SUSTAINABLE TREATMENT TECHNOLOGIES USING MIXED WASTE MEDIA TO MITIGATE AGRICULTURAL CONTAMINANTS IN LAND DRAINAGE

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DECLARATION

I declare that this dissertation entitled “Sustainable treatment technologies using mixed waste media to mitigate agricultural contaminants in land drainage” is the result of my own work, except where explicitly stated otherwise, for which references are made. This thesis has not been submitted in whole or in part in support for another degree to any University or Institution.

Golnaz Asghari-Ezzati

ACKNOWLEDGEMENT

“This is the favour of my Lord"

دعوی مکن برترم از دیگران به علم   چون کبر کردی از همه دونان فروتری
از من بگوی عالم تفسیرگوی را   گر در عمل نکوشی نادان مفسری
بار درخت علم ندانم مگر عمل   با علم اگر عمل نکنی شاخ بی‌بری
علم آدمیتست و جوانمردی ادب   ورنی ددی به صورت انسان مصوری
هر علم را که کار نبندی چه فایده   چشم از برای آن بود آخر که بنگری   (سعدی)

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فَلِلَّهِ الحمد رب السماوات و رب الأرض رب العالمين

ABSTRACT

Intensification of agriculture in the European Union has resulted in nutrient losses from farms, which have contributed to a deterioration in water quality. As soil in drainage water ditch networks has limited capacity to attenuate nutrients leaving farms, efforts to reduce nutrient loads have been unsuccessful. Therefore, innovative solutions and experimental approaches are needed to intercept nutrients in ditches before final discharge to receiving waters. The existing ditch networks on farms may offer an opportunity for implementation of nutrient attenuation measures, by combining the natural attenuation capacity of the ditch with in-ditch engineered structures containing media capable of adsorbing nutrients. Although these structures have gained in popularity as a mitigation option, their configuration or optimal placement in the landscape has not yet been fully considered. The selection of appropriate media depends on the type of nutrient losses, the nutrient loads, media adsorption capacity and lifetime. In addition, the identification of an optimal location for the placement of in-ditch engineered structures is crucial for successful implementation as such structures are capable of only removing a proportion of nutrient loads exiting the farm, so the natural attenuation capacity of the ditch is important to further reduce the load.

This thesis proposes two innovative mitigation techniques to remove both nitrogen (N) and phosphorus (P) in an agricultural drainage system: an in-ditch engineered system filled with reactive media and a natural solution which utilises soil chemistry of the ditch network for nutrient removal.

In order to develop the first technique, a novel, internationally applicable decision support tool (DST) was developed to select locally sourced media for single or dual mitigation of N and P. The developed DST was validated in several case studies and it was then used to select an optimal combination of media for the removal of ammonium (NH_4^+) and P in water draining from an intensive dairy farm in south-east Ireland. Normally, large-scale column tests need to be conducted to develop design criteria for engineered structures, but as these are time consuming and expensive, rapid small-scale column tests (RSSCTs) were used, for the first time, to assess the media performance and longevity in simultaneous N and P removal in comparison with large-scale columns. The adsorption capacity and lifetime of the selected media in large- and small-scale column studies were consistent and the generated data using RSSCTs were successfully used to model P and N removals in the large-scale filters. This indicated that RSSCTs may be used to accurately and quickly develop design criteria for in-ditch engineered structures.

In the second technique, the natural P remediation capacity of the ditch network of the study site was investigated with a view to identifying the optimum location for the placement of an engineered structure and to examine the capacity of a ditch in retaining or mobilising P. Experimental analyses indicated that the ideal location for installation of an in-ditch structure was at the point where a sharp increase in nutrient concentration was observed, which was due to discharges from the farm yard. The results also showed that P inputs into the drainage network accumulated in the sediments and bankside over time. This not only contributed to degradation of water quality leaving this farm, but the stored nutrients in the ditch network, as a result of decades of application, had also changed the chemistry of sediments to act as a secondary source of P, adding to the already polluted water.

Arising from the findings of this thesis, in order to limit nutrient losses from intensive farms into drainage waters, implementation of an enhanced remediation technique is essential where natural attenuation is insufficient to eliminate pollution. An efficient mitigation measure starts with characterisation of the type of nutrient losses and then the development of appropriate in-ditch engineered structures filled with media to remove the identified nutrients. However, cognisance must also be taken of potential pollution swapping as a result of using the media, appropriate structure dimension and optimal location, and the nutrient remediation or immobilisation capacity of the ditches. This thesis provides a design framework that will contribute to sustainable, environmentally friendly farm management.

Table of Contents

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

A	Constant of proportionality (mg g^{-1})(L) $^{(-1/B)}$
Al	Aluminium
Al-WTR	Alum-based water treatment residual
AOD	Above ordnance datum
B	Diffusional kinetic
BDST	Bed depth service time
bgl	Below ground level
C_o	Influent concentration (mg L^{-1})
Ca	Calcium
CAN	Calcium ammonium nitrate
C_e	The concentration of P in solution at equilibrium (mg L^{-1})
CH_4	Methane
C_t	Effluent concentration (mg L^{-1})
DIN	Dissolved inorganic nitrogen
DOC	Dissolved organic carbon
DRP	Dissolved reactive phosphorus
DST	Decision support tool
EBCT	Empty bed contact time
EC	Electrical conductivity (µS cm^{-1})
EEA	European environment agency
EPA	Environmental protection agency
EPC_0	Equilibrium P concentration
ERRSQ	Errors squared
EU	European Union

Fe	Iron
FAO	Food and agriculture organization
FWMC	Flow weighted mean concentration
FH2020	Food Harvest 2020
FW2025	Food Wise 2025
g	Gravity (m s^{-2})
GHG	Greenhouse Gas
H_2O	Dihydrogen monoxide (water)
HRT	Hydraulic retention time
K	Potassium
k	Binding energy (L mg^{-1})
K_{sat}	Hydraulic conductivity (m s^{-1})
LU	Livestock Unit
M	Weight
M3	Mehlich-III
MAC	Maximum allowable concentration
Mg	Magnesium
Ms	Manganese
N	Nitrogen
Na	Sodium
NAP	Nitrates action programme
N_r	Reactive nitrogen
N_2O	Nitrous oxide
ND	Nitrate directive
NH_4^+	Ammonium
NH_4-N	Ammonium-nitrogen

NO_3^-	Nitrate
NO_3-N	Nitrate-nitrogen
NO_x	Nitrogen oxide
NUE	Nitrogen use efficiency
OM	Organic matter
P	Phosphorus
P_{baro}	Pressure of the baro-diver (cm H_2O)
P_{diver}	Pressure of the diver (cm H_2O)
PP	Particulate phosphorus
PSM	Phosphorus sorbing material
Q	Water flow (L s^{-1})
q_{max}	Maximum adsorption capacity (g Kg^{-1})
ρ	Density of water (1000 kg m^{-3})
R	R programming language
RDO	Rugged dissolved oxygen (mg L^{-1})
rpm	Revolutions per minute
RSSCT	Rapid small scale column test
S	Phosphorus sorbed in isotherm test (mg P L^{-1})
S	Average retention efficiency (%)
Si	Silicon
Smax	(mg kg^{-1})
Su	Sulphur
Ti	Titanium
TP	Total Phosphorus
TRP	Total Reactive Phosphorus
USDA	United States department of agriculture

USEPA	United States environmental protection agency
V	Volume
V_B	Empty bed volumes of filtered solution (no units)
WFD	Water framework directive
WL	Water Level (cm)
WQ	Water quality

Chapter 1

Introduction

1.1. Overview

Excess nutrient losses from intensive agricultural sites across the European Union (EU) have contributed to significant impairment of water quality in receiving waters (FAO, 2017a; EEA, 2018). Coastal, aquatic and terrestrial eutrophication, as well as soil and water acidification, suggest the need for the development of integrated nutrient management strategies to address this problem (EU, 2014a). Farming in the EU contributes to between 40 and 80 % of nitrogen (N) and 20 to 40 % of phosphorus (P) entering surface waters (EPA, 2014). Direct discharges along surface and near surface pathways (Thomas et al., 2016) and groundwater discharge deliver P to surface water bodies, while reactive nitrogen (N_r) leaches through soil and subsoil to groundwater and onwards to associated surface water bodies (Fenton et al., 2009; Mellander et al., 2018). On any agricultural landscape, heterogeneous soils, subsoil and geology have a combined natural attenuation or water purification function (Jahangir et al., 2013; McAleer et al., 2017). This offers some protection against N and P surpluses, but agricultural systems are inherently leaky and enhanced attenuation is needed at "breakthrough" points (where P is transported between fields) and delivery points in the landscape to protect water quality (Thomas et al., 2016).

One option for enhanced remediation is to install an engineered structure that intercepts nutrients along the transfer continuum (source-mobilisation-delivery to water bodies-impact) (Haygarth et al., 2005). On Irish farms the ditch network offers an opportunity to intercept surface and subsurface waters before final discharge from the farm. Such ditch networks are extensive on grassland farms and are currently being mapped and divided into typologies of risk (Moloney et al., 2020). These ditch systems offer a site for engineered structures, as landowners are reluctant to sacrifice land for purposes other than production. Researchers have attempted to combine individual nutrient removal technologies at laboratory and field scales (Goodwin et al., 2015; Ahnen et al., 2016; Gottschal et al., 2016) to examine the efficiency of employing a "treatment train" (Majsztrik et al., 2017), a sequenced combination of natural and engineered mitigation measures, for complex contaminant mixtures. Such solutions may include the installation of ecologically engineered structures filled with organic/inorganic materials, placed at key points in the landscape to protect water quality. Denitrifying bioreactors, containing carbon (C)-rich media such as woodchip, are a commonly used engineered structure to reduce nitrate (NO_3^-) in surface and subsurface runoff from agricultural fields and land drainage systems (Christianson et al., 2011). However, N can be transformed along the transfer continuum. For example, on heavy textured (high clay content) soils NO_3^- is transformed to ammonium (NH_4^+). This process depends on physical and biogeochemical characteristics of the soil (O'Sullivan et al., 2015; Coyle et al., 2016). Therefore, an efficient removal of NH_4^+ requires materials with high retention or ion exchange capacity for NH_4^+ (Demir et al., 2002).

To date, the efficiency of numerous media-based engineered structures in treating a single contaminant, predominantly N and more recently P, has been widely reported (Addy et al., 2016; Christianson and Schipper, 2016). Yet, many of the media examined may pose potentially negative impacts on the environment through "pollution swapping" (the unplanned creation of secondary contaminants during the treatment of targeted contaminants e.g. the creation of nitrous oxide (N_2O) during the treatment of NO_3^-), which has often been overlooked (Stevens and Quinton, 2009; Healy et al., 2012, 2014). Considering the simultaneous loss of N (either as NO_3^- and NH_4^+) and dissolved reactive phosphorus (DRP) and possible occurrence of pollution swapping during mitigation of drainage water, there is a need to develop an interceptor containing media that mitigates all contaminants arising from agricultural activities and contaminant remediation measures (Fenton et al., 2014). However, a knowledge gap exists with respect to suitable combinations of media to be used in engineered structures while considering the three pillars of sustainability (environmental, social, economic).

Generally, the performance and practicality of mitigation technologies utilising single or blended media in engineered structures depends on several factors including nutrient adsorption capacity, removal of pollutants such as suspended solids/particles/pesticides, hydraulic conductivity and porosity, availability, practicality, cost, and life-time (Schipper et al., 2010b; Ahsan et al., 2011; Payne et al., 2014). Yet, until now, there is no decision support tool (DST) that incorporates all these factors and provides the user with a list of appropriate media considering specific criteria (logistics and economics). In addition, in farms, various types and combinations of nutrients are lost, therefore such a tool would need to consider different farm nutrient pollution scenarios, i.e. provide options for the dual mitigation of N and P.

The next important step in developing design criteria of an efficient engineered structure is related to the initial characterisation of the physical, chemical and biological properties of selected medium/media, while taking cognizance of potential negative side effects such as leaching of organic C and metals and emission of greenhouse gases (GHGs). This step is often completed using large-scale column studies (of around 1 m in length) which are costly to operate and labour intensive. In addition, generation of data may take up to several months. Much smaller-scale column tests (of around 0.4 m in length or less) have been used to generate models to predict the P removal performance of media (Callery et al., 2017). These have overcome the time and financial burden of large-scale column studies. However, to date, these studies have only examined the efficacy of a single medium to remove a single contaminant of interest (mainly P). As drainage water (and wastewater) may contain many contaminants, the use of one or more media, selected to remove specific contaminants, needs to be examined in small-scale column studies, with a view to generating data to model the performance of large-scale columns. If this approach proves successful, it may negate the need for long-term and expensive large-scale column studies.

On intensive input dairy farms, the ditch network has been identified by Fenton et al. (2018) as an ideal location for engineered structures to mitigate drainage waters before final discharge occurs to surface water bodies. There has been much research with regard to the classification and attenuation capacity of such networks (e.g. Shore et al., 2016). Such systems have ad-hoc abilities to store and release nutrients and, therefore, a thorough examination and characterisation of bank and base horizons could identify an optimal location for the installation of engineered structures along these systems. It is important to note that an engineered structure is designed to treat only a small percentage of the nutrients discharging in a ditch system, hence, a percentage of the water remains untreated by the structure. As a result, the water purification function of the ditch system could be utilised to further protect water quality by exposing different soil chemistries and horizons to drainage waters, thereby capturing and storing these nutrients. Successful soil P management, and placement of such engineered structures in a ditch network and optimization of their nutrient removal efficiency, requires a precise and site-specific characterisation (Kronvang et al., 2007) to understand the soil and water chemistry interacting along the ditch. This may help in identifying the type and style of nutrient removal structure to be used (Penn et al., 2017; Rosen and Christianson, 2017). It may also help the decision makers to make more informed choices about how to manage a polluted site and minimise DRP losses.

There are several components that should be improved upon to enable an in-ditch engineered structure to become a reality on intensive dairy farms:

i) the process of medium/media selection
ii) the development of a more efficient process to elucidate adsorption capacity of selected media
iii) quantification of ditch P storage capacity and mobility

1.2. Research objectives

The main objective of this research was to develop an efficient, sustainable and cost effective mitigation technique to prevent pollution losses and remove mixed contaminants in an agricultural drainage ditch by intercepting nutrients with locally sourced media.

The specific aims of the study to achieve this objective were:

1. the development of a DST to facilitate identification of a ranked list of locally sourced materials, to be used in isolation or in combination, to maximise mixed-contaminant mitigation whilst minimising pollution swapping (Chapter 4)
2. to assess the accuracy of rapid, small-scale column studies, conducted cheaply and quickly in the laboratory, in estimating the removal of NH_4^+ and DRP from water replicating the characteristics of agricultural drainage ditch water and to compare the modelled results to those of much larger-scale laboratory columns (Chapter 5)
3. to study P retention and mobilisation dynamics in an open ditch network, investigate P storage capacity, and identify the best location for placement of an engineered-structure filled with adsorptive media (Chapter 6)

1.3. Thesis structure

Chapter 2 comprises a literature review focusing on intensive agriculture and the increase in stocking rate and the usage of N and P fertilisers. This increase has consequences for nutrient losses in drainage water that has significantly degraded water and soil quality. Therefore, mitigation measures such as engineered solutions are required to remediate these contaminants flowing through in-field ditches before they reach water bodies. However, engineered structures only mitigate a percentage of the total flow and are designed to treat a section of the nutrient load to avoid blockage of the ditch during high flow conditions. Thus, the natural attenuation of the ditch is important and can boost this remediation potential even during high flow events. Hence, it is important to investigate the capacity of the ditch in providing natural attenuation before placement of an in-ditch engineered structure in a ditch.

Chapter 3 describes and characterises the study site (an intensive dairy farm in Co. Wexford, Ireland) used in part of this study. The elevated concentrations of NH_4^+ and DRP in the drainage network leaving the catchment influenced the selection of media to be used in column experiments for the mitigation of the selected contaminants (Chapter 5) and DRP losses in an open-ditch network (Chapter 6).

Chapter 4 discusses various media-based nutrient mitigation options and examines the selection of locally sourced media with maximum adsorption capacity for remediation of mixed nutrient contaminants in agricultural drainage waters. A user-friendly **Far**m **Mi**tigation Decision Support **T**ool, **FarMit**, was developed that takes local conditions into account and is applicable for any nutrient pollution scenario in any geographical location.

Chapter 5 discusses characterisation and performance of selected media in Chapter 4 for the removal of NH_4^+ and DRP in column adsorption experiments. Small- and large-scale column tests were conducted to evaluate the accuracy of small-scale columns in predicting the concentrations of the final discharge from large-scale columns.

Chapter 6 discusses water and ditch soil/subsoil chemistry (connectivity of ditch to farm yard) and investigates the P retention/mobilization capacity in an open ditch network, soil

P storage, and better site management decisions to minimize DRP losses on the farm. Demarcating natural attenuation and pollution hotspots may enable identification of an optimal location for the installation of an engineered structure and provide possible changes in the management of discharges from the connecting farm yard.

Chapter 7 presents the overall conclusion of previous chapters and provides recommendations for future research.

1.4. Contributing to existing knowledge

1.4.1. Peer-reviewed publications (published)

To date, two peer review papers have been published from this work, based on Chapter 4 and 6 respectively:

Ezzati, G., Healy, M.G., Christianson, L., Feyereisen, G.W., Thornton, S., Daly, K., Fenton, O., 2019. Developing and validating an adaptable decision support tool (FarMit) for selection of locally sourced media for dual mitigation of nutrients in drainage water from intensively farmed landscapes. Ecological Engineering: X, 2, 100010. https://doi.org/10.1016/J.ECOENA.2019.100010

Ezzati, G., Fenton, O., Healy, M.G., Christianson, L., Feyereisen, G.W., Thornton, S., Chen, Q., Fan, B., Ding, J., Daly, K., 2020. Impact of P inputs on source-sink P dynamics of sediment along an agricultural ditch network. Journal of Environmental Management, 257, 109988. https://doi.org/10.1016/j.jenvman.2019.109988

Additionally, a paper has been published as part of an INSPIRATION-ITN project, which examines an intensive dairy farm (the same farm as in the present study) and utilises a 12-year dataset, including a field campaign undertaken during the present study.

Clagnan, E., Thornton, S.F., Rolfe, S.A., Wells, N.S., Knöller, K., Murphy, J., Tuohy, P., Daly, K., Healy, M.G., **Ezzati, G.**, von Chamier, J., Fenton, O., 2019. An integrated assessment of nitrogen source, transformation and fate within an intensive dairy system to inform management change. PLOS ONE, 14, 7, e0219479. https://doi.org/10.1371/journal.pone.0219479

In addition, a paper has been published in association with the China Agricultural University, Beijing, China. A PhD student was placed on secondment in Teagasc and helped with the ditch survey undertaken in Chapter 6.

Fan, B., Wang, J., Fenton, O., Daly, K., **Ezzati, G.**, Chen, Q., 2018. Strategic differences in phosphorus stabilization by alum and dolomite amendments in calcareous and red soils. Environmental Science and Pollution Research, 26, 5, 4842-4854.
https://doi.org/10.1007/s11356-018-3968-9

The published journal papers are presented in Appendix A.

1.4.2. Poster presentations

Ezzati, G., Healy, M.G., Christianson, L., Feyereisen, G.W., Thornton, S., Daly, K., Fenton, O. Sustainable treatment technologies using mixed waste media to mitigate agricultural contaminants in land drainage. INSPIRATION 4th Workshop: Agronomy management from “field” to “fork”. Oct. 14-19. 2018. Wexford, Ireland.

Ezzati, G., Healy, M.G., Feyereisen, G.W., Christianson, L., Daly, K., Thornton, S., Fenton. O., 2017. Feasibility Matrix to Identify Locally Sourced Mixed Media to Mitigate Agricultural Pollutants in Land Drainage. Soil and Water Management and Conservation General Poster II. Oct. 22-25, 2017. Tampa, FL, US.

Dhaese, K., Koopmans, K., **Ezzati, G.**, Christianson, L.E. Nitrate removal rate in an ‘in-ditch’-woodchip bioreactor in Flanders (Belgium). Land Use and Water Quality Conference, June. 3-6, 2019. Aarhus, Denmark.

1.4.3. Oral presentations

INSPIRATION-ITN Network Management Committee Meetings:

- Netherlands, March 2019
- Ireland, October 2018
- Belgium, March 2018 [EU commission Interim Project Evaluation]
- Greece, September 2017
- UK, March 2017

Erasmus Mundus for the Community- EM2 , Warsaw, Poland, April 2017

1.5. INSPIRATION-ITN Marie Curie Actions H2020

Network-wide training and skill development

1.5.1. Secondments to partner organisations

February-April 2019, University of Sheffield, Sheffield, UK
April-May 2018, PcFruit, Sint Truiden, Belgium
May-June 2017, Tellabs, Co. Carlow, Ireland

1.5.2. Workshops

WS1: Project and time management skills, strategies for effective knowledge transfer, science dissemination and outreach, March 2017, Sheffield, UK

WS3: Innovative methods for solute flux measurement in the subsurface environment, September 2017, Athens, Greece

WS4: Agronomy management from “field” to “fork”: Developing sustainable practices & mitigation of environmental impacts, incl. field visit for technology demonstration, October 2018, Wexford, Ireland

WS 5/7: Careers workshop/ Entrepreneurship (consultant-led) incl. commercialisation, project finance, market research, media inputs, patents, IPR, spin-outs for technology R&D, August 2019, Sheffield, UK

WS6: Integrating sustainability into agricultural practice: assessment methods, technology appraisal, management concepts, March 2019, Wageningen, Netherlands

1.5.3. Seasonal Schools

SS1: Winter School on developing science into practice, including stakeholder involvement, with input from non-academic partners and invited external organisations, March 2017, Sheffield, UK

SS2: Novel monitoring techniques to assess contaminant sources, natural processes and remediation performance with focus on nutrient and C cycles, September 2017, Athens, Greece

SS3: Numerical modelling and interpretation of pollutant fluxes and cycles between atmosphere, soil and groundwater at different scales, January 2019, Liege, Belgium.

1.6. Research dissemination as Marie Curie Early Stage Researcher

Face to face: Science Week for primary school students –Showcasing and introducing the use of natural media for mitigation of drainage water (INSPIRATION project), 12-15. 11. 2018, Johnstown Castle Research Centre, Co. Wexford, Ireland.
Face to face: Johnstown Castle Farm Visit for Marie Curie INSPIRATION Consortium (including early stage researchers/supervisors/beneficiaries), 15. 10. 2018, Johnstown Castle Research Centre, Co. Wexford, Ireland.

Stand exhibition- Posters and Demonstration: European Researchers Night powered by Marie Curie Actions at Cork Discovers: A world of research, 28. 09. 2018, University College Cork, Co. Cork, Ireland.

INSPIRATION ITN seminar for BE-based ESRs, 7. 05. 2018, Flemish Institute for Technological Research (VITO), Mol, Belgium.

Project Presentation, 14. 05. 2018, Department of Architecture Geology Environment and Construction, University Liege.

Face to Face: Johnstown Castle and INSPIRATION’s field site visit for participants in Ramiran International Conference 07. 04. 2017, Johnstown Castle Research Centre, Co. Wexford, Ireland.

Online forum for Q&A in “I am a scientist, get me out of here!” with primary school student across Ireland in FOOD ZONE, 06-11. 11. 2017, Online.

Print Media: Teagasc Women in STEM (science, technology, engineering, mathematics), 11. 2017, Teagasc Publication.

Face to Face: Science Week Interaction with school students- Showcasing project’s experiments in growth chambers, 14-15. 11. 2017, Johnstown Castle Research Centre, Co. Wexford, Ireland.

Video: WP4- Investigating loss of phosphorus from agricultural drainage water to open ditch: Soil sampling-phosphorus loss into ditch, available from inspiration_itn in twitter and online at http://inspirationitn.group.shef.ac.uk/

Chapter 2

Literature Review

2.1. Overview

Intensive dairy systems are inherently leaky systems with low nutrient use efficiencies. Such low efficiencies lead to high nutrient surpluses which can be stored in soil profiles, and when conditions are favourable, can be lost to connected water bodies for decades (Fenton et al., 2011a). Nutrient losses can occur along surface and subsurface pathways and on marginal heavy textured land. The installation of tile drainage further complicates the proportionality of such pathway losses. Land drainage can also be installed on well to moderately drained land to control the water table depth. The ditch networks serve these tile drainage systems and act as a conduit between the farm and surface water bodies.

The European Union Water Framework Directive (EU WFD) (OJEC, 2000) aims to achieve “at least” good status in all water bodies by designated reporting periods. States must develop and implement “programmes of measures” (POM) to aid with minimizing nutrient losses to water bodies. In Ireland, the Nitrates Directive National Action Plan (NAP) (DAFM, 2006) is imposed on a national territory basis and is Ireland’s POM. Such measures are considered “baseline”, whereas the vast majority of stored subsurface nutrients cannot be mitigated using current POM.

The concept of “hydrological and biogeochemical time lags” shows that both legacy N (Fenton et al., 2011a; Van Meter et al., 2016) and P (Schulte et al., 2011; Wall et al., 2013), released from subsurface horizons, will affect water quality for decades to come. Therefore, there is a need for “above baseline” engineered options at delivery points in the landscape to intercept these nutrients before they enter a water body. There is a vast array of such options in the literature, such as the COST Action 869 database (Cost, 2011) or Rural Sustainable Drainage Systems (Quinn et al., 2014), where mitigation measures are installed at breakthrough or delivery points (Thomas et al., 2016) in the landscape to treat water before it reaches surface water bodies. Probably the best examples of in situ engineered structures on farms are in New Zealand (Schipper et al., 2010a) and the USA (Hassanpour et al., 2017), where tile drainage systems on arable farms in states such as North/South Dakota have denitrifying bioreactors (woodchip biological reactors that treat NO_3^-) at the final outlet to ensure drainage waters have minimal loads of N_r. Other systems concentrate on P mitigation and have been used to intercept surface runoff on golf courses and urban areas (Penn et al., 2017).

Recently, there is a move towards acknowledging that both N and P are lost from drainage systems and that engineered structures need to be designed for both. Therefore, these is a need to re-visit several aspects of the design process such as how media are selected, how design criterion are elucidated, and how the natural system in which these structures are placed could be better utilized to take advantage of their inherent water purification functions.

This chapter discusses intensive input agriculture, nutrient losses from farming systems, EU legislation, drainage systems and specifically ditch systems and associated mitigation options, including sustainable engineered solutions, appropriate media-based mitigation options, limitations and media characterization, and identification of optimal locations in a farm system to implement these measures.

2.2. Agricultural intensification

According to the Food and Agriculture Organisation of the United Nations (FAO UN) (FAO, 2017a; UN, 2019), the current level of food production needs to increase by 60 % in order to satisfy the increase in protein-rich animal food for a world population of more than 9 billion in 2050 and 11 billion by the end of this century (Figure 2.1) (Pison, 2019). World population growth poses a challenge to produce enough food, but this needs to be done sustainably to ensure the prudent use of water, atmosphere, soil, nutrients and biodiversity (EU, 2014a,b), and compliance with environmental legislation. This may constrain agricultural expansion.

The global use of pesticides and mineral/organic fertiliser, mainly as N and P (Gruber and Galloway, 2008; FAO, 2017a), as a response to population growth and higher food demand, has increased considerably (and it is projected to continue to increase to service a world population of 9 billion in 2050 (Alexandratos and Bruinsma, 2012) (Figure 2.2).

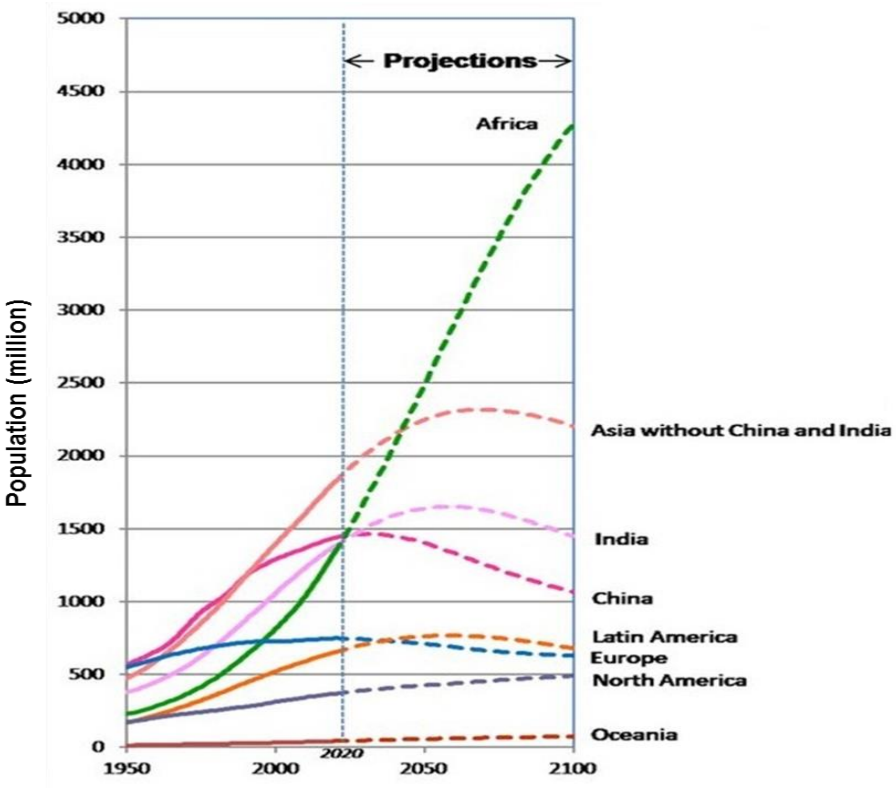


Figure 2.1. *World population growth by 2100 based on UN-medium scenario projection in 2019. Adapted from Pison (2019).*

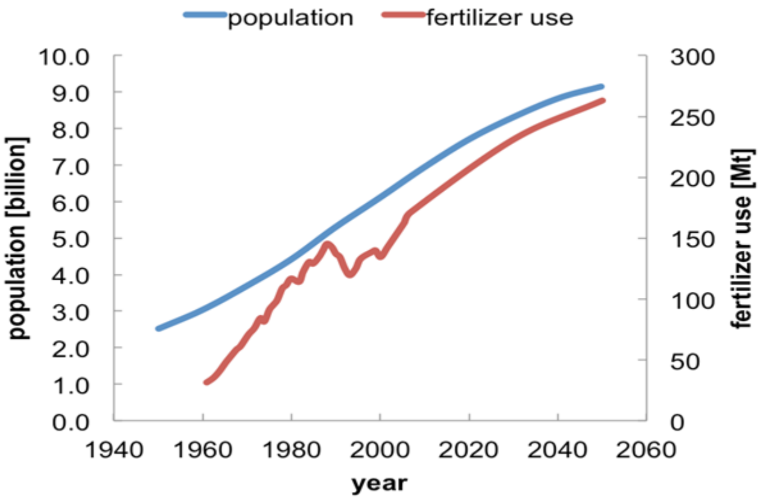


Figure 2.2. *Projected world population (based on median growth) and fertiliser consumption to 2050. Source: Alexandratos and Bruinsma (2012).*

In 2017, 1.3 Mt and 11.6 Mt of P and N fertilisers were used across EU states (Eurostat, 2019a) and the average livestock density reached 0.8 livestock units per hectare of agricultural farms, with Ireland reported to be one of the countries with high values for total livestock density among Member States (Eurostat, 2019b) (Figure 2.3).

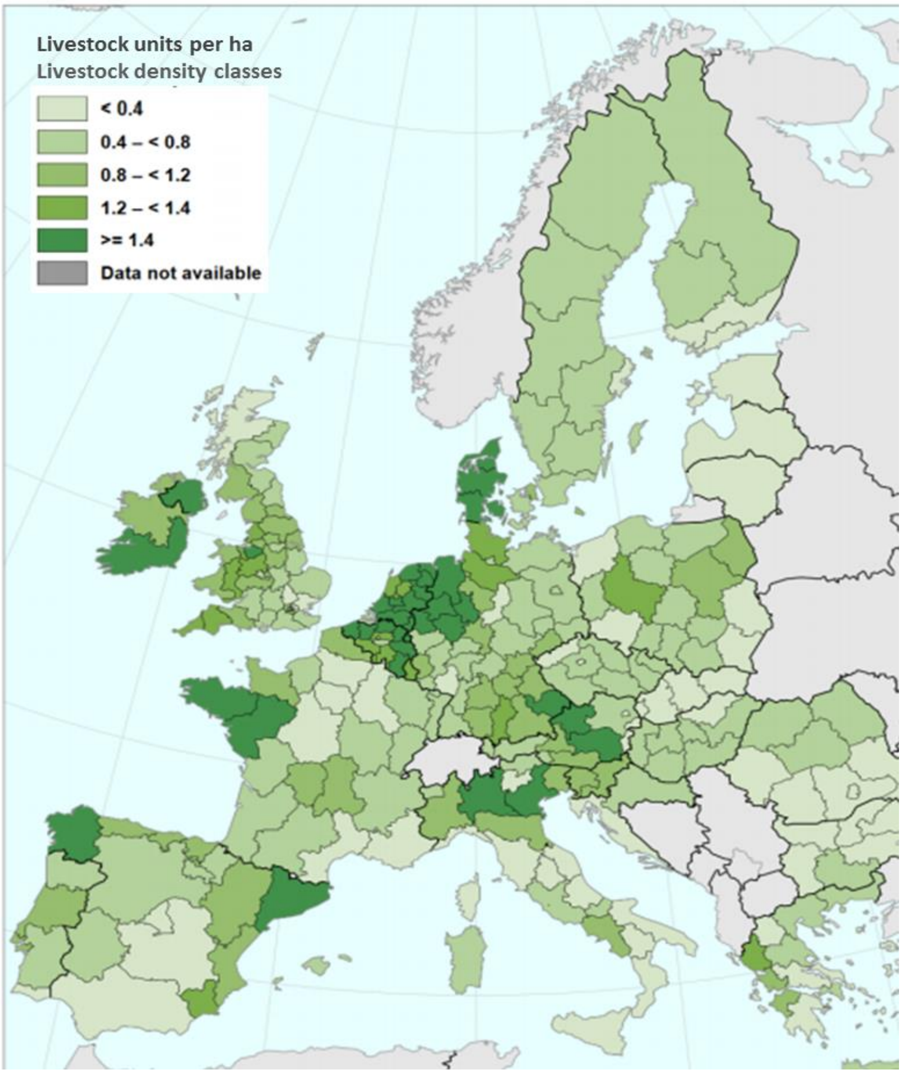


Figure 2.3. *Livestock density in EU-28 as in 2016. Adapted from Eurostat (2019b).*

Increased fertiliser use has not only resulted in greater agricultural production, but has also contributed to the vulnerability of natural resources including ecosystem services and aquatic biodiversity (Schindler, 2006; Withers and Haygarth, 2007; Kay et al., 2009). An increase in stocking rate density has led to higher N losses to water bodies due to higher production of urine and slurry (Selbie et al., 2015) and dairy soiled water (DSW; a mixture of relatively dilute slurry and effluent arising from the washing-down of the farmyard (Minogue et al., 2015)). Agricultural intensification (intensive input) has also lead to more waste generation (Jhansi et al., 2013), excessive loading of nutrients and sediment to receiving waters, and altered channel morphology, hydrology and water temperature (Mainstone and Parr, 2002; Elser et al., 2007; Lewis and Wurtsbaugh, 2008).

Agricultural intensification has also contributed substantially to GHG emissions from soils (FAO, 2003). The livestock and crop production sectors produce approximately 21 % of total GHGs in the world (FAO, 2016) (Figure 2.4), which has almost doubled during the past 50 years (Tubiello et al., 2014). Overgrazing, unsustainable land use and improper soil management have also increased erosion, and have resulted in land degradation and breaches of the soil's capacity to store nutrients (FAO, 2011). According to the FAO and Intergovernmental Technical Panel on Soils (ITPS) (2015), 33 % of the Earth's soil is already degraded, and it is projected that over 90 % could become degraded by 2050 which may lead to a 50 % loss in crop yields.

In response to increases in food demand, countries such as Ireland have set ambitious growth strategies for the agri-food sector. These include *Food Harvest 2020* (DAFM, 2010), which aims to increase primary output in agriculture, fisheries and forestry by 33 % compared to 2007-2009, and *Food Wise 2025* (FW2025; DAFM, 2015), which aims to increase exports from the agri-food sector by 85 % and increase primary production by 60 % by 2025. Intensive farms in Ireland, which are mostly located in south-west and south-east of the country, are therefore subject to apply for a "derogation" (exemption/relaxation from agricultural restrictions) of 210 kg N ha^{-1} (DAFM, 2017), which if successful, will allow them to carry a higher stocking rate. This will inevitably put pressure on already vulnerable natural resources such as water and air quality. Due to the abolition of the milk quota, coupled with ambitious expansion targets, the N surplus on intensive dairy farms is likely to increase, as will the storage of subsurface nutrients. Therefore, water quality is likely to suffer. In addition, as marginal land makes up a large percentage of dairy farms (30 % of milk comes from heavy textured soils), artificial drainage will enable grazing and trafficking of land to occur for longer periods of the year. This will have implications for the release of nutrients through drainage and ditch systems. It is projected that the Irish dairy cow herd will increase by 16 % between 2014 and 2020 and N fertiliser use is projected to increase by 21 % during the same period of time (EPA, 2016a).

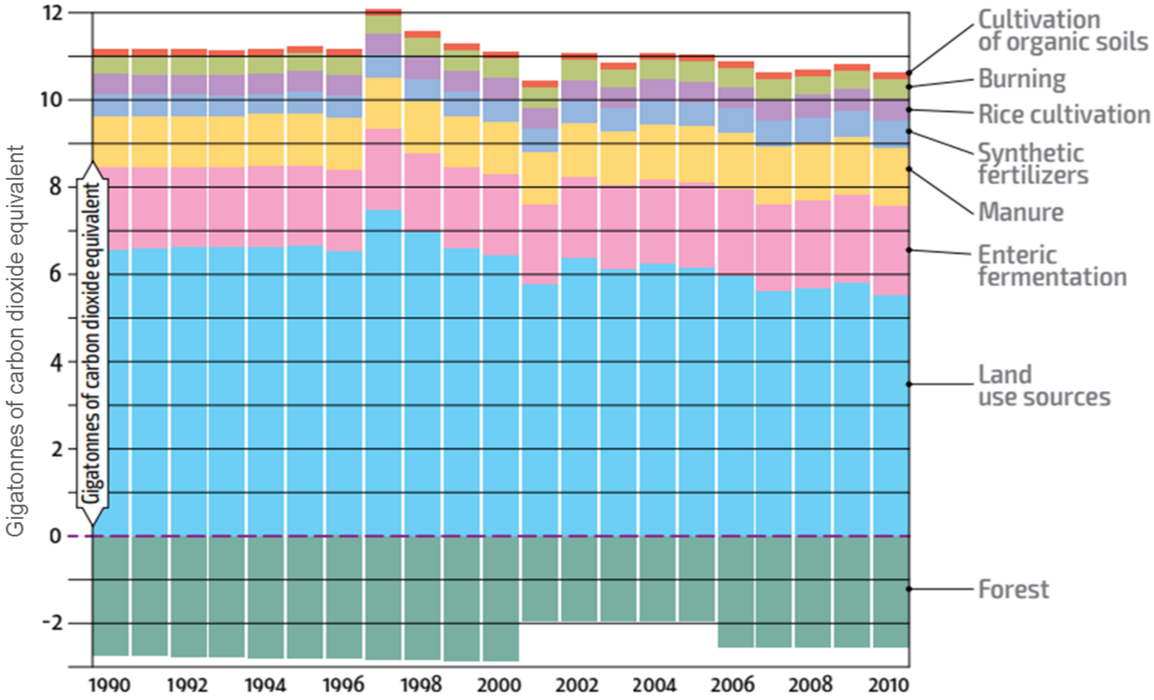


Figure 2.4. *Annual greenhouse gas emissions from agriculture and forestry in the world. Source: FAO (2016).*

Agriculture in Ireland is the largest contributor to GHG emissions and accounts for over 30 % of the total emissions in the country (EPA, 2019). Nationally, 81 % of agricultural lands are devoted to grass (silage, hay and pasture), 9 % to grazing and 9 % to crop production (Teagasc, 2016), and about 11.2 % of farms are considered to be dairy farms (IFA, 2017). According to the EPA (2019), 43 % of the national N surplus and 31 % of the national P surplus are derived from the dairy sector (Figure 2.5). By 2015, the amount of P and N fertiliser use reached about 30000 kg and 325000 kg respectively (Wall and Dillon, 2017). FW2025 has recognized that intensive agriculture and the expansion of the dairy industry need to be both agronomically and environmentally sustainable and therefore has proposed over 400 sustainable growth recommendations to be implemented by different stakeholders (DAFM, 2015). For example, a prohibited period of chemical fertiliser application has been identified for different regions in Ireland in order to increase fertiliser use efficiency and minimize risk of nutrient losses.

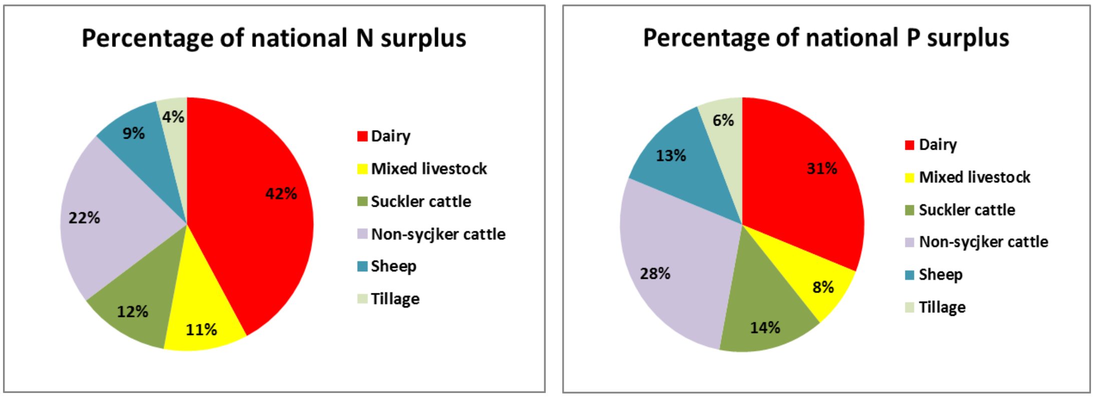


Figure 2.5. *Share of estimated total national N and P surplus attributed to each farm type (representing 61 % of farms and 76 % of utilized agricultural areas from 2008-2015 showing dairy sector as the largest contributor). Adapted from EPA (2019).*

Maintaining long-term soil productivity and nutrient balances depends on farm management (Teagasc, 2016). For example, artificial land drainage of pasture land is typically installed in heavy textured soils (soils high in clay, with poor water penetration) to increase grass utilisation and reduce costs. In Ireland, over 33 % of milk production originates on heavy soils (Humphreys et al., 2011), therefore maintaining productivity and intensification necessities installation of such artificial drainage networks on poorly drained gley soils. These drainage networks regulate water table and transmit water from agricultural lands to ditches or collector drains (Herzon and Helenius 2008; Veraart et al., 2017), so they frequently receive large quantities of nutrient-rich runoff (agrochemicals, organic matter (OM), drug residues, sediments) (FAO, 2017b) or shallow groundwater from adjacent fields.

Nutrients originating from DSW might also reach a water body through different pathways, such as leakage in storage facilities or runoff to nearby water bodies (Ruane et al., 2011). Here, catchment monitoring studies have shown total P losses of < 1 kg ha^{-1} yr^{-1} in the wettest years on all farms, including farms with predominantly poorly drained soils and associated high run-off potential (Melland et al., 2012; Murphy et al., 2015; Shore et al., 2016; EPA, 2019). Nitrogen losses are believed to be highly variable spatiotemporally, as other unaccounted input/output factors such as biological N fixation, immobilisation and mineralization make it difficult to establish a concrete relationship between N balances and N leaching (Humphreys et al., 2008; Burchill et al., 2016, EPA, 2019).

In addition, the already stored N and P accumulated over decades due to fertiliser application and low N use efficiency (NUE), creates subsurface stores of nutrients not available to the crop, but available to be mobilised and delivered to water bodies. This continued release has created a time lag between implementation of mitigation measures and improvement in water quality (Wall et al., 2013) (Figure 2.6). Quantification of such time lags, which is based on soil nutrient accumulation (biogeochemical legacy) and groundwater distribution (hydrologic legacy) (Van Meter and Basu, 2015), is challenging due to the long and complex N leaching pathways via soils, ground waters and rivers (Fenton et al., 2011a). In addition, different processes control the retention and remobilisation of P, which are also linked to water-sediment interactions (Sharpley et al., 2013). The time lags vary between regions for all kinds of reasons such as climatic factors, soil/subsoil chemistry, hydrogeology and farm management (Stark and Richards, 2008). Time lags may also mask the effectiveness of measures during the early stages of implementation. Managing the expectations of policy and regulators means that time lag needs to be presented as a viable reason why water quality targets are not being met, while at the same time investigation continues to diminish point and diffuse losses through implementation of POM.

A recent study by Melland et al. (2018) showed that in meso-scale catchments (1-100 km^2) around the world (n=25), scientists should account for long time lags, from 4 to 20 years, to measure tangible water quality changes when designing measurement programmes. The review indicated the need to consider the limitations of combining response data from multiple catchment scales and over multiple soil, subsurface and geological conditions, when gauging the effectiveness of practice change policies on water quality (Melland et al., 2018). Other factors that need to be taken into consideration are potential pollution swapping, identification of the degree to which water quality targets are likely to be attained, and estimation of the temporal and spatial scale of effectiveness of practice change (Roberts and Craig, 2014). The latter may incorporate the variation between different indicators of improved water quality according to the appropriate monitoring period and location, and calculation of the ratio of costs to benefits arising from practice changes (Stoeckl et al., 2014).

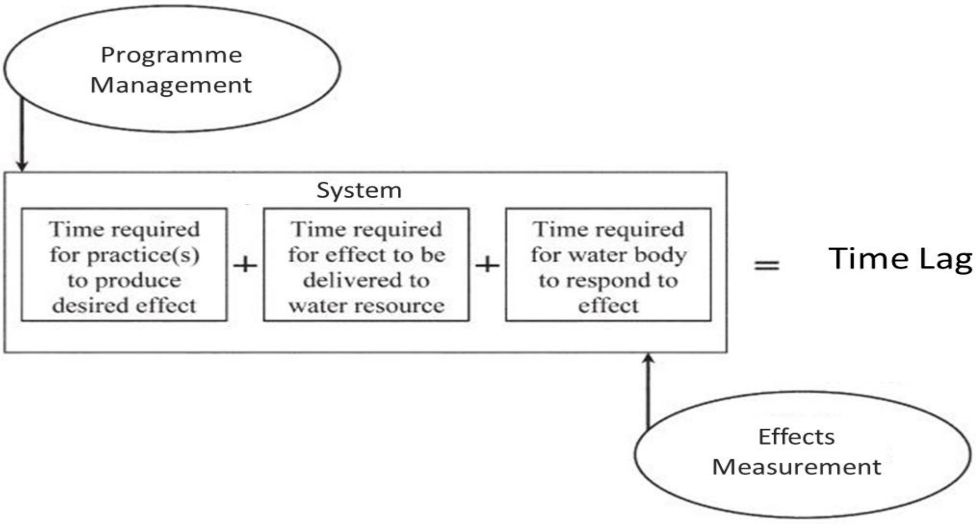


Figure 2.6. *Schematic diagram showing major elements of time lag in response of water quality to mitigation measures: Programme management, system, effects measurement. Adapted from Meals and Dressing (2010).*

2.3. Phosphorus in soil

Phosphorus is a key limiting nutrient for plants (Kröger et al., 2013) and a key component in fundamental biochemical reactions including genetic material (DNA, RNA), energy transfer (adenosine triphosphate) and structural support of organisms (phospholipids and hydroxypatite) (Ruttenberg, 2001). Conversion of unavailable P locked in bedrock, soils and sediments to dissolved P as orthophosphate (the directly available form of P) occurs through geochemical and biochemical reactions. During photosynthesis, mineral orthophosphte, carbon and other essential nutrients are utilized, while biological productivity is controlled by the availability of P. The global biogeochemical P cycle is built upon four major components: exposure of P-bearing rocks to weathering and uplift, physical erosion/chemical weathering resulting in the production of soil which transports dissolved and particulate P to rivers, transport of P to large water bodies, and sedimentation of P with organic and mineral matter and deposition in sediments (Ruttenberg, 2003). These components create two fluxes that circulate P through living organisms: a land-based flux (which transfers P from soil to plants, animals, and back to soil) and a water-based flux (which circulates P among aquatic animals) (Liu and Chen, 2014).

The total global amount of P in the world’s soil is estimated to be 90 to 200 x 10^3 Mt, although only a small fraction is available to biota (Liu and Chen, 2008). The equilibrium of orthophosphate between the soil surface and soil solution is controlled by sorption and desorption. The metal oxides of iron (Fe) and aluminium (Al), clay minerals, and organic ligands enhance the adsorption of orthophosphate in soil (Sims and Pierzynski, 2005) and the desorption reactions include precipitation of orthophosphate ions with cations, depending on soil pH, calcium (Ca) (in alkaline soils), and Fe and Al (in acidic soils).

Figure 2.7 presents the dynamic interrelationships between different forms of P occurring in soil-plant-animal systems (Boitt, 2017). The P cycle undergoes many abiotic and biotic reactions in the soil to maintain equilibrium conditions (Frossard et al., 2011). The biotic processes include uptake and assimilation of dissolved P into particulate organic P by plants, macrophytes, plankton, periphyton and microbes; and the abiotic processes include adsorption of dissolved P by sediments, immobilisation of dissolved P by mineral precipitation and erosion, biochemical remobilisation of particulate P in sediment, and exchange of dissolved P between soil and the overlying water column (Boitt, 2017; Frossard et al., 2011).

Phosphorus does not undergo oxidation-reduction reactions. Therefore, the P cycle lacks the complexity of the N cycle (Mullen, 2005). However, the P cycle has been affected by human activities, causing serious ecological problems (Liu and Chen, 2014). The mining and application of P after the middle of the 20th entry have doubled the amount of mobilised P produced by preindustrial weathering processes (Carpenter and Bennett, 2011; Ludwig and Steffen, 2018). Hence, if the P being exported is not replaced by additional inputs of P, crop productivity will be severely limited (Hedley and McLaughlin, 2005). This bioavailable P needs to be supplied by soluble P-containing mineral/organic fertilisers (slurry, manures) (Pierzynski et al., 2005). At the same time, agricultural P fertilisers are major source of P input to surface freshwaters due to soil erosion (Carpenter and Bennett, 2011).

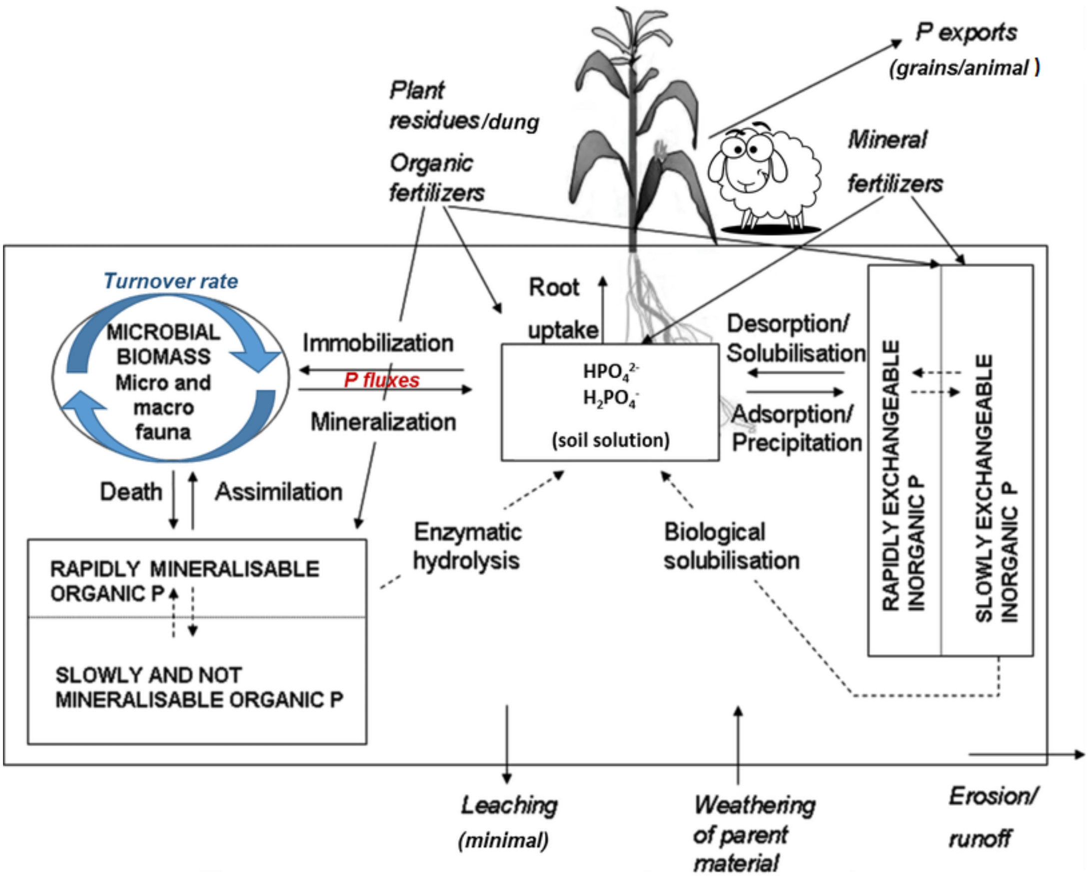


Figure 2.7. *Phosphorus cycle in soil-plant-animal system. Source: Boitt (2017).*

In Ireland, a national P soil index system (1-4) is used to determine the levels of nutrients in the soil and recommend P fertiliser applications. The national P index classifies soils into deficient (1), low (2), optimum (3) and excessive (4) in available P. However, this may not provide a holistic guide as most of Irish soils are P-deficient and below the optimum value for productive agriculture (Teagasc, 2019), which is due to the differences in P buffering capacities (the ability to supply soluble P as a function of capacity) in grassland soils (Wall et al., 2011). The P sorption and P buffering capacity control the supply and availability of P in the soil solution and hence influence fertiliser uptake and critical soil P values (Daly et al., 2015), and are highly correlated with soil/subsoil properties and chemistry (Dougherty et al., 2011). Therefore, an efficient use of P fertiliser and nutrient management requires a more soil-specific approach to increase P-supplying capacity and reach optimal range under reduced P input legislation.

2.4. Nitrogen in soil

The N cycle provides N as an essential source of energy for living organisms to produce amino acids and proteins (Pidwirnym, 2006). The dominant source of N, mainly present as di-nitrogen gas (N_2), is the atmosphere, followed by dissolved N_2 in oceans, and organic/inorganic matter in terrestrial and marine ecosystems (Mills, 2012). Nitrogen is taken up as either NO_3^- ions or NH_4^+ ions by plants, depending on density of ions at the root wall cells and soil type and abundance of oxygen.

Nitrogen loading originates from a mixture of animal waste and fertiliser inputs, comprising both inorganic (urea, calcium ammonium nitrate (CAN)) and/or organic (DSW, manure, slurry and urine) components. As the subsurface is heterogeneous, surplus N can be transformed at different rates through biological processes within the N cycle, especially nitrification and denitrification, in which NH_4^+ is oxidised to NO_3^- and then reduced to N_2 (Rivett et al., 2008) (Figure 2.8). This and other pathways (e.g. nitrification, DNRA (dissimilatory nitrate reduction to ammonium) and anammox) are composed of sequential reactions (Clagnan et al., 2019), with the production and possible release of intermediate and undesirable N compounds, such as NO_3-N, nitrite (NO_2-N) and N_2O, to the environment.

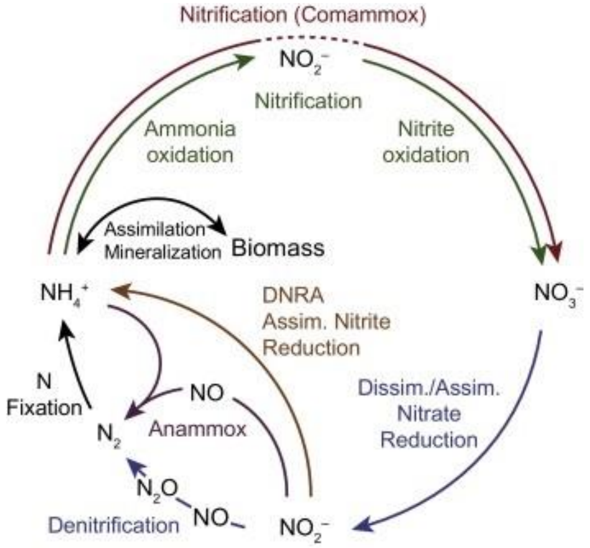


Figure 2.8. *Nitrogen cycle. Adapted from Daims et al. (2016)*

Current policy instruments, such as the EU WFD regulate N use for water quality protection and treat the farm as a homogeneous block; however, the ability of the soil/subsoil and underlying geology to attenuate a N surplus is highly variable and linked to the subsurface heterogeneity (Jahangir et al., 2013; MacAleer et al., 2017).

2.5. Nutrient losses from farm systems

The losses of N and P, and release of sediment-associated contaminants in drainage water (Walling et al., 2003) are site-specific and depend on many factors such as geology, climate condition (Mellander et al., 2018), annual rainfall (Vero et al., 2016), farm management (Cichota and Snow, 2009), drainage status of the soil, soil and subsoil type, and the permeability of the soil (Schulte et al., 2005). The nutrient losses (N and P) impair the quality of water and stream habitat by moving through soil, subsoil and aquifers to the subsurface or groundwater in many different time scales from months (provided that the soil is well drained and highly permeable) to years (for moderately drained and low permeable soils) (Fenton et al., 2011b).

2.5.1. Phosphorus losses

The application of organic and inorganic fertilisers (Preedy et al., 2001; Haygarth et al., 2005) results in critical and incidental P losses to both surface and subsurface water bodies (Heathwaite and Dils, 2000; Leinweber et al., 2002) (Figure 2.8). This contributes to a large proportion of water quality problems such as eutrophication (Schindler, 2006; Brennan et al., 2017) at both local and regional scales (Torrent et al., 2007; Dale et al., 2010; Kröger et al., 2013), and has degraded "high status" water bodies in Europe (Gonzales et al., 2018).

The transfer of P bound to soil to water bodies happens via two main pathways, surface runoff and subsurface flow (leaching). Phosphorus is transferred as dissolved P (DP) and particulate P (PP) (Figure 2.9). Haygarth et al. (2005) developed the "pollutant transfer continuum" concept which describes the transfer of P from source to water (Thomas et al., 2016). This four-tiered P-transfer continuum model (comprising source, mobilisation, delivery, and impact components) explains the interdisciplinary and inter-scale nature of P losses and shows that increasing the connectivity between in-field water and nearby water bodies would increase the risk of P being transferred (Daly et al., 2015, Moloney, 2020) and, therefore, increase the risk of deteriorating the water quality.

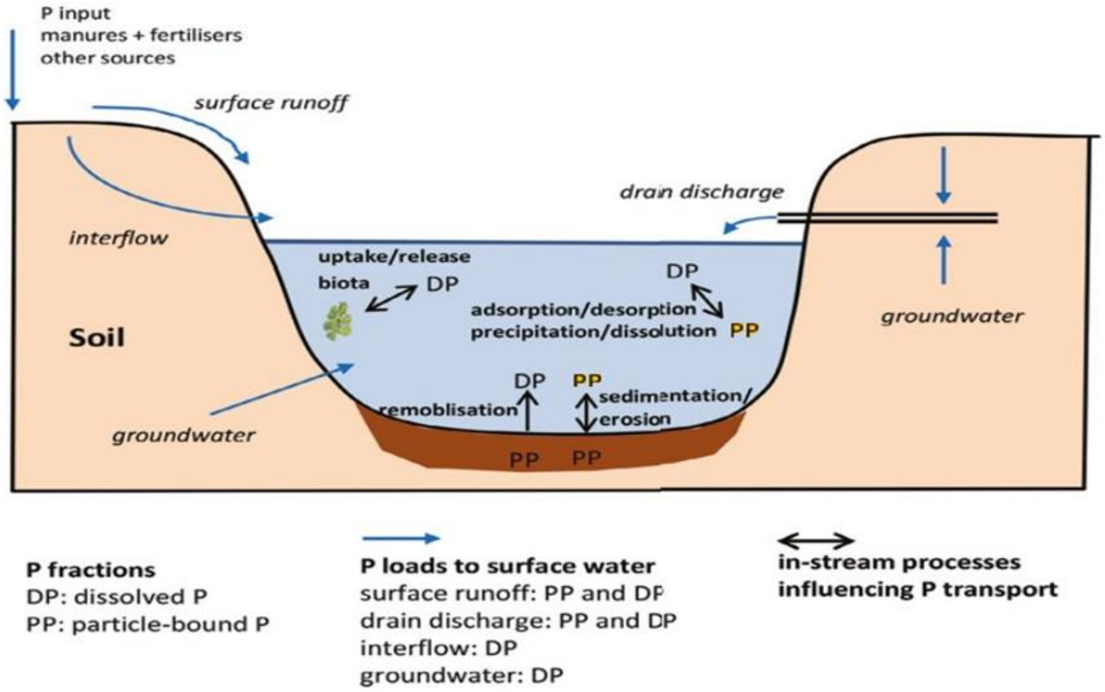


Figure 2.9. *Main P load pathway transfer from diffuse sources to surface water. Source: Grift (2017).*

Mineral fertiliser and manure add a greater amount of P to water compared to agricultural soils (DAFM, 2017). Other factors such as soil erosion, physical transfer of P with soil particles, soil P concentrations and manure input, also constitute pathways of P transfer from soil to water (Haygarth et al., 2005; Haygarth and Sharpley, 2000). According to Thomas et al. (2016), soil properties such as Al, Fe, calcium carbonate, clay, pH and OM define the capacity of soils to bind and immobilise P. Therefore, the transfer of total P to surface runoff is more likely from some soils than others (Daly et al., 2001, 2015).

Generally, soil type (Campbell and Foy, 2008) and its drainage status (Sims et al., 1998), and the type of water resources (surface or groundwater) play an important role in mobilising or retaining P. Kurz et al. (2005) showed that poorly drained sites with elevated soil P levels (average of 17 mg P L^{-1} measured as Morgan's P) have more potential for losing DRP to water bodies. Generally, nutrient losses in wet soils that are characterized by a heavy texture are associated with overland flow, while on free-draining light-textured soils, nutrients are lost through leaching (Kiely et al., 2007). Hence, P retention and potential of P loss to water is site-specific and depends on soil hydrology, water flow velocity, and biological/chemical characteristics of running water and underlying sediments (Withers and Jarvie, 2008).

Managing P resources on farms is a serious challenge for farmers, as they not only need to consider increasing food demand and rising P fertiliser costs, but also soil fertility (Daly et al., 2015). Therefore, prioritising a precise site characterisation and a soil-specific approach is required for efficient soil P management, successful reduction of P losses and sustainable intensification (both economically and environmentally) (Kronvang et al., 2007). As significant amounts of sediment and nutrients are transported in surface runoff pathways (McDowell and Monaghan, 2015), it was previously believed that reducing sediment transport was enough to control non-point P losses (Penn et al., 2017). Hence, soil infiltration and sedimentation were encouraged to reduce nutrient loss (McDowell and Laurenson, 2014). However, as P losses, originating from farmyards and silage/manure storage areas, includes PP and dissolved inorganic and organic P, its remediation is more complicated than originally thought (Macdowel and Laurenson, 2014; Kröger et al., 2013).

In addition, terrestrial legacy P (Sharpley et al., 2013) that has accumulated in sediments and river/lake systems will continue releasing DRP to water bodies via surface and subsurface pathways, and the timescale of retention and remobilisation of P are linked to water and sediment residence time (Sharpley et al., 2011), with the magnitude of time lag ranging from months, to years, to decades depending on the site hydrology and drainage status (Meals and Dressing, 2010), even if no inputs (fertiliser) are spread on farms during this period. This means that water quality improvement through diffuse P source mitigation must factor in time for P sources to transfer to and within river networks (Wall et al., 2013). Hence, a site-specific designing of monitoring program and mitigation measure is required to appropriately address the lag between implementing the measures and an improvement in water quality.

2.5.2. Nitrogen losses

Reactive N surplus in agricultural catchments accumulate in the rooting zone of soils due to low N-use efficiency (NUE) (Bouwman et al., 2017). Nitrogen leaching originates from inorganic or organic fertiliser applications to soil, as both the soil particles and NO_3^- are negatively charged and, therefore, NO_3^- can move easily through water (Kung et al., 2000; Fenton et al., 2008). Several factors increase the rate of N leaching. These include a well-drained soil, heavy rainfall, high inputs of N, especially outside the growing season, and the concentration of NO_3^- in the soil (Huebsch et al., 2013).

Depending on the soil, subsoil and bedrock conditions, N leaches along surface or pathways as either NO_3^- (well-drained soil) or NH_4^+ (heavy textured soils) (Clagnan et al., 2018a). The N biotransformation includes nitrification (chemical oxidation caused by autotrophic bacteria), denitrification (conversion of NO_3^- to N_2 gas called *full denitrification* or to N_2O gas called *partial denitrification*), anaerobic ammonium oxidation (annamox) and DNRA (Deni and Pennincks, 1999).

Nitrogen transformational processes within water and soil/subsoil continua and soil drainage classes (Alterra, 2011) define the type of excess N leaching along surface or pathways to be as either NH_4^+ and/or NO_3^- (Figure 2.10). The fate of N losses depends on the soil function, which is governed by the soil type and agricultural land uses (O'Sullivan et al., 2015). This means that adequate denitrification in poorly drained or lower permeability soils would ensure that the N surplus leaving the rooting zone does not lead to elevated groundwater N concentrations. Therefore, the soil would have a high naturally N purification capacity (Schulte et al., 2014), whereas well-drained soils would create unsuitable conditions for denitrification (higher aerobicity, lower water saturation and higher residence time) which leads to greater NO_3^- losses (Clagnan et al., 2018a).

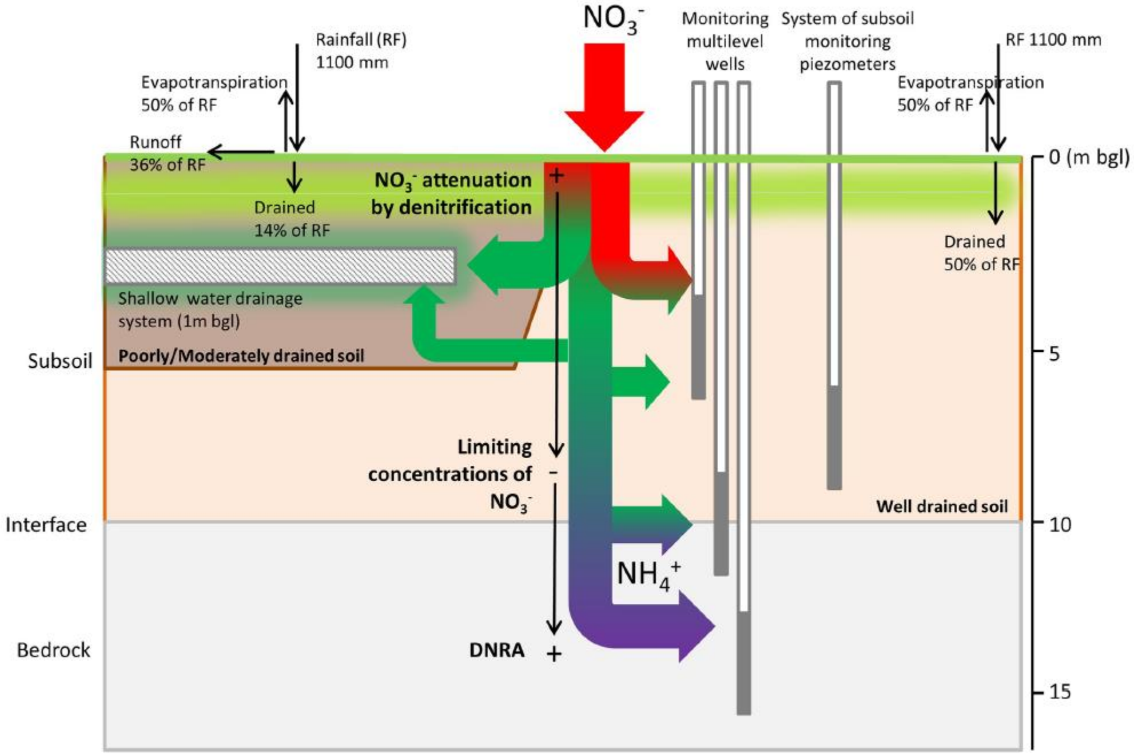


Figure 2.10. Conceptual diagram of N loss pathway on the Johnstown Castle Dairy Farm with elevated NH_4^+ concentration in drainage water: (1) migration pathway in poorly-imperfectly drained soils with high NO_3-N attenuation (2) migration pathway under moderately-well drained conditions with no NO_3-N attenuation is lower, leading to its transformation in NH_4-N. Source: Clagnan et al. (2019).

2.6. Regulations of N and P losses

The EU WFD (OJEC, 2000) aims to achieve at least "good status" of ground and surface waters through implementation of mitigation measures to reduce nutrient loads entering receiving waters. These mitigation measures are enacted by the Nitrates Directive (OJEC, 1991), while the EU WFD guidelines monitor their effectiveness. In recent years, focus has been placed on the potential impact of agricultural intensification on the degradation of natural resources and water quality (McDowell et al., 2008; Preston et al., 2011; Sutton et al., 2011). A high proportion of EU countries have less than good ecological status of water bodies due to multiple anthropogenic pressures (Figure 2.11) (EEA, 2018).

The negative impact of intensification on ecological status has been observed by the

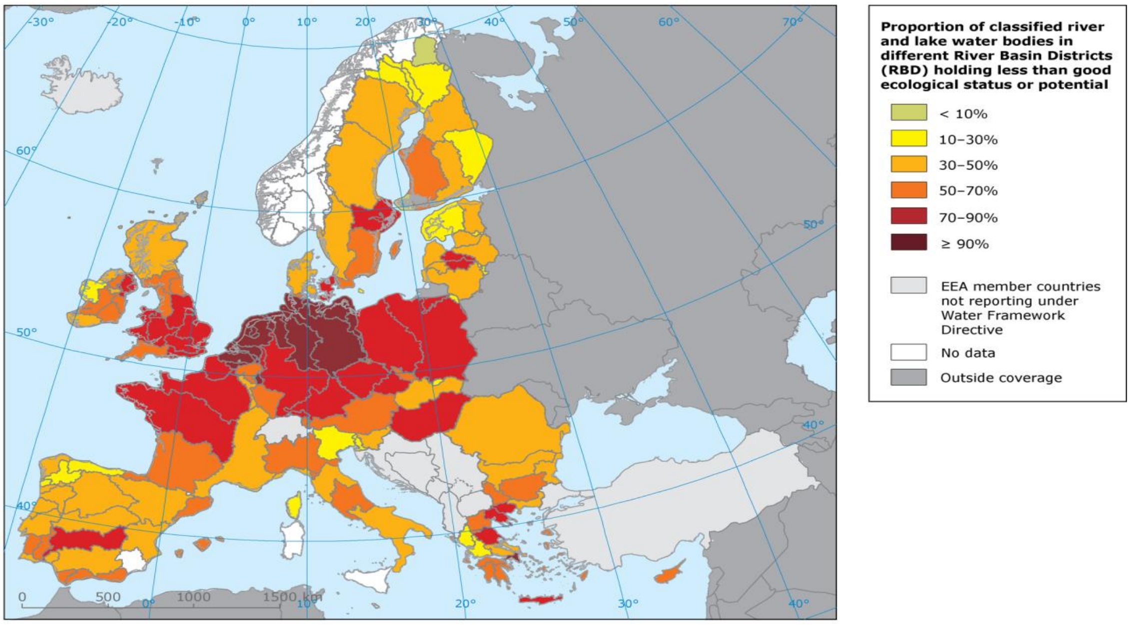


Figure 2.11. *Proportion of classified river and lake water bodies holding less than good ecological status. Adapted from EEA (2018).*

positive correlation between increase in N/P concentrations in freshwater ecosystems and an increase in poor and bad ecological status; therefore, agriculture in drained catchments (imbalance between agricultural nutrient inputs and outputs) has been identified as one of the most important predictors of good ecological status in rivers (EEA, 2018; Grizzetti et al., 2017).

In contrast to the general downward trend of nutrient concentrations in Europe's river from 2000-2015 (Figure 2.12), groundwater NO_3^- has no overall decline (EEA, 2018) (Figure 2.13) and even exceeded limits set by the Drinking Water Directive in many water supplies (EEA, 2016). According to the EEA (2018), between 2013 and 2015, 12 out of 22 countries had average groundwater NO_3^- concentrations above the EU quality standard of 50 mg NO_3^- L^{-1} (or 11.3 mg NO_3-N L^{-1}) as described in the EU Groundwater Directive (OJEC, 2006). These figures show that further reduction in level of nutrients are necessary to achieve "good" status of water bodies across the EU and, therefore, full implementation of EU WFD (EEA, 2018).

During 2014-2016 in Ireland, 38% of monitored river sites had average NO_3^- concentrations > 8 mg L^{-1} and over 26% had average phosphate concentrations > 0.035

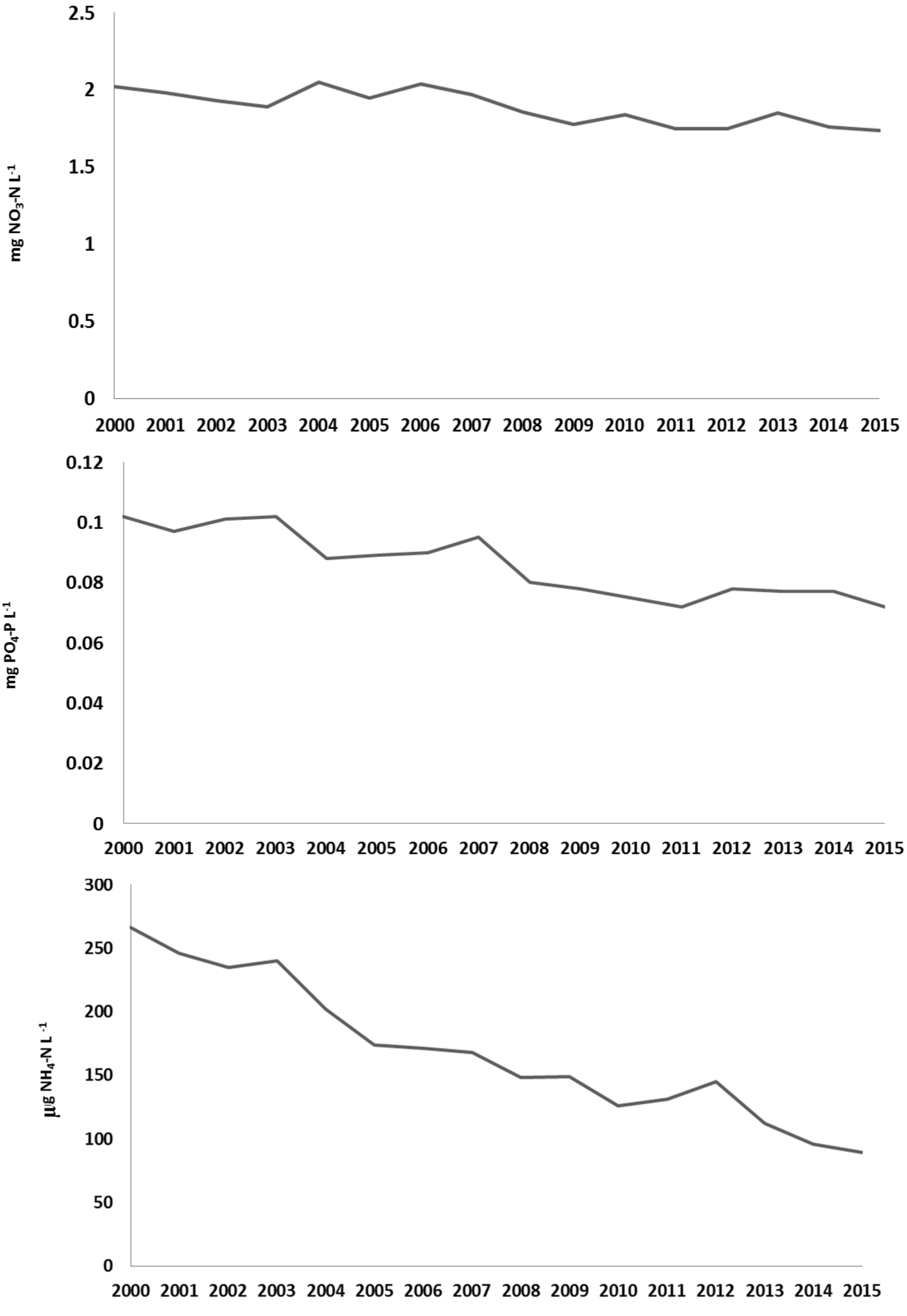


Figure 2.12*. Average annual mean concentrations of nitrate (top), phosphate (middle) and ammonium (bottom) in rivers across Europe. Adopted from EEA (2018, 2019).*

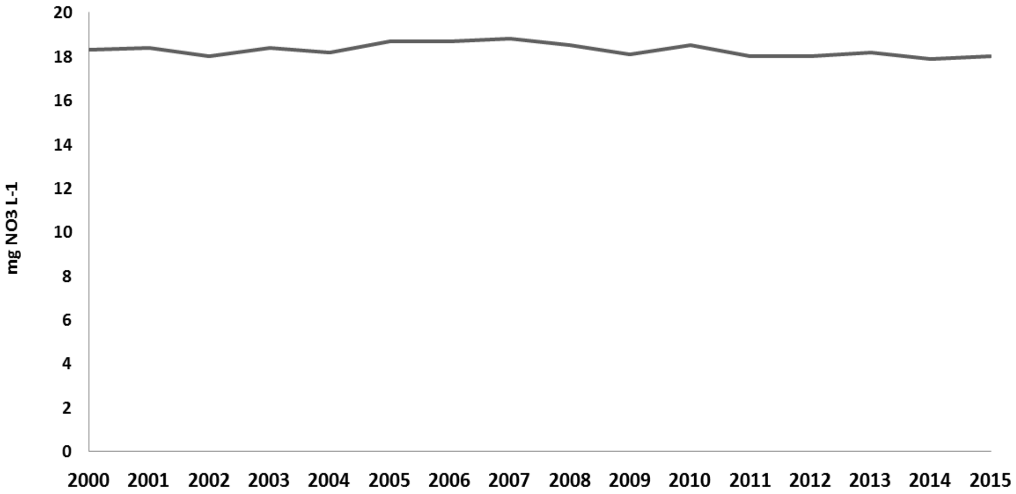


Figure 2.13*. Average annual mean* NO_3^- *concentrations in groundwater across Europe. Adapted from EEA (2018).*

mg L^{-1} which were mostly located in the south and south-east of the country (EPA, 2017). According to EPA (2016), the annual rate of change since 2007 of nitrate concentrations in 50% of river sites improved slightly or remained stable whereas phosphate concentrations in 74.4% of rivers remained constant and decreased in 22.1% of rivers. Here, the first NAP came into operation in 2006 (DEHLG and DAF, 2004) and was designed to improve water quality and prevent pollution of surface waters and groundwater from agricultural sources by measures such as limiting the number of animals and the amount of manure applied per hectare. The NAP sets the maximum allowable concentration (MAC) as 11.3 mg NO_3-N L^{-1} and 0.23 mg NH_4-N L^{-1} for drinking water (EU, 2014c). For estuarine water bodies, Irish legislation stipulates a mean annual dissolved inorganic N (DIN) concentration of <2.6 mg L^{-1} combined with mean annual acceptable molybdate reactive phosphorus (MRP) concentration of 15 mg L^{-1} (EPA, 2014). In lotic systems, a mandatory annual mean total P concentration of 25 mg L^{-1} and ortho-phosphate concentration of <0.035 mg L^{-1} are set (Statutory Instruments 2009; Mellander et al., 2014; EPA, 2013).

The NAP is reviewed every four years and considers managing nutrient source pressures of significant importance (Wall et al., 2011) and is utilised for mitigation of diffuse agricultural pollution (Zhang et al., 2012). Hence, the fourth iteration of Ireland’s NAP (NAP4), which will run until the end of 2021, has defined a fertiliser input program in order to target the application based on soil N and P requirements (Table 2.1). This would ensure efficient use of N and P at the correct time during the growing season and would avoid cattle fertiliser applications on fields with high available N or high soil P status, or on “critical source areas” (areas with large amount of P, and a high risk of P mobilisation and transport) (Thomas et al., 2016).

Table 2.1. *Annual maximum fertilisation rates of N on grassland in Ireland.*

Grassland stocking rate (kg ha^{-1} yr^{-1})	Available nitrogen (kg ha^{-1})
170	206
Grassland stocking rate greater than 170 (kg ha^{-1} yr^{-1})	
171-210	282
211-250	250
>250	250*

*The application of N from livestock manure (including that deposited by the animals themselves) shall not exceed 250 kg N ha^{-1} yr^{-1} (for holding granted with derogation).

Table 2.2. *Annual maximum fertilisation rates of P on grassland in Ireland.*

Grassland stocking rate (kg ha^{-1} yr^{-1})	Phosphorus Index			
	1	2	3	4
	Available Phosphorus (kg ha^{-1})			
<85	27	17	7	0
86-130	30	20	10	0
131-170	33	23	13	0
Grassland stocking rate greater than 170 (kg ha^{-1} yr^{-1})				
171-210	36	26	16	0
211-250	39	29	19	0
>250	39	29	19	0

2.7. Mitigation measures to reduce nutrient losses in drainage ditches

Numerous pilot and farm-scale studies have investigated the efficiency of various agricultural mitigation measures to target nutrient losses, contamination in different water bodies and GHG emissions for a range of agricultural activities (Campbell et al., 2004; McKergow et al., 2008; Kay et al., 2009; Merriman et al., 2009; Monaghan, 2009; Sharpley et al., 2010; Newell Price et al., 2011; Wall et al., 2011). Source mitigation at farm level to reduce the risk of nutrient transfer are not only cost saving (Zhang et al., 2012; Buckley and Carney, 2013), but are more beneficial than other measures such as mobilisation or delivery control measures (Collins et al., 2014). Long-term monitoring studies in the U.S. have shown that the high nutrient export from predominantly agricultural crop production (<70 %) watersheds to surface or groundwater can successfully be prevented or reduced by implementation of best management practices e.g. filter strips or water control basins (Makarewicz et al., 2009) and engineering-based solutions such as denitrifying bioreactors (Christianson et al., 2012). Nutrient mitigation measures include natural or engineered options. After careful characterization of farm nutrient losses, the most appropriate solution can be developed, which may incorporate the natural attenuation function with engineered solutions to maximize the efficiency of the mitigation measure.

2.7.1. Natural Attenuation

All soils can perform multiple functions of primary productivity (food, fuel and fibre), carbon sequestration, housing biodiversity, recycling nutrients, as well as water purification (Coyle et al., 2016). The supply of each function highly depends on land use management and local soil properties including soil drainage (Schutle et al., 2015). The concept of 'Functional Land Management' (Schutle et al., 2014) was developed to optimize the supply of soil functions including its water purification function. In Ireland, a high proportion of land (99 %) provides high water attenuation capacity (supply of denitrification as a partial proxy for water purification) that helps the groundwater nitrate concentrations remain below thresholds (Byrne and Fanning, 2015), even in intensively grazed agricultural landscapes.

Many studies have reported significant nutrient losses from tile drain outlets, while enhancing drainage capacity of poorly-drained soils could positively or negatively impact nutrient losses (Kalita et al., 2007; Algoazany et al. 2007; Gentry et al., 2007; Vidon and Cuadra, 2010). Drainage reduces N and P loads through flow reductions (Skaggs et al., 2012) and increases denitrification, which contribute to further N reductions (Skaggs et al., 2010). However, controlling the discharges into ditches and maintaining the network is important to prevent possible increase in the amount of sediment losses from agricultural fields to water bodies (Randall and Goss, 2001) (Figure 2.14).

Meanwhile, the natural attenuation of the soil, defined as the use of processes occurring in the natural soil environment to contain the spread of contamination (Mulligan and

***Figure 2.14**. Left: Sediment accumulation in pipe discharging directly into ditches, Johnstown Castle, Co. Wexford, Ireland, 2018. Right: In-field ditches with elevated concentrations of DRP and NO_3^- in Sint-Truiden, Belgium, 2018.*

Yong, 2004), may reduce contaminant concentration and transform contaminants to less harmful forms (Bjerg et al., 2003). This has encouraged farmers to rely on the natural attenuation of the soil to remediate excessive nutrient loads (Figure 2.15). The usefulness of this technique has been used in 'monitored natural attenuation' systems (Speight, 2017) (Figure 2.16), which are engineered natural attenuation systems, whose effectiveness in achieving site-specific remediation within a specific time-frame is compared to other techniques.

***Figure 2.15.** A partially open extensive ditch on the farm, receiving nutrients from pipes, relying on natural attenuation of the soil to remediate excess nutrient loads. Johnstown Castle, Co. Wexford, Ireland, 2017.*

The natural attenuation capacity of soils is due to the bedrock chemistry through which water migrates. Various studies have highlighted this natural attenuation capacity of N (EPA US, 2007; Jahangir et al., 2016) and P (Mellander et al., 2015; Shore et al., 2016) on agricultural farms and showed that many aspects of soil/subsoil and aquifer biogeochemistry prevent N and P losses, even in drained landscapes. Studies have even reported remediation of heavy metal contamination through natural attenuation occurring around mining areas (Krishna et al., 2010).

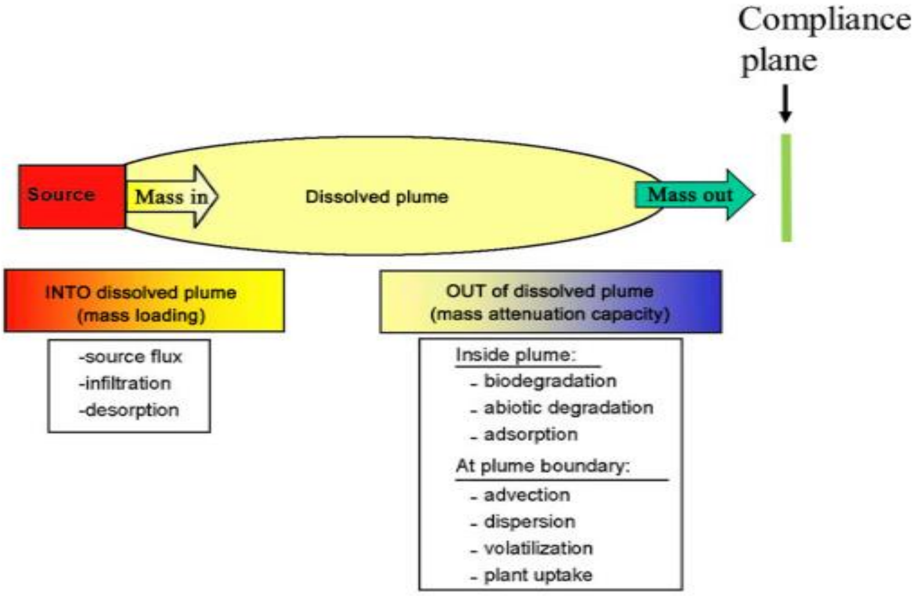


Figure 2.16. *Concept of monitored natural attenuation. Source: Brusseau et al. (2019).*

The processes responsible for natural attenuation include volatilisation, leaching, dilution, dispersion, photo-oxidation, biodegradation by on-site bacteria and fungi, and phytoremediation, and adsorption of contaminates to clay minerals and OM in the soil (Scow and Hicks, 2005; Nelson et al., 2014). Complete remediation may take from 1 to 50 years, depending on several factors including history of contamination (soil legacy), microbial community, concentration/chemistry of contaminants, soil chemistry, and temperature (Alvarez and Illman, 2005; Ouvard et al., 2013). Additionally, natural attenuation often follows first-order kinetics, meaning that the rate of attenuation will decrease over time as contaminants become sequestered in the soil (Nelson et al., 2014). Shore et al. (2016) and Daly et al. (2017) showed that exposed drainage ditch sediments with appropriate soil chemistry can act as natural DRP traps, as soil properties such as Al, Fe, calcium carbonate, clay, pH and OM define the capacity of soils to bind and immobilise P (Thomas et al., 2016). Therefore, the transfer of total P into surface runoff is more vulnerable in some soils than in others (Daly et al., 2001, 2015). Similarly, heavy textured soils offer high water purification function in terms of N (higher denitrification rate) due to an abundance of microbial communities in soils with high clay content (Li et al., 2018).

In general, the best result arising from mitigation measures is when natural attenuation, as a non-engineered treatment with a very slow biodegradation processes (Mulligan and Yogn, 2004), is used in conjunction with other remediation techniques (Krishna et al., 2010) such as source removal or controlled engineered solutions like controlled drainage systems. This is because natural remediation systems on their own are not sufficient to remediate large fluxes of contaminates that may occur in intensive dairy farms.

2.7.2. Engineered mitigation options

Ecologically engineered solutions eliminate nutrient problems in drainage water at field and watershed-scales through a multidisciplinary approach (Kröger et al., 2013) to make a "treatment train" (a sequence of various mitigation measures) of various mitigation practices which appears to be the best technique to meet water quality standards (Dinnes et al., 2002, Christianson, 2011).

Some of the most commonly used engineered measures are constructed wetlands (Blackwell et al., 2002; Kadlec, 2012), buffers (Braskerud, 2002; Fogg et al., 2005), controlled drainage and in-ditch techniques (Strock et al., 2010; Woli et al., 2010; Puckett, 2014), which are highlighted in Table 2.3.

In short, constructed wetlands are artificial sinks for N_r and other organic and inorganic contaminants that have been used for treating domestic sewage, industrial and agricultural wastewater and leachate through biogeochemical reactions (Rozema et al., 2016). As little research has quantified all delivery pathways of transformed nutrients in and around wetlands (Jahangir et al., 2016), variable removal efficiencies have been reported (Kadlec, 2012). Buffers, strips of permanent area designed within and between

Table 2.3. *Comparison between engineered mitigation options: wetlands, buffers, controlled drainage and in-ditch structures.*

	Targeted contaminants	**Mechanism**	**Main disadvantages**	**Advantages**	**Limiting factors**
Constructed Wetland	BOD, COD & particulate pollutants Nitrogen (mainly nitrate) in field runoff, river/stream improvement	Biologically active system depending on microbial and plant activity	Not good for mitigation of dissolved P	Efficient year-around Efficient in storm-water runoff Biodiversity conservation	Very low temperature requires certain design considerations Carbon availability at high nitrate loadings Management practices Large areal requirement
Buffer strips	Sediments /particulate materials Removal of N in organic/particulate form Very good for removing sediment-bound P	Not good for soluble P and nitrate	Limited microbial process and subsurface denitrification Sediment build-up at top of buffer	Easy adaptation to existing farming practices Good for poorly drained and permeable soils (not sandy or heavy textured soil)	Large buffer width required Creates uncultivated land area Type of vegetation/non-growing season Groundwater distance to surface slope < 5% High velocity flow/snowmelt/ice cover
Controlled drainage	Excess nutrient discharges Managing excess and deficit soil-water conditions			Lower pollutant loads Trapping nutrients with a long hydraulic residence time during dry seasons	Regular maintenance Conduits of field pollutants during wet seasons Depth and drain spacing Hydrology of the area
In-ditch structures for filtration	Excess nutrient loads	Intercept water with materials that have chemical contaminant removal capacity	High cost (depending on target removal rate/size of the farm) Appropriate material selection	Efficient under different climate condition Flexibility of design (in-ditch/in-field/edge of field)	Location to install the structures Hydrology of the catchment may result in bypassing riparian zones and discharging into water bodies Short life time Hydraulic characteristics of material(s) Retention time Cost of materials Filter material characteristics: Carbon availability for denitrification of NO_3^-; P/NH_4^+ binding/retention capacity
1. Biological removal (denitrifying bioreactors)		Carbon-based materials: microbially mediated process of denitrification (conversion of nitrate to N gas			
2. Sorption filters		Sorption/precipitation/Ion exchange			

agricultural fields to slow runoff, have been recognised as a designed measure to control nonpoint source pollution from agricultural fields and mitigate negative impact on water quality (Yuan et al., 2009). Although the efficiency of buffers is site-specific and studies provide highly variable results, buffers are known to have high sediment trapping capacity, which depends on the buffer width (wider buffers have higher potential for trapping sediments) (Fogg et al., 2005).

Generally, there are limitations and major financial drawbacks associated with buffers and wetlands, which influence their practicality such as loss of productive land by using buffer strips or initial high cost of constructing wetlands (IDALS, 2009). Other options such as controlled drainage may actually improve the yield (thus the income), whereas in-ditch techniques provide more flexibility without the need of turning a piece of productive land into a non-productive area. A well-managed drainage system that was initially developed to improve drainage water quality via a decreasing nutrient load (Dinnes et al., 2002), can mitigate nutrient losses, increase fertiliser nitrogen-use efficiency and reduce GHG emissions (Strock et al., 2017; Castellano et al., 2019). According to Ballantine and Tanner (2012), controlled drainage systems yield significant benefits for water quality and nutrient-water use efficiency. Cooley et al. (2013) showed that a well-controlled drainage network not only offers agronomic benefits such as improving the crop yields and reducing surface runoff, but may also improve soil quality and reduce soil erosion. The effectiveness of drainage can result in an increase in crop growth of up to 30 %, and an increase in N and P uptake of 45 % and 62 %, respectively, on 20-yr drained soil compared to undrained soil (Brown et al., 2013).

Among various options, in-field (in-ditch/along the ditch) structures filled with filtration materials and the use of different adsorbents (natural, manufactured or recycled from various sources) have gained more popularity as a cost-effective, easy to install, and low-maintenance technology during recent years (Delgado and Berry, 2008; Bhatnagar and Sillanpaa, 2011; Bibi et al., 2015). To date, the performance of in-ditch structures has mainly been evaluated in terms of their ability to treat a single contaminant, predominantly NO_3^- (Addy et al., 2016; Christianson and Schipper, 2016) and more recently P (Penn et al., 2014a). Recent studies have examined combining individual nutrient removal technologies (Goodwin et al., 2015; Ahnen et al., 2016;

Gottschal et al., 2016) such as a combination of in-ditch structures (Christianson et al., 2017) to examine the efficiency of employing a treatment train in the remediation of complex contaminant mixtures (Tsitonaki, 2008). The different types of engineered structures for the removal of N and P are explained in the following sections. However, a knowledge gap exists with respect to (1) identifying the suitable medium/or combination of media for the remediation of multiple water quality parameters and (2) site/contaminant-specific design criteria such as the occurrence of single or mixed nutrient losses, logistics/availability of selected filter material to the user (farmer) and associated costs, ditch capacity in retaining/mobilising nutrients, for an engineered structure to target simultaneous contaminant remediation.

2.7.2.1. Denitrifying bioreactors for nitrate remediation

Denitrifying bioreactors (i.e. biofilters), as a recently established engineered-based agricultural best management practice (Bock et al., 2018), are in situ engineered structures filled with C-sourced materials such as woodchip, straw, corn cob or compost. They have gained in popularity for the treatment of excess NO_3^- loadings in drainage water due to their low cost, low maintenance and energy input (Kim et al., 2003).

Denitrifying bioreactors capture and biologically degrade organic and inorganic pollutants to fuel heterotrophic activity and provide non-toxic discharges using microorganisms (Schipper et al., 2010a). They are used in tile drainage systems and intercept nutrients and convert NO_3^- to N_2 gas (Christianson et al., 2011, 2013; Healy et al., 2014). In the microbial process of heterotrophic denitrification, NO_3^- uses a C-source as an electron donor to be converted to gaseous forms of N (Coyne, 2008) so the media serve as an electron donor, helping the bioreactor to create required anaerobic conditions (Shipper et al., 2010). Therefore, full denitrification removes N effectively from biological cycling (Rütting et al., 2011; Burgin et al., 2013). Biofilters are versatile and can be designed to facilitate a wide range of applications and nutrients from different emission sources such as pesticides (Ranaivoson et al., 2012) in a variety of agricultural settings from subtropical climates to snow-covered areas (Addy et al., 2016). However, they react differently in adsorbing heavy metals or volatile organics (Saliling et al., 2007; Schipper et al. 2010a,b). Therefore, the correct choice of structure design and filter medium depends on the contaminated site, climate conditions and topography of the region. Wood-based denitrifying bioreactors (Figure 2.17) have gained more popularity due to their relative low cost, ease of handling, low maintenance, good capacity for turbid water and long lifetime (Sharrer et al., 2016). Woodchip's high porosity and permeability and surface roughness mean that they are an effective suspended solids (TSS) and chemical oxygen demand (COD) adsorbent for subsurface agricultural drainage water (Feyereisen et al., 2016; Hoover et al., 2016; Pluer et al., 2016; Sharrer et al., 2016). On the other hand, they have little DRP removal capacity (Choudhury et al., 2016).

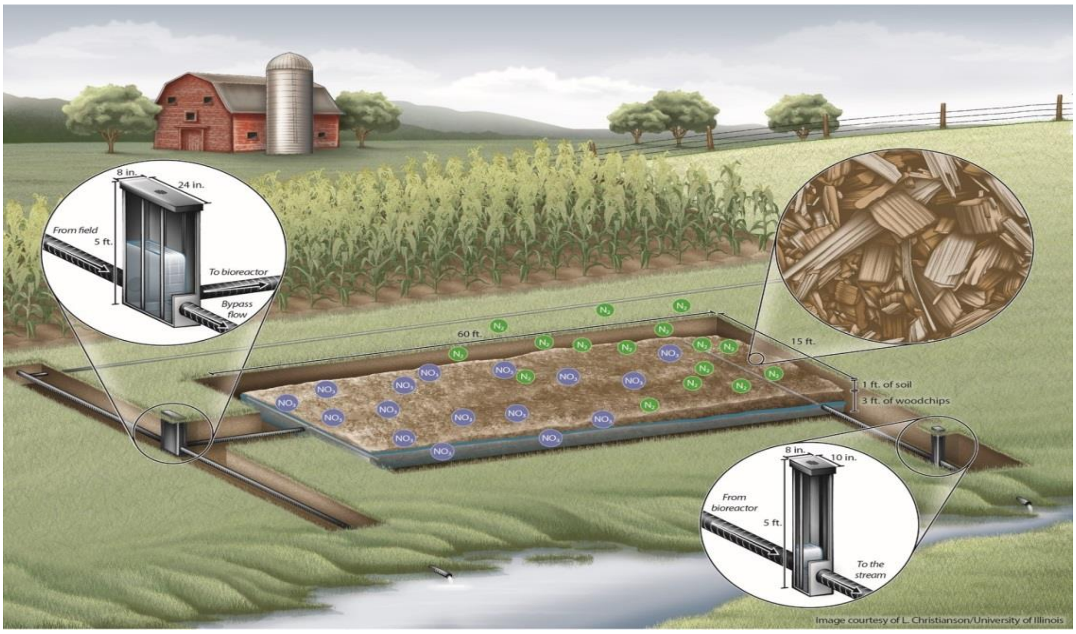


Figure 2.17. *Generalized illustration of a woodchip denitrifying bioreactor for nitrate treatment in subsurface drainage. Credit: L. Christianson/University of Illinois.*

2.7.2.2. Sorption filters

2.7.2.2.1 NH_4^+ removal structures

Typically, N losses from land drainage systems can occur as either NO_3^- (Nangia et al., 2010) or NH_4^+ (Clagnan et al., 2019). The occurrence of different types of N is explained by the fact that the physical and biogeochemical factors that control the transformation of N along subsurface pathways vary widely along the soil-subsoil-bedrock continuum (Rivett et al., 2008; Fenton et al., 2009c). Ammonium pollution in agricultural landscapes is not only dependent on soil chemistry, but it also originates from diffuse sources which make it difficult to control or mitigate (Huang et al., 2017).

Consequently, there has been little research on NH_4^+ removal structures (Rabah and Darwish, 2013) in comparison to NO_3^- removal structures (Section 2.7.2.1).

Among various NH_4^+ removal technologies such as air stripping (Guštin and Marinšek-Logar, 2011), reverse osmosis (Bodalo et al., 2005), microwave radiation (Lin et al., 2009) (which is mostly used for industrial wastewater treatment), ion-exchange and adsorption, media-based treatment options have proved to be efficient, cost-effective and simple to apply (Turan, 2016; Huang et al., 2017). According to Huang et al. (2017), zeolite, activated carbon, biochar and carbon-based materials are effective for NH_4^+ removal, although their efficiency depends on country of origin, pyrolisis conditions and vegetation type (for biochar). In recent years, there has been a growing number of studies using natural adsorbents (Wang et al., 2014; Gupta et al., 2015) for remediation of NH_4^+ losses in ditch networks. Huang et al. (2017) has proposed a criteria-tree for identifying the most suitable adsorbents to remove NH_4^+ from agricultural drainage water in large (field) scale filters (Figure 2.18).

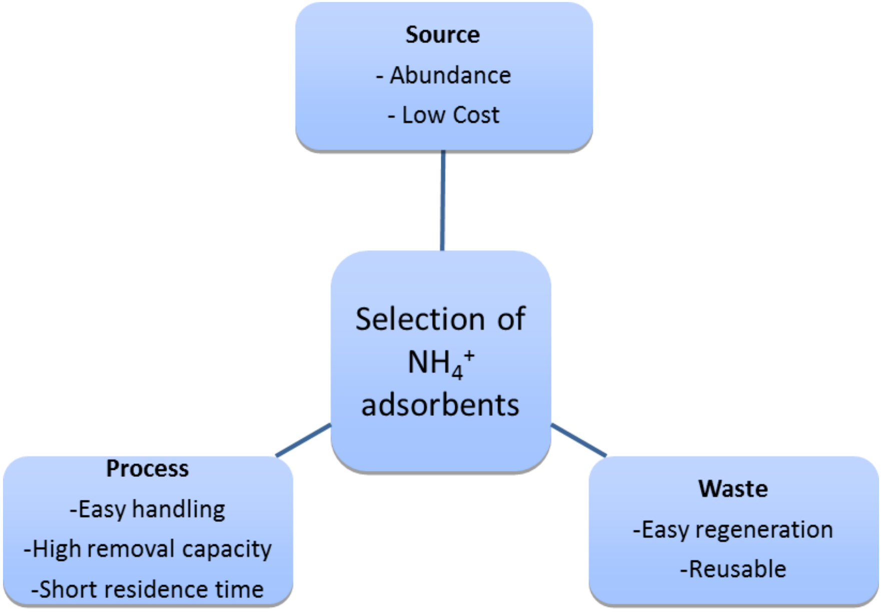


Figure 2.18. *Criteria for selecting cost-effective ammonium adsorbent material: source (availability and cost), process (easy operation and efficiency), waste (environmental friendliness). Adapted from Huang et al. (2017).*

An efficient engineered solution for removing NH_4^+ losses in agricultural drainage water is the installation of in-ditch control structures comprising appropriate adsorption media (Fenton et al., 2016). However, as adsorption capacity of filter media may vary by region, developing an efficient structure filled with an adsorptive material requires an initial adsorption characterization to match site-specific conditions.

2.7.2.2.2 P removal structures

Phosphorus losses from an agricultural catchment can occur in dissolved and/or particulate (McDowell and Sharpley, 2001) and in reactive forms readily available to organisms for algae growth (Barsanti and Gualtieri, 2014). This fraction of P is measured as DRP and its interception and remediation can be achieved by using a P-sorbing filter (Lyngsie, 2013; Penn et al., 2017) (Figure 2.19). The necessity of constructing P removal structures is justified by the ready bioavailability of dissolved P, poor performance of best management practices to reduce P losses from legacy soil, and high P legacy in soils as a continuous source of pollution to drainage water (Penn and Bowen, 2018).

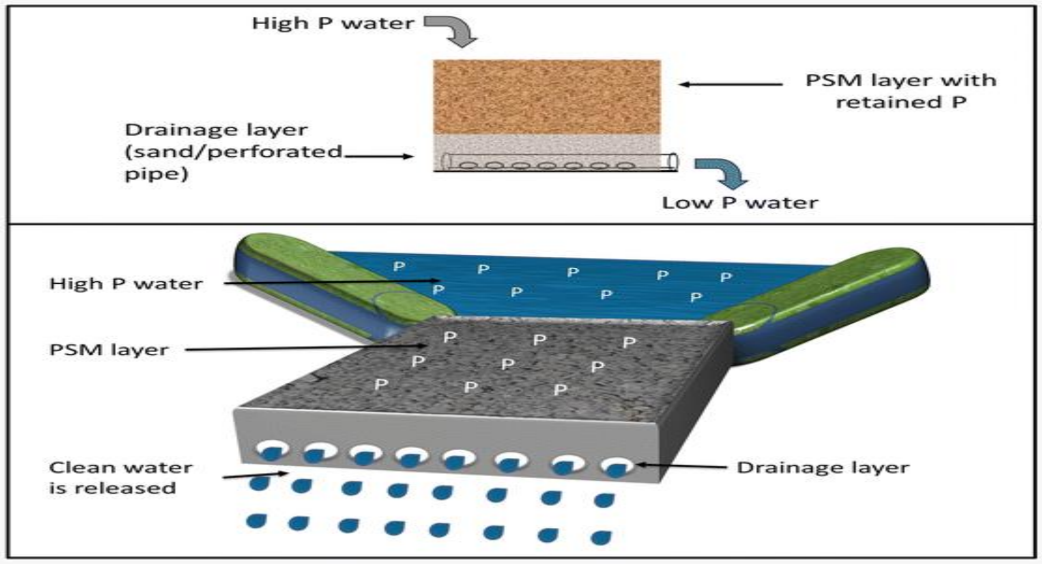


Figure 2.19. *Diagram illustrating basic premise of a P removal structure filled with P sorbing material . Source: Penn and Bowen (2018).*

The P-adsorption ability of a media depends on its redox potential, pH, the content of Al, Ca and Fe (Cucarella and Renman, 2006; Standford and Larson, 2015), and the Fe to P ratio (Healy et al., 2010; Reisner and Pradeep, 2014). Commonly used media for use in P removal are industrial by-products such as red mud, crushed concrete, fly ash and Bayer residue (Li et al., 2006; Egemose et al., 2012; Grace et al., 2015), metal mine ochre (Fenton et al., 2009a), and acid mine drainage residual (Pen et al., 2007). The configuration of an appropriate P removal structure also depends on the soil chemistry of the site (Penn et al., 2017). This means that a thorough examination of site characteristics (in terms of nutrient losses and attenuation/mobilisation potential) needs to take place before the installation of any structure.

2.7.3. Pollution swapping and limiting factors

Until recently, the focus of most studies has been on NO_3^- removal (Christianson et al., 2011), while generation of N_2O, ammonia (NH_3), NH_4^+, carbon dioxide (CO_2), and methane (CH_4), as a result of the biophysical and biogeochemical processes within the denitrifying bioreactors filled with woodchips, have often been neglected (Greenan et al., 2009; Schipper et al., 2010; Woli et al., 2010; Fenton et al., 2014; Healy et al., 2015). These negative impacts on the environment are the result of incomplete denitrification, which also releases dissolved organic carbon (DOC) and tannins during bioreactor start-up (Schipper et al., 2010; Warneke et al., 2011; Christianson et al., 2012; Hartz et al., 2017). Additionally, significant increases in woodchip P content in bags placed near the bioreactor outlets and along the bioreactor floor are reported (Christianson et al., 2016). This is aligned with the observation of Sharrer et al. (2016), who showed that woodchip leaching from denitrifying bioreactors could be an important source of P during bioreactor start-up, with most rapid P release within first 24 h of operation.

In terms of P sorption materials, contaminant release has been reported from both organic and inorganic filter media (Trois et al., 2010; Christianson and Schipper, 2016) and there may be adverse consequences associated with using industrial by-products. Metal leaching may occur arising from the use of fly ash, crushed concrete and Bayer residue (Grace et al., 2016) and the high Ca, Fe, and mostly Al content of furnace slag is believed to cause environmental problems, including elevated pH of water (Sanford and Larson, 2015). The materials react differently in adsorbing heavy metals or volatile organics (Sailing et al., 2007; Schipper et al., 2010). In addition, their low economic and geographical availability are other important issues in ensuring treatment sustainability (Yin et al., 2017). Other limiting factors for efficiency of such engineered structures filled with media include a positive linear relationship between nitrogen oxide (NO_x) removal and solute hydraulic retention times (HRTs) (Greenan et al., 2009; Chun et al., 2009; Bruun et al, 2016; Pluer et al., 2016; Hoover et al., 2016). Similarly, enhanced P removal efficiency as a function of a longer HRT has been observed (Sanford and Larson, 2015).

Therefore, many of the previously tested media that have been found to be successful in the remediation of a single contaminant may potentially be net polluters. The concept of pollution swapping is widely recognized (Stevens and Quinton, 2009) now, yet no single mitigation measure has been found that can eliminate all contaminants simultaneously. An ambitious goal would be to completely remove all pollutants without pollution swapping, though few studies have taken this into consideration (Healy et al., 2015). Only recent laboratory studies have investigated the dual removal of NO_3^- and DRP (Ibrahim et al., 2015; Choudhury et al., 2016; Christianson et al., 2017). Fenton et al. (2014) proposed the use of a Permeable Reactive Interceptor (PRI), in which a bioreactor is designed with additional remediation sequences to simultaneously mitigate NO_3^-, NH_4^+, DRP and DOC through the use of interconnected cells (Ibrahim et al., 2015).

Due to the limited bioavailability of C, engineered structures have a decreasing removal capacity over time. Therefore, selection of the medium/media is another important factor when considering lifetime of an engineered structure. For example, the efficiency of denitrifying bioreactors depends on the long-term ability of C-rich media in sustaining and enhancing denitrification over several decades (Moorman et al., 2010; Schipper et al., 2010; Long et al., 2011; Christianson et al., 2012). David et al. (2016) examined a woodchip bioreactor during the first three years of operation and showed that aging woodchip influenced the performance of the bioreactor negatively due to decreased amount of degradable C in the woodchips during the second and third years of operation. Temperature is also a limiting factor in the performance of denitrifying bioreactors (Cameron and Shipper, 2010). Chen et al. (2012) reported decreased removals from 80 % to 30 % following a 10^{o}C temperature drop, while Ahnen et al. (2016) reported good performance at temperature of 1 to 5 °C.

2.7.4. Adaptation of engineered solutions by farmers

In general, discharges of agricultural system-driven mixed contaminants to water bodies are a common problem. Therefore, considering these simultaneous nutrient losses, the correct choice of nutrient removal structure design and filter media will be defined based on specifics of a site, including climate, topography of the region, and site-specific nutrient contamination (Christianson and Helmers, 2011; Penn et al., 2017; Rosen and Christianson, 2017) to address mitigation of all contaminants produced as a result of both agricultural activities and contaminant remediation measures.

The performance and practicality of mitigation technology utilizing single or blended media depends on the long-term ability of C-rich media in sustaining and enhancing denitrification over several decades (for NO_3^- removal) (Moorman et al., 2010; Schipper et al., 2010) or adsorption capacity (saturation time) for NH_4^+ and DRP removal. Therefore, the physical, chemical, and biological properties of the media characterise an engineered structure's hydraulic conductivity, porosity, carbon: nitrogen ratio (C:N), microbially available C, availability, practicality, cost, and life-time (Ahsan et al., 2011; Christianson et al., 2012; Christianson et al., 2017). Additionally, potential negative side effects such as leaching of organic C, leaching of metals, and emission of GHGs must be considered. However, a knowledge gap exists with regard to a decision tool that has considered these factors. Farmers, as major stakeholders in the agricultural industry, need holistic advice (Schnyder et al., 2019) that considers practicality at farm-scale, ease of operation and cost. Until now, most of the advice has neither evaluated the whole-farm context nor has considered any potential adverse environmental effects (Schnyder et al., 2019).

Dissemination of information to farmers and stakeholders has shifted from a "procedure-like" (EPA, 2019) one-way approach, to a more dynamic and adaptive approach which is intended to be farmer-led and support them in their decision making. In recent years, online platforms have started to emerge (e.g. Nutrient Management Planning https://nmp.teagasc.ie (Teagasc, 2018)). However, a knowledge gap still exists with respect to a DST that is not only easily understood by the farmer, but also considers different factors in farm management such as environmental risk. Therefore, there is a need of a DST that provides farmers with a catalogue of sustainable nutrient mitigation options that incorporate environmental, economic, and social metrics.

Hence, more substantial research and work are needed to provide a user-friendly tool for farmers that not only targets mitigation of pollution caused by nutrient losses, but also considers perception of farmers on a suitable solution (Kerebel et al., 2013) specific to their local (cost/applicability/availability/logistics) conditions. Other criteria that influence the uptake of DSTs by farmers (Rose et al., 2016) are usability, performance, relevance to user and presenting outcomes resulting from different options (such as pollution swapping with regard to media-based engineered solutions for mitigation of nutrient contamination).

2.8. Adsorption isotherms to develop an in-ditch engineered structure design criteria

Frequently, mitigation options consider only a single medium filter which may or may not release secondary pollutant. The use of one medium will also accelerate saturation time and thus requires earlier replacement of the filter. Regardless of the number of media used in any remediation technology, and prior to deployment, it is necessary to characterize the adsorption capacity of these media. Frequently, this is done in batch-scale experiments, which are quick, cheap and easy-to-perform (Crini and Badot, 2008).

The amount of adsorbed molecules on the surface of the solid (adsorbent) depends on the concentration of the solution, and equilibrium is reached when adsorption (movement of molecules of adsorptive from solution and attaching to solid phase) and desorption (molecules of adsorptive detaching from solid phase to enter solution) are equal. This equilibrium found in batch adsorption systems is calculated as:

$$q_e = \frac{(C_o - C_e)V}{m} \qquad \text{[Eqn. 2.1]}$$

where q_e (mg g^{-1}) is equilibrium of the solid-phase, C_e (mg L^{-1}) is equilibrium of the liquid-phase, C_o (mg L^{-1}) is initial concentration of the solution, and m (g) is mass of adsorbent. The equilibrium concentration data are then fitted to adsorption isotherm models, with the two most commonly known to be Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906).

However, the materials that are intended to fill engineered structures and remove nutrients must not only have a capacity to adsorb P but also perform well under expected field conditions. Yet, batch tests fail to replicate in-field conditions, which experience varying temperatures, humidity, flow dynamics, pollutant load, and therefore often fail to accurately estimate the lifespan of the media (Pratt and Shilton, 2009). Batch isotherms use excessive nutrient concentrations and much longer retention times compared to field conditions (Penn et al., 2017). In order to overcome the limitation of batch studies in the accurate estimation of long-term performance of a medium, the closest simulation to in-field conditions are known to be large-scale adsorption columns (Monrabal-Martinez et al., 2017), which are an integral part of any media characterisation procedure (Ali and Gupta, 2007), to represent continuous flow conditions in the field (Pratt et al., 2012)

However, large-scale column experiments occupy large spaces, require a lot of equipment (Figure 2.20), are labour-intensive, and time consuming and expensive to run (Penn et al., 2014b). In addition, simultaneous mixed contaminant removal using more than one medium has only been investigated recently in long-term experiments running for several months. Therefore, rapid small-scale column tests (RSSCTs) could provide accurately enough data for the development of a field-scale engineered structure filled with adsorption media. RSSCTs offer a quick estimation of media performance in real-world conditions (Callery and Healy, 2017) using the minimum quantity of medium and contaminant solution (Poddar et al., 2013). This technique is mostly useful for assessing capacity or kinetic characteristics of untested materials and to avoid the possibility of metals or other polluting substances leaching from the media (Velghe et al., 2012).

Figure 2.20. *Space and required equipment to run large-scale column test. Johnstown Castle Research Centre, Co. Wexford.*

2.9. Identifying the location for placement of an in-ditch engineered structure

The major problem in choosing the correct mitigation option and implementing an efficient measure to reduce/eliminate excess nutrients in drainage water is identifying where nutrients are being stored and released in the ditch systems (EC, 2014). Therefore, before considering mitigation of nutrient loads in the ditch, it is important to initially characterise the ditch network and demarcate hotspots of nutrient losses and natural attenuation areas in the agricultural landscape. Penn et al. (2007) pointed out that demarcating hotspots of P losses and natural attenuation areas allows for a more accurate siting of engineered structures with P sorbing material *(*PSM) to control dissolved fractions in open ditches or at the end of tile drainage. In addition, the natural attenuation function of ditches is also controlled by connectivity to the source of pollution, such as a farm yard (Figure 2.21), which is associated with greatest risk of P loss to ditches (Moloney et al., 2020). A practical remediation strategy would then be to reduce this connectivity or to reduce the volume of contaminated discharges into the ditch (Dollinger et al., 2015).

The soil-subsoil-sediment chemistry along the ditch network and between the source and the ditch (Mellander et al., 2016) should be thoroughly examined. This would then define if the sediments in the ditch are acting as a pollution sink (retaining contaminants from the drainage water) or a pollution source (releasing contaminants to the drainage water) (Smith et al., 2004).

Figure 2.21. *Farm yard run-off parallel to an open ditch network. Johnstown Castle Dairy Farm, Co. Wexford.*

In general, characterization of the ditch network and establishing the connectivity between the ditch and the source of pollution allow for the utilization of the unique features of the overall drainage network to disconnect nutrient transfers to surface water bodies (Moloney et al., 2020). This is done by placing engineered structures with appropriate carbon-based or sorbing materials more strategically at breakthrough or delivery points to intercept nutrients and protect water quality. Additionally, it is important to consider the existing surplus of nutrients in the soil (Hamilton, 2012), which may impair water quality and therefore create a time lag between initiation of implementing mitigation measures and observing a measurable improvement in the target water body (Van Meter et al., 2016; Fiorellino et al., 2017).

Methodologies such as “sustainable drainage design” or “rural sustainable drainage systems” (Quinn et al., 2014) aim to trap nutrients before they reach delivery points (Thomas et al., 2016), which would ultimately enable on-farm management and in-ditch decisions to prevent further losses and improve water quality. Ideally, a drainage network in a sustainable intensification system should not only provide opportunities for nutrient use efficiency and increased crop production, but will also have positive financial and environmental impacts by offering opportunities for implementing cost efficient mitigation measures (Pretty et al., 2018).

Chapter 3

Farm characterisation and identification of nutrient losses

3.1 Overview

This chapter investigates nutrient losses in the installed drainage network at Johnstown Castle Dairy Farm. The data generated from this chapter were used in the selection of media for use in the laboratory column experiments to mitigate mixed contaminants on this site (Chapters 4 and 5).

3.2. Agriculture in Co. Wexford, South East Ireland

Wexford County, located in South East (SE) Ireland, is considered to be one the most intensive farming areas of the country. Wexford has 4,426 farms, of which a significant proportion are dairy (Teagasc, 2015). The dairy sector is a significant enterprise (1193 suppliers) of the county, while specialist beef farms is the dominant agricultural system (Teagasc, 2015). According to the Census of Agriculture in 2010, the average farm size in Wexford increased from 18 to 41 ha from 1915 to 2010 (a 128 % increase) (CSO, 2019), which is higher than the national average of 32.7 ha (Teagasc, 2015).

Monitoring and remediating the drainage water leaving Johnstown Castle Dairy Farm (located in Co. Wexford) is of great importance as it enters the River Kildavin (Slaney River Lower Part, Wexford) and contributes to its water quality. The Slaney River is categorized as *low-quality* (less than good status) (EPA, 2012), and is considered to be mainly eutrophic (EPA, 2016a). The potential cause of the pollution is believed to be diffuse agricultural pollution.

In addition, the geology and the soil-type (predominantly brown earth, gley, and brown podzolics) of Wexford makes it susceptible to contamination (EPA, 2016b). The DIN concentrations in the Lower and Upper Slaney Estuary were some of the highest among water bodies in Ireland (EPA, 2017). However, nationally the overall trend between 2007-2016 showed some reduction of the N load, but the total P load has remained unchanged (EPA, 2018) (Figure 3.1 and Figure 3.2).

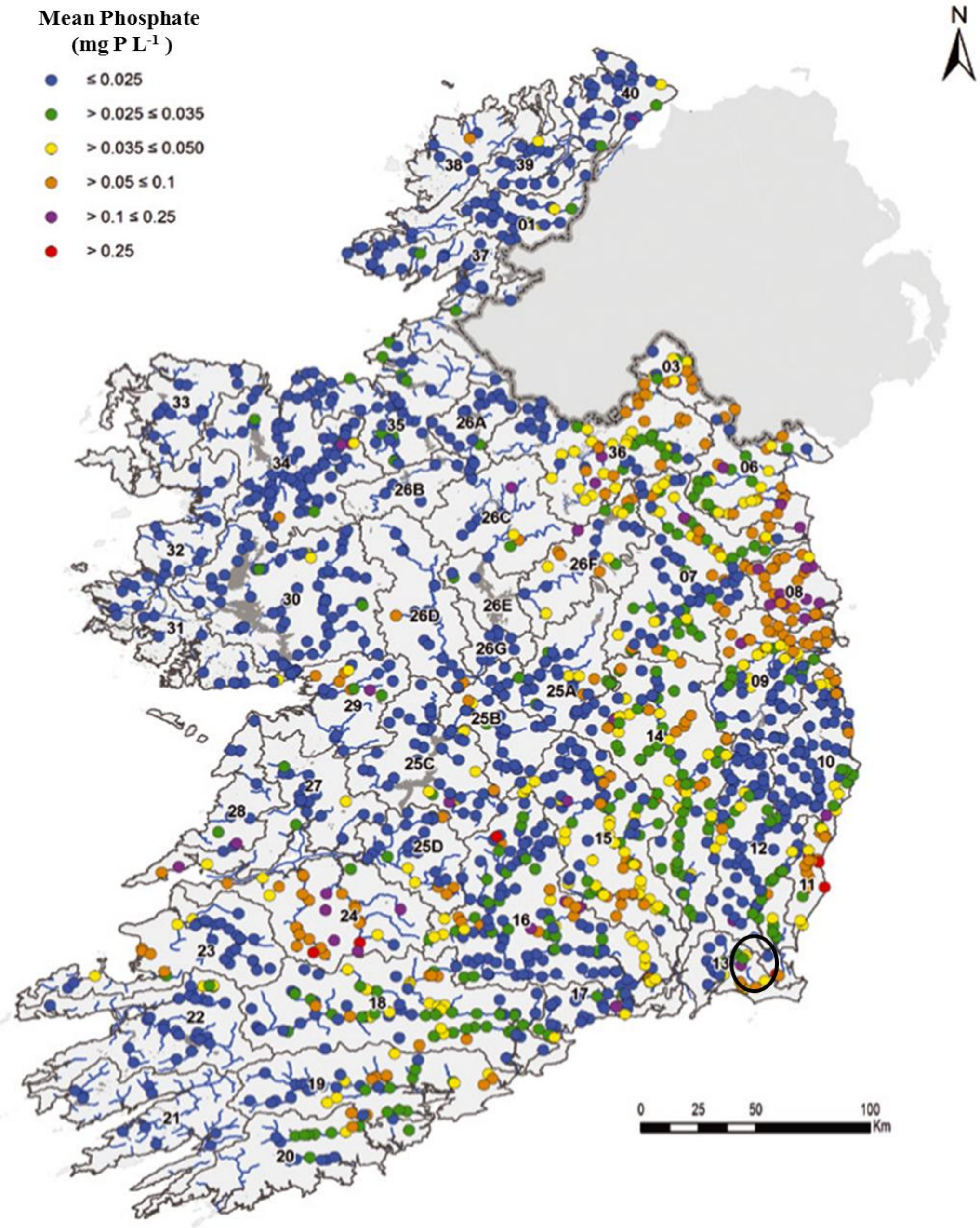


Figure 3.1. *Mean phosphate concentrations (mg L^{-1}) in rivers across Ireland during the period of 2014-2016. Adapted from EPA (2018); Black circle: Lower Slaney River in Co. Wexford, SE Ireland.*

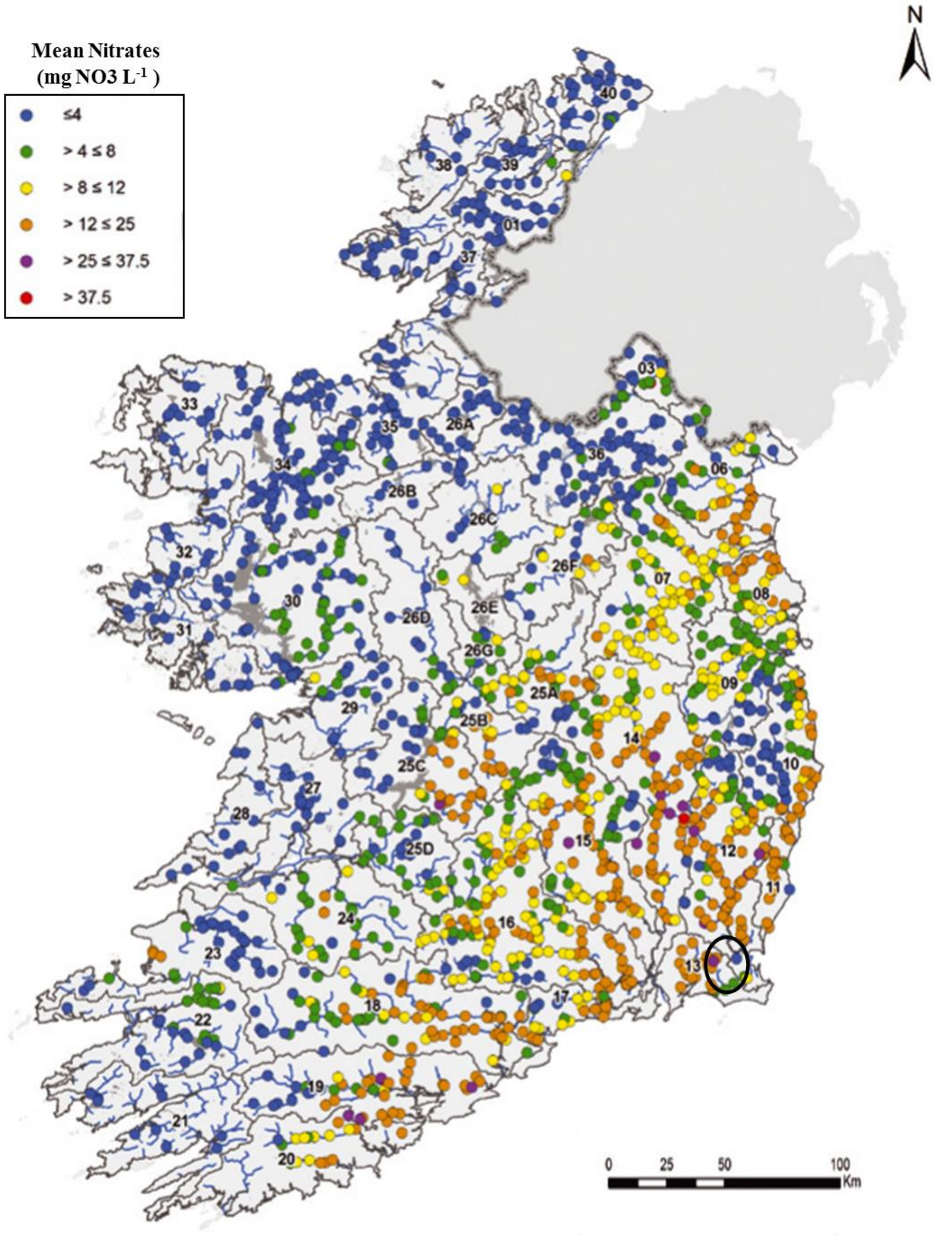


Figure 3.2. *Mean nitrate concentrations (mg L^{-1}) in rivers across Ireland during the period of 2014-2016. Adapted from EPA (2018); Black circle: Lower Slaney River in Co. Wexford, SE Ireland.*

Meanwhile, soil fertility remains a limiting factor as about 60 % of Irish soils are below optimum soil fertility levels (Teagasc, 2019), with only 11 % of all dairy farms surveyed between 2007-2013 perceived as being optimum for soil test P (Teagasc, 2015). In general, the high levels of P losses to water bodies in Wexford is associated with an increase in chemical P fertiliser inputs, but also P application history is a major component in terms of P storage in the subsoil (Fenton et al., 2017). Therefore, measures such as nutrient management planning are important to limit maximum farm P applications to crop requirements, stocking rate and soil test P levels (Teagasc, 2019).

3.2. Site description

The field site used in the present work is at Johnstown Castle, Co. Wexford, which contains an intensive dairy farm (190.4 ha) (52°17‘52” N and 06°29’48” W) operating at 3.1 Livestock Units per hectare (LU ha^{-1}) and having a grazing season length of 243 days. The elevation ranges from 34 to 120 m above ordnance datum (AOD) and the area has a cool maritime climate with an annual temperature of 9.6 ^{o}C. Figure 3.3 presents the satellite imagery of the Johnstown Castle farms overlaid with the drainage status map, drainage system (surface and subsurface) and existing sampling points.

An artificial random drainage system has been installed on poorly and imperfectly drained soil within the dairy and beef farms and in-field drains discharge to the ditch network. The entire drainage network is 10.25 km and comprises 1.01 km of open drains and 9.24 km of subsurface drains installed at approximately 1.2-2.9 m depth below the ground surface. The main ditch within the farm runs parallel to a farmyard and is 850 m in length. It consists of a 500 m primary open ditch network with some sections being fully cased and connected to different parts of the network.

There is an in situ synoptic meteorological station (Figure 3.3) on the dairy farm which records daily rainfall, wind speed and hours of sunshine. The 30-year mean annual rainfall (1981-2011) on site is approximately 1040 mm with a maximum intensity between September and November. Approximately half of the precipitation is drained at different rates into well to poorly drained soils on site.

Due to glaciated origins of the area, soil and associated drainage classes are heterogeneous (saturated hydraulic conductivity ranges from 0.0001 to 0.029 m d^{-1}; Jahangir et al., 2013). This grassland area consists of poorly and imperfectly drained gleys to well drained silty clay loam (topsoil) and dense gravels intermixed with clay at 0.6-10.0 m subsoil geology. The bedrock geology is ordovician sediments of sandstone and shales at 10 m below ground level (bgl) (Jahangir et al., 2013).

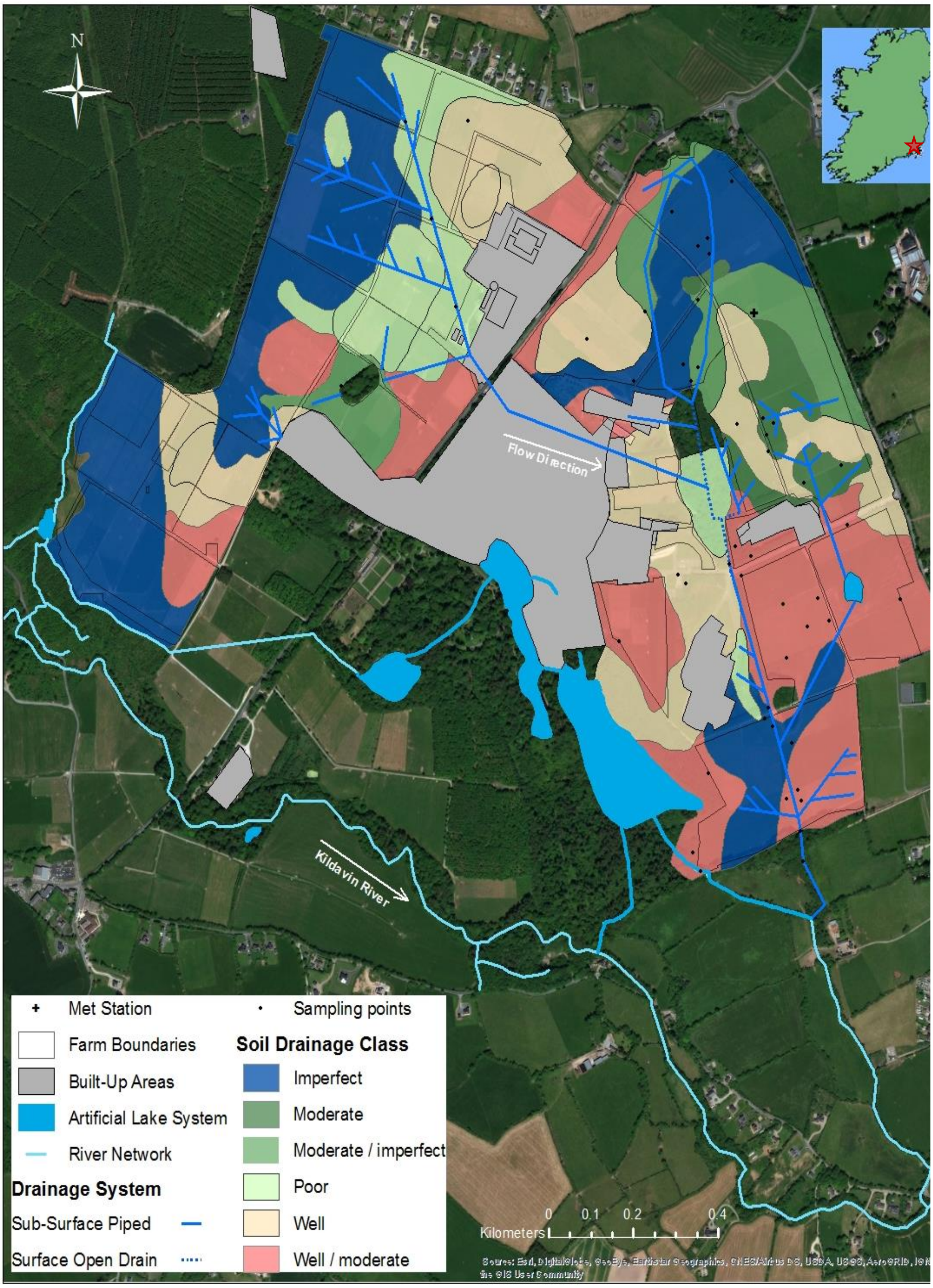


Figure 3.3. *The soil drainage class, artificial lake system, river network and drainage system of Johnstown Castle Beef and Dairy Farm.*

The N inputs on Johnstown Castle farm arise from urea and CAN and the central area of the dairy farm receives DSW. The total N balance during the period of 2011-2015 is approximately 360 kg N ha^{-1} (Clagnan et al., 2019) compared with an average of 223 kg N ha^{-1} (Tracey et al., 2008). The N-surplus is stored in the soil or leached from the system in the absence of NH_3 volatilisation. The P inputs on the farm come from manures and animal feed and 4 %, 10 % and 16 % superphosphate fertiliser. The total amount of P fertiliser used on this site is about 27.5 tons (data for 2018).

3.3. Delineation of Johnstown Castle mini-catchment boundary

In order to study the high and low risk areas of N and P along the surface and subsurface pathways of losses in the field site, a water sampling campaign using multiple sampling points, presented in Figure 3.3, was conducted in June-July 2017. This fieldwork, in addition to a 12-year water quality (WQ) dataset, contributed to data used in Clagnan et al. (2019), which showed that water purification across the field varied. The study also showed that an incomplete denitrification in poorly drained sites transferred NO_3^- to NH_4^+ (Clagnan et al., 2019). The present study continued this work, but from a P perspective.

To develop a necessary secondary dataset for delineation of a mini-catchment and to detect areas with natural attenuation capacity along the existing drains and streams, the existing 12-year WQ data (of groundwater and surface water sampling points), along with previous studies examining the soil type and nutrient concentrations in groundwater and drains, were collated. The quarterly long-term water quality data indicated elevated N concentration in the open ditches contributing to surface water quality in form of ammonium (ranging from 0.006 to 3.94 mg L^{-1} NH_4-N) and sporadic DRP sampling with concentrations ranging from 0.004 to 2.97 mg L^{-1}.

All primary data of the study site and the contour map of the area were incorporated in the Geographic Information System (GIS) to delineate a boundary for a mini-catchment with an area of 189.0 ha. Finally, new sampling points in the ditch were selected to provide higher resolution data to study the nutrient losses in the open ditch and demarcating hotspots with high nutrient concentrations (area lacking natural attenuation) (Figure 3.4 and Chapter 6). Eight sampling points (Locations A, B, C, D, E, F, G, H in Figure 3.4) along the ditch network were selected. Site H represents the sampling point at the end of the catchment and is excluded in the P investigation in Chapter 6.

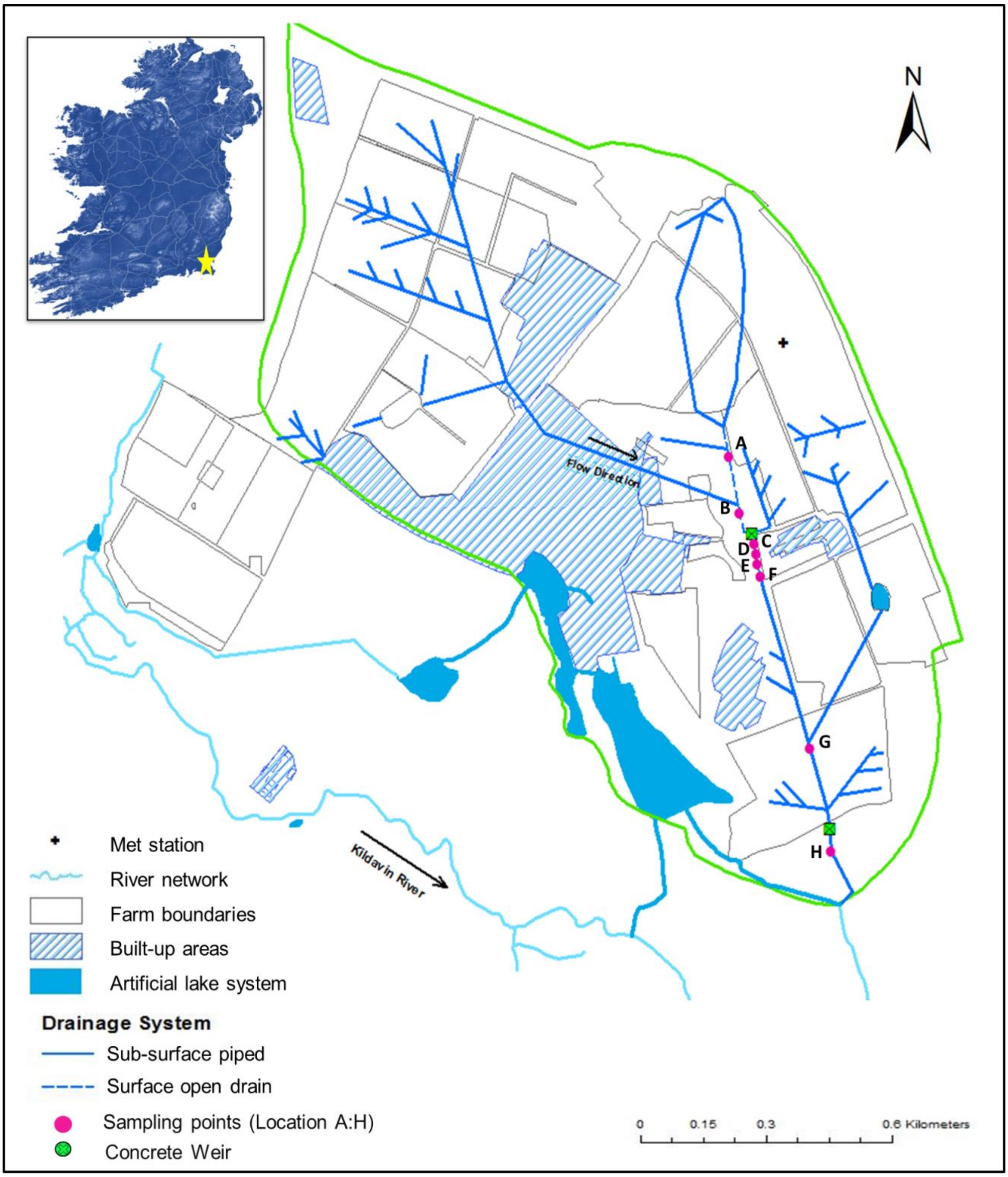


Figure 3.4. *The mini-catchment boundary, drainage system, concrete weirs and new sampling points along the open ditch network of Johnstown Castle Dairy Farm, Co. Wexford.*

3.4. Water sampling and analysis

In order to locate step changes in nutrient concentrations along the ditch network (Figure 3.5), grab samples were collected regularly from the surface water and the open ditch from Jan 2017 to July 2018 (n=100) (presented in Chapter 6). In addition, bimonthly water samples were collected from groundwater boreholes and piezometers.

Figure 3.5. *Sampling of surface water (left) and groundwater (right).*

Initially, water at each sampling location was pumped to a flow cell connected to an in situ multiparameter probe (Fort Collins; Multi-parameter; Troll 9500, USA) to measure temperature, electrical conductivity (EC), rugged dissolved oxygen (RDO) and pH under steady-state conditions (Figure 3.6). Then, duplicate 50 ml water samples were collected in screw top tubes and one sample was filtered in the field using 0.45 µm pore size filters. The samples were then transferred to a water laboratory on the same day. The filtered samples were analysed for mineral N (NH_4-N, NO_2-N, total oxidised nitrogen (TON)) and DRP calorimetrically using a nutrient analyser (Aquachem600 Labmedics Analytics, Thermo Clinical Labsystems, Finland). The unfiltered sample were analysed for total phosphorus (TP) (with acid persulphate digestion) (Askew and Smith, 2005). Nitrate concentration was calculated by subtracting NO_2-N from TON.

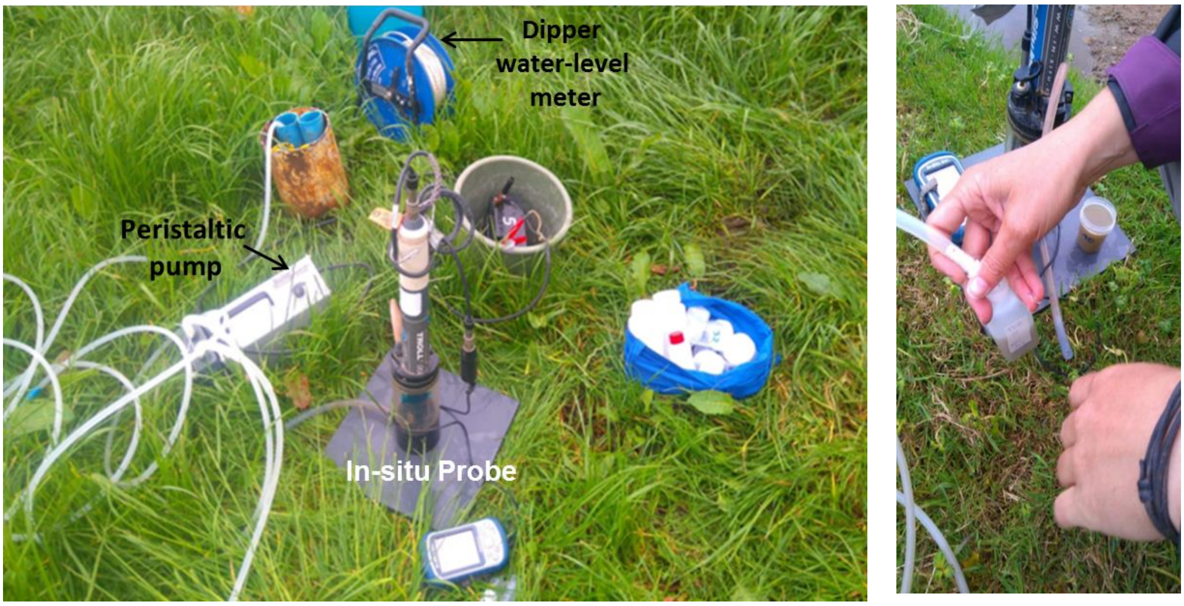


***Figure 3.6**. Nutrient and biogeochemical water sampling.*

In order to monitor the flow in the ditch network, two Corbett-type weirs were installed in the middle of the open ditch and at the end of the mini-catchment (Figure 3.4 and 3.7). The flow was calculated using the following equation:

$$Q = 0.0452 * (WL^{2.2472}) \qquad \text{[Eqn. 3.1]}$$

where Q is the discharge (L s^{-1}); and WL is the water level (cm) at the throat of the weir.

In order to measure the water level passing through the weirs, a stilling well was installed at the inlet of each weir. Water level data loggers (“TD-Divers”; van Essen Instruments), were deployed inside each well (Figure 3.7) so that the diver’s pressure sensor was at the same level as the bottom of the weir. The divers measured the height of the water column by measuring the water pressure using the built-in pressure sensor. The height above the diver’s pressure sensor was calculated using the following equation:

$$WL = 98.6.65 \, \frac{P_{diver} - P_{baro}}{\rho.g} \qquad \text{[Eqn. 3.2]}$$

where P_{diver} is the pressure in the diver (cm H_2O), P_{baro} is atmospheric pressure measured by a Baro-Diver (cm H_2O), g is the acceleration due to gravity (9.81 m s^{-2}), and ρ is the density of water (1000 kg m^{-3}). The Baro-Diver installed in the catchment was used for accurate barometric compensation and the high resolution (10-minute) data on temperature and pressure stored in divers were downloaded using Diver-Office Software.

The water flow data collected from July 2017 - July 2018 were consistent at both locations showing a minimum and maximum flow of 0.85- 23 L sec^{-1}. These data were used to develop the column study design (Chapter 5) and to calculate the nutrient load (Chapter 6).

The drainage water flow data plotted against time is presented in Appendix B.

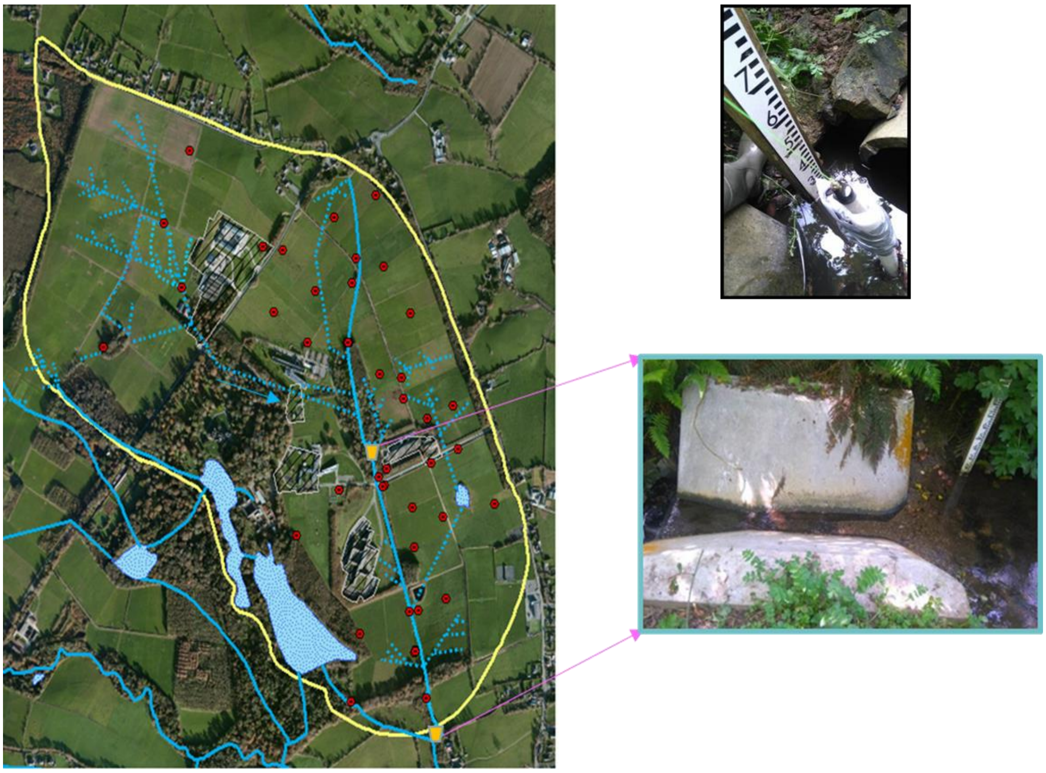


Figure 3.7. *Two Corbett-type weirs installed in the middle and end of the ditch network (left), and deploying divers in stilling wells at the inlet of the weirs to collect water-flow data (right).*

Table 3.1. *Summary statistics of N and P concentrations and biogeochemical data for open ditch network during January 2017 - July 2018.*

Sampling Location	**Sample size**	**NH_4-N**	**NO_3-N**	**DRP**	**TP**	**pH**	**Temp.**	**EC**	**RDO**
		mg L^{-1}					˚C	µS cm^{-}	mg L^{-1}
A	10								
Max		1.44	4.21	0.12	0.22	8.44	12.99	471.1	10.67
Min		0	0.39	0.02	0.01	6.86	8.06	251.9	9.12
Mean		0.30	3.17	0.04	0.08	7.26	9.873	364.13	9.99
Median		0.03	3.59	0.03	0.05				
B	10								
Max		0.28	5.24	0.08	0.11	7.27	10.07	388.8	9.64
Min		0	3.25	0.008	0.00	5.95	9.03	366.9	8.93
Mean		0.053	4.33	0.03	0.05	6.82	9.3	375.3	9.24
Median		0.016	4.43	0.01	0.05				
C	18								
Max		0.68	4.74	0.114	0.33	8.2	12.58	426.7	12.56
Min		0	1.94	0.02	0.02	6.97	7.92	236.7	8.21
Mean		0.099	3.73	0.05	0.08	7.23	9.625	348.5	10.18
Median		0.014	3.8	0.04	0.05				
D	10								
Max		6.38	5.284	0.61	2.29	7.56	12.6	423.8	10.75
Min		0.08	0	0.04	0.03	6.9	9.16	342	8.98
Mean		2.65	1.771	0.22	0.53	7.183	11.31	392.9	9.86
Median		2.868	0.856	0.12	0.15				
E	16								
Max		18.77	17.98	2.97	4.89	8.6	14.93	720	11.7
Min		0	1.42	0.008	0.01	6.34	7.99	252	8.89
Mean		2.24	5.09	0.27	0.53	7.32	11.14	466.1	10.28
Median		0.12	4	0.03	0.08				
F	18								
Max		1.55	9.89	1.25	1.32	8.6	14.88	560.8	10.86
Min		0	0	0.02	0.03	7.05	9.15	346.2	9.98
Mean		0.196	1.48	0.43	0.53	7.56	11.58	423.2	10.56
Median		0.06	3.181	0.14	0.16				
G	18								
Max		18.47	4.32	2.75	4.29	9.24	12.61	632.1	11.9
Min		0	0	0.004	0.01	6.98	8.22	233.2	8.09
Mean		1.3	3.11	0.22	0.24	7.90	9.51	385.06	10.102
Median		0.03	3.9	0.06	0.10				
H: End of catchment	18								
Max		10.38	4.41	2.11	1.54	9.08	13.08	537.4	12.04
Min		0	0	0	0.01	6.57	8.42	372.4	0.00
Mean		0.7	3.5	0.201	0.2	7.55	10.75	455.0	6.92
Median		0.1	3.7	0.0875	0.11				

The high-resolution water sampling (Table 3.1) indicated high concentrations of NH_4-N and DRP leaving the catchment that discharges directly into the adjacent river. Concentration ranged from 0-18.77 mg NH_4-N L^{-1} and 0-2.97 mg DRP L^{-1}. The data exceeded the MAC of 0.23 mg L^{-1} of NH_4-N for surface drinking water and 0.035 mg L^{-1} of DRP for surface water (EU, 2014c).

3.5. Implications of the findings

The results indicated that no attenuation capacity was offered by the ditch system in this study site. This necessitates the implementation of an engineered measure that would mitigate the nutrients and clean the water before it leaves the catchment. The most efficient measure for this system would be the installation of an in-ditch engineered structure filled with adsorptive media in parts of the ditch that has low or no natural attenuation capacity for NH_4-N and DRP.

3.6. Summary

This chapter investigates the nutrient losses on Johnstown Castle Dairy Farm. The results showed elevated concentrations of N (as NH_4-N) and DRP leaving the catchment.

Chapter 4 investigates the selection of an appropriate mixture of media that can mitigate both NH_4-N and DRP in Johnstown Castle, or any other type of nutrient pollution that may occur in drainage waters worldwide.

Chapter 4

Developing and validating a decision support tool (DST) for media selection to mitigate nutrients in drainage waters

4.1. Overview

In this chapter, a DST was developed to select locally sourced single medium/mixed media to attenuate mixed nutrient contamination. This tool provides a rapid, easily modifiable screening of many media-based treatments (75 media). The DST was tested in various case studies in Ireland, Belgium and USA, and was validated through several SWOT (Strength, Weakness, Opportunity, Threat) workshops.

This study has been published in Ecological Engineering-X:

Ezzati, G., Healy, M., Christinson, L., Feyereisen, G., Daly, K., Thornton, S., 2019. Developing and validating an adaptable decision support tool (FarMit) for selection of locally sourced media for dual mitigation of nutrients in drainage water from intensively farmed landscapes. Ecological Engineering-X. https://doi.org/10.1016/J.ECOENA.2019.100010

4.2. Introduction

Decades of research have shown that aquatic environments are under pressure due to population growth, waste generation (FAO, 2011; Jhansi et al., 2013), excessive loading of nutrients (Billen et al., 2013; Erisman et al., 2011; Addy et al., 2016; Fenton et al., 2017), pesticides (Gramlich et al., 2018), and sediment inputs (Sherriff et al., 2015). Nutrients such as N_r (NO_3-N and NH_4-N) and DRP in drainage waters from intensively farmed agricultural sites have contributed significantly to impairment of water quality (Daly et al., 2017; Fenton et al., 2017; Rosen and Christianson, 2017; Clagnan et al., 2018 a,b).

The interception of single pollutants along surface or near surface drainage loss pathways using in situ engineered structures filled with biological (e.g. woodchip in a denitrifying bioreactor) or reactive (e.g. steel slag in a P-sorbing structure) media is receiving increasing research attention (e.g. Penn et al., 2017). The removal rates of N and P using these media can be high. For example, Hassanpour et al. (2017) measured 50 % NO_3^- removal from drainage water using woodchip media in a denitrifying bioreactor over a 3-year period and Okello (2016) reported a 74 % removal of DRP in drainage water using iron-coated sand in a reactive P-sorbing filter. However, the simultaneous removal of these pollutants in drainage water using dual media has mostly been examined at laboratory-scale (Healy et al., 2012, 2014; Ibrahim et al. 2015; Hua et al., 2016; Christianson et al., 2017; Fenton et al., 2017; Stroek et al., 2017). In addition, the transferability of these results to other locations due to the availability, suitability or delivered cost of media is often overlooked. An example here is the use of iron ochre to sorb P in drainage water; the availability of the ochre may not be a problem, but the form of ochre may be contaminated with heavy metals and its use may therefore be prohibitive (Fenton et al., 2009a).

There is a vast catalogue of media in the literature that are reported to mitigate pollutants leaving farms. However, there is currently no DST available to select a suitable medium, or a combination of media, for the targeted removal of NO_3^-, NH_4^+ and DRP, considered separately or together, while also considering factors other than pollutant removal capacity. These factors may include the media lifetime, hydraulic conductivity, the potential for “pollution swapping”, capacity to attenuate other (non-target) contaminants (e.g. pesticides, organic carbon, etc.), and availability and local price of the media.

Decision Support Tools, usually software-based, manipulate data (often obtained through literature review or expert opinion) and recommend management actions through clear decision stages (SIP, 2018). In a review of DSTs for use in agriculture, Rose et al. (2016) found that in the UK 49 % of farmers used some kind of DST to inform decisions whereas all advisors used DSTs, and software versions were the preferred form of DST platform. In terms of selecting media to mitigate drainage water impacts, there is no DST that provides all the relevant information in one platform. Therefore, the objectives of this chapter were to: (1) develop a globally-applicable, user-friendly DST to assist selection of locally sourced media, in order to reduce NO_3^-, NH_4^+ and DRP, as single or mixed pollutants, from drainage water at farm-scale (2) evaluate the effectiveness and practicality of the DST in two phases: (a) applying it in different geographical/farming-practice case studies, and (b) validating the framework through SWOT (strength, weakness, opportunities, and threats) analysis.

To meet these objectives, several steps were implemented to build a platform on which the DST could be developed. These included identifying a number of scenarios for N and P losses from farms and compiling a database of media for mitigation of nutrient losses. Figure 4.1 illustrates the steps taken in developing the FarMit (**Far**m **Mi**tigation **T**ool) DST.

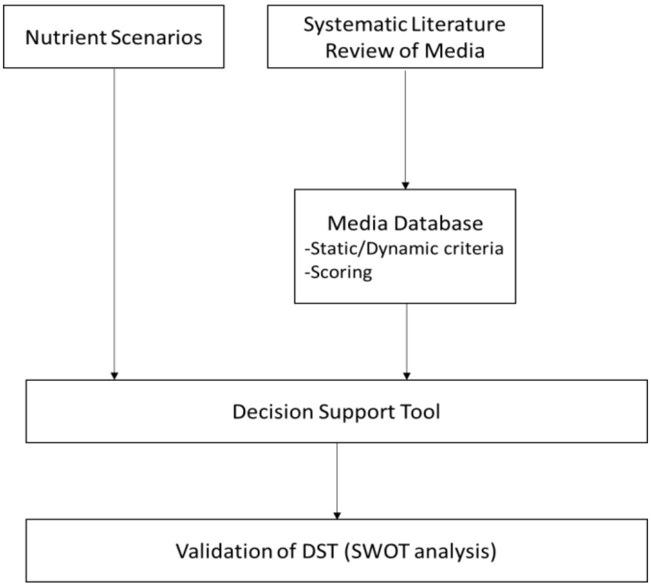


Figure 4.1. *Flowchart for the development of FarMit DST*

4.3. Materials and methods

4.3.1. Nutrient scenarios

Testing water samples for nutrients collected at the drainage discharge point can provide a spatial and temporal profile of single or mixed pollutants at a given site. Typically, N_r losses from land drainage systems may occur as NO_3-N (Nangia et al., 2010) or NH_4-N (Clagnan, 2017), depending on various physical and biogeochemical factors that control the transformation of N_r (Rivett et al., 2005; Fenton et al., 2009a; Clagnan et al., 2018a). Phosphorus losses from agricultural land, which are either retained or mobilized, may occur in particulate and dissolved forms (McDowell and

Sharpley, 2001). Based on the complexities of nutrient losses from agricultural land, a conceptual model of different possible diffuse nutrient loss scenarios that may occur at farm-scale was developed.

The FarMit DST is based around identifying materials to treat three nutrient loss scenarios (Figure 4.2).

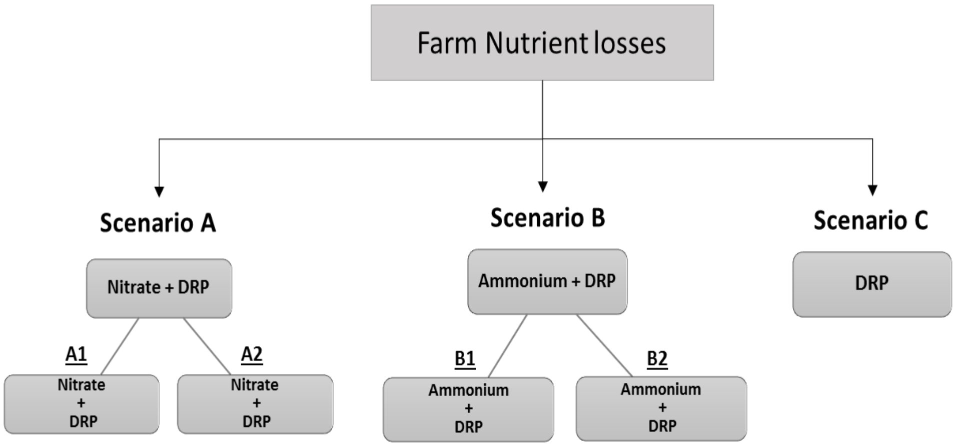


Figure 4.2. *Farm pollution scenarios: A: Farm pollution with leaching of NO_3-N and retention of P, or Farm pollution with leaching of NH_4-N and mobilization of P, B: Farm pollution with leaching of NO_3-N and retention of P, or Farm pollution with leaching of NH_4-N and mobilization of P, C: Farm pollution with DRP mobilization and no leaching of N.*

In Scenario A, mineralised N_r in the soil, in the form of NO_3^-, leaches to shallow pathways along low permeable layers or artificial drainage systems (e.g. Clagnan et al., 2018a,b) or along deeper groundwater pathways (Brouyere et al., 2003). In Scenario B, subsurface conditions, such as limited N_r and oxygen supply, combined with high soil C, may induce transformation of NO_3^- to NH_4^+ (by DNRA). In Scenarios A and B, DRP losses may also occur along surface, near surface, or deeper groundwater pathways. These losses could originate from the soil/subsoil, geological strata, or media used within an engineered bioreactor used to treat water and wastewater. Therefore, site-specific conditions (soil chemistry and drainage composition) or media characteristics may lead to the retention of P losses or the mobilisation of P. Finally, Scenario C represents a farm with only loss of P, where N_r in either form does not exceed a threshold or MAC. This may be due to the high attenuation capacity of the site, with conversion of N_r into gaseous forms (e.g. di-nitrogen or nitrous oxide), isolation from potential sources, or adaptation of perennial crop farming systems (Stanek et al., 2017).

4.3.2. Systematic literature review to form media database

The five steps of a systematic review were followed, as outlined in Khan et al. (2003). The problem to be addressed was specified as follows (Step 1): what media have been used in the literature to attenuate NO_3^-, NH_4^+ and DRP from drainage waters? What is the efficacy of a medium to remove NO_3^-, NH_4^+ and DRP, or other pollutants in drainage waters? What is the hydraulic conductivity of the media? What is the lifetime of the media? What pollution swapping may occur using these media?

Next (Step 2), relevant work within the literature was identified. For this purpose, several keywords were selected to ensure relevancy for the literature search of over 175 media-based water treatment studies published during the last 20 years (150 papers were considered in final review). These included: water/wastewater treatment, water quality, agricultural waste, denitrification, denitrifying bioreactor, nutrient pollution, leaching, nutrient removal, adsorption, drainage, nitrate, phosphorus, and ammonium. The database search engines used were Google Scholar, Agricultural Research Database (AGRICOLA), International System for Agricultural Science and Technology (AGRIS), Web of Science, Scopus, American Society of Civil Engineering (ASCE), and the National Agricultural Library. To assess the quality of these relevant studies (Step 3), the following criteria were imposed: use of standard methods, and experimental design including replication and data interpretation. This enabled a database of 75 distinct media types to be assembled. Data were then synthesised (Step 4) in tables and grouped as follows: wood-based (Table 4.1), vegetation/phytoremediation (Table 4.2) and inorganic materials (Table 4.3).

Table 4.1. *Wood-based nutrient remediation applications.*

Positive properties/ Advantages	Disadvantages	Example of amendments to overcome disadvantages	Example of Positive consequence of amendments	Example of Negative consequence of amendments	Other References
Low cost, easy handling, low maintenance, good capacity for turbid water, long life time, surface roughness, high porosity and permeability, Effective adsorbent of Nitrate, Suspended solids (TSS), Chemical oxygen demand (COD)	Low C availability limit the denitrification rate (Cameron and Schipper, 2010; Warneke et al., 2011) Removal efficiency depends on type of wood (Grace et al., 2016) Little dissolved reactive phosphorus (DRP) removal capacity (Fenton et al., 2016) Better performance at lower turbidity (Choudhury et al., 2016)	a) Addition of a soluble C source (such as methanol or glycerine) to increase microbial-available C (Hartz et al., 2017) ; Application of acetate (NCERA, 2017) b) Addition of Biochar to enhance microbial activity (Lassiter & Easton, 2013) c) Coupling with solid settling tank (Chudhury et al., 2016) d) Weathering woodchips (Hoover et al., 2016) e) Pre-installation washing of woodchip (Ibrahim et al., 2015) f) Biochar amendments (Lassiter and Easton, 2013; Pluer et al., 2016) g) Mixture of woodchips with zeolite and pea gravel (Ibrahim et al., 2015) h)Woodchip with corn cob (Feyereisen et al., 2016) i) Ammendment with water treatment residuals (Kim et al., 2003; Razali et al., 2007; Zoski et al., 2013; Gottschall et al., 2016) j) Woodchip lined with 40 mm heavy duty agricultural liner (Wagner et al., 2015)	a) 1.4:1 (C applied: N denitrified, on a mass basis) for methanol and 2.0:1 for glycerine : Complete denitrification and reduction of bioreactor size ; increase in Nitrate-N reduction from 38 % to 98 % b) Pottential increase in denitrification rate and P adosrption (up to 75 %) while decreasing nitrogen leaching as a result of enhancig microbial activity c) Increase of TP removal to 71 % d)Better performance and higher reduction in initial C losses e) Lower NO_3^- production f) Pottential increase in denitrification rate and P adosrption (up to 75%) while decreasing nitrogen leaching as a result of enhancig microbial activity (Lassiter & Easton, 2013) g) First successful implementation of PRI for simultaneous nutrient remediation h) Lower NO_x production (0.9 % against 9.7 % with woodchip only) i) Significant higher removal rate of DRP and Nitrate	b) Biochar addition reduced reduction by 10% (NCERA, 2017) d) Higher NH_4^+, DRP and dissolved organic carbon losses e) No significant P removal f) No significant increase in P removal (Pluer et al., 2016); Depending on retention time and type of biochar (Roser, 2016) g) Pollution swapping; Short longevity of pea gravel depending on wastewater strength i) Particle size (Kim et al., 2003) and pH (Kim et al., 2003; Razali et al., 2007); Increase in total coliform; Life time could be an issue depending on flow strength and retention time, hydraulagic condition, land management (Zoski et al., 2013); No significant change in Ammonium removal efficiency (Gottschal et al., 2016) j) Unsatisfactory pesticide removal efficiency	Van Driel et al., 2006; Saliling et al., 2007; Greenan et al., 2009; Chun et al., 2009a,b; Cameron & Schipper, 2010; Schipper et al., 2010a,b; Moorman et al., 2010; Robertson, 2010; Christianson et al., 2010a,b, 2011, 2012a,b, 2013, 2016; Ruane et al., 2011; Lassiter & Easton, 2013; Dassanayake et al., 2015; Feyereisen et al., 2015a,b; Ahnen et al., 2016; Brunn et al., 2016; David et al., 2016; Fenton et al., 2016; Ghane et al., 2016; Hoover et al., 2016; Lepine et al., 2016; Sharrer et al., 2016

Table 4.2. *Vegetation-based nutrient remediation/Phytoremediation (dead fibrous material, carbon-based processed biomass).*

Medium	**Proven removal potential**			**Positive properties/ Advantages**	**Disadvantages**	**Limitations**	**Reference**
	NO_3-N	**NH_4-N**	**DRP**				
Vetiver grass	×		×	Over 80 % nutrient removal efficiency (Ash & Truong, 2004; Troung and Hart ,2001; Bedewi,2010; Mayorca, 2007; Donaldson and Grimshaw, 2013) Good Ammonium, BOD5, SS and coliform removal		Plant Uptake, lifetime , geographical limitation due to various types of plants according to climate condition, vegetation cover, age of decomposition, practicality	Troung et al., 2000; Troung and Hart, 2001; Ash & Truong, 2004; Mayorca, 2007; Bonsong and Chansiri, 2008; Bedewi, 2010; Donaldson and Grimshaw, 2013; Oku et al., 2016
Rye grass	×				Poor P treatment		Zheli et al., 2012; Chen et al., 2013
Peat , Sphangum Peat Cocopeat	×	×		Maintenance-free operation, minimum consumption of non-renewable energy, and the possibility of using treated effluent for spray irrigation (Patterson, 2001) Very good NH_4^+, BOD_5 and TSS removal efficiency and prolonged lifetime	Absence of completely anaerobic zone Insignificant P removal potential (Danley-Thomson et al., 2015)		Patterson, 2001; Patterson, 2004; Perez et al., 2005; Headley, 2006; Kalmykova et al., 2008; Batista et al., 2009; Christianson et al., 2012; Ezzati and Asghari, 2015; Danley-Thomson et al., 2015a,b; Jin et al., 2017
Yard waste Green waste Waste cellulose (leaf compost, wood mulch, saw dust)	×	×		~ ~ No need for replacement for up to 10 years (Robertson et al., 2000)	Inefficient for long-term operation (Christianson et al., 2012) ~ ~		Robertson et al., 2000; Cameron & Schipper, 2010; Christianson et al., 2012
Compost	×			High removal capacity shortly after operation Complete NO_3^- removal within first week (Trois et al., 2010)	Unsustainable due to large amount of N leaching		Gilbert et al., 2008; Trois et al., 2010
Pine bark	×				Releases large amounts of phenolic compounds and hydroxylated benzene rings Pathogens like Enterobacter and Pantoea aglomerans prevents the applicability of the pine bark in full-scale operations		Trois et al., 2010

Walnut , almond, coconut shell charchoal			×	Potential for cation/metal removal	Time and temperature of heating, time limited (Kazemipour et al., 2008)	Kazemipour et al., 2008; Ahsan et al., 2011; Agarwal et al., 2011; Bhatnagar et al., 2010; Penn et al., 2011
Corn stalks Corn cob	×			Good Nitrate Removal	Additional carbon release (Feyereisen et al., 2016)	Greenan et al., 2006; Cameron and Shipper, 2010; Feyereisen et al., 2015a, 2016
Barley straw	×	×				Feyereisen et al., 2015a; Healy et al., 2014
Cardboard	×				High CO_2 emission Poor P removal	Healy et al., 2012, 2014
Wheat straw	×			High NO_3^- removal	Need frequent replacement (Soares & Abeliovich, 1998)	Sailing et al., 2007; Cameron and Schipper, 2010
Rice husk			×	Excellent metal removal capacity		Daifullah et al., 2003; Ahmaruzzaman and Gupta, 2011
Tea/Coffee waste				Potential for adsorption of cationic compounds	Particle concentration effect on adsorption (Djati Utomo & Hunter, 2010)	Djati Utomo and Hunter, 2010; Wang et al., 2014
Fly ash			×			Li et al., 2006; We et al., 2006; Alinnor, 2007; Nascimento et al., 2009
Bottom ash		×	×	Significant P removal		Lin & Yang, 2002; Grace et al., 2015
Biochar	×	×	×		Adsorption capacity depends on biochar production condition, type of biochar, water characteristics, equilibrium, etc	Ezzati and Asghari, 2015; Dalahmed, 2016; Pluer et al., 2016
Coal Charcoal-bio	×	×	×	Relative adsorption capacity for all nutrients		Ahsan et al., 2001
Granular activated carbon	×					Grace et al., 2015
Raw Brown Coal		×		Better removal at higher concentration and higher pH		Nazari et al., 2017

Table 4.3. *Inorganic materials for nutrient remediation.*

Medium	**Removal Potential**			**Positive properties/ Advantages**	**Disadvantages/ Limitation**	**Example of amendments to overcome disadvantages**	**Example of Positive consequence of amendments**	**Reference**
	NO_3-N	**NH_4-N**	**DRP**					
Aluminium-based water treatment sludge (AL-WTR)			×	Constantly good P removal efficiency Potential for applying as dairy waste amendment for mitigation of nutrient losses in surface runoff (Healy et al., 2015b; Murnane et al., 2015)	Metal leaching (Grace et al., 2016)			Kim et al., 2003; Yang et al., 2006; Razali et al., 2007; Penn et al., 2007; Wendling et al., 2013; Zoskiet al., 2013; Zhao et al., 2007; Malecki-Brown et al., 2009
Crushed concrete			×	Very good P removal and good metal capacity	Metal leaching Not effective as stand-alone filter (Berg et al., 2005)			Ahsan et al., 2001; Rahman et al., 2004; Colman et al., 2005; Berg et al., 2005; Egemose et al., 2012; Grace et al., 2015
Bayer residue /Red mud			×	Good P and metal removal	Leaching of contaminants thus pre-storage treatment is needed Liu et al., 2011)			Hua et al., 2014; Grace et al., 2015; Herron et al., 2016; Chen et al., 2016 ; Lie et al., 2011
Granulated blast furnace slag			×	Potential for metal adsorptions				Grace et al., 2015
Metal mine ochre			×	High P adsorption				Fenton et al., 2009
Acid mine drainage residual			×	99 % of P, zinc (Zn), and Cu	Clogging			Penn et al., 2007
Steel slag	×		×	Capturing over 54 % of P load	Adsorption highly depends on flow rate, , particle size and retention time			Penn et al., 2011, 2012
Furnace slag		×	×					Sanford & Larson, 2016; Grace et al., 2015

Natural zeolites	×	×	×	Very good removal of NH_4^+				Widiastuti et al., 2011; Bhatnagar and Sillanpaa, 2011; Grace et al., 2015
Limestone			×	Good metal removal capacity	Average TSS and BOD_5 removal capacity Contact time (Siedek, 2010) Size of filter	Combination of limestone and granular activated carbon (Kanawade, 2016) Smaller filter covered with biofilm (Maung, 2006)	Double Nitrate removal (58 %) Higher turbidity, suspended solids, and coliform bacteria removal rate	Ahsan et al., 2001; Siedek, 20110
Crushed glass	×	×		Over 90 % BOD_5, TSS removal and around 80% oil and grease level reduction	Higher value usage such as recycling			Aqua Test, Inc. & Stuth Co., Inc., 1997; Healy et al., 2010
Recycled shredded-tire chips	×		×	Over 90% removal of BOD_5, Escherichia coli and fat-oil-grease reduction of 65 % TP	Intermediate Nitrate removal Higher value usage such as recycling levy			Garcia-Perez et al., 2016)
Sand	×	×	×	Complete nitrification, almost complete BOD_5 and TSS reduction 80 % Oil level reduction	Sand and soil characteristics are linked to geological processes thus the mineral content of them is a vital factor in defining removal capacity. Permeability against water flow: Possible surface clogging (Rodgers et al., 2004)			CWC, 1997; Gill et al., 2001; Healy et al., 2007; Healy et al, 2011
Natural soil (top soil)		×	×	Excellent removal of organic carbon, TN, and bacteria Very good P removal capacity				Healy et al., 2010, Sanford and Larson, 2016
Natural rock phosphate (Apatite)			×	Very good P removal				Troesch et al., 2016

Natrolite (partially processed mineral zeolite)		×	×			Ahsan et al., 2001; Siedek, 20110
Andesite			×			Ahsan et al., 2001
Saw dust	×					Schipper and Vukovic, 1998; Rodgers et al., 2006
Expanded clay			×			Sanford & Larson, 2016
Flue Gas Desulfurization Gypsum			×			Bryant et al., 2011; 2012
Pea gravel		×	×	Low cost	Particle size Lifetime	Healy et al., 2007; AAFC, 2015; Ibrahim et al., 2016
Pond culture	×		×		Removal rate depends on several limiting factors such as presence of organic substrate, temperature, etc	Erbanová et al., 2012
Synthetic						
Pyrite modified by calcination	×	×				Wang Et al., 2012; Chet et al., 2014
Thermally-modified calcium-rich attapulgite			×			HongbinYin et al., 2017
K1 Kaldness media :plastic MB3 /AMB	×					Saliling et al., 2007; Pfeiffer and Wills, 2011
Synthetic zeolites	×			Cu removal capacity		Peña et al., 2000; Querrol et al., 2002
Laboratory expanded shale			×			Sanford & Larson, 2016
Peat modified with iron(III) hydroxy ions			×	Significant higher removal than raw peat		Robals et al., 2015
Cationic cellulose nanopapers	×					Mautner et al., 2017

Media were then assigned nine criteria with an equal weight (seven static and two dynamic), based on Steps 1-4, and a corresponding scoring system (Step 5 data interpretation) was developed for each criterion. In the static component, these criteria were NO_3-N, NH_4-N and DRP removal capacity (Static Criteria 1-3 in the FarMit DST), removal of other pollutants of concern (Static Criterion 4), hydraulic conductivity (Static Criterion 5), lifetime of media before saturation (Static Criterion 6), and negative externalities such as emission of GHGs, contaminant leaching, or the presence of other pollutants in the final effluent (Static Criterion 7) (Table 4.4). For example, Criterion 1 (% NO_3-N removal) had a score range of -1, 0, 1, 2, 3, 4 corresponding to < 10 %, 10-30 %, 30-50 %, 50-70 %, 70-85 %, and >85 % reduction, respectively. Although many studies report % removal, there are other factors that affect this criterion, such as hydraulic residence time in denitrifying bioreactors and contact time in P-sorbing filters.

In the dynamic component of FarMit, media were scored according to geographically-based criteria such as availability and delivery cost to the treatment site or farm. These criteria are country/region-specific and will change over time. As the amount of media needed will vary depending on the drainage flow and composition at the site of concern, local knowledge is required and only the end-user can obtain the most appropriate ranking of media by assigning scores to these two components. The score ranges for these two final dynamic criteria are presented in Table 4.4.

The nutrient combinations identified (A, B and C) in Figure 4.2 and the scoring system developed as part of Step 5 (Table 4.4) for all criteria (1-9) were combined to form the FarMit DST (Figure 4.1). In order to test the DST, case studies from Ireland, Belgium (Flanders), and the USA (highlighted in grey in Table 4.5) were used.

Table 4.4. *Static (1-7) and Dynamic (8-9) criteria and corresponding scoring ranges*

Criteria	Performance within each criterion	Score
[1] Static scores based on an average performance reported		
1- NO_3-N Removal Rate	NO_3-N concentration reduction > 85%	4
	NO_3-N concentration reduction: 70-85%	3
	NO_3-N concentration reduction: 50-70%	2
	NO_3-N concentration reduction: 30-50%	1
	NO_3-N concentration reduction: 10-30%	0
	NO_3-N concentration reduction < 10% and increase in concentration	-1
2- NH_4 –N Removal Rate	NH_4-N concentration reduction > 85%	4
	NH_4-N concentration reduction: 70-85%	3
	NH_4-N concentration reduction: 50-70%	2
	NH_4-N concentration reduction: 30-50%	1
	NH_4-N concentration reduction: 10-30%	0
	NH_4-N concentration reduction < 10% and increase in concentration	-1
3- DRP Removal Rate	P concentration reduction > 85%	4
	P concentration reduction: 70-85%	3
	P concentration reduction: 50-70%	2
	P concentration reduction: 30-50%	1
	P concentration reduction: 10-30%	0
	P concentration reduction < 10% and increase in concentration	-1
4- Removal of other pollutants of concern	Removal of other nutrient/pollutant> 80%	2
	Removal of other nutrient/pollutant< 80%	1
5- [2] Hydraulic conductivity	Very good: > 4 cm/h	3
	Good: 1.5-4 cm/h	2
	Acceptable/depending on compactness: <1.5 cm/h	1
6- Lifetime	Lifetime >10 years	2
	Lifetime : 5-10 years	1
	Lifetime <5 years	0
7- Negative externalities	GHG emission	-3
	Contaminant leaching/other pollutants in effluent	-2
	Expensive pre-treatment	-1
[3] Dynamic scores subject to change based on geographical region		
8- Scale of Availability	Scale of Availability: farm scale	4
	Scale of Availability: local/country scale	3
	Scale of Availability: EU/continent scale	2
	Scale of Availability: International scale	1
9- Cost	Cost (low)	3
	Cost (medium)	2
	Cost (high)	1

[1] Extracted from the developed Media Database (Tables 4.1, 4.2, 4.3) based on average performance of conducted studies

[2] Required additional data from other sources

[3] Scoring should be defined by individual users (requires case study knowledge on temporal/spatial factors)

Table 4.5. *Site-specific case studies in Ireland, Belgium and USA based on land drainage discharges, shallow groundwater and drainage ditch nitrogen and phosphorus concentrations (spatial and temporal data considered). Locations highlighted in greyscale were used to validate the DST.*

Site details/reference	**Location**	**Geology /soil drainage-soil type**	**Mean NO_3-N (mg L^{-1})**	**Mean NH_4-N (mg L^{-1})**	**Mean DRP (mg L^{-1})**	**Pollution Scenario**		**Study Period**
						Description	**Type**	
IRELAND								
Intensive dairy farm/Teagasc Dairy Production Centre (Huebsch et al., 2013)	Curtin's, Fermoy, Co. Cork	Limestone/free-brown earth	11.6	0.3	< 0.035	NO_3-N dominates with P retained in the soil-subsoil-geology. Only one specific borehole had NH_4-N breaches caused by localised conditions.	A1	2001- 2010
Dairy research farm, (Huebsch et al., 2013; Fenton et al., 2017)	Kilworth-Moorepark, Fermoy, Co. Cork	Limestone/free-brown earth	11.1	< 0.05*	<0.035	NO_3-N dominates with P retained in the soil-subsoil-geology.	A1	2001-2010 and 18 months from 2012
Beef research farm, Johnstown Castle (Fenton et al., 2009a,b; Clagnan et al. 2018b)	Foals House, Co. Wexford	Glacial deposits underlain by Pre-Cambrian greywacke-schist-massive schistose quartzites/moderate-Typical groundwater gley	7.5± 4.5*	0.1	<0.035	NO_3-N dominates shallow groundwater with P retained in the soil-subsoil-geology. Also some NH_4-N in shallow groundwater.	A1/ B1	2007-2009 and 2009-2017
Beef research farm, Johnstown Castle (Ibrahim et al., 2013; Peyton et al., 2016; Clagnan et al., 2018b)	Foals House, Co. Wexford	Glacial deposits underlain byPre-Cambrian greywacke-schist-massive schistose quartzites/poor-typical groundwater gley	0.45± 0.63	< 0.1	>0.035	Drainage water dominated by DRP only	C	2009- 2017
Commercial dairy farm (Clagnan et al., 2018a)	Castleisland, Co. Kerry	Limestone-sandstone-shale/poor-typical surface water gley	2.92 ± 1.46	0.43 ± 0.46	>0.035	NH_4-N dominates with DRP, low NO_3-N	B2	Aug 2015- Aug 2016
Commercial dairy farm (Clagnan et al., 2018a)	Athea, Co. Limerick	Shale/poor-humic surface water gley	0.47 ± 0.37	0.17± 0.18	>0.035	NH_4-N dominates with DRP, low NO_3-N	B2	Aug 2015- Aug 2016
Commercial dairy farm (Clagnan et al., 2018a; Daly et al. (2017)	Rossmore, Co Tipperary	Sandstone-shale/moderate-typical surface water gley	0.76 ± 0.80	0.22± 0.21	0-0.84*	NH_4-N dominates with DRP, low NO_3-N	B2	Aug 2015-Aug 2016 and Oct 2015-May 2016

Dairy research farm (Necpalova et al., 2012)	Solohead, Co. Tipperary	Devonian sandstone/poorly drained Gleys (90%) and grey brown Podzolics (10%)	< 1	0.33± 0.95	>0.035	NH_4-N dominates with DRP, low NO_3-N	B2	2008- 2010
Dairy farm, Johnstown Castle Environmental Research Centre (unpublished data)	Co. Wexford	Pre-Cambrian greywacke-schist-massive schistose quartzite/poor to moderately well-gleyic cambisol		0.98	0.055	NH_4-N dominates with DRP, low NO_3-N	B2	Jan 2016- Dec 2017
FLANDERS, BELGIUM								
Site details/reference	**Location**	**Geology /soil drainage-soil type**	**Mean NO_3-N (mg L^{-1})**	**Mean NH_4-N (mg L^{-1})**	**Mean DRP (mg L^{-1})**	**Pollution Scenario**		**Study Period**
						Description	**Type**	
Grassland/maize/fruits and nuts*	Kaalbeek, Alken, Limburg	Moderately to poorly drained-sandy loam- heavy subsoil	11.84		0.357	NO_3-N dominates with high concentration of P being mobilized	A2	Jan 2015- Dec 2016
Fruits and nuts*	Nieuwerkerken, Limburg	Moderately to poorly drained- sandy loam- heavy subsoil	10.85		0.07		A2	Jan 2017- March 2018
Grains, legumes, ornamental plants/ maize/grassland*	Sint-Pieters-Kapelle, Middelkerke, W Flanders	Very poorly drained- heavy clay-heterogeneous topsoil: Polder	<5.6	0.495	1.2	NH_4-N dominates with high concentrations of DRP	B2	Sep 2014- Dec 2016
Maize/grassland/potato*	Moerkantsebaan, Essen, Antwerp	Insufficient drainage-sand (dominant)/loamy sand	7.83		1.56	NO_3-N above very good status but below good status	A2 / C	Jan 2014 – Jul 2016
Grassland/fruit and nuts/maize*	Herk-de-Stad, Limburg	Moderately drained-sandy loam-heavy subsoil		2.82	0.83	Very high NH_4-N with DRP mobilized	B2	Jan 2014- Nov2015
Grassland/maize/grassland corn/vegetables*	Bree, Limburg	Moderately drained-loamy sand/light sandy loam	24.02		0.0278	Very high NO_3-N with most of DRP retained	A1	Jan 2015- Nov 2016
Potato/maize/other crops*	Leisele, Alveringem, West-Flanders	Insufficient to moderately drained/loam (dominant) and sandy loam	10.41		1.67	NO_3-N above good status but below very good status	A2/ C	Jan 2017- April 2018

Grassland/grains, legumes/vegetables*	Aarschot-Flemish Brabant, Limburg	Moderately to poorly drained-sandy loam/loamy sand/light sandy loam/loam/gley soil:	< 5.6		1.45	No N pollution; DRP	C	Jan 2014- Nov 2016
Maize/grassland/vegetables and herbs/grains *	Bollisenbeek, Peer, Limburg	Very well to poorly drained-sand and loamy sand, subsoil with humus/iron	21.60		>0.07	High NO_3-N and DRP > MAC	A2	Jan 2015- Dec 2017
USA								
Site details/reference	**Location**	**Geology /soil drainage-soil type**	**Mean NO_3-N ($mg\ L^{-1}$)**	**Mean NH_4-N ($mg\ L^{-1}$)**	**Mean DRP ($mg\ L^{-1}$)**	**Pollution Scenario**		**Study Period**
						Description	**Type**	
Agricultural field with crop rotation, Northeast Research and Demonstration Farm (Christianson et al., 2012a)	Northeast Iowa	n.a.	13.18			NO_3-N dominates	A1	2010
Agricultural field with crop rotation, Green County (Christianson et al., 2012a)	Central Iowa	n.a.	15.18			NO_3-N dominates	A1	2008
Dairy farm, Ridgely Farm (Rosen and Christianson, 2017)	Chesapeake Bay catchment, Caroline Co., Maryland	Sassafras sandy loam (47%)	8.17± 10.5	11.25± 11.8	2.52± 2.8	Both N species; DRP	A2/ B2	
Organic field (rotation of various crops), Queen Anne Farm (Rosen & Christianson, 2017)	Queen Anne's Co., Maryland	Ingleside sandy loam (29.5%)	9.49± 5.0		0.15± 0.2	NO_3-N dominates; DRP	A2	
Grazed pasture and hayed pasture (Vadas et al., 2015)	Platteville, Wisconsin	Tama/moderately eroded-silt loam/sandy clay loam		1.4	1.5	Based on flow weighted nutrient concentration for DRP and NH_4-N	B2	Aug 2010-Jul 2012

Corn and soybean production **	Blue Earth County, Minnesota	Minnetonka/ poorly drained-silty clay loam/sandy clay loam/sandy clay/silty clay	15.76 (FWMC)			NO_3-N dominates		WY2011-2017
Corn and soybean production **	Dodge County, Minnesota	Readlyn/somewhat poorly drained- silt loam/sandy clay loam/silty clay loam/sandy clay/silty clay	26.18 (FWMC)			NO_3-N dominates		WY2013-2017
Grains (sugar beet-corn-dry bean-soybean-wheat crop rotation) **	Norman County, Minnesota	Grimstad/somewhat poorly drained-fine sandy loam/silt loam/clay loam/silty clay loam/sandy clay/silty clay	22.36 (FWMC)			NO_3-N dominates		WY2013-2017
Grains (sweetcorn-peas-soybean crop rotation) **	Renville County, Minnesota	Canisteo-Glenco/poorly drained-silt loam/clay loam/silty clay loam/sandy clay/silty clay	15.08 (FWMC)			NO_3-N dominates		WY2012-2017
Grains (corn-soybean) production **	Wilkin County, Minnesota	Elmville /somewhat poorly drained-very fine sandy loam	17.27 (FWMC)			NO_3-N dominates		WY2013-2017
Grains (corn-alfa alfa rotation) **	Wright County, Minnesota	Cordova/poorly drained-clay loam/sandy clay loam/silty clay loam/sandy clay/silty clay	20.02 (FWMC)		0.27 (FWMC)	NO_3-N dominates		WY2012-2017
Corn and soybean production ***	Salt Fork Vermillion River, Illinois	Poorly drained-Drummer	12.00			NO_3-N dominates	A1	WY2011-2012
Corn production (David et al., 2015)	Upper Mississippi River basin, Illinois	Poorly drained-Drummer	16.00			NO_3-N dominates	A1	WY2010-2012

Unpublished data from regional/national database:* VMM; ** Discovery Farms Minnesota; *** USDA

FWMC= Flow weighted mean concentration; WY=Water Year: the year beginning on 1 October and ending 30 September the following year

4.3.4. Testing of FarMit DST using different case studies

Three case studies each with their own distinctive nutrient scenario from Ireland, Belgium and the USA were used to test the DST (see Table 4.5 for details). Nutrient losses from drainage systems are ubiquitous, but water quality regulation standards differ worldwide. For example, in an Irish dairy system, cattle are kept outdoors for most of the year with both organic and inorganic fertilizer being land spread. Studies have shown high N surpluses on dairy farms due to low N utilisation efficiencies, e.g. Clagnan et al. (2018a) found a range from 211 to 292 kg N ha^{-1} on heavy textured sites. As drainage waters are not governed directly by water quality legislation, other standards for surface or groundwater (e.g. drinking water standards) can be used to quantify the level of pollution. For example, in Ireland surface waters are of "high" and "good" status if their DRP is <0.025 mg L^{-1} and < 0.035 mg L^{-1}, respectively (EU, 2014c; EPA, 2016b). For NO_3-N, an average drinking water concentration of 11.3 mg L^{-1} applies for groundwater, whereas a lower standard of <0.9 mg L^{-1} and <1.8 mg L^{-1} are indicative of surface waters with "high" and "good" status, respectively (EPA, 2016b). Although a drinking water standard, and not specific to drainage waters, an indicative NH_4-N concentration of <0.23 mg L^{-1} may be considered to be non-polluting.

The region of Flanders in Belgium is mostly dominated by fruit production and arable farming in the east, with livestock production and production of vegetables for the frozen food market in the west (Flemish Agriculture and Fisheries, 2017). This region comprises 75 % of agricultural production in Belgium, and is considered by the Government of Flanders, Investment and Trade Body to be a "global leader in intensive farming". The water standard for NO_3-N should be < 11.3 mg L^{-1} and the same standard for NH_4-N as in Ireland applies. In terms of DRP, there is a range of concentrations for "very good" and "good" status of surface water from 0.04 to 0.06 mg DRP L^{-1} and 0.07 to 0.14 mg DRP L^{-1}, respectively.

Finally, the sites selected in the USA were in the states of Iowa, Minnesota, Wisconsin and Maryland, in which the dominant agricultural systems are corn, soybean, livestock, vegetables, fruits, and tree nuts (Hatfield, 2012). As with Ireland, NO_3-N standards in the USA are specific to drinking water, and not drainage water, but with a slightly lower standard at 10 mg NO_3-N L^{-1}, which is termed a "maximum contaminant level". In terms of DRP in the USA, there is a limit of 0.037 mg DRP L^{-1} (USEPA, 2000) in surface waters.

4.3.5. Validation of DST (SWOT analysis)

The procedure of Andersson-Sköld et al. (2014) was followed to validate the DST. The FarMit DST was validated by running several SWOT (Strength, Weakness, Opportunity, Threat) analysis sessions with end-users. This allowed the DST to be critically reviewed by independent stakeholders and external experts (researchers/scientists in the fields of water/soil quality monitoring/remediation and environmental protection, agricultural consultants/advisors) at the following SWOT analysis workshops:

i. PCFruit, Fruit Research Centre, Belgium (May 2018; five attendees)

ii. Department of Environment Research Centre of Teagasc, Agriculture and Food Development Authority of Ireland, Ireland (December 2018; 14 attendees)

iii. Water Research Group/ Groundwater Protection Group in Sheffield University, UK (February 2019; 10 attendees)

iv. Network Meeting of EU Horizon2020 Early Stage Researchers representing different partner countries in the INSPIRATION (Managing soil and groundwater impacts from agriculture for sustainable Intensification) Independent Training Network (ITN), Netherlands (March 2019; 14 attendees)

The process was carried out by presenting the FarMit DST to participants, starting with a summary of current media-based mitigation measures for removing/remediating nutrients in drainage water at farm-scale. The attendees were then divided into groups of three to four and participants were given a chart explaining each criterion. The groups were then asked to use the DST with a view to making best management decisions from a farmer/advisor point of view. The opinions of groups on the performance of FarMit DST with regard to its strengths and weaknesses as attributes of the DST and opportunities and threats as attributes of the environment were recorded and discussed among attendees.

4.4. Results

The FarMit DST is available online as an Excel-based tool. It may be used by first accessing the 'INPUT' tab on the file. Figure 4.3 shows the user interface of FarMit DST. The results of the three case studies are now presented.

Figure 4.3. *The user interface of FarMit DST.*

4.4.1. Case studies

4.4.1.1. Ireland

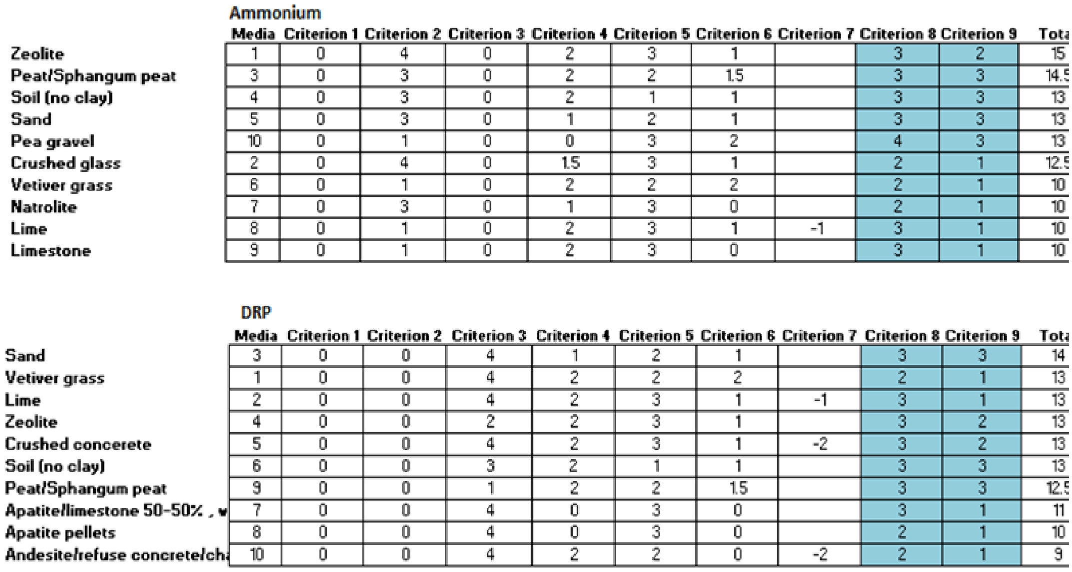
The results of the Irish case study are presented in Figure 4.4. The following steps were taken to obtain the final results:

1- Based on the drainage water test results (Table 4.5), the "Ammonium/DRP" icon in the DST user interface was selected (Figure 4.3).

2- The DST recommends the top 10 media based on *static* criteria for treatment of this scenario. For example, the top three media for NH_4-N removal are zeolite, crushed glass and peat/sphagnum peat with a cumulative score of 10, 9.5 and 8.5, respectively. The equivalent media for DRP removal are vetiver grass, lime and sand with cumulative scores of 10, 9 and 8, respectively.

3- The *dynamic* criteria 8 and 9 were assigned scores considering local conditions and resources available at farm-scale. For example, in Ireland sand and gravel can be delivered to site at 0.21 and 0.15 € kg^{-1}, while zeolite, lime, and limestone cost over 0.70, 0.95, and 1.3 €, respectively. Any media priced below and over 0.5 € kg^{-1} were assigned scores of 3 and 2, respectively, while media over 2 € kg^{-1} (e.g. andesite, charcoal, nitrolite, etc.) were assigned a score of 1. The DST sums the total scores of static and dynamic criteria.

4- After pressing "Run", the DST presented a high to low ranking of media for the mitigation of pollutants in the Irish case-study. These are presented graphically (by a histogram) and in table format.



Ammonium

	Media	Criterion 1	Criterion 2	Criterion 3	Criterion 4	Criterion 5	Criterion 6	Criterion 7	Criterion 8	Criterion 9	Tota
Zeolite	1	0	4	0	2	3	1		3	2	15
Peat/Sphangum peat	3	0	3	0	2	2	1.5		3	3	14.5
Soil (no clay)	4	0	3	0	2	1	1		3	3	13
Sand	5	0	3	0	1	2	1		3	3	13
Pea gravel	10	0	1	0	0	3	2		4	3	13
Crushed glass	2	0	4	0	1.5	3	1		2	1	12.5
Vetiver grass	6	0	1	0	2	2	2		2	1	10
Natrolite	7	0	3	0	1	3	0		2	1	10
Lime	8	0	1	0	2	3	1	-1	3	1	10
Limestone	9	0	1	0	2	3	0		3	1	10

DRP

	Media	Criterion 1	Criterion 2	Criterion 3	Criterion 4	Criterion 5	Criterion 6	Criterion 7	Criterion 8	Criterion 9	Tota
Sand	3	0	0	4	1	2	1		3	3	14
Vetiver grass	1	0	0	4	2	2	2		2	1	13
Lime	2	0	0	4	2	3	1	-1	3	1	13
Zeolite	4	0	0	2	2	3	1		3	2	13
Crushed concerete	5	0	0	4	2	3	1	-2	3	2	13
Soil (no clay)	6	0	0	3	2	1	1		3	3	13
Peat/Sphangum peat	9	0	0	1	2	2	1.5		3	3	12.5
Apatite/limestone 50-50% , w	7	0	0	4	0	3	0		3	1	11
Apatite pellets	8	0	0	4	0	3	0		2	1	10
Andesite/refuse concrete/ch	10	0	0	4	2	2	0	-2	2	1	9

Figure 4.4. *Irish Case Study results: Ammonium (top) and DRP (bottom).*

The order of the top five media for NH_4-N removal was (from best to worst): zeolite, peat/sphagnum peat, soil (no clay), sand and pea gravel. The top five media for DRP removal were (from best to worst): sand, lime, vetiver grass, zeolite, and crushed concrete. The ranking implied the influence of wide (local) application of some media over others in the dynamic criteria scoring. For example, zeolite is highly available despite being imported, therefore it has higher availability with lower delivery cost. Similarly, the extensive peat harvest/extraction from peat deposits along with the geology of Ireland, which provides limestone rocks or sand with various compositions, influenced the dynamic criteria scoring and therefore the final ranking of media.

4.4.1.2. Belgium

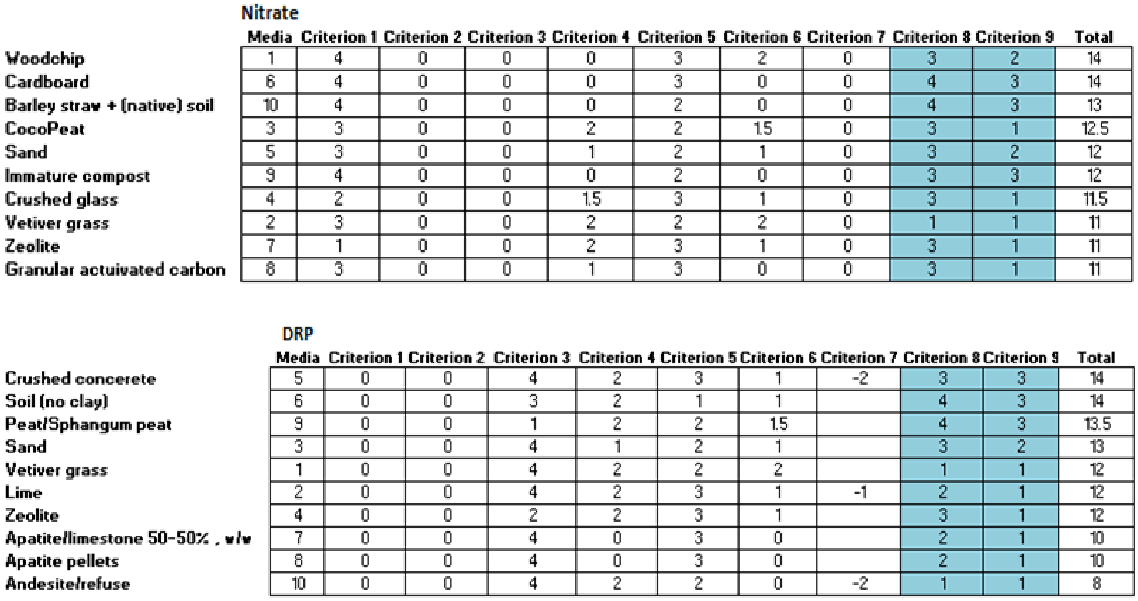
The results of the Belgian case study are presented in Figure 4.5. The following four steps were taken to obtain the final results:

1- Based on the drainage water test results (Table 4.5), the “Nitrate/DRP” icon in the user interface was selected (Figure 4.3).

2- The DST recommends the top 10 media for treatment of this scenario. For example, the top three media based on *static* criteria for NO_3-N removal are woodchips, vetiver grass, and coco-peat, with a cumulative score of 9, 9 and 8.5, respectively. The media for DRP removal are similar to the Irish case study.

3- The *dynamic* Criteria 8 and 9 were assigned scores considering local conditions and resources available at farm-scale. This information was confirmed through consultation and face-to-face communication with a local private soft fruit company. A medium such as woodchip costs about €15 m^{-3} to be delivered to a farm, which is considered inexpensive (i.e. Score 3) and similar to barley straw, or pea gravel. Some media such as apatite, limestone or vetiver grass are considered to be very costly, and must be imported to the site (with an associated high delivery cost). This was therefore assigned a Score of 1. The DST sums the total scores of the static and dynamic criteria.

4- After pressing “Run”, the DST presented a high to low ranking of media for the Belgian case-study.



Nitrate

	Media	Criterion 1	Criterion 2	Criterion 3	Criterion 4	Criterion 5	Criterion 6	Criterion 7	Criterion 8	Criterion 9	Total
Woodchip	1	4	0	0	0	3	2	0	3	2	14
Cardboard	6	4	0	0	0	3	0	0	4	3	14
Barley straw + (native) soil	10	4	0	0	0	2	0	0	4	3	13
CocoPeat	3	3	0	0	2	2	1.5	0	3	1	12.5
Sand	5	3	0	0	1	2	1	0	3	2	12
Immature compost	9	4	0	0	0	2	0	0	3	3	12
Crushed glass	4	2	0	0	1.5	3	1	0	3	1	11.5
Vetiver grass	2	3	0	0	2	2	2	0	1	1	11
Zeolite	7	1	0	0	2	3	1	0	3	1	11
Granular actuivated carbon	8	3	0	0	1	3	0	0	3	1	11

DRP

	Media	Criterion 1	Criterion 2	Criterion 3	Criterion 4	Criterion 5	Criterion 6	Criterion 7	Criterion 8	Criterion 9	Total
Crushed concerete	5	0	0	4	2	3	1	-2	3	3	14
Soil (no clay)	6	0	0	3	2	1	1		4	3	14
Peat/Sphangum peat	9	0	0	1	2	2	1.5		4	3	13.5
Sand	3	0	0	4	1	2	1		3	2	13
Vetiver grass	1	0	0	4	2	2	2		1	1	12
Lime	2	0	0	4	2	3	1	-1	2	1	12
Zeolite	4	0	0	2	2	3	1		3	1	12
Apatite/limestone 50-50% , w/w	7	0	0	4	0	3	0		2	1	10
Apatite pellets	8	0	0	4	0	3	0		2	1	10
Andesite/refuse	10	0	0	4	2	2	0	-2	1	1	8

Figure 4.5. *Belgian Case Study results: Nitrate (top) and DRP (bottom).*

The top five ranked media for mitigation of NO_3^- were (from best to worst): woodchips, cardboard, barley straw with native soil, coco-peat and sand. Soil (no clay) together with crushed concrete, peat/sphagnum peat, sand, and vetiver grass together with lime and zeolite, were the highest ranked media for mitigation of DRP. The feedback from face to face communication with farmers indicated that considering the availability of resources at farm scale, waste cellulose (combination of leaf compost, wood mulch and saw dust) could gain more interest than woodchips. In addition, availability of locally sourced barley straw and peat with high NO_3^- removal potential could consequently change the scores for the dynamic criteria to compensate for a low score for a static criterion (e.g. lifetime). Farmers perceived “pollution swapping” as being important and the final material needed to have a low pollution swapping potential. This was perceived as important to avoid monetary fines in terms of water regulations in the future.

4.4.1.3. USA

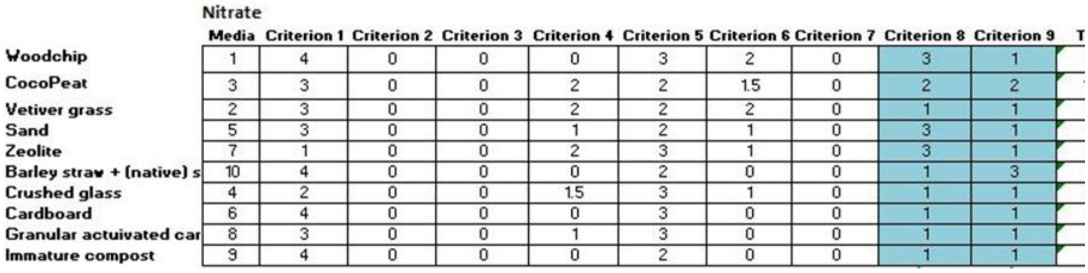
The results of the US case study are presented in Figure 4.6. The following four steps were taken to obtain the final results:

1- Based on the drainage water test results as in Table 4.5**,** the “Nitrate” icon on in the user interface was selected (Figure 4.3).

2- The DST recommends the top 10 media for treatment of NO_3^- pollution scenario (similar to Belgium Case Study for NO_3^- related media).

3- The *dynamic* Criteria 8 and 9 were assigned scores based on a comparative scale using online information in consultation with the USA stakeholder, considering local conditions and resources available at farm-scale within the vicinity of case study region. The use of woodchips (to be used in denitrifying bioreactors) receive financial support from the government and the existence of numerous wholesale suppliers/or producers of coco-peat (coconut coir), vetiver grass, and zeolite made these media accessible and available. The DST then summed the total scores of static and dynamic criteria.

4- After pressing "Run", the DST recommended a high to low ranking of media for USA case-study.



Nitrate

	Media	Criterion 1	Criterion 2	Criterion 3	Criterion 4	Criterion 5	Criterion 6	Criterion 7	Criterion 8	Criterion 9	T
Woodchip	1	4	0	0	0	3	2	0	3	1	
CocoPeat	3	3	0	0	2	2	1.5	0	2	2	
Vetiver grass	2	3	0	0	2	2	2	0	1	1	
Sand	5	3	0	0	1	2	1	0	3	1	
Zeolite	7	1	0	0	2	3	1	0	3	1	
Barley straw + (native) s	10	4	0	0	0	2	0	0	1	3	
Crushed glass	4	2	0	0	1.5	3	1	0	1	1	
Cardboard	6	4	0	0	0	3	0	0	1	1	
Granular actuivated car	8	3	0	0	1	3	0	0	1	1	
Immature compost	9	4	0	0	0	2	0	0	1	1	

Figure 4.6. *US Case Study results: Nitrate.*

The DST recommended woodchips, coco-peat, vetiver grass together with sand and zeolite, barley straw with native soil, as the highest ranked media from best to worst. This result supports the common use of denitrifying woodchip bioreactors in the USA as a well-established NO_3^- remediation technology (Christianson et al., 2012a). The installation of woodchip bioreactors at the end of tile drainage systems is also financially supported by the US Department of Agriculture Natural Resources Conservation Service (USDA NRCS) (NRCS, NHCP, 2015). Such schemes, along with the major local productions, industry needs and wholesale suppliers/distributors/importers, have a direct influence on media availability and cost and, consequently, the scoring and final selection. The output of the FarMit DST considers only selection of a medium/media. Future research is required to test the medium/media under controlled laboratory conditions to elucidate design and operational parameters.

4.4.2. SWOT analysis

The overall SWOT analysis results from different workshops is summarised in Table 4.6. It was perceived that the major strengths of the FarMit DST were its easy concept and worldwide applicability for targeting dual removal of nutrient pollution, regardless of farming practice and considering specific local economic conditions and media-availability to individual users. Weaknesses identified included the absence of a sustainability factor (i.e. possible reusability of saturated media as a fertilizer or a soil amendment) and impracticality of using certain media regardless of their high ranking in nutrient mitigation. The major opportunity provided by FarMit was that it may be a long-term efficient decision support framework that can be implemented at the initial stage of decision making. The threats were seen as the risk of extreme weather events or social/economical/political changes that may have an impact of availability and price of media for farmers.

4.5. Discussion

4.5.1. Performance of DST in case-study applications

The DST application in different case studies representing different geographical locations and showcasing different farming practices, provided a ranking of media with high potential to remove nutrients in drainage water for various farm pollution scenarios. SWOT analysis showed the DST to be an effective tool to communicate management options to different stakeholders. It provided a list of options to the stakeholder and the results are clear enough to provide applicable information.

Table 4.6. *Summary of SWOT analysis results: strength and weakness (attributes of the tool), and opportunities and threats (attributes of the environment) of FarMit DST identified through different workshops.*

STRENGTH	WEAKNESS	OPPORTUNITIES	THREATS
Clear concept, provides quick view of best media, and easy to understand		Flexibility of the tool to be further developed	
User friendly without any complications, thus suitable for any software skill level.		Easy to change scores from time to time depending on environmental circumstances	The use of the tool/scorings depend on local/national legislations
Time saving by providing a list of best media	Lack of a factor showing raw/waste nature of a medium	Positive impact on decision making as an easy to access tool	
Static criteria do not change from region to region but are of paramount important in any mitigation option regardless of farm size.	Lack of a criterion for environmental sustainability and post-implementation cost (disposal of used media and associated costs)		Impact of local geographical conditions on removal efficiency (e.g. weather, humidity,
Low-cost DST which is easy to disseminate		Enabling knowledge transfer between different stakeholders	
Robust selection of media (based on literature review and actual experiments)			
Informative and encouraging to consider several options	Bar graphs may be misleading for non-scientific community	Supporting document to be used for legal purposes	
The ranking list is provided based on an order from most efficient	The tool doesn’t consider unfeasibility of having certain medium at site, regardless of its good adsorption capacity	Possibility to add a factor considering the applicability at site	Farmers’ constraint might not let them to choose top ranked media based on lower “Cost” or higher “Availability”

Providing the user with options helps in making a more informed selection considering environmental impacts	Does not consider GHG emission caused by transport of media		Information on availability/efficiency of some media at shorter time period depends on extreme weather condition, land use changes, growing/failure of an industry, etc. Changes in Geopolitical landscapes have direct impact on commercial deals and import/export agreements Fluctuation of exchange rate in case of importation can change the cost
Considers negative externalities (pollution swapping) thus prevents further post-treatment in near/far future	“Pollution Swapping” has not been considered in many studies so not sufficient information on all 75 media in this regard	Draws the attention toward the critical issue of creating a new pollutant as the result of mitigating a existing pollutant. Change habits and therefore improve accidental (further) environmental pollution Influence mindset by considering several criteria of importance for overall pollution remediation	
Considers two types of nutrient (N & P) pollutions emerging as singled or simultaneously			

Considers environmental, economical, and logistical criteria into account	Some media may appear exotic and unknown depending of geographical location where the tool is applied	
Taking user's income ("Cost") into account	The scoring range for "Cost" is not narrow enough to make differentiation easier	Possibility to add a weighting factor to show importance of dynamic criteria
	Lack of differentiating between organic/inorganic components of media and information on nonlocal media [1]	
Provide decision support framework which is efficient at longer terms.		Possibility of data collection regarding farmers' preferences in order to improve decision making processes
		Encourage farmer to monitor the water quality more often to avoid possible contamination of water by the end of medium's lifetime
Can be further developed to include new emerging media , as well as results from new laboratory and field experiments on currently listed media	Lack of information on amount of required media and their exact lifetime [2]	

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[1] All 75 media are differentiated based on being wood-based, vegetation/phytoremediation based or inorganic in Table 4.1, Table 4.2, Table 4.2, respectively, documenting detailed list of advantages/disadvantages of media and already tested amendments to improve their efficiency.

[2] Acquisition of this information requires batch or column adsorption studies and modelling of adsorption capacity of selected media based on nutrient load and targeted removal percentage of pollution in a defined time period.

The results were consistent with the hypothesis that the dynamic criteria (availability and delivery cost of media to site) would vary spatially and temporarily. This was due to reasons such as geopolitical situation and proximity to a national border (e.g. to the French border for Flanders in Belgium), size of the country and therefore availability of wholesale manufacturers/suppliers/distributers, local production (e.g. wood-based or corn-based media like corn cob/stover may suit farmers in USA better than Belgium or Ireland), levies on recyclable materials (e.g. glass in Ireland or cardboard in Belgium), financial support from government (e.g. installation of woodchip denitrifying bioreactors in USA), the extent of application of media according to the dominant industry/use, etc. A good example for the latter is zeolite, which is a natural mineral medium with high potential for removal of both NH_4-N and DRP. Although imported in Ireland, this has wide application in Ireland and thus higher availability with lower delivery cost compared to Belgium, for example. Conversely, coco-peat is more available in Belgium than Ireland due to the wide application of coco-based media for other purposes (e.g. coco-chips in pesticide biofilter), while this medium is readily available and may be purchased at a relatively low cost in the USA.

4.5.2. SWOT analysis

Generally, the ranking of media is similar based on static (non-geographical) criteria for comparable case studies in different locations, although it is expected to change when considering the dynamic criteria (8 and 9) at specific sites. The operator may choose from 75 options (Appendix C) according to their local knowledge and personal preference. This was considered as a strength in the SWOT analysis. This flexibility enabled the operators (farmer/adviser/engineer) to make a quick and informed medium selection based on possible future costs. This strength of the FarMit DST was welcomed in Belgium, where farmers were willing to take an active role in implementing sustainable solutions to minimize pollution caused by nutrient losses and they may opt for natural/organic media with zero pollution swapping and longer saturation time regardless of nutrient adsorption capacity. For example, despite the high availability of cardboard or crushed concrete at farm-scale and their high nutrient removal efficiency, the stakeholder (farmer) was concerned about the media lifetime and potential negative externalities. Therefore, the preference was to implement a more sustainable, but more expensive, alternative (e.g. zeolite).

In addition, if an operator wishes to avoid expensive pre-treatment or post-treatment of media due to pollution swapping caused by, for example, leaching of heavy metals (e.g. andesite and re-used concrete), they may wish to select a medium further down the ranking that may be more expensive but which has a lower environmental footprint. In addition, after the selection and operation of an engineered treatment system, the FarMit DST can be used again to minimize the effects of pollution swapping. For example, woodchip has been shown in some studies to release DRP (e.g. Fenton et al., 2016). In these cases, the DST can be used to select a Scenario C medium instead.

Another SWOT strength, as well as opportunity of FarMit, is the flexibility to be further developed and to adjust with time of application, as the dynamic criteria may also change over time. For example, a non-native plant such as vetiver grass has a high pollutant removal efficiency (Ash and Truong, 2004; Mayorca, 2007; Donaldson and Grimshaw, 2013) and can be purchased at a relatively low cost in the USA. It was initially only available at international-scale to Ireland and Belgium (where it was imported from Asia), but now has a growing market in Europe (with ensuing lower supply costs and higher availability). Here, the SWOT threats lie in the fact that changes in geopolitical landscapes impact commercial trade directly and extreme weather might change availability (and price) of local products.

The SWOT analysis identified a lack of a criteria considering environmental sustainability and post-implementation cost (e.g., disposal of used media and associated costs). This can be addressed in the future as the tool has the flexibility to be further developed.

4.6. Limitations and future recommendations

Phytoremediation and organic materials, presented in Table 4.2, have limitations (such as type of vegetation plant, geology, geographical features), which may affect the results of their application (e.g. peat). Similarly, soils and sands may differ in metal content and geochemistry, which could influence their nutrient adsorption capacity. Therefore, the user can subsequently decide to test several highly ranked media in batch studies to confirm their performance in specific contexts. This would then help to screen suitable materials and identify the most efficient type or chemistry of locally sourced media (thus with highest nutrient mitigation potential or longer lifetime) to be used in the site under examination.

In terms of final selection for an engineered structure, further media testing may be needed to elucidate on-site removal capacity, which may differ from literature or even laboratory conditions e.g. woodchip and denitrification rate. Additionally, the design of a system for dual nutrient mitigation will usually require the user to consider the sequence of media needed to address pollution swapping (Fenton et al., 2016).

Future development of this FarMit DST should consider incorporation of other factors by individual users (e.g. circular economy/agronomic value of saturated media) for scoring and finalising media selection, as well as aligning the ranking of media for removal performance based on similar conditions, e.g. residence time, and to factor in other issues that influence the removal efficiency, e.g. atmospheric conditions such as temperature. Furthermore, dynamic criteria could outweigh all other components if weightings are assigned. This would exclude all media for which access is not possible (e.g. vetiver grass in some areas). Another factor which could be included in the DST at a later stage would be maintenance costs pertaining to the selected medium/media at the field site.

The flexibility of the FarMit DST provides a tool with the capability to be updated by adding media emerging from new studies as well as new tests on the current 75 media reviewed, but in different experimental settings. This would consequently update the "static component" of the DST as new results indicate higher or lower removal rates, lifetime, or new insights into the pollution swapping potential of a media.

4.7. Conclusions

A decision support tool ("FarMit") was developed and validated. This tool enables the end-user to select locally sourced media which can be used in drainage ditch structures to mitigate polluted outflows. The tool provides seven static criteria for 75 media and the operator provides dynamic criteria (availability and delivery cost) to adjust the final ranked list for local conditions.

SWOT analysis, conducted in a series of workshops, showed the tool to be systematic, transparent and user-friendly, providing the user with a wide catalogue of options, and considers users' local economic and market conditions. Despite the fact that the tool does not provide an end-use for the saturated medium (media) or insight about re-use potential, it provides the opportunity of knowledge transfer between different stakeholders, and therefore can positively impact decision making.

4.8. Summary

This chapter is summarised in the following bullet points:

- Different nutrient pollution scenarios that would occur on farms were identified.
- A DST was developed to select media for mitigation of nutrients in drainage water.
- This DST enables users to choose media specific to pollution and local conditions.
- The DST considers static/dynamic criteria to ensure environmental/logistics compliance.
- The DST was tested using case studies in Ireland, Belgium and USA.
- SWOT analysis found the DST to be systematic, flexible and transparent.

The suitable media for mitigation of nutrient losses at the study site (Chapter 3) were selected using the DST developed herein. The next chapter investigates the dual nutrient removal efficiency of selected mixed media in small and large-scale adsorption column tests. The objective is to investigate possibility of using small-scale columns to predict effluent concentrations leaving large-scale columns.

Chapter 5

Use of rapid small-scale column tests for simultaneous prediction of phosphorus and nitrogen retention in large-scale filters

5.1. Overview

The objectives of this chapter are to examine the efficacy of the RSSCT modelling approach in simultaneous prediction of DRP and NH_4-N effluent concentrations in large-scale filters filled with mixed media.

The content of this chapter has been submitted to the Journal of Agricultural Water Management:
Ezzati, G., Healy, M., Christianson, L.E., Daly, K., Fenton, O., Feyereisen, G., Thornton, S., Callery, O. Use of rapid small-scale column tests for simultaneous prediction of phosphorus and nitrogen retention in large-scale filters.

5.2. Introduction

Intensification of agriculture through crop growth strategies and increased animal stocking rates has been enacted in many countries of the EU (Van Zanten et al., 2016). This may result in unabated diffuse and point-source nutrient (N and P) losses to water bodies, causing multiple effects on environmental systems while traveling along biogeochemical pathways and continua from soil to water bodies (Galloway et al., 2003; Sharpley et al., 2011). As surface and subsurface storage components of these mixed nutrients are large, critical and incidental losses which are deleterious for the aquatic system, will occur (Schulte et al., 2014; Ascott et al., 2018). Therefore, alongside existing best management practices to mitigate surface and groundwater nutrient losses, there is a need for a number of additional measures that can intercept and mitigate nutrients before they leave the farm system. Engineered remediation technologies are amongst these measures and have moved beyond proof of concept in recent years (e.g. Christianson and Schipper, 2016). These include installation of structures filled with P sorbing materials (Penn et al., 2014a; Sanford and Larson, 2016) to intercept surface runoff, in-ditch control structures designed to remove both P and N in drainage waters (Fenton et al., 2016), and denitrifying bioreactors connected to tile systems that are filled with carbon-based media that convert NO_3^- to di-nitrogen gas (Christianson et al., 2013; Healy et al., 2014, Fenton et al., 2016).

In Chapter 4, a DST was developed to assist users in the selection of locally sourced media for use in mitigating pollution associated with excess nutrients in drainage waters. Within this DST, several water contamination scenarios were identified, such as NO_3^- only, DRP only, or a mixed discharge of NH_4^+ and DRP. On heavy textured soils, where land drainage has been installed to extend the grazing season, there is a large body of evidence (e.g. Clagnan et al., 2019) that identifies NH_4^+ and DRP as the main nutrients of concern in both shallow and groundwater drainage systems. The aim of the current study is to design and quantify the effectiveness of filters containing appropriate media capable of retaining both NH_4^+ and DRP.

Prior to deployment of filters in field situations, it is advisable to characterise the adsorption capacity of the media using batch experiments. These tests are quick, cheap, and easy-to-perform (Crini and Badot, 2008), but fail to replicate in-field conditions, in which there may be additional variables, such as fluctuating water temperatures, flow dynamics and pollutant loads. Consequently, they often fail to accurately estimate lifespan or effectiveness of the media (Pratt and Shilton, 2009). As the accurate estimation of long-term performance of a medium is only possible under continuous flow conditions in the field (Pratt et al., 2012), the closest simulation to in-field conditions is to allow nutrient-rich water to flow through large-scale adsorption columns which are frequently operated in the laboratory (Nwabanne and Igbokwe, 2012; Monrabal-Martinez et al., 2017). However, these tests are costly and may take a long period to reach steady-state conditions (Penn et al., 2014b).

RSSCTs, which use only a minimum quantity of medium and contaminant solution, have been developed to reproduce the results of large-scale column studies (Poddar, 2013). Callery et al. (2016) used RSSCTs to predict the long-term P retention performance of large-scale, single medium adsorption filters. Callery and Healy (2017) developed the model further to predict medium saturation, as well as filter-pore and effluent concentration data. This RSSCT and modelling approach has never been attempted to examine a mixed contaminant scenario such as that found in heavy textured soils i.e. DRP and NH_4^+. Such a scenario would necessitate the presence of more than one medium in a filter that would have both a capacity for P adsorption and N removal. Therefore, the objective of the current study is to examine the efficacy of the RSSCT modelling approach in predicting DRP and NH_4^+ effluent concentrations in large-scale filters. If this methodology proves successful, this approach may provide an accurate and quick method of predicting the performance of filter media that may negate the need for long-term and expensive large-scale column studies.

5.3. Materials and methods

5.3.1. Media selection

The DST, developed in Chapter 4, was used to generate a list of media capable of mitigating DRP and NH_4^+ in drainage water (Table 5.1- Stage 1). Batch and adsorption isotherm experiments were conducted to identify media with the highest adsorption capacities for DRP and NH_4^+ (Table 5.1- Stage 2). Figure 5.1 shows some of the different media selected by the DST.

Table 5.1. *Stages of media selection for dual nutrient mitigation. At the end of each selection stage, media failing the criteria are omitted from the table.*

Stage 1 Selection of media using a DST[1]	Stage 2 Batch & Adsorption isotherm tests	Stage 3 K_{sat} tests
Peat soil	Peat soil	
Puraflo peat	Puraflo peat	
Compost	Compost	
Woodchip	Woodchip	
Dewatered alum-sludge		
Soil (air dried at 40 °C)		
Sand	Eight types of sands[2]	Five types of sand[2]
Turkish (Yildizeli) zeolite (particle size: 1-3 and 3-5 mm)	Turkish (Yildizeli) zeolite (particle size :1-3 and 3-5 mm)	Turkish (Yildizeli) zeolite (particle size: 1-3 and 3-5 mm)
Barley straw	Barley straw (cut into 2 mm)	
Maize		
Silage		

[1] Chapter 4

[2] Collected from quarries in the south of Ireland

Figure 5.1. *Some of the different waste materials used as in Table 5.1. Top left: Peat soil, sand, woodchip, zeolite, Puraflo^{TM} (from left to right); Bottom left: Eight types of sand. Right column: Different grading of zeolite.*

The batch experiments were conducted as follows: 2 g of locally sourced media, identified in Stage 1, were placed in 50 ml-capacity glass containers. Each medium was overlain with 35 ml of distilled water, which was amended with KH_2PO_4 and NH_4Cl to produce DRP and NH_4-N solutions with concentrations ranging from 1 mg L^{-1} to 40 mg L^{-1}. The containers were then sealed and placed in an end-over end shaker for 24 h. Following this, the samples were allowed to settle for 1 h and then centrifuged at 3500 rpm for 10 min, before the supernatant was withdrawn and filtered using 0.45-µm filters. A multipoint Langmuir isotherm (McBride, 2000) was used to estimate the adsorption capacity of each medium. The specific adsorption (q_e) (the mass of nutrient adsorbed per unit mass of amendment at equilibrium) (g kg $^{-1}$) was calculated from the following equation:

$$q_e = (C_0 - C_e) * \frac{V}{M} \qquad \text{[Eqn. 5.1]}$$

where C_e is the concentration of nutrient (DRP or NH_4-N) in solution at equilibrium (mg L^{-1}), C_0 is initial concentration, V is the volume of solution (L), and M is the weight of adsorbent medium (g). q_{max}, the estimate of the maximum monolayer adsorption capacity of the media, was calculated by plotting q_e/C_e against C_e and using the slope and intercept from the following equation:

$$\frac{C_e}{q_e} = \frac{1}{b} * \ q_{max} + C_e/q_{max} \qquad \text{[Eqn. 5.2]}$$

where b is the coefficient associated with adsorption energy (L mg^{-1}) to form a complete monolayer on the surface.

The average retention efficiency S (%) was calculated as follows:

$$S \ = \frac{C_e - \ C_o}{C_o} * 100 \qquad \text{[Eqn. 5.3]}$$

where C_e and C_0 are as defined above.

A constant head method (ASTM D2434; ASTM, 2000) was used to measure the saturated hydraulic conductivity (K_{sat}, m d^{-1}) of the media selected in Stage 2 (Table 5.1- Stage 3). This parameter helps in avoiding filter clogging and is considered to be one of the factors that ensures effective operation of filters (Segismundo et al., 2017). The elemental composition of selected media was analysed with a Rigaku NEX CG energy dispersive X-ray fluorescence bench-top spectrometer (EDXRF; Rigaku, Austin, USA).

5.3.2. Preparation of filter columns

In this experiment, two sets of filter columns were constructed: small columns, with lengths ranging from 0.1 to 0.4 m, and large columns, with lengths of 0.4 m. For both scales, the selected media for DRP retention and NH_4^+ removal was sand and zeolite, respectively. The packing density for both sand and zeolite was 1.8 g cm^{-3} and 0.92 g cm^{-3}, respectively.

Figures 5.2 and 5.3 shows the large-scale columns which were manufactured using acrylic tubes with an internal diameter of 0.10 m. Each column was instrumented with an inlet pipe at the base and an outlet pipe, which was positioned 0.38 m from the base (after the second media).

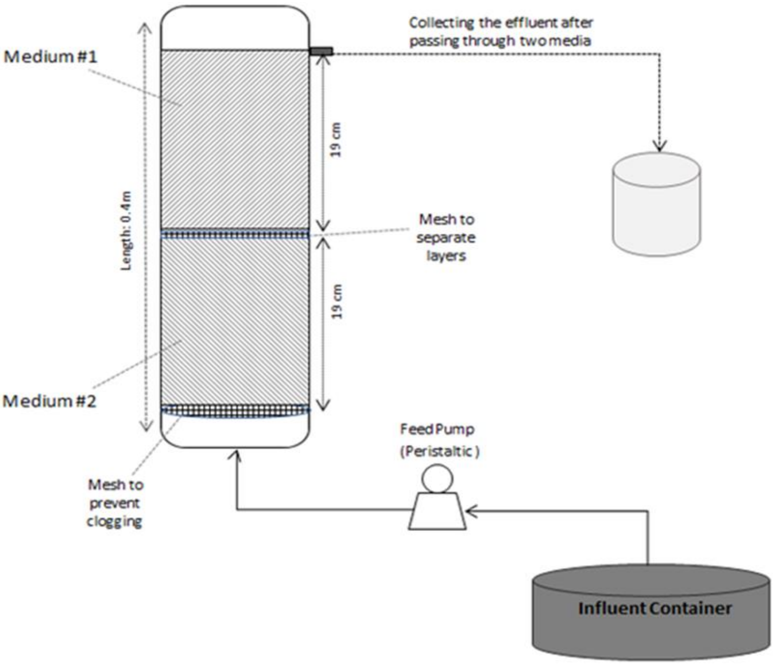


Figure 5.2. *Schematic diagram of large-scale columns*

The media overlay a fine metal mesh, positioned 0.01 m from the base to prevent clogging and to allow for uniform water distribution. The columns were positioned vertically and fixed on a steel frame, with flow entering the bottom of the columns. For the large columns, the media configurations were as follows: sand over zeolite or zeolite over sand (each at n=3) and each layer was 0.19 m deep, giving a total depth of filter media of 0.38 m.

Figure 5.3. *Large scale columns located in temperature-controlled room.*

Figure 5.4 shows a schematic diagram of small-scale columns, for which polycarbonate tubes with an internal diameter of 0.01 m and lengths of 0.1, 0.2, 0.3, and 0.4 m were used (Figure 5.5-middle). Plastic syringes were connected to either end of the columns, into which acid-washed glass wool (2 g) was placed to retain the media and prevent biofilm formation. The columns were positioned vertically and fixed in retort stands, with flow entering the bottom of the columns.

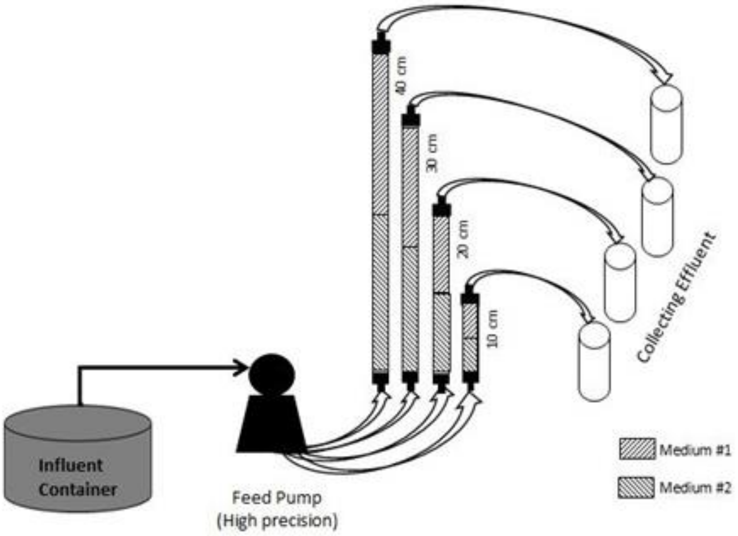


Figure 5.4. *Schematic diagram of small columns.*

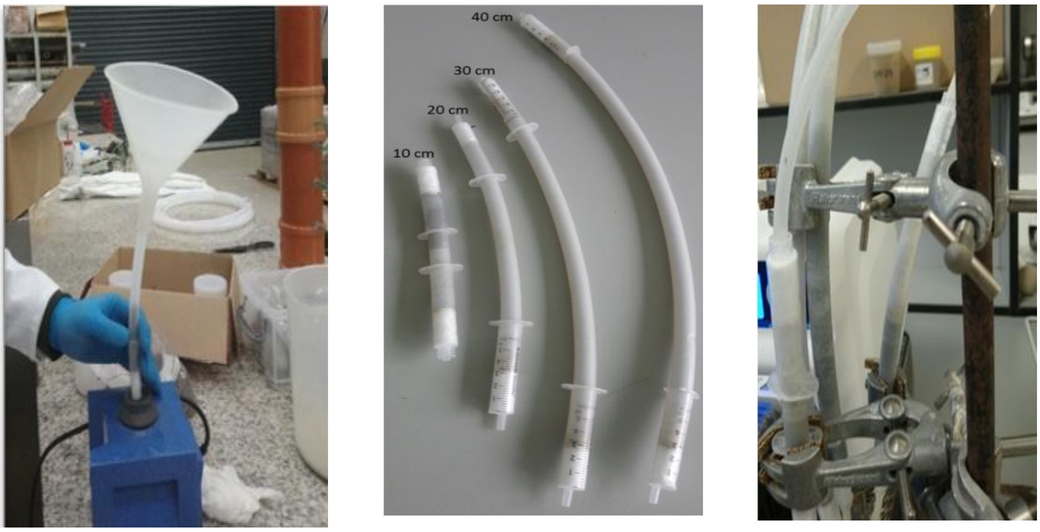


Figure 5.5. *Small-scale column set-up. Packing columns with media (left), small columns with different lengths (middle), fixing the columns to retort stand (right).*

As media configuration change made no difference to retention (Section 5.3.2), a single configuration was chosen i.e. zeolite over sand. To achieve a similar packing density to the large columns for each column length, a mass of 12.4, 24.9, 37.4 and 49.7 g of sand and 6.3, 12.7, 19.1 and 25.5 g of zeolite were used for the 0.1, 0.2, 0.3 and 0.4 m columns, respectively.

5.3.3. Operation of the filter units

Prior to the start of the experiment, potable water was pumped through the small and large columns to remove background concentrations of DRP and NH_4^+. When the outlet concentrations were < 0.01 mg DRP L^{-1} and < 0.01 mg NH_4-N L^{-1}, the experiment commenced. KH_2PO_4 and NH_4Cl were used to produce influent water for the large and small columns with concentrations of 1 mg DRP L^{-1} and 1 mg NH_4-N L^{-1}.

Peristaltic pumps were used to pump the influent water to the large columns at a HLR of 156 cm d^{-1}, which is similar to the HLR applied in onsite wastewater filtration systems (Hermann et al., 2013). The large columns were operated for 42 d, with the pumps operational for 5 h per day (Figure 5.6).

Figure 5.6. *Large scale column operation (left) and sampling (right) from 6 columns packed with sand and zeolite in different configurations.*

For operation of the small columns (Figure 5.7), influent water (1 mg DRP L^{-1} and 1 mg NH_4-N L^{-1}) was pumped into the base of the columns at a HLR 52.8 cm d^{-1} for 6 h per day. The HLR was chosen so as the median empty bed contact time (EBCT) of the small columns was similar to the large columns. The duration of the small column experiment was 11 d, which was the length of time over which both DRP and NH_4-N removals dropped below 100 %.

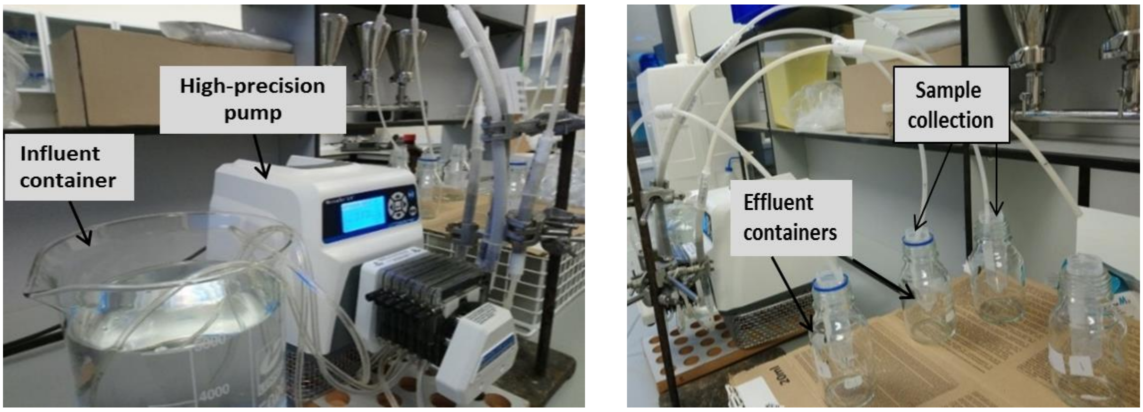


Figure 5.7. *Small scale columns operation (left) and sampling (right).*

5.3.4. Data collection and analysis

For both column scales, the influent (daily) and effluent (different time points) were sampled in 50 mL tubes and filtered immediately through 0.45 µm filters and analysed for DRP and NH_4-N within 24 h using a Thermo Konelab 20 analyser (Technical Lab Services, Ontario, Canada). During the first four days of operation of the large columns, the effluent was sampled after every bed volume. After reaching steady-state conditions (defined as the point at which the effluent concentration began to stabilise), sampling was increased to every 5 bed volumes for another 2 days, and later on increased to every 10 bed volumes. For the small columns, sampling was conducted every two hours. On each sampling occasion, two samples were taken from each column: a sample (5 ml) was taken directly from the effluent (marking the end of the 2-h period and compared with the influent daily concentration) and a sub-sample (50 ml) was taken from the total filtered volume in that 2-h composite period.

In order to model the effluent concentrations of nutrients leaving the large and small columns, the adsorption model of Callery and Healy (2017) was used, assuming that pseudo-second order kinetics was occurring for both nutrients (Zang et al., 2010; Jiang et al., 2013; Olgun et al., 2013; Sieczka and Koda, 2016; Riahi et al., 2017; Zhan et al., 2017; Wasielewski et al., 2018):

$$C_t = C_0 - [((A\,V_B^{(\frac{1}{B})} M))/VB] * [t/(t+K)] \qquad \text{[Eqn. 5.4]}$$

where C_t is the filter effluent concentration (mg L^{-1}), C_o is the influent concentration (mg L^{-1}); A, B and K are coefficients representing a constant of proportionality (mg g^{-1}), a constant of system heterogeneity (i.e. existence of multiple types of adsorption sites in the medium) (no units), and a time constant (min), respectively; V_B is the empty bed volumes of filtered solution (no units), M is the mass of adsorbent (g), V is the volume of filtered solution (L), and the empty bed contact time (min).

The coefficients (A, B, and K), determined from the small column study, were fitted using the Levenberg-Marquant algorithm via Solver in Excel to give the least error squared (ERRSQ) of difference between the predicted and the actual effluent concentrations. They were then applied to predict the effluent concentration of the large columns.

As the concentration of NH_4^+ effluent in the 0.2 to 0.4 m columns was zero during the early bed volumes of the experiment (i.e. 100 % retention was achieved initially), data for the modelling process was taken after 12 bed volumes for all column sizes. From this period onwards, the % retention in the columns dropped below 100 %.

5.3.5. Statistics

To assess if there were any differences in % of nutrient retention capacity based on media configuration in the large columns i.e. sand over zeolite or zeolite over sand, a z-test was conducted. A p value of < 0.05 rejected the null hypotheses i.e. no difference in terms of retention based on the configuration.

5.4. Results and discussion

5.4.1. Selection of media

The final selected media for the small and large column experiments were coarse sand sourced from the south west of Ireland with a high Fe content and natural Turkish (Yildizeli) zeolite (particle size 1-3 mm). Batch experiment results indicated that both the sand and zeolite had good DRP and NH_4^+ removals, and had good K_{sat} values for the column experiments (Table 5.2).

The sand had a q_{max} of 8.34 g DRP kg^{-1} with a binding energy, k, of 2.87 L mg^{-1} (Table 5.2). This q_{max} was higher than other sands commonly used in filter systems (e.g. Danish sands, which have 0.02 to 0.13 g DRP kg^{-1}; Fenton et al., 2008). Zeolite, which is an aluminosilicate mineral, also had good DRP retention, similar to the results of other studies (Lin et al., 2014; Ibrahim et al., 2015; Gérard, 2016).

Zeolite, used in the current study to target NH_4^+ removal, had an Al content of 12.8% (Table 5.2), which is within the range of commonly used filter P materials (i.e. 1.3 to > 40 %) (Cucarella and Renman, 2009). According to Penn et al. (2017), high Fe and Al content of a P-sorption material indicates ligand exchange (ion binding to a metal) as the main mechanism for DRP retention rather than precipitation, which would occur in high calcium content materials.

Zeolite had a q_{max} of 39.5 g NH_4-N kg^{-1} with a binding energy of 9.8 L mg^{-1} (Table 5.2). Various ranges of q_{max} for zeolite are found in the literature due to variations in country of origin and chemical element (Wasielewski et al., 2018) e.g. 15.3-25 g NH_4-N kg^{-1} (Langwald, 2008; Zhang et al., 2010; Kotoulas et al., 2019), 31.9 g NH_4-N kg^{-1} (Ham et al., 2018), and 40.3 g NH_4-N kg^{-1} (Ibrahim et al., 2015). These have resulted in 84 % to complete NH_4-N removal (99 %), depending on operational conditions such as influent concentration, temperature, pH, and adsorbent dosage.

Table 5.2. *Batch experiment and constant head data for maximum adsorption capacity of media (q_{max}; g kg^{-1}), binding energy (k; L mg^{-1}); and selected elemental composition based on XRF analysis of sand and zeolite used in the column experiments.*

	q_{max} (g kg^{-1})		k (L mg^{-1})		K_{sat} (m s^{-1})	Na	Mg	Al	Si	Fe	K	Ca	Ti	S	Mn	P
	DRP	NH_4-N	DRP	NH_4-N		% of total composition[1]										
Sand	8.34	0.6	2.87		7.41×10^{-4}	1.3	1.0	11.8	70.9	8.6	4.0	0.1	1.2	0.4	0.2	0.1
Zeolite	6.33	39.52	2.2	9.8	7.39×10^{-4}	-	1.3	12.8	70.0	2.8	7.4	4.3	-	-	0.1	-

[1] Na: Sodium; Mg: Magnesium; Al: Aluminium; Si: Silicon; Fe: Iron; K: Potassium; Ca: Calcium; Ti: Titanium; Su: Sulphur; Ms: Manganese; P: Phosphorus. Elements presented only for those having > 0.1% of total composition.

5.4.2. Retention of DRP and NH_4-N in the columns

For the large columns, the DRP retention was initially high at >95 % for the first two empty bed volumes, V_B, of filtered solution, and decreased gradually to 13 % after >100 L of filtered volume (43 V_B) (Figure 5.8). The configuration of the media did not affect DRP or NH_4^+ retentions ($p > 0.05$).

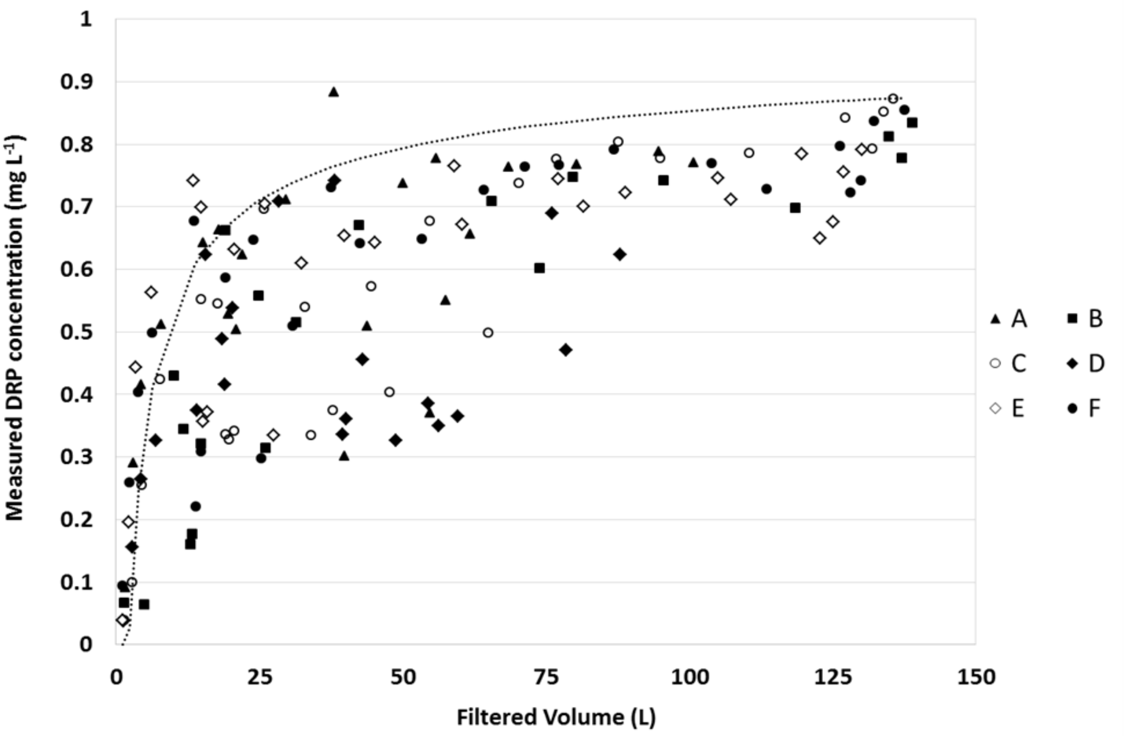


Figure 5.8. *Measured DRP concentration (y-axis) vs. filter volume (x-axis) for both configurations (sand over zeolite (A, B and C) and zeolite over sand (D, E, F)) of the large filter columns. The dashed line is the model fit using coefficients from small columns.*

One hundred percent NH_4-N retention was achieved for the first 25 L filtered volumes (11 V_B), but decreased to 80 % after 120 L filtered volumes (52 V_B) (Figure 5.9). Similar trends in NH_4-N retention using zeolite were also documented by other studies (Alshameri et al., 2014; Huang et al., 2015; Kotoulas et al., 2019). Clinoptilolite zeolite is known to be a very good ion-exchanger (Wasielewski et al., 2018), and a high adsorption rate has been associated with diffusion of NH_4-N ions (Huang et al., 2010) through macropores and mesopores to the surface of zeolite (Shaban et al., 2017).

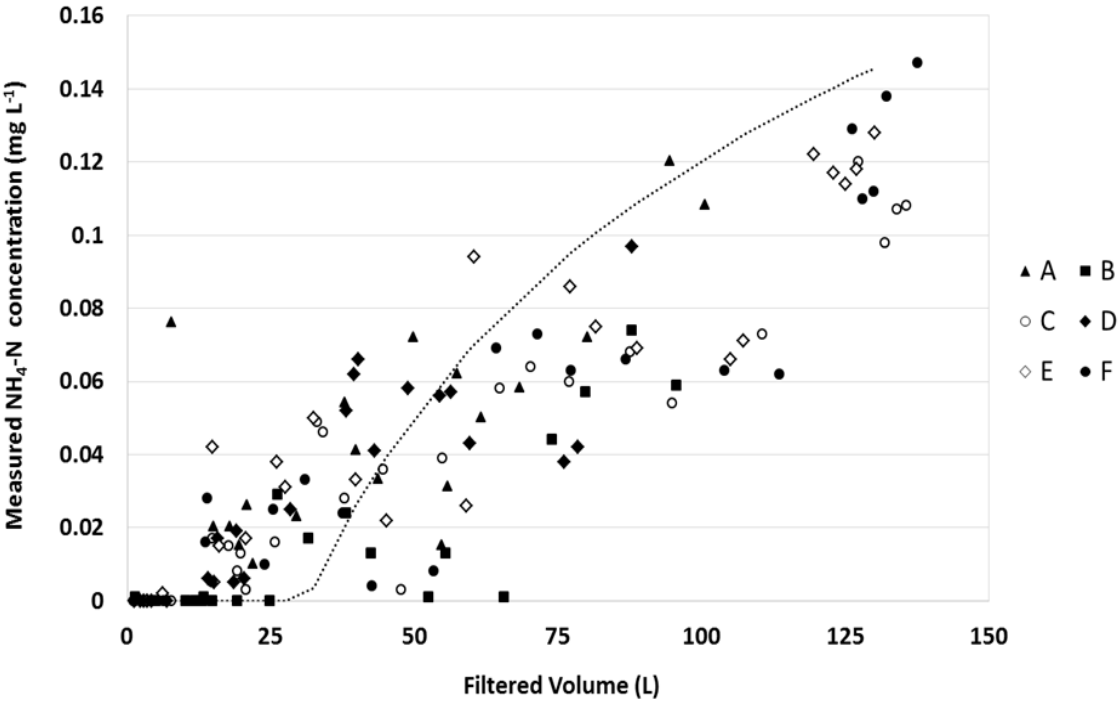


Figure 5.9. Measured NH_4-N concentration (y-axis) vs. filter volume (x-axis) for both configurations (sand over zeolite (A, B and C) and zeolite over sand (D, E, F)) of the large filter columns. The dashed line is the model fit using coefficients from small columns.

The small columns were P-saturated after 1L of filtered volume (V_B=50 for the 0.3 m column), whereas the NH_4^+ saturation of the columns took substantially longer to occur; the 0.1 m column was 80 % saturated after approximately 10 L filter volumes (V_B=1550) and duration of complete removal was related to the length of the column (Figure 5.10). Unlike many batch adsorption experiments and large-scale column tests examining the NH_4^+ removal efficiency of zeolite, RSSCTs operated under continuous loading of a few hours per day has never been investigated. However, the results here are in agreement with other studies, which showed a positive relationship between removal efficiency, mass of adsorbent and contact time (Kotoulas et al., 2019).

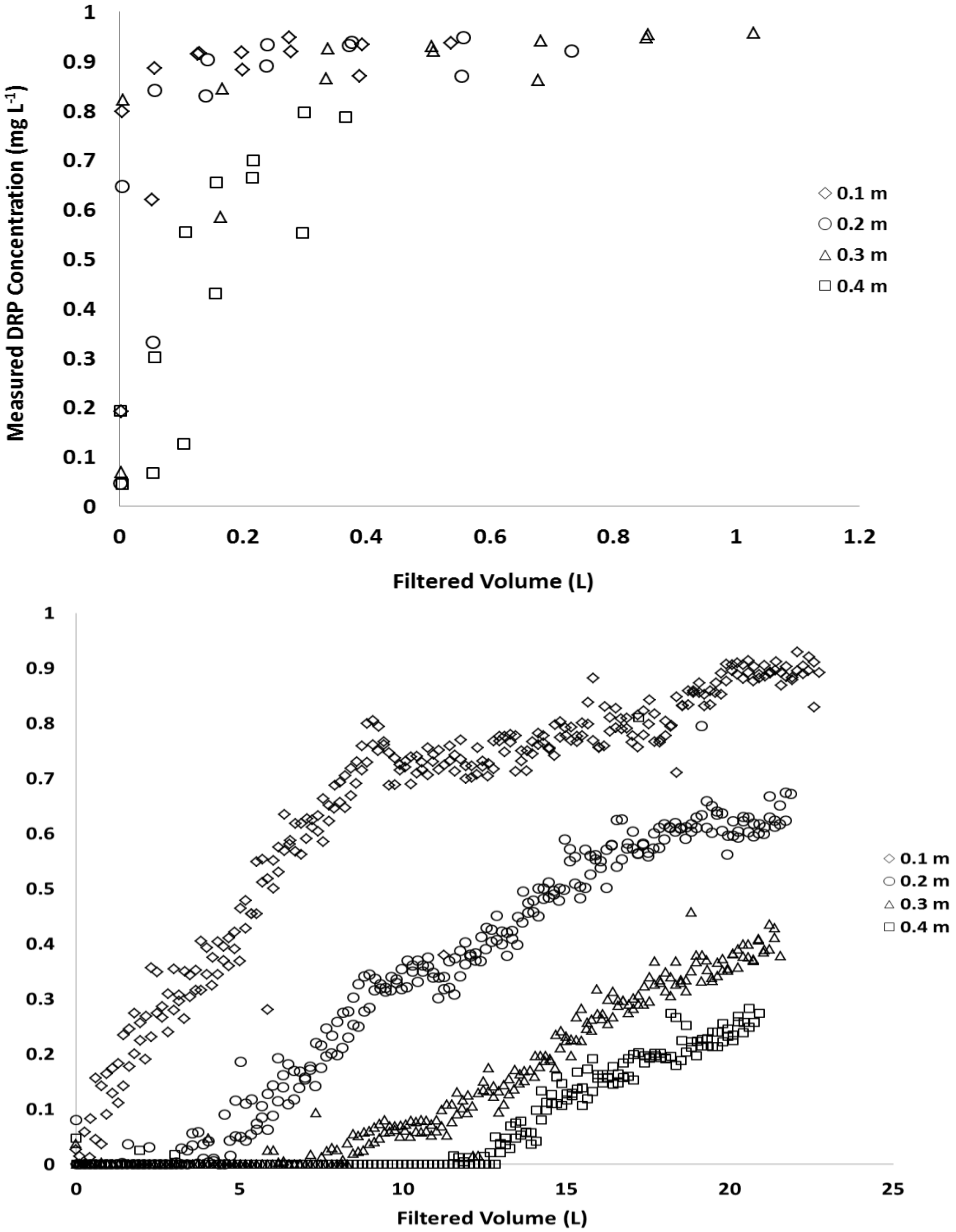


Figure 5.10. *Measured DRP (top) and NH_4-N concentrations (bottom) vs. filter volume from the small columns.*

5.4.3. Predicting DRP effluent concentration in large columns using scale column data

The model developed using the small column data (Table 5.3, ERRSQ=5.56) was able to predict DRP effluent in the large columns. Figure 5.8 superimposes the modelled data from the small columns onto the measured data from the large columns and Figure 5.11 presents the observed versus modelled data using coefficients from small column tests for each individual column and configuration.

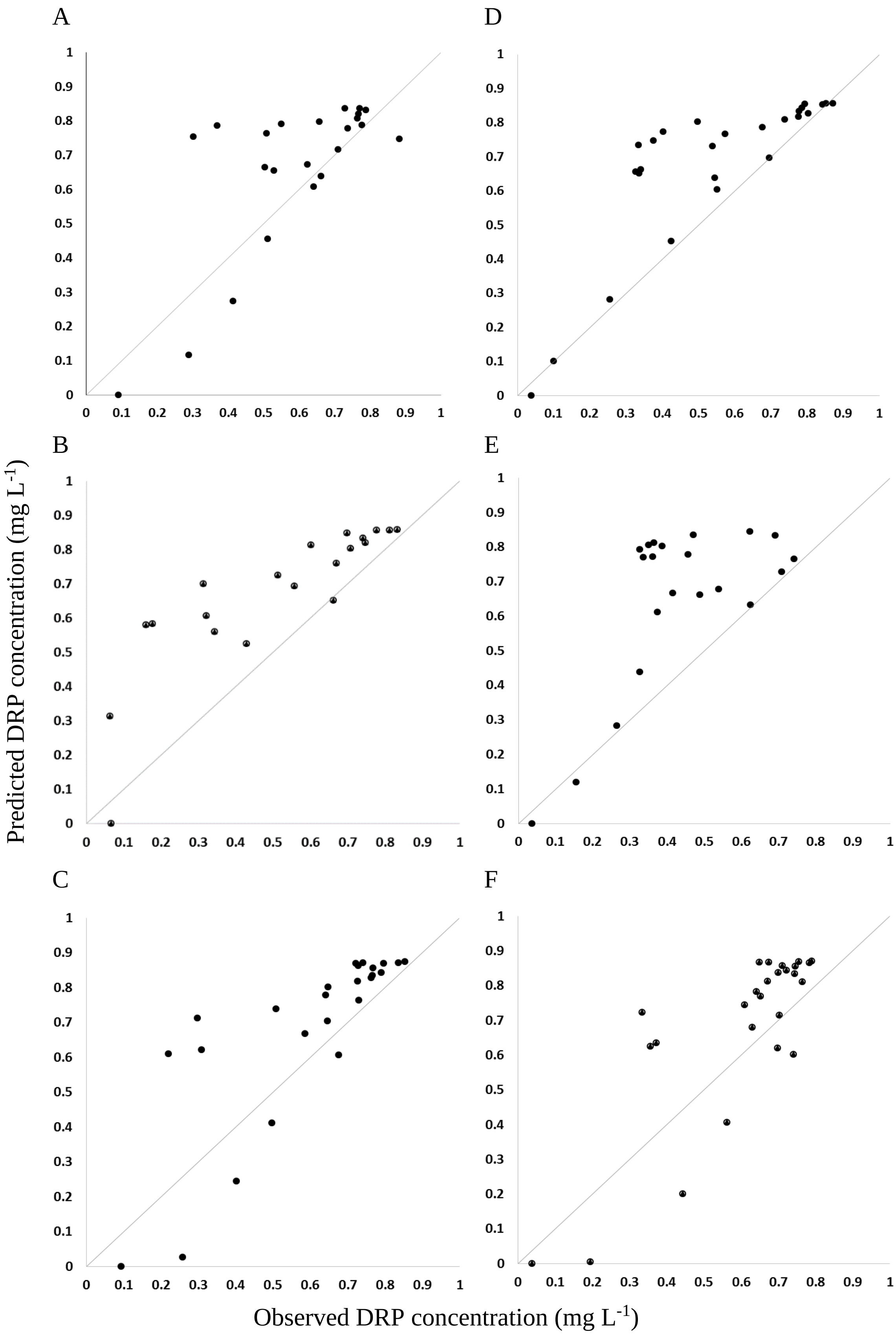


Figure 5.11. *Observed DRP concentrations versus predicted DRP concentrations. Configuration 1 (zeolite at the bottom, sand at the top) (A, B, C) and Configuration 2 (zeolite at the top and sand at the bottom) (D, E, F).*

The constant of heterogeneity, B, was a dominant coefficient in predicting effluent concentrations. This is indicative of potentially multiple adsorption mechanisms responsible for nutrient removal which can be explained by the fact that the model is predicting combined removal efficiency of two media with different elemental compositions (Table 5.2) which are packed into one filter column. According to Callery and Healy (2017), the curve produced by Eqn. 5.4, which is based on second-order kinetics, can indicate the importance of intraparticle diffusion (Ko et al., 2000) for model prediction within small columns at different lengths. This is shown in Figures 5.8 and 5.10 where the tailing of the breakthrough curve has likely been caused by intra-particle diffusion (Doekar and Mandavgane, 2015). This may become significant as the surface of the medium/media become saturated or as EBCT increases (Callery and Healy, 2017).

Table 5.3. *Comparison of model parameters, coefficients and ERRSQ values, obtained when (a) fitting Eqn. 5.4 to DRP concentration data from large columns using model coefficients determined from small columns, (b) parameters at different depths of small columns.*

Model Coefficients	**(a) Parameters determined using small column data**	**(b) Parameters at different lengths of small columns**			
		Small column depth (m)			
		0.1	0.2	0.3	0.4
A	0.03	280.56	447.05	206.32	669.24
B	2.13	18684.43	18681.93	18687.69	18682.58
K	901	897.99	846.75	972.76	877.25
ERRSQ	5.56	0.04	0.04	0.08	0.052

A: Constant of proportionality
B: Constant of system heterogeneity
K: Constant of time

5.4.4. Predicting NH_4-N effluent concentration from large columns using small columns

Complete NH_4-N removal was observed during the initial operational period of the large and small columns, which is consistent with other studies (Balci and Dince, 2002; Sharifnia et al., 2016; Mazloomi and Jalali, 2016; Kotoulas et al., 2019). Consequently, the small columns were operated for a longer period of time (11 d in total) to generate enough data for the successful prediction of NH_4-N effluent concentrations leaving the large columns.

Eqn. 5.4 predicted the behaviour of the filters in retaining NH_4-N (Figure 5.9) and Figure 5.12 presents observed versus modelled data using coefficients from small column tests for each individual column. The constant of heterogeneity in NH_4-N adsorption, B, was less than DRP (Table 5.4), which may be due to the fact that zeolite was the only medium in the columns capable of NH_4-N retention (and not sand as observed in the batch experiment). However, the high K values indicate that the adsorption rate did not follow a linear regression with filter depth, as initially proposed by filter bed depth service time (BDST) (Hutchins, 1973) which has been used by many adsorption studies. The BDST model assumes that intraparticle diffusion is negligible (Ayoob and Gupta, 2007) which becomes an important factor as a medium's surface becomes more saturated (Doekar and Mandavgane, 2015; Callery and Healy, 2017).

The proposed model in this study is therefore describing a real-world adsorption system in which several factors control the adsorption (Crini and Badot, 2010), meaning that larger amounts of media and increased contact time may not produce directly proportionally higher adsorption. A similar lack of proportionality between the length of columns (amount of adsorbent) and increase in NH_4-N retention has been reported by Sarioğlu (2004).

Although the experiments were carefully designed to provide similar environmental conditions for all columns, there was a small difference between data generated from various large scale columns. In order to avoid any bias, the average effluent data was calculated to generate model parameters.

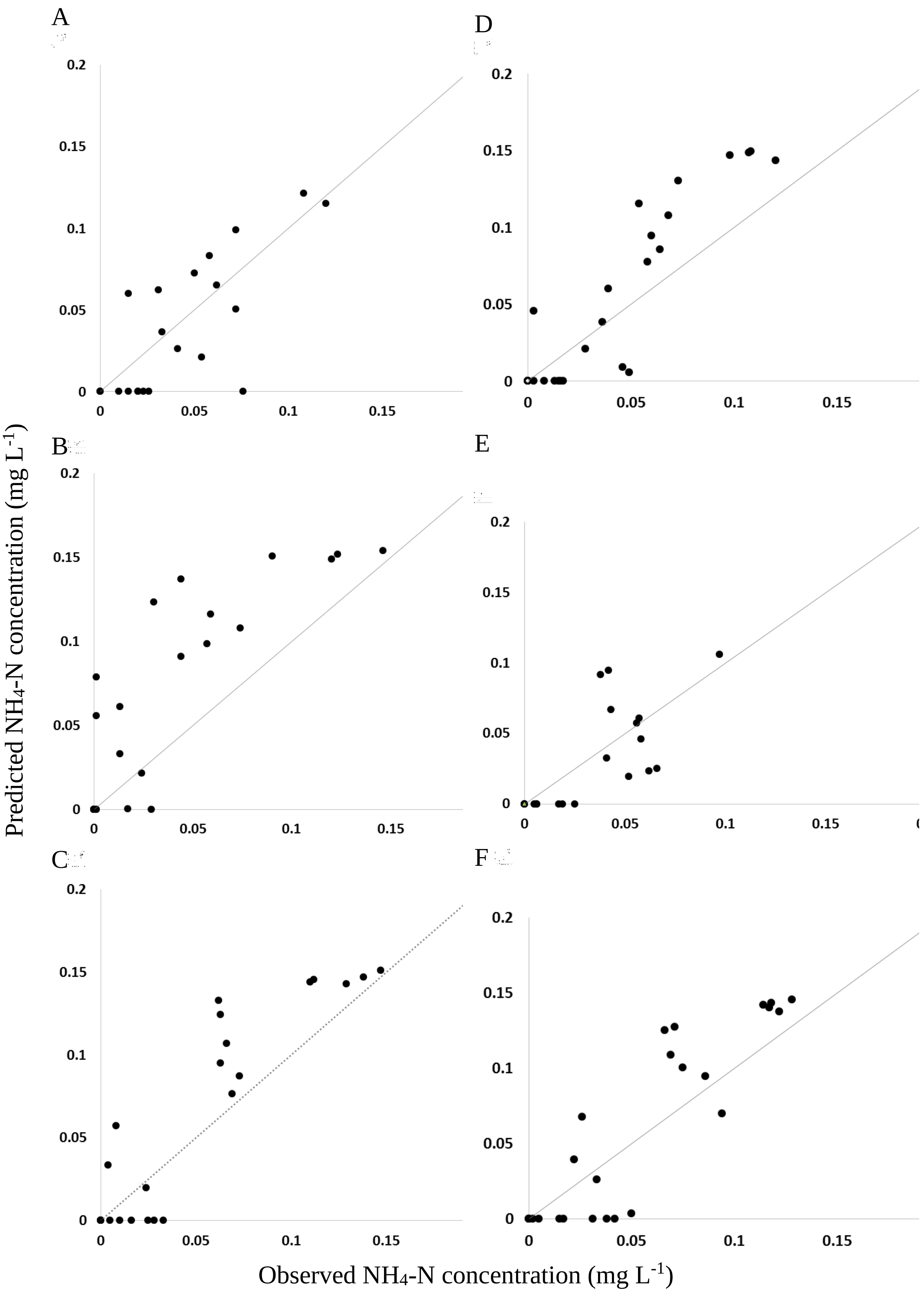


Figure 5.12*. Observed NH_4-N concentrations versus predicted NH_4-N concentrations. Configuration 1 (zeolite at the bottom, sand at the top) (A, B, C) and Configuration 2 (zeolite at the top and sand at the bottom) (D, E, F). Black centres- small-scale columns*

Table 5.4. *Comparison of model parameters, coefficients and ERRSQ values, obtained when (a) fitting Eqn. 5.4 to* NH_4*-N concentration data from large columns using model coefficients determined from small columns, (b) model parameters at different depths of small columns.*

	(a) Parameters determined using small column data	**(b) Parameters at different lengths of small columns**			
		Small column depth (m)			
Model coefficients		0.1	0.2	0.3	0.4
A	0.057	0.051	0.048	0.11	0.11
B	1.13	1.13	1.10	1.04	1.04
K	1961.61	1961.61	1961.61	1961.63	1961.60
ERRSQ	0.13	0.11	0.12	5.23	1.75

A: Constant of proportionality
B: Constant of system heterogeneity
K: Constant of time

5.4.5. Implications of study for drainage filters

To date, large-scale columns have been mainly used to estimate nutrient saturation and longevity of media to replicate operational conditions (Peyne et al., 2014; Lopez-Ponnada et al., 2017; Monrabal-Martinez et al., 2017). However, moving from large-scale columns to RSSCTs would gain financial and labour advantages, whilst not sacrificing the accuracy of model outcomes. This may include considerable savings on: time required for constructing and operating the columns, labour hours and number of staff required, space required to house the structure and experimental set up, number/capacity of containers, amount of influent (chemical and distilled water), procurement of adsorbent(s) (media) and sampling equipment e.g. tubes, syringes, filter pours; number of pumps, cost of laboratory analysis of water samples; and overhead costs, including electricity and light.

The results of this study validated the model, showing that it could upscale RSSCTs accurately to describe the pattern of large-scale column performance. However, it is important to design the experiment carefully so as the media becomes saturated over the duration of the experiment. In the current study, the modelling parameters of Eqn. 5.4 were incapable of modelling NH_4-N in the filter effluent in the large columns until the retention of NH_4-N in the small columns dropped to below 100%.

5.5. Conclusions

In this study, rapid small-scale column tests were used to predict effluent DRP and NH_4-N concentrations from much larger columns with good accuracy. As large-scale laboratory filter column tests are time consuming and expensive, but are considered to replicate in-field conditions well, the methodology used in this study will save operational, financial and labour costs, whilst providing accurate model predictions of DRP and NH_4-N. Future work should consider modelling biological N systems, where adsorption is not the dominant removal mechanism and the structure if filled with a C-sourced media e.g. in woodchip-based systems that convert nitrate to di-nitrogen.

5.6. Summary

This chapter is summarised in the following bullet points:

- Small-scale filters were used to generate data to model P and N removals in much larger scale filters.
- Models derived from small-scale column tests predicted DRP and NH_4-N concentrations leaving large-scale columns with great accuracy.
- The order of packing the media did not influence adsorption or modelling outcomes.
- Moving to small scale tests provides operational, financial and labour savings and facilitates developing design criteria of an in-ditch engineered structure filled with media.
- Simultaneous modelling of DRP and NH_4-N was based on second-order kinetics.
- Future research should focus on modelling of biological N transformations.

The next chapter looks into ditch characterisation and P losses in the open ditch network at the study site. This would enable identification of “hot spot” areas without natural attenuation and therefore suitable locations for the installation of engineered structures.

Chapter 6

Impact of P inputs on source-sink P dynamics of sediment along an agricultural ditch network

6.1. Overview

This chapter investigates the retention and mobilisation of P along the open ditch network of the study site, establishes connectivity between the ditch and source of pollution, and identifies the best location for placing an in-ditch engineered structure filled with media.

The contents of this chapter have been published in the Journal of Environmental Management:

Ezzati, G., Fenton, O., Healy, M.G., Christianson, L., Feyereisen, G.W., Thornton, S., Chen, Q., Fan, B., Ding, J., Daly, K., 2020. Impact of P inputs on source-sink P dynamics of sediment along an agricultural ditch network. Journal of Environmental Management, 257, 109988. https://doi.org/10.1016/j.jenvman.2019.109988

6.2. Introduction

Diffuse and point-source nutrient pollution from agriculture results in degradation of water quality (Sutton et al., 2011), including loss of aquatic biodiversity (FAO, 2011) and ecosystem services (Schindler et al., 2010). Incidental and legacy P losses from agriculture to water (Haygarth et al., 2005) are major sources which contribute to eutrophication (Verheyen et al., 2015). The European Union Water Framework Directives (OJEC, 2000) sets a target to achieve at least "good" status in all water bodies by 2020 and member states must implement POM to minimise point and diffuse P losses (Kronvang et al, 2007; Sharpley, 2016; Macintosh et al., 2018; Melland et al., 2018). For example, in Ireland the Nitrates Directive has been implemented as a baseline set of measures to protect water bodies from nutrient and sediment loss. However, legacy P stores which are stored over decades of excessive P applications are difficult to mitigate and therefore further measures are needed to tackle such losses (Sharpley et al., 2013; Vadas et al., 2005; Fiorellino et al., 2017). Typically, water infiltrates into soil and interacts with legacy P stores along the transfer continuum. This water often discharges to drainage ditches which may act as corridors for nutrient movement (Needelman et al., 2007). However, concentrations of dissolved P in these networks may change due to dilution, direct discharges from pipes connected with a source, or as a result of sediment chemistry.

Clagnan et al. (2019) examined the connectivity of surplus nutrients lost from intensive dairy systems to adjoining ditch networks and found elevated DRP at all sampling locations. Moloney et al. (2020) classified the on-farm ditch networks according to P loss risk and concluded that the risk was attributed to connectivity of the farm yards to ditches as well as legacy P stored in the sediment. There is a constant interplay between dissolved P in water and bankside-sediment/sediment chemistry in which physiochemical properties such as Al, Fe, calcium carbonate, clay, pH and OM, which enable mobilisation or immobilisation of P along the transfer continuum (Thomas et al., 2016). Shore et al. (2016) classified drainage ditch networks based on physical and chemical attributes such as Fe, Al, and Ca contents, with ditch maintenance that includes both removal and leaving vegetated sections being key to aid attenuation along ditch networks (Haggard et al., 2004; Smith et al., 2005).

The challenge for catchment managers and water policy is determining where these measures should be carried out. In addition, a synoptic view of the role of bank side and soil-sediments in the retention and mobilisation of P along these networks has shown that subsurface horizons rich in Al could attenuate P or make it less soluble (Daly et al., 2017). Therefore, a ‘right measure, right place’ approach to drainage measure implementation could be effective (Delgado and Berry, 2008; Dollinger et al., 2015; Daly et al., 2017). According to Haggard et al. (2004), sediments are spatially heterogeneous and can act as temporary stores of P or a transient storage pool that may be released back into water depending on in situ conditions. Smith et al. (2004) investigated the transient nature of P stored in ditches and found that sediment physiochemical properties affect ditch capacity to become a source, sink or regulator of DRP in ditch water. Hence, characterisation of ditch networks and closer monitoring of mobilisation of P is important in terms of their influence on the potential for nutrient losses to water (Kurz et al., 2005) and ditch management e.g. cost-effective installation of an in-ditch P sorbing structure requires demarcating hotspots of P loss whilst avoiding natural attenuation areas (Penn et al., 2007).

There is a lack of basic understanding of how a ditch network functions as a natural attenuation area both laterally and vertically, with no studies considering how this changes along the network. Therefore, the primary objective of the current study was to identify optimal locations for implementing mitigation measures along an agricultural ditch, by examining the source-sink dynamics for P along a ditch network. This was done by examining high resolution spatial trends of P retention and mobilisation in bankside sediment and ditch basal sediment along a ditch connected to an intensive dairy farm, and to couple this signature with spatial and temporal dissolved reactive P trends. The connectivity between surface (runoff) and subsurface (groundwater and artificial drainage system) flow pathways was established, and extensive field and laboratory work was conducted to elucidate bankside and sediment and water characteristics at key sampling locations along the ditch network. This was used to evaluate the potential of the ditch becoming a P source for drainage water. Finally, the equilibrium P concentration of the sediments was investigated to study their dynamics with water.

6.3. Materials and methods

6.3.1. Site description and identification of sampling locations

The Johnstown Castle catchment, delineated in Figure 6.1, and presented in detail in Chapter 3, contains an intensive dairy farm (190.4 ha). Due to its glaciated origins, soils at the site are heterogeneous, varying in drainage class from well to poorly drained soils (saturated hydraulic conductivity ranges from 0.0001 to 0.029 m d^{-1} (Jahangir et al., 2013)). The grassland areas of the site consist of poorly and imperfectly drained gleys to well drained silty clay loam (topsoil) and dense gravels intermixed with clay at 0.6 to 10.0 m subsoil geology.

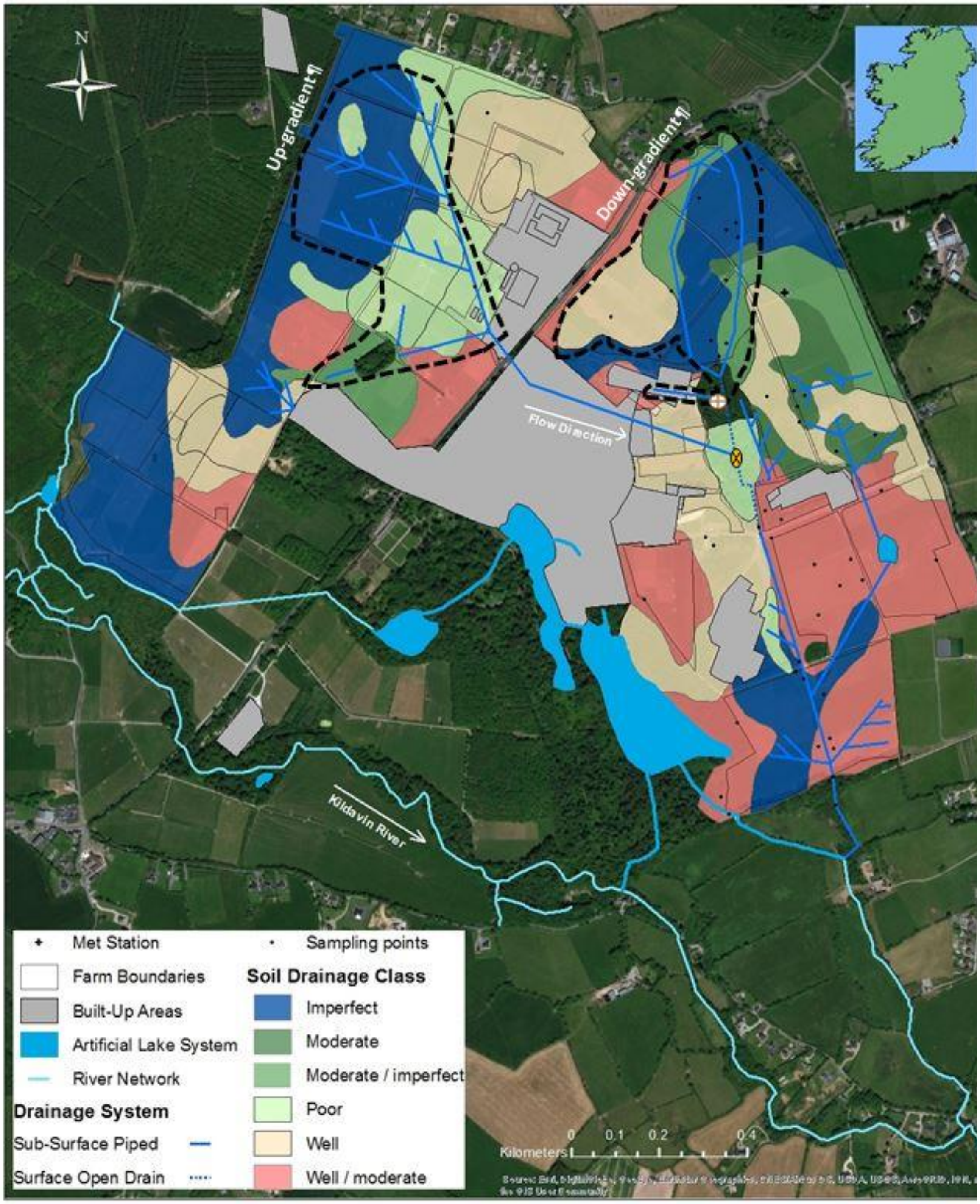


Figure 6.1. *Johnstown Castle Intensive Dairy farm showing the up-gradient and down-gradient surface/subsurface drainage system and runoff areas and their entry point into the open ditch system, soil drainage class, and sampling points across the farm documented by Kurz et al. (2005) and Clagnan et al. (2019).* ⊗ *No.1 ;* ⊕ *No.2*

In poorly drained areas, an artificial drainage system has been installed and in-field drains discharge into a ditch network with high connectivity to the surrounding landscape. The total length of the drainage system within the catchment boundary is 10.25 km, comprising 1.01 km of ditches with drains installed at approximately 1.2 to 2.9 m depth. The main ditch within the farm (Figure 6.2) is 850 m in length and runs parallel to the farmyard (Figures 6.3 and 6.4). This ditch starts with a shallow depth of 30 cm and gradually gets deeper to 270 cm, with 20 m AOD change in elevation, and is the focus of this current study.

Figure 6.2. *Main open ditch network at high flow (left) and low flow (right).*

Figure 6.3. *Farm yard housing dairy cows. Johnstown Castle.*

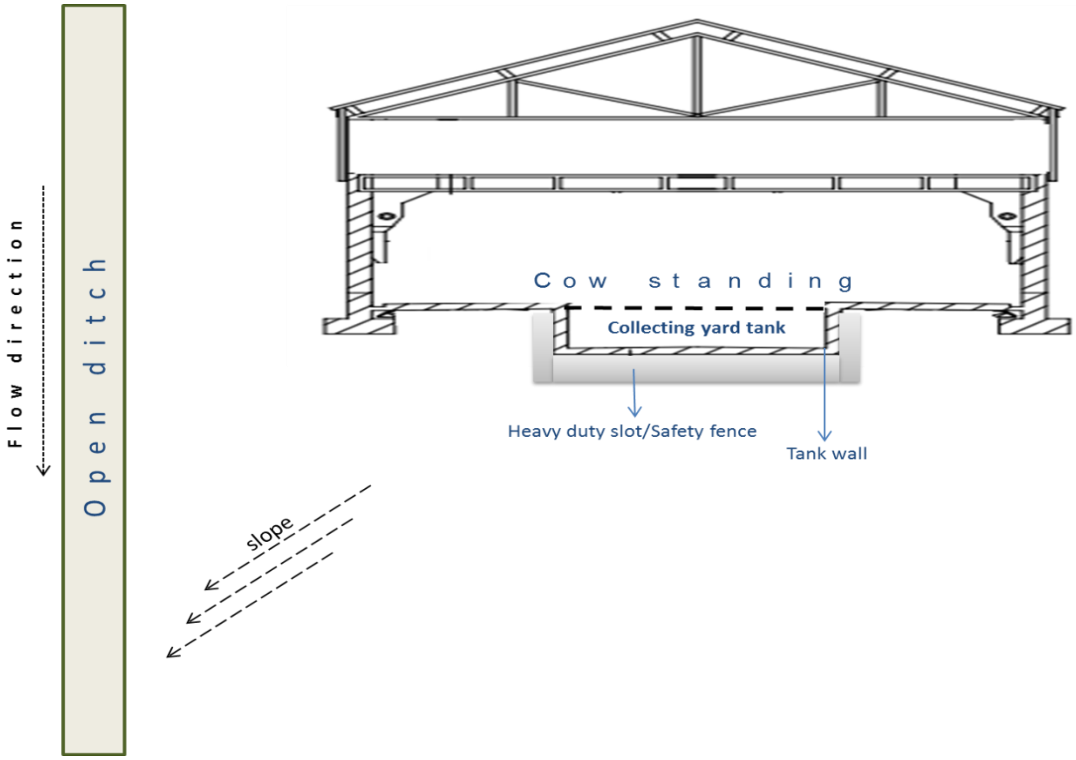


Figure 6.4. *Simple diagram showing the open ditch and the storage facility underneath the farmyard for collecting slurry and DSW.*

In terms of runoff and sub-surface drainage, an area of 94 ha (Kurz et al. 2005), including of an up-gradient (24 ha) and down-gradient (70 ha) (Figure 6.1), contributes to discharges entering the ditch through concrete pipes at No 1 and 2 (Figure 6.5). The down-gradient contribution area enters the ditch at No 2 and is represented by the sampling point A. The up-gradient area (Figure 6.1) enters the ditch at No 1. Other sources of water into the ditch stem from direct rainfall or groundwater. A groundwater well between the ditch and the farmyard (Figure 6.5, Well 2 total depth of ~ 5 bgl) indicates an average water table height of < 1 m bgl with a hydraulic gradient of 0.5, indicating discharge to the ditch through the bankside subsoil horizons and through the base of the ditch.

Figure 6.5 shows the groundwater elevation in the area of the ditch with contour beside the farm yard running perpendicular to the flow of the ditch. This places the water-table at 1 m below the farmyard which interacts with the depth of the concrete slurry storage

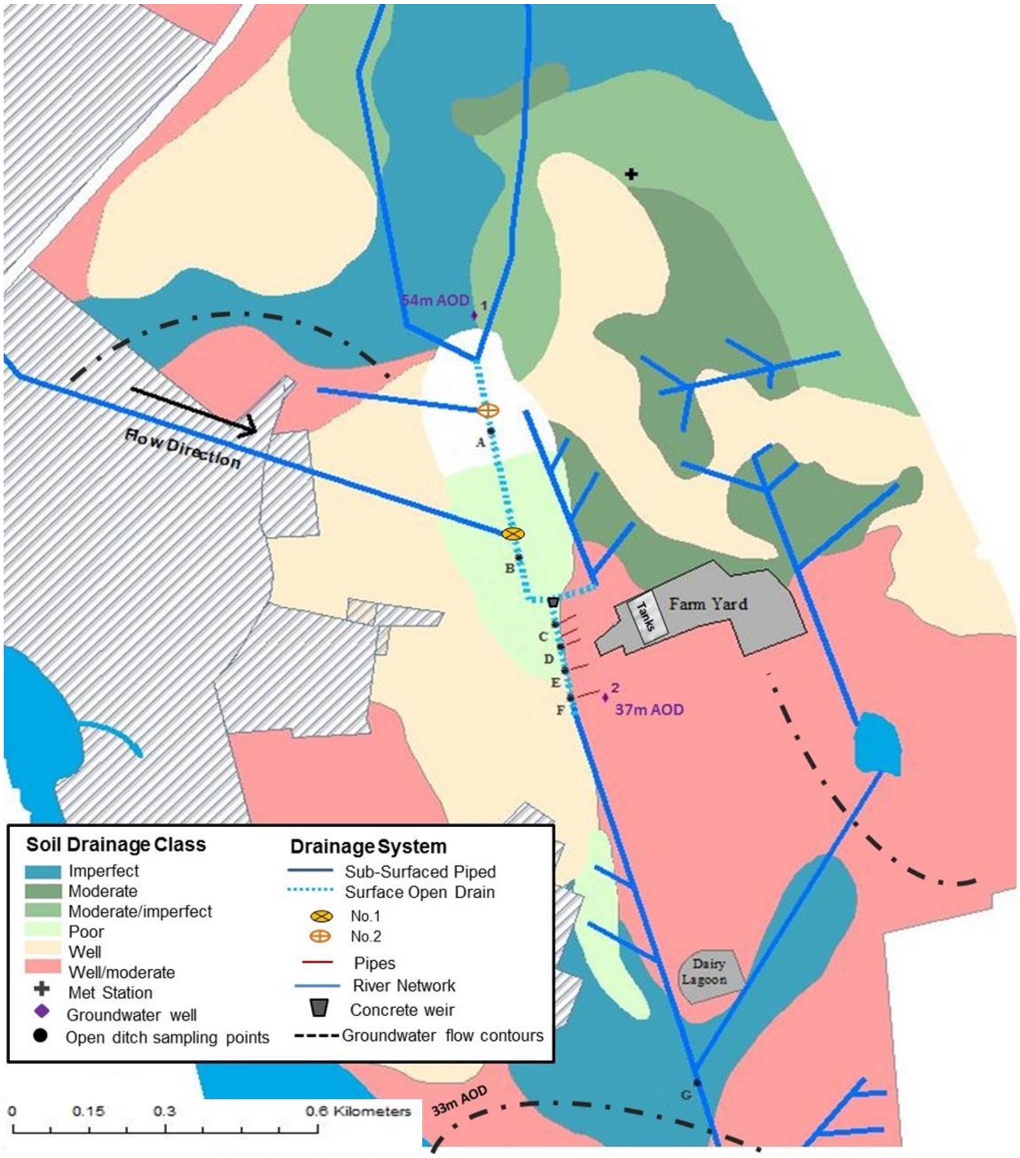


Figure 6.5. *In ditch grab water and soil-subsoil-sediment sampling points (Sites A-G). Position of farmyard, entry points of up-gradient and down-gradient discharge to the ditch (⊗ No.1; ⊕ No.2), position of pipes discharging directly into the ditch and water table height (m AOD) around the ditch network. Groundwater flow is perpendicular to groundwater contours i.e. into ditch.*

facilities. On the opposite side of the ditch poorly drained soils have not been artificially drained and are presently out of production. Based on their connectivity and landscape position, Moloney et al. (2020) identified agricultural ditches as being high risk areas of P loss on Irish farms. At the Johnstown Castle site, water quality and P dynamics of bankside and sediment samples along the length of the ditch were collected to provide a detailed appraisal of the impacts of sources entering the ditch. Seven sediment and water sampling points (Sites A, B, C, D, E, F, G in Figure 6.4) along the ditch network were selected for sample collection.

6.3.2. Bankside and sediment sampling and analysis

Sediment samples from the bankside and base locations of the ditch were collected in October 2017. Grass and plants were removed and the bankside profile was sampled at depth intervals of 30 cm from top to base (Figure 6.6).

The number of samples collected at each sampling points varied according to the depth of the ditch along the total length and are listed as follows: A: 1; B: 3; C: 4; D: 4; E: 8; F: 10; G: 9. Location-Code represents the depth interval number (e.g. A1 as shown in Table 6.2 and 6.3). Similarly, sediments from the base of the ditch were collected at the same location as bankside samples. Figure 6.7 shows the collected samples with a range of different colours indicative of different elemental composition (chemistry) of individual samples.

Figure 6.6. *Bankside sampling with 30 cm intervals (left) after removing grass and plants (right).*

Figure 6.7. *Collected bankside and sediment samples.*

6.3.3. Soil Chemistry analysis

All sediment samples were oven dried (40°C) and sieved (2 mm) to remove stones and debris, and were stored at room temperature prior to analysis. The modified Mehlich 3-P (M3P) method (Mehlich, 1984) was used to determine labile extractable P, Al, Fe, Ca using a soil solution ratio of 1:10 in Mehlich 3 reagent (0.2M CH_3COOH + 0.25MNH_4NO_3+ 0.015M NH_4F + 0.13M HNO_3+0.001M EDTA). Two grams of samples were shaken on a reciprocating shaker (Figure 6.7) for 5 min and the supernatant was filtered (Figure 6.8) to determine concentrations of labile extractable P, Al, Fe and Ca. Sediment pH was analysed on 2:1 soil-water ratio and OM was measured based on loss-on-ignition of 4 g of samples at 500ºC (Schulte, 1995) (Figure 6.8).

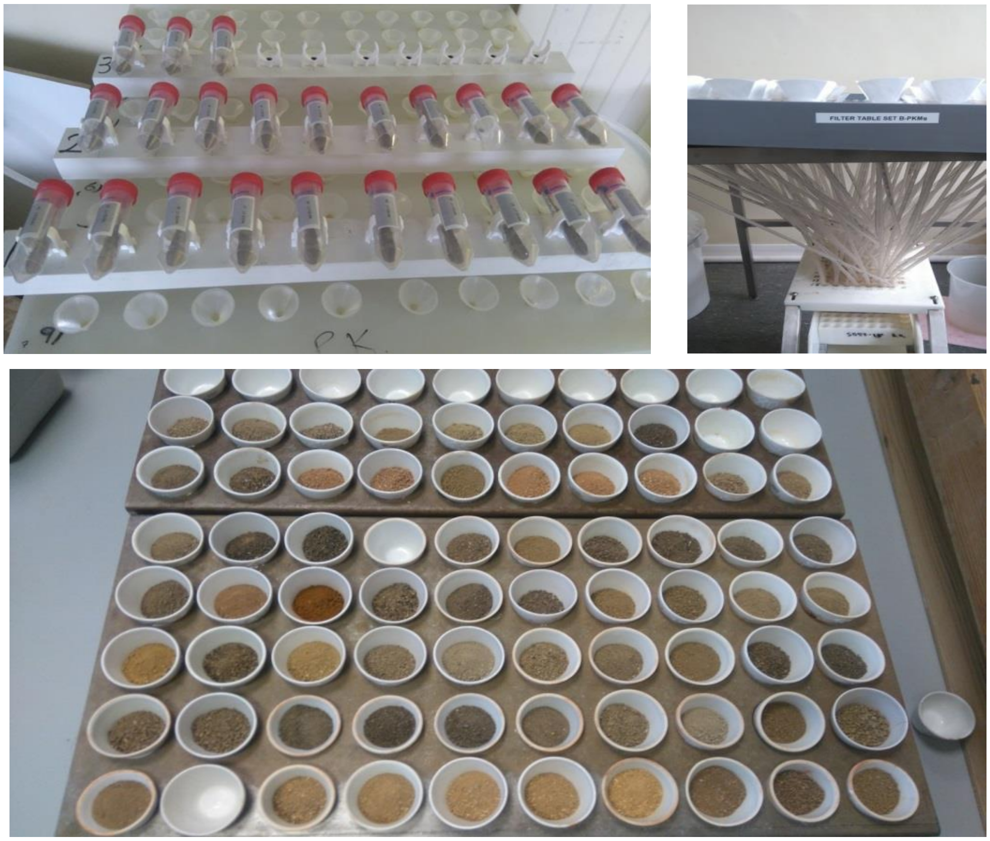


Figure 6.8. *Reciprocating shaker and filtration of samples in Mehlich-3 test (top) and measuring organic matter of samples in crucibles after ashing in the oven (bottom).*

6.3.4. Phosphorus sorption isotherm and equilibrium P concentration

The P sorption properties of the bankside and sediment samples were described by a P sorption isotherm derived for all locations and depths along the ditch. Sediment samples from the bankside and base locations were equilibrated with six solutions with concentrations of 0, 5, 10, 15, 20 and 25 mg P L^{-1} (Paulter and Sims, 2000). Analyses were carried out in duplicate by adding 30 ml of initial P solutions to 2 g sediment in 50 ml centrifuge tubes. The tubes were shaken on an end over end shaker at room temperature for 24 h, centrifuged and filtered, and the final concentration of P in solution was measured colorimetrically. The difference between initial concentration and final equilibrium P concentration was calculated as P sorbed to the soil. The linear form of the Langmuir isotherm equation was fitted to the sorption data as follows:

$$C/_S = 1/_{S_{max}} * k + \ C/_{S_{max}} \qquad \text{[Eqn. 6.1]}$$

This equation was used to derive the maximum sorption capacity (S_{max}; mg kg^{-1}) and k (L mg^{-1}), the constants related to the P binding energy in sediment.

The P sink/source dynamics of bankside and sediment samples was described the equilibrium P concentration (EPC_0) which represents a solution P concentration at the sediment-water interface where P is neither sorbed nor released. This parameter is often used to describe the role of sediment in freshwater systems in regulating P concentrations where sediment will adsorb/desorb P in order to reach a target P concentration at equilibrium, or EPC_0. If EPC_0 measured in sediment is higher than freshwater DRP, the sediment will release P to the water column in order to reach that equilibrium solution P concentration. If the sediment EPC_0 is lower than surrounding DRP, this favours net P adsorption from water into sediment in an effort to maintain a lower P concentration in solution at equilibrium (McDowell et al., 2015). The EPC_0 in bankside and sediment samples collected along the ditch was measured using 1g sediment equilibrated with 20 ml of solution P concentration of 0, 0.1, 0.25, 0.5, 1 mg L^{-1} and shaken at room temperature for 24 h, centrifuged and filtered through 0.45 µm filters to measure the concentration of P in solution measured colorimetrically (Murphy and Riley, 1962). The EPC_0 was calculated from the slope of the linear plot of P sorbed on the solid phase against final solution P concentration.

6.3.5. Data treatment

Statistical analyses were carried out using R-Programming Language. The Null-hypothesis for all tests was considered to have no variance and no difference between groups and p-value of 0.05 was used to accept or reject hypothesis.

6.3.6. Ditch water sampling and analysis

Grab water samples from sampling points A to G (Figure 6.5) were collected from January 2017 to July 2018. Filtered (0.45 µm) water samples were collected in 50 ml tubes and analysed for DRP using colorimetric analysis (Aquachem600 Labmedics Analytics, Thermo Clinical Labsystems, Finland) and digested with acid persulphate to determine total dissolved P (TDP). Unfiltered samples were analysed for total reactive P (TRP) using colorimetry (Aquachem) and PP was calculated by subtracting TDP from TP. Additionally, ditch water at each location was pumped to a flow cell connected with an in situ Multiparameter Probe (In Situ Inc. Ltd., USA) to measure temperature, electrical conductivity (EC), RDO, and pH under steady-state conditions.

6.4. Results and discussion

6.4.1. Trends in water quality along the open ditch

Table 6.1 presents summary statistics of DRP, TP, PP, and TRP across sampling points for the sample period January 2017 to July 2018. The distribution of these data is shown as boxplots in Figure 6.9. Values of DRP and TP at sample points A to C were lower in comparison to values recorded further downstream from D to G. Average DRP and TP values between A and C were 0.042 and 0.168 mg L^{-1}, respectively, and increased to 0.237 mg DRP L^{-1} and 0.48 mg TP L^{-1} between D and G.

A step change in P concentrations was observed at sample point D indicating a point source contribution possibly due to inputs from the farmyard located between sampling points D and E. Field work during the present study identified several pipes directly discharging (odorous) into the ditch from the farmyard area and these were also tested when running water discharged from the pipes and recorded DRP concentrations ranging from 0.011 to 0.093 mg L^{-1} and TP ranging from 0.027 to 1.72 mg L^{-1} (red straight lines between farmyard and ditch in Figure 6.3).

The results at point E are indicative of direct discharges from the farm yard as evidenced by maximum DRP and TP of 2.976 mg L^{-1} and 4.89 mg L^{-1} respectively. Downstream from D, these parameters remained high and increased along the length of the ditch with highest mean DRP at F (0.434 mg L^{-1}) almost 10 times higher than A and twice that

***Table 6.1**. Summary statistics of phosphorus concentrations and biogeochemical data for sites A-G in the ditch during January 2017-July 2018.*

Sampling Location	**Sample size**	**DRP**	**TP**	**PP**	**TRP**	**pH**	**Temp**	**EC**	**RDO**
		mg L^{-1}					℃	µS cm^{-1}	mg L^{-1}
A	10								
Max		0.120	0.227	0.227	0.052	8.44	12.99	471.1	10.67
Min		0.020	0.014	0.004	0.021	6.86	8.06	251.9	9.12
Mean		0.041	0.080	0.077	0.037	7.26	9.873	364.1333	9.99
Median		0.030	0.053	0.042	0.038				
B	10								
Max		0.088	0.110	0.110	0.093	7.27	10.07	388.8	9.64
Min		0.008	0.009	0.009	0.019	5.95	9.03	366.9	8.93
Mean		0.036	0.051	0.031	0.043	6.82	9.3	375.3	9.24
Median		0.019	0.053	0.013	0.040				
C	18								
Max		0.114	0.330	0.284	0.090	8.2	12.58	426.7	12.56
Min		0.021	0.028	0.005	0.025	6.97	7.92	236.7	8.21
Mean		0.054	0.087	0.066	0.045	7.23	9.625	348.5	10.18
Median		0.043	0.055	0.040	0.039				
D	10								
Max		0.610	2.290	0.318	1.210	7.56	12.6	423.8	10.75
Min		0.047	0.031	0.005	0.048	6.9	9.16	342	8.98
Mean		0.228	0.536	0.135	0.363	7.183	11.31	392.9	9.86
Median		0.123	0.156	0.100	0.132				
E	16								
Max		2.976	4.890	0.180	2.980	8.6	14.93	720	11.7
Min		0.008	0.017	0.001	0.007	6.34	7.99	252	8.89
Mean		0.272	0.536	0.036	0.432	7.32	11.14	466.1	10.28
Median		0.031	0.086	0.010	0.071				
F	18								
Max		1.258	1.320	0.784	1.230	8.6	14.88	560.8	10.86
Min		0.027	0.034	0.003	0.025	7.05	9.15	346.2	9.98
Mean		0.434	0.537	0.096	0.451	7.56	11.58	423.2	10.56
Median		0.147	0.165	0.058	0.167				
G	18								
Max		2.759	4.290	0.234	2.781	9.24	12.61	632.1	11.9
Min		0.004	0.016	0.000	0.025	6.98	8.22	233.2	8.09
Mean		0.220	0.242	0.037	0.225	7.90	9.51	385.06	10.102
Median		0.062	0.105	0.005	0.094				

Temp: Temperature; EC: Electric conductivity; RDO: Rugged dissolved oxygen.

recorded at E. Maximum DRP values recorded at F of 1.258 mg L^{-1}, suggested that high P inputs are not attenuated by bankside and sediment along the ditch but continued to increase downstream at G, were some extreme values were recorded, reaching maximum DRP almost twice than F. Highest values at G are likely due to the direct discharges into the ditch from the yard (positioned at 37m AOD) along with inputs from another ditch and potentially the diffuse inputs coming from surrounding fields including a dairy lagoon, which are accumulated down slope (33m AOD).

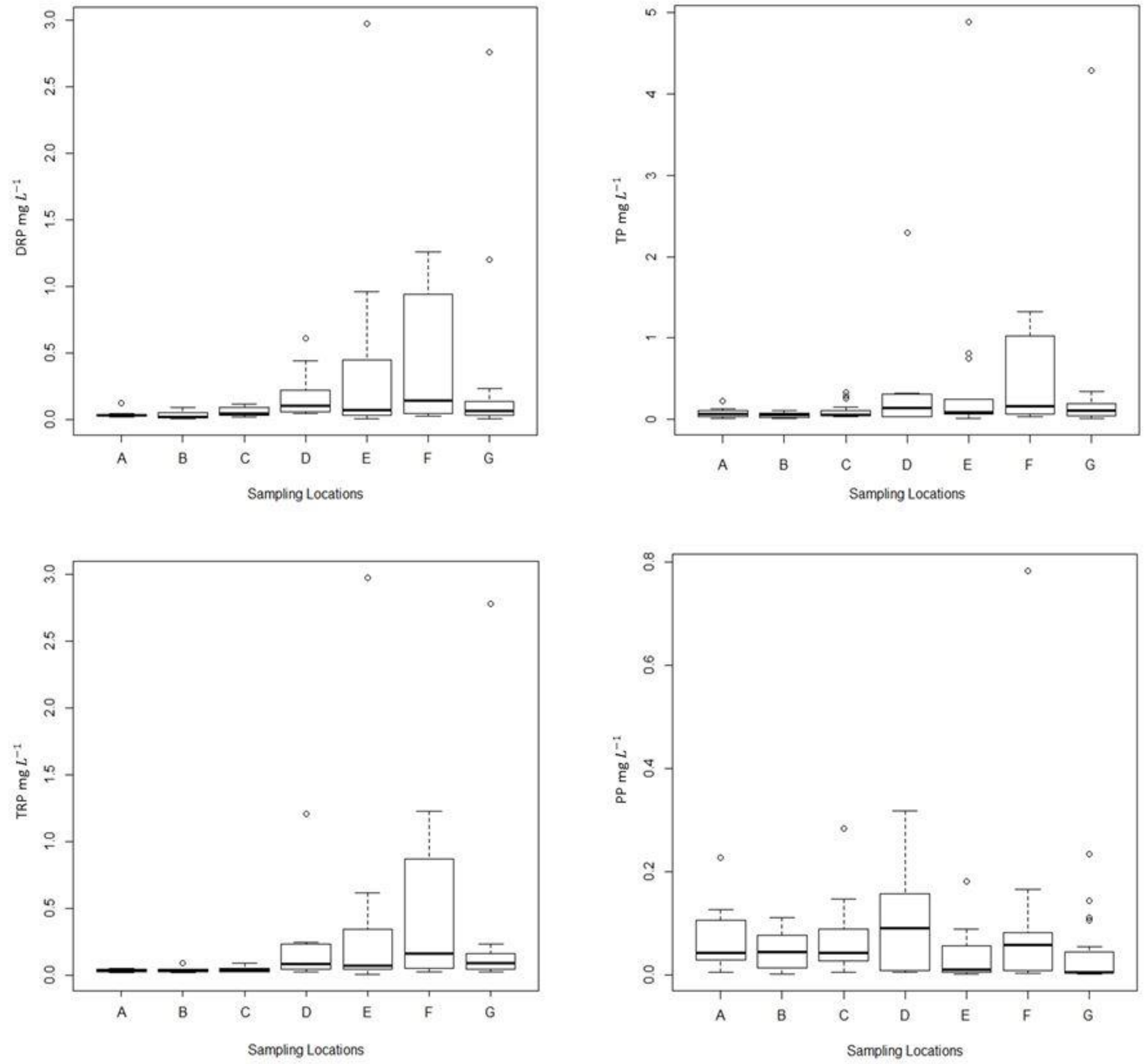


Figure 6.9. *Boxplots showing distribution of water quality data: DRP,TP, PP, and TRP (mg/l) at sampling locations A-G.*

A step-change in TP values was also observed at D. Maximum TP of between 0.11-0.33 mg L^{-1} between A-C, rose to 1.32-4.89 mg L^{-1} from D to G and these values align with previously reported TP values in agricultural ditches with a direct connection to a farmyard (Harrison et al., 2019). At catchment scale, Harrison et al. (2019) reported mean TP values >1.5 mg L^{-1} in a riparian survey of ditches connected to farmyards and Moloney et al. (2020) have identified this type of ditch as highest risk for P loss, if its landscape position allows for a direct connection into watercourses, compared to disconnected and secondary ditches.

Over the length of the ditch, average PP values were similar at all sample points except D, where a sharp increase to 0.135 mg L^{-1} was observed, coinciding with potential point source inputs from the farmyard. However, mean PP values further downstream fell back to within the range observed at upstream points, indicating some attenuation of the particulate fraction from this point onward. Point source inputs to the ditch were evident at sample point D, as soluble P remained high along the length of the ditch. However, the sharp increase in PP reverted to lower concentrations, indicating some ability to attenuate particulate fractions downstream.

6.4.2. Bankside and sediment characteristics

The biogeochemical properties of bankside and sediment samples for each depth interval are represented by Mehlich extractable Al, Fe, Ca, % OM and pH, and are presented in Table 6.2. Sediment and bankside pH ranged from 5.38 to 7.9, with high pH values coinciding with highest values of Ca at sample points E, F and G.

In general, most of the bankside and sediment samples had a neutral pH and moderately low Al and Fe values compared to those recorded in previous studies on Irish soils and sediments (Daly et al., 2015; Daly et al., 2017). High extractable Ca was evident at sample points E, F and G, perhaps as a consequence of a change in soil characteristics or soil type along this reach of the ditch, as illustrated in Figure 6.7. Extractable metals Al, Fe and Ca have been reported to have a high affinity for P in both soils and sediment (Gächter and Müller, 2003; Mellander et al., 2012; Daly et al., 2017). However, the

Table 6.2. *Bankside and sediment biogeochemical properties from each depth represented by Mehlich extractable Al, Fe, Ca, with % organic matter (OM) and pH.*

Sampling Location		**Depth**	**pH**	**OM**	**M3Ca**	**M3Al**	**M3Fe**
	Code	(cm)		(%)		mg kg^{-1}	
A	**A1**	0-30	6.9	3.2	12568	213	230
	Sediment		6.0	1.8	977	259	134
B	**B1**	0-30	5.38	8.0	12363	448	259
	B2	30-60	5.42	5.5	10592	511	308
	B3	60-100	5.66	5.0	1172	449	401
	Sediment		7.2	3.1	1530	173	26
C	**C1**	0-30	6.1	6.8	1811	338	284
	C2	30-60	6.2	4.8	15012	309	269
	C3	60-90	7.3	2.8	14563	234	418
	C4	90-110	7.5	5.2	34854	65	781
	Sediment		7.9	1.0	698	68	139
D	**D1**	0-30	6.5	5.2	1996	469	149
	D2	30-60	6.5	2.0	792	362	67
	D3	60-90	6.4	0.8	303	130	142
	D4	90-110	6.7	1.7	870	205	323
	Sediment		7.8	1.4	986	91.88	190
E	**E1**	0-30	7.1	5.6	25454	180	264
	E2	30-60	7.2	6.1	21864	200	276
	E3	60-90	7.4	5.0	22672	285	193
	E4	90-120	7.4	3.9	19943	373	215
	E5	120-150	7.5	2.9	13851	411	178
	E6	150-180	7.6	1.4	849	256	236
	E7	180-210	7.9	2.4	20217	369	146
	E8	210-240	7.9	1.0	20175	362	154
	Sediment		7.8	2.9	91	89.54	239
F	**F1**	0-30	6.8	4.6	19997	493	225
	F2	30-60	5.9	4.4	1397	399	230
	F3	60-90	6.0	3.9	12546	456	226
	F4	90-120	6.2	3.8	12148	277	164
	F5	120-150	6.0	3.8	11765	328	179
	F6	150-180	6.1	3.2	11054	191	157
	F7	180-210	6.4	5.7	17744	307	278
	F8	210-240	6.6	7.1	22538	343	245
	F9	240-270	6.7	7.4	26862	484	266
	F10	270-290	6.7	6.1	23473	476	191
	Sediment		7.2	3.3	1705	158.73	336

G						
G1	0-30	6.3	21.3	45266	376	261
G2	30-60	6.5	18.1	38003	312	226
G3	60-90	6.6	17.7	42736	372	280
G4	90-120	7.1	6.5	2728	399	275
G5	120-150	6.7	10.1	25664	315	260
G6	150-180	7.1	8.0	27634	251	225
G7	180-210	7.1	5.4	19883	256	282
G8	210-240	7.4	17.7	18495	244	266
G9	240-270	7.8	1.3	15364	129	204
Sediment		7.6	1.5	1015	143.4	266

bankside/sediment analysis of our study showed low levels of Al (range of 355 mg kg^{-1} between bankside of all sites) and Fe (range of 351 mg kg^{-1} between all sites except C4, which showed sharp increase to 781 mg kg^{-1}), with moderate to high M3Ca values (range of 4223 mg kg^{-1} with lowest values recorded at D and highest at G in the imperfectly drained area of the farm).

The % OM ranged from 1.8 to 21.3 % from point A to G, demonstrating the variability in soil types and drainage classes on surrounding fields at the site, with highest values recorded at surface bankside samples on imperfectly drained soils and lowest values along the length of the ditch dominated by well drained soils (Figure 6.8).

Appendix D presents the comparison between P adsorption isotherms of different bankside interval depths and sediments.

6.4.3. Trends in Bankside and sediment P dynamics along the ditch network

Mehlich3 extractable P varied along the length and depth of the ditch network, with values exceeding the agronomic optimum of 50 mg kg^{-1} recorded at all sample points except A and C. Values in Table 6.3 indicate a shift toward higher M3P values at E which continued downstream reaching highest M3P values recorded at the surface bankside samples at G of 101-108 mg kg^{-1} at depth of 90 cm.

Table 6.3. *Phosphorus sorption expressed by Langmuir Smax, k, R^2; EPC_0 and PEBC, and Mehlich extractable P from each interval depth of the bankside and sediment.*

Sampling Location		**Depth**	**Langmuir**			**Equilibrium Phosphorus**			**M3P**
			Smax	**k**	**R^2**	**EPC_0**	**PEBC**	**R^2**	
	Code	(cm)	(mg kg^{-1})	(L mg^{-1})		(mg L^{-1})	(L Kg^{-1})		(mg kg^{-1})
A	**A1**	0-30	208.33	0.85	0.98	0.40	12.22	0.99	32.81
	Sediment		200.0	0.728	0.98	0.06	14.92	1.00	42.98
B	**B1**	0-30	285.71	1.093	0.95	0.07	16.20	1.00	14.22
	B2	30-60	333.33	1.87	0.97	0.03	18.04	1.00	13.05
	B3	60-100	322.58	1.55	0.98	0.14	16.61	1.00	31.49
	Sediment		196.07	0.850	0.98	0.44	13.00	0.99	19.72
C	**C1**	0-30	357.14	0.58	0.95	1.71	17.11	0.92	83.98
	C2	30-60	294.11	1.03	0.99	0.62	12.51	1.00	40.57
	C3	60-90	357.14	2.33	0.97	0.06	18.58	1.00	26.97
	***C4**	90-110	n/a	n/a	0.42	0.01	19.94	1.00	9.1
	Sediment		131.57	0.5278	0.96	0.28	10.96	1.00	20.33
D	**D1**	0-30	250.0	0.85	0.97	0.07	14.93	1.00	13.81
	D2	30-60	370.62	1.57	0.977	0.05	9.60	0.99	11.42
	D3	60-90	116.27	0.741	0.98	0.04	10.41	0.99	7.87
	D4	90-110	81.96	2.440	0.91	0.04	14.00	0.99	15.7
	Sediment		163.93	2.902	0.97	0.25	10.47	1.00	28.09
E	**E1**	0-30	285.71	0.66	0.98	2.05	9.55	0.99	97.36
	E2	30-60	285.7	0.56	0.95	1.75	9.64	1.00	86.39
	E3	60-90	256.41	0.81	0.96	0.75	10.87	1.00	59.73
	E4	90-120	294.11	0.79	0.97	0.84	10.99	1.00	68.65
	E5	120-150	243.90	0.69	0.96	0.35	11.65	1.00	38.25
	E6	150-180	187.68	0.75	0.97	0.14	13.43	1.00	26.4
	E7	180-210	400.0	2.50	0.9	0.00	19.88	1.00	5.4
	E8	210-240	303.03	1.73	0.97	0.01	19.53	1.00	7.15
	Sediment		192.30	0.55	0.95	0.36	9.42	0.98	31.79
F	**F1**	0-30	256.41	1.0	0.97	0.21	14.18	1.00	25.81
	F2	30-60	217.39	0.75	0.96	0.12	14.31	1.00	14.23
	F3	60-90	222.22	1.32	0.98	0.15	15.17	1.00	19.02
	F4	90-120	185.18	0.675	0.96	0.18	13.41	1.00	17.37
	F5	120-150	188.67	0.73	0.97	0.27	12.26	0.99	20.71
	F6	150-180	151.51	0.55	0.97	0.35	11.10	0.99	20.08
	F7	180-210	250.0	0.68	0.97	1.62	8.41	0.99	60.73
	F8	210-240	250.0	0.68	0.97	1.11	11.94	0.99	59.18
	F9	240-270	344.82	1.38	0.99	0.58	15.04	1.00	53.27
	F10	270-290	333.33	1.50	0.98	0.42	13.73	1.00	28.77
	Sediment		285.71	0.89	0.96	0.41	14.18	1.00	50.1

G	**G1**	0-30	285.71	0.49	0.99	4.61	7.01	0.94	101.49
	G2	30-60	357.14	0.38	0.98	4.17	9.80	0.94	108.84
	G3	60-90	416.66	0.48	0.97	2.98	9.82	0.89	111.36
	G4	90-120	344.82	0.93	0.98	0.78	12.55	1.00	89.79
	G5	120-150	285.71	0.74	0.98	1.19	13.03	0.88	86.78
	G6	150-180	303.033	0.67	0.97	1.21	10.73	0.99	72.77
	G7	180-210	256.41	0.92	0.98	1.00	11.28	0.99	80.19
	G8	210-240	250.0	0.95	0.98	0.65	11.04	0.99	70.75
	G9	240-270	178.57	0.708	0.97	0.46	10.64	0.99	40.88
	Sediment		227.27	0.88	0.98	0.24	12.56	1.00	38

* Freundlich K (mg kg$^{-1)}$, n (L mg^{-1}), R^2

The step change in water quality P values recorded at D, signalling point source inputs, was also observed in bankside and sediment P data; however, this occurred at the next downstream sample point (E). Welch's t-test results showed significant differences in M3P and EPC_0 values from D to E (p-value <0.05) and D and G (p-value of 0.0084), and significant differences in EPC_0 values between B and G (p-value= 0.009). This implies that whilst point source P impacted water quality at D, these inputs may be mobilised downstream where they start to accumulate as M3P in sediment, starting at E.

At upstream points between A and C, M3P values were generally low; however, accumulation of extractable P is evidenced by increasing M3P values from E, downstream to G and likely due to P deposition by water draining the site. Box plots in Figure 6.10 illustrate the shift upwards in extractable P along the length of the ditch.

Phosphorus sorption isotherm parameters Smax and k representing sorption capacity and P binding energies are presented alongside EPC_0 along the length and depth of the ditch in Table 6.3 with the spread of data represented as boxplots in Figure 6.9. Values of k ranged from 0.3 to 2.9 L mg^{-1} with lowest values recorded at sample point G and coinciding with high M3P values at this point. This parameter, representing P binding and affinity, decreased along the length of the ditch, from point E onward, and coincided with the upward shift in extractable P bankside and sediment samples from E to G. Bankside and sediment locations downstream were characterised by loosely bound P and high extractable P, thereby increasing the likelihood of P loss to the overlying water.

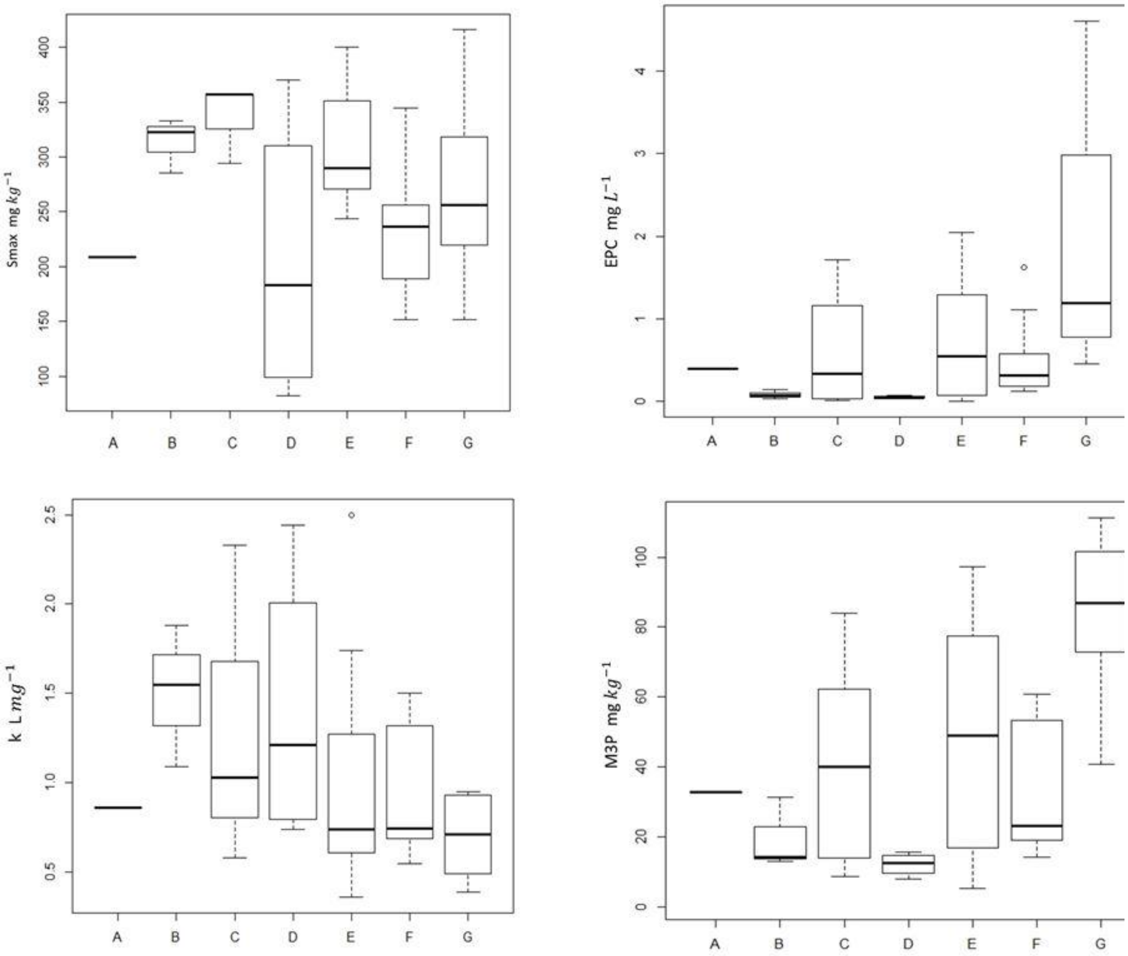


Figure 6.10. *Boxplots showing the distribution of Smax, EPC$_0$, K, and M3P values at sampling locations A-G.*

The EPC$_0$ parameter in this study was measured along the length and depth of the ditch to identify whether this ditch acts as a source or sink at bankside and sediment locations along its reach. However, EPC$_0$ illustrated in Figure 6.10 and tabulated in Table 6.3 highlighted the variability in EPC$_0$ with highest values recorded at surface bankside locations and a trend toward increasing values from A to G along the length of the ditch. The boxplots in Figure 6.9 illustrate increases in EPC$_0$ from A to G, coinciding with M3P recorded at downstream points compared to upstream sample points. Highest EPC$_0$ and M3P values downstream at G, indicate accumulation and deposition of P, that is loosely bound P (low k values) and released to water (EPC_0) therefore acting as a source of P to the overlying water and water draining into the ditch.

At all bankside depths at G, k values were low (<1 mg L^{-1}) and EPC_0 values ranged from 0.24 to 4.61 mg L^{-1}. The P dynamics at this point on the ditch indicate that deposition of P from upstream sources and water draining the site has altered the sediment P sorption characteristics towards net release of P to water. This is largely driven by accumulated P in bankside and sediment, that is loosely bound (low k values), making this junction at source of P leaving the ditch. The relationship between k and EPC_0 in bankside and sediment samples is illustrated in Figure 6.11 (a), showing the influence of binding energies on potential P release. Bankside and sediment k values accounted for 40 % of the variation in EPC_0 values. Moloney et al. (2020) found a similar regression coefficient between k and EPC_0 measured in ditch sediment across 10 farms and also reported the influence of accumulated labile P in ditch sediment on EPC_0 values. A similar relationship between M3P and EPC_0 was observed and is plotted in Figure 6.11 (b) demonstrating the positive relationship between accumulated labile P (M3P) and EPC_0 values, therefore supporting the suggestion that P deposition in ditches can act as a source of P to overlying water, thereby increasing the sediment EPC_0.

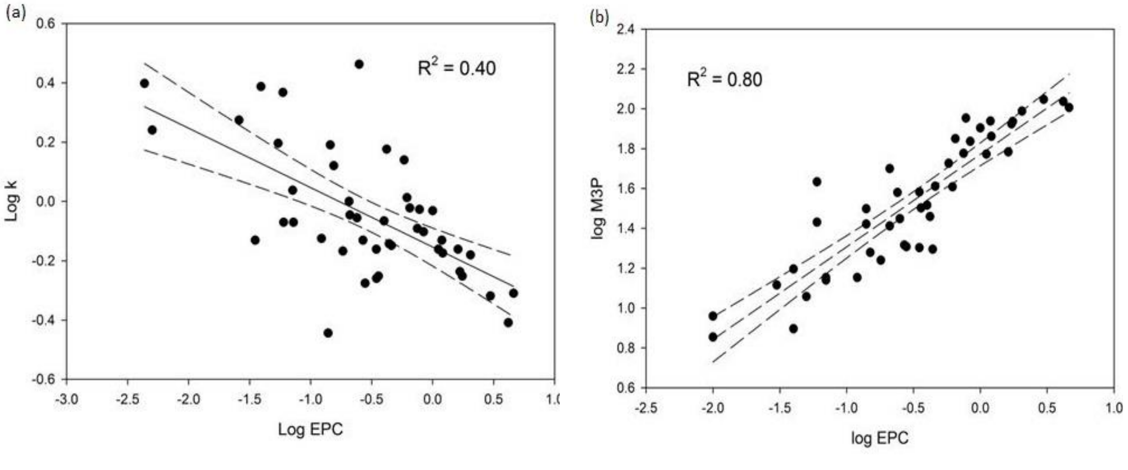


Figure 6.11. *Scatter plot showing (a) regression line between log* EPC_0 *and log K and (b) regression line between log* EPC_0 *and log M3P in all bankside and sediment samples.*

6.4.5. Impacts on water quality and source-sink properties of ditch sediments

The water quality and bankside-sediment data are both indicative of diffuse and point sources of P coming into the ditch network. A step change in water quality was observed at D, due to point source inputs from the yard, but the effect on sediment P dynamics and deposition occurred further downstream at E. These data signal the influence of the farm yard on water quality and sediment P deposition in agricultural ditches. These inputs acted as a direct point source of P into the ditch and a source of P accumulation in sediment, causing deterioration in water quality and altered P sorption dynamics of the bankside and sediment. Changes in sediment P were characterised by higher extractable P (M3P) and lower P binding energies. Furthermore, P inputs into the ditch altered the EPC_0 reducing the attenuation capacity of bankside and sediments in the ditch. This is also evidenced by the positive correlation between M3P and EPC_0 highlighting the influence of P inputs on sediment ability to attenuate P.

The accumulated P in surface layers of E, coupled with lower k values, and consistently high DRP and TP concentrations show release of P from bankside sediment. This is similar to some deeper intervals of site F and all intervals of G which were saturated with P and k values get lowers as P deposited into system. This had consequently resulted in more releasing of accumulated P into the water and thus higher DRP concentrations. This observation is also supported by EPC_0 values which are presented in Figure 6.12 with mean bankside and sediment EPC_0 at each sampling point along the ditch, plotted against mean DRP values at each point. The plot includes the 1:1 line of equality between EPC_0 and DRP values where points below the line indicate sediment acting as a P source and points above line indicate a P sink (Smith et al., 2004). In Figure 6.11 most of the EPC_0 values along this ditch, with the exception of values recorded at A and B, acted as source of P, releasing P to water.

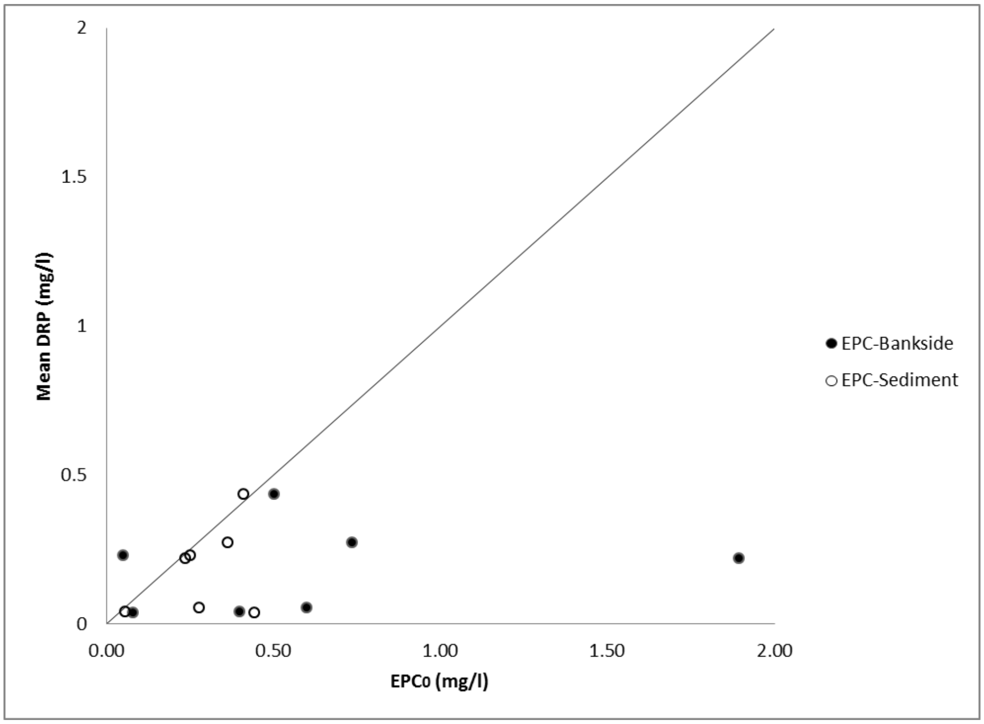


Figure 6.12. *Mean DRP values collected at sampling points as a function of average EPC_0 at bankside and EPC_0 of sediment. Close circle: Average EPC_0 from bankside (mg L^{-1}), Open circle: EPC_0 (mg L^{-1}) values from sediment. Values below 1:1 line indicate that the point act as a potential source of P.*

It is also necessary to implement mitigation interventions (McDowell and Nash, 2012) to clean ditch water before it leaves the farm (king et al., 2015).

This study identified the location for successful installation of an in-ditch nutrient interceptor at point D-E when the nutrient pollution starts to elevate and before they accumulate at point G. Using the ditch network and maximising their natural attenuation capacity by implementing in-ditch engineered structures filled with medium/media with nutrient adsorption/remediation capacity will retain P before entering into surface water. Here again, we should consider the high legacy P in deeper soil layers of the bankside which will continue releasing P into the water. Therefore, there will not be an immediate impact of water quality even after removing the source pollution.

6.5. Conclusion and recommendations

This study examined hydrochemistry and sediment P trends along the length and depth of an agricultural ditch network on an intensive dairy farm. High spatial resolution grab samples of ditch water were collected over 18 months alongside measurements of bankside and sediment P chemistry at depth intervals at points along the ditch. Phosphorus concentrations in the water increased along the length of the ditch, due to inputs from a point source, identified by the presence of pipes discharging from the farm yard directly into the ditch. This caused a step-change in water P concentrations at this point as mean DRP and TRP values increased >10-fold from upstream to downstream points, indicating little or no attenuation of reactive P in the ditch by sediment. Particulate P increased sharply at the sample point closest to point source inputs from the yard, but values fell back in line with upstream values, indicating some attenuation of PP along the length of the ditch. Inputs from point and diffuse sources were transferred downstream resulting in deposition of P in sediment, which inhibited any natural attenuation of soluble P along the length of the ditch. The highest accumulation of P in the ditch sediment was recorded at the furthest downstream sampling point and P inputs into the ditch not only affected water quality, but also altered the sorptive properties of the sediment toward acting as a secondary source of P to water leaving the ditch network. The effects of P inputs from the yard on water quality and sediment P characteristics did not coincide at the same point on the ditch, rather, the step change in water quality occurred at D whilst changes in sediment P were only evident further downstream at D, indicating transfer and deposition in ditch sediment. The results demonstrated that such P inputs have altered the physico-chemical characteristics of the ditch sediment which highlights the need to remediate sediment to restore its natural P attenuation capacity and reverse its role as a secondary source of P to water. Water quality policy design will need to account for physico-chemical time lag phases in sediment remediation before any improvements are observed. Preventing further point source inputs to the ditch requires substantial restructuring in the farm yard, such as, redirecting yard runoff entering ditches, directly or indirectly, by e.g. blocking the pipes and collecting runoff for water treatment.

6.6. Summary

This chapter investigates the P mobilisation/retention dynamics along the ditch network at Johnstown Castle intensive dairy farm and the results are summarised in the following bullet points:

- Point source inputs from farm yard to the ditch have accumulated in the sediments.
- High P inputs into the ditch had altered sediment P dynamics by turning them into a source of P.
- Soil chemistry and P attenuation was heterogeneous laterally and vertically
- In-ditch measures are needed to remediate water and sediment
- A physico-chemical lag time was identified

The next chapter will summarise conclusions and implications of the entire thesis and will discuss recommendations for future work.

Chapter 7

Conclusions and Recommendations

7.1. Overview

Ireland has set ambitious food growth strategies to promote its intensive agricultural production. While government policies consider agronomic and environmental sustainability to be of equal importance, growth projections of the dairy sector (DAFM, 2010, 2015) suggest higher nutrient losses to the environment are inevitable. In addition, legacy P and N stored within the soil profile will continue discharging to ditch networks for decades, even after the removal of the source of pollution or implementation of any mitigation measure.

Therefore, there is a need to impose conservation practices, which may also include the use of engineered structures as an in situ remediation technique, to target point and diffuse losses of nutrients from farms. Such structures have gained popularity due to their lower costs and higher efficiency compared to other engineered mitigation measures, and are commonplace on drained landscapes in the USA (Hassanpour et al., 2017) and New Zealand (Schipper et al., 2010a). To date, many studies have used in-field/in-ditch engineered structures filled with reactive media to reduce or remediate nutrient losses. However, a dearth of knowledge exists with regard to the selection of appropriate media for the remediation of specific contaminants (NO_3^-, NH_4^+ and DRP, as single or mixed contaminants), and local conditions are infrequently considered. In addition, the efficacy of such structures may only be accurately quantified by first conducting large-scale column studies, which are expensive and time and labour intensive. As ditch systems have an inherent natural nutrient attenuation capacity, they could be used to supplement engineered technologies, which can only treat a fraction of the total amount of nutrients discharging from an agricultural system.

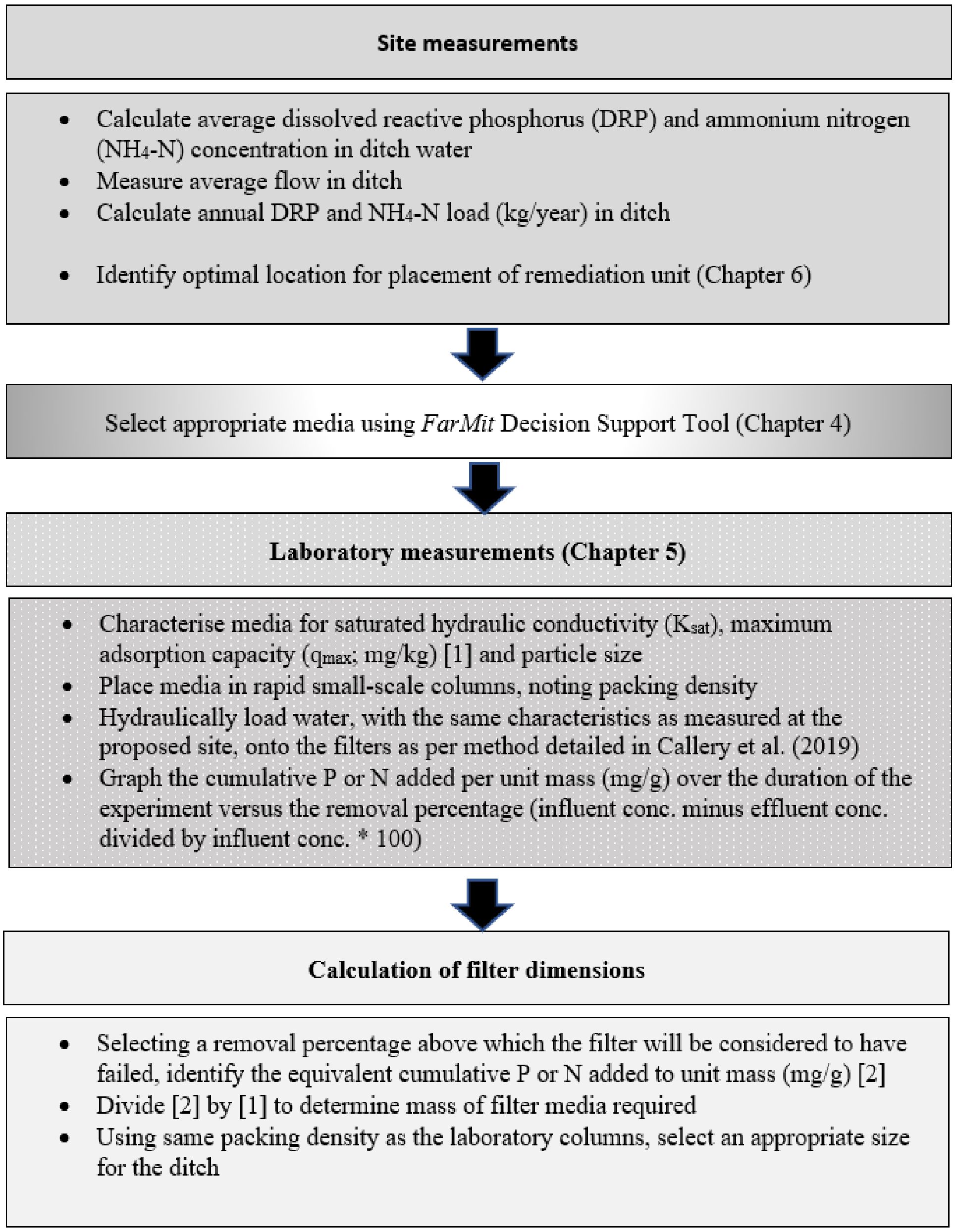
The main objective of this research was to develop an efficient, sustainable, and cost-effective mitigation technique to prevent pollution losses and remove mixed contaminants in an agricultural drainage system. Two mitigation techniques were explored: (1) an engineered solution in which filters, filled with locally sourced media selected for their ability to mitigate N and P, were used to intercept nutrients in drainage networks, and (2) a natural solution, which took advantage of the soil chemistry in drainage networks to remove nutrients. To address the first mitigation technique, a DST was developed to identify locally sourced materials to be used to remediate N and P in drainage water. These materials were placed in rapid, small-scale laboratory columns to predict their performance and longevity, and the modelled results were compared to those of large-scale columns. To address the second mitigation technique, P retention and mobilisation dynamics in an open ditch network were investigated to assess P retention/mobilisation capacity, investigate connectivity between the source of pollution (farm yard) and the ditch, and identify an optimum location for the placement of an engineered structure filled with adsorptive media.

7.2. Summary of the main findings and their implications

- A novel, globally applicable and user-friendly DST was developed, which incorporated various parameters for the selection of an appropriate, locally sourced medium or a combination of media to target contaminants in drainage waters. The DST utilised a catalogue of 75 organic/inorganic and natural/synthetic materials. The DST provides a fast, versatile, flexible, and easily modifiable media selection process for various nutrient-based water drainage problems. It assists users in making informed choices on appropriate media-based mitigation measures according to various technical, economic and logistical factors, while considering other important factors such as pollution swapping.

- Rapid, small-scale column tests (RSSCTs), comprising columns 0.1 to 0.4 m long and 0.01 m in diameter, were used, for the first time, to generate data to accurately model the DRP and NH_4-N removal in large-scale columns in a fraction of the time. The associated financial, operational and labour advantages of using RSSCTs are the time required for constructing and operating the columns, labour hours, space to house the structure, number/capacity of containers, amount of influent (chemical and distilled water), procurement of adsorbent(s), sampling equipment, number of pumps, cost of laboratory analysis of water samples, and overhead costs including electricity and light. An important finding of this study was that the media needs to become saturated over the duration of the experiment in order to accurately model its performance.

- The flowchart for development of an efficient field-scale engineered structure filled with adsorptive media, using the data ascertained from different chapters, is presented in Figure 7.1:



Site measurements

- Calculate average dissolved reactive phosphorus (DRP) and ammonium nitrogen (NH_4-N) concentration in ditch water
- Measure average flow in ditch
- Calculate annual DRP and NH_4-N load (kg/year) in ditch
- Identify optimal location for placement of remediation unit (Chapter 6)

Select appropriate media using *FarMit* Decision Support Tool (Chapter 4)

Laboratory measurements (Chapter 5)

- Characterise media for saturated hydraulic conductivity (K_{sat}), maximum adsorption capacity (q_{max}; mg/kg) [1] and particle size
- Place media in rapid small-scale columns, noting packing density
- Hydraulically load water, with the same characteristics as measured at the proposed site, onto the filters as per method detailed in Callery et al. (2019)
- Graph the cumulative P or N added per unit mass (mg/g) over the duration of the experiment versus the removal percentage (influent conc. minus effluent conc. divided by influent conc. * 100)

Calculation of filter dimensions

- Selecting a removal percentage above which the filter will be considered to have failed, identify the equivalent cumulative P or N added to unit mass (mg/g) [2]
- Divide [2] by [1] to determine mass of filter media required
- Using same packing density as the laboratory columns, select an appropriate size for the ditch

Figure 7.1. *Flow chart for implementation of on-site design.*

- Investigating the existence of lack of natural attenuation capacity of a ditch system, before the development of appropriate engineered mitigation measures, is of significant importance because engineered structures are designed to only treat a percentage of the total load discharging through the ditch system. Therefore, any additional help in terms of natural attenuation and management of the ditch network through dredging, for example, to expose binding sites for P attenuation would be advantageous.

- Continuous drainage of water from a farm yard into a ditch may alter the physico-chemical characteristics of the ditch sediment, turning it into a secondary source of P to water. There was an elevated P concentration in the drainage water closest to the point source inputs from the yard, which indicated an ideal location for placement of an engineered, in-ditch structure.

- High levels of P accumulated in the sediments and on the surface and deeper bankside depths of a ditch may indicate a high "P legacy" in the system. This highlights the necessity to remediate sediments to restore their natural P attenuation capacity. Therefore, physico-chemical lag phases in sediment remediation must be considered in developing appropriate engineered solutions before any improvements are observed, as sediments will keep releasing P into the ditch discharge waters for some time.

7.3. Recommendations for future research

- Future development of the DST should incorporate other criteria, such as the possible re-use of the media after it becomes saturated in the engineered structure. Therefore, aspects pertaining to the circular economy should be considered.

  Aligning the ranking of media for removal performance based on similar conditions like residence time, and factoring in other issues that influence the removal efficiency (e.g. temperature), may provide users with more holistic options. A user may also wish to have more flexibility in the dynamic criteria, so that it would outweigh all other components if weightings are assigned. This would exclude all media that may be unavailable due to the geographical location where the DST is being used. Consideration of the maintenance costs pertaining to the selected medium/media may be another factor to consider.

- The RSSCT modelling approach needs to be modified to incorporate biological N removal in C-source filter media, such as woodchip, where adsorption is not the dominant removal mechanism and NO_3^- is converted to N_2.

  Small-scale column tests should be designed to have consistently less than complete (100 %) removal from the columns. This can be done by increasing the concentration of influent when the filter medium is known to have high retention capacity.

  The question of what happens to the saturated media is always difficult. In the first instance, the media is expected to adsorb nutrients from drainage waters. Next, once saturation has occurred, the same filter media is expected to act as a fertilizer, offering plant-available nutrients to grassland in the adjoining areas to the ditch network.

  Future work should examine the concept of a circular economy and find ways to close the bio-economy loop within the farm. Other uses may include: reuse of media as farm roadway aggregate or as a soil conditioner to enhance soil health in compacted areas of the farm.

- Placement of an engineered structure, containing locally sourced media with a high DRP and NH_4^+ removal capacity, in a ditch must be considered to remediate the drainage water, where natural attenuation is insufficient to eliminate pollution from an intensive dairy farm.

  Furthermore, future work should consider the installation of a sediment trap in the up-gradient farm to trap sediments gaining access to the underground drainage network. The entire ditch network should be over-engineered (trapezoidal shape) to increase water storage capacity. This would slow down the water and create a longer overall retention time.

Careful consideration should also be given to the management of dairy soiled water (DSW) on the farm. This could be facilitated by opening up the last section of underground concrete pipe on site and installing an integrated constructed wetland to receive both drainage waters and DSW from the farmyard.

Further investigation into the interaction between groundwater and surface water should be undertaken and a more accurate water balance of the site should also be undertaken. This would lead to a greater understanding of the load of N and P travelling along different pathways on the site.

- A long-term research programme should be initiated whereby water quality could be monitored using high resolution techniques such as in situ nutrient sensors (instead of grab sampling), field portable soil analyzers such as handheld XRF to investigate soil and sediment chemistry (instead of soil sampling and costly/time consuming laboratory analysis), isotope techniques to identify sources of P losses; and earth observation techniques to track changes in water and soil quality.

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Appendix A

Ezzati, G., Healy, M.G., Christianson, L., Feyereisen, G.W., Thornton, S., Daly, K., Fenton, O., 2019. Developing and validating an adaptable decision support tool (FarMit) for selection of locally sourced media for dual mitigation of nutrients in drainage water from intensively farmed landscapes. Journal of Ecological Engineering : X, 2, 100010. https://doi.org/10.1016/J.ECOENA.2019.100010

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Developing and validating a decision support tool for media selection to mitigate drainage waters

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A R T I C L E I N F O

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A B S T R A C T

The nitrate nitrogen (NO_3-N) and ammonium (NH_4-N) and/or dissolved reactive phosphorus (DRP) load in drainage water from farms can be managed by reactive or biological media filters. The nutrient content of the drainage water can be obtained directly from water analysis, which immediately focuses attention on filter media selection. There are many factors that may be important before choosing a medium or media e.g. nutrient removal capacity, lifetime, hydraulic conductivity, the potential for "pollution swapping", attenuation of non-target contaminants (e.g. pesticides, organic carbon, etc.), and local availability and transportation cost of media to site. In this study, a novel decision support tool (DST) was developed, which brought all these factors together in one place for five nutrient scenarios. A systematic literature review was conducted to create a database containing 75 media with an associated static scoring system across seven criteria (% of nutrient concentration reduction, removal of other pollutants, lifetime, hydraulic conductivity, negative externalities) and a dynamic scoring system across two criteria (delivery cost and availability). The DST was tested using case studies from Ireland, Belgium and USA with different agricultural practices and nutrient scenarios. It was then validated by SWOT (strength, weakness, opportunities and threats) analysis. The DST provided a rapid, easily modifiable screening of many media-based treatments for specific dual or single nutrient-based water drainage problems. This provides stakeholders (farmers/regulators/advisors) with a versatile, flexible and robust yet easy-to-understand framework to make informed choices on appropriate media-based mitigation measures according to users' relevant technical, economic and logistical factors.

1. Introduction

Decades of research have shown that aquatic environments are under pressure due to population growth, waste generation (FAO, 2011; Jhansi et al., 2013), excessive loading of nutrients (Billen et al., 2013; Erisman et al., 2011; Addy et al., 2016; Fenton et al., 2017), pesticides (Gramlich et al., 2018), and sediment inputs (Sherriff et al., 2015). Nutrients such as reactive nitrogen (nitrate (NO_3-N) and ammonium (NH_4-N)) and dissolved reactive phosphorus (DRP) in drainage waters from intensively farmed agricultural sites have contributed significantly to impairment of water quality (Daly et al., 2017; Fenton et al., 2017; Rosen and Christianson, 2017; Clagnan et al., 2018a,b). The interception of single pollutants along surface or near surface drainage loss pathways using in-situ engineered structures filled with biological (e.g. woodchip in a denitrifying bioreactor) or reactive (e.g. steel slag in a P-sorbing structure) media is receiving increasing research attention (e.g. Penn et al., 2017). The removal rates of nitrogen (N) and phosphorus (P) using these media can be high. For example, Hassanpour et al. (2017) measured 50% NO_3 removal from drainage water using woodchip media in a denitrifying bioreactor over a 3-year period and Okello (2016) reported a 74% removal of DRP in drainage water using iron-coated sand in a reactive P-sorbing filter. However, the simultaneous removal of these pollutants in drainage water using dual media has mostly been examined at laboratory-scale (Healy et al., 2012, 2014; Ibrahim et al. 2015; Hua et al., 2016; Christianson et al., 2017; Fenton et al., 2017). In addition, the transferability of these results to other locations due to the availability, suitability or delivered cost of media is often overlooked. An example here is the use of iron ochre to sorb P in drainage water; the availability of the ochre may not be a problem, but the form of ochre may be contaminated with heavy metals and its use

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may therefore be prohibitive (Fenton et al., 2009b).

There is a vast catalogue of media in the literature that are reported to mitigate pollutants leaving farms. However, there is currently no decision support tool (DST) available to select a suitable medium, or a combination of media, for the targeted removal of NO_3, NH_4 and DRP, considered separately or together, while also considering factors other than pollutant removal capacity. These factors may include the media lifetime, hydraulic conductivity, the potential for "pollution swapping" (i.e. the creation of greenhouse gases (GHGs) or leaching of contaminants that may occur during operation), capacity to attenuate other (non-target) contaminants (e.g. pesticides, organic carbon, etc.), and availability and local price of the media.

Decision Support Tools, usually software-based, manipulate data (often obtained through literature review or expert opinion) and recommend management actions through clear decision stages (SIP, 2018). In a review of DSTs for use in agriculture, Rose et al. (2016) found that in the UK 49% of farmers used some kind of DST to inform decisions whereas all advisors used DSTs, and software versions were the preferred form of DST platform. In terms of selecting media to mitigate drainage water impacts, there is no DST that provides all the relevant information in one platform. Therefore, the objectives of this study were to: (1) develop a globally-applicable, user-friendly DST to assist selection of locally sourced media, in order to reduce NO_3, NH_4 and DRP, as single or mixed pollutants, from drainage water at farm-scale (2) evaluate the effectiveness and practicality of the DST in two phases: (a) applying it in different geographical/farming-practice case studies, and (b) validating the framework through SWOT (strength, weakness, opportunities, and threats) analysis.

To meet these objectives, several steps were implemented to build a platform on which the DST could be developed. These included identifying a number of scenarios for N and P losses from farms and compiling a database of media for mitigation of nutrient losses. Fig. 1 illustrates the steps taken in developing the FarMit (**Far**m **Mit**igation Tool) DST.

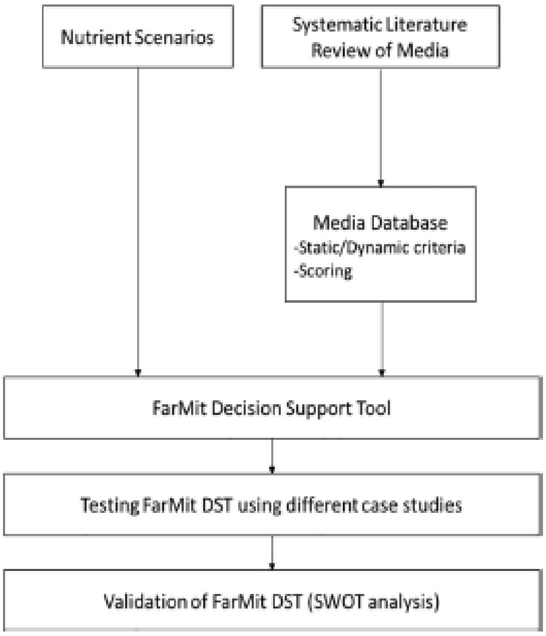

Fig. 1. Flowchart for the development of FarMit DST.

2. Materials and methods

2.1. Nutrient scenarios

Testing water samples for nutrients collected at the drainage discharge point can provide a spatial and temporal profile of single or mixed pollutants at a given site. Typically, reactive nitrogen (N_r) losses from land drainage systems may occur as NO_3-N or NH_4-N, depending on various physical and biogeochemical factors that control the transformation of N_r (Fenton et al., 2009a; Clagnan et al., 2018a). Phosphorus losses from agricultural land, which are either retained or mobilized, may occur in particulate and dissolved forms (McDowell and Sharpley, 2001). Based on the complexities of nutrient losses from agricultural land, a conceptual model of different possible diffuse nutrient loss scenarios that may occur at farm-scale was developed.

The FarMit DST is based around identifying materials to treat three nutrient loss scenarios (Fig. 2). In Scenario A, mineralised N_r in the soil, in the form of NO_3, leaches to shallow pathways along low permeable layers or artificial drainage systems (e.g. Clagnan et al., 2018a,b) or along deeper groundwater pathways. In Scenario B, subsurface conditions, such as limited N_r and oxygen supply, combined with high soil carbon (C), may induce transformation of NO_3 to NH_4 (by dissimilatory nitrate reduction to ammonium, DNRA). In Scenarios A and B, DRP losses may also occur along surface, near surface, or deeper groundwater pathways. These losses could originate from the soil/subsoil, geological strata, or media used within an engineered bioreactor used to treat water and wastewater. Therefore, site-specific conditions (soil chemistry and drainage composition) or media characteristics may lead to the retention of P losses or the mobilisation of P. Finally, Scenario C represents a farm with only loss of P, where N_r in either form does not exceed a threshold or maximum allowable concentration (MAC). This may be due to the high attenuation capacity of the site, with conversion of N_r into gaseous forms (e.g. di-nitrogen or nitrous oxide), isolation from potential sources, or adaptation of perennial crop farming systems (Stanek et al., 2017).

2.2. Systematic literature review to form media database

The five steps of a systematic review were followed, as outlined in Khan et al. (2003). The problem to be addressed was specified as follows (Step 1): what media have been used in the literature to attenuate NO_3, NH_4 and DRP from drainage waters? What is the efficacy of a medium to remove NO_3, NH_4 and DRP, or other pollutants in drainage waters? What is the hydraulic conductivity of the media? What is the lifetime of the media? What pollution swapping may occur using these media?

Next (Step 2), relevant work within the literature was identified. For this purpose, several keywords were selected to ensure relevancy for the literature search of over 175 media-based water treatment studies published during the last 20 years (150 papers were considered in final review). These included: water/wastewater treatment, water quality, agricultural waste, denitrification, denitrifying bioreactor, nutrient pollution, leaching, nutrient removal, adsorption, drainage, nitrate, phosphorus, and ammonium. The database search engines used were Google Scholar, Agricultural Research Database (AGRICOLA), International System for Agricultural Science and Technology (AGRIS), Web of Science, Scopus, American Society of Civil Engineering (ASCE), and the National Agricultural Library. To assess the quality of these relevant studies (Step 3), the following criteria were imposed: use of standard methods, and experimental design including replication and data interpretation. This enabled a database of 75 distinct media types to be assembled. Data were then synthesised (Step 4) in tables and grouped as follows: wood-based (Table S1), vegetation/phytoremediation (Table S2) and inorganic materials (Table S3). Media were then assigned nine criteria (seven static and two dynamic), based on Steps 1–4, and a corresponding scoring system (Step 5 data interpretation)

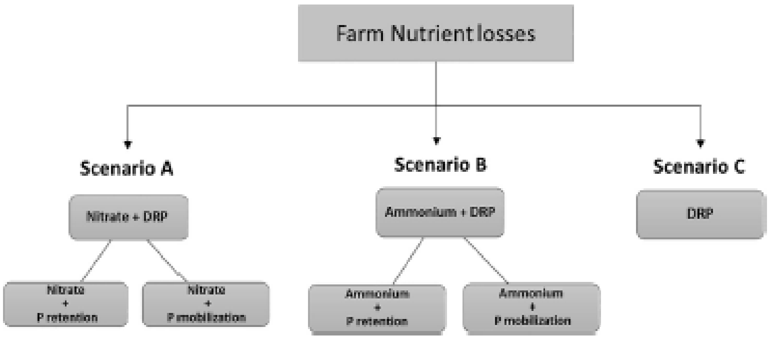

Fig. 2. Farm pollution scenarios: A: Farm pollution with leaching of NO_3-N and retention of P, or Farm pollution with leaching of NH_4-N and mobilization of P, B: Farm pollution with leaching of NO_3-N and retention of P, or Farm pollution with leaching of NH_4-N and mobilization of P, C: Farm pollution with DRP mobilization and no leaching of N.

Table 1
Static (1–7) and dynamic (8–9) criteria and corresponding scoring ranges.

Criteria	Performance within each criterion	Score
Static scores based on an average performance reported[1]		
1-NO_3-N removal rate	NO_3-N concentration reduction > 85%	4
	NO_3-N concentration reduction: 70–85%	3
	NO_3-N concentration reduction: 50–70%	2
	NO_3-N concentration reduction: 30–50%	1
	NO_3-N concentration reduction: 10–30%	0
	NO_3-N concentration reduction < 10% and increase in concentration	−1
2-NH_4 –N removal rate	NH_4-N concentration reduction > 85%	4
	NH_4-N concentration reduction: 70–85%	3
	NH_4-N concentration reduction: 50–70%	2
	NH_4-N concentration reduction: 30–50%	1
	NH_4-N concentration reduction: 10–30%	0
	NH_4-N concentration reduction < 10% and increase in concentration	−1
3-DRP removal rate	P concentration reduction > 85%	4
	P concentration reduction: 70–85%	3
	P concentration reduction: 50–70%	2
	P concentration reduction: 30–50%	1
	P concentration reduction: 10–30%	0
	P concentration reduction < 10% and increase in concentration	−1
4-Removal of other pollutants of concern	Removal of other nutrient/pollutant > 80%	2
	Removal of other nutrient/pollutant < 80%	1
5-Hydraulic conductivity[2]	Very good: > 4 cm/h	3
	Good: 1.5–4 cm/h	2
	Acceptable/depending on compactness: < 1.5cm/h	1
6-Lifetime	Lifetime > 10 years	2
	Lifetime : 5–10 years	1
	Lifetime < 5 years	0
7-Negative externalities	GHG emission	−3
	Contaminant leaching/other pollutants in effluent	−2
	Expensive pre-treatment	−1
Dynamic scores subject to change based on geographical region[3]		
8-Scale of Availability	Scale of Availability: farm scale	4
	Scale of Availability: local/country scale	3
	Scale of Availability: EU/continent scale	2
	Scale of Availability: International scale	1
9-Cost	Cost (low)	3
	Cost (medium)	2
	Cost (high)	1

[1] Extracted from the developed Media Database (Tables S2–S4) based on average performance of conducted studies.
[2] Required additional data from other sources.
[3] Scoring should be defined by individual users (requires case study knowledge on temporal/spatial factors).

was developed for each criterion. In the static component, these criteria were NO_3-N, NH_4-N and DRP removal capacity (Static Criteria 1–3 in the FarMit DST), removal of other pollutants of concern (Static Criterion 4), hydraulic conductivity (Static Criterion 5), lifetime of media before saturation (Static Criterion 6), and negative externalities such as emission of GHGs, contaminant leaching, or the presence of other pollutants in the final effluent (Static Criterion 7) (Table 1). For example, Criterion 1 (% NO_3-N removal) had a score range of −1, 0, 1, 2, 3, 4 corresponding to < 10%, 10–30%, 30–50%, 50–70%, 70–85%, and > 85% reduction, respectively. Although many studies report % removal, there are other factors that affect this criterion, such as hydraulic residence time in denitrifying bioreactors and contact time in P-sorbing filters.

In the dynamic component of FarMit, media were scored according to geographically-based criteria such as availability and delivery cost to the treatment site or farm. These criteria are country/region-specific and will change over time. As the amount of media needed will vary depending on the drainage flow and composition at the site of concern, local knowledge is required and only the end-user can obtain the most appropriate ranking of media by assigning scores to these two components. The score ranges for these two final dynamic criteria are presented in Table 1.

The nutrient combinations identified (A, B and C) in Fig. 2 and the scoring system developed as part of Step 5 (Table 1) for all criteria (1–9) were combined to form the FarMit DST (Fig. 1). In order to test the DST, case studies from Ireland, Belgium (Flanders), and the USA (highlighted in grey in Table S4) were used.

2.3. Testing of FarMit DST using different case studies

Three case studies each with their own distinctive nutrient scenario from Ireland, Belgium and the USA were used to test the DST (see Table S4 for details). Nutrient losses from drainage systems are ubiquitous, but water quality regulation standards differ worldwide. For example, in an Irish dairy system, cattle are kept outdoors for most of the year with both organic and inorganic fertilizer being land spread. Studies have shown high N surpluses on dairy farms due to low N utilisation efficiencies, e.g. Clagnan et al. (2018a) found a range from 211 to 292 kg N ha^{-1} on heavy textured sites. As drainage waters are not governed directly by water quality legislation, other standards for surface or groundwater (e.g. drinking water standards) can be used to quantify the level of pollution. For example, in Ireland surface waters are of “high” and “good” status if their DRP is < 0.025 mg L^{-1} and < 0.035 mg L^{-1}, respectively (EU, 2014; EPA, 2016). For NO_3-N, an average drinking water concentration of 11.3 mg L^{-1} applies for groundwater, whereas a lower standard of < 0.9 mg L^{-1} and $<$ 1.8 mg L^{-1} are indicative of surface waters with “high” and “good” status, respectively (EPA, 2016). Although a drinking water standard, and not specific to drainage waters, an indicative NH_4-N concentration of < 0.23 mg L^{-1} may be considered to be non-polluting.

The region of Flanders in Belgium is mostly dominated by fruit production and arable farming in the east, with livestock production and production of vegetables for the frozen food market in the west (Flemish Agriculture and Fisheries, 2017). This region comprises 75% of agricultural production in Belgium, and is considered by the Government of Flanders, Investment and Trade Body to be a “global leader in intensive farming”. The water standard for NO_3-N should be < 11.3 mg L^{-1} and the same standard for NH_4-N as in Ireland applies. In terms of DRP, there is a range of concentrations for “very good” and “good” status of surface water from 0.04 to 0.06 mg DRP L^{-1} and 0.07 to 0.14 mg DRP L^{-1}, respectively.

Finally, the sites selected in the USA were in the states of Iowa, Minnesota, Wisconsin and Maryland, in which the dominant agricultural systems are corn, soybean, livestock, vegetables, fruits, and tree nuts (Hatfield, 2012). As with Ireland, NO_3-N standards in the USA are specific to drinking water, and not drainage water, but with a slightly lower standard at 10 mg NO_3-N L^{-1}, which is termed a “maximum contaminant level”. In terms of DRP in the USA, there is a limit of 0.037 mg DRP L^{-1} (USEPA, 2000) in surface waters.

2.4. Validation of DST (SWOT analysis)

The procedure of Andersson-Sköld et al. (2014) was followed to validate the DST. The FarMit DST was validated by running several SWOT (Strength, Weakness, Opportunity, Threat) analysis sessions with end-users. This allowed the DST to be critically reviewed by independent stakeholders and external experts (researchers/scientists in the fields of water/soil quality monitoring/remediation and environmental protection, agricultural consultants/advisors) at the following SWOT analysis workshops:

i. PCFruit, Fruit Research Centre, Belgium (May 2018; 5 attendees)
ii. Department of Environment Research Centre of Teagasc, Agriculture and Food Development Authority of Ireland, Ireland (December 2018; 14 attendees)
iii. Water Research Group/ Groundwater Protection Group in Sheffield University, UK (February 2019; 10 attendees)
iv. Network Meeting of EU Horizon2020 Early Stage Researchers representing different partner countries in the INSPIRATION (Managing soil and groundwater impacts from agriculture for sustainable Intensification) Innovative Training Network (ITN), Netherlands (March 2019; 14 attendees)

The process was carried out by presenting the FarMit DST to participants, starting with a summary of current media-based mitigation measures for removing/remediating nutrients in drainage water at farm-scale. The attendees were then divided into groups of three to four and participants were given a chart explaining each criterion. The groups were then asked to use the DST with a view to making best management decisions from a farmer/advisor point of view. The opinions of groups on the performance of FarMit DST with regard to its strengths and weaknesses as attributes of the DST and opportunities and threats as attributes of the environment were recorded and discussed among attendees.

3. Results

The FarMit DST is available in the supplemental Excel file. It may be used by first accessing the ‘INPUT’ tab on the file. The results of the three case studies are now presented.

3.1. Case studies

3.1.1. Ireland

The results of the Irish case study are presented in the supplemental Excel file (Tab: EXAMPLES). The following steps were taken to obtain the final results:

1- Based on the drainage water test results (Table S4), the “Ammonium/DRP” icon in the DST user interface was selected.
2- The DST recommends the top 10 media based on *static* criteria for treatment of this scenario. For example, the top three media for NH_4-N removal are zeolite, crushed glass and peat/sphagnum peat with a cumulative score of 10, 9.5 and 8.5, respectively. The equivalent media for DRP removal are vetiver grass, lime and sand with cumulative scores of 10, 9 and 8, respectively.
3- The *dynamic* criteria 8 and 9 were assigned scores considering local conditions and resources available at farm-scale. For example, in Ireland sand and gravel can be delivered to site at 0.21 and 0.15 € kg^{-1}, while zeolite, lime, and limestone cost over 0.70, 0.95, and 1.3 €, respectively. Any media priced below and over 0.5 € kg^{-1} were assigned scores of 3 and 2, respectively, while media over 2 € kg^{-1} (e.g. andesite, charcoal, nitrolite, etc.) were assigned a score of 1. The DST sums the total scores of static and dynamic criteria.
4- After pressing “Run”, the DST presented a high to low ranking of media for the mitigation of pollutants in the Irish case-study. These are presented graphically (by a histogram) and in table format.

The order of the top five media for NH_4-N removal was (from best to worst): zeolite, peat/sphagnum peat, soil (no clay), sand and pea gravel. The top five media for DRP removal were (from best to worst): sand, lime, vetiver grass, zeolite, and crushed concrete. The ranking implied the influence of wide (local) application of some media over others in the dynamic criteria scoring. For example, zeolite is highly available despite being imported, therefore it has higher availability with lower delivery cost. Similarly, the extensive peat harvest/extraction from peat deposits along with the geology of Ireland, which provides limestone rocks or sand with various compositions, influenced the dynamic criteria scoring and therefore the final ranking of media.

3.1.2. Belgium

The results of the Belgian case study are presented in the supplemental Excel file (Tab: EXAMPLES). The following four steps were taken to obtain the final results:

Table 2
Summary of SWOT analysis results: strength and weakness (attributes of the tool), and opportunities and threats (attributes of the environment) of FarMit DST identified through different workshops.

Strength	Weakness	Opportunities	Threats
Clear concept, provides an overview of best media, and easy to understand		Flexibility for the DST to be further developed	
User friendly without any complications, thus suitable for any software skill level.		Easy to change scores from time to time depending on environmental circumstances	The use of the tool/scorings depend on local/national legislation
Time saving, as it provides a list of best performing media	Not showing raw/waste nature of a medium	Positive impact on decision making as it is an easy to use tool	
Static criteria do not change from region to region, but are important in any mitigation option regardless of farm size.	Does not consider environmental sustainability and post-implementation cost (disposal of used media and associated costs)		Impact of local geographical conditions on removal efficiency (e.g. weather, humidity)
Low-cost DST which is easy to disseminate		Enabling knowledge transfer between different stakeholders	
Robust selection of media (based on literature review and actual experiments)			
Informative and presents several media options	Bar graphs may be misleading for non-scientific community	Supporting document to be used for legal purposes	
A ranking list (from best to worst) of potential media is provided	Lack the factor of unfeasibility at site, regardless of its good adsorption capacity	Possibility to add a factor considering the applicability at site	Farmers' constraints might not let them to choose top ranked media based on lower "cost" or higher "availability"
Provides the user with options which helps in making a more informed selection that considers environmental impacts	Does not consider greenhouse gas emissions caused by transport of media		Information on availability/efficiency of some media depends on extreme weather conditions, land use changes, growing/failure of an industry, etc.
			Changes in geopolitical landscapes may have a direct impact on commercial and import/export agreements
			Fluctuation of exchange rate in the case of importation can alter the cost
Considers negative externalities (pollution swapping), thus prevents further post-treatment in near/far future	"Pollution Swapping" has not been considered in many studies so not sufficient information on all 75 media in this regard	Highlights pollution swapping as an issue	
		Knowledge presented could affect end decision thereby moving to a material with a lower environmental footprint	
		Influence mindset by considering several criteria of importance for overall pollution remediation	
Considers both N and P individually or simultaneously			
Considers environmental, economic and logistical criteria	Some media listed may not be familiar to the user depending of geographical location where the tool is applied		
The DST considers the users' incomes	The scoring range for "Cost" is narrow	Possibility to add a weighting factor to show importance of dynamic criteria	
	Lack of differentiating between organic/inorganic components of media and information on nonlocal media[1]		
Provides a decision support framework comprising long term goals		Possibility of data collection regarding farmers' preferences in order to improve decision making processes	
		Encourages farmers to monitor water quality more often to avoid possible contamination of water by the end of medium's lifetime	
Can be further developed to include new emerging media, as well as results from new laboratory and field experiments on currently listed media	Lack of information on amount of required media and their exact lifetime[2]		

[1] All 75 media are differentiated based on being wood-based, vegetation/phytoremediation based or inorganic in Table S2, Table S3, Table S4, respectively, documenting detailed list of advantages/disadvantages of media and already tested amendments to improve their efficiency.

[2] Acquisition of this information requires batch or column adsorption studies and modeling of adsorption capacity of selected media based on nutrient load and targeted removal percentage of pollution in a defined time period.

1- Based on the drainage water test results (Table S4), the "Nitrate/DRP" icon in the DST user interface was selected.
2- The DST recommends the top 10 media for treatment of this scenario. For example, the top three media based on *static* criteria for NO_3-N removal are woodchips, vetiver grass, and coco-peat, with a cumulative score of 9, 9 and 8.5, respectively. The media for DRP removal are similar to the Irish case study.
3- The *dynamic* Criteria 8 and 9 were assigned scores considering local conditions and resources available at farm-scale. This information was confirmed through consultation and face-to-face communication with a local private soft fruit company. A medium such as woodchip costs about €15 m^{-3} to be delivered to a farm, which is

considered inexpensive (i.e. Score 3) and similar to barley straw, or pea gravel. Some media such as apatite, limestone or vetiver grass are considered to be very costly, and must be imported to the site (with an associated high delivery cost). This was therefore assigned a Score of 1. The DST sums the total scores of the static and dynamic criteria.

4- After pressing "Run", the DST presented a high to low ranking of media for the Belgian case-study.

The top five ranked media for mitigation of NO_3 were (from best to worst): woodchips, cardboard, barley straw with native soil, coco-peat and sand. Soil (no clay) together with crushed concrete, peat/sphagnum peat, sand, and vetiver grass together with lime and zeolite, were the highest ranked media for mitigation of DRP. The feedback from face-to-face communication with farmers indicated that considering the availability of resources at farm-scale, waste cellulose (combination of leaf compost, wood mulch and saw dust) could gain more interest than woodchips. In addition, availability of locally sourced barley straw and peat with high NO_3 removal potential could consequently change the scores for the dynamic criteria to compensate for a low score for a static criterion (e.g. lifetime). Farmers perceived "pollution swapping" as being important and the final material needed to have a low pollution swapping potential. This was perceived as important to avoid monetary fines in terms of water regulations in the future.

3.1.3. USA

The results of the US case study are presented in Supplement Excel Sheet (Tab: EXAMPLES). The following four steps were taken to obtain the final results:

1- Based on the drainage water test results as in Table S4, the "Nitrate" icon on the DST user interface was selected.
2- The DST recommends the top 10 media for treatment of NO_3 pollution scenario (similar to Belgium Case Study for **NO_3**-related media).
3- The *dynamic* Criteria 8 and 9 were assigned scores based on a comparative scale using online information in consultation with the USA stakeholder, considering local conditions and resources available at farm-scale within the vicinity of case study region. The use of woodchips (to be used in denitrifying bioreactors) receive financial support from the government and the existence of numerous wholesale suppliers/or producers of coco-peat (coconut coir), vetiver grass, and zeolite made these media accessible and available. The DST then summed the total scores of static and dynamic criteria.
4- After pressing "Run", the DST recommended a high to low ranking of media for USA case-study.

The DST recommended woodchips, coco-peat, vetiver grass together with sand and zeolite, barley straw with native soil, as the highest ranked media from best to worst. This result supports the common use of denitrifying woodchip bioreactors in the USA as a well-established NO_3 remediation technology (Christianson et al., 2012a). The installation of woodchip bioreactors at the end of tile drainage systems is also financially supported by the US Department of Agriculture Natural Resources Conservation Service (USDA NRCS) (NRCS, NHCP, 2015). Such schemes, along with the major local productions, industry needs and wholesale suppliers/distributors/importers, have a direct influence on media availability and cost and, consequently, the scoring and final selection. The output of the FarMit DST considers only selection of a medium/media. Future research is required to test the medium/media under controlled laboratory conditions to elucidate design and operational parameters.

3.2. SWOT analysis

The overall SWOT analysis results from different workshops is summarised in Table 2. It was perceived that the major strengths of the FarMit DST were its easy concept and worldwide applicability for targeting dual removal of nutrient pollution, regardless of farming practice and considering specific local economic conditions and media-availability to individual users. Weaknesses identified included the absence of a sustainability factor (i.e. possible reusability of saturated media as a fertilizer or a soil amendment) and impracticality of using certain media regardless of their high ranking in nutrient mitigation. The major opportunity provided by FarMit was that it may be a long-term efficient decision support framework that can be implemented at the initial stage of decision making. The threats were seen as the risk of extreme weather events or social/economical/political changes that may have an impact of availability and price of media for farmers.

4. Discussion

4.1. Performance of DST in case-study applications

The DST application in different case studies representing different geographical locations and showcasing different farming practices, provided a ranking of media with high potential to remove nutrients in drainage water for various farm pollution scenarios. SWOT analysis showed the DST to be an effective tool to communicate management options to different stakeholders. It provided a list of options to the stakeholder and the results are clear enough to provide applicable information.

The results were consistent with the hypothesis that the dynamic criteria (availability and delivery cost of media to site) would vary spatially and temporarily. This was due to reasons such as geopolitical situation and proximity to a national border (e.g. to the French border for Flanders in Belgium), size of the country and therefore availability of wholesale manufacturers/suppliers/distributers, local production (e.g. wood-based or corn-based media like corn cob/stover may suit farmers in USA better than Belgium or Ireland), levies on recyclable materials (e.g. glass in Ireland or cardboard in Belgium), financial support from government (e.g. installation of woodchip denitrifying bioreactors in USA), the extent of application of media according to the dominant industry/use, etc. A good example for the latter is zeolite, which is a natural mineral medium with high potential for removal of both NH_4-N and DRP. Although imported in Ireland, this has wide application in Ireland and thus higher availability with lower delivery cost compared to Belgium, for example. Conversely, coco-peat is more available in Belgium than Ireland due to the wide application of coco-based media for other purposes (e.g. coco-chips in pesticide biofilter), while this medium is readily available and may be purchased at a relatively low cost in the USA.

4.2. SWOT analysis

Generally, the ranking of media is similar based on static (non-geographical) criteria for comparable case studies in different locations, although it is expected to change when considering the dynamic criteria (8 and 9) at specific sites. The operator may choose from 75 options (Table S5) according to their local knowledge and personal preference. This was considered as a strength in the SWOT analysis. This flexibility enabled the operators (farmer/adviser/engineer) to make a quick and informed medium selection based on possible future costs. This strength of the FarMit DST was welcomed in Belgium, where farmers were willing to take an active role in implementing sustainable solutions to minimize pollution caused by nutrient losses and they may opt for natural/organic media with zero pollution swapping and longer saturation time regardless of nutrient adsorption capacity. For example, despite the high availability of cardboard or crushed concrete at farm-scale and their high nutrient removal efficiency, the stakeholder (farmer) was concerned about the media lifetime and potential negative externalities. Therefore, the preference was to implement a more sustainable, but more expensive, alternative (e.g. zeolite).

In addition, if an operator wishes to avoid expensive pre-treatment or post-treatment of media due to pollution swapping caused by, for example, leaching of heavy metals (e.g. andesite and re-used concrete), they may wish to select a medium further down the ranking that may be more expensive but which has a lower environmental footprint. In addition, after the selection and operation of an engineered treatment system, the FarMit DST can be used again to minimize the effects of pollution swapping. For example, woodchip has been shown in some studies to release DRP (e.g. Fenton et al., 2016). In these cases, the DST can be used to select a Scenario C medium instead.

Another SWOT strength, as well as opportunity of FarMit, is the flexibility to be further developed and to adjust with time of application, as the dynamic criteria may also change over time. For example, a non-native plant such as vetiver grass has a high pollutant removal efficiency (Ash and Truong, 2004; Mayorca, 2007; Donaldson and Grimshaw, 2013) and can be purchased at a relatively low cost in the USA. It was initially only available at international-scale to Ireland and Belgium (where it was imported from Asia), but now has a growing market in Europe (with ensuing lower supply costs and higher availability). Here, the SWOT threats lie in the fact that changes in geopolitical landscapes impact commercial trade directly and extreme weather might change availability (and price) of local products.

The SWOT analysis identified a lack of a criteria considering environmental sustainability and post-implementation cost (e.g., disposal of used media and associated costs). This can be addressed in the future as the tool has the flexibility to be further developed.

5. Limitations and future recommendations

Phytoremediation and organic materials, presented in Table S2, have limitations (such as type of vegetation plant, geology, geographical features), which may affect the results of their application (e.g. peat). Similarly, soils and sands may differ in metal content and geochemistry, which could influence their nutrient adsorption capacity. Therefore, the user can subsequently decide to test several highly ranked media in batch studies to confirm their performance in specific contexts. This would then help to screen suitable materials and identify the most efficient type or chemistry of locally sourced media (thus with highest nutrient mitigation potential or longer lifetime) to be used in the site under examination.

In terms of final selection for an engineered structure, further media testing may be needed to elucidate on-site removal capacity, which may differ from literature or even laboratory conditions e.g. woodchip and denitrification rate. Additionally, the design of a system for dual nutrient mitigation will usually require the user to consider the sequence of media needed to address pollution swapping (Fenton et al., 2016).

Future development of this FarMit DST should consider incorporation of other factors by individual users (e.g. circular economy/agronomic value of saturated media) for scoring and finalising media selection, as well as aligning the ranking of media for removal performance based on similar conditions, e.g. residence time, and to factor in other issues that influence the removal efficiency, e.g. atmospheric conditions such as temperature. Furthermore, dynamic criteria could outweigh all other components if weightings are assigned. This would exclude all media for which access is not possible (e.g. vetiver grass in some areas). Another factor which could be included in the DST at a later stage would be maintenance costs pertaining to the selected medium/media at the field site.

The flexibility of the FarMit DST provides a tool with the capability to be updated by adding media emerging from new studies as well as new tests on the current 75 media reviewed, but in different experimental settings. This would consequently update the "static component" of the DST as new results indicate higher or lower removal rates, lifetime, or new insights into the pollution swapping potential of a media.

6. Conclusions

A decision support tool ("FarMit") was developed and validated. This tool enables the end-user to select locally sourced media which can be used in drainage ditch structures to mitigate polluted outflows. The tool provides seven static criteria for 75 media and the operator provides dynamic criteria (availability and delivery cost) to adjust the final ranked list for local conditions.

SWOT analysis, conducted in a series of workshops, showed the tool to be systematic, transparent and user-friendly, providing the user with a wide catalogue of options, and considers users' local economic and market conditions. Despite the fact that the tool does not provide an end-use for the saturated medium (media) or insight about re-use potential, it provides the opportunity of knowledge transfer between different stakeholders, and therefore can positively impact decision making.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecoena.2019.100010.

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Research article

Impact of P inputs on source-sink P dynamics of sediment along an agricultural ditch network

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ABSTRACT

Phosphorus (P) loss from intensive dairy farms is a pressure on water quality in agricultural catchments. At farm scale, P sources can enter in-field drains and open ditches, resulting in transfer along ditch networks and delivery into nearby streams. Open ditches could be a potential location for P mitigation if the right location was identified, depending on P sources entering the ditch and the source-sink dynamics at the sediment-water interface. The objective of this study was to identify the right location along a ditch to mitigate P losses on an intensive dairy farm. High spatial resolution grab samples for water quality, along with sediment and bankside samples, were collected along an open ditch network to characterise the P dynamics within the ditch. Phosphorus inputs to the ditch adversely affected water quality, and a step change in P concentrations (increase in mean dissolved reactive phosphorus (DRP) from 0.054 to 0.228 mg L^{-1}) midway along the section of the ditch sampled, signalled the influence of a point source entering the ditch. Phosphorus inputs altered sediment P sorption properties as P accumulated along the length of the ditch. Accumulation of bankside and sediment labile extractable P, Mehlich 3 P (M3P) (from 13 to 97 mg kg^{-1}) resulted in a decrease in P binding energies (k) to < 1 L mg^{-1} at downstream points and raised the equilibrium P concentrations (EPC$_0$) from 0.07 to 4.61 mg L^{-1} along the ditch. The increase in EPC$_0$ was in line with increasing dissolved and total P in water, demonstrating the role of sediment downstream in this ditch as a secondary source of P to water. Implementation of intervention measures are needed to both mitigate P loss and remediate sediment to restore the sink properties. In-ditch measures need to account for a physicochemical lag time before improvements in water quality will be observed.

1. Introduction

Diffuse and point-source inputs from agriculture result in degradation of water quality (Sutton et al., 2009), including loss of aquatic biodiversity (FAO, 2011) and ecosystem services (Schindler et al., 2010). Incidental and legacy P losses from agriculture to water (Haygarth et al., 2005) are major sources which contribute to eutrophication (Verheyen et al., 2015). The European Union Water Framework Directives (OJEC, 2000) requires member states to achieve at least "good" status in all water bodies and implement "programmes of measures" to minimise point and diffuse P losses (Kronvang et al., 2007; Sharpley, 2016; Macintosh et al., 2018; Melland et al., 2018). In Ireland the Nitrates Directive regulates P use on farms as a baseline measure to protect water bodies from nutrient and sediment loss. However, legacy P stores which are stored over decades of excessive P applications are difficult to mitigate and further measures may be needed before any impact on water quality is observed (Sharpley et al., 2013; Vadas et al., 2005; Fiorellino et al., 2017). Typically, water infiltrates into soil and interacts with legacy P stores along the transfer continuum. This water often discharges to drainage ditches acting as corridors for nutrient movement (Needelman et al., 2007). However, concentrations of dissolved P in these networks can vary due to direct discharges from pipes connected

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with a source, or as a result of sediment chemistry (Moloney et al., 2020).

Clagnan et al. (2019) examined the connectivity of surplus nutrients lost from an intensive dairy system to adjoining ditch networks and found elevated DRP in drainage water. Moloney et al. (2020) classified the on-farm ditch networks according to P loss risk and concluded that the highest risk was attributed to connectivity of the farm yards to ditches in combination with legacy P stored in the sediment. There is a constant interplay between dissolved P in water and bankside-sediment/sediment chemistry in which physiochemical properties such as aluminium (Al), iron (Fe), calcium (Ca), clay, pH and organic matter (OM) can enable mobilisation or immobilisation of P along the transfer continuum (Thomas et al., 2016). Shore et al., 2016 classified drainage ditch networks based on physical and chemical attributes and highlighted the role of vegetationfor nutrient and water attenuation along the networks (Haggard et al., 2004; Smith et al., 2005). The challenge for catchment managers and water policy is identifying the locations where these measures should be implemented. T Ditch bank side soil and sediments have a fundacion in the retention and mobilisation of P along these networks (Daly et al., 2017; Delgado and Berry, 2008; Dollinger et al., 2015; Daly et al., 2017; Fenton et al., 2017). Daly et al. (2017) found that subsurface horizons rich in Al could attenuate P or make it less soluble and concluded that a 'right measure, right place' approach to drainage measure implementation could be effective. However, Haggard et al. (2004) reported that sediments are spatially heterogeneous and can act as temporary stores of P or a transient storage pool that may be released back into water depending on *in situ* conditions. This transient nature of sediment P can influence the ditch capacity to become a source, sink or regulator of DRP in ditch water Smith et al. (2005). Hence, characterisation of ditch networks and closer monitoring of mobilisation of P is important in terms of their influence on the potential for nutrient losses to water (Kurz et al., 2005) and ditch management.

There is a lack of basic understanding of how a ditch network functions as both mobilisers and an attenuators of nutrients area both laterally and vertically and how this might change along the network. The primary objective of the current study was to identify optimal locations for implementing mitigation measures along an agricultural ditch, by considering the source-sink dynamics for P. Spatial variation in bankside soil and sediment P properties were measured along a ditch connected to an intensive dairy farm, and coupled with spatial and temporal DRP trends in the drainage water. The connectivity between surface (runoff) and subsurface (groundwater and artificial drainage system) flow pathways was established. An intensive dairy farm located in Southeast Ireland was chosen as a case-study site for this work. The catchment draining the farm was delineated and the main ditch carrying water from the farm to an outlet point provided the location for soil and sediment sampling and monitoring of water quality on the farm. Along this ditch, bankside soil and sediment samples were taken at locations and characterised for their P sorptive properties and P source/sink dynamics. Water quality draining the ditch was monitored for soluble, particulate and total P fractions over an 18 month period to profile P concentrations in the overlying water in the ditch so that a location for a potential mitigation option could be identified.

2. Materials and methods

2.1. Site description and identification of sampling locations

The Johnstown Castle catchment, delineated in Fig. 1, contains an intensive dairy farm (190.4 ha) located in SE Ireland in North Atlantic Europe (52°17′52″ N and 06°29′48″ W). The 30-year mean annual rainfall on this site is approximately 1000 mm, of which approximately half is drained at different rates into well to poorly drained soils (Fig. 1). Due to its glaciated origins, soils at the site are heterogeneous, varying in drainage class from well to poorly drained soils (saturated hydraulic conductivity ranges from 0.0001 to 0.029 m d^{-1} (Jahangir et al., 2013)). The grassland areas of the site consists of poorly and imperfectly drained Gleys to well drained silty clay loam (topsoil) and dense gravels intermixed with clay at 0.6–10.0 m subsoil geology. In poorly drained areas, an artificial drainage system has been installed and in-field drains discharge to a ditch network with high connectivity to the surrounding landscape (Fig. 2). A detailed description of the drainage network is provided in Clagnan et al. (2019). The total length of the drainage system within the catchment boundary is 10.25 km, comprising of 1.01 km of ditches with drains installed at approximately 1.2–2.9 m depth. The main ditch within the farm runs parallel to the farmyard and is 850 m in length. This ditch starts with shallow depth of 30 cm and gradually gets deeper to 270 cm, with 20 m above ordnance datum (AOD) change in elevation, and is the focus of this current study.

In terms of runoff and sub-surface drainage, an area of 94 ha (Kurz et al., 2005) – delineated up-gradient (24 ha) and down-gradient (70 ha) in Fig. 1 – contributes to discharge which enters the ditch through concrete pipes at No 1 & 2 (Fig. 2). The down-gradient contribution area enters the ditch at No 2 and is represented by the sampling point A. The up-gradient area (Fig. 1) enters the ditch at No 1. Other sources of water into the ditch stem from direct rainfall or groundwater. A groundwater well between the ditch and the farmyard (Fig. 2, Well 2 total depth of ~5 below ground level (bgl)) indicates an average water table height of <1 m bgl with a hydraulic gradient of 0.5, indicating discharge to the ditch through the bankside subsoil horizons and through the base of the ditch. Fig. 2 shows the groundwater elevation in the area of the ditch with contour beside the farm yard running perpendicular to the flow of the ditch. This places the water-table at 1 m below the farmyard which interacts with the depth of the concrete slurry storage facilities. On the opposite side of the ditch poorly drained soils have not been artificially drained and are presently out of production. Based on their connectivity and landscape position, Moloney et al. (2020) identified agricultural ditches as being high risk areas of P loss on Irish farms. At the Johnstown Castle, water quality and P dynamics of bankside and sediment samples along the length of the ditch were collected to provide a detailed appraisal of the impacts of sources entering the ditch. Seven sediment and water sampling points (Locations A, B, C, D, E, F, G in Fig. 2) along the ditch network were selected for sample collection.

2.2. Bankside and sediment sampling and analysis

Sediment samples from the bankside and base locations of the ditch were collected in October 2017. Grass and plants were removed and the bankside profile was sampled at depth intervals of 30 cm from top to base. The number of samples collected at each sampling points varied according to the depth of the ditch along the total length and are listed as follows: A: 1; B: 3; C: 4; D: 4; E: 8; F: 10; G: 9. Location-Code represents the depth interval number (e.g. A1) as shown in Tables 2 and 3. Similarly, sediments from the base of the ditch were collected, at the same location as bankside samples.

2.2.1. Soil chemistry analysis

All sediment samples were oven dried (40 °C) and sieved (2 mm) to remove stones and debris, and stored at room temperature prior to analysis. Sediment pH was analysed on 2:1 soil-water ratio paste and OM was measured based on loss-on-ignition of 4 g of samples at 500 °C (Schulte, 1995). The modified Mehlich 3-P (M3P) method (Mehlich, 1984) was used to determine labile extractable P, Al, Fe, Ca using a soil solution ratio of 1:10 in Mehlich 3 reagent (0.2 M $CH3COOH$ + 0.25M$NH4NO3$+ 0.015 M $NH4F$ + 0.13 M $HNO3$+0.001 M EDTA). Two gram samples were shaken on a reciprocating shaker for 5 min and the supernatant was filtered to determine concentrations of labile extractable P, Al, Fe and Ca.

2.2.2. Phosphorus sorption isotherm and equilibrium P concentration

The P sorption properties of the bankside and sediment samples were

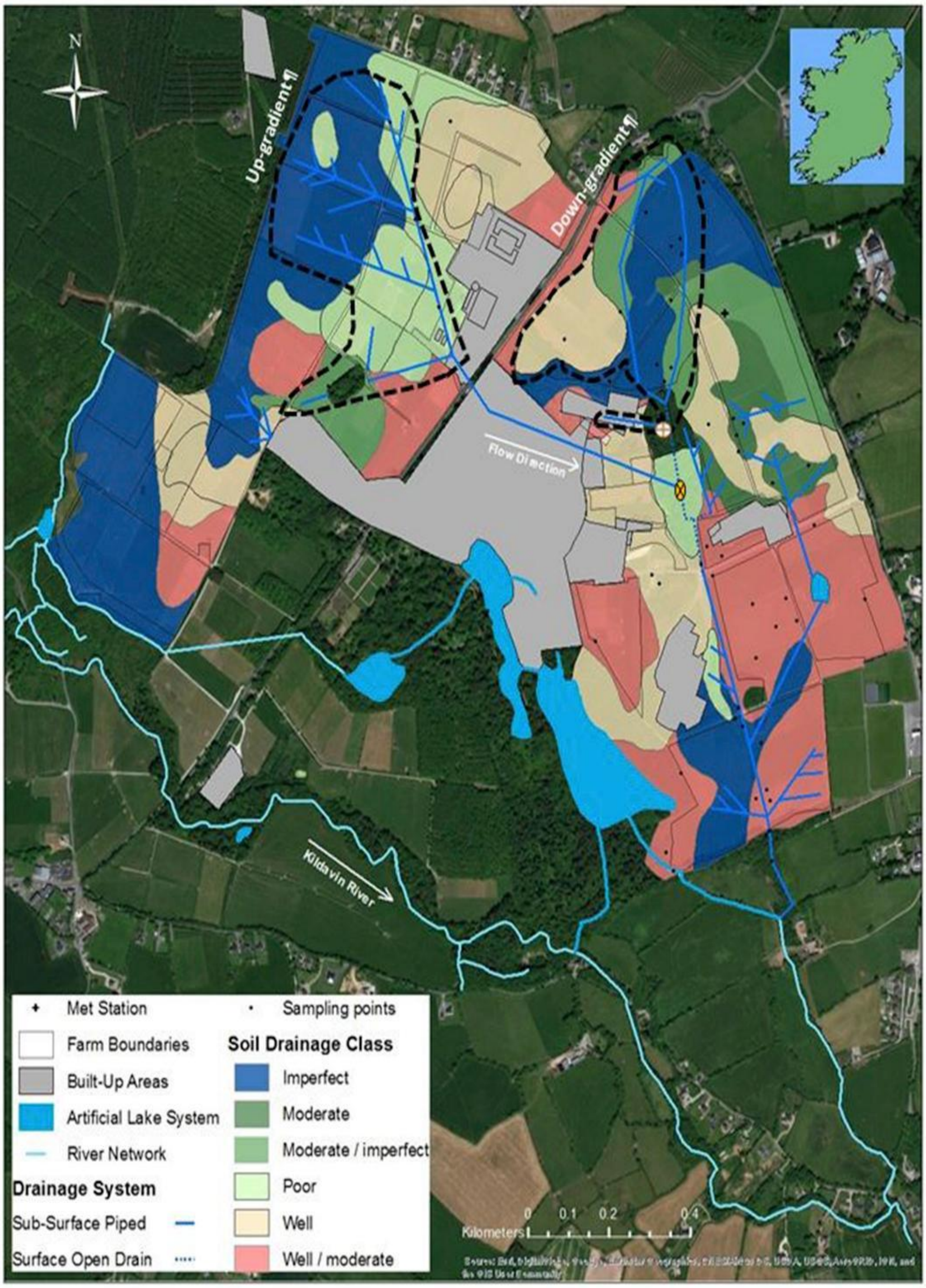

Fig. 1. Johnstown Castle Intensive Dairy farm showing the up-gradient and down-gradient surface/subsurface drainage system and runoff areas and their entry point into the open ditch system, soil drainage class, and sampling points across the farm documented by Kurz et al. (2005) and Clagnan et al. (2019). ⊗ No.1; ⊕ No.2.

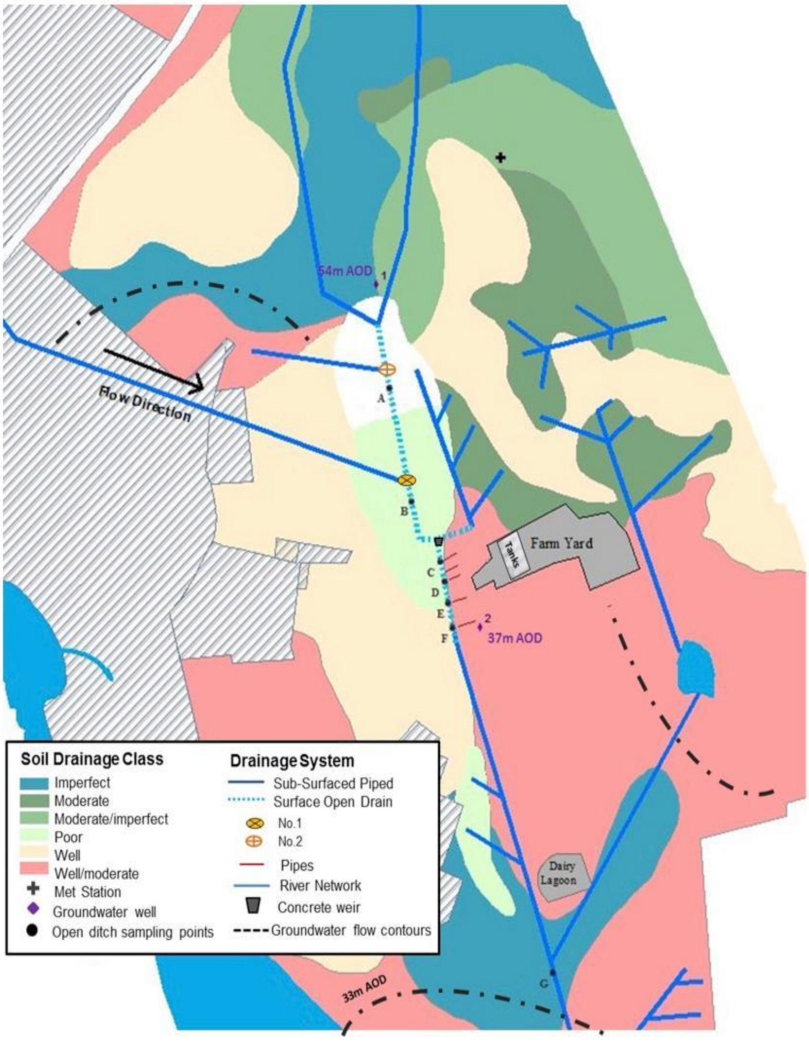

Fig. 2. In ditch grab water and soil-subsoil-sediment sampling points (Locations A-G). Position of farmyard, entry points of up-gradient and down-gradient discharge to the ditch (⊗ No.1; ⊕ No.2), position of pipes discharging directly into the ditch and water table height (m AOD) around the ditch network. Groundwater flow is perpendicular to groundwater contours i.e. into ditch.

described by a P sorption isotherm derived for all locations and depths along the ditch. Sediment samples from the bankside and base locations were equilibrated with six solutions with concentrations of 0, 5, 10, 15, 20 and 25 mg P L^{-1} (Paulter and Sims, 2000). Analyses were carried out in duplicate by adding 30 ml of initial P solutions to 2 g sediment in 50 ml centrifuge tubes. The tubes were shaken on an end over end shaker at room temperature for 24 h, centrifuged and filtered, and the final concentration of P in solution was measured colorimetrically. The difference between initial concentration and final equilibrium P concentration (C) was calculated as P sorbed to the soil (S). The linear form of the Langmuir isotherm equation ($C/S = 1/S_{max} *k + C/S_{max}$) was fitted to the sorption data and was used to derive the maximum sorption capacity (S_{max}; mg kg^{-1}) and k (L mg^{-1}), the constants related to the P binding energy in sediment.

The P sink/source dynamics of bankside and sediment samples was described the EPC_0 which represents a solution P concentration at the sediment-water interface where P is neither sorbed nor released. This parameter is often used to describe the role of sediment in freshwater systems in regulating P concentrations where sediment will adsorb/desorb P in order to reach a target P concentration at equilibrium, or EPC_0. If EPC_0 measured in sediment is higher than freshwater DRP, the sediment will release P to the water column in order to reach that equilibrium solution P concentration. If the sediment EPC_0 is lower than surrounding DRP, this favours net P adsorption from water into sediment in an effort to maintain a lower P concentration in solution at equilibrium (McDowell and Monaghan, 2015). The EPC_0 in bankside and sediment samples collected along the ditch was measured using 1 g sediment equilibrated with 20 ml of solution P concentration of 0, 0.1, 0.25, 0.5, 1 mg L^{-1} and shaken at room temperature for 24 h, centrifuged and filtered through 0.45 μm filters to measure the concentration of P in solution measured colorimetrically (Murphy and Riley, 1962). The EPC_0 was calculated from the slope of the linear plot of P sorbed on the solid phase against final solution P concentration.

2.2.3. *Data treatment*

Statistical analyses were carried out using R-Programming Language. The Null-hypothesis for all tests was considered to have no variance and no difference between groups and p-value of 0.05 was used to accept or reject hypothesis.

2.3. *Ditch water sampling and analysis*

Grab water samples from sampling points A to G (Fig. 2) were collected from Jan 2017 to July 2018. Filtered (0.45 μm) water samples were collected in 50 ml tubes and analysed for DRP using colorimetric analysis (Aquachem600 Labmedics Analytics, Thermo Clinical Labsystems, Finland) and digested with acid persulphate to determine total dissolved P (TDP). Unfiltered samples were analysed for total reactive P (TRP) using colorimetry (Aquachem) and particulate P (PP) was calculated by subtracting total dissolved phosphorus (TDP) from total phosphorus (TP). Additionally, ditch water at each location was pumped to a flow cell connected with an *in-situ* Multiparameter Probe (In Situ Inc. Ltd., USA) to measure temperature, electrical conductivity (EC), rugged dissolved oxygen (RDO), and pH under steady-state conditions.

3. Results and discussion

3.1. *Trends in water quality along an open ditch*

Table 1 presents summary statistics of DRP, TP, PP, and TRP across sampling points for the sample period January 2017 to July 2018. The distribution of these data is shown as boxplots in Fig. 3. Values of DRP and TP at sample points A to C were lower in comparison to values recorded further downstream from D to G. Average DRP and TP values between A and C were 0.042 and 0.168 mg L^{-1}, respectively and increased to 0.237 mg DRP L^{-1} and 0.48 mg TP L^{-1} between D and G. A step change in P concentrations was observed at sample point D indicating a point source contribution possibly due to inputs from the farmyard (Fig. 2) located between sampling points D and E. Field work during the present study identified several pipes directly discharging (odorous) into the ditch from the farmyard area and these were also tested when running water discharged from the pipes and recorded DRP concentrations ranging from 0.011 to 0.093 mg L^{-1} and TP ranging from 0.027 to 1.72 mg L^{-1} (red straight lines between farmyard and ditch in Fig. 2). The results at point E are indicative of direct discharges from the farm yard as evidenced by maximum DRP and TP of 2.976 mg L^{-1} and 4.89 mg L^{-1} respectively. Downstream from D, these parameters remained high and increased along the length of the ditch with highest mean DRP at F (0.434 mg L^{-1}) almost 10 times higher than A and twice that recorded at E. Max DRP values recorded at F of 1.258 mg L^{-1}, suggested that high P inputs are not attenuated by bankside and sediment along the ditch but continued to increase downstream at G, were some extreme values were recorded, reaching maximum DRP almost twice than F. Highest values at G are likely due to the direct discharges into the ditch from the yard (positioned at 37 m AOD) along with inputs from another ditch and potentially the diffuse inputs coming from surrounding fields including a dairy lagoon, which are accumulated down slope (33 m AOD). A step-change in TP values was also observed at D. Maximum TP of between 0.11 and 0.33 mg L-1 between A-C, rose to 1.32–4.89 mg L-1 from D to G and these values align with previously reported TP values in agricultural ditches with a direct connection to a farmyard (Harrison et al., 2019; Moloney et al., 2020). At catchment scale, Harrison et al. (2019) reported mean TP values > 1.5 mg L-1 in a riparian survey of ditches connected to farmyards and Moloney et al.,

Table 1

Summary statistics of ditch water phosphorus (P) fractions and hydrochemistry at sample points A-G along the length of ditch during January 2017–July 2018.

Location	Sample size	DRP	TP	PP	TRP	pH	Temp.	EC	RDO
		mg L^{-1}					°C	μS cm^{-1}	mg L^{-1}
Site A	10								
Max		0.120	0.227	0.227	0.052	8.44	12.99	471.1	10.67
Min		0.020	0.014	0.004	0.021	6.86	8.06	251.9	9.12
Mean		0.041	0.080	0.077	0.037	7.26	9.873	364.1333	9.99
Median		0.030	0.053	0.042	0.038				
Site B	10								
Max		0.088	0.110	0.110	0.093	7.27	10.07	388.8	9.64
Min		0.008	0.009	0.009	0.019	5.95	9.03	366.9	8.93
Mean		0.036	0.051	0.031	0.043	6.82	9.3	375.3	9.24
Median		0.019	0.053	0.013	0.040				
Site C	18								
Max		0.114	0.330	0.284	0.090	8.2	12.58	426.7	12.56
Min		0.021	0.028	0.005	0.025	6.97	7.92	236.7	8.21
Mean		0.054	0.087	0.066	0.045	7.23	9.625	348.5	10.18
Median		0.043	0.055	0.040	0.039				
Site D	10								
Max		0.610	2.290	0.318	1.210	7.56	12.6	423.8	10.75
Min		0.047	0.031	0.005	0.048	6.9	9.16	342	8.98
Mean		0.228	0.536	0.135	0.363	7.183	11.31	392.9	9.86
Median		0.123	0.156	0.100	0.132				
Site E	16								
Max		2.976	4.890	0.180	2.980	8.6	14.93	720	11.7
Min		0.008	0.017	0.001	0.007	6.34	7.99	252	8.89
Mean		0.272	0.536	0.036	0.432	7.32	11.14	466.1	10.28
Median		0.031	0.086	0.010	0.071				
Site F	18								
Max		1.258	1.320	0.784	1.230	8.6	14.88	560.8	10.86
Min		0.027	0.034	0.003	0.025	7.05	9.15	346.2	9.98
Mean		0.434	0.537	0.096	0.451	7.56	11.58	423.2	10.56
Median		0.147	0.165	0.058	0.167				
Site G	18								
Max		2.759	4.290	0.234	2.781	9.24	12.61	632.1	11.9
Min		0.004	0.016	0.000	0.025	6.98	8.22	233.2	8.09
Mean		0.220	0.242	0.037	0.225	7.90	9.51	385.06	10.102
Median		0.062	0.105	0.005	0.094				

Temp: Temperature; EC: Electric conductivity; RDO: Rugged dissolved oxygen.DRP: dissolved reactive phosphorus. TP: total P. PP: particulate P. TRP: total reactive P.

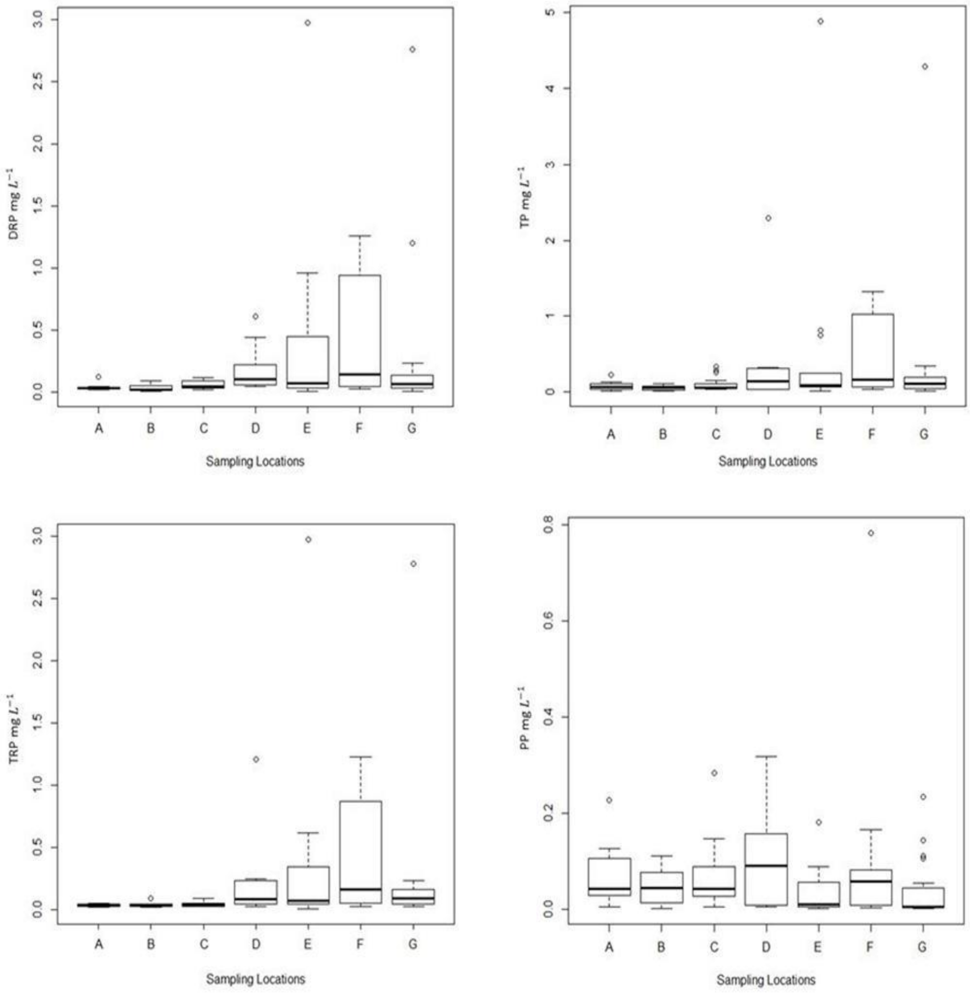

Fig. 3. Boxplots showing distribution of water quality data: DRP, TP, PP, and TRP (mg/l) at sampling locations A-G. The midline represents the median.

(2020) have identified this type of ditch as highest risk for P loss, if its landscape position allows for a direct connection into watercourses, compared to disconnected and secondary ditches.

Over the length of the ditch, average PP values were similar at all sample points except D, where a sharp increase to 0.135 mg L^{-1} was observed, coinciding with potential point source inputs from the farmyard. However, mean PP values further downstream fell back to within the range observed at upstream points, indicating some attenuation of the particulate fraction from this point onward. Point source inputs to the ditch were evident at sample point D, as soluble P remained high along the length of the ditch. However, the sharp increase in PP reverted to lower concentrations, indicating some ability to attenuate particulate fractions downstream.

3.2. Bankside and sediment characteristics

The biogeochemical properties of bankside and sediment samples for each depth interval are represented by Mehlich extractable Al, Fe, Ca, % OM and pH, and are presented in Table 2. Sediment and bankside pH ranged from 5.38 to 7.9, with high pH values coinciding with highest values of Ca at sample points E, F and G. In general, most of the bankside and sediment samples had a neutral pH and moderately low Al and Fe values compared to those recorded in previous studies on Irish soils and sediments (Daly et al., 2015, 2017). High extractable Ca was evident at sample points E, F and G, perhaps as a consequence of a change in soil characteristics or soil type along this reach of the ditch as illustrated in Fig. 2. The % OM ranged from 1.8 to 21.3% from point A to G, demonstrating the variability in soil types and drainage classes on surrounding fields at the site, with highest values recorded at surface bankside samples on imperfectly drained soils and lowest values along the length of the ditch dominated by well drained soils (Fig. 2).

Extractable metals Al, Fe and Ca have been reported to have a high affinity for P in both soils and sediment (Gächter and Müller, 2003; Mellander et al., 2012; Daly et al., 2017). However, the bankside/sediment analysis of our study showed low level of Al (range of 355 mg kg^{-1} between bankside of all locations) and Fe (range of 351 mg kg^{-1} between all locations except C4 which showed sharp increase to 781 mg kg^{-1}), with moderate to high M3Ca values (range of 4223 mg kg^{-1} with lowest values recorded at D and highest at G in the imperfectly drained area of the farm).

Table 2

Bankside and sediment physic-chemical properties Mehlich extractable Al, Fe and Ca, % organic matter (OM) and pH from bankside samples at 30 cm each depth intervals and sediment at the base of the ditch, taken at sample points A to G along the length of ditch.

Location	Depth	pH	OM	M3Ca	M3Al	M3Fe
Code	(cm)		(%)	mg kg^{-1}		
Site A						
A1	0–30	6.9	3.2	12,568	213	230
Sediment		6.0	1.8	977	259	134
Site B						
B1	0–30	5.38	8.0	12,363	448	259
B2	30–60	5.42	5.5	10,592	511	308
B3	60–100	5.66	5.0	1172	449	401
Sediment		7.2	3.1	1530	173	26
Site C						
C1	0–30	6.1	6.8	1811	338	284
C2	30–60	6.2	4.8	15,012	309	269
C3	60–90	7.3	2.8	14,563	234	418
C4	90–110	7.5	5.2	34,854	65	781
Sediment		7.9	1.0	698	68	139
Site D						
D1	0–30	6.5	5.2	1996	469	149
D2	30–60	6.5	2.0	792	362	67
D3	60–90	6.4	0.8	303	130	142
D4	90–110	6.7	1.7	870	205	323
Sediment		7.8	1.4	986	91.88	190
Site E						
E1	0–30	7.1	5.6	25,454	180	264
E2	30–60	7.2	6.1	21,864	200	276
E3	60–90	7.4	5.0	22,672	285	193
E4	90–120	7.4	3.9	19,943	373	215
E5	120–150	7.5	2.9	13,851	411	178
E6	150–180	7.6	1.4	849	256	236
E7	180–210	7.9	2.4	20,217	369	146
E8	210–240	7.9	1.0	20,175	362	154
Sediment		7.8	2.9	91	89.54	239
Site F						
F1	0–30	6.8	4.6	19,997	493	225
F2	30–60	5.9	4.4	1397	399	230
F3	60–90	6.0	3.9	12,546	456	226
F4	90–120	6.2	3.8	12,148	277	164
F5	120–150	6.0	3.8	11,765	328	179
F6	150–180	6.1	3.2	11,054	191	157
F7	180–210	6.4	5.7	17,744	307	278
F8	210–240	6.6	7.1	22,538	343	245
F9	240–270	6.7	7.4	26,862	484	266
F10	270–290	6.7	6.1	23,473	476	191
Sediment		7.2	3.3	1705	158.73	336
Site G						
G1	0–30	6.3	21.3	45,266	376	261
G2	30–60	6.5	18.1	38,003	312	226
G3	60–90	6.6	17.7	42,736	372	280
G4	90–120	7.1	6.5	2728	399	275
G5	120–150	6.7	10.1	25,664	315	260
G6	150–180	7.1	8.0	27,634	251	225
G7	180–210	7.1	5.4	19,883	256	282
G8	210–240	7.4	17.7	18,495	244	266
G9	240–270	7.8	1.3	15,364	129	204
Sediment		7.6	1.5	1015	143.4	266

3.3. *Trends in Bankside and sediment P dynamics along the ditch network*

Mehlich3 extractable P varied along the length and depth of the ditch network, with values exceeding the agronomic optimum of 50 mg kg^{-1} recorded at all sample points except A and C. Value in Table 3 indicate a shift toward higher M3P values at E which continued downstream reaching highest M3P values recorded at the surface bankside samples at G of 101–108 mg kg^{-1} at depth of 90 cm. The step change in water quality P values recorded at D, signalling point source inputs, was also observed in bankside and sediment P data; however, this occurred at the next downstream sample point (E). Welch's *t*-test results showed significant differences in M3P and EPC$_0$ values from D to E (p-value <0.05) and D and G (p-value of 0.0084), and significant differences in EPC$_0$ values between B and G (p-value $= 0.009$). This implies that whilst point source P impacted water quality at D, these inputs may be mobilised downstream where they start to accumulate as M3P in sediment, starting at E. At upstream points between A and C, M3P values were generally low; however, accumulation of extractable P is evidenced by increasing M3P values from E, downstream to G and likely due to P deposition by water draining the site. Box plots in Fig. 4 illustrate the shift upwards in extractable P along the length of the ditch.

Phosphorus sorption isotherm parameters Smax and k representing sorption capacity and P binding energies are presented alongside EPC$_0$ along the length and depth of the ditch in Table 3 with the spread of data represented as boxplots in Fig. 4. Values of k ranged from 0.3 to 2.9 L mg^{-1} with lowest values recorded at sample point G and coinciding with high M3P values at this point. This parameter, representing P binding and affinity, decreased along the length of the ditch, from point E onward, and coincided with the upward shift in extractable P bankside and sediment samples from E to G. Bankside and sediment locations downstream were characterised by loosely bound P and high extractable P, thereby increasing the likelihood of P loss to the overlying water. The EPC$_0$ parameter in this study was measured along the length and depth of the ditch to identify whether this ditch acts as a source or sink at bankside and sediment locations along its reach. However, EPC$_0$ illustrated in Fig. 4 and tabulated in Table 3 highlighted the variability in EPC$_0$ with highest values recorded at surface bankside locations and a trend toward increasing values from A to G along the length of the ditch.

The boxplots in Fig. 4 illustrate increases in EPC$_0$ from A to G, coinciding with M3P recorded at downstream points compared to upstream sample points. Highest EPC$_0$ and M3P values downstream at G, indicate accumulation and deposition of P, that is loosely bound P (low k values) and released to water (EPC$_0$) therefore acting as a source of P to the overlying water and water draining into the ditch.

At all bankside depths at G, k values were low (<1 mg L^{-1}) and EPC$_0$ values ranged from 0.24 to 4.61 mg L^{-1}. The P dynamics at this point on the ditch indicate that deposition of P from upstream sources and water draining the site has altered the sediment P sorption characteristics towards net release of P to water. This is largely driven by accumulated P in bankside and sediment, that is loosely bound (low k values), making this junction at source of P leaving the ditch.

The relationship between k and EPC$_0$ in bankside and sediment samples is illustrated in Fig. 5 (a), showing the influence of binding energies on potential P release. Bankside and sediment k values accounted for 40% of the variation in EPC$_0$ values. Moloney et al. (2020) found a similar regression coefficient between k and EPC$_0$ measured in ditch sediment across 10 farms and also reported the influence of accumulated labile P in ditch sediment on EPC$_0$ values. A similar relationship between M3P and EPC$_0$ was observed and is plotted in Fig. 5 (b) demonstrating the positive relationship between accumulated labile P (M3P) and EPC$_0$ values, therefore supporting our suggestion that P deposition in ditches can act as a source of P to overlying water, thereby increasing the sediment EPC$_0$.

3.4. *Impacts on water quality and source-sink properties of ditch sediments*

The water quality and bankside-sediment data are both indicative of diffuse and point sources of P coming into the ditch network. A step change in water quality was observed at D, due to point source inputs from the yard, but the effect on sediment P dynamics and deposition occurred further downstream at E. These data signal the influence of the farm yard on water quality and sediment P deposition in agricultural ditches. Inputs from the yard acted as a direct point source of P into the ditch and a source of P accumulation in sediment, causing deterioration in water quality and altered P sorption dynamics of the bankside and sediment. Changes in sediment P were characterised by higher extractable P (M3P) and lower P binding energies. Furthermore, P inputs into the ditch altered the EPC$_0$ reducing the attenuation capacity of bankside

Table 3

Phosphorus (P) sorption isotherm parameters describing sorption maxima Smax, P binding energies k, and Langmuir model R^2 measured in bankside and sediment samples. Equilibrium P concentrations EPC_0 is derived from isotherms at low initial P concentrations. Accumulation of P is expressed as labile P using Mehlich extractable P from bankside samples at 30 cm depth intervals to the base and sediment samples taken from sample point A to G along the length of the ditch.

Location	Depth	Sorption properties			Equilibrium Phosphorus		M3P
Code	(cm)	Smax (mg kg^{-1})	k (L mg^{-1})	R^2	EPC_0 (mg L^{-1})	R^2	(mg kg^{-1})
Site A							
A1	0–30	208.33	0.85	0.98	0.40	0.99	32.81
Sediment	Base	200.0	0.728	0.98	0.06	1.00	42.98
Site B							
B1	0–30	285.71	1.093	0.95	0.07	1.00	14.22
B2	30–60	333.33	1.87	0.97	0.03	1.00	13.05
B3	60–100	322.58	1.55	0.98	0.14	1.00	31.49
Sediment	Base	196.07	0.850	0.98	0.44	0.99	19.72
Site C							
C1	0–30	357.14	0.58	0.95	1.71	0.92	83.98
C2	30–60	294.11	1.03	0.99	0.62	1.00	40.57
C3	60–90	357.14	2.33	0.97	0.06	1.00	26.97
*C4	90–110	n/a	n/a	0.42	0.01	1.00	9.1
Sediment	Base	131.57	0.5278	0.96	0.28	1.00	20.33
Site D							
D1	0–30	250.0	0.85	0.97	0.07	1.00	13.81
D2	30–60	370.62	1.57	0.977	0.05	0.99	11.42
D3	60–90	116.27	0.741	0.98	0.04	0.99	7.87
D4	90–110	81.96	2.440	0.91	0.04	0.99	15.7
Sediment	Base	163.93	2.902	0.97	0.25	1.00	28.09
Site E							
E1	0–30	285.71	0.66	0.98	2.05	0.99	97.36
E2	30–60	285.7	0.56	0.95	1.75	1.00	86.39
E3	60–90	256.41	0.81	0.96	0.75	1.00	59.73
E4	90–120	294.11	0.79	0.97	0.84	1.00	68.65
E5	120–150	243.90	0.69	0.96	0.35	1.00	38.25
E6	150–180	187.68	0.75	0.97	0.14	1.00	26.4
E7	180–210	400.0	2.50	0.9	0.00	1.00	5.4
E8	210–240	303.03	1.73	0.97	0.01	1.00	7.15
Sediment	Base	192.30	0.55	0.95	0.36	0.98	31.79
Site F							
F1	0–30	256.41	1.0	0.97	0.21	1.00	25.81
F2	30–60	217.39	0.75	0.96	0.12	1.00	14.23
F3	60–90	222.22	1.32	0.98	0.15	1.00	19.02
F4	90–120	185.18	0.675	0.96	0.18	1.00	17.37
F5	120–150	188.67	0.73	0.97	0.27	0.99	20.71
F6	150–180	151.51	0.55	0.97	0.35	0.99	20.08
F7	180–210	250.0	0.68	0.97	1.62	0.99	60.73
F8	210–240	250.0	0.68	0.97	1.11	0.99	59.18
F9	240–270	344.82	1.38	0.99	0.58	1.00	53.27
F10	270–290	333.33	1.50	0.98	0.42	1.00	28.77
Sediment	Base	285.71	0.89	0.96	0.41	1.00	50.1
Site G							
G1	0–30	285.71	0.49	0.99	4.61	0.94	101.49
G2	30–60	357.14	0.38	0.98	4.17	0.94	108.84
G3	60–90	416.66	0.48	0.97	2.98	0.89	111.36
G4	90–120	344.82	0.93	0.98	0.78	1.00	89.79
G5	120–150	285.71	0.74	0.98	1.19	0.88	86.78
G6	150–180	303.033	0.67	0.97	1.21	0.99	72.77
G7	180–210	256.41	0.92	0.98	1.00	0.99	80.19
G8	210–240	250.0	0.95	0.98	0.65	0.99	70.75
G9	240–270	178.57	0.708	0.97	0.46	0.99	40.88
Sediment		227.27	0.88	0.98	0.24	1.00	38

and sediments in the ditch. This is also evidenced by the positive correlation between M3P and EPC_0 highlighting the influence of P inputs on sediment ability to attenuate P.

The accumulated P in surface layers of E, coupled with lower k values, and consistently high DRP and TP concentrations show release of P from bankside sediment. This is similar to some deeper intervals of F and all intervals of G which were saturated with P and k values get lowers as P deposited into system. This caused a release of accumulated P into the water and thus higher DRP concentrations. This observation is also supported by EPC_0 values which are presented in Fig. 6 with mean bankside and sediment EPC_0 at each sampling point along the ditch, plotted against mean DRP values at each point. The plot include the (1:1) line of equality between EPC_0 and DRP values where points below the line indicate sediment acting as a P source and points above line indicate a P sink (Smith et al., 2005). In Fig. 6 most of the EPC_0 values along this ditch, with the exception of values recorded at A and B, acted as source of P, releasing P to water.

The results highlighted the need for a mitigation intervention (McDowell and Nash, 2012) to clean ditch water before it leaves the farm (King et al., 2015).

This study identified the appropriate location for installation of an in-ditch nutrient interceptor at point D-E when the nutrient pollution starts to elevate before accumulating at point G. In-ditch engineered structures filled with medium/media with nutrient adsorption/remediation capacity can retain P before leaving the ditch and entering a surface water body (Ezzati et al., 2019). However, mitigation options should consider the high legacy P in deeper soil layers of the bankside and sediment samples which will continue releasing P into the water,

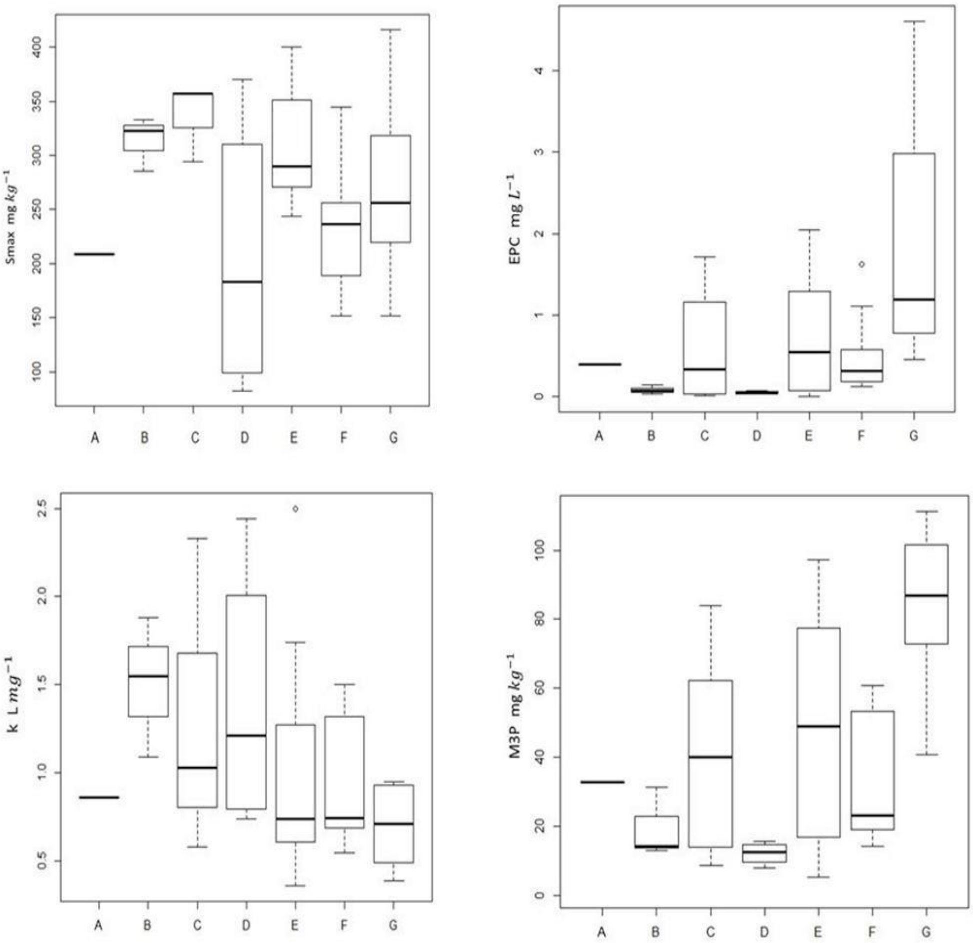

Fig. 4. Boxplots showing the distribution of Smax, EPC$_0$, k, and M3P values in all bankside and sediments at sampling locations A-G. The midline represents the median.

and which will delay and short term impacts on water quality.

4. Conclusion and recommendations

This study examined hydrochemistry and sediment P trends along the length and depth of an agricultural ditch network on an intensive dairy farm. High spatial resolution grab samples of ditch water were collected over 18 months alongside measurements of bankside and sediment P chemistry at depth intervals at points along the ditch. Phosphorus concentrations in water increased along the length of the ditch, due to inputs from a point source, identified by the presence of pipes discharging from the farm yard directly into the ditch. This caused a step-change in water P concentrations at this point as mean DRP and TRP values increased >10-fold from upstream to downstream points, indicating little or no attenuation of reactive P in the ditch by sediment. Particulate P increased sharply at the sample point closest to point source inputs from the yard, but values fell back in line with upstream values, indicating some attenuation of PP along the length of the ditch. Inputs from point and diffuse sources were transferred downstream resulting in deposition of P in sediment, which inhibited any natural attenuation of soluble P along the length of the ditch. The highest accumulation of P in the ditch sediment was recorded at the furthest downstream sampling point and P inputs into the ditch not only affected water quality but altered the sorptive properties of the sediment toward acting as a secondary source of P to water leaving the ditch network. The effects of P inputs from the yard on water quality and sediment P characteristics did not coincide at the same point on the ditch, rather, the step change in water quality occurred at D whilst changes in sediment P were only evident further downstream at D, indicating transfer and deposition in ditch sediment. The results demonstrated that such P inputs have altered the physico-chemical characteristics of the ditch sediment which highlights the need to remediate sediment to restore its natural P attenuation capacity and reverse its role as a secondary source of P to water. Water quality policy design will need to account for physico-chemical the lag phases in sediment remediation before any improvements are observed. Preventing further point source inputs to the ditch requires substantial restructuring in the farm yard, such as, redirecting yard runoff entering ditches, directly or indirectly, by e.g. blocking the pipes and collecting runoff for water treatment.

Close circle: Average EPC$_0$ from bankside (mg L^{-1}), Open circle: EPC$_0$ (mg L^{-1}) values from sediment. Values below 1:1 line indicate that the point act as a potential source of P.

Author contribution section

All authors provided interpretation and analysis of data, written text

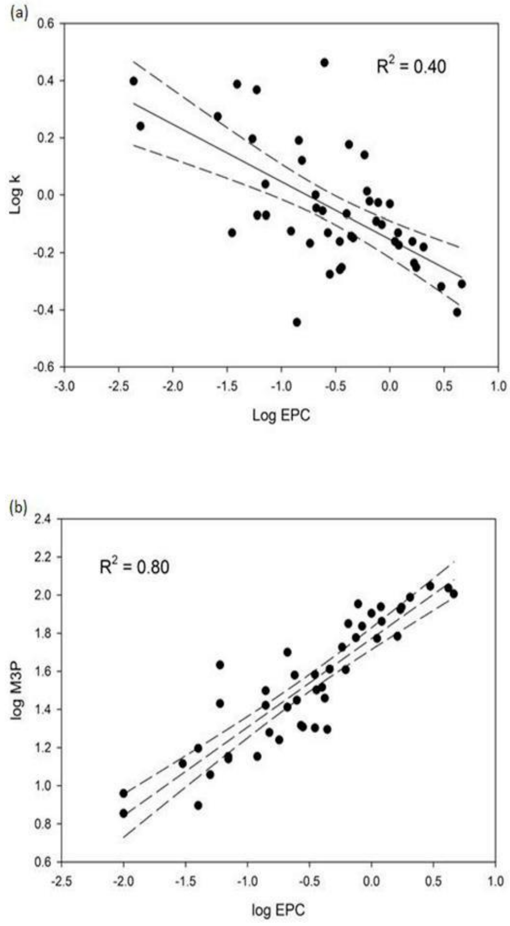

Fig. 5. Scatter plot showing (a) regression line between log EPC_0 and log K. and (b) regression line between log EPC_0 and log M3P in all bankside and sediment samples.

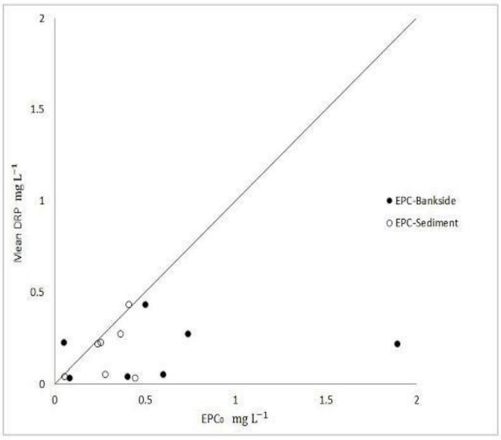

Fig. 6. Mean DRP values collected at sampling points as a function of average EPC_0 at bankside and EPC_0 of sediment.

and review of drafts of the manuscript. All authors contributed analytical data from field samples and laboratory assays to the database.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2019.109988.

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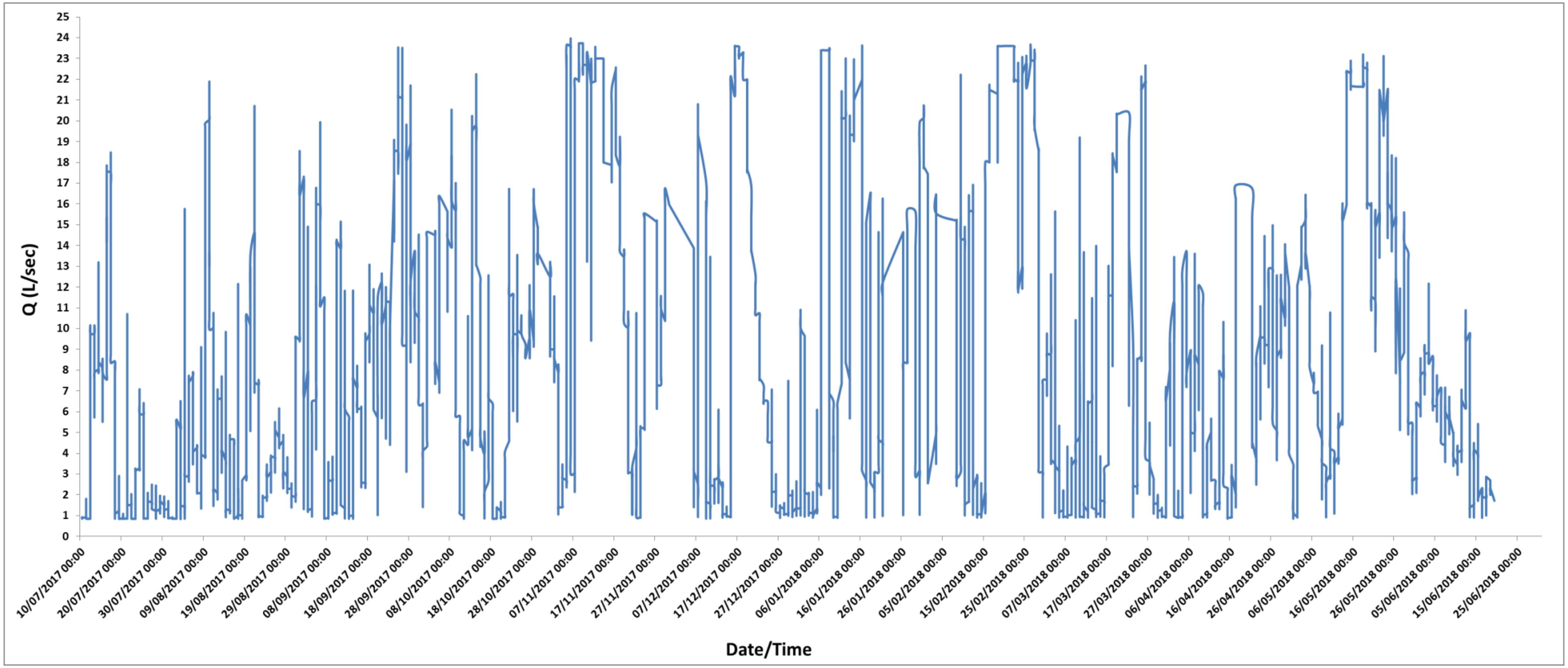
Appendix B

Appendix B. Water flow data from open ditch network: July 2017- July 2018.



Appendix C

Appendix C. Ranking list of 75 media for removal of NO3-N, NH4-N, and DRP based on static criteria.

	Criterion							Total Score based on Static Criteria			Ranking based on Static Criteria		
	1	2	3	4	5	6	7						
MEDIUM	**NO3-N Removal Rate**	**NH4-N Removal Rate**	**DRP-Removal Rate**	**Removal of other pollutant**	**Hydraulic conductivity**	**Life time**	**Negative Externality**	**NO3-N Removal**	**NH4-N Removal**	**DRP removal**	**NO3-N Removal**	**NH4-N Removal**	**DRP removal**
Lime		1	4.0	2.0	3.0	1.0	-1	5.0	6.0	9.0	9	8	2
Soil (no clay)	1.0	3.0	3.0	2.0	1.0	1.0		5.0	7.0	7.0	15	4	6
Woodchip	4	0.0	0.0		3.0	2.0		9.0	5.0	5.0	1	12	16
Peat/Sphangum peat		3.0	1.0	2.0	2.0	1.5		5.5	8.5	6.5	14	3	9
Vetiver grass	3.0	1.0	4.0	2.0	2.0	2.0		9.0	7.0	10.0	1	4	1
Andesite/refuse concrete/charcoal	0.0	1.0	4.0	2.0	2.0		-2	2.0	3.0	6.0	46	26	10
Sand	3.0	3.0	4.0	1.0	2.0	1.0		7.0	7.0	8.0	5	4	3
Natrolite/refuse concrete/charcoal	0.0	1.5	4.0	2.0	2.0		-2	2.0	3.5	6.0	46	24	10
Refuse concrete/nitrolite/charcoal-bio	0.0	1.5	3.0	2.0	2.0		-2	2.0	3.5	5.0	46	24	16
Crushed glass	2.0	4.0	0.0	1.5	3.0	1.0		7.5	9.5	5.5	4	2	14
Bottom ash	1.0	1.0	3.0		1.0		-2	0.0	0.0	2.0	70	67	51
Alum slugde:waste product from potable water	0.0		3.0	2.0	1.0		-2	1.0	1.0	4.0	60	59	28
Apatite/limestone 50-50% , w/w			4.0		3.0			3.0	3.0	7.0	38	26	6
Andesite/waste paper/refuse concrete	0.0	1.0	2.0	2.0	2.0		-2	2.0	3.0	4.0	46	26	28
Refuse concrete/waste paper/nitrolite	0.0	1.0	2.0	2.0	2.0		-2	2.0	3.0	4.0	46	26	28
Refuse concrete/waste paper/limestone	0.0	1.0	2.0	2.0	2.0		-2	2.0	3.0	4.0	46	26	28
Refuse cement and waste paper	0.0	1.0	3.0	1.0	2.0		-2	1.0	2.0	4.0	60	41	28
Lime stone with granulated activated carbon		2.0		2.0	2.5		-2	2.5	4.5	2.5	43	15	50
Zeolite	1.0	4.0	2.0	2.0	3.0	1.0		7.0	10.0	8.0	5	1	3

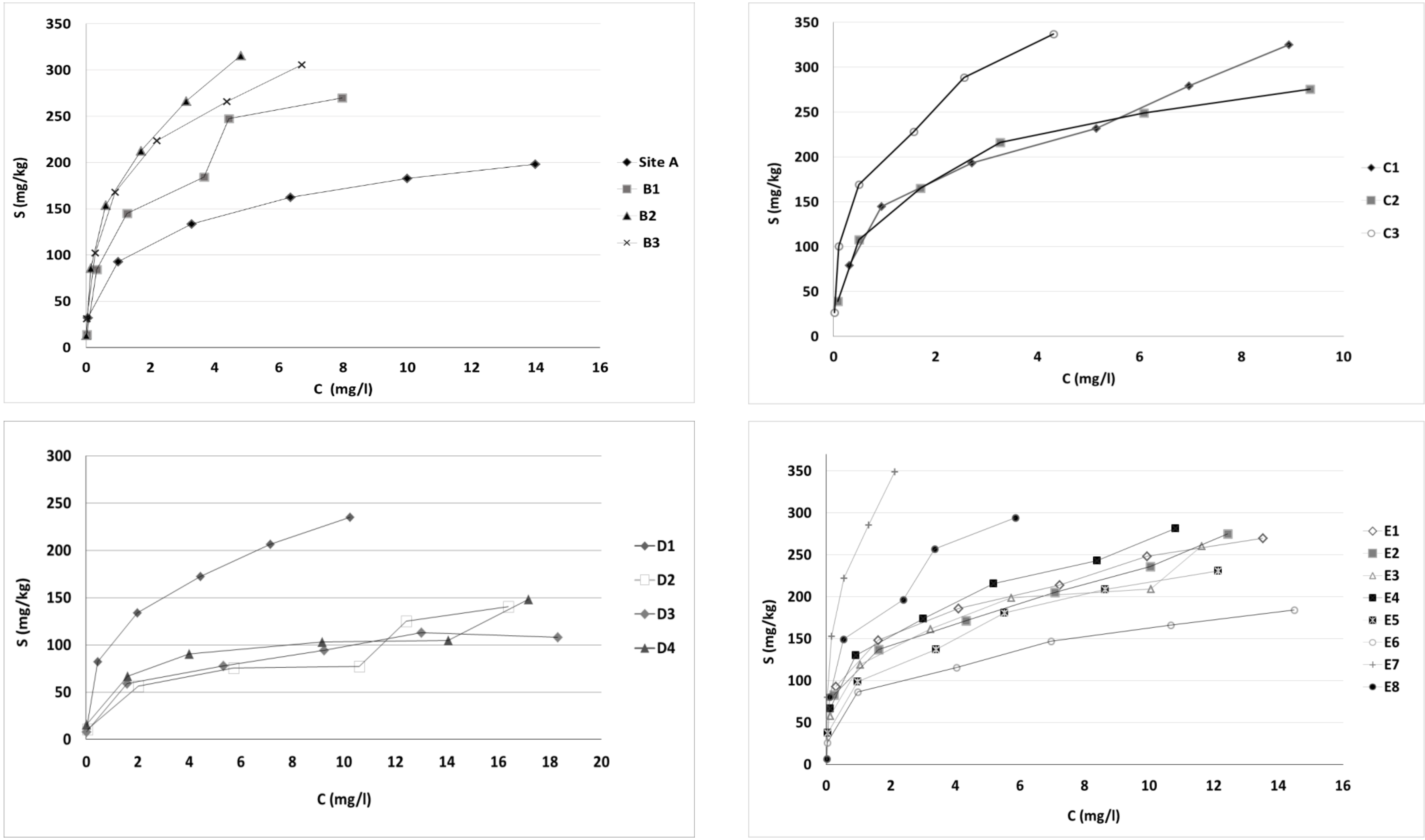
Apatite pellets			4.0		3.0			3.0	3.0	7.0	38	26	6
Ochre			4.0		3.0		-2	1.0	1.0	5.0	60	59	16
Waste cellulose (leaf compost, wood mulch, saw dust)	3	3			2.0			5.0	5.0	2.0	15	12	51
Fly ash	0.0	1.0	*2.0*	2.0	1.0		-2	1.0	2.0	3.0	60	41	36
Limestone	0.0	1.0	1.0	2.0	3.0			5.0	6.0	6.0	15	8	10
Pea gravel		1.0	0.0		3.0	2.0		5.0	6.0	5.0	15	8	16
Steel slag	2.0		2.0	2.0	2.0	1.0	-2	5.0	3.0	5.0	15	26	16
Recycled shredded tyres	2.0		3.0		3.0	1.0	-2	4.0	2.0	5.0	26	41	16
Barley straw	2.0	1.0			2.0	0.0		4.0	3.0	2.0	26	26	51
Ryegrass	1.0			2.0	2.0	0.0		5.0	4.0	4.0	15	16	28
Refuse concrete and waste paper	0.0	0.0	3.0	0.0	2.0		-2	0.0	0.0	3.0	70	67	36
Furnace slag		1.0	2.0		3.0			3.0	4.0	5.0	38	16	16
Natrolite	0.0	3.0	2.0	1.0	3.0			4.0	7.0	6.0	26	4	10
Andecite/limestone/refuse concrete/waste paper	0.0		3.0		2.0		-2	0.0	0.0	3.0	70	67	36
Andecite/waste paper/charcoal-bio/refuse concrete	0.0		3.0		2.0		-2	0.0	0.0	3.0	70	67	36
Cardboard	4.0	0.0			3.0			7.0	3.0	3.0	5	26	36
Barley straw + (native) soil	4.0				2.0	0.0		6.0	2.0	2.0	9	41	51
Granular actuivated carbon	3.0			1.0	3.0			7.0	4.0	4.0	5	16	28
Stratified layers of sand,granular activated carbon,& pyritic fill	2.0			1.0	3.0			6.0	4.0	4.0	9	16	28
Crushed concerete			4.0	2.0	3.0	1.0	-2	4.0	4.0	8.0	26	16	3
Sawdust (30% Volume)	3.0			0.0	2.0			5.0	2.0	2.0	15	41	51
bayer residue	0.0	1.0	1.0	2.0	2.0			4.0	5.0	5.0	26	12	16
corncorb+woodchip	1.0				2.0	1.0		4.0	3.0	3.0	26	26	36
Immature compost	4.0				2.0	0.0		6.0	2.0	2.0	9	41	51
Corn corb	2.5				2.0	0.0	-2	2.5	0.0	0.0	43	67	70

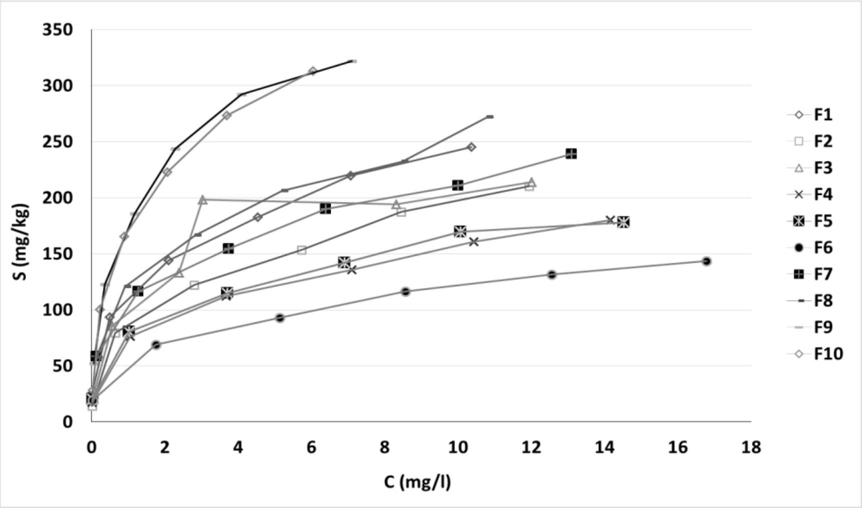
Yard waste	2.0				2.0	0.0		4.0	2.0	2.0	26	41	51
Woodchip/pea gravel	2.0	-1.0			3.0	2.0	-2	5.0	2.0	3.0	15	41	36
Corn Stover	0.5				2.0			2.5	2.0	2.0	43	41	51
Rice husk			3.0	2.0	1.0		-1	2.0	2.0	5.0	46	41	16
Tea/Coffee waste	0.0		0.0	1.0	1.5		-1	1.5	1.5	1.5	58	57	64
Pine bark	0.0				3.0	2.0	-2	3.0	3.0	3.0	38	26	36
Ryegrass/artificial aquatic mats biofilm	2.0			2.0	2.0		-1	5.0	3.0	3.0	15	26	36
Sandy Loam soil	0.0	-1.0			2.0		-2	0.0	-1.0	0.0	70	75	70
Woodchips+Acetate	4				3.0		-1	6.0	2.0	2.0	9	41	51
Logepole pine needles(LPN)	4.0	1.0			3.0		-3	4.0	1.0	0.0	26	59	70
Wheat straw	3.0				2.0	0.0		5.0	2.0	2.0	15	41	51
Lodepole pine woodchips	2.0	0.0			3.0		-3	2.0	0.0	0.0	46	67	70
Pyrite modified by calcination	3.0	1.0		1.0	1.0			5.0	3.0	2.0	15	26	51
Shells	0.0	0.0	1.0	1.0	3.0			4.0	4.0	5.0	26	16	16
Sawdust with sand	0.0			0.0	1.5			1.5	1.5	1.5	58	57	64
Thermally-modified calciumrich attapulgite			4.0		1.0			1.0	1.0	5.0	60	59	16
Charcoal (from coconut)	0.0	0.0	1.0	3.0	1.0		-2	2.0	2.0	3.0	46	41	36
CocoPeat	3.0		0.0	2.0	2.0	1.5		8.5	5.5	5.5	3	11	14
Charcoal-bio	1.0	2.0	0.0	0.0	2.0		-2	1.0	2.0	0.0	60	41	70
Biochar	1.0	-1			1.0	0.0		2.0	0.0	1.0	46	67	66
Expanded clay			0.0		1.0			1.0	1.0	1.0	60	59	66
Flue Gas Desulfurization Gypsum			2.0		1.0			1.0	1.0	3.0	60	59	36
K1 Kaldness media : plastic MB3/ AMB	0.5				3.0			3.5	3.0	3.0	36	26	36
Corn Cob + Modified Coconut Coir + Modified biochar	2				2.0			4.0	2.0	2.0	26	41	51
Woodchip lined with 40-mm heavy duty agricultural liner	0.5				3.0			3.5	3.0	3.0	36	26	36
Expanded shale			2.0		1.0			1.0	1.0	3.0	60	59	36

Raw Brown Coal		2.0	0.0		2.0			2.0	4.0	2.0	46	16	51
Base wash Brown Coal		3.0	0.0		2.0		-1	1.0	4.0	1.0	60	16	66
Pond culture	0.0		0.0		1.0		-1	0.0	0.0	0.0	70	67	70
Cationic cellulose nanopapers	2.0				2.0		-1	3.0	1.0	1.0	38	59	66
Peat modified with iron(III) hydroxy ions			3.0		3.0		-1	2.0	2.0	5.0	46	41	16

Appendix D

Appendix D. Comparison between Adsorption Isotherm between bankside intervals and sediments at sampling locations.

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250
300
350
C (mg/l)
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4
6
8
10
12
14
16
18
F1
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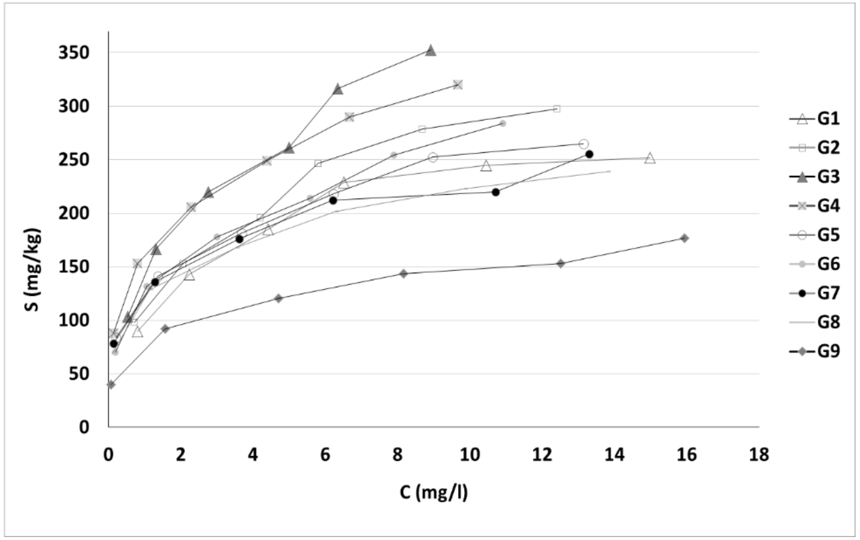
F9
F10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200
250
300
350
C (mg/l)
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4
6
8
10
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14
16
18
G1
G2
G3
G4
G5
G6
G7
G8
G9