}) and 245 kg ha^{-1} (1.73 g K pot^{-1}), respectively. Pots were sown with perennial ryegrass (*Lolium perenne* L.) seeds at a rate equivalent to 28 g m^{-2} and placed in a glasshouse for three months under the following conditions: average temperature of 11.1° C (±3.9° C) and relative humidity of 82 % (± 12 %). Pots were then placed in controlled growth chambers operated in the following conditions: (1) photoperiod of 16 h light (2) daytime temperatures of 14° C and night-time temperatures of 8° C, with respectively relative humidities of 85 % and 75 %, and (3) photosynthetically active radiation of 450 ± 50 µmol m^{-2} s^{-1}. The pots were randomly placed in the chambers and were held between 60 to 90 % field capacity by weighting them regularly. The grass was harvested six times when it attained a length of 22-26 cm. At the end of the experiment, and for each pot, six soil cores were taken, oven-dried at 40 °C for three days, composited and subjected to soil P fractionation analysis. Phosphorus use efficiency and magnitude of grass response to P fertilisations in these soils were evaluated, the details of which are in Chapter 3.

4.3.2 Soil P fractionation

A modified Hedley fractionation procedure (Hedley et al., 1982) was used for each soil and P treatment to determine the different fractions before and after the experiment. The iron-oxide paper strip method (Menon et al., 1989) was used as an alternative to the traditionally used but laborious resin-P method (Chardon et al., 1996).

Table 4.1. Selected physico-chemical properties of the six soils used in the study. Values in parenthesis represent standard deviations, except for the fractions Fe-Al bound P, Organic P and Residual P, which are standard errors of the mean.

Soil property	Units	Galway peat	Galway peaty mineral	Cork mineral	Cork peaty mineral	Wexford mineral	Wexford peaty mineral
Classification[*]		Ombric Histosol	Haplic Cambisol	Haplic Stagnosol	Haplic Stagnosol	Haplic Cambisol	Haplic Podzol
Texture		Sandy Loam	Sandy Loam	Clay Loam	Sandy Clay Loam	Loam	Sandy Loam
Clay	g kg^{-1}	42	98	297	71	182	101
Silt	g kg^{-1}	20	184	345	58	365	186
Sand	g kg^{-1}	174	360	266	203	366	572
Organic Matter	g kg^{-1}	764	358	91	668	87	141
pH		5.3	6.6	5.1	4.5	6.0	6.2
Dry bulk density	g cm^{-3}	0.2	0.6	0.6	0.2	1.2	0.7
Total C	g kg^{-1}	403.0	177.0	42.0	347.0	30.9	70.0
Organic C	g kg^{-1}	387.4	152.6	39.5	341.9	26.2	65.3
Total N	g kg^{-1}	16.3	14.2	3.6	22.0	3.0	4.4
Mehlich-3	mg kg^{-1}						
Al		2.6 (0.4)	61.5 (9.8)	884.9 (13.9)	605.0 (25.5)	947.0 (2.6)	991.4 (46.4)
Fe		222.1 (18.1)	238.5 (6.0)	262.4 (4.0)	507.4 (15.2)	117.0 (2.0)	256.4 (10.1)
Ca		7812.6 (175.5)	8216.0 (126.5)	656.1 (2.7)	2414.0(19.4)	1103.1 (3.8)	2105.6 (39.3)
P		13.7 (0.7)	6.5 (0.0)	20.6 (0.2)	31.1 (1.1)	23.3 (0.2)	25.6 (0.6)
Labile P	mg kg^{-1}	33.5 (0.1)	4.2 (0.4)	2.0 (0.2)	38.4 (2.7)	3.0 (0.7)	1.4 (0.2)
Fe-Al bound P	mg kg^{-1}	47.4 (1.0)	111.0 (8.6)	20.4 (0.8)	103.1 (3.1)	194.1 (4.2)	37.0 (0.8)
Organic P	mg kg^{-1}	146.4 (0.3)	350.7 (5.3)	186.2 (1.2)	535.3 (5.0)	332.5 (6.1)	307.5 (2.2)
Ca bound P	mg kg^{-1}	43.5 (3.0)	287.5 (91.6)	12.3 (1.8)	47.9 (3.5)	127.9 (7.4)	118.7 (8.7)
Residual P	mg kg^{-1}	335.1 (2.4)	369.9 (23.8)	148.3 (0.9)	376.9 (7.8)	516.9 (2.7)	158.1 (2.7)
Total P	mg kg^{-1}	605.8 (8.5)	1116.7 (10.5)	369.1 (2.6)	1101.5 (29.1)	1174.2 (0.9)	622.6 (5.6)

Additionally, the iron-oxide paper strip test is more suitable for soils of different nature, as its ability to determine dissolved and loosely bound P is not influenced by physical or chemical properties of the soils (Robinson and Sharpley, 1994). Duplicate 0.5 g samples of dried soil were weighed in 50 mL polypropylene tubes and shaken in 40 mL of 0.01 M $CaCl_2$ with iron-oxide paper strips for 16 h using a reciprocal shaker operated at 6 rpm. Phosphorus adsorbed to the iron strips was dissolved by shaking the strips for 1 h in 40 ml 0.1 M H_2SO_4. This fraction was identified as the FeO strip-P. The soil suspension was then centrifuged at approximately 51845 m s^{-2} for 20 min and the supernatant was decanted. The soil was then sequentially extracted with: (1) 30 ml of 0.5 M $NaHCO_3$ at pH 8.5 ($NaHCO_3$-P) (2) 0.1 M NaOH (NaOH-P), and (3) 1 M H_2SO_4 (H_2SO_4-P), each of them at the same shaking and centrifuging settings as described for the FeO strip-P. The residual P fraction resisting the 1 M H_2SO_4 extraction was calculated as the difference between total P (P_t) and the sum of FeO strip-P + $NaHCO_3$-P + NaOH-P + H_2SO_4-P. Total P was determined by ICP-OES in a separate 0.5 g dried sample using the microwave-assisted acid digestion method (USEPA, 1996). Inorganic P (P_i) concentrations for all the extractants were determined within 24 h using the ascorbic acid-molybdenum blue method (Kuo, 1996). The P_t concentration in the different extractants (except for the FeO strip-P, where only P_i was determined) was determined by acid potassium persulfate digestion. Organic P concentrations (P_o) in the $NaHCO_3$ and NaOH fractions were calculated as the difference between P_t and P_i.

The different chemically extracted fractions were grouped into operationally defined pools of increasing recalcitrance as follows: (1) the FeO strip-P represented the labile P pool and comprised P dissolved in the soil solution along with loosely adsorbed P, (2) the $NaHCO_3$-P_i and NaOH-P_i represented the Fe-Al bound P pool and included moderately sorbed and/or fixed P_i by Al and Fe oxides/hydroxides, (3) analogous to the Fe-Al bound P, the $NaHCO_3$-P_o + NaOH-P_o represented the organic P pool, (4) the H_2SO_4-P represented the Ca-bound P pool and comprised stable P contained in primary minerals such as apatite, and (5) the residual P pool, calculated as the difference between the P_t and the sum of the previous pools, comprised highly stable organometallic complexes and organic materials such as lignin (Gama-Rodrigues et al., 2014; Condron and Newman, 2011; Negassa and Leinweber, 2009; Schlichting et al., 2002; Cross and Schlesinger, 1995).

4.3.3   Statistical analysis

In order to analyse and evaluate the impact of the increasing P fertiliser applications on the different soil P pools, the percentage change for each soil and P pool were calculated as the difference between the P concentration after and before the experiment divided by the original P concentration. Path analysis was used to examine the cause-and-effect relationships between the soil P pools and P fertiliser, and to differentiate between the direct and indirect effects of these relationships. Phosphorus concentrations (in mg kg^{-1}) at each P application dose (kg ha^{-1}) for each soil pool the end of the experiment were used in the path analysis. The conceptual diagram in Figure 4.1 was proposed as a general model to test P transformations and dynamics in the different soils. Phosphorus fertiliser was the sole independent variable that may affect the different soil P pools. Therefore, the soil P pools were considered as dependent variables. A basic assumption of the model is that, under cultivation conditions where soils are mainly aerated most time of the year, P movements between the soil P pools occur from the most recalcitrant pools to the less recalcitrant ones and not vice-versa, as might happen under flooded conditions where the redox conditions would change (Castillo and Wright, 2008). This is represented in the model by the different arrows between the independent variable and the dependent variables, and within the dependent variables following the assumption mentioned above (Figure 4.1). Each potential relationship in the model (cause) is measured by a partial regression coefficient (direct effect). They are analogous to the covariance between two variables and are referred to as path coefficients (β). Indirect effects are referred to as the effects between two variables that are mediated by another intervening variable (Raykov and Marcoulides, 2006). Both unstandardized (raw score units) and standardized (standard deviation units) path coefficients were calculated. The use of unstandardized path coefficients enabled comparison for the same variable relationship across the different soils, whereas standardized path coefficients were better for comparing different variable relationships within the same soil (Beaujean, 2014).

The generic model represented in Figure 4.1 is a saturated model with zero degrees of freedom, that is, there are as many estimated parameters as data points (observations). By definition, saturated models exhibit perfect fit to the data and hence they cannot be confirmed or invalidated by the path analysis (Raykov and Marcoulides, 2006). However, this model was used as a benchmark against which nested (modified) models with positive degrees of freedom could be tested. Modifications of the saturated model were done by dropping from the model the non-significant path coefficients stepwise until final models were tenable, analogous to

backward selection in regression analysis, so that the likelihood to miss a plausible variable was excluded. The Chi square test (χ^2), at a significance level of 0.05, was used to validate the nested model from the preceding one until the most restrictive, yet

Figure 4.1. Path diagram with the proposed relationships between the different soil P pools and P fertiliser applications. Errors represent the variance of each of the dependent variables (five soil P pools).

plausible, model was achieved for each soil (Raykov and Marcoulides, 2006). Comparative Fit Index (CFI), Expected Cross Validation Index (ECVI), Akaike's Information Criterion (AIC), and Goodness of Fit Index (GFI) were also considered to evaluate the fit strength of the models generated. Analyses were carried out in R statistical software, version 3.4.2 (R Core Team, 2017) using the "lavaan" and "semPlot" packages (Epskamp, 2017; Rosseel, 2012).

4.4   Results and discussion

4.4.1   Soils characterization

The physico-chemical characteristics of the soils before the application of fertiliser are shown in Table 4.1. The range of OM content reflects a broad variation, spanning from 8.7 to 76.4 %, representing the contrasting soil types in high status catchments in Ireland (White et al., 2014). Soil pH was acidic for Cork peaty mineral, Cork mineral and Galway peat, with values of 4.5, 5.1 and 5.3, respectively, in contrast with near-to-neutral values for the other soils. Total P in the soils ranged between 369.1 to 1174.2 mg kg^{-1}. From a pedogenic point of view, Galway peat, classified as Ombric Histosol, had similar values to those reported by Yang and Post (2011), but less than other semi-natural or cultivated Histosols reported elsewhere (Schlichting et al., 2002). The other soils in this study had considerably larger P_t concentrations compared to those in the Yang and Post (2011) pedogenic study. There was a significant positive correlation ($r^2 = 0.7$, $p < 0.05$) between soil pH and Ca-bound P fraction, indicating that pH favoured retention of P in this stable fraction from past P additions (Castillo and Wright, 2008; Schlichting et al., 2002). There were no other significant correlations between the remaining fractions and other soil properties. Organic P and residual P were by far the predominant fractions in all the soils, with values ranging from 24.2 to 50.4 % and from 25.4 to 55.3 % of the P_t, respectively, whereas labile P was the smallest fraction and did not exceed 5.5 % of the P_t in any soil (Table 4.1).

4.4.2   Changes in P pools over the study duration

Figure 4.2 shows the percentage change before and after the pot study in labile P, Fe-Al-bound P, Ca-bound P, organic P and residual P pools in each soil over all P applications. The labile P fraction (Figure 4.2a) increased with increasing rates of P applications in all the soils, as expected. Part of the P applied in the form of fertiliser was taken up by the grass, while the rest reacted with the soil matrix and was adsorbed to soil particles. There were negative changes in labile P in Galway peat, Cork peaty mineral and, to a lesser extent, Galway peaty mineral and Wexford mineral, until P applications exceeded threshold values of approximately 45, 35, 25 and 10 kg ha^{-1}, respectively, indicating a partial depletion of the original pool by grass growth and uptake. Here, grass growth may have been impeded due to lack of available P, until the rates of application were enough to support plant growth and replenish the labile P pool.

Galway peat and Cork peaty mineral, the soils with the most OM content (Table 4.1), had relatively low maximum positive percentages of change (around 200 %), whereas more mineral soils, such as Wexford peaty mineral and Cork mineral, had maximum positive percentage changes exceeding 2500 %. The magnitude at which the labile P pool changed across the P applications is an indication of the ability of each soil to sorb and retain freshly applied P into this fraction. Therefore, high percentage change values mean that large amounts of added P ended up in this pool, whereas low values indicate that only a small amount was tied up here. Phosphorus concentration in the soil solution phase immediately after fertiliser applications is typically very high (saturated solution), and undergoes rapid adsorption reactions on the surface of the soil particles until equilibrium is reached, thus decreasing its concentration to levels typically very small compared to the solid phases (McLaughlin et al., 2011). Mineral soils demonstrated a high ability to adsorb P in the surface areas of their mineral fraction, whereas this adsorption capacity in organic soils was much smaller (Figure 4.2a).

Phosphorus not retained in the labile pool of the organic soils was taken up by the plant roots in higher proportions than in mineral soils, as P was readily available in the soil solution and not loosely bound to soil mineral particles. This was evidenced by the higher P uptakes of the organic soils compared to mineral soils (Figure 4.3). At high P doses, when it is likely that P has been applied in excess of crop requirements, organic soils with a low % change in labile P showed higher P uptake by the plant roots compared to mineral soils with higher % changes but lower P uptake (Figure 4.3). Organic soils have low sorption and retention capacities for P (Guppy et al., 2005, Daly et al., 2001), so the relative inability of these soils to retain P applied in excess of crop requirements increases the risk of P loss to the aquatic environment (Roberts et al., 2017; Daly et al., 2001). The iron-oxide paper strip method, used as a proxy for the labile P pool, may also have acted as a sink for some dissolved organic P (Robinson and Sharpley, 1994). Although inositol hexaphosphate is the predominant molecule among the organic P compounds, it is relatively resistant to mineralisation.
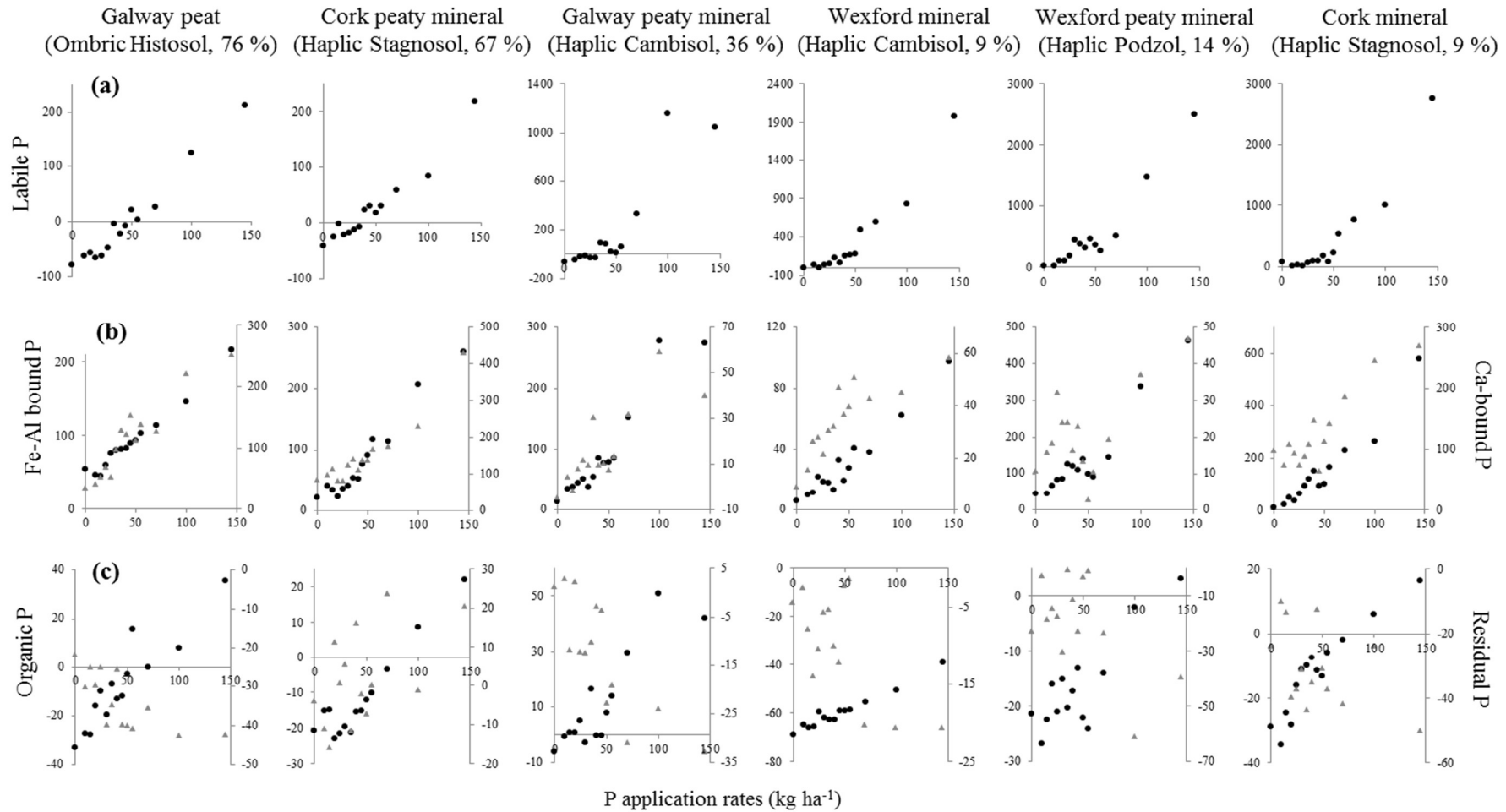
Figure 4.2. Percentage change in (**a**) Labile P fraction, (**b**) Fe-Al bound P (left vertical axis, ● symbol) and Ca-bound P (right vertical axis, ▲ symbol) fractions, and (**c**) Organic P (left vertical axis, ● symbol) and Residual P (right vertical axis, ▲ symbol) fractions across P applications in the six soils studied. Percentages represent the organic matter content.

However, it is likely that other more degradable molecules, such as phospholipids and nucleic acids, are more abundant in organic soils and therefore prone to be mineralised in the extraction phase with H_2SO_4, overestimating labile P (Quiquampoix and Mousain, 2005; Ivanoff et al., 1998). To minimise this potential source of error and improve the interpretation of labile P pools,studies to efficiently estimate bioavailable P, especially in organic soils where degradable organic P is likely to be present in a higher proportion compared to mineral soils.

The Fe-Al bound and Ca-bound P fractions increased proportionally to the P applications in all the soils (Figure 4.2b). There was no clear pattern of P accumulation across the different soils for both P pools, although higher maximum percentage changes (up to 600 %) were measured in the Fe-Al bound P in the mineral soils (Cork mineral and Wexford peaty mineral). The short duration of this study likely hindered a better observation of any potential trend between organic and mineral soils. None of the soils had negative percentage changes, indicating that there was no depletion of these pools at low P doses during the experiment. With the exception of Cork peaty mineral, the magnitude of change in the Ca-bound P fraction was smaller than the Fe-Al bound P, supporting the hypothesis that this pool is considered a more stable fraction to short-term changes and least reactive to freshly applied P (Cross and Schlesinger, 1995). With no P applied (zero P rate), the percentage of change in these two fractions was positive at the end of the experiment, indicating that P was released from other pools and retained in these fractions. Likely, part of the P contained in the organic P and residual P fractions was mineralized and transferred to these pools.

There was a build-up in the organic P pool across the P treatments (Figure 4.2c), indicating that some of the applied P was entering in this pool. However, the magnitude of the change was small, up to 80 % in absolute values, highlighting the limited ability of this soil pool to retain added P compared to the labile P fraction. Again, there was no pattern of percentage of change between organic and mineral soils. With the exception of Galway peaty mineral soil, negative changes were measured for most of the P applications to the soils. The negative values in this fraction may be attributed to mineralization of the partially decomposed OM by the microbial community. It has been reported that mineralization of organic materials is enhanced by heterotrophic microorganisms when P is not a limiting element (Pisani et al., 2015; Wright and Reddy, 2001).

Figure 4.3. Relationship between % change in labile P and P uptake for the six soils at each of the 14 fertiliser applications examined in this study. P Uptake was calculated by multiplying the cumulative grass dry matter yield at each P dose by the average herbage P content. The miniature graph represents % change up to 350 in the y-axis to facilitate reading data in that area. Values in parenthesis in the legend represent organic matter content.

Small P fertiliser additions may generate more plant available P derived from the mineralization of organic P fractions, so that this pool may play an important role in soil P fertility, acting as a source of plant available P in those soils where it is a relevant reservoir (Menezes-Blackburn et al., 2018; George et al., 2017; Condron and Newman, 2011; Guo et al., 2000). With the exception of Cork peaty mineral, where there was a tendency to build up P, changes in residual P (Figure 4.2c) declined across P treatments. The low pH of the Cork peaty mineral soil may have favoured precipitation of some of the applied P with Fe and Al oxides that were part of the primary minerals in this soil. The reduction of the residual P pool in the rest of the soils (Figure 4.2c) indicated that P may have been partially mineralized and therefore mobilised to other pools. The residual pool is considered the most recalcitrant and hence least available of all the fractions, as it is associated with very stable organo-metallic materials (Turner et al., 2005). However, previous research has shown that this pool can act as a source of P for arable crops and forest trees plantations in the short and long-term experiments under low or no P inputs (Velásquez et al., 2016; Condron and Newman, 2011). To our knowledge, our results are the first to confirm this tendency under pasture (ryegrass) monoculture.

4.4.3   Pathways of transformations in soil P pools

Path analysis uses the data generated by the P fractionation technique in a theoretical model to differentiate between direct and indirect effects from one variable on others (Tiecher et al., 2018; Gama-Rodrigues et al., 2014; Kang et al., 2009; Zheng et al., 2004). These interrelations are evaluated as partial correlations between the variables but, unlike routine multiple regression analysis in which a single dependent variable is considered, path analysis conducts a multivariate multiple regression analysis where several dependent variables are subjected to regression analysis simultaneously on one or more independent variable. Unstandardized path coefficients are shown in Table 4.2 and in Figures 4.4-4.6, whereas the standardized values are shown in Table 4.3. Phosphorus fertiliser had a significant impact on the majority of the soil P pools, although at different magnitudes. The labile P pool was significantly affected by P fertiliser applications in all the soils, with the highest effect in the most organic soils, with a β = 0.70 for Galway peat and β = 0.27 for Cork peaty mineral soil. This indicates that any added P in excess of plant requirements may pose an elevated risk of P transfer to surface waters in the organic soils under rainfall events in field conditions, as supported in Figure 4.3.

The Fe-Al bound pool was a significant direct sink for freshly applied P for all the soils, as widely reported (Castillo and Wright, 2008; Zheng et al., 2004). Phosphorus fertiliser had the highest impact on the Fe-Al bound P in the Cork peaty mineral soil ($\beta = 1.73$), likely due to the very low pH of this soil that favoured immobilization and physico-chemical sorption reactions between the freshly applied P and the amorphous and poorly crystalline Fe-Al oxides/hydroxides in this soil. The Fe-Al bound P pool contributed indirectly to the replenishment of labile P in most of the soils, especially in Cork mineral ($\beta = 0.46 \times 0.43$). However, there was no indirect relationship between added P and the labile pools through the Fe-Al bound P pool for the most organic soils (Galway peat, Cork peaty mineral). The lack of relationship between these two pools in these soils supports the idea that, as a consequence of low pH, mobilization reactions of P in soils (sorption/desorption and precipitation/dissolution) play an important role in P availability. The organic P pool had a considerable direct relationship with P fertiliser in all soils except Galway peaty mineral. The Cork peaty mineral soil had the highest response ($\beta = 0.85$). There was no substantial indirect effect of the organic pool to Fe-Al bound and labile P pools, with the exception of Wexford peaty mineral, where a moderate relationship between the organic P and Fe-Al bound P was calculated ($\beta = 0.58$; Table 4.2 and Figure 4.6). These results show that P applications increased organic P reserves over short periods of time. Other studies reported a slight increase in the moderately labile organic P pools in incubation and short-term (0 to ≤ 10 y) field studies (Negassa and Leinweber, 2009). However, as was reported in the previous section, the organic P pool experienced a negative change at low P rates in the majority of soils. These results highlight the potential role of the organic P pool as a source of P for plant uptake through mineralization when added P does not meet crop requirements for growth (Negassa and Leinweber, 2009; Castillo and Wright, 2008; Turner et al., 2007; Zheng et al., 2004). The role of the soil organic pools as a source of plant available P could be well evaluated in middle and long-term unfertilised experiments by path analysis in future studies.

Table 4.2. Unstandardized partial regression coefficients. Direct (diagonal, bold) and indirect (off diagonal) contribution of P fertiliser applications on the different soil P pools. Significant levels at $p \leq 0.05$, 0.01 and 0.001 represented by [*], [**] and [***], respectively. NS = not significant.

Variable	Residual P	Ca-bound P	Organic P	Fe-Al bound P	Labile P
Galway Peat					
Residual P	**-0.49***				
Ca-bound P	NS	**0.69***			
Organic P	-0.24*	NS	**0.53***		
Fe-Al bound P	NS	NS	NS	**0.55***	
Labile P	NS	NS	NS	NS	**0.70***
Galway Peaty Mineral					
Residual P	**1.12**				
Ca-bound P	-0.17*	**1.27***			
Organic P	NS	0.94***	**NS**		
Fe-Al bound P	-0.43***	NS	NS	**1.19***	
Labile P	0.08**	0.13***	NS	0.07***	**0.15**
Cork Mineral					
Residual P	**NS**				
Ca-bound P	NS	**0.18***			
Organic P	-0.38***	NS	**0.54***		
Fe-Al bound P	NS	1.62***	NS	**0.46***	
Labile P	NS	NS	-0.10**	0.43***	**0.09***
Cork Peaty Mineral					
Residual P	**NS**				
Ca-bound P	-0.13**	**1.00***			
Organic P	NS	0.685*	**0.85***		
Fe-Al bound P	NS	NS	NS	**1.73***	
Labile P	0.08*	0.12*	0.03**	NS	**0.27***
Wexford Mineral					
Residual P	**-0.55**				
Ca-bound P	-0.24*	**0.29***			
Organic P	-0.25*	NS	**0.45***		
Fe-Al bound P	NS	NS	NS	**1.21***	
Labile P	NS	NS	NS	0.10*	**0.25***
Wexford Peaty Mineral					
Residual P	**NS**				
Ca-bound P	-0.14**	**0.17**			
Organic P	-0.18***	0.55***	**0.38***		
Fe-Al bound P	NS	NS	0.58***	**0.74***	
Labile P	NS	NS	NS	0.18***	**0.04***

Table 4.3. Standardized partial regression coefficients. Direct (diagonal, bold) and indirect (off diagonal) contribution of P fertiliser applications on the different soil P pools. Significant levels at $p \leq 0.05$, 0.01 and 0.001 represented by [*], [**] and [***], respectively. NS = not significant.

Variable	Residual	Ca-bound P	Organic P	Fe-Al bound P	Labile P

Galway Peat

Residual P	**-0.61*****				
Ca-bound P	NS	**0.89*****			
Organic P	-0.26*	NS	**0.70*****		
Fe-Al bound P	NS	NS	NS	**0.96*****	
Labile P	NS	NS	NS	NS	**0.94*****

Galway Peaty Mineral

Residual P	**0.46****				
Ca-bound P	-0.29*	**0.90*****			
Organic P	NS	**0.79*****	**NS**		
Fe-Al bound P	-0.429***	NS	NS	**0.68*****	
Labile P	0.40***	0.39***	NS	0.26***	**0.32****

Cork Mineral

Residual P	**NS**				
Ca-bound P	NS	**0.71*****			
Organic P	-0.38***	NS	**0.74*****		
Fe-Al bound P	NS	0.48***	NS	**0.52*****	
Labile P	NS	NS	-0.17**	0.89***	**0.21***

Cork Peaty Mineral

Residual P	**NS**				
Ca-bound P	-0.23**	**0.87*****			
Organic P	NS	0.43*	**0.46***		
Fe-Al bound P	NS	NS	NS	**0.91*****	
Labile P	0.12*	0.25*	0.26**	NS	**0.51*****

Wexford Mineral

Residual P	**-0.45****				
Ca-bound P	-0.37*	**0.39***			
Organic P	-0.34*	NS	**0.51*****		
Fe-Al bound P	NS	NS	NS	**0.93*****	
Labile P	NS	NS	NS	0.34*	**0.63*****

Wexford Peaty Mineral

Residual P	**NS**				
Ca-bound P	-0.43**	**0.42****			
Organic P	-0.35***	0.343***	**0.59*****		
Fe-Al bound P	NS	NS	0.34***	**0.68*****	
Labile P	NS	NS	NS	0.82***	**0.18***
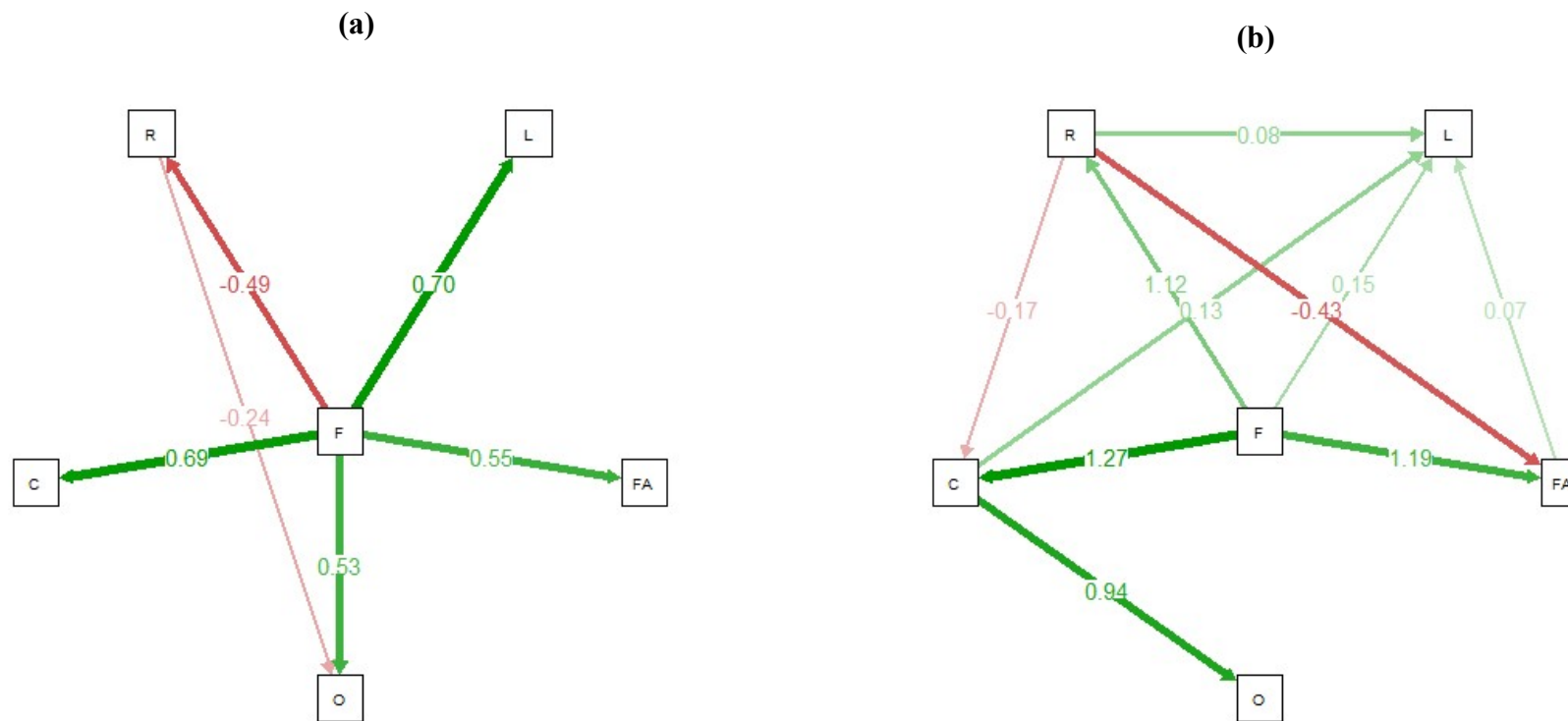
Figure 4.4. Path relationships between soil P pools and P fertiliser in (a) Galway peat soil and (b) Galway peaty mineral soil. Numbers represents unstandardized partial regression coefficients, being the width of the path proportional to the strength of the coefficients, and with green and red colours in the paths representing positive and negative relationships, respectively. F = P fertiliser applied, L= Labile P pool, FA=Fe-Al bound P pool, O= Organic P pool, C= Ca-bound P pool and R=Residual P pool.
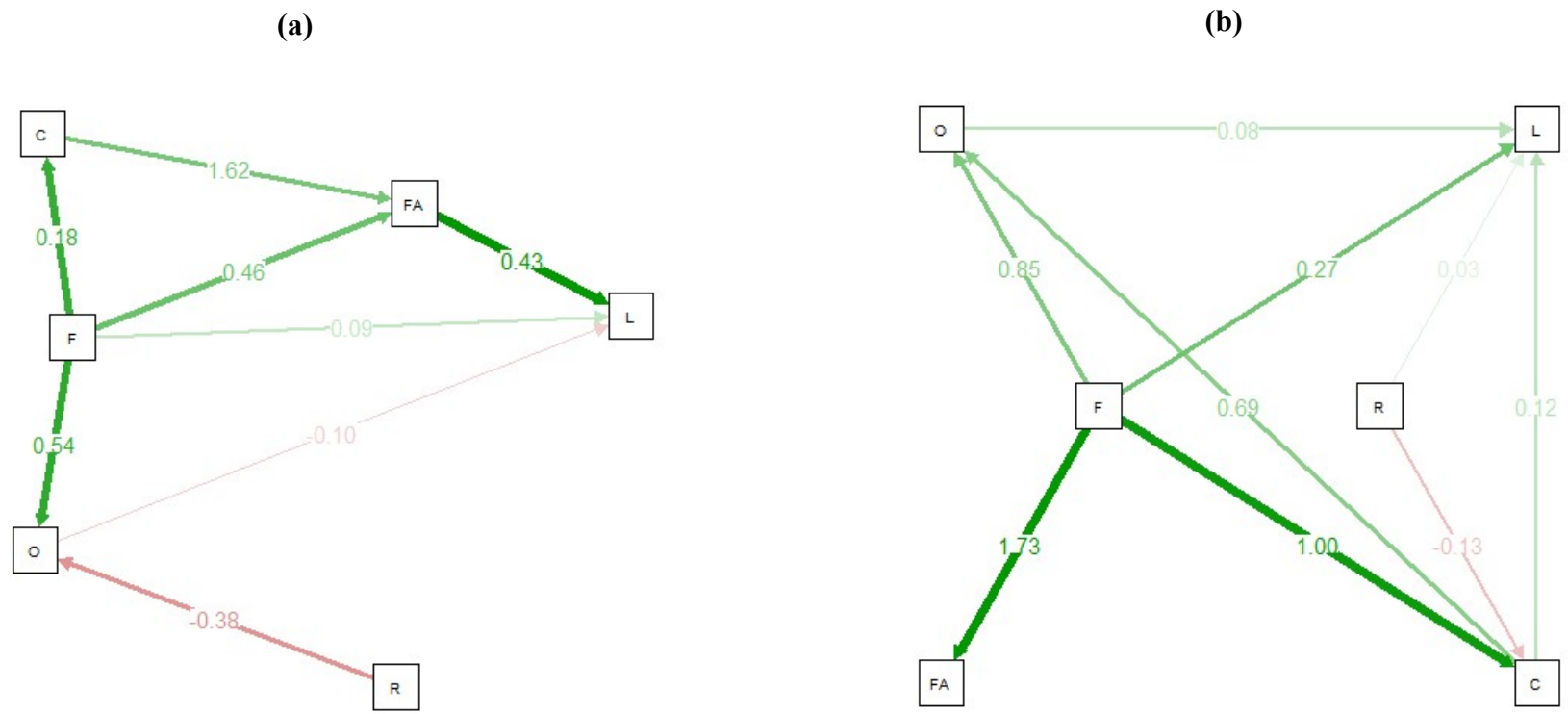
Figure 4.5. Path relationships between soil P pools and P fertiliser in (a) Cork mineral soil and (b) Cork peaty mineral soil. Numbers represents unstandardized partial regression coefficients, being the width of the path proportional to the strength of the coefficients, and with green and red colours in the paths representing positive and negative relationships, respectively. F = P fertiliser applied, L= Labile P pool, FA=Fe-Al bound P pool, O= Organic P pool, C= Ca-bound P pool and R=Residual P pool
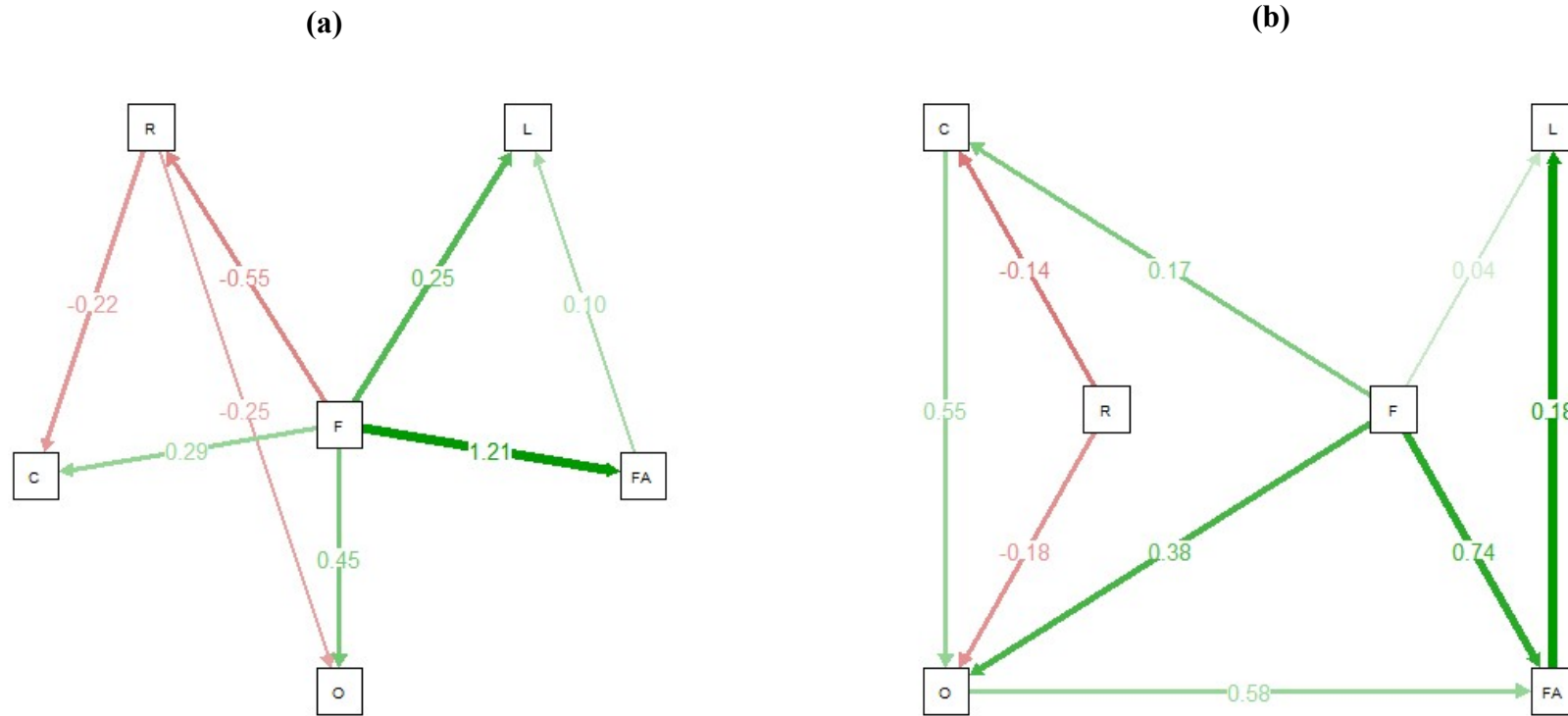
Figure 4.6. Path relationships between soil P pools and P fertiliser in (a) Wexford mineral soil and (b) Wexford peaty mineral soil. Numbers represents unstandardized partial regression coefficients, being the width of the path proportional to the strength of the coefficients, and with green and red colours in the paths representing positive and negative relationships, respectively. F = P fertiliser applied, L= Labile P pool, FA=Fe-Al bound P pool, O= Organic P pool, C= Ca-bound P pool and R=Residual P pool

Phosphorus fertilisation had a large direct impact on the Ca-bound pools in all the soils, especially in Galway peaty mineral, Cork peaty mineral and Galway peat, with path coefficients of 1.27, 1.00 and 0.69, respectively. These soils had the highest Mehlich-III extracted Ca concentrations (Table 4.1), which may explain the higher affinity for P applied in this pool. The Ca-bound P pool exerted little indirect effect on the labile P across the different soils, but had a moderate influence in both organic and Fe-Al bound P pools, suggesting that mobilization of P retained in this pool is possible but unlikely to become available, at least in the short-term. The hypothesis of partial mineralisation of this relatively stable pool towards moderately labile fractions has been suggested in previous studies, which speculated that recalcitrant organic P included in this pool may be mineralised under aerobic conditions (Zheng et al., 2004; Guo et al., 2000; Schlichting et al., 2002). Residual P showed a significant direct interaction with P fertiliser applications in half of the soils, with a negative effect in the Galway peat ($\beta = -0.49$) and Wexford mineral soils ($\beta=-0.55$), suggesting that this recalcitrant P can be mobilised when P is not limiting (Wright and Reddy, 2001). The residual P pool was an important sink for the P applied in Galway peaty mineral, as indicated by the large positive direct effect of the path coefficient ($\beta = 1.12$). Although not statistically significant ($p > 0.05$), the path coefficients in Cork mineral and Wexford peaty mineral soils were also negative (data not shown), indicating an overall tendency of the P retained in this pool to be mobilised and become a potential source of P for plant growth.

When the different pathways of P transformations are compared considering the amount of OM of the soils used in this study, there were no significant transformations among the soil pools in the soil with the highest OM content (Galway peat, 76 % OM). Likewise, Cork peaty mineral, the second largest in OM content (66 %), had limited transformations among its pools, with relatively low enrichment of the labile pool via the Ca-bound P pool ($\beta = 1.0 \times 0.12$) and the organic P pool ($\beta = 0.85 \times 0.03$). Plant growth in these two soils may be restricted under low or nonfertilized management regimes due to their limited ability to replenish labile P, leaving them dependant on continuous fertilisation. On the other hand, added P was indirectly transformed into moderately labile Fe-Al bound P pools to a greater extent in mineral soils, indicating an enhanced ability to build up P reserves compared to organic soils, and were therefore more resilient to non-fertilised management regimes. However, this trend in mineral and organic soils is likely to be so due to the short length of this experiment, and further work in medium and long-term field conditions should be conducted.

4.5 Conclusions

Under P deficient scenarios, this chapter showed that external P additions accumulated mainly in the labile P pool across the different soil types, followed by the Fe-Al bound P pool. However, organic soils displayed a more limited ability to build-up labile P and, to a lesser extent, Fe-Al bound P reserves, compared to mineral soils, rendering them vulnerable to P losses when fertiliser is applied in excess of the crop requirements for growth. Additionally, there was a higher P uptake in the grass yield of these organic soils than in mineral soils, indicating that P fertiliser applications to P-deficient organic soils tend to remain in the soil solution and therefore should be restricted to growing periods when there is a demand for P and the risk of precipitation is low. Soil pH should be optimized prior any fertilisation event, even in P deficient soils, as it influences the retention of applied P. Organic and residual P pools were partially mineralized in most of the soils, indicating mobilisation towards more labile pools. Therefore, they may be considered as a potential source of P for plants.

Transformations of P between the different P pools under fertilisation were well explained by path analysis, and showed the potential of the more recalcitrant pools to mobilise P into more labile P in all the soils. Only the most OM-rich soil had no significant P turnover from the more recalcitrant to labile pools, rendering it dependant to external P applications that may elevate the risk of incidental P losses. Current fertiliser recommendations are mostly based on single agronomic soil P tests that only measure readily available P in the labile P pool, but do not take into consideration the interrelationships with recalcitrant P pools, which may be a potential source of P.

4.6 Summary

This chapter showed the contrasting ability of the different soil types to retain soluble and freshly applied P into the soil matrix, where organic soils had diminished sorption capacities compared to mineral sols. Path analysis suggested a dynamic turnover of non-labile pools to supply P to the labile pool in mineral soils. Chapter 5 examines the runoff losses of P in an organic soil when subjected to different P application rates and timing regimes.

Chapter 5

Split phosphorus fertiliser applications in organic soils reduce incidental losses in surface runoff

5.1   Overview

The objectives of this study were to (1) to evaluate P concentrations in runoff from a rainfall simulation experiment in which P was applied as single and split applications and at different P doses, and (2) to assess the decay rate and persistence of P losses in overland flow derived from the different P applications. The experimental design of the rainfall experiment was based on a farm survey conducted in three different catchments in Ireland on the frequency of P applications that are typically applied, and was conducted within the project in which this thesis is encompassed.

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5.2   Introduction

Incidental losses of P to surface waters, originating from recently added fertilisers to agricultural soils, is a significant pressure on water quality (Delgado and Scalenghe, 2008; Carpenter, 2008; Hart et al., 2004; Haygarth and Jarvis, 1999).

As a result of reclamation of marginal land for grassland production and the application of P fertiliser, P exports from these soils have been reported to be potential major contributors of water deterioration in Ireland (Roberts et al., 2017) and in other parts of the world (Simmonds et al., 2015; Zheng et al., 2014; Guérin et al., 2011; Janardhanan and Daroub, 2010; Castillo and Wright, 2008). However, although some research has been conducted regarding the mechanisms of surface runoff from organic soils (Simmonds et al., 2017; Holden and Burt,

2002), little is known about the potential magnitudes of P loss following P applications nor the mitigation of those losses.

Given the low sorption capacity of organic soils for added P, one of the mechanisms that has been proposed to mitigate P exports is the optimisation of P fertiliser applications in order to better match P requirements with crop demands (Hart et al., 2004). Multiple smaller applications of P fertiliser that account for the same amount of P applied in one single application can both fulfil crop demands and decrease incidental P losses during rainfall-runoff events. However, very little research has reported P losses in this scenario, especially from organic soils. Burkitt et al. (2011) reported this "little and often" approach as a common practice in some parts of Australia, although they did not report consistent data on the number of applications being carried out by landowners.

In this study, we hypothesise that the frequency of P applications on organic/histic soils can reduce the magnitude, decay rate and persistence of P concentrations in runoff following a rainfall event. A laboratory rainfall-runoff experiment was conducted. Two different P fertiliser applications were applied in one single dose or split into two doses on intact organic soil blocks and subjected to eight simulated rainfall events over a period of 85 days.

5.3   Materials and methods

5.3.1   Sites description and farm survey

Farm surveys were carried out in three high status river catchments, namely, the River Urrin in the Southeast, the River Allow in the Southwest, and the River Black in the Midwest of the Republic of Ireland over the 2014/2015 winter period. A total of 39 farms (16, 10 and 13 for the Urrin, Allow and Black catchments, respectively) were surveyed to assess the frequency of P applications of mineral and organic fertilisers across 520 fields. Surveyed data accounted for the number and type of P applications (N-only fertiliser applications, like Calcium Ammonium Nitrate (CAN) or urea, are not included in these data) and the percentage of OM content of each field. As any particular field may have received applications of mineral fertiliser only, organic fertiliser only, or a combination of both types of fertiliser in different proportions, the total numbers of organic and mineral fertiliser applications were calculated. The absolute

values were then converted to proportions of the total number of fields with relation to each soil.

5.3.2 *Soil sample collection, characterisation and fertiliser application regime*

Intact soil blocks, each approximately 0.6 m long, 0.4 m wide and 0.2 m deep, under permanent perennial ryegrass (*Lolium perenne* L.) were collected from a drystock farm in Tuam, Co. Galway (53°3' N 9° 0' W) in June 2017. This farm is situated within the River Black catchment, one of the three catchments included in the farm survey (Roberts et al., 2017). Subsamples taken from the same locations as the soil blocks were air dried, sieved through 2-mm sieve, thoroughly homogenised and analysed for physico-chemical properties. Percentage OM was determined using loss on ignition test at 360° C (Schulte and Hopkins, 1996), particle size analysis was determined with the hydrometer method (ASTMD, 2002), total C and N were estimated by combustion (McGeehan and Naylor, 1988), total and plant available P were determined by the acid perchloric digestion (Sommers and Nelson, 1972) and Morgan's P test (Morgan, 1941) procedures, respectively. Mehlich-3 soil test was used to determine Al, Ca, Fe and P (Mehlich, 1984). A P saturation ratio (PSR) for organic soils was estimated as $[P/(Al+5*Fe)]_{Mehlich-3}$, where P, Al and Fe are Mehlich-3 extractable forms on a molar basis (Guérin et al., 2007).

Phosphorus treatments consisted of different rates of P fertiliser in the form of single super-phosphate (16 % P). Artificial fertiliser was chosen as the predominant form of added P over organic fertilisers (slurry) based on the results of the farm survey conducted in this study. Fertiliser recommendations for organic soils in Ireland are limited to maintenance amounts to replace P removed in crop offtakes, which can be up to 30 kg ha^{-1} depending on the stocking rate and/or grazing regime (Coulter and Lalor, 2008). However, in a nutrient management survey published recently (Roberts et al., 2017), added P can be almost 1.5 times higher than the P requirements for organic soils. Based on this, the fertiliser application rates and timings investigated were: one single application of 30 kg P ha^{-1} (675 mg P flume^{-1}), a 30 kg P ha^{-1} applied in two split applications of 15 kg P ha^{-1} (337.5 mg P flume^{-1}) (one at day 0 and the second at day 55), one single application of 55 kg P ha^{-1} (618.8 mg P flume^{-1}) and 55 kg P ha^{-1} applied in two split applications of 27.5 kg P ha^{-1} (one at day 0 and the second at day 55). Each treatment was replicated at n=3, and a study control (soil only, also replicated at three times) was included in the experimental design.

5.3.3   Rainfall simulation setup

The grassed, intact soil cores were trimmed and packed in runoff boxes, each 1 m long by 0.225 m wide by 0.05 m deep, with side walls 2.5 cm higher than the soil surface. Each runoff box was instrumented with three holes, each 0.5 cm in diameter, at the base to facilitate natural drainage of the soil (Regan et al., 2010) and an overflow weir at the end to allow runoff water to be collected in the simulated rainfall experiments (Figure 5.1). Prior to

Figure 5.1. Flumes layout under the rainfall simulator.

placing the soil in the runoff boxes, cheese cloth was placed at the base before packing the soil slabs to prevent soil loss through the drainage holes. Typically, two blocks were used to fill each runoff box, and packed to ensure that no gap existed between the cores. Melted candle wax was applied between the walls and the soil surface to seal any gap and avoid runoff losses. The runoff boxes were placed outdoors under natural conditions for two months prior to the start of the experiment to facilitate natural settlement of the cores. Grass in the boxes was trimmed to a length of 4-6 cm before any P treatment application, as typically P fertiliser is applied, along with N fertiliser, after a field has been grazed (Burkitt et al., 2011).

The runoff boxes were placed in a rainfall simulator at a slope of 6 %, similar to the average slope of fields high in OM (> 20 %) of the Roberts et al. (2017) study. The rainfall simulator

consisted of a single 1/4HH-SS14SQW nozzle (Spraying Systems Co., Wheaton, IL) attached to a 4.5-m-height metal frame with a rotating disc (Figure 5.2). The simulator was calibrated to achieve an intensity of 10.2 ± 0.1 mm h^{-1} and a droplet impact energy of 260 kJ mm^{-1} h^{-1} at 90 % uniformity. The water used in the simulations had a DRP concentration of less than 0.005 mg L^{-1}. Prior to the start of the experiment, the drainage holes were plugged and the soil was saturated under the simulator until ponding was observed in the surface. The drainage holes were then unplugged to allow the soil to drain freely for 24 h to replicate field

Figure 5.2. Rainfall simulator rotating disc.

conditions before any P application. Due to higher infiltration of water in organic soils compared to mineral soils, drainage holes were plugged at each rainfall simulation to mitigate the direct loss of water in the drainage (Zheng et al., 2014).

After one day, the different P treatments were applied (day 0). Eight rainfall simulations were carried out at days 2, 7, 15, 30, 57, 62, 70 and 85, respectively. Each event lasted for 30 min after continuous runoff was observed. Water in the runoff was collected at 10-min intervals within this 30-min rainfall period and analysed immediately after the end of each simulation. Between each rainfall simulation, the soil boxes were left outdoors under natural weather conditions with the drainage holes unplugged and at a 6 % slope. Temperature and rainfall parameters were recorded from a local weather station (www.iruse.ie).

5.3.4 Water analysis

Water samples were tested for suspended solids (1.2 μm pore size), DRP, TP, total dissolved P (TDP). Suspended solids were measured only for the first three rainfall events and discontinued thereafter as the concentration for all the P treatments (including control) were similar (24.5 ± 5.5 mg L^{-1}) and remained constant over these three first events. Dissolved reactive phosphorus was measured colorimetrically using a nutrient analyser (Konelab 20, Thermo Clinical Laboratories Systems), and TP and TDP were determined after acid persulfate digestion using a BioTector Analyzer (BioTector Analytical Systems Ltd.) Dissolved reactive phosphorus and TPD determination was performed in filtered samples using 0.45-μm filter disks. Particulate P (PP) was calculated by subtracting TPD from TP, and dissolved unreactive P (DUP) was calculated by subtracting DRP from TDP.

5.3.5 Data analysis

Flow weighted mean concentrations (FWMC) were calculated to adjust the variability of the discharge water for each rainfall simulation event using (Cooke et al., 2005):

$$FWMC = \frac{\sum_1^n (v_i \times c_i)}{\sum_1^n v_i} \tag{5.1}$$

where v_i is the volume, in litres, in the ith sample and c_i is the concentration, in mg L^{-1}, in the ith sample. A repeated-measures ANOVA was performed in SPSS (IBM SPSS 24 Core Systems) followed by the Tukey's HSD multiple comparison test. Data were log-transformed in order to meet constancy of variance and normality of errors. A monophasic exponential equation was used to model the decay of P concentration in runoff with time:

$$P = \alpha \times e^{-\beta*t} \tag{5.2}$$

where P is the concentration of P in runoff (in mg L^{-1}), t is the time in days since P application, and α and β are the equation parameters representing the maximum P (in mg L^{-1}) at time zero and the decay rate of P, respectively. For the split P treatments (2×15 kg P ha^{-1} and 2×27.5 kg P ha^{-1}), two equations were fit for each portion of the treatments. The regression analyses were conducted using a nonlinear mixed-effects model in *R* statistical software, version 3.4.2 (R Core Team, 2017) using the *nlme* function in the *nlme* package (Pinheiro et al., 2017). From

the models generated, the time at which the concentration of P would decrease to 50, 75 and 87.5 % of the maximum (corresponding with the half-life, quarter-life and one-eighth-life of the peak P value, respectively) and the corresponding P concentration were estimated. Additionally, the cumulative P losses (mg L^{-1}) were calculated as the area under the curve for each treatment by integrating Eqn. 2 between time zero and infinity:

$$CP = \frac{\alpha}{\beta}$$ [5.3]

where α and β are the model parameters in Eqn.2.

5.4   Results and discussion

5.4.1   Farm survey

Figure 5.3 shows the number of fertiliser applications for organic and mineral soils, differentiating between organic and mineral P fertiliser for each application. To our knowledge, this is the first study to survey and report the frequency of P fertiliser applications. From the 520 fields sampled, 456 fields (88 %) were mineral and 64 (12 %) were organic. There were 39 mineral soils (9 %) and 10 organic soils (16 %) that did not receive any P fertiliser application (data not presented in Figure 5.3). Nearly 40 % of the organic soils received one single application, followed by 28 % and 16 % of the fields receiving two and three applications, respectively, with no further applications beyond this point. Mineral soils had a higher number of P applications, up to seven or eight (with a marginal number of soils receiving nine to eleven applications). These fields were typically under more intense management, with tighter rotational grazing regimes linked to dairy farms and silage and hay production enterprises. By contrast, organic fields were generally under dry stock farms with a more extensive land use.

Regarding the type of fertiliser applied, mineral fertiliser was predominant across the number of fertiliser applications, especially in those soils receiving one single application. This trend was observed in both soil types. For fields receiving two or three applications, the proportion was more balanced. The mineral fertiliser used in the fields receiving two or more applications was typically a combination of different nutrients (NPK) to balance plant offtakes (Roberts et al., 2017).

Organic soils have been reported to have low sorption capacities for P (Guppy et al., 2005; Daly et al., 2001). Therefore, the risk of P losses to adjacent water bodies is high when these soils are placed into agricultural production and receive external P applications to increase
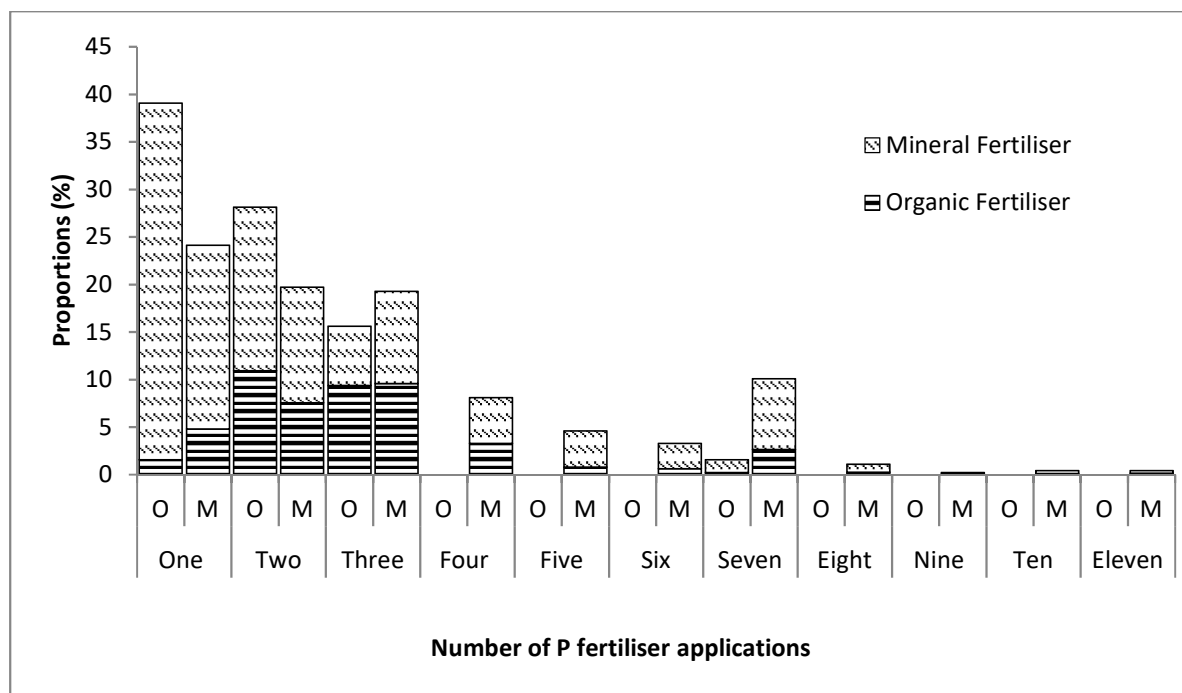
Figure 5.3. Number of fields (proportion in relation to the total number of organic (n=64) and mineral (n=456) soils) receiving increasing number of P fertiliser applications of organic and/or mineral fertiliser. O = organic soils, M = mineral soils.

grass yields. Phosphorus applied in excess of crop requirements in these soils remains in the soil solution, so the likelihood of P loss is increased during rainfall events. However, P losses from these soils may be minimised using a combination of timing and rates of P fertiliser applications (Roberts et al., 2017).

5.4.2 Soil general properties

Based on the soil profile and the OM content, the soil used in this study was classified as a humic lithosol in the Irish Soil Information System (Creamer et al., 2014). Table 5.1 shows the

main physicochemical parameters. The PSR of the soil (0.02) was below the 0.05 value at which it is considered to be a threshold for P concentration in runoff (Guérin et al., 2007).

5.4.3   Phosphorus forms and concentrations in runoff

Among the different forms of P measured in the runoff, DRP was predominant, and on average comprised 89 % of the TP for the P-receiving treatments (65 % for the control). These proportions are consistent with previous studies reporting soluble P in grassland soils, which ranged from 60 to up to 96 % of TP (Kleinman et al., 2002, Nash et al., 2000; Fleming and Cox, 1998; Greenhill et al., 1983). Other studies reported PP as the main form in water runoff using organic P fertiliser such as dairy (Murnane et al., 2015; Brennan et al., 2011) or pig slurry (O'Flynn et al., 2012). The moderately smooth slope at which runoff boxes were subjected in this study, along with the use of soluble commercial P fertiliser and the absence of animals causing damage to the soil, are likely responsible for the low particulate P losses in the overland flow observed (Hart et al., 2004).

Phosphorus treatments, timing of rainfall and their interactions had a significant ($p < 0.001$) effect on the concentration of DRP in the runoff. Among the treatments, FWMC DRP losses in the runoff during the first rainfall event from the single application of 30 kg ha^{-1} (44.6 mg L^{-1}) were more than three times greater than for the first application of its split application, 15 kg ha^{-1} (13.3 mg L^{-1}) (Figure 5.4). Similarly, FWMC DRP losses were almost five times greater for the single application of 55 kg ha^{-1} (97.8 mg L^{-1}) than from its split application of 27.7 kg ha^{-1} (21.8 mg L^{-1}). This highlights that P applications and losses of P in the runoff were not linearly related. Rather, the concentration of P increased exponentially at higher P applications. Other studies also reported a nonlinear relationship between P applications and P concentration in the overland flow (Burkitt et al., 2011; McDowell and Catto, 2005). This is better illustrated when the parameters of the models generated for each treatment were calculated (Table 5.2): whilst the maximum FWMC DRP concentration at time zero (α)

Table 5.1. Selected chemical and physical properties of the soil in the rainfall simulations study. Numbers in parenthesis represent standard deviations (n=3).

pH	OM	Particle Size				Mehlich-3				Total C	Total N	Total P	Morgan's P	PSR[1]
		Clay	Silt	Sand	Texture	Al	Fe	Ca	P					
		%							mg Kg^{-1}				mg L^{-1}	
5.5 (0.3)	54.1 (2.1)	13.9 (1.5)	27.3 (1.6)	58.8 (0.5)	Sandy Loam	328.7 (79.6)	350.7 (46.5)	3771.0 (289.1)	29.3 (3.1)	276.8 (7.7)	16.5 (0.1)	884.0 (39.5)	9.1 (2.2)	0.022 (0.001)

increased with higher P applications, the decay rate (β) remained relatively constant for the different P applications. For example, the FWMC DRP concentration at day 15 was very similar for all the P applications, despite the large differences in the FWMC DRP concentrations between P applications at days 2 and 7. We hypothesise that decay rates may differ among soils of different pedogenesis, depending on the mineralogy and hydrological parameters affecting the P sorption capacity of each soil type. When the simulated cumulative DRP concentrations are considered (CP in Table 5.2), the maximum values correspond to the highest P treatments. The CP was higher for the single applications than for the sum of the split treatments (577.0 and 264.7 mg L^{-1} versus 305.7 and 132.3 mg L^{-1} for the 55 and 30 kg ha^{-1} applications, respectively).
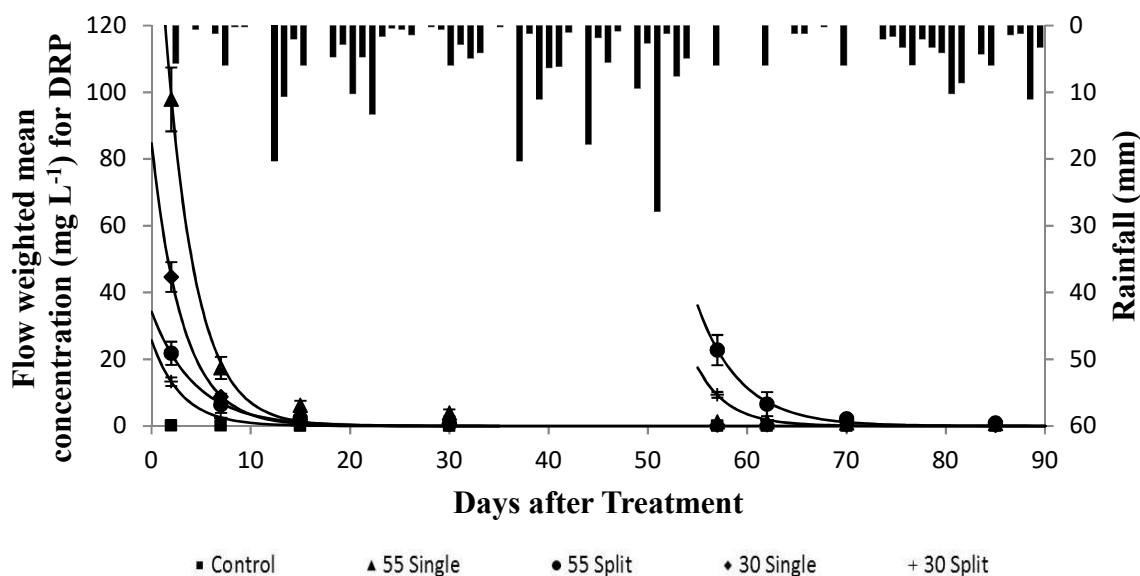
Figure 5.4. Rainfall (right y-axis) and DRP concentration (left y-axis) in runoff (including standard deviations) for each P fertiliser treatment over a period of 85 days. Fertiliser applications correspond with DAT 2 and DAT 57 (spikes in the graph).

As FWMC DRP losses in single applications were higher than those obtained from the split applications, the relevance of multiple, but smaller, applications instead of the same total P in one single fertiliser application, may be proposed as a strategy to improve P management and reduce P losses.

Table 5.2. Model parameters, time to reach 50, 75 and 87.5 % of the maximum P concentration (as DRP) in runoff, along with the P concentration (as DRP) at these referred times, for the different P fertiliser applications. Numbers in parenthesis represent standard deviations (n=3).

Treatments	α	β	CP[1]	t(50 %)	P conc.	t(75%)	P conc.	t(85%)	P conc.
	mg L^{-1}		mg L^{-1}	days	mg L^{-1}	days	mg L^{-1}	days	mg L^{-1}
Single 55 kg ha^{-1}	190.4 (12.7)	0.33 (0.02)	577.0	2.1	95.2	4.2	47.6	6.3	23.8
1st 27.5 kg ha^{-1}	34.2 (2.9)	0.23 (0.02)	148.7	3.0	17.1	6.0	8.5	9.1	4.3
2nd 27.5 kg ha^{-1}	36.1 (4.1)	0.23 (0.02)	157.0	3.0	18	6.0	9.0	8.9	4.5
Single 30 kg ha^{-1}	84.7 (2.1)	0.32 (0.01)	264.7	2.2	42.3	4.3	21.1	6.5	10.6
1st 15 kg ha^{-1}	25.6 (2.2)	0.33 (0.03)	77.6	2.1	12.8	4.2	6.4	6.3	3.2
2nd 15 kg ha^{-1}	17.5 (1.6)	0.32 (0.03)	54.7	2.2	8.8	4.4	4.4	6.6	2.2

The organic soils in the current study had higher P incidental losses in runoff than from other studies in which mineral soils received similar inorganic P applications. For instance, Burkitt et al. (2011) measured DRP losses in surface runoff of approximately 10 and 4 mg L^{-1} after three days of P application in an oxyaquic hydrosol receiving 40 and 13.3 kg ha^{-1} P fertiliser, respectively. These results support previous studies indicating that organic soils are regarded as having poor adsorbancy of P (Simmonds et al., 2015; Guppy et al., 2005; Daly et al., 2001). To our knowledge, no study to date has examined incidental P losses in surface runoff after P fertiliser applications in soils with high content of OM, either in field or in laboratory conditions. Hence, this study can be regarded as a starting point for further experiments investigating incidental P losses under field conditions following recently applied P fertiliser.

The rainfall regime for a specific region/country that may affect any P application is an important point to consider in any P risk assessments and consequently in the P use management in fields. In Ireland, for example, frequent rainfall events occur across the whole year, with April, May, June and July being the months of least rainfall (national average of 80 mm per month). This increases to 100 mm in February, March, August and September (Walsh, 2012). Additionally, rainfall events are higher in the west of the country, where the majority of peat-derived and other organic soils are located (Hammond, 1981). Therefore, it is likely that a rainfall event will occur close to the time of a P fertiliser application, especially at the beginning of the growing season when the temperature starts to rise (February-March) and farmers begin to apply organic P (accumulated from the preceding winter session) and/or artificial fertilisers to enhance grass growth. In this scenario, a "little and often" approach may be more desirable as the losses are smaller than in a single application.

The intensity of the rainfall events, their ability to saturate the soil, and therefore to promote surface runoff, is the most important factor of the model used in this experiment. This means that under other rainfall intensities apart from those recorded here, the P loads in the rainfall events may be different that those reported here.

5.4.4   Decay rate and persistence of phosphorus in runoff

The time to reduce FWMC DRP concentrations to half the initial values in the different P treatments ranged between two and three days. In a similar manner, it would take between four and six days and between six and nine days to reduce P concentrations to 75% and 85 % of the

initial peak value (Table 5.2). The estimated FWMC DRP concentrations at these decay times were all high, indicating that more time would be required to return to baseline concentrations similar to those measured in the control (no P added) soils. Although P concentrations in surface runoff are not equivalent to those for freshwater quality standards, they may be regarded as guidelines in risk assessment plans (Tierney and O'Boyle, 2018). Despite its potential utility, few studies have reported half times in runoff studies, varying between one and four days (Burkitt et al., 2011; Nash et al., 2005). Nevertheless, decay times, such as the ones estimated in the current study, can be seen as guidelines to ascertain the risk of P losses when the probability of rainfall events is taken into account in local recommendation guidelines.

Dissolved reactive P from the different treatments remained significantly different ($p < 0.01$) over the duration of the experiment when compared with the control, except for the single 30 kg ha^{-1} application on day 85 ($p = 0.08$). Relatively low P applications such as those at 30 kg ha^{-1} had a significant effect on DRP exports which lasted at least 70 days, highlighting the persistent effect that P applications can have on surface runoff. For the split applications, DRP losses were significant for at least 30 days. Hart et al. (2004) reported that the most significant proportion of P exports in runoff on mineral soils may last up to 50 days after P applications. The longer periods of time over which P applications had significant effects in the current study compared to those reported in Hart et al. (2004) may be explained by the low P retention abilities of the organic soil used in this experiment. As previously mentioned, in countries such as Ireland, the probability for a relevant rainfall event to occur close to the time of fertiliser application is high, highlighting the elevated risk of P transfer when P applications are made in one dose compared to a smaller but more frequent approach.

5.5   Conclusions

Our initial hypothesis in which frequency of P applications would decrease P loads in runoff was supported by our results, where significantly reduced P concentrations in surface runoff were obtained from split applications compared to the same P amount applied in one single application. This suggests that, in soils with low P sorption abilities such as histic and other peat-derived soils, the 'little and often' approach may be regarded as a good strategy to minimise P exports in surface runoff from organic soils following P fertiliser application. In

this scenario, the risk of P loss in runoff is closely linked to climatology, so that rainfall events occurring all year around, such as in Ireland and other temperate countries, can drastically affect incidental P losses when they are applied in one single dose rather than smaller, but multiple, applications. However, it has been shown that decay rates at which P was exported in the surface runoff were similar across different P application rates and timings, suggesting that is a characteristic related to the specific ability of the soil to retain P in the overland flow and not added P rates.

Our results also showed that the time required to reduce P concentration in overland flow to a baseline value can take two to three months, and is likely associated with the limited ability of organic soils to retain added P. The time to reduce peak concentrations to 75 or 85 % ranged between six and nine days from the time of fertiliser application. Although P exports at these times and standard freshwater quality concentrations are not equivalent, cognisance of the time periods of potentially elevated P concentrations following P fertiliser applications should be taken into account in the nutrient management of farms.

5.6   Summary

This chapter has explored the P loads in surface runoff in an rainfall simulation experiment using different P applications and timing regimes. For any given amount of applied P, split applications produced significantly lower P in surface runoff than the single applications, suggesting that the timing regime should be considered in order to minimise P losses in overland flow. Chapter 6 explores the P and N loads in leaching water derived from different P rates and timings of slurry in a column experiment.

Chapter 6

Impacts of single and split dairy slurry applications on the column leachate of two soils with contrasting organic matter content

6.1   Overview

The aim of this work was to compare leaching losses of P and N from two soils of contrasting organic matter content receiving different doses of dairy slurry in one single application or split in two, and determine the potential risk of nutrient loss arising from these slurry applications on the leached water.

6.2   Introduction

Land application of animal-derived manures such as dairy slurry is a common practice to improve soil fertility, but it may also pose a risk of nutrient and C losses to the surrounding environment. Although surface runoff is considered to be the main pathway of nutrient losses from fertiliser applications, leachate or subsurface processes may also be a key component of the transport mechanism from agricultural soils to water in some soil types, particularly organic soils (Hart et al., 2004; Simmonds et al., 2017).

With intensification of agricultural practices across Europe, marginal soils such as peat soils and other peat-derived soils are being cultivated to meet food demands. Organic soils have low P retention properties due to intense competition reactions of organic acids for the scarce cationic sorption sites of the mineral fraction (Gerke, 2010; Guppy et al., 2005; Daly et al., 2001). Moreover, organic soils can develop significant preferential flow pathways due to their high hydrophobicity when they are exposed to drying and wetting processes. However, few studies have been conducted in organic soils receiving organic fertiliser applications, and the potential impact of subsurface transfer of P and N in these soils remains poorly understood (Riddle et al., 2018; Parvage et al., 2015).

In Chapter 5, the impact of single versus split applications of fertiliser on nutrient content in runoff from organic soils was quantified. This chapter builds on this work by evaluating the risk of nutrient transfer derived from these fertiliser practices to the groundwater. Therefore, the aim of this chapter was to examine losses of P and N in subsurface flow following single and split applications of dairy slurry at different doses to soils of contrasting organic matter content. The soils were placed in polyvinyl chloride (PVC) columns, maintained under constant conditions of temperature and humidity, and subjected to simulated rainfall. The slurry treatments (equivalent to 15, 30 and 55 kg P ha^{-1}) were made in one single application or split into two applications over a total study period of 34 weeks.

6.3   Materials and methods

6.3.1   *Soil collection and analysis*

Organic and mineral soils were collected from two dry-stock farms located in a "high status" catchment (Roberts et al., 2017). Approximately 150 kg of each soil type was collected from the top 0.2 m, air-dried, manually sieved to pass a 2-mm sieve, and thoroughly mixed. A subsample from each soil type was analysed for physico-chemical properties. At the time of soil collection, intact soil cores (n=3) were taken to determine fresh bulk density and gravimetric water content, according to British standards (BS 1377-2, 1990)

Cation exchange capacity was estimated using the method described by Ross (1995). pH (1:1 in H$_2$O) was determined according to McLean (1982). Total OM was determined using the loss on ignition test at 360° C (Schulte and Hopkins, 1996). Total C and N were estimated by combustion (McGeehan and Naylor, 1988). Total and plant available P were determined by the acid perchloric digestion (Sommers and Nelson, 1972) and the Morgan's P test (Morgan, 1941) procedures, respectively. Particle size analysis was determined using the hydrometer method (ASTMD, 2002). The Mehlich-3 soil test was used to determine Al, Ca, Fe and P (Mehlich, 1984). As a measure of the degree of P saturation of the soils, the P saturation ratio (PSR) for acidic soils was calculated:

$$[P/(Al+\gamma*Fe)]_{Mehlich\text{-}3} \qquad\qquad [6.1]$$

where P, Al and Fe are Mehlich-3 extractable forms on a molar basis and γ is a weighing factor, set at 1 for the mineral soil and 5 for the organic soil, to compensate for the low extraction efficiency of Fe in organic soils (Guérin et al., 2007).

Additionally, P sorption isotherm experiments were conducted to determine the total sorption and bonding capacities of both soils. Twenty-five mL of varying concentrations (0, 5, 10, 30 and 60 mg P L^{-1}) of a KH_2PO_4 stock solution were added to 50 mL polyethylene centrifuge tubes each containing 1 g of soil (n=3). Samples were shaken for 24 h at 250 epm in a reciprocating shaker, allowed to settle for 1 h, filtered through a 0.45 μm membrane filter, and the filtrate was analysed for DRP using a nutrient analyser (Konelab 20, Thermo Clinical Lab systems, Finland). A linearized Langmuir adsorption equation (Kovar and Pierzynski, 2009) was used to fit the data:

$$\frac{C}{S} = \frac{1}{kS_{max}} + \frac{C}{S_{max}} \tag{6.2}$$

where C is the concentration of P after equilibration (in mg L^{-1}) and S is the total amount of P retained (mg kg^{-1}), S_{max} represents the maximum amount of P that can be sorbed by the soil (mg kg^{-1}), and k is a constant related to the bond strength of added P to soil (L mg^{-1} P).

6.3.2   Slurry collection and analysis

Dairy slurry was collected from the Teagasc Agricultural Research Centre, Moorepark, Fermoy, Co. Cork, and kept refrigerated (10 ± 1 °C) prior to the start of the experiment. Homogenised subsamples were tested in triplicate for TP, total N (TN), DRP, ammonium (NH_4), pH and DM. Total P and TN were measured using acid persulfate digestion and by combustion oxidation, respectively. Dry matter was measured by drying at 105° C for 24 h and pH was determined using a pH probe (LF 96 Meter, WTW, Germany). A subsample of fresh slurry was centrifuged before being filtered (0.45 μm) and analysed for DRP and NH_4. All the parameters were determined using the standard methods (APHA, 2005).

6.3.3   Soil columns setup

Prior to placement in the columns, the gravimetric water content of the two soils was modified using distilled water to attain the same value as that measured at the time of sampling. The soil was packed in forty-two 0.3-m deep and 0.1-m internal diameter PVC columns (21 for each soil type) (Figure 6.1), each instrumented with perforated bases to allow free drainage. A 0.05-m layer of gravel was placed at the bottom of the columns, which was overlain by 0.2 m of soil, compacted in 0.05 m depth intervals to attain the same fresh bulk density as obtained in the field. At each depth interval, the soil was pressed against the column to avoid the occurrence of preferential flow paths.

Figure 6.1. PVC columns containing packed soil

The experiment was conducted in a temperature ($10 \pm 1 \,^{\circ}$C) and humidity (85 ± 8 %)-controlled room, representative of climatic conditions in Ireland (Walsh, 2012). Each column was irrigated weekly with 160 mL of distilled water, applied homogeneously onto the surface in two aliquots each of 80 mL over a 2 h period. This rate of water addition was representative of the yearly average precipitation in Ireland (19 mm per week, 980 mm per year; Walsh, 2012). Prior to the start of the experiment, the columns were allowed to incubate for a period of 16 weeks to stabilise the pulse in C and N mineralisation following drying and wetting processes in the soil (Borken and Matzner, 2009).

The treatments (each at n=3) examined were: (1) one single application of 15 kg P ha^{-1} (11.8 mg P column^{-1}) (2) a 15 kg P ha^{-1} applied in two split applications of 7.5 kg P ha^{-1} (5.9 mg P column^{-1}) each (3) one single application of 30 kg P ha^{-1} (23.6 mg P column^{-1}) (4) a 30 kg P

ha^{-1} applied in two split applications of 15 kg P ha^{-1} (11.8 mg P column^{-1}) each (5) one single application of 55 kg P ha^{-1} (43.2 mg P column^{-1}) (6) 55 kg P ha^{-1} applied in two split applications of 27.5 kg P ha^{-1} (21.6 mg P column^{-1}) each, and (7) a study control (soil only). Based on the content of TP of the dairy slurry, the amounts of slurry applied were 36, 72 and 132 g for the single 15, 30 and 55 kg ha^{-1}, respectively. The amount of TN added was 64.6, 129.2 and 236.9 kg ha^{-1} for applications of 15, 30 and 55 kg P ha^{-1}, respectively. The duration of the experiment was 34 weeks.

Single applications were made after the incubation period, at week 17, and split applications on week 17 and 25, respectively. The doses were selected based on current fertiliser recommendations on organic soils in Ireland, where the maximum allowance for P is 30 kg P ha^{-1}, depending on the stocking rate and/or grazing regime (Coulter and Lalor, 2008). However, a recent study reported that the P applied may be up to 1.5 times higher than the advised amounts for organic soils (Roberts et al., 2017). Due to the low sorption abilities of organic soils to retain P (Guppy et al., 2005; Daly et al., 2001), lower application rates (15 kg ha^{-1}) were included in the experiment.

6.3.4   Leachate collection and analysis

Leached water was collected weekly in plastic containers using funnels placed beneath each column (Figure 6.2). Volumes of leached water were measured and homogenised before subsampling. Unfiltered subsamples were analysed for TP, TN, total organic carbon (TOC), total inorganic carbon (TIC) using a Biotector Analyser (Biotector Analytical Systems Ltd), and the pH was measured using with a pH probe (LF 96 Meter, WTW). Filtered subsamples

Figure 6.2. Containers and funnels used to weekly collect leached water.

(0.45-μm pore size) were analysed for DRP, NH_4-N, total oxidised nitrogen (TON) and nitrite-N (NO_3-N) using a nutrient analyser (Konelab 20, Thermo Clinical Laboratories Systems, Finland), and total dissolved nitrogen (TDN), dissolved organic and inorganic carbon (DOC and DIC) and TDP using a Biotector analyser (Biotector Analytical Systems Ltd). Nitrate-N (NO_2-N) was calculated as the difference between TON and NO_3-N, total particulate N (TPN) as the difference between TN and TDN, organic N (N_{org}) as the difference between TDN and TON + NH_4-N, DUP as the difference between TDP and DRP, and particulate P as the difference between TP and TDP.

6.3.5   Data analysis

Each week, the cumulative mass of leached water from every column was measured and tested for the water quality parameters of interest. This enabled the mass release from each column to be measured and expressed as a loss per unit surface area of each column. These data were then extrapolated to produce a weekly gravimetric loss per hectare (kg ha^{-1}) for each treatment. Additionally, in order to estimate the percentage of the nutrients applied that was released in the leached water, a mass balance was estimated for P and N as the difference between the cumulative losses of each nutrient and the control soil divided by the amount of the nutrient applied at each slurry treatment. Despite the repeated nature of the measurements, the use of the maximum (total) cumulative values of each nutrient as a single meaningful measure reduced the multivariate response to an univariate response, thus enabling the use of classical analysis methods (Davis, 2002). The data were subjected to normality and homogeneity of variance analyses. Differences in the loads in leachate (kg ha^{-1}) were evaluated using a two-way ANOVA, and simple effects analyses were performed by the Bonferroni test at α=0.05 when the main and/or interaction effects were significant ($p < 0.05$). Data analyses were performed in SPSS (IBM SPSS 24 Core Systems) using the GLM-Univariate procedure.

6.4   Results and discussion

6.4.1   Soil and slurry characteristics

Table 6.1 shows selected physical and chemical properties of both soils and their Langmuir equation parameters. The organic and mineral soils were classified as a humic lithosol and typical brown earth, respectively, under the Irish soil classification system (Creamer et al., 2014), whose equivalents to the FAO soil classification system (IUSS Working Group WRB, 2014) are lithic leptosol and haplic phaeozem. The organic soil had nearly seven times more OM content (54.1 %) than the mineral soil (8.0 %), although the Mehlich-III extractable Ca was slightly lower (2831 mg kg^{-1} for the organic soil and 3042 mg kg^{-1} for the mineral soil), yielding a moderately acidic pH for the former (5.5) and near-to neutral pH for the latter (6.3). The P sorption ability (S_{max}) of the organic soil (1278 mg kg^{-1}) was higher than in the mineral soil (896 mg kg^{-1}), whilst the constant k, related to the bonding energy of added P to soil sorption sites, was roughly similar in both soils (Table 6.1).

The decreased S_{max} of the mineral soil may have been partly attributable to its higher pH compared to the organic soil. pH has been shown to be inversely related to the S_{max} due to the alteration of the forms of P-fixing compounds such as clays and Al and Fe oxides that lead to desorption processes; lower soil pH favours the presence of free iron and aluminium oxides in soil matrix, whereas higher pH (6.5 – 7.5) exert an opposite effect, lowering the concentration of free iron and aluminium oxides (Roy and De Datta, 1985). However, it is likely that the main reason for the higher P-sorption ability of the organic soil over the mineral soil is due to the activation of new sorption sites that were occluded by the native OM of the soil by the breaking of the soil structure when it was sieved prior packing in the columns, as it will be explained in the next subsection

Mehlich-3 extractable P concentrations were low-to-optimum for the organic soil (29.3 mg kg^{-1}) with respect to agronomic recommendations (Mallarino et al., 2013) and very high for the mineral soil (72.3 mg kg^{-1}), possibly due to excessive fertiliser applications in the years prior to sample collection. The PSR of the mineral soil (0.084) was above the critical threshold of 0.05, indicating a potential source of P losses (Guérin et al., 2007). Despite S_{max} (maximum amount of P that can be sorbed by the soil) in the organic soil being higher than in the mineral soil, the PSR was more elevated for the latter, indicating that P was less strongly retained by the mineral soil (Beauchemin and Simard, 1999).

Table 6.1. Selected physico-chemical characteristics (± standard deviations) of the two soils used in this study.

Soil properties		Soil type	
		Organic	Mineral
pH[1]		5.5 (0.3)	6.3 (0.1)
OM	%	54.1 (2.1)	8.0 (0.2)
Dry bulk density	g cm^{-3}	0.41	0.99
Particle Size			
Clay	%	13.9 (1.5)	16.9 (1.3)
Silt	%	27.3 (1.6)	37.4 (0.3)
Sand	%	58.8 (0.5)	45.7 (1.0)
Texture (USDA)		Sandy Loam	Loam
Total C	mg kg^{-1}	276.8 (7.7)	39.2 (4.1)
Total N	mg kg^{-1}	16.5 (0.1)	3.6 (0.5)
Total P	mg kg^{-1}	884.0 (39.5)	770.0 (60.1)
Mehlich III			
P	mg kg^{-1}	29.3 (3.1)	72.3 (3.1)
Al	mg kg^{-1}	328.7 (79.6)	591.7 (15.6)
Fe	mg kg^{-1}	350.7 (46.5)	334.0 (22.6)
Ca	mg kg^{-1}	2831.7 (51.7)	3042.0 (289.1)
CEC[2]	meq/100 g	32.4 (5.6)	17.5 (0.2)
PSR[3]		0.022 (0.001)	0.084 (0.002)
Langmuir parameters			
S$_{max}$	mg kg^{-1}	1278.9	896.5
k	m^3 g^{-1}	0.09	0.12

[1] Organic matter. [2] Cation exchange capacity. [3] Phosphorus saturation ratio.

This seems to be in contradiction with the k values obtained from the Langmuir equation, where mineral soil had a slightly higher bonding energy compared to the organic soil (Table 6.1). As defined in Eqn. [6.2], k is a constant derived from the sorption isotherms where increasing amounts of P are added to the soil, thus reflecting the overall binding energy across all the saturation process derived from the sorption isotherm trials. However, this constant may not necessarily reflect the binding energy of P to the soil at a specific, intermediate phase of the saturation process. In neutral and alkaline soils, Ca-containing compounds will have some effect on P sorption, which may not be captured by the PSR formula (Ige et al., 2005).

Total phosphorus, TN, NH4-N, DM and pH values in the dairy slurry fertiliser were 354.7 ±1.9 mg kg^{-1}, 1519.6 ± 64.4 mg kg^{-1}, 590.0 ± 0.2 mg kg^{-1}, 5.3 ± 0.1 (%) and 6.5 ± 0.0, respectively. All the columns drained freely throughout the duration of the experiment, with an average 96 % leachate recovery for both soils.

6.4.2   Phosphorus in leachate

Considering the organic soil, with the exception of the single application of 55 kg ha^{-1} (Figure 6.3 – A1), there was no statistically significant difference ($p > 0.05$) in the mass of DRP released between the slurry treatments and the study control. Similarly, there were no statistically significant differences in the DRP mass released across all treatments from the mineral soil (Figure 6.3- B1). Comparing the mass of DRP released from both soils when subjected to the same application rate, there were no statistically significant differences for the control, single 55 and split 55 kg ha^{-1} applications ($p > 0.05$), suggesting that DRP losses in the leachate at these slurry applications (no slurry application in the case of the control) were of the same magnitude for both soils. However, mineral soil had significantly higher DRP releases in the single 15, single 30, split 15 and split 30 kg ha^{-1} treatments than the equivalent treatments in the organic soil. With regard to TP, treatment had no impact on the mass release from the organic soil (Figure 6.3 – A2), whereas there were significant differences between the control and the single 30 and single 55 kg ha^{-1} treatments in the mineral soil (Figure 6.3- B2). The split slurry applications seemed to have little effect on the P release, as the cumulative curve (Figure 6.3) did not show any clear pattern for these applications in both soils. In general, the amounts of P losses observed in this study are somewhat lower than other similar leachate studies in which undisturbed organic and mineral soils columns were used. For example, Parvage et al. (2015) reported TP losses of 6.72 kg ha^{-1} after three days of continuous leachate from peat soil columns receiving 22 kg P ha^{-1} in the form of composted horse manure. In comparison, the total TP losses in the current study were lower than 2 kg ha^{-1} after a much longer period of 19 weeks. Despite the higher S_{max} of the organic soil compared to the mineral soil in this experiment, the maximum amount of P that can be retained by each soil is higher for the mineral soil than for the organic soil due to the higher bulk density of the mineral soil compared to the organic soil. Thus, for the organic soil, the proportion of P applied in the slurry was 1.94, 3.88 and 7.11 % of the S_{max} for the 15, 30 and 55 kg ha^{-1} treatments, respectively.
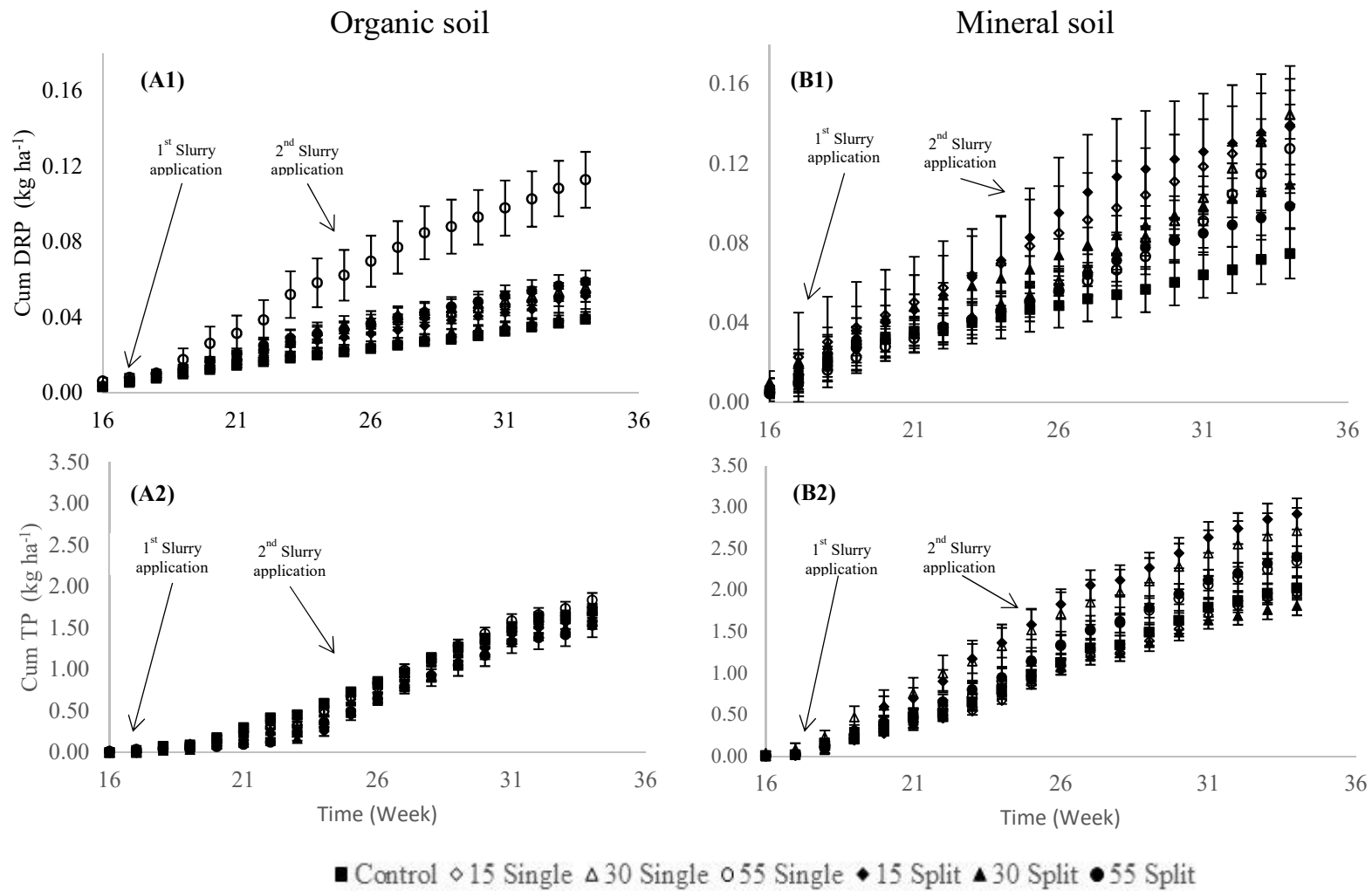
Figure 6.3. Average cumulative concentrations of dissolved reactive P (DRP) and total P (TP) for each treatment and soil type. Error bars represent standard deviations.

For the mineral soil, the proportions were 0.98, 1.78 and 3.26 % of the S_{max}. These figures reflect the ability of both soils to retain added soluble P, likely due to the destruction of occluded sorption sites by OM in the process of soil packing into the columns that became active. When the amount of P released in leachate is calculated as the percentage of what was applied in the slurry (Table 6.2), most of the P applied was retained in the soils, with percentages lower than 2 % for the organic soil.

For the mineral soil the values were similar, although a 7.3 % recovery was obtained for the 15 split applications. Although organic soils are considered to have low sorption capacities for P due to competition between phosphate anions and humic/fulvic acids and occlusion of OM for sorption sites (Daly et al., 2001; Guppy et al., 2005), the amounts of P obtained in leachate highlight the elevated ability of the organic soil used in this study to retain freshly added P. The disruption of the soil structure when packing the columns, with the breakage of soil aggregates, likely enhanced the ability of the soil to immobilise soluble P applied in the slurry by the activation of sorption sites that were occluded by the native OM of the soil (Margenot et al., 2017; Muukkonen et al., 2009).

Table 6.2. Percentage recovery of TP in leachate, calculated as the difference between the total P obtained at each treatment and the control divided by the amount of P applied in the slurry.

Slurry application (kg ha⁻¹)	Soil type	
	Organic	Mineral
Single		
15	1.62	0.93
30	0.43	1.99
55	0.71	0.97
Split		
15	1.55	7.32
30	0.61	0.69
55	0.16	1.06

Disturbed soil columns may have created new reaction surfaces and, consequently, increased the soils' ability to sorb: the presence of new carbonates (Sø et al., 2011), clay minerals (Gérard, 2016), and Al and Fe oxide (Antelo et al., 2007) sorption sites from the breakage of the soil aggregates may have further promoted the P retention capacity. In the case of Al and Fe oxides,

this enhanced sorption ability may have been promoted by the formation of tertiary compounds between the metals and organic acids, especially abundant in soils with high OM content (Riddle et al., 2018; Gerke, 2010). Additionally, in organic soils, subsurface flow is the predominant path of P transport due to the tendency to develop macropores and cracks following drying and wetting cycles under natural conditions as a consequence of its hydrophobicity (Simmonds et al., 2017; Litaor et al., 2006). Disturbed organic soils likely destroyed the pore network, and therefore contributed to the observed small mass release of P in the leachate.

These results suggest that the alteration of the soil structure by, for instance, tillage practices in annual crops or in intensively managed grasslands before reseeding may be regarded as a palliative recommendation to enhance the P retention ability of these soils. This may minimise the risk of P losses into surrounding water, if and when the risk of erosion and the subsequent loss of soil particles is correctly managed. However, ploughing is not considered a suitable practice for organic soils due to economic and environmental reasons (Paul et al., 2018; Ilnicki, 2003), leaving extensive grassland or wetland restoration uses as the wisest, most sustainable options for these soils. However, environmental impacts derived from management practices in organic soils under grassland practices remain poorly understood and warrants further field investigation.

6.4.3   Nitrogen and carbon in leachate

There was no statistical difference in the NH_4-N released from the treatments applied ($p > 0.05$) in the organic soil, except for the single 55 kg ha^{-1} treatment (Figure 6.4 – A1). For the mineral soil, single applications of 30 and 55 kg ha^{-1} and the split application of 55 had a statistically significant effect ($p < 0.001$) in the NH_4-N release compared to the control (Figure 6.4 – B1). When soil types were compared, all treatments were significantly higher for the mineral soil in comparison to the organic soil. The NH_4-N in the leachate from the mineral soil ranged from 6 to 36 kg ha^{-1} compared to the very low values for the organic soil, which ranged from 0.1 to 0.3 kg ha^{-1}. Given that the pH of the organic soil was acidic (5.5) and the relatively low temperature at which soil columns were studied (10° C), the losses of NH_4-N through conversion to NH_3 gas were likely to be low (Vymazal, 2007).
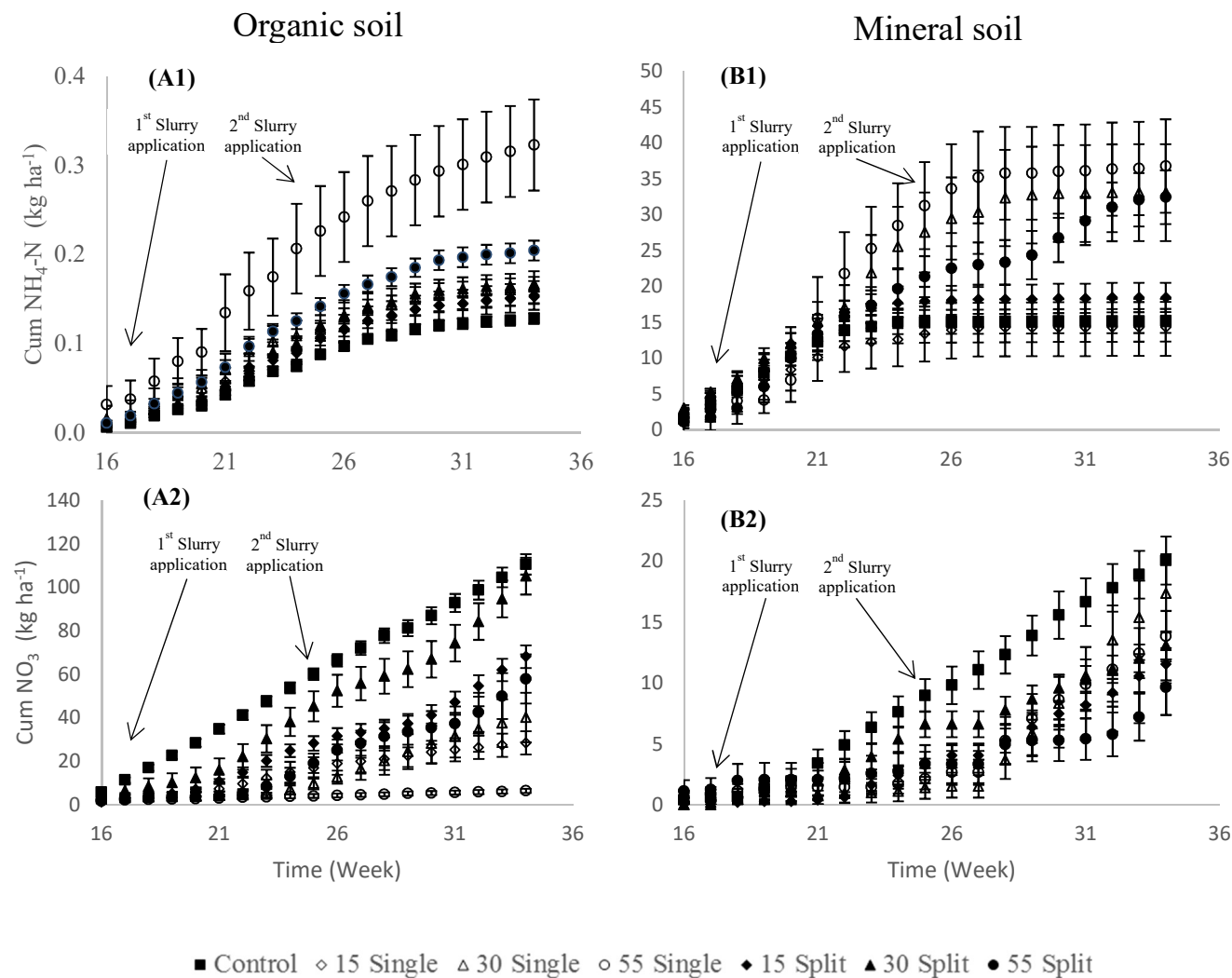
Figure 6.4. Average cumulative concentrations of ammonium (NH_4-N) and nitrate (NO_3-N) for each treatment and soil type. Error bars represent standard deviations.

The NH_4-N released in leached water as a percentage of the NH_4-N applied in the slurry was lower than 1 % in the organic soil, but ranged from 18 to 54 % in the mineral soil (Table 6.3). Therefore, it is likely that NH_4-N applied in the slurry, which was equivalent to 38 % of the TN, was mainly held in the cationic sorption soil sites of the organic soil due to its relatively high CEC (32.4 meq/100 g) or subjected to a more intense nitrification process. By contrast, the lower CEC of the mineral soil (17 meq/100 g) may have promoted mobilization of the positively charged NH_4-N through the columns.

Over the duration of the study, cumulative NO_3-N losses from all treatments were substantially higher from the organic soil columns than from the mineral soil columns, indicating a more efficient nitrification process. For the organic soil, leached losses of NO_3-N were significantly lower in all treatments than from the control, except for the split 30 kg ha^{-1} (Figure 6.4- A2). Comparatively, NO_3-N releases from the amended columns were not statistically different than from the control in the mineral soil. The high concentration of NO_3-N in the control columns in the organic soil may be due to an ammonification-nitrification process of the native OM of the soil, which was substantially higher than the mineral soil (Table 6.1).

Table 6.3. Percentage recovery of NH_4-N in leachate, calculated as the difference between the total NH_4-N obtained in leachate water at each treatment and the control divided by the amount of NH_4-N applied in the slurry.

Slurry application (kg ha^{-1})	Soil type	
NH$_4$-N	Organic	Mineral
Single		
15	0.59	32.48
30	0.31	53.67
55	0.37	33.30
Split		
15	0.58	49.11
30	0.32	17.78
55	0.25	28.58

The high volume of slurry applied onto the columns (36, 72 and 132 g of slurry for the single 15, 30 and 55 kg ha^{-1}, respectively) may have clogged the surface, particularly following water application, thus creating anoxic conditions wherein denitrifying bacteria may have been more

active than in the unamended soil columns (Vymazal, 2007). In the mineral soil, the nitrification process may have occurred to a lesser extent than in the organic soil, possibly due to the lower C/N ratio as a consequence of the smaller initial amount of OM in the soil compared to the organic soil. As was the case for the P, split slurry applications did not have a significant impact in the mass released in leachate over the period of study. Only the mineral soil showed an increased in the NH_4-N load for the second application of the split 55 kg ha^{-1} treatment four weeks after it was applied.

The daily and cumulative TOC released from both the organic and mineral soil columns were similar. In both cases, with the exception of the 55 kg ha^{-1} treatment, there were no significant differences between the treatments and the study control (Figure 6.5). This similarity in both soils may be due to high volume of slurry applied in the columns receiving this dose. Although the TOC content of the dairy slurry was not measured, this can be up to 13000 mg kg^{-1} (Murnane et al., 2018), thus creating a lag time until heterotrophic microorganisms could use the excess of applied TOC that ended up in the leachate water a few weeks after the application of the 55 kg ha^{-1} treatment. This may be evidenced by the fact that, among treatments, TOC loads in leachate were all significantly higher in the mineral soil than the organic soils (Figure 6.5), suggesting that organic carbon was used by denitrifying bacteria more efficiently in the organic soil compared to the mineral soil.

These results indicated that, although NH_4-N and NO_3-N may be the predominant pollutants in subsurface waters derived from mineral soils receiving agricultural wastes, organic soils experienced increased rates of nitrification resulting in higher NO_3-N releases that, in turn, may be conduct to elevate rates of denitrification, given the typically high amounts of inherent organic compounds in these soil types that could act as electron donors for the conversion of NO_3-N to N_2O. Despite that denitrification predominantly occurs under anaerobic or anoxic conditions, it has been reported that this process can also occur before the oxygen has been totally depleted or under low-oxygen conditions (Vymazal, 2007). The predisposition of organic soils to endure temporary flooding may render them vulnerable to increased rates of denitrification when agricultural sources of N are applied. Further field studies are needed to quantify and evaluate the impact of agricultural wastes on gaseous N release for these soil types.
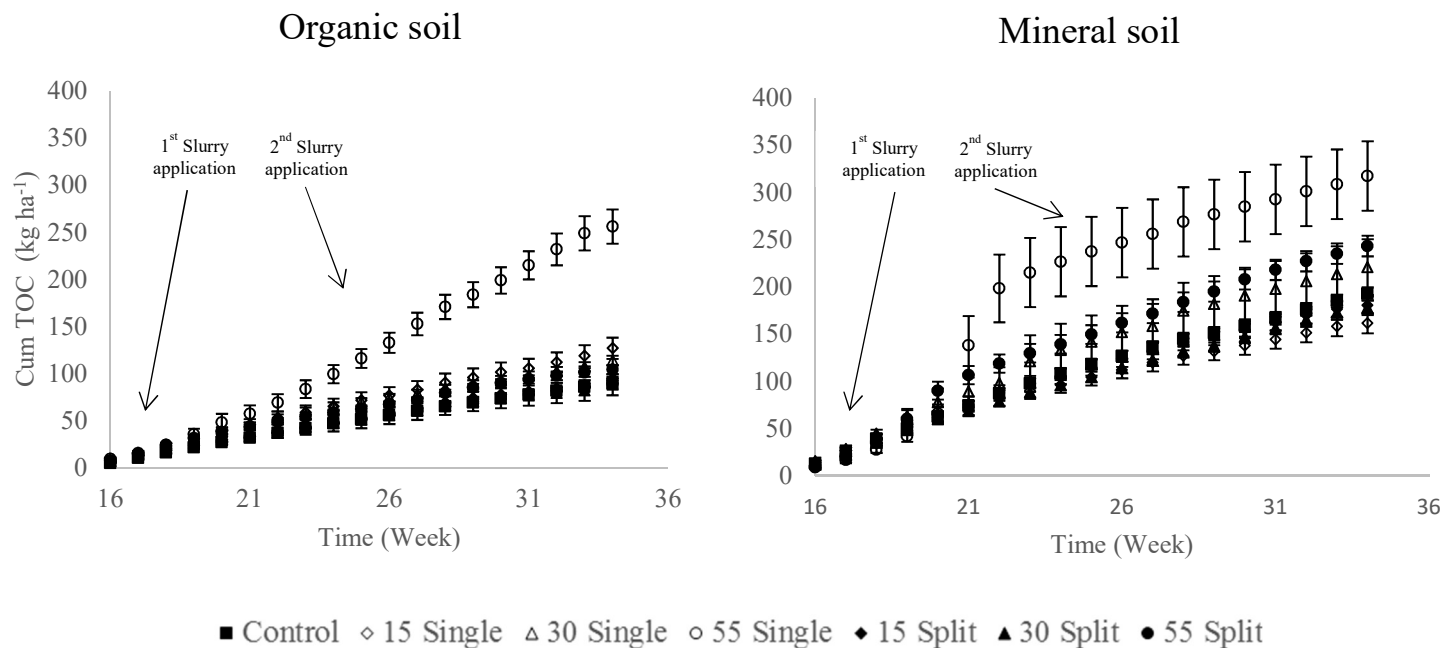
Figure 6.5. Average cumulative concentrations of total organic carbon (TOC) for each treatment and soil type. Error bars represent standard deviations.

6.5 Conclusions

Irrespective of the soil type, total cumulative P loads in leached water after a period of 19 weeks were very small for all the treatments, reflecting the high ability of both soils to retain P from slurry in the soil matrix. However, this elevated sorption ability was not likely due to the soils' chemical properties under natural conditions, but rather a consequence of the breakage of soil aggregates during the packing process of the soil into the columns that exposed new sorption sites that were previously occluded, therefore artificially increasing their P retention capacities. In general, split applications did not produce a significantly lower P release in the leachate when compared with their single counterparts, although this lack of effect may have been masked by the artificially enhanced ability of the soils used here to retain P.

Although NH_4-N loads in leachate increased proportionally with the slurry application rate in the mineral soil, the losses for the organic soil were negligible, indicating higher retention and nitrification abilities in this soil type. However, the NO_3-N released in leachate from the organic soil was greater than from the mineral soil at all the treatments. Nonetheless, the masses measured in the leachate were inversely proportional to the application rates, along with the fact that TOC losses were smaller in the organic soil compared to the mineral soil, indicating that denitrification was likely the predominant process occurring. Once again, split applications of fertiliser had little effect on N released in leached water, suggesting that these fertiliser management practices may have little impact on N losses in leached water. This indicates that the amount of fertiliser, as opposed to its application regime, would seem to exert the highest effect in nutrient losses.

Further studies at field-scale under natural conditions and/or laboratory-based experiments using intact, undisturbed soil cores are needed to better quantify losses of P derived from fertilisation practices.

6.6 Summary

This chapter presents the results obtained from a column experiment where leaching water was collected over a period of 19 weeks after three different slurry applications were applied either in one single application or split in two. There were no significant P loads for any soil type and treatment, probably due to the breaking of the soil structure and the soil pore system which

increased the soils' ability to sorb and retain the applied soluble P. Field experiments on organic soils and in natural conditions should be performed to evaluate the potential risk of P losses from these soils, especially in the context of HSW where organic soils are more abundant. Chapter 7 will summarise conclusions from the entire thesis and make recommendations for further research

Chapter 7

Conclusions and Recommendations

7.1   Overview

The intensification of agricultural production in Ireland has been recently promoted by two policy reports: Food Harvest 2020 and Food Wise 2025. These reports aim to increase agricultural exports, mainly from the beef and dairy sectors. This implies that grasslands are one of the primary agro-ecosystems to be broadened in order to meet the requirement for agricultural intensification. While these policies claim to be ecologically sustainable, some of the practices considered inevitably imply reclamation of natural and semi-natural grasslands and the drainage of some wetland areas for conversion to pasture production. These habitats tend to be located in upland areas within high status water bodies, and are often associated with peats, peat-derived soils, and other organic soils that have been identified as particularly vulnerable to P losses due to their poor P retention abilities.

The primary objective of this thesis was to evaluate the use of P fertilisers on organic soils in order to assess the potential magnitude of P losses from these soils and to identify good management practices that could reduce the amount of P lost. To address this, a series of agronomic, soil chemistry, rainfall and leaching experiments were carried out to gain insight into P assimilation and transport of applied P and the mechanisms of soil P cycling in these soils.

7.2   Summary of main findings

- Under conditions of deficient soil P bioavailability, most organic soils responded well to P fertiliser applications, likely due to the lack of interaction of the added soluble P with the soil matrix. These results indicate that soluble P was immediately available for plant uptake in organic soils. Therefore, the concept of "build-up", whereby soil P reserves need to be increased first in a soil deficient in available P by adding P

fertilisers, should not be applied in organic soils due to their intrinsic inability to retain added P.

- Irrespective of soil type, herbage P content increased shortly after initial P fertilisation, followed by a reduction with time. This suggests that one single fertiliser application at the beginning of the growing season may not meet the P requirements for grazing animals towards the end of the grazing period.

- The analysis of the different soil P pools further supported the evidence that organic soils have limited ability to build up soil P reserves in comparison to mineral soils, showing once again the elevated risk of P loss and negative environmental impacts when these soils are managed as mineral soils. Additionally, it was shown that organic soils had higher P offtakes in the grass yield compared to mineral soils, where added P was to a greater extent immobilised in the soil matrix and hence unavailable for plant uptake, at least in the short term.

- There was poor mobilisation from more recalcitrant soil P pools to the labile pools in organic soils compared to mineral soils. This low turnover implies, again in the short-term, the importance of continuous external P applications in order to maintain productivity in organic soils. In contrast, mineral soils had a better potential to supply P from the non-labile to the labile P pools.

- Grass response was limited by the very low pH of one of the organic soils, likely due to the immobilization of P fertiliser by the formation of tertiary compounds between organic acids, Al/Fe cations and the orthophosphate. Even under conditions of P deficiency, fertilisation did not produce a defined grass response for this organic soil.

- Phosphorus loads in runoff were markedly higher for single fertiliser applications than for split applications. Moreover, it took approximately six and nine days for the P concentration in runoff to reduce by 75 % and 85 %, respectively, of the initial peak P concentration following P applications. The concentrations at these periods were still several times higher than the baseline P concentrations when no P fertiliser was applied. In fact, it took between two to three months to reach baseline P concentrations following

P applications in surface runoff in organic soils, which indicates the elevated risk of P loss as a consequence of the poor P retention.

- Phosphorus losses via subsurface pathway did not show a clear pattern with regard the different fertiliser rates and timing regimes investigated. Nitrification was the main process occurring in organic soils, irrespective of the different slurry treatments. Indirect evidence suggests that denitrification was also a relevant mechanism in the organic soil receiving slurry.

7.3   Main implications arising from the findings

- When organic soils are managed as mineral soils, the risk of P transfer from the soil to the surrounding waters greatly increases as added P tends to remain, to a greater extent, in the soil solution. Fertilisation of organic soils should be therefore tailored to meet plant requirements during the growing year in order to avoid over-fertilisation, which may result in an increased risk of environmental damage and additional economical costs for the landowners. Furthermore, many organic soils tend to be located within high status catchments, which are vulnerable even when subjected to relatively low intensity activities (Ni Chathain et al., 2013). Therefore, agricultural activities in these areas, particularly those relating to fertilisation, should be restricted, controlled and even prohibited if water quality is to be preserved.

- Another important implication for the management of organic soils is the interaction of pH with the freshly added P. The acidity of some organic soils tends to be very low, especially shortly after reclamation, and this characteristic can be the main limiting factor affecting productivity in these soils. Therefore, liming should be prioritised before any P fertilisation plan. Increasing the pH of organic soils may promote the formation of Ca-P compounds that may remain sparingly soluble at elevated pH levels. However, liming has been shown to increase ammonia volatilization and stimulate nitrification in organic soils (Parent and Khiari, 2003), and these side effects need to be evaluated in further research.

- Phosphorus reserves in organic soils did not play a significant role as suppliers of available P of the labile P fraction, possibly due to the relatively short period of time during which this was evaluated in the current study (eight months). This suggests that the resilience of the P locked in the non-labile pools in organic soils is more pronounced than in mineral soils, indicating that longer periods of time under cultivation are required to mobilise it. This more pronounced resistance may be due to the presence of complex organic acids, such as humic, fulvic and low weight molecular compounds, which have the ability to form tertiary compounds with other metals and anions simultaneously (Gerke, 2010; Antelo et al., 2007). Under this scenario, the ability of native microbial communities to unlock these complexes may be hampered due to the changes in the habitat conditions of these soils when they are brought intro agricultural production, which consequently result in longer solubilisation and mineralisation periods.

- Split applications may be a good management decision for P loss mitigation following P fertilisation, especially in countries/regions with elevated rainfall amounts. From an environmental point of view, frequent but smaller P fertiliser applications in organic soils can have two positive implications: (1) it significantly reduces the P loads generated in overland flow when a rainfall event occurs shortly after P application and (2) plants have better access to soluble P throughout the year, resulting in higher herbage P concentrations for ruminants and enhanced grass yield as the P limitations for plant growth are overcome.

- Knowledge of the decay rates of P loads in surface runoff and the time periods at which initial P concentrations are reduced to 50, 75 or any other percentage, can be a useful tool for assessing the potential risk of P loss. This information could be integrated with forecasted rainfall events and considered in the nutrient management advice for local farmers to mitigate P losses after fertiliser applications.

- Nitrification is a process occurring naturally in drained organic soils, so any type of nitrogenous fertiliser application, either mineral or organic, should be discouraged.

7.4   Recommendations for future research

- Morgan's test for soil P availability is not a reliable test for organic soils. Therefore, further investigation should be undertaken to establish a suitable soil P test for organic soils that describes P bioavailability. Previous studies have shown that WEP or $CaCl_2$ soil tests can be good indicators of bioavailable P (Simmonds et al., 2015; Castillo and Wright, 2008). Due to their relative ease of use, further research on organic soils should be undertaken to evaluate these indicators as predictors of P mobility in these soils.

- Field experiments are needed in order to calibrate optimum grass yields with P fertiliser applications in organic soils. However, the typically remote location of organic soils and the relatively small area compared to more traditional agricultural soils, leave them unlikely to receive the deserved attention if water quality in these catchment areas is to be preserved. Additionally, the role of the non-labile P pools in organic soils as potential sources of available P is not clear and should be investigated in long-term field experiments.

- Further research is needed to investigate the different types of organic acids, their chemistry and abundance. Knowing their molecular composition and stoichiometry will help to better understand the reactions produced when soluble P is added to these soil types. Additionally, a better understanding of the microbial communities (bacteria and fungi) will provide insight on the potential of these soils to supply P in its available form for plant uptake.

- Organic soils have a high porosity and a loosely-structured nature, and therefore P losses via leaching pathways are expected to be relevant under undisturbed conditions following P applications. Field studies are required to quantify the magnitude and the forms of P transported from subsurface flow, which is an important prerequisite in the development of mitigation strategies.

- The use of slow release P fertilisers (e.g. reactive rock phosphate) has been proposed for organic soils with soil pH < 6.0 as an alternative to more traditional, highly soluble P fertilisers to reduce surface losses (McDowell et al., 2010; McDowell and Catto, 2005), and for organic soils with soil pH > 6.5 to reduce P losses in leachate (Simmonds et al., 2016). Field trials in Ireland should be conducted using this strategy to evaluate P losses from organic soils

7.5   Concluding remarks

Organic soils are increasingly brought into production as a consequence of the expansion of the agri-food sector, which can pose a threat for the water quality of the areas where these soils are located when P fertilisers are applied in order to increase the productivity of these marginal areas. This thesis has proven the limited ability of these soils to build-up P reserves, and therefore the elevated risk of P losses derived from agricultural practices if P fertiliser applications are not accurately applied to meet grass requirements. In this scenario, the use of organic soils for agricultural production may be regarded as environmentally hazardous and less suitable than, for instance, intensification of existing agricultural land if food demand is to be met. When organic soils are cropped, liming should be prioritised before any P fertilisation plan as the typically low pH of these soils tend to block soluble P for plant uptake. The potential of the non-labile soil P pools to supply available P was shown to be very limited, at least in the short term, and further, longer-term field experiments investigating P mobilisation and mineralisation of recalcitrant P pools should be promoted. "Little and often" strategy, where smaller but frequent fertiliser applications are applied through the year, may be regarded as an effective mitigation strategy from an environmental point of view, but may not be viable economically. Furthermore, the cognisance of the time at which P loads in surface runoff reach baseline levels could be used in the nutrient management advice for local farmers to mitigate P losses after fertiliser applications when information regarding forecasted rainfall events is available.

The elevated risk of P loss from these ecosystems highlighted by this thesis, along with the fact that peats and similar habitats become sources of large net carbon dioxide emissions after reclamation and drainage, should discourage any policy of farming use and promote their conservation.

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Appendix A

Contrasting yield responses to phosphorus applications on mineral and organic soils from extensively managed grasslands: Implications for P management in high ecological status catchments. *Journal of Plant Nutrition and Soil Science,*

González Jiménez, J.L., Healy, M. G., Roberts, W. M., Daly, K.,

Article associated with Chapter 3

Appendix A

Contrasting yield responses to phosphorus applications on mineral and organic soils from extensively managed grasslands: Implications for P management in high ecological status catchments

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Abstract

Phosphorus (P) loss from grassland production is one of the main causes affecting high status water bodies in Europe. Soils with a high content in organic matter (OM), even if extensively managed, are particularly vulnerable to P losses due to their poor P sorption capacities, and can affect the water quality of high status catchments if the dynamics of applied P in these soils is not well understood. The aim of this study was to assess dry matter yield, herbage P content, and P use efficiency in six soils deficient in P and ranging in OM content from 8.7% to 76.4% in a pot experiment under increasing P applications using the Mitscherlich equation. Of the six soils investigated, there was a better response in dry matter yield and greater P use efficiency in the soils with greater OM content than the mineral soils. The Mitscherlich model described grass response precisely in organic soils due to the higher plant availability of applied P as a consequence of the poor P sorption capacities of these soils. Despite the higher availability of applied P for plants in organic soils, the P requirements to meet the threshold herbage P content for dietary P supply to ruminants were still very high, which may pose a risk of P loss to the environment if P fertiliser is applied based on recommendations obtained from plant analysis. These results indicate that P fertilisation of organic soils in sensitive catchments poses a potentially high risk of P transfer to water bodies.

Key words: build up / fertilizer / herbage P content / Mitscherlich / P uptake / P use efficiency

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1 Introduction

Phosphorus (P) is one of the most important elements for grass and animal health, and is typically applied as fertiliser to replace P exported in products (meat, milk, grass) in either chemical or organic (manure and/or slurry) forms. When applied in excess of crop requirements, it may transfer to the surrounding water bodies *via* leaching and overland flow, causing eutrophication (*Carpenter*, 2008).

In the European Union (EU), the Water Framework Directive (WFD; *OJEC*, 2000) has established targets for all the member states to achieve at least "good" ecological status for all water bodies and maintain "high" ecological status. High status water bodies (HSW) are those reflecting minimally disturbed ecological conditions (called reference conditions; *Pardo* et al., 2012), and are sensitive even to small anthropogenic activities such as extensively managed grasslands with low P inputs. Additionally, in line with the general intensification of agriculture in Europe (*EEA*, 2013), many countries have set growth strategies for the agri-food sector in recent years. For example, the Irish Government has enacted Food Harvest 2020 (*DAFF*, 2010) and Food Wise 2025 (*DAFM*, 2015). Whilst these strategies promote agricultural expansion in a sustainable manner, it inevitably requires reclamation of marginal land in sensitive catchments, whose suitability for agricultural production may be compromised.

Histosols account for soils with an elevated proportion of partially decomposed organic material derived from plants, and represent about 7% of the total land area in Europe, with Finland (9.84 M ha), Sweden (9.08 M ha), United Kingdom (4.45 M ha), and the Republic of Ireland (1.27 M ha) among the countries with the largest areas covered by this soil type (*Montanarella* et al., 2006). In Ireland, approximately 66% of this area is located in upper parts of mountain ranges (*Renou-Wilson* et al., 2011). It is in these upland areas where HSW under extensive grassland enterprises are more vulnerable to loss of high ecological status (*White* et al., 2014; *Roberts* et al., 2016). Organic soils, comprising mainly histosols and other related organic matter-rich soils such as histic and humic top horizons (*Creamer* et al., 2014), typically have a high percentage of organic matter (OM) content, low pH, and low aluminium (Al) and iron (Fe) content, and are therefore associated with a low P sorption capacity (*Daly* et al., 2001; *Guppy* et al., 2005; *Kang* et al., 2009). Consequently, the commonly

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applied concept of "build-up and maintenance" for mineral soils (_Olson_ et al., 1987; _Voss_, 1998), where a soil deficient in P has first to increase its reserves before it becomes plant available, may increase the likelihood of P losses _via_ leaching and/or runoff when applied to organic soils. Whilst some preliminary work suggests that organic soils under P fertilisation show similar herbage production than mineral soils _O'Connor_ et al., 2001), the relevance of the concept of build-up of soil P under P fertiliser applications in organic soils is poorly understood (_Daly_ et al., 2001, 2015; _Roberts_ et al., 2017).

Historically, crop production is based on the law of the diminishing returns, in which the yield response of a crop to incrementally increasing amounts of an applied nutrient asymptotically declines (_Black_, 1993). Among the different models used to explain these yield response curves, the Mitscherlich equation is one of the best available due to its inherent nature to represent biological concepts such as the maximum yield attainable and the efficiency of the added nutrient in increasing the yield or the initial fertility of the soil (_Black_, 1993). Currently, P fertiliser recommendations in Ireland are based on (1) a national P index that classifies mineral soils into _deficient, low, optimum_ and _excessive_ in available P using Morgan's P extractant as a soil P test and (2) minimum herbage P concentration of 3 g kg^{-1} that ensures dietary requirements for ruminants. There is a positive relationship between soil Morgan's P levels and the risk of P loss to waters, so that soils classified as _deficient/low_ in the national P index system are deemed to receive P fertiliser, whereas soils classified as _optimum/excessive_ are considered to receive only maintenance or no P fertiliser additions, respectively (_Schulte_ and _Herlihy_, 2007; _Lalor_ and _Coulter_, 2008). However, it has been reported that Morgan's extractant overestimates P availability in organic soils and therefore is not a suitable indicator of P status in these soil types (_Roberts_ et al., 2017).

The objectives of this study were to (1) examine and quantify grass responses to P fertiliser in soils with contrasting amounts in OM using the Mitscherlich equation, and (2) evaluate these responses with a view to developing appropriate strategies for P applications that optimise biomass and herbage P content and reduce the potential risk to water quality. To achieve these objectives, a pot experiment, in which six soils ranging in OM content received different P fertilisation rates, was conducted. Cumulative dry matter (DM) yield and herbage P concentration data were evaluated to assess the management of P on organic soils.

2 Material and methods

2.1 Soil sampling

Soil samples were collected from six sites, representing predominant grassland soils in high status catchments in the Republic of Ireland. The sites selected included two sites at the River Black catchment in Co. Galway, two sites at the River Allow catchment in Co. Cork, and two sites at the River Urrin catchment in Co. Wexford (_Roberts_ et al., 2017). Soils were selected based on their OM content and deemed to be deficient in P as no P fertiliser applications were made in the

years before soil collection, with the exception of Galway peaty mineral, which received an average of 32 kg P ha^{-1} the year before soil collection. At each site, three bulk samples were randomly selected to a depth of 20 cm below the soil surface, air dried and manually sieved through a 1.2 cm mesh. They were then thoroughly mixed to get a homogenised sample. Fresh bulk density was determined at each site at the time of sampling and gravimetric water content (on a wet basis) was calculated to recreate field conditions when packing the soil in the pots.

A subsample from each homogenised soil sample was oven-dried at 40°C for three days, sieved through a 0.2-cm mesh and analysed for physico-chemical characteristics. Soil pH (v/v, 1:2) in water was measured according to _van Reeuwijk_ (2002). The soil OM content was determined using loss-on-ignition at 550°C for 16 h (_Storer_, 1984), which is the standard procedure implemented in the accredited labs in which the soil samples were analysed. Particle size was determined by the hydrometer method (_Day_, 1965). The core method (_Wilke_, 2005) was used for the determination of both fresh and dry bulk density. Analysis for total carbon and total nitrogen were carried out on a LECO Truspec C-N analyser (LECO Corporation, Michigan, USA). The plant available phosphorus was determined using Morgan's extractant. Total P was determined using the U.S. EPA method 3052 (_USEPA_, 1996), in which a 0.5 g sample was suspended in 2 mL of deionized water, followed by a combination of 7.5 mL nitric acid (69% purity), and 2.5 mL concentrated hydrochloric acid. The mixture was then digested at 180°C in a microwave over a ramping time period of 20 min and held for another 20 min at the same temperature. The digestate was analysed using ICP-OES. The Mehlich-3 soil test was used to determine the concentration of Al, calcium (Ca), Fe, and magnesium (Mg) for each soil (_Mehlich_, 1984).

2.2 Pot experiment

Before starting the experiments, soils were rewetted to bring them to the gravimetric water content at the time of sampling and packed in 18.5 L-capacity pots (30 cm upper diameter 30 × cm height) up to 3 to 4 cm below the rim. This large size of the pots maximized the growth potential of the grass, in addition to ensuring that the water status of the containers remained more stable in comparison to smaller pots (_Spomer_ et al., 1997). A 3 cm-deep layer of gravel/coarse sand mix was placed over the drainage holes in the pots. The pots were left outdoors under natural conditions for two weeks to equilibrate before application of the P treatments. Fourteen P fertiliser treatments, with two replications per treatment, in the form of single superphosphate (16% P content) were applied uniformly to the surface of each soil at rates equivalent to 0, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 70, 100, and 145 kg P ha^{-1}. One week prior to the application of superphosphate, all pots received an initial application of N as calcium ammonium nitrate and potassium (K) as potassium chloride, at a rate equivalent to 55 kg ha^{-1} and 245 kg ha^{-1}, respectively. Maintenance applications of N at the same rate as the initial one were applied after each harvest to ensure no N limitation to ryegrass growth during the experiment. After nutrient applications, all pots were left to incubate for two weeks. Pots were sown with perennial ryegrass (_Lolium perenne_ L.) at a rate

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equivalent to 28 g m^{-2} and maintained in environment-controlled chambers according to a randomized complete block design under conditions similar to those that occur in the growing months in Ireland (*Walsh*, 2012): (1) photoperiod of 16 h light, (2) day and night temperatures of 14°C and 8°C (± 2°C), (3) relative humidity of 85 ± 10% during the day and 75 ± 10% during the night, and (4) photosynthetically active radiation (PAR) of 450 ± 50 μmol m^{-2} s^{-1}. Pots were held between 60 to 90% field capacity by weighting them regularly and watering three times per week using tap water with a maximum dissolved reactive P (DRP) concentration of 0.0025 mg L^{-1}. Aphids were treated with insecticide every time they were detected. The grass was cut manually when it attained a length of 22 to 26 cm above the soil surface. A total of six harvests were taken. The total duration of the experiment, from the planting of ryegrass seeds to the last grass harvest, was eight months.

2.3 Herbage yield, herbage P content, P uptake, P balance and P Use Efficiency (PUE)

All grass collected at each harvest was oven-dried at 70°C for 72 h and weighed. This combination of temperature and drying time ensured complete drying of the ryegrass blades while minimizing potential losses due to partial combustion of the plant tissues. Cumulative DM yield for each soil type and P fertiliser treatment was calculated by summing the harvests of the six cuts. Total P uptake was calculated by multiplying the cumulative DM yield at each P rate by the average herbage P content. The P balance was calculated as the difference between the total P uptake and the P fertiliser applied. The Phosphorus Use Efficiency (PUE) was estimated using (*Johnston* et al., 2014):

$$PUE = \frac{(U_p - U_0)}{F_p}, \tag{1}$$

where U_P is the P uptake (kg ha^{-1}) by ryegrass at a given P rate, U_0 is the P uptake (kg ha^{-1}) by ryegrass at a zero P rate, and F_p is the applied P rate (in kg ha^{-1}).

2.4 Mitscherlich model

The Mitscherlich model was used to describe the yield response to applied P. The Mitscherlich equation (*Black*, 1993) is defined by:

$$Y = A\left[1 - e^{-c(x+b)}\right], \tag{2}$$

where Y is the cumulative dry matter yield (kg DM ha^{-1}), x is the amount of P fertiliser added (kg P ha^{-1}), b is the initial plant available P in the soil determined by the Morgan's P soil test (kg P ha^{-1}), A is the maximum yield obtained as x increases indefinitely (kg DM ha^{-1}), and c is a proportionality constant related to how quickly Y reaches A.

The coefficient of determination (R^2) was computed using:

$$R^2 = (sst - sse)/sst, \tag{3}$$

where *sst* is the total sum of squares (total variation) and *sse* is the variation not explained by the regression. Optimum

rates of P fertiliser values were considered to be at 95% of the theoretical maximum yields from each response equation. The choice of this proportion is arbitrary, but choosing an optimum P value of 95% of the maximum yield ensures that the estimates of the maximum theoretical yield are likely to be within a relatively broad 5% of the standard error of the estimate and near-maximum grass production.

2.5 Statistical analysis

Data sets were tested prior to analysis for normality (Shapiro–Wilk test) and homogeneity (Bartlett's test) of variance. For each soil type, the total DM yield was subjected to a one-way analysis of variance. Regression analyses were carried out using R statistical software, version 3.4.2 (*R Core Team*, 2017).

3 Results and discussion

3.1 Soil physico-chemical properties

Table 1 shows the main properties of the soils used in this study. Organic matter content showed a broad spectrum, ranging from 8.7% (Wexford Mineral) to 76.4% (Galway Peat). Cork peaty mineral had a strongly acidic pH (4.5), followed by Cork mineral and Galway Peat (5.1 and 5.3, respectively), with soils from Wexford and Galway peaty mineral having the largest values. Cork mineral and Wexford mineral had the highest values in clay content, with approximately 297 and 182 g kg^{-1}, respectively, followed by Wexford peaty mineral with 101 g kg^{-1}. Mehlich-3 extractable Al and Fe ranged from 2.6 to 991.44 mg kg^{-1} and from 116.99 to 507.39 mg kg^{-1}, respectively, with the highest values of Al for the soils from the Wexford site. Mehlich-3 extractable Al contains crystalline (*e.g.*, gibbsite) and amorphous Al (*Kuo*, 1996) and does not necessarily imply phytotoxicity as the soluble, plant available Al may only be a small fraction. This is in line with *Fay* et al. (2007), who reported the highest concentration of Al in the south east of the country. Extractable Ca was lowest for the more acidic soils, and increased at more neutral pH values, except for Galway peat, which had the second highest value (7812 mg kg^{-1}) of the soils examined, and an acidic pH (5.3).

3.2 Herbage yield

There was no statistically significant response to P treatments ($p > 0.05$) for both soils from Cork. In contrast, both soils from Galway and Wexford peaty mineral had a significant total DM response to P fertiliser applications ($p < 0.0001$). The response of Wexford mineral soil was weaker but still statistically significant ($p < 0.04$). Cork peaty mineral was moderately acidic (4.5), leading to immobilization and sorption reactions between applied P and Al and Fe oxides. Soil pH has a direct impact on the availability of added P, as adsorption and precipitation reactions with Al and Fe oxides make it plant unavailable (*McLaughlin* et al., 2011; *Oburger* et al., 2011). Previous studies showed that P applications can have a limited effect on grass yield in organic soils deficient in P, so that liming should be a priority to increase the yield in these soils

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Table 1: Soils classification and main parameters of the soils used in the study.

Site	Soil Classification[a]	pH	OM[b]	Particle size			Texture[c]	Fresh bulk density	Dry bulk density	Total C	Total N	Morgan's P	Total P	Mehlich-3			
				Sand	Silt	Clay								Al	Ca	Fe	Mg
			(%)	(%)				(g cm^{-3})		(%)		(mg L^{-1})		(mg kg^{-1})			
Galway Peat	Drained Ombro-trophic Peat	5.3	76.4	73.7	8.6	17.7	Sandy Loam	0.9	0.2	40.3	1.6	6.2	96.3	2.63	7812.6	222.1	422.3
Galway Peaty Mineral	Humic Surface-water Gley	6.6	35.8	56.0	28.7	15.2	Sandy Loam	1.3	0.6	17.0	1.4	0.9	609.6	61.5	8216.0	238.5	109.8
Cork Mineral	Typical Surface-Water Gley	5.1	9.1	29.3	38.0	32.7	Clay Loam	1.2	0.6	4.2	0.3	1.7	145.2	884.9	656.1	262.4	137.6
Cork Peaty Mineral	Humic Surface-water Gley	4.5	66.8	61.0	17.6	21.4	Sandy Clay Loam	0.9	0.2	34.7	2.2	5.9	182.7	605.0	2114.0	507.4	193.6
Wexford Mineral	Typical Brown Earth	6.0	8.7	40.1	40.0	19.9	Loam	1.5	1.2	3.1	0.3	1.2	1065.2	947.0	1103.1	117.0	199.8
Wexford Peaty Mineral	Typical Brown Podzolic	6.2	14.1	66.6	21.6	11.8	Sandy Loam	1.0	0.7	7.0	0.4	0.5	290.0	991.4	2405.6	256.4	517.0

[a] World Reference Base 2014;
[b] Organic Matter;
[c] U.S Soil Taxonomy.

(*Valkama* et al., 2016). The content of clay in Cork mineral soil was approximately 300 g kg^{-1} which, along with the slightly acidic pH (5.1), implies a significant interaction with freshly applied P. Clay content and extractable Al and Fe have been correlated with P sorption capacity of soils elsewhere (*Bolland* et al., 2003; *Gérard*, 2016). According to the concept of build-up and maintenance, added P was rapidly sequestered in Cork mineral and, to a lesser extent, in Wexford mineral soils *via* sorption and fixation reactions with mineral and clay components into unavailable P forms to fill sorption sites and redress the P deficiency. In this scenario, soil P is largely unavailable for plant uptake until it can reach a threshold or critical point over several fertilization sessions at which time it is soluble and available for uptake. *Daly* et al. (2015) demonstrated this concept across a range of mineral acid and neutral soils, where the relationship between the ratio of extractable Al:P and plant available, soluble P indicated that P in soils with low amounts of physico-chemically sorbed P relative to amounts of Al (high Al:P) was fixed and insoluble. However, as more P is added to soil and sorbed to mineral components, the Al:P is lowered and P is released as plant available and soluble forms. Under the concept of build-up, mineral soils can sorb P after P fertilizations and make it slowly available in succeeding harvests, when the P in soil solution becomes depleted by plant uptake. The poor response of sites deficient and low in soil P has been observed in previous studies (*Herlihy* et al., 2004; *Valkama* et al., 2016).

Galway peat had the strongest yield response to P fertilisations, followed by Galway peaty mineral and Wexford peaty mineral. All these soils had a considerable percentage of OM (Tab. 1). Organic soils typically have a low P retention due to the little mineral fraction present in the soil (*Daly* et al., 2001; *Guppy* et al., 2005). Moreover, humic acids derived from the partial decomposition of the OM are mostly negatively charged, and therefore compete with orthophosphates for sorption sites in mineral particles (*McDowell* and *Condron*, 2001). On the other hand, humic acids can form complexes with metals such as Al^{+3} and Fe^{+3} and, in turn, adsorb P, thereby contributing to the sorption capacities of the soils (*Gerke*, 2010). The determination of organically bound Al/Fe through the sodium pyrophosphate extraction method (*van Reeuwijk*, 2002) and the development of phosphate saturation indices (PSI) that relate the oxalate-extractable P, Al, and Fe (*Janardhanan* and *Daroub*, 2010) can be a good way to evaluate the potential of OM to sorb P in organic soils.

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In the current study, the results indicate that the negative relationship between OM and yield response was the predominant event taking place in the organic soils studied, likely due to the low "labile" or organically bound Al/Fe concentrations. Under this scenario, the build-up concept is then limited by the amount of OM present in the soils, and freshly applied P will remain in the soil solution, supplying P directly to the plant. Considering the particular climatology of Ireland with frequent rainfall events over the year, the presence of P in the soil solution increases the risk of losses *via* leaching and runoff to water bodies. Therefore, organic soils that have been drained and brought into agricultural production should be fertilised only in the growing period (March–April), when the grass requirements for P are highest, to minimize the risk of P losses due to their inability to sorb and retain applied P in the soil matrix.

Additionally, the national P index, where soils are classified from deficient to excessive in available P based on Morgan's soil test, should not be applied to organic soils, as it has been suggested that the acidic Morgan's extractant may overestimate available P in these soils, probably due to the hydrolysis of part of the organic P forms (*Roberts* et al., 2017). Other soil tests such as water-extractable P have been used in organic soils as a proxy for the plant-available P (*Castillo* and *Wright*, 2008) and may be more suitable for describing the P status of these type of soils.

3.3 Mitscherlich model

The Mitscherlich response curves for each soil type and the equation parameter values, along with the R^2 values, are shown in Fig. 1 and Tab. 2, respectively. Values of *A* (the maximum yield attainable under unlimited P supply) ranged between 7,300 and 11,000 kg DM ha^{-1}. Galway peat and Galway peaty mineral had the highest values of *A* (11,000 and 10,100 kg DM ha^{-1}, respectively), whereas Wexford mineral soil was the least productive. The greater response in organic soils compared to mineral soils under similar soil P status is in agreement with other studies (*Valkama* et al., 2016). The reason for this is likely due to diminished P sorption capacity in organic soils, leaving applied P in the soil solution and readily available for plant uptake. There was a large range in values for *c* (the proportionality constant, *i.e.*, how fast the yield approaches *A*), which ranged from 0.04 for soils with high R^2 to 1.1 for the soil with lower R^2 values. The proportionality constant *c* has been correlated with the buffering capacity of soils in previous studies (*Brennan* and *Bolland*, 2003). The *c* parameter in Cork Mineral, Wexford mineral and, to a lesser extent, Cork peaty mineral had the highest values, supporting the concept of P build-up in these soils. The main strength of the Mitscherlich model to describe yield

response curves lies in its ability to give a good description of the yield when the range of P applications is large and a maximum yield is achieved at high P rates (*Colwell* et al., 1988). This is the case for the soils from Galway and for Wexford peaty mineral, where the response to P fertiliser was well described along the whole set of P rates (high R^2). However, the Mitscherlich model becomes less accurate when an asymptote is not reached at higher P rates. Both soils from Cork and Wexford mineral did not reach maximum yields at maximum or near maximum P rates, so the accuracy of the Mitscherlich model was relatively poor.

3.4 Herbage P content

The average herbage P concentration across the fourteen P applications declined in all the sites over the timeline of the pot trial. The second cut at each soil had the highest herbage P concentrations for all the soils, with values above the threshold limit of 3 g kg^{-1}, followed by a steady decline in each subsequent cut and remaining stable around
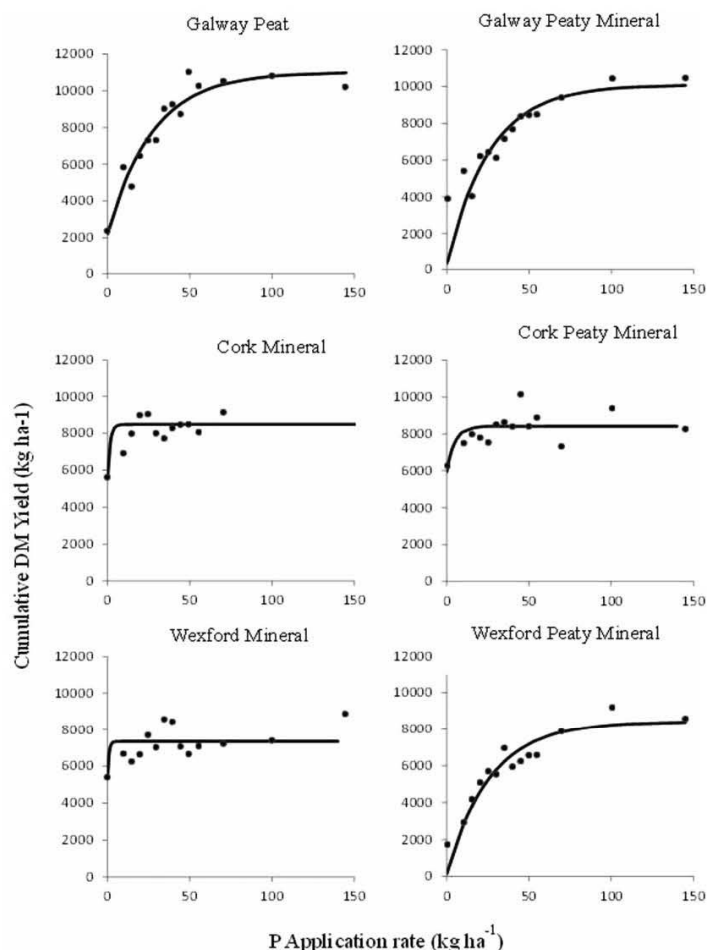

Figure 1: Cumulative DM yield response to increasing P fertiliser rates for each soil. Dots represent average observed values and lines the fit regression curves from the Mitscherlich equation.


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Table 2: Parameters of the fit Mitscherlich equation for each soil site. Parameter *A* is in kg DM ha^{-1}. Standard errors in brackets.

Site	Max yield attainable under unlimited P-supply, *A* (kg ha^{-1})	Optimum P rate	Proportionality constant, *c*	R^2
Galway Peat	11020 (476)	82	0.04 (4.3×10^{-3})	0.93
Galway Peaty Mineral	10100 (831)	78	0.04 (8.5×10^{-3})	0.67
Cork Mineral	8482 (277)	5	0.64 (2.0×10^{-1})	0.43
Cork Peaty Mineral	8415 (223)	14	0.21 (5.3×10^{-2})	0.39
Wexford Mineral	7348 (227)	3	1.10 (3.6×10^{-1})	0.31
Wexford Peaty Mineral	8415 (499)	79	0.04 (6.0×10^{-3})	0.88

1.5–2 g kg^{-1} after the 5th cut for all the soils (data not shown). The decline on herbage P concentration observed in this experiment agrees with other studies (*Bailey* et al., 1997, and references within), although this pattern is not consistent in the literature (*Burkitt* et al., 2010). The decline of herbage P throughout the year after one single P application at the start of the grazing period can have negative implications in the health of ruminants if the P requirements are not met for the intermediate to late grazing period (*Sheil* et al., 2016). Under this scenario, a "little and often" approach, where P fertiliser applications allocated for the whole year are split in two or more smaller rates, would be more suitable to maintain herbage P concentrations within the critical range of 3 to 3.5 g kg^{-1}.

Figure 2 shows the cumulative DM yield plotted against the average P concentration in the herbage. Galway peat and Cork peaty mineral soils reached the threshold herbage P concentration of 3 g kg^{-1} at near-maximum yield, around the 50 to 55 kg ha^{-1} P fertiliser application rate, whereas the other soils reached it when the P fertiliser applications were at 100 to 145 kg ha^{-1}. Herbage P concentration continued to increase in Galway peat, Cork peaty mineral and, to a lesser extent, Wexford peaty mineral beyond the critical concentration, although the yield remained the same, thus reflecting a luxurious consumption of P in these soils. Results showed that the P fertiliser requirements to reach a critical P level of 3 g kg^{-1} were higher than those required to reach 95% of the maximum yields from the Mitscherlich model. This is also in agreement with previous findings (*Morton* et al., 1999; *Schulte* and *Herlihy*, 2007). As a result, the fertiliser P required to obtain a critical herbage P concentration around 3 g kg^{-1} would satisfy the P fertiliser requirements to obtain near-to-maximum yields, maximizing grass production. However, these high fertiliser rates can pose an elevated risk of P losses for organic soils due

to their poor P retention capacities as it has been shown above, and hence P fertilizer recommendations derived from plant analysis may not seem suitable for these soils.
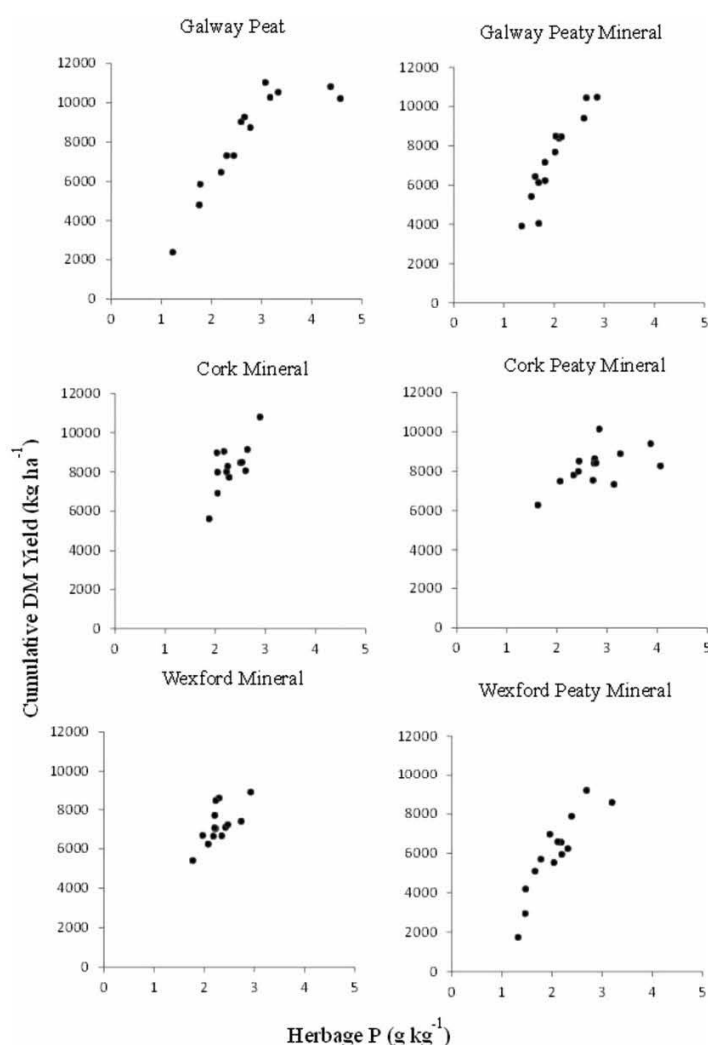
Figure 2: Cumulative grass DM yield *versus* herbage P content for each soil.

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3.5 P uptake, P balance and P Use Efficiency (PUE)

The P uptake, P balance, and PUE at each P fertiliser rate and site are shown in Fig. 3. Phosphorus uptake increased in all sites as the P fertiliser rates increased. Galway peat had the highest P uptakes at the maximum P fertiliser rates. This increase in P uptake with increased P application rates is in line with the fact that uptake is a function of the DM yield and the herbage P content, which in turn increased with P fertilisations.

The P balance was negative at zero P fertiliser rate for all soils and at 10 kg P ha^{-1} for Galway peat, Cork mineral, Cork peaty mineral and Wexford mineral, which indicated a depletion of any stable P reserves in the soil. The P balance became positive for the rest of treatments in all soils, indicating an accumulation of P in the soils. The positive P balance obtained in all soils and almost all P treatments reflected that inputs (P fertiliser) exceeded offtakes (P uptake by the grass), so the surplus of P applied to the soil was either retained in the soil or lost *via* leaching throughout the duration of the experiment, or a combination of both.

The greatest PUE were at low P rates, decreasing in all soils as P rates increased. Galway peat soil had the highest P efficiency, with an average PUE of 54% across P treatments. Cork mineral and Cork peaty mineral had moderate-to-high PUE at low P rates, but decreased markedly as P application rates raised, attaining an average efficiency of 33% and 35%, respectively. Wexford mineral, Wexford peaty mineral and Galway peaty mineral had a low P efficiency over all P application rates, with averages efficiencies of 20%, 28%, and 25%, respectively. With the exception of Galway peat, the mean PUE of the other soils were similar to those reported in other studies with ryegrass for low soil P status (*Herlihy* et al., 2004) and agrees with the tendency for there to be a low PUE in the same year of P application (*Johnston* et al., 2014). The overall P efficiency of Galway peat, with a high OM content (76%) was considerably higher than the other soils, indicating that interactions between P fertiliser and the soil mineralogy were minimal and hence applied P was readily available in the soil solution for plant uptake throughout the duration of the experiment.

4 Conclusions

In this study, grass response to P fertiliser varied between organic and mineral soils with P deficiencies. When grass yield was modelled using the Mitscherlich equation, mineral soils had a weak response to P applications due to the need to first build up their soil P reserves, whereas more organic soils showed a large response to P applications, which indicated no requirement to build up P reserves. This illustrates the potential risk of P losses to waters if P fertilisers are applied to organic soils even when they are deficient in P. Additionally, the high fertiliser P requirements derived from plant analysis to meet the critical herbage P concentration may not be suitable for organic soils if environmental aspects have to be considered. Losses from these soils can be minimized if P is applied during the growing season only, and under a "little and often" approach rather than one single application, as P will be taken up by the plants shortly after its application. However, these implications might not be feasible in reality, as fields with organic soils may be located far from the farmyard and therefore may be fertilised in one single application to reduce costs and time. In this scenario, bringing new organic soils into agricultural production may be less desirable than intensification of existing agricultural land if they are within high status or sensitive catchments.
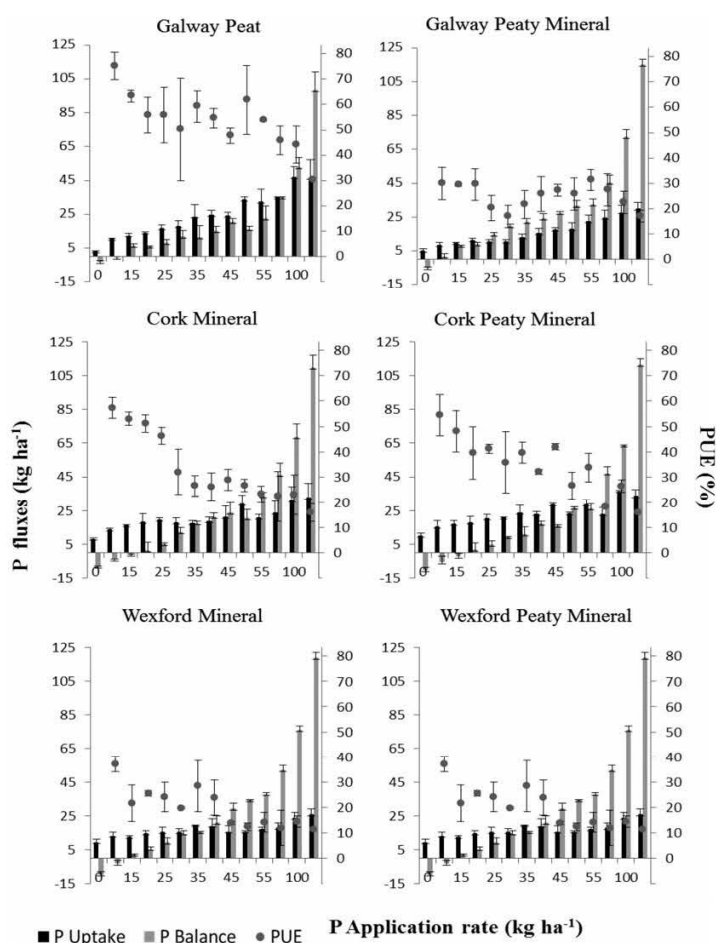

Figure 3: Phosphorus (P) uptake and P balance (kg ha^{-1}) and P use efficiency (PUE) (%) for each P fertiliser rate and soil site. Error bars represent standard deviations.

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Appendix A

Effects of fertiliser on phosphorus pools in soils with contrasting organic matter content: A fractionation and path analysis study. *Geoderma.*

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Article associated with Chapter 4

Appendix A

Effects of fertiliser on phosphorus pools in soils with contrasting organic matter content: A fractionation and path analysis study
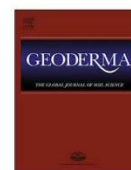
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ARTICLE INFO

ABSTRACT

With the intensification of agricultural production in many European countries, more marginal soils with elevated organic matter (OM) content are being brought into cultivation. However, little is known about the transformations in the constituent phosphorus (P) pools of organic soils receiving applications of P fertiliser. Soil P fractions were measured before and after receiving fertiliser in a controlled experiment to determine the change in the soil pools and path analysis was used to evaluate the relationships between P pools. In this study, P deficient soils ranging in OM content from 8 to 76%, were placed in large pots, planted with ryegrass and subjected to P fertiliser applications ranging from 10 to 145 kg ha^{-1}, and monitored over an eight-month study period. High OM soils had a diminished ability to build-up the labile pool from freshly applied P, with relatively low increases up to 200% of the initial value, compared to mineral soils in which the labile pool increased to > 2500% of the initial concentration. Additionally, organic soils had higher P uptakes in the grass yield than mineral soils, indicating a higher availability of added P in the soil solution than mineral soils due to their limited sorption ability. In general, there was a reduction in the organic P pool over applications from 0 to 55 kg ha^{-1}, which was indicative of partial mineralization, but was followed by an accumulation of added P over applications from 55 to 145 kg P ha^{-1}. The residual P pools did not build-up with P additions, but data indicated the occurrence of mineralization in most of the soils with decreases of around 40% of the initial concentrations. Organic and residual pools therefore displayed potential to supply P to more labile P pools across all soils of this study. Path analysis indicated that applied P was the only source of labile P in the soil with the highest OM content, leaving it dependent on continuous P applications to supply P for productivity, whereas in the rest of the soils there were interrelations between the non-labile and labile pools. Low pH strongly immobilised the applied P and should be corrected before the initiation of any fertilisation program, even in soils deficient in plant available P. The results demonstrated that P added as fertiliser to organic soils does not accumulate as in mineral soils, which may leave them susceptible to P losses in surface runoff. Therefore, organic soils under agricultural production located in high status catchments should receive low P applications and only during periods with low probability of precipitation to minimise the possibility of P exports to receiving waters.

1. Introduction

The maintenance of grasslands for livestock production often requires the application of nutrients in the form of fertilisers to balance the exports derived from that productivity. Among the nutrients incorporated, phosphorus (P) is of special consideration because of its essential contribution to plant growth, but also for its complex chemistry within the soil matrix (Epstein and Bloom, 2004; Pierzynski and McDowell, 2005). When applied in excess of the crop requirements, P accumulates in soil which may increase the risk of P losses to water bodies leading to eutrophication (Carpenter, 2008).

Histosols and other peat-derived soil, often described as organic soils (Creamer et al., 2014), typically contain large amounts of organic matter (OM) at the surface and have poor P retention capacities (Guppy et al., 2005; Daly et al., 2001). With a total land area of approximately 7% in Europe (Montanarella et al., 2006), organic soils have received relatively little attention regarding P management. In the Republic of Ireland, approximately 840,000 ha of organic soils are currently or potentially under agricultural production (Renou-Wilson et al., 2011). Many of these soils are located in upland, remote areas and set within high ecological status or pristine water bodies identified under the European Water Framework Directive (OJEC, 2000). This regulation

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Table 1
Selected physico-chemical properties of the six soils used in the study. Values in parenthesis represent standard deviations, except for the fractions Fe-Al bound P, Organic P and Residual P, which are standard errors of the mean.

Soil property	Units	Galway peat	Galway peaty mineral	Cork mineral	Cork peaty mineral	Wexford mineral	Wexford peaty mineral
Classification[a]		Ombric Histosol	Haplic Cambisol	Haplic Stagnosol	Haplic Stagnosol	Haplic Cambisol	Haplic Podzol
Texture		Sandy loam	Sandy loam	Clay loam	Sandy clay loam	Loam	Sandy loam
Clay	$g\,kg^{-1}$	42	98	297	71	182	101
Silt	$g\,kg^{-1}$	20	184	345	58	365	186
Sand	$g\,kg^{-1}$	174	360	266	203	366	572
Organic matter	$g\,kg^{-1}$	764	358	91	668	87	141
pH		5.3	6.6	5.1	4.5	6.0	6.2
Dry bulk density	$g\,cm^{-3}$	0.2	0.6	0.6	0.2	1.2	0.7
Total C	$g\,kg^{-1}$	403.0	177.0	42.0	347.0	30.9	70.0
Organic C	$g\,kg^{-1}$	387.4	152.6	39.5	341.9	26.2	65.3
Total N	$g\,kg^{-1}$	16.3	14.2	3.6	22.0	3.0	4.4
Mehlich-3	$mg\,kg^{-1}$						
Al		2.6 (0.4)	61.5 (9.8)	884.9 (13.9)	605.0 (25.5)	947.0 (2.6)	991.4 (46.4)
Fe		222.1 (18.1)	238.5 (6.0)	262.4 (4.0)	507.4 (15.2)	117.0 (2.0)	256.4 (10.1)
Ca		7812.6 (175.5)	8216.0 (126.5)	656.1 (2.7)	2414.0(19.4)	1103.1 (3.8)	2105.6 (39.3)
P		13.7 (0.7)	6.5 (0.0)	20.6 (0.2)	31.1 (1.1)	23.3 (0.2)	25.6 (0.6)
Labile P	$mg\,kg^{-1}$	33.5 (0.1)	4.2 (0.4)	2.0 (0.2)	38.4 (2.7)	3.0 (0.7)	1.4 (0.2)
Fe-Al bound P	$mg\,kg^{-1}$	47.4 (1.0)	111.0 (8.6)	20.4 (0.8)	103.1 (3.1)	194.1 (4.2)	37.0 (0.8)
Organic P	$mg\,kg^{-1}$	146.4 (0.3)	350.7 (5.3)	186.2 (1.2)	535.3 (5.0)	332.5 (6.1)	307.5 (2.2)
Ca bound P	$mg\,kg^{-1}$	43.5 (3.0)	287.5 (91.6)	12.3 (1.8)	47.9 (3.5)	127.9 (7.4)	118.7 (8.7)
Residual P	$mg\,kg^{-1}$	335.1 (2.4)	369.9 (23.8)	148.3 (0.9)	376.9 (7.8)	516.9 (2.7)	158.1 (2.7)
Total P	$mg\,kg^{-1}$	605.8 (8.5)	1116.7 (10.5)	369.1 (2.6)	1101.5 (29.1)	1174.2 (0.9)	622.6 (5.6)

[a] World Reference Base 2014 (IUSS Working Group WRB, 2014).

encourages member states to maintain "high" ecological water status where it exists and to achieve at least "good" ecological status for all water bodies. However, with the intensification of agricultural practices across Europe, these sites often receive high P inputs similar to those usually applied in areas under intensive livestock production (Roberts et al., 2017), and recent studies have linked the loss of "high ecological status" in these catchments to these practices (White et al., 2014). Therefore, it is essential to understand the impact of fertiliser applications on the P chemistry in organic soils and to evaluate possible negative effects of P management, if the quality of the sensitive catchments to agricultural practices is to be maintained.

Phosphorus applied to soils undergoes a series of physico-chemical (dissolution-precipitation and desorption-adsorption) transformations regulated by soil characteristics such as mineralogy composition, surface area, pH, extractable iron-aluminium (Fe-Al) hydroxides and OM content (Guérin et al., 2011; Janardhanan and Daroub, 2010; Frossard et al., 2000; Porter and Sanchez, 1992). Phosphorus fertiliser recommendations on mineral soils are based on their ability to sorb and gradually build-up P over time until a critical level is reached, followed by the maintenance of that level by replacing the P removed by consecutive harvests (Voss, 1998; Olson et al., 1987). However, the ability of organic soils to sorb and retain P applied is impeded by the inherent large amounts of OM that compete for sorption sites (Guppy et al., 2005; Daly et al., 2001), so that the approach of build-up of P and maintenance on these soils for fertiliser recommendations has been questioned (Roberts et al., 2017; Daly et al., 2015).

The sequential P fractionation procedure, developed by Hedley et al. (1982), extracts P bound from diverse inorganic and organic compounds of different lability using solutions of increasing extracting strength (Cross and Schlesinger, 1995). Despite its limitations when providing P speciation at the P fraction level and the likelihood to overestimate organic P (Turner et al., 2005), the Hedley method is one of the most comprehensive methodologies used to evaluate the soil P cycle and dynamics into "operationally-defined fractions" of different availability and nature (Condron and Newman, 2011; Negassa and Leinweber, 2009). However, only a few studies have applied this technique in OM-rich soils (Schlichting et al., 2002; Cross and Schlesinger, 1995) and, to our knowledge, none exists in organic soils where the effect of P applied in the different soil P pools has been evaluated using this technique. Therefore, there is a lack of knowledge

about the interaction of freshly applied P with the different soil P fractions when organic acids are in direct competition for the same reaction sites as the P applied. Phosphorus assimilation and turnover in agricultural organics soils is poorly understood and needs further research in order to improve their management and minimise potential P loses to the environment.

Sequential P fractionation techniques alone do not provide insight on the relationships and transformations between the soil P pools under different treatments, nor behavioural comparison of soils of different pedogenesis receiving the same treatments (Gama-Rodrigues et al., 2014; Zheng et al., 2004). Path analysis has been shown to be a valuable tool to evaluate the cause-and-effect interrelations between P pools in different soil types and under a variety of management regimes (Tiecher et al., 2018; Zheng et al., 2004; Beck and Sanchez, 1994; Tiessen et al., 1984).

Therefore, the objectives of this study were (1) to assess the changes in the different soil P fractions receiving increasing amounts of P fertiliser, and (2) to examine which pools acted as sinks or sources for P so as to gain a better understanding of the soil P cycle. To address these objectives, six soils deficient in available P and ranging in OM content were placed in large pots and received fourteen increasing amounts of P fertiliser under ryegrass growth, and were subjected to P fractionation and path analyses.

2. Materials and methods

2.1. Pot experiment

Six grassland soils deficient in P and representing a range of OM content, were selected from three high status catchments in the Republic of Ireland (Table 1). All soils were under a low intensity grazing system and received no P applications in the years prior to soil collection, with the exception of Galway peaty mineral, which received P applications of approximately $32\,kg\,P\,ha^{-1}y^{-1}$ in the years prior to the soil collection. The soils were collected from the surface horizon (0–20 cm), air dried, and sieved through a 12 mm mesh. A subsample was taken from each soil and analysed for selected physico-chemical properties and to determine initial P concentrations in the different P pools defined below (Table 1).

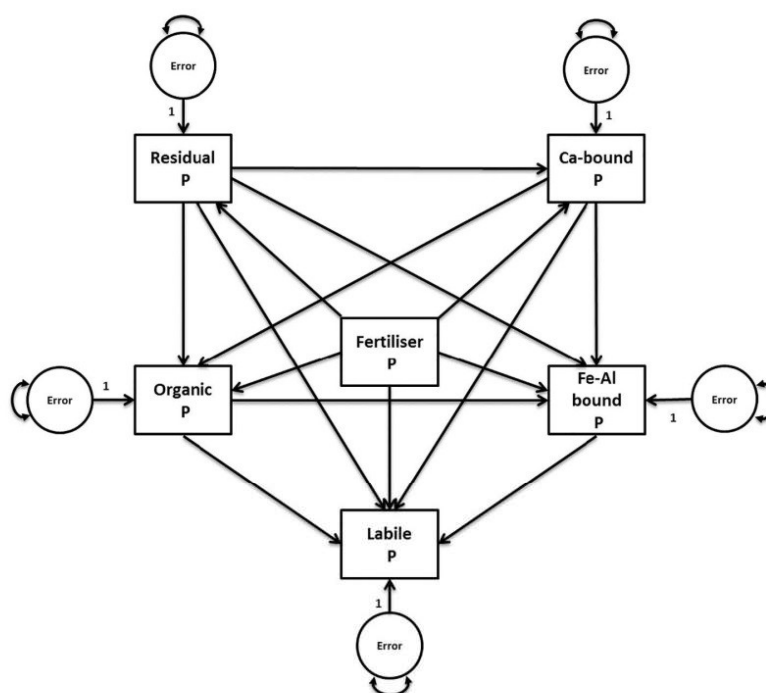Soils were rewetted to their field gravimetric water content and

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Fig. 1. Path diagram with the proposed relationships between the different soil P pools and P fertiliser applications. Errors represent the variance of each of the dependent variables (five soil P pools).

placed in 18.5 L pots (0.3 m upper diameter, 0.3 deep). Each soil received fourteen P fertiliser applications (n = 2) as single superphosphate (16% P content) at rates equivalent to 0, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 70, 100 and 145 kg P ha^{-1}. Each pot received an initial application of nitrogen (N) as calcium ammonium nitrate and potassium (K) as potassium chloride, at a rate equivalent to 55 kg ha^{-1} and 245 kg ha^{-1}, respectively. Pots were sown with perennial ryegrass (*Lolium perenne* L.) seeds at a rate equivalent to 28 g m^{-2} and placed in a glasshouse for three months under the following conditions: average temperature of 11.1 °C (± 3.9 °C) and relative humidity of 82% (± 12%). Pots were then placed in controlled growth chambers operated in the following conditions: (1) photoperiod of 16 h light (2) daytime temperatures of 14 °C and night-time temperatures of 8 °C, with respectively relative humidities of 85% and 75%, and (3) photosynthetically active radiation of 450 ± 50 μmol m^{-2} s^{-1}. The pots were randomly placed in the chambers and were held between 60 and 90% field capacity by weighting them regularly. The grass was harvested six times when it attained a length of 22–26 cm. At the end of the experiment, and for each pot, six soil cores were taken, oven-dried at 40 °C for three days, composited and subjected to soil P fractionation analysis. Phosphorus use efficiency and magnitude of grass response to P fertilisations in these soils were evaluated, the details of which are in González Jiménez et al. (in press).

2.2. Soil P fractionation

A modified Hedley fractionation procedure (Hedley et al., 1982) was used for each soil and P treatment to determine the different fractions before and after the experiment. The iron-oxide paper strip method (Menon et al., 1989) was used as an alternative to the traditionally used but laborious resin-P method (Chardon et al., 1996). Additionally, the iron-oxide paper strip test is more suitable for soils of different nature as its ability to determine dissolved and loosely bound

P is not influenced by physical or chemical properties of the soils (Robinson and Sharpley, 1994). Duplicate 0.5 g samples of dried soil were weighed in 50 ml polypropylene tubes and shaken in 40 ml of 0.01 M CaCl$_2$ with iron-oxide paper strips for 16 h using a reciprocal shaker operated at 6 rpm. Phosphorus adsorbed to the iron strips was dissolved by shaking the strips for 1 h in 40 ml 0.1 M H$_2$SO$_4$. This fraction was identified as the FeO strip-P. The soil suspension was then centrifuged at approximately 51,845 m s^{-1} for 20 min and the supernatant was decanted. The soil was then sequentially extracted with: (1) 30 ml of 0.5 M NaHCO$_3$ at pH 8.5 (NaHCO$_3$-P) (2) 0.1 M NaOH (NaOH-P), and (3) 1 M H$_2$SO$_4$ (H$_2$SO$_4$-P), each of them at the same shaking and centrifuging settings as described for the FeO strip-P. The residual P fraction resisting the 1 M H$_2$SO$_4$ extraction was calculated as the difference between total P (P$_t$) and the sum of FeO strip-P + NaHCO$_3$-P + NaOH-P + H$_2$SO$_4$-P. Total P was determined by ICP-OES in a separate 0.5 g dried sample using the microwave-assisted acid digestion method (USEPA, 1996). Inorganic P (P$_i$) concentrations for all the extractants were determined within 24 h using the ascorbic acid-molybdenum blue method (Kuo, 1996). The P$_t$ concentration in the different extractants (except for the FeO strip-P, where only P$_i$ was determined) was determined by acid potassium persulfate digestion. Organic P concentrations (P$_o$) in the NaHCO$_3$ and NaOH fractions were calculated as the difference between P$_t$ and P$_i$.

The different chemically extracted fractions were grouped into operationally defined pools of increasing recalcitrance as follows: (1) the FeO strip-P represented the labile P pool and comprised P dissolved in the soil solution along with loosely adsorbed P (2) the NaHCO$_3$-P$_i$ and NaOH-P$_i$ represented the Fe-Al bound P pool and included moderately sorbed and/or fixed P$_i$ by Al and Fe oxides/hydroxides (3) analogous to the Fe-Al bound P, the NaHCO$_3$-P$_o$ + NaOH-P$_o$ represented the organic P pool (4) the H$_2$SO$_4$-P represented the Ca-bound P pool and comprised stable P contained in primary minerals such as apatite (5) the residual P pool, calculated as the difference between the P$_t$ and the sum of the

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previous pools, comprised highly stable organometallic complexes and organic materials such as lignin (Gama-Rodrigues et al., 2014; Condron and Newman, 2011; Negassa and Leinweber, 2009; Schlichting et al., 2002; Cross and Schlesinger, 1995).

2.3. Statistical analysis

In order to analyse and evaluate the impact of the increasing P fertiliser applications on the different soil P pools, the percentage change for each soil and P pool were calculated as the difference between the P concentration after and before the experiment divided by the original P concentration. Path analysis was used to examine the cause-and-effect relationships between the soil P pools and P fertiliser, and to differentiate between the direct and indirect effects of these relationships. Phosphorus concentrations (in $mg\,kg^{-1}$) at each P application dose ($kg\,ha^{-1}$) for each soil pool the end of the experiment were used in the path analysis. The conceptual diagram in Fig. 1 was proposed as a general model to test P transformations and dynamics in the different soils. Phosphorus fertiliser was the sole independent variable that may affect the different soil P pools. Therefore, the soil P pools were considered as dependent variables. A basic assumption of the model is that, under cultivation conditions where soils are mainly aerated most time of the year, P movements between the soil P pools occur from the most recalcitrant pools to the less recalcitrant ones and not vice-versa, as might happen under flooded conditions where the redox conditions would change (Castillo and Wright, 2008). This is represented in the model by the different arrows between the independent variable and the dependent variables, and within the dependent variables following the assumption mentioned above (Fig. 1). Each potential relationship in the model (cause) is measured by a partial regression coefficient (direct effect). They are analogous to the covariance between two variables and are referred to as path coefficients (β). Indirect effects are referred to as the effects between two variables that are mediated by another intervening variable (Raykov and Marcoulides, 2006). Both unstandardized (raw score units) and standardized (standard deviation units) path coefficients were calculated. The use of unstandardized path coefficients enabled comparison for the same variable relationship across the different soils, whereas standardized path coefficients were better for comparing different variable relationships within the same soil (Beaujean, 2014).

The generic model represented in Fig. 1 is a saturated model with zero degrees of freedom, that is, there are as many estimated parameters as data points (observations). By definition, saturated models exhibit perfect fit to the data and hence they cannot be confirmed or invalidated by the path analysis (Raykov and Marcoulides, 2006). However, this model was used as a benchmark against which nested (modified) models with positive degrees of freedom could be tested. Modifications of the saturated model were done by dropping from the model the non-significant path coefficients stepwise until final models were tenable, analogous to backward selection in regression analysis, so that the likelihood to miss a plausible variable was excluded. The Chi square test (χ^2), at a significance level of 0.05, was used to validate the nested model from the preceding one until the most restrictive, yet plausible, model was achieved for each soil (Raykov and Marcoulides, 2006). Comparative Fit Index (CFI), Expected Cross Validation Index (ECVI), Akaike's Information Criterion (AIC), and Goodness of Fit Index (GFI) were also considered to evaluate the fit strength of the models generated. Analyses were carried out in R statistical software, version 3.4.2 (R Core Team, 2017) using the "lavaan" and "semPlot" packages (Epskamp, 2017; Rosseel, 2012).

3. Results and discussion

3.1. Soils characterization

The physico-chemical characteristics of the soils before the

application of fertiliser are shown in Table 1. The range of OM content reflects a broad variation, spanning from 8.7 to 76.4%, representing the contrasting soil types in high status catchments in Ireland (White et al., 2014). Soil pH was acidic for Cork peaty mineral, Cork mineral and Galway peat, with values of 4.5, 5.1 and 5.3, respectively, in contrast with near-to-neutral values for the other soils. Total P in the soils ranged between 369.1 and 1174.2 $mg\,kg^{-1}$. From a pedogenic point of view, Galway peat, classified as Ombric Histosol, had similar values to those reported by Yang and Post (2011), but less than other semi-natural or cultivated Histosols reported elsewhere (Schlichting et al., 2002). The other soils in this study had considerably larger P_t concentrations compared to those in the Yang and Post (2011) pedogenic study. There was a significant positive correlation ($r^2 = 0.7$, $p < 0.05$) between soil pH and Ca-bound P fraction, indicating that pH favoured retention of P in this stable fraction from past P additions (Castillo and Wright, 2008; Schlichting et al., 2002). There were no other significant correlations between the remaining fractions and other soil properties. Organic P and residual P were by far the predominant fractions in all the soils, with values ranging from 24.2 to 50.4% and from 25.4 to 55.3% of the P_t, respectively, whereas labile P was the smallest fraction and did not exceed 5.5% of the P_t in any soil (Table 1).

3.2. Changes in P pools over the study duration

Fig. 2 shows the percentage change before and after the pot study in labile P, Fe-Al-bound P, Ca-bound P, organic P and residual P pools in each soil over all P applications. The labile P fraction (Fig. 2a) increased with increasing rates of P applications in all the soils, as expected. Part of the P applied in the form of fertiliser was taken up by the grass, while the rest reacted with the soil matrix and was adsorbed to soil particles. There were negative changes in labile P in Galway peat, Cork peaty mineral and, to a lesser extent, Galway peaty mineral and Wexford mineral, until P applications exceeded threshold values of approximately 45, 35, 25 and $10\,kg\,ha^{-1}$, respectively, indicating a partial depletion of the original pool by grass growth and uptake. Here, grass growth may have been impeded due to lack of available P, until the rates of application were enough to support plant growth and replenish the labile P pool. Galway peat and Cork peaty mineral, the soils with the most OM content (Table 1), had relatively low maximum positive percentages of change (around 200%), whereas more mineral soils, such as Wexford peaty mineral and Cork mineral, had maximum positive percentage changes exceeding 2500%. The magnitude at which the labile P pool changed across the P applications is an indication of the ability of each soil to sorb and retain freshly applied P into this fraction. Therefore, high percentage change values mean that large amounts of added P ended up in this pool, whereas low values indicate that only a small amount was tied up here. Phosphorus concentration in the soil solution phase immediately after fertiliser applications is typically very high (saturated solution), and undergoes rapid adsorption reactions on the surface of the soil particles until equilibrium is reached, thus decreasing its concentration to levels typically very small compared to the solid phases (McLaughlin et al., 2011). Mineral soils demonstrated a high ability to adsorb P in the surface areas of their mineral fraction, whereas this adsorption capacity in organic soils was much smaller (Fig. 2a).

Phosphorus not retained in the labile pool of the organic soils was taken up by the plant roots in higher proportions than in mineral soils, as P was readily available in the soil solution and not loosely bound to soil mineral particles. This was evidenced by the higher P uptakes of the organic soils compared to mineral soils (Fig. 3). At high P doses, when it is likely that P has been applied in excess of crop requirements, organic soils with a low % change in labile P showed higher P uptake by the plant roots compared to mineral soils with higher % changes but lower P uptake (Fig. 3). The fertiliser and agronomic responses of this trial are detailed in González Jiménez et al. (in press). Organic soils have low sorption and retention capacities for P (Guppy et al., 2005; Daly et al.,
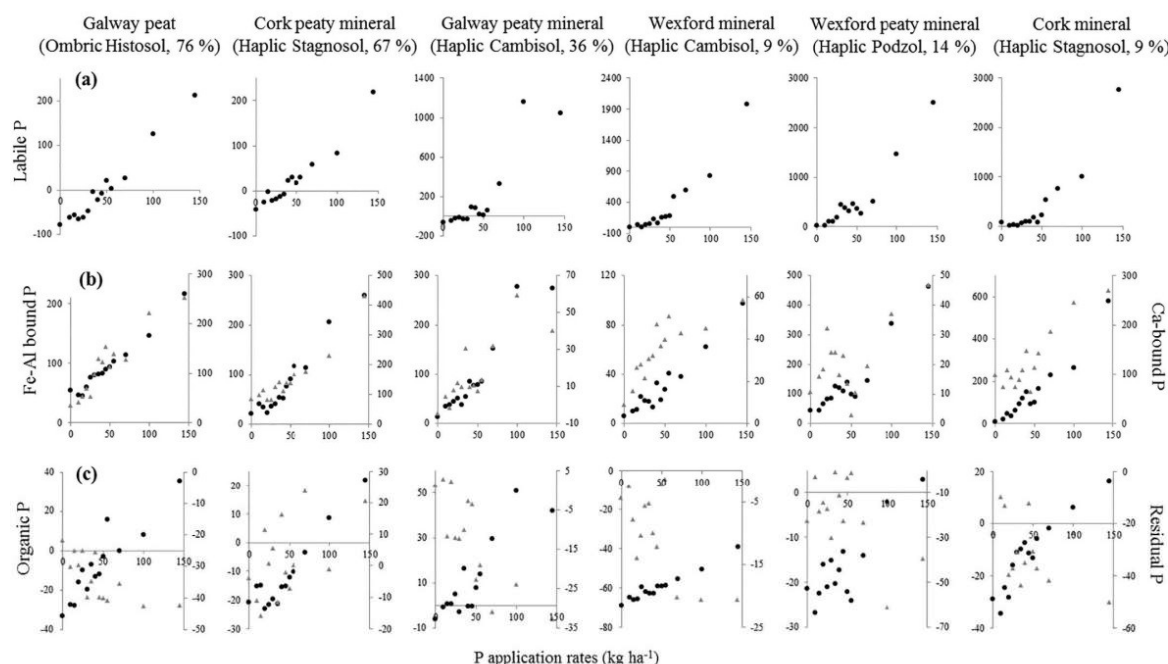
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Galway peat (Ombric Histosol, 76 %)   Cork peaty mineral (Haplic Stagnosol, 67 %)   Galway peaty mineral (Haplic Cambisol, 36 %)   Wexford mineral (Haplic Cambisol, 9 %)   Wexford peaty mineral (Haplic Podzol, 14 %)   Cork mineral (Haplic Stagnosol, 9 %)

P application rates (kg ha⁻¹)

Fig. 2. Percentage change in (a) labile P fraction, (b) Fe-Al bound P (left vertical axis, ● symbol) and Ca-bound P (right vertical axis, ▲ symbol) fractions, and (c) Organic P (left vertical axis, ● symbol) and Residual P (right vertical axis, ▲ symbol) fractions across P applications in the six soils studied. Percentages represent the organic matter content.

2001), so the relative inability of these soils to retain P applied in excess of crop requirements increases the risk of P loss to the aquatic environment (Roberts et al., 2017; Daly et al., 2001). The iron-oxide paper strip method, used as a proxy for the labile P pool, may also have acted as a sink for some dissolved organic P (Robinson and Sharpley, 1994). Although inositol hexaphosphate is the predominant molecule among the organic P compounds, it is relatively resistant to mineralization. However, it is likely that other more degradable molecules, such as phospholipids and nucleic acids, are more abundant in organic soils and therefore prone to be mineralized in the extraction phase with H_2SO_4, overestimating labile P (Quiquampoix and Mousain, 2005; Ivanoff et al., 1998). To minimise this potential source of error and improve the

interpretation of labile P pools, diffusive gradients in thin films (Zhang et al., 2014; Ding et al., 2010) could be used in future studies to efficiently estimate bioavailable P, especially in organic soils where degradable organic P is likely to be present in a higher proportion compared to mineral soils.

The Fe-Al bound and Ca-bound P fractions increased proportionally to the P applications in all the soils (Fig. 2b). There was no clear pattern of P accumulation across the different soils for both P pools, although higher maximum percentage changes (up to 600%) were measured in the Fe-Al bound P in the mineral soils (Cork mineral and Wexford peaty mineral). The short duration of this study likely hindered a better observation of any potential trend between organic and mineral soils.

Fig. 3. Relationship between % change in labile P and P uptake for the six soils at each of the 14 fertiliser applications examined in this study. P Uptake was calculated by multiplying the cumulative grass dry matter yield at each P dose by the average herbage P content. The miniature graph represents % change up to 350 in the y-axis to facilitate reading data in that area. Values in parenthesis in the legend represent organic matter content.

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None of the soils had negative percentage changes, indicating that there was no depletion of these pools at low P doses during the experiment. With the exception of Cork peaty mineral, the magnitude of change in the Ca-bound P fraction was smaller than the Fe-Al bound P, supporting the hypothesis that this pool is considered a more stable fraction to short-term changes and least reactive to freshly applied P (Cross and Schlesinger, 1995). With no P applied (zero P rate), the percentage of change in these two fractions was positive at the end of the experiment, indicating that P was released from other pools and retained in these fractions. Likely, part of the P contained in the organic P and residual P fractions was mineralized and transferred to these pools.

There was a build-up in the organic P pool across the P treatments (Fig. 2c), indicating that some of the applied P was entering in this pool. However, the magnitude of the change was small, up to 80% in absolute values, highlighting the limited ability of this soil pool to retain added P compared to the labile P fraction. Again, there was no pattern of percentage of change between organic and mineral soils. With the exception of Galway peaty mineral soil, negative changes were measured for most of the P applications to the soils. The negative values in this fraction may be attributed to mineralization of the partially decomposed OM by the microbial community. It has been reported that mineralization of organic materials is enhanced by heterotrophic microorganisms when P is not a limiting element (Pisani et al., 2015; Wright and Reddy, 2001). Small P fertiliser additions may generate more plant available P derived from the mineralization of organic P fractions, so that this pool may play an important role in soil P fertility, acting as a source of plant available P in those soils where it is a relevant reservoir (Menezes-Blackburn et al., 2018; George et al., 2017; Condron and Newman, 2011; Guo et al., 2000).

With the exception of Cork peaty mineral, where there was a tendency to build up P, changes in residual P (Fig. 2c) declined across P treatments. The low pH of the Cork peaty mineral soil may have favoured precipitation of some of the applied P with Fe and Al oxides that were part of the primary minerals in this soil. The reduction of the residual P pool in the rest of the soils (Fig. 2c) indicated that P may have been partially mineralized and therefore mobilised to other pools. The residual pool is considered the most recalcitrant and hence least available of all the fractions, as it is associated with very stable organometallic materials (Turner et al., 2005). However, previous research has shown that this pool can act as a source of P for arable crops and forest trees plantations in the short and long-term experiments under low or no P inputs (Velásquez et al., 2016; Condron and Newman, 2011). To our knowledge, our results are the first to confirm this tendency under pasture (ryegrass) monoculture.

3.3. Pathways of transformations in soil P pools

Path analysis uses the data generated by the P fractionation technique in a theoretical model to differentiate between direct and indirect effects from one variable on others (Tiecher et al., 2018; Gama-Rodrigues et al., 2014; Kang et al., 2009; Zheng et al., 2004). These interrelations are evaluated as partial correlations between the variables but, unlike routine multiple regression analysis in which a single dependent variable is considered, path analysis conducts a multivariate multiple regression analysis where several dependent variables are subjected to regression analysis simultaneously on one or more independent variable. Unstandardized path coefficients are shown in Table 2 and in Figs. S1–S3 of the Supplementary material (standardized values are shown in Table S1 of the Supplementary material).

Phosphorus fertiliser had a significant impact on the majority of the soil P pools, although at different magnitudes. The labile P pool was significantly affected by P fertiliser applications in all the soils, with the highest effect in the most organic soils, with a $\beta = 0.70$ for Galway peat and $\beta = 0.27$ for Cork peaty mineral soil. This indicates that any added P in excess of plant requirements may pose an elevated risk of P transfer to surface waters in the organic soils under rainfall events in field

Table 2

Unstandardized partial regression coefficients. Direct (diagonal, bold) and indirect (off diagonal) contribution of P fertiliser applications on the different soil P pools. NS = not significant.

Variable	Residual	Ca-bound P	Organic P	Fe-Al bound P	Labile P
Galway peat					
Residual P	**−0.49*****				
Ca-bound P	NS	**0.69*****			
Organic P	−0.24*	NS	**0.53*****		
Fe-Al bound P	NS	NS	NS	**0.55*****	
Labile P	NS	NS	NS	NS	**0.70*****
Galway peaty mineral					
Residual P	**1.12****				
Ca-bound P	−0.17*	**1.27*****			
Organic P	NS	0.94***	**NS**		
Fe-Al bound P	−0.43***	NS	NS	**1.19*****	
Labile P	0.08**	0.13***	NS	0.07***	**0.15****
Cork mineral					
Residual P	**NS**				
Ca-bound P	NS	**0.18*****			
Organic P	−0.38***	NS	**0.54*****		
Fe-Al bound P	NS	1.62***	NS	**0.46*****	
Labile P	NS	NS	−0.10**	0.43***	**0.09***
Cork peaty mineral					
Residual P	**NS**				
Ca-bound P	−0.13**	**1.00*****			
Organic P	NS	0.685*	**0.85***		
Fe-Al bound P	NS	NS	NS	**1.73*****	
Labile P	0.08*	0.12*	0.03**	NS	**0.27*****
Wexford mineral					
Residual P	**−0.55****				
Ca-bound P	−0.24*	**0.29***			
Organic P	−0.25*	NS	**0.45*****		
Fe-Al bound P	NS	NS	NS	**1.21*****	
Labile P	NS	NS	NS	0.10*	**0.25*****
Wexford peaty mineral					
Residual P	**NS**				
Ca-bound P	−0.14**	**0.17****			
Organic P	−0.18***	0.55***	**0.38*****		
Fe-Al bound P	NS	NS	0.58***	**0.74*****	
Labile P	NS	NS	NS	0.18***	**0.04***

* Significant level at $p \leq 0.05$.
** Significant level at $p \leq 0.01$.
*** Significant level at $p \leq 0.001$.

conditions, as supported but Fig. 3.

The Fe-Al bound pool was a significant direct sink for freshly applied P for all the soils, as widely reported (Castillo and Wright, 2008; Zheng et al., 2004). Phosphorus fertiliser had the highest impact on the Fe-Al bound P in the Cork peaty mineral soil ($\beta = 1.73$), likely due to the very low pH of this soil that favoured immobilisation and physico-chemical sorption reactions between the freshly applied P and the amorphous and poorly crystalline Fe-Al oxides/hydroxides in this soil. The Fe-Al bound P pool contributed indirectly to the replenishment of labile P in most of the soils, especially in Cork mineral ($\beta = 0.46 \times 0.43$). However, there was no indirect relationship between added P and the labile pools through the Fe-Al bound P pool for the most organic soils (Galway peat, Cork peaty mineral). The lack of relationship between these two pools in these soils supports the idea that pH plays an important role in mobilisation reactions of P in soil.

The organic P pool had a considerable direct relationship with P fertiliser in all soils except Galway peaty mineral. The Cork peaty mineral soil had the highest response ($\beta = 0.85$). There was no substantial indirect effect of the organic pool to Fe-Al bound and labile P pools, with the exception of Wexford peaty mineral, where a moderate relationship between the organic P and Fe-Al bound P was calculated ($\beta = 0.58$; Table 2 and Fig. S3). These results show that P applications increased organic P reserves over short periods of time. Other studies reported a slight increase in the moderately labile organic P pools in

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incubation and short-term (0 to ≤10 y) field studies (Negassa and Leinweber, 2009). However, as was reported in the previous section, the organic P pool experienced a negative change at low P rates in the majority of soils. These results highlight the potential role of the organic P pool as a source of P for plant uptake through mineralization when added P does not meet crop requirements for growth (Negassa and Leinweber, 2009; Castillo and Wright, 2008; Turner et al., 2007; Zheng et al., 2004). The role of the soil organic pools as a source of plant available P could be well evaluated in middle and long term unfertilised experiments by path analysis in future studies.

Phosphorus fertilisation had a large direct impact on the Ca-bound pools in all the soils, especially in Galway peaty mineral, Cork peaty mineral and Galway peat, with path coefficients of 1.27, 1.00 and 0.69, respectively. These soils had the highest Mehlich-III extracted Ca concentrations (Table 1), which may explain the higher affinity for P applied in this pool. The Ca-bound P pool exerted little indirect effect on the labile P across the different soils, but had a moderate influence in both organic and Fe-Al bound P pools, suggesting that mobilisation of P retained in this pool is possible but unlikely to become available, at least in the short-term. The hypothesis of partial mineralization of this relatively stable pool towards moderately labile fractions has been suggested in previous studies, which speculated that recalcitrant organic P included in this pool may be mineralized under aerobic conditions (Zheng et al., 2004; Guo et al., 2000; Schlichting et al., 2002).

Residual P showed a significant direct interaction with P fertiliser applications in half of the soils, with a negative effect in the Galway peat ($\beta = -0.49$) and Wexford mineral soils ($\beta = -0.55$), suggesting that this recalcitrant P can be mobilised when P is not limiting (Wright and Reddy, 2001). The residual P pool was an important sink for the P applied in Galway peaty mineral, as indicated by the large positive direct effect of the path coefficient ($\beta = 1.12$). Although not statistically significant ($p > 0.05$), the path coefficients in Cork mineral and Wexford peaty mineral soils were also negative (data not shown), indicating an overall tendency of the P retained in this pool to be mobilised and become a potential source of P for plant growth.

When the different pathways of P transformations are compared considering the amount of OM of the soils used in this study, there were no significant transformations among the soil pools in the soil with the highest OM content (Galway peat, 76% OM). Likewise, Cork peaty mineral, the second largest in OM content (66%), had limited transformations among its pools, with relatively low enrichment of the labile pool via the Ca-bound P pool ($\beta = 1.0 \times 0.12$) and the organic P pool ($\beta = 0.85 \times 0.03$). Plant growth in these two soils may be restricted under low or nonfertilised management regimes due to their limited ability to replenish labile P, leaving them dependent on continuous fertilisation. On the other hand, added P was indirectly transformed into moderately labile Fe-Al bound P pools to a greater extent in mineral soils, indicating an enhanced ability to build up P reserves compared to organic soils, and were therefore more resilient to nonfertilised management regimes. However, this trend in mineral and organic soils is likely to be so due to the short length of this experiment, and further work in medium and long-term field conditions should be conducted.

4. Conclusions

Under P deficient scenarios, this work showed that external P additions accumulated mainly in the labile P pool across the different soil types, followed by the Fe-Al bound P pool. However, organic soils displayed a more limited ability to build-up labile P and, to a lesser extent, Fe-Al bound P reserves, compared to mineral soils, rendering them vulnerable to P losses when fertiliser is applied in excess of the crop requirements for growth. Additionally, there was a higher P uptake in the grass yield of these organic soils than in mineral soils, indicating that P fertiliser applications to P-deficient organic soils tend to remain in the soil solution and therefore should be restricted to growing periods when there is a demand for P and the risk of precipitation is

low. Soil pH should be optimized prior any fertilisation event, even in P deficient soils, as it influences the retention of applied P. Organic and residual P pools were partially mineralized in most of the soils, indicating mobilisation towards more labile pools. Therefore, they may be considered as a potential source of P for plants.

Transformations of P between the different P pools under fertilisation were well explained by path analysis, and showed the potential of the more recalcitrant pools to mobilise P into more labile P in all the soils. Only the most OM-rich soil had no significant P turnover from the more recalcitrant to labile pools, rendering it dependent to external P applications that may elevate the risk of incidental P losses. Current fertiliser recommendations are mostly based on single agronomic soil P tests that only measure readily available P in the labile P pool, but do not take into consideration the interrelationships with recalcitrant P pools, which may be a potential source of P.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2018.11.049.

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