



School of Science

Department of Science

MSc in Environmental Science

**NUTRIENT REDUCTION CAPACITY OF A NOVEL
BIOSWALE SYSTEM FOR THE REDUCTION OF
NUTRIENTS FROM FARMYARD DIRTY WATER**

Author Edward Lanigan

Supervisors:

Dr. Kieran Germaine

Dr. David Dowling

Acknowledgements

I would first like to thank my supervisors Dr. Kieran Germaine and Dr. David Dowling. They were always willing to offer me support and guidance about my research or writing. They allowed me the freedom to make this work my own but also guided me in the right the direction whenever they thought I needed it. Without their constant encouragement and support I'm not sure this project would have reached completion.

I would also like to thank the Joe Connelly, Brendan Walsh and Eddie Brennan of Clogrennane Lime for supplying me with all the dolomite I required for my project for free, as well as allowing me to use their XRF.

I would also like to extend my gratitude to Pat O'Brien and the staff of Delmec Engineering, Graiguecullen Carlow, for allowing me the use of their facility. I used my skills in engineering to make the steel structure which was used for the column experiment both in chapters three and five.

I would like to thank my postgraduate friends a fantastic group of individuals. Through the frustrations and fun, they were there for me.

I must express my very profound gratitude to my parents for providing me with unfailing support and continuous encouragement throughout my years of study. To my kids Rachel, Robbie and Carson for reminding me of what really matters in life. Finally, to my wife Tara who supported me in so many ways throughout, a Humanities graduate who took the time many times to read my thesis and offer many valuable suggestions.

Thank you.

Abstract

The protection of clean water is of paramount importance to both humans and the aquatic environment. The aquatic environment in Ireland is subjected to impacts from many different human activities and pressures. Pollution from agriculture comes in the form of point sources from farmyards, containing animals and diffuse pollution, where nutrients and pesticides are washed off land and into the rivers through rainfall.

Farmyard dirty water (FYDW) is created when rainwater gets mixed with agricultural waste streams. FYDW can be a mixture of urine, animal feces, organic matter, milk parlor waste and inorganic pollutants that contain nutrients. These waste streams cause serious pollution of ground and surface water bodies. FYDW may also contain potentially pathogenic micro-organisms, pesticides and antibiotics. These constituents can have detrimental effects on the aquatic environment as well as affecting human health.

At present, there are two ways of dealing with FYDW, land spreading which is regulated in the European Union (EU) and open to misuse, and Integrated Constructed Wetland (ICW) which can require large areas of land.

In 2015 a feasibility study was carried out on campus at the Institute of Technology, Carlow. This study examined the ability of a small scale bioswale containing an aquatic plant layers of soil, wood bark and a submerged layer of pea gravel. The study conducted over 3 months found good reductions in chemical oxygen demand (COD), nitrate, and ammonium but not reactive phosphate.

The objective of this study is to develop a novel bioswale for the treatment of FYDW. The system is relatively small in comparison to ICWs, the novel bioswales could provide a more cost-effective way of reducing pollutants present in FYDW.

The objective of this study was to evaluate materials that could be used in a bioswale to remove phosphorus (P), three experiments were carried out under controlled conditions. The first experiment was a screening of several materials and examination of effective flow rates for phosphorus (P) removal. The material should act as a choke layer to prevent smaller particles from the soil above from descending into the drainage

layer into the bottom of the system. Dolomite removed 87.8-99.6% of P from solution. Shale removed 98.1% and soil removed 98.5%.

The second experiment used Langmuir sorption isotherms to examine the effectiveness of dolomite, shale and soil in the removal of P from solution. The results of the second experiment gave theoretical values for the sorption of P in mg per kg of material with soil, shale and dolomite. The experimental values for the sorption isotherms were 0.545 mg g⁻¹ for dolomite, 0.143 mg g⁻¹ for shale and 0.587 mg g⁻¹ for soil. This enabled the building of 6 small scale bioswales, 3 for each type of bioswale, the dolomite and shales bioswales. The final experiment seen the construction of PVC pipes with 5 layers of the materials, soil, willow bark, shale or dolomite and limestone as a drainage stone. Three pipes had a layer of dolomite and three had a layer of shale. The findings from these experiments showed that dolomite and shale both had high levels of removal of reactive phosphate removal from solution. The percentage reductions were 97.65% for shale columns and 95.23% for dolomite columns. Under negative redox conditions there was a significant difference between the two types of bioswales. The shale bioswales had a better total phosphate removal than the dolomite bioswales under the same conditions. The overall conclusion was to use soil as this was required for the plant and had good P removal properties, shale and dolomite in any future bioswale. The final experiment also examined the removal of ammonium and nitrate from solution. The systems removal rates of ammonium were above 94.0%, with the dolomite bioswale systems having a higher percentage removal rate than the shale systems. For both types of bioswales it was noted that there was a steady decline in the removal of both nitrate and ammonium.

The Langmuir isotherm experiments conducted on the materials for the removal of P and the values obtained for the removal of ammonia and P from solution, should now allow for the development of a large scale bioswale construction and the monitoring of nutrient removal from such over an extended period of time.

Table of Contents

Chapter 1.0: Introduction	1
1.1 Farmyard Dirty Water (FYDW).....	10
1.2 Associated environmental impacts of FYDW and Regulations.....	12
1.3 Current methods of dealing with FYDW	14
1.3.1 Land Spreading	14
1.3.2 Integrated Constructed Wetlands	14
1.4 P, speciation and negative environmental effects	19
1.5 Phosphate remediation materials.....	Error! Bookmark not defined.
1.6 Physical and Chemical Characteristics effecting Sorption of Phosphate.....	20
1.7 Sorption Isotherm Mathematical description	22
1.8 Feasibility Study.....	24
1.9 Aims and objectives of the present study.....	31
Chapter 2.0: Materials and methods	
2.1 Chemical and Physical Analysis	32
2.3 Preliminary column trial and optimal flow rates for removal of phosphates by dolomite and shale.....	35
2.4 Batch studies Soil, Shale and Dolomite	36
2.5 Multi horizon packed bed filtration system.....	37
Chapter 3.0:	
Preliminary analysis of several materials and optimal flow rate: Removal of phosphate from aqueous solution.....	36
3.0 Introduction: Preliminary trial of several materials	43
3.1 Results	44
3.2 Optimal flow rate for the retention of phosphate by dolomite and shale	42
3.3 Discussion	46
3.4 Conclusions	54
Chapter 4.0:	
Langmuir adsorption isotherm; Batch study of phosphate adsorption on soil shale and dolomite.....	50

4.1 Introduction	51
4.2 Total and reactive phosphate comparison of results	51
4.3 Results of sorption isotherms and XRF.....	559
4.4 General discussion.....	63
4.5 Conclusion.....	66
Chapter 5.0:	
Reduction of Nutrients in synthetic waste water by multi horizon packed bed bioswale filtration system.	72
5.1 Introduction	73
5.2 Results	70
5.3 Reactive Phosphate removal efficiency of the mini-bioswales.....	74
5.4 Total Phosphate removal efficiency of the mini-bioswales	77
5.5 Results of ammonium and nitrate reductions in the mini bioswales.....	82
5.6 Discussion	87
5.7 Conclusions	92
Chapter 6.0:	
Overall Discussion.....	94
Chapter 7.0:	
Concluding remarks and future research.....	102
References.....	i-xiv

1.0 Introduction

Water is one of the most important substances on our planet and is necessary for all life. Most of the water on our planet (96%) is found in the oceans, the remaining 4% is fresh water. 1.7% of global water can be found in ice caps and glaciers, another 1.7% is found as ground water and less than 0.01% is found in freshwater rivers and lakes (known as surface waters). Both ground water and fresh surface waters, accounting for a mere 1.71% of water on our planet, are essential for the vast majority of the estimated 6.5 million species of terrestrial life, (NOAA, 2017). For humans, safe, clean, high quality surface and ground water resources are critical for drinking water, domestic, agricultural and industrial uses. It is ironic that these same human activities can lead to serious pollution of these critical water resources, impacting not only on the health and well-being of over 7 billion humans that are reliant on them but also the billions of other terrestrial and marine life forms on planet Earth.

The aquatic environment in Ireland is subjected to impacts from many different human activities and pressures. These activities, either acting alone or together, can damage the quality of Ireland's surface water and groundwater resource. Characterization by the Environmental Protection Agency (EPA) of these pressures has identified the most prevalent pressures causing damage to the quality of water bodies. These are:

1. Agriculture affects 53% of water bodies, (EPA Water Quality Report, 2019).
2. Discharges from urban and domestic wastewater treatment systems affects 29% of water bodies, (EPA Water Quality Report, 2019).
3. Hydro-morphological alterations that change the flow and structure of water bodies affects 24% of water bodies, (EPA Water Quality Report, 2019).
4. Forestry affects 16% of water bodies, (EPA Water Quality Report, 2019).

Other less common but significant pressures include pollution from diffuse urban run-off and industry and pressures caused by peat extraction, mining and quarrying. Agricultural pressures, which are the most prevalent, include point source pollution associated with farmyards and other places where animals congregate, and diffuse pollution associated with nutrients (phosphorus and nitrogen), sediment and pesticide runoff from land, (Bartley P, Johnston P, 2006).

In relation to wastewater, the primary pressure is from urban wastewater discharges, but domestic wastewater (septic tanks) can have impacts at the local scale. Diffuse urban

discharges, including runoff from paved areas, leaking sewers, and misconnections from domestic plumbing systems into the wrong pipes, are also significant contributors, (Montenegro, C.T, 2013). Protecting these essential sources of water is critical to ensure their suitability as abstraction sources for producing safe drinking water and for agricultural and industrial uses. Hence, there is a significant amount of legislation dealing with water quality and water monitoring. In Europe, one of the main pieces of legislation covering water quality in river, lakes, groundwater, transitional and coastal waters is the EU Water Framework Directive (WFD), Directive 2000/60/EC. The objective of the WFD is to protect, restore and prevent any further deterioration of surface waters, groundwater and water dependent ecosystems.

Under the WFD the quality of surface waters is assessed by looking at a range of aquatic organisms whose presence and abundance indicates the ecological health of different water bodies. These biological quality elements include phytoplankton, microalgae, aquatic plants, macroinvertebrates and fish. Changes in the composition and abundance of these different biological communities are measured against what would be expected in the absence of pollution and impacts from human activities are measured (Parmar, Rawtani and Agrawal, 2016).

Physicochemical and hydro-morphological quality elements are used to assess the ecological natural waters. Surface waters are categorised into five different classes or Ecological Statuses: High, Good, Medium, Poor and Bad. The Ecological status indicates if a natural water body is being damaged by pollution or habitat degradation, (Gorzal, Kornijów and Buczyńska, 2018).

Waters in high and good ecological status show only minor or slight changes from natural conditions whereas waters at less than good status (moderate, poor or bad) range from moderately to severely damaged by pollution or habitat degradation (Figure 1.1). This system replaces a previously used scheme developed by the Irish (EPA) known as the Quality rating system or Q-value. The Q-scheme method is used whereby a Quality-index is assigned to a river or stream based on macroinvertebrate data. The Q-index is a quality measurement ranging from Q1-Q5 with Q1 being of the poorest quality and Q5 being pristine / unpolluted. Ground water is assessed based on the chemical status and quantitative status and there are only two classes Good and Poor, (EPA Water Quality Report 2019).

Table 1.1 Relationship between Q-Values, Ecological status and Water quality used in Surface water Quality Assessment in Ireland.

Q Value	WFD Status	Pollution Status	Status Class	Water Quality
Q5, Q4-Q5	High	Unpolluted	A	Satisfactory
Q4	Good	Unpolluted	A	Satisfactory
Q3-Q4	Moderate	Slightly polluted	B	Unsatisfactory
Q3, Q2-Q3	Poor	Moderately polluted	C	Unsatisfactory
Q2, Q1-Q2, Q1	Bad	Seriously polluted	D	Unsatisfactory

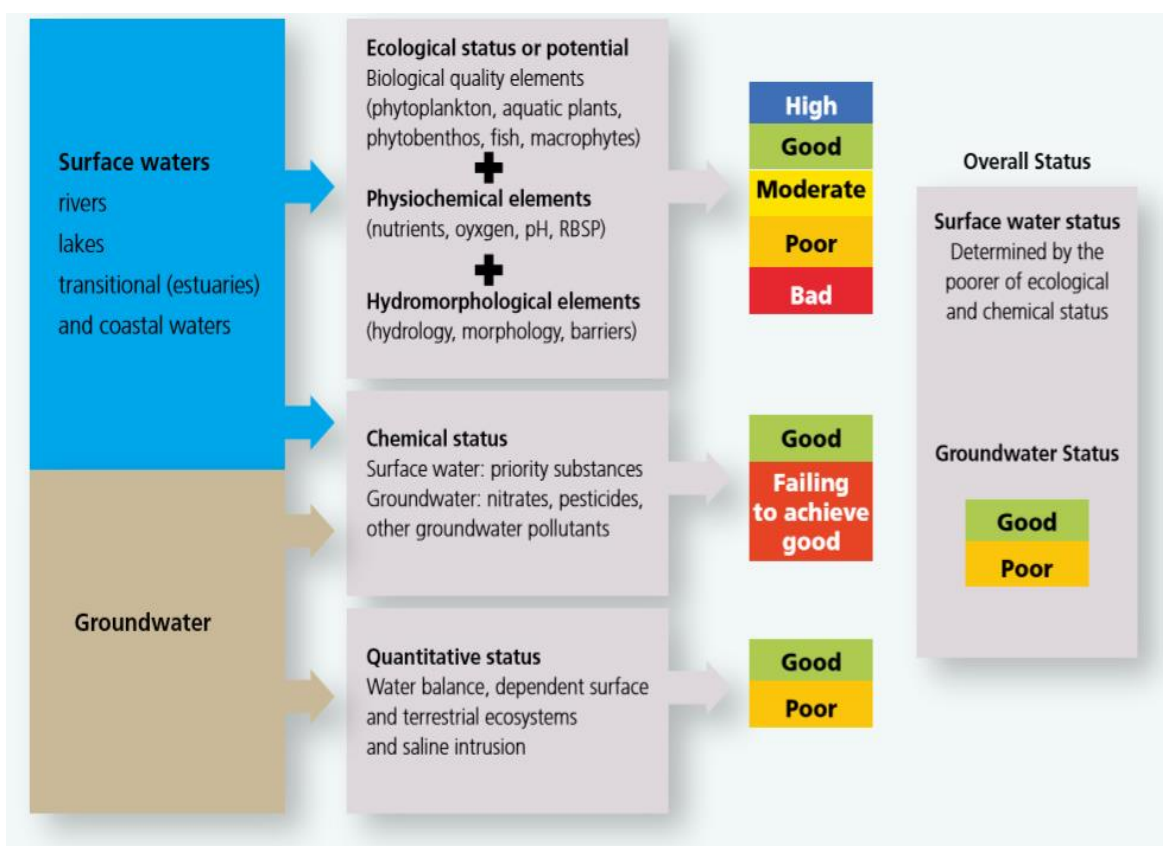


Figure 1.1 System use to classify surface and ground water quality Status in Ireland and the EU, under the WFD.

The Irish EPA is responsible for monitoring surface and ground water quality in Ireland and each year they produce a report on their findings. In 2019 their report showed a continued decline in the number of high-status Rivers (12.9% in 2007-2012 to 8.5% in 2013-2018) and slight increase in the number of Poor Status Rivers (14.8% - 17.7%) (Figure 1.2).

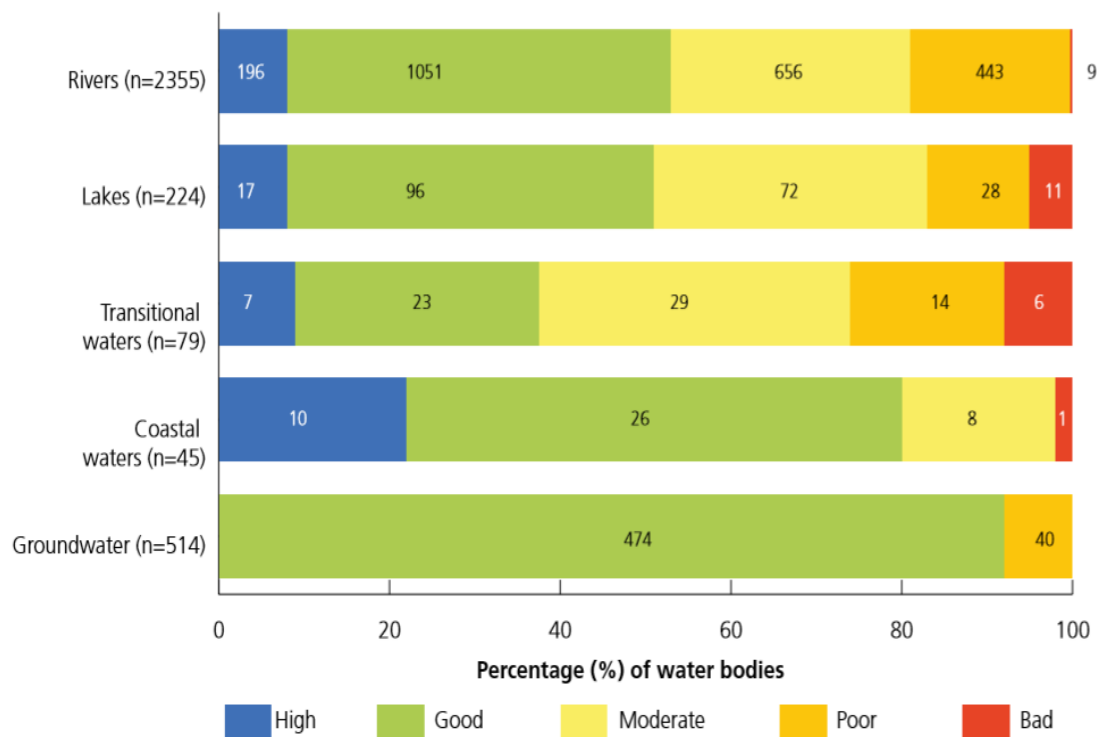


Figure 1.2 The Status of Water Quality in Ireland (2013-2018) (EPA Water Quality Report 2019).

The EPA report outlined a marked increase in the proportion of sites with increasing nutrient concentrations in this assessment. Over a quarter of sites surveyed displayed an increase in both nitrogen (N) (26.8%) and P concentrations (26.0%). This increase in nutrients is also seen in the loads of nutrients from rivers entering the marine environment; loads of total nitrogen (TN) and TP have increased by 16% and 31%, respectively, since 2012-2014. River sites with increasing nutrient concentration are mostly located in the more intensively farmed areas in the south, south-east and east of the country, where the soils are more freely draining and vulnerable to leaching, (EPA Water Quality Report 2019).

Increased nutrients in aquatic systems can result in eutrophication, major fish kills and trophic dead zones. P is a growth limiting nutrient in aquatic systems and therefore increasing P concentrations are related to increased risk of eutrophication. In rivers, average P concentrations of less than 0.025 mg/l P and less than 0.035 mg/l P have been established in Ireland as legally binding environmental quality standards (EQS) to support the achievement of high and good ecological status respectively. Concentrations of phosphate consistently greater than 0.035 mg/l P in rivers are likely to lead to eutrophication which can cause harm to plants and animals. In lakes average TP

concentrations of less than 0.010 mg/l P and less than 0.025 mg/l P have been established in Ireland as legally binding environmental quality standards (EQS) to support the achievement of high and good ecological status. Concentrations of total phosphorus (TP) consistently greater than 0.025 mg/l P will cause eutrophication, (EPA Water Quality Report 2019).

During the monitoring period 2016-2018, the EPA found that phosphate concentrations in 64% of monitored river sites are classed as either high or good quality (i.e. less than 0.035 mg/l) (Table 1.2). The remaining 36% of river sites are classed as being of moderate, poor or bad quality. They also reported that 71% of monitored lakes are classed as either high or good quality nutrient condition based on the environmental quality standard (i.e. less than 0.025 mg/l P). The remaining 29% of lake sites are classed as being of moderate or worse quality having average TP concentrations greater than 0.025 mg/l P, (EPA Water Quality Report 2019).

Table 1.2.1 P concentrations in rivers in Ireland 2016-2018 (EPA 2019)

3-Year Average mg/l (P)	Categories of phosphorus concentrations in rivers					
	< 0.025	0.025-0.035	0.035-0.05	0.05-0.1	0.1-0.25	>0.25
No. of rivers	364	87	86	125	41	8
% of rivers	51.2	12.2	12.1	17.6	5.8	1.1

Table 1.2.2 P concentrations in lakes in Ireland 2016-2018 (EPA 2019)

3-Year Average mg/l P	Categories of phosphorus concentrations in lakes				
	< 0.010	0.010-0.025	0.025-0.05	0.05-0.1	>0.1
No. of lakes	71	87	41	22	3
% lakes	32	39	18	10	1

The EPA Water Quality report indicated that 93% of ground water sources complied with the WFD threshold standard of 0.035 mg/l P. However, there has also been a 5.4% decrease in the percentage of monitoring points with concentrations less than 0.015 mg/l P. As part of the Oslo Paris Convention for the Protection of the Marine Environment of

the North-East Atlantic (OSPAR), the EPA monitors of nutrient inputs from 19 major Irish rivers to estuarine and coastal waters. Measuring these inputs provides a useful indicator of trends in the transfer of nutrients from land-based sources which are calculated based on nutrient concentrations, which are measured 12-times a year, and river flows, which is measured continuously. Since 2014, the trend has seen an increase in nutrient inputs to the marine environment. Average TN in 2016–2018 increased by 8,806 tons (16%) since 2012–2014, the majority of which is coming from the catchments to the south and southeast of the country and average to TP rose by 329 tons (31%) over the same period, (EPA Water Quality Report 2019). There is clearly a need to reduce the levels of P entering surface waters and thereby reduce the levels entering the marine environment. Since agriculture has been identified as one of the main sources of P entering surface waters, ways must be found to reduce the levels of P being released by agricultural activities.

The contribution of the agricultural sector to the Irish economy, both from direct and indirect employment and taxation, is significant. In 2019 the actual worth to the national economy was in the region of 14.5 billion euro in exports alone. Agriculture directly accounts for 7.7% of the national workforce and this figure increases to 10% (or approximately 173,000 people) when indirect employment from the Agri-food sector is considered. In geographical terms, farms account for 69,798 km² of Ireland's land mass, approximately 71%, (Agriculture - Ireland - European Commission, 2020). Figures from the Department of Agriculture, Food and Marine 2011 outline that the agricultural sector was worth 2.5% of Ireland's GDP, twice the EU average, (Agriculture and Food Development Authority, Teagasc, 2015).

Economic benefits of agriculture are significant, but agriculture also has major impacts on the environment. These include but not limited to soil erosion, loss of biodiversity, emissions of CO₂ and methane, loss of forestry and eutrophication of ground and surface waters. The impact of soil erosion will, in time, affect the production of food globally. It is of particular concern where conventional upland farming practices continue to be applied, (Montgomery, 2007). In the EU it is estimated that 12 million hectares of agricultural land suffer from severe erosion with an are estimated loss of 0.47% in annual profits each year amounting to around €1.25 billion, (Panagos et al., 2018). Reclamation of land through drainage of organic soils accounts for the release of some 780 million tonnes of CO₂ annually, this represents nearly a quarter of the combined emissions from

the forestry, agricultural and land use sectors, (Tubiello et al., 2016). Agriculture contributes significantly to the loss of biodiversity world-wide, large-scale land use and its physical manipulation along with the uses of pesticides and fertilizers are resulting in loss of flora and fauna, (McLaughlin and Mineau, 1995). Pollinators such as bees, provide a vital service and are critical to sustainable food production. Observations of wild bee populations in orchards found a linear decrease in the abundance and species richness of wild bees in response to increasing amounts of conventional pesticides (Park et al., 2015). Agriculture contributes significantly to the eutrophication of natural water bodies. Leip et al. (2015) estimate that in Europe, manure and mineral fertilizer applications account for 17-26% of the P load and 23%-47% of the N load entering natural water bodies.

Nutrients losses of N and P from agricultural systems through diffuse and point source to surface and ground waters has been highlighted as one of the main threats to water quality in Ireland, (Bradley et al., 2015).

While P is naturally present in water systems in limited amounts, it is human activities that are responsible for large increases in P levels and subsequent processes of algal blooms and their decomposition which lead to decreased dissolved oxygen resulting in fish kills, (Correll, 1998). N, carbon (C) and P are elements required for eutrophication to take place, while C may be obtained from the atmosphere, P mainly reaches aquatic bodies through surface waters, Schindler et al, (2016). Several long-term studies on the effects of N and P on eutrophication in lakes in North America and Europe were reviewed by, Schindler et al., (2016). They state that there was no evidence to suggest that controlling N inputs can mitigate algal blooms and that eutrophication may be controlled by reducing inputs of P from human sources, including agriculture. There are several natural Environmental factors that affect eutrophication these include; increased water temperature due to seasonal variation, decreased salinity, high dissolved oxygen levels, availability of light and carbon dioxide, (Yang et al., 2008).

Eutrophication will likely occur in rivers above the value of $30 \mu\text{gL}^{-1}$. The results of a laboratory study conducted on 5 Irish tillage soils at varying inclines between 10- and 15-degree slopes, with a simulated rainfall intensity of 30mmh^{-1} found surface runoff P concentrations in excess of $30 \mu\text{gL}^{-1}$ when their Morgan's P, Mehlich 3 P, and water extractable P concentrations exceed 9.5 mg L^{-1} , 67.2 mg kg^{-1} , and 4.4 mg kg^{-1} , respectively, (Regan et al., 2010)..

Figures from the central statistics office shows Ireland has over 6.5 million cows and 1.5 million pigs, (Central Statistics Office 2020). Of the 6.5 million, 1.5 million are dairy cows each produces 9784 litres of nutrient rich waste when mixed with rainfall containing 587 mg l⁻¹ and 568 mg l⁻¹ of P, (Minogue et al, 2015). Using these figures, cows could produce as much as 62 billion liters of nutrient rich wastewater per year in Ireland. This nutrient rich waste may be used but it can also pollute surface waters through point and diffuse sources. Currently two chief methods for dealing with pollutants arising from intensive agricultural activities, these are:

- a) Storage and subsequent spreading of slurries and manures, and
- b) The creation of man-made Integrated Constructed wetlands (ICW) with a view to mitigating the pollution effects associated with farmyard effluents.

The spreading of farmyard waste in Ireland is governed by seasonal rules under Council Directive 91/676/EEC, also covered is the storage of slurries and manures, (Nitrates Explanatory Handbook for Good Agricultural Practices for the Protection of water Regulation 2017). The storage of this dirty water also requires good storage infrastructure. Both requirements may be open to abuse resulting in eutrophication of natural waters, (Mustafa et al., 2009). The first method of dealing with these effluents is beneficial for crop growth, however a concern associated with slurries and manures storage and spreading is eutrophication of surface water. Leaking tanks a point source and diffuse source though soil leaching of nutrients into water bodies during periods of heavy rain fall (McDonald 2019).

Integrated Constructed Wetlands (ICWs) are an alternative method to land spreading. ICWs are a series of shallow ponds that are lined by an impermeable synthetic liner or clay-based material. They may be constructed with a substrate of soil, gravel and sand, into which vascular macrophytic plants are sown. ICWs mitigate effluents by retaining solids and particulates, this allows bio-filtration to extract nutrients such as nitrate and phosphate from waste effluents. Prior to the use of ICWs in the treatment of farm effluent, they were used for several decades in Europe in the treatment of urban waste streams and industrial effluents (Vymazal, 2010). ICWs have two major limitations for the treatment of FYDW. ICW require a land area of 1.3 times the farmyard area, (Scholz 2007) and

secondly most ICWs are not capable of recycling the effluent back through the wetlands should the effluent not meet regulations for discharge.

Having another option for dealing with the pollutants, associated with FYDW such as a bioswale would be important, when either land spreading of such associated agricultural wastes is not possible due to NAP rules or where ICW's are not feasible due to land requirements.

In 2015 a project was undertaken by the EnviroCore Research Centre in the Institute of Technology Carlow to develop an alternative to the ICW model. The development of a Novel Bioswale system for the treatment of FYDW was the main objective of the project (Merriman, Arnabat, and Germaine & Dowling unpublished report 2015). The system employs various natural layers of filtration material which the wastewater must percolate down through, a re-circulatory pump and an impermeable barrier. This system was to be the first of its kind in both Ireland and Europe. The location that was chosen was Teagasc, Oakpark Research Centre, Carlow. Figure 1.3 shows the finished system and a schematic diagram of the various layers and associated pipe work are detailed in section 1.8.



Figure 1.3: Novel Bioswale located at Teagasc Research Centre Oak Park Carlow. showing irrigation system working on the bioswale. What may be seen in the photo is the Gabion stone wall, wetland plants, number 57 stone and the sprinklers. Not seen in the photo is the 5000-litre storage tank for holding the FYDW. Also not seen as it is underground is layers of engineered soil, willow wood chips, pea gravel perforated pipe, outflow concrete sump and three large underground interconnected cisterns.

The advantages of the Bioswale System are its small footprint, low construction costs and potential for efficient and reliable treatment of contaminated water. The system has the potential to be applied to the treatment of urban run-off and domestic wastewater in small communities. The central theme of the project was to develop an affordable, reliable method for the treatment of FYDW and in doing so, protect the quality of both surface and ground water (Merriman, Arnabat, and Germaine & Dowling unpublished report 2015). The system will monitor the nutrients of total and reactive P, nitrates and ammonium.

1.1 Constituents of FYDW

Farmyard waste is a mixture of urine, animal feces, organic matter, dairy parlour washings and inorganic pollutants. During periods of rainfall, rainwater gets mixed with the farmyard waste and combines to produce dirty water. Nutrients contained in this wastewater include P and N in various forms. Microbiological contamination includes faecal coliforms and faecal streptococci. Faecal material contains labile organic carbon, and microbiological nutrients which contribute to the problem of biological oxygen demand, (Edwards et al., 2008). Other harmful compounds include fertilisers, pesticides and antibiotics (Robertson and MacCormack, 1977 & Hooda et al., 2000). These components can have detrimental effects on the aquatic environment as well as affecting human health.

The presence of ammonia and nitrate in surface water has negative health impacts on both human and aquatic life. Fish and other aquatic animals are sensitive to ammonia, even at concentrations as low as 0.02mg l^{-1} . In surface waters, most ammonia is converted to ammonium due to the slightly acidic nature of surface waters. Nitrate enters surface water from human activities as organic matter where through mineralisation it is converted to nitrate (Hooda et al., 2000). Pollution of rivers used for the abstraction of potable water by agricultural runoff have major implications for human health. High levels of nitrate in potable water exceeding 50mg l^{-1} can cause methemoglobinemia (blue baby syndrome) in infants, (Royal Commission on Environmental pollution 1977, WHO 1985).

Microorganisms living in watercourses feed on organic matter. Organic wastes that enter water from silage, slurry or runoff are a rich source of food for these microorganisms. The loading of organic waste into water bodies will see rapid deoxygenation of the water, as the populations of microorganisms rapidly grow. Biological Oxygen Demand (BOD) is a measure of the oxygen demand exerted by inoculants of microorganisms at a specified volume of water, usually one litre, over a period of five days, at 20°C in the dark. River class 1B, (Good Ecological Status) rivers have a standard for BOD of $<1.5\text{mg L}^{-1}$ as set out by the Water Framework Directive, (Gray, 2005). Runoff from farms will have different BOD loading depending on the type of farm and the livestock kept on them.

Liquid effluents draining from places of storages may contain BOD loadings of 1000-12000 mg L⁻¹. Silage, pig slurries and cattle slurries are the worst containing BOD concentrations of 30000-80000, 20000-30000 and 10000-20000 respectively, (Hooda et al., 2000). The extent of the increase in BOD caused by runoff will depend on the assimilative capacity of the river or lake and the concentration of BOD in the runoff, as well the hydraulic loading.

Chemical Oxygen Demand (COD) a method used to determine the oxygen demand of organic waste may be used in conjunction with BOD to give a useful indication of how much of the organic waste may be present. A high COD/BOD ratio indicates that there is a lot of non-biodegradable solids in the waste (Robertson and MacCormack, 1977). Rivers classified as poor or bad quality will have levels higher than 5mg O₂ L⁻¹ BOD. These rivers can have dissolved oxygen levels less than 10% saturation and would be considered anaerobic and fish kills will certainly occur, (Gray, 2005).

FYDW can harbour high levels of potentially pathogenic bacteria, viruses, and parasites. Faecal coliforms and faecal streptococci are members of two bacterial groups that are found in the organic waste and runoff from farms. Elevated levels of faecal coliforms and faecal streptococci can be used as bioindicators regarding river water pollution, (Water.epa.gov, 2015).

The preparation, mixing, loading and cleaning of tankers with pesticides and fertilisers can result in leaks and spillages into FYDW. The majority of pesticide residues that reach water bodies do so through diffusion from land to water. Invertebrate species and particularly arthropods are sensitive to them, (Schriever and Liess, 2007). Parasites on livestock are disease causing and the use of sheep dip containing pesticides decreases this problem, however this leaves the issue of the disposal of this waste. Sheep dip contains organo-phosphorus. This chemical can have deleterious impacts on the environment, on analysis of 20 catchments on the River Tweed in Scotland 17 samples showed signs of sheep dip organophosphates, (Hooda et al., 2000).

1.2 Associated environmental impacts of FYDW and Regulations

The environmental status of surface waters across Europe are defined by the biological, chemical and morphological conditions. The benchmark for surface water is high status where the impact of human pressures is low. As the impact of human activity increases the status of the surface waters decreases from high to low status. Quality elements used to determine the status of a water body are the “composition and abundance of aquatic flora” or “composition, abundance and age structure of fish fauna” (Classification EPA, Ireland, 2016).

In Ireland there has been a decline in the number of river sites classed as high quality from 82 sites in 2001-2003 to 21 sites 2013-2015. High to good quality status for coastal water has risen from 68% in 2012 to 76% in 2015, primarily due to decreases in algae blooms. The status of almost half (47%) of transitional waters are poor to moderate status, leaving room for significant improvement. During the period between 2013-2015, a considerably high figure of 54% of lakes are classified as having moderate to poor status, an increase of 3% since 2012, (EPA 2016).

There is a minor effect on the quality of Ireland’s groundwater with just 1% of Ireland’s groundwater classified as having poor chemical status. The main contributory factors to nutrients entering natural waters are discharges from agricultural and domestic waste waters. In 2012 it was estimated that 53% of pollution in rivers arose from agricultural activities with 30% (n=3500) of farms found to be in breach of Good Agricultural Practices, 52% of these breaches were due to poor management of livestock manures/organic fertilizers with a further 16% attributed to poor storage, (EPA 2016).

The Nitrates Directive (91/676/EEC) was first implemented in 1991, its main purpose was to protect natural water bodies through good agricultural practices, (Nitrates Explanatory Handbook for Good Agricultural Practices for the Protection of water Regulation, 2017). In every EU member state, it is now mandatory to have a National Nitrate Action Program (NNAP) that sets out rules of management of manures and fertilizers. The regulations not only cover N compounds but also cover phosphorous compounds. The national action program in Ireland was drawn up from the Nitrates Directive in 2005 and is contained in a handbook ‘*Good Agricultural Practices for Protection of Waters Regulations 2006*’.

Farmers abiding by the rules and regulations contained in the handbook is not only imperative for the good of the environment but failure to do so is breaking the law and may result in fines. Financial supports such as the Single Payment Scheme may be withdrawn for farmers failing to comply. Some rules and regulations contained in the handbook include:

- Over fertilization of crops is prohibited, a maximum limit of 170 kg N per hectare per year is applied for spreading of manure and slurry. A derogation to this limit was made in 2014, raising the limit for intensive farming to 210 kg of N per hectare.
- Buffering zones ranging from 3 to 200 metres are in place for organic fertilizers depending on the water body. For example, lake shorelines, slopes towards watercourses and water for human consumption all have different buffering zones.
- The spreading of fertilizers is prohibited during November and December. Spreading at other times of the year is prohibited if other conditions are not met, such as ground conditions that may cause nutrients to run off into natural water or if the weather conditions are unsuitable (water logged land, land likely to flood, frozen or snow covered, rain forecast within 48 hours).
- Storage capacity on Irish farms varies depending on location, ranging from 16 to 22 weeks.
- Clean water must be diverted away from dirty water areas. Water that does become dirty must be collected along with organic fertilizers and silage effluent from the holdings must be stored.

Countries in EU have directives that protect the surface and ground waters against pollution, such as the Nitrates, Bathing and Water Framework Directive. In Ireland we have the 1977 (Water Quality Standards for P) Regulations, 1998. Farmers are incentivised to maintain their land in good environmental condition through the agricultural environmental program (AEP). Farmers receive a single farm payment which may be lowered if noncompliance to P limits are found, (Amery and Schoumans, 2014).

All countries throughout the EU have P application limits. Limits depend on the soil P status, type of crop sown and in some cases the yield. Irish P limits vary with the P content of the soil. High soil P content limits the application of fertilizers. Soil P content is determined using the Morgan's test which give results as mg L⁻¹. Soils are then classified

from index 1 to 4. Soils with index 1 are classified as having a P content of 0.0-3.0 mg P L⁻¹. Index 3 is classified as 5.1-8.0 mg P L⁻¹. Testing of soils is not mandatory for a farmer. However, in the absence of soil index levels or when results are older than 5 years an index of 3 is assumed, (Amery and Schoumans, 2014). Application of fertilizer is not only guided by the soil index level but is also affected by several other factors. As with the nitrate directive the same rules for applying dirty water and manures must be adhered to. Buffer zones concerning water for human consumption are in place, 100-200 m at surface waters, 25 m near bore holes and springs or wells, (Statutory Instruments, S.I. No 31/2014). The N/P ratio of 2/8 in manures normally means an excess of P on agricultural land, (Amery and Schoumans, 2014). The Nitrate directive (91/676/EEC) contains regulations regarding N applications. These regulations may directly reduce but do not totally remove the risk of P pollution from organic fertilizers due to the excess P applied to the land.

1.3 Current methods of dealing with FYDW

Organic fertilizers are a valuable resource, but the amount produced on a farm can exceed the requirements of the farm itself. Storage can be costly whether in slatted or steel tanks or open lagoons. Identifying cost effective methods of managing excess volumes of this waste is of critical importance to maintain the balance between a cost-effective agriculture industry and a clean environment. As mentioned previously there are two main methods of dealing with this nutrient rich waste, (Barber and Quinn, 2012).

1.3.1 Land Spreading

While the negative impacts from manures and slurries through diffuse and source pollution have been discussed, there are also beneficial uses of these wastes as a source of nutrients for crops when used correctly. Mineral fertilizers reliance may be reduced through proper management of manures and slurries. In 2014 the cost of chemical fertilizer per nutrient was approximately €1.00 per kg N, €2.00 per kg P, and €1.00 per kg K, (Teagasc, 2017). Considering this, getting the maximum available nutrients from natural fertilizers is important. The value of N fertilizer may be increased by changing the rates, times of application and placement of manures, and in doing so increasing the present N fertilizer values from 20-60% to 40-80%, (Schröder, 2005). Land spreading can have a negative effect on ground and surface waters through diffuse runoff nutrient in manure and slurries that have been spread on the land can make it into water after periods of heavy rainfall and in doing so cause eutrophication of surface waters. Diffuse

water pollution from agriculture accounts for approximately 25% of all reasons for waterbodies not achieving the desired water quality, (Barber and Quinn, 2012).

1.3.2 Integrated Constructed Wetlands

Integrated Constructed Wetlands (ICW) are the main alternative method for dealing with waste waters from farms. ICWs range in size (from relatively small 3000 m² to comparatively large 22,000 m²) and are used for agricultural, industrial and domestic waste waters, (Scholz et al., 2007). Integrated constructed wetlands while providing a good means of pollution reduction from FYDW have a disadvantage in that they require an extensive area especially considering that many farm holdings in Ireland are relatively small. A review published in 2017 examining the footprint and removal efficiency of several constructed wetland. The review examined several different types of CW, tidal flow (TF), effluent recirculation (ER), artificial aeration (AA) vertical flow constructed wetland (VFCW), horizontal flow constructed wetland (HFCW), and hybrid constructed wetland (HCW). When both municipal wastewater footprint per population equivalent are of equal importance then TF-VFCW, AA-HCW and ER-HCW in the removal of COD, NH₄⁺-N, and TP (Ilyas and Masih, 2017).

Before an ICW can be employed it must undergo a period of maturation. This involves the development of an extensive submerged plant root system. Plants can act as filters removing nutrients and pollutants from farm waste silage, manure, slurry or another runoff, (Wen et al., 2010). The submerged roots are contained in two zones, an aerobic zone and an anaerobic zone. These zones develop where the pollution from the effluent is trapped by roots, aquatic soil, algae and micro biotic fauna (Han and Park, 2014).

The mechanisms that enable the reduction and removal of pollutants from wastewater include, the process of accumulation of nutrients in soil, roots and sediments, the chemical precipitation and adsorption through phyto-utilization of nutrients to plants and the intricate chemical pathways of algae (Hoagland et al., 2001).

Most of the water quality improvements that occur in an ICW's system are caused by bacteria that are present on sediments, soils and submerged plants, where chemical changes are catalysed by microbes making available the nutrients to plants, (Schaechter, 2009).

Biochemical reactions cause nitrification, a biological two-step process of oxidation where ionised and un-ionised ammonia is converted to nitrate and nitrite by aerobic chemoautotrophic bacteria. The process by which this occurs depends upon the conditions in the sediments or soils it takes place within. Nitrate is then either taken up through assimilation by plants and also converted to nitrogenous gases by facultative bacteria causing denitrification. Denitrification is the reduction of nitrate and nitrite to N gas and nitrous oxide. Anammox bacteria use nitrite as an electron acceptor in the oxidation of ammonium to N gas, (Schaechter, 2009). When oxygen levels are extremely low, denitrification will occur without nitrification occurring.

There are two main categories of ICWs: 1: surface flow and 2: subsurface flow. The surface flow process allows wastewater to flow at the height of the lower stems of plants in the wetlands, these plants are constantly submerged. In the case of a sub-surface flow system the plants grow in a gravel based medium in flooded channels, wastewater nutrients are reduced as the wastewater percolates through the wetlands root zone, (Vymazal 2010).

There are no definitive guides to determine the appropriate size of ICW systems as there are many parameters that can influence such a decision. For example, the influent chemical and biological characteristics and the expected parameters of the effluent, topography, precipitation rates, evaporation and transpiration and residence time, (Vymazal 2010).

A case study of an ICW at Annestown Dunhill Co. Waterford made recommendations that a constructed wetland needs to be at least 1.3 times the size of the farmyard area to achieve appropriate effluent values of 1 mg l^{-1} molybdate reactive P (MRP), (Scholz et al., 2007). Methods on how to determine the size of ICWs required, vary. Sizes are sometimes quoted based on scientific trials that take into account the parametric values of hydraulic retention time and volume sizes. Others use anecdotal evidence that consider the type of effluent and its final requirements. Tanner and Koostermann (1997) outlined a guide based on herd size for cows, stating that to treat the effluent from three cows would require a surface flow system consisting of three ponds 7.1 m^2 . This will only give a specific water quality and changes in influent parameters would affect the quality of the outflow.

Integrated constructed wetland systems have been used for the past few decades with varying success. The Annetstown constructed wetland system has performed well over a period of 6 years, achieving removal rates of 99% ammonia-nitrogen and 74% nitrate-nitrogen, and a removal rate of 91.85% effluent values of 0.94 ± 0.628 phosphorous, (Mustafa et al., 2009). The ICW is very efficient for nutrient removal when compared with figures given in Gray 2005 for wetlands which indicates a phosphorous removal level of 10-70% and 40-80% for N. The system had a total area of 0.76 ha consisting of 6 cells, three densely packed with helophytes and the last three, sparsely filled with vegetation. Effluent entering the ICW coming from the dairy farm of 0.5 ha with 77 cows was treated with this ICW system.

1.4 Phosphorus importance to life, speciation and negative environmental effects

P is a vital nutrient to all life. It is an essential component of living organisms. Calcium phosphate accounts for roughly 20 percent of human bones and teeth. It's an important component of DNA and RNA, (Childers et al., 2011). The growth of plants is greatly affected by the bioavailability of P. Insufficient supply of P to plants negatively affects plant metabolism. Plant metabolism is more negatively impacted during early development than later in the plant life cycle (Grant et al., 2001).

P is present in aquatic systems either as particulate organic, inorganic forms or soluble organic and as orthophosphates. P can most frequently be found in the forms H_2PO_4^- and HPO_4^{2-} . Dissolved P forms are removed from waters either through chemical precipitation forming Al, Fe or Ca oxides or through assimilation by organisms, (Spivakov, Maryutina and Muntau, 1999). P enters aquatic systems naturally through weathering of rock, excretion by aquatic life and decaying plants (Thiébaud, 2008).

Irish P regulations deem that eutrophication will occur where rivers exceed 0.03mg P L^{-1} , (Gray, 2005 & Mustafa et al., 2009) and lakes levels exceed 0.02 mg P L^{-1} , (Lucey et al., 1999). Rivers with P levels of 0.07 mg P L^{-1} or greater are classified as Q3 rivers and are considered moderately polluted, (Toner et al., 2005).

Any future treatment system will have to consider the potential environmental impact of P discharges into a water body, with the current environmental status of the water body also effecting discharge limits. The P concentration in the treated FYDW and the assimilative capacity of the surface water are important factors when considering whether a water body may be able to take the discharge without been negatively affected. The P discharge limits for an urban wastewater treatment plant could be compared to a bioswale for the treatment of FYWD to see if they are favorable. Limits exceeding 1mg P l^{-1} would be a concern. The type of water body would also be an issue with ultraoligotrophic lakes having P values of $< 5\text{ ug l}^{-1}$. The suitability of a river would depend on the combination of the river's status and assimilative capacity. For example, when discharging an effluent into a river the factors to consider include, the volume of the discharge, its concentration and the flow rate. A river of good ecological status would have to meet P values not exceeding 30 ug l^{-1} after the effluent from a treatment system has entered. Table 1 shows

the limits for urban water discharge, the limits for the ecological status of both rivers and lakes and their associated P values.

Farmyard dirty water has considerable levels of P. Martínez-Suller et al., 2010, carried out a study to determine the composition of farmyard dirty water from dairy farms. The study found total phosphate levels ranging from 21-103 mg L⁻¹ with a mean value of 44 mg L⁻¹. Levels of P from such effluents have the potential to cause major eutrophication through point and diffuse sources, if facilities are mismanaged or seasonal rules for spreading of these wastes are abused.

The assimilation of P by plants, depends on the P load in the effluent, the biomass in the wetland and its age. Long term storage of P in ICWs is correlated to biomass growth, death, and decay. Another important sink in wetlands for P is soil (Mustafa et al., 2009).

Phosphorous in wetlands may be grouped into two categories organic and inorganic. The ratio of these forms is affected by soil type, vegetation, and topography. The features of the surrounding watershed and how the surrounding land is used, play a key role in the forms is phosphorous in constructed wetlands. Bioavailable phosphorous in the dissolved form are readily available for plants and microorganisms (Figure 1.4), (Zhang et al., 2019). Other forms of phosphorous, such as particulate and organic forms must undergo transformation through biotic processes to be assimilated by microorganisms and vegetation. The immobilisation of P also occurs through the abiotic processes of sedimentation, precipitation and adsorption by the formation of phosphorous compounds with Fe, Al and Ca, (Prochaska & Zouboulis, 2006; Jordan et al., 2005, and Pant, Reddy and Lemon, 2001). Substrates in wetland soils have been found to have P content in the range of 30 to 500mg P kg⁻¹, values up to 10,000mg P kg⁻¹ have been reported in sediments receiving P from confined animal operations (Dunne and Reddy, 2005).

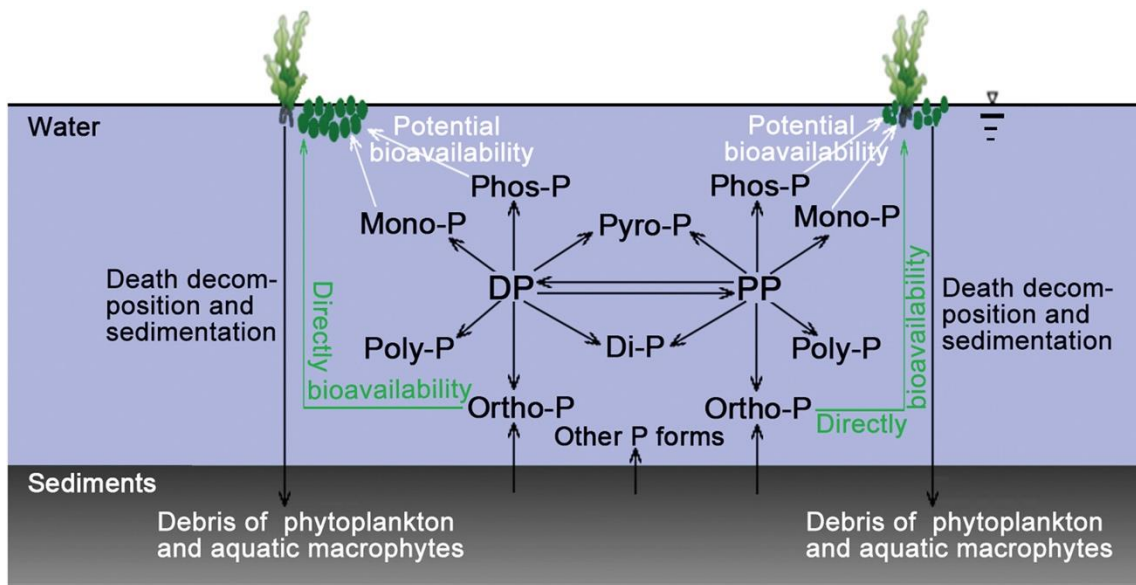


Figure 1.4, Zhang et al. (2019) Cycling of dissolved P (DP) and particulate P (PP) fractions in water system of a eutrophic lake. The main classes of DP and PP are phosphonate (Phos-P), orthophosphate (Ortho-P), monoester phosphate (Mono-P), diester phosphate (Di-P), pyrophosphate (Pyro-P) and polyphosphate (Poly-P).

Negative environmental impacts of P in aquatic systems and the importance of P as a nutrient in crop growth have seen many studies try to develop ways of removing P from waste waters, mitigating against negative environmental damage and develop means of P retention and subsequent reuse. Ju et al. (2014) studied the effectiveness of electrolysis on ammonium and phosphate removal in a laboratory scale tidal flow constructed wetland system. Systems were small scale with a 13cm diameter Perspex pipe, an upper layer of zeolite (particle size 0.5-2.0mm) (35cm depth) containing *Juncus effusus* and a lower submerged anaerobic layer (particle size 3-6mm) (25 cm depth) bio-ceramic substrate. Stable reductions of $\geq 95\%$ from an initial concentration of 10 mg PO_4^{3-} were observed for the electrolysis system, while a similar system without the use of electrolysis with an initial concentration of 10 mg PO_4^{3-} had a decrease in between 43.8 % to 19.8%. Significantly better reductions in the electrolysis system were attributed to the formation of ferric iron coagulants, (Ju et al., 2014). Reductions of $\text{NH}_4^+\text{-N}$ down to 80% from an upper value of 60 mg l^{-1} was mainly attributed to the upper layer of the systems. Electrolysis played an insignificant role in the ammonium removal, both systems had the same reductions for ammonium, (Ju et al., 2014).

Novel phosphate binding polymeric hydrogels were synthesized and developed for the aquaculture industry to deal with their associated wastewater effluents. The phosphate

binding capacity of the gels were $47 \text{ mg PO}_4^{3-} \text{ g}^{-1}$. Phosphate effluents in the experiment decrease by more than 99%. (Kioussis, Wheaton and Kofinas, 1999).

Bastin et al. (1999), examined in batch studies the removal capacity of iron oxide-gypsum for P with solutions ranging from 0.001 to 10 mg P L^{-1} . It was found that the material was effective in the removal of P and unaffected at pH between 4 and 8, however, higher pH values led to significant increases in P removal.

1.6 Physical and Chemical Characteristics effecting Sorption of Phosphate

Sorption may be subdivided into three categories adsorption, absorption and ion exchange. Adsorption solutes may be bonded by van der Waals or covalent bonds at the sorbate surface as hydrated species. Absorption is the incorporation of the solute into the mineral structure occurring at the surface and bonding may be both physical and chemical. Ion exchange solutes changes places with a similar charged species on a mineral surface, this type of exchange may force precipitation reactions to occur (Laidler, Meiser and Sanctuary, 2003). The extent to which a sorbate becomes sorbed onto a surface depends on the concentration of sorbate in solution, the temperature of the solution and the characteristics of the sorbent and sorbate, (Tchobanoglous et al., 2003)

The fundamental characteristics of phosphate as a sorbate include molecular structure, solubility and polarity. The important factors affecting sorption is the temperature and pH of the solute, with pH, either slightly alkaline or slightly acidic conditions are best depending on available ions. (Laidler, Meiser and Sanctuary, 2003). These characteristics have been investigated in much detail. Xiao et al. (2013) investigated the effect that river sediment surface properties have on adsorption of phosphate and found that with an increasing particle size of the sediments, there was a subsequent decrease in total surface area which led to a decrease in the adsorption capacity for phosphate. This means that the adsorption capacity of a material will increase as the material particle size decreases, (Dunne and Reddy 2005).

Environmental conditions and the type of minerals present in soils and substrates significantly affect immobilisation of phosphate in wetlands. Alkaline conditions favour

the removal of phosphate from solution through adsorption onto mineral surface of calcium while in acidic conditions the formation of Fe and Al precipitates, (Dunne and Reddy 2005). Both ion-exchange and precipitation reactions will depend not only depend on the pH but also the surface chemistry of the sorbate. Phosphate has varying degrees of affinity for several cations. The geochemical composition of rocks plays a pivotal role in these reactions, (Prochaska & Zouboulis, 2006; Jordan et al., 2005, and Pant, Reddy and Lemon, 2001).

Wetland soils and sediments are an important sink for phosphate immobilization. Important phosphate mineral formation that occurs in calcium rich soils are hydroxyapatite ($\text{Ca}_5(\text{PO}_4)\text{OH}$) and beta tricalcium phosphate ($\text{B-Ca}_3(\text{PO}_4)_2$) formation, , (Prochaska & Zouboulis, 2006; Jordan et al., 2005). In acidic conditions formations of Al and Fe minerals predominate with the formation of variscite (AlPO_4), strengite (FePO_4) and vivianite ($\text{Fe}_3(\text{PO}_4)_2$) (Dunne and Reddy, 2005). Significant rises in temperature will affect adsorption in a positive manner. Rajput. (2014), found that phosphorous sorption onto soils was higher at 35 degrees Celsius than at 25 degrees Celsius.

Underlying geological material mainly determines the mineral composition of soil. An exception to this is carbon and N. These are added to soil through the fixation of atmospheric gases. Moderate to high precipitation causes leaching and depletion of cations Na, K, Ca, Mg, and this is another process that will change the mineral composition of soils. Selective dissolution and recrystallization processes change the chemical compositions of soils through formations of clay minerals and Fe and Al oxides, (Artiola, Pepper and Brusseau, 2007). Phosphate is immobilized in acidic soils when it replaces the hydroxyl groups on hydrous Al and Fe oxides, initially the bond between the ions is monodentate before becoming a stronger bidentate bond (Artiola, Pepper and Brusseau, 2007). The mechanics of sorption occurs in places such as natural and constructed wetlands. Adsorption occurs when soluble inorganic phosphate moves from soil porewater to soil mineral surfaces where it accumulates at the surface. The ability of the soil to retain phosphate increase with increasing clay content. Absorption occurs when soluble inorganic phosphate penetrates the soil solid phase. The equilibrium between the phosphate adsorbed and desorbed is referred to as the phosphate buffering capacity, (Dunne and Reddy, 2005).

The data in Tables 1.6.1, 1.6.2 and 1.6.3 below are from several sorption isotherm studies for shale, dolomite and soil. The important characteristics of geochemistry of the substrate, its particle size, for soil organic matter. Conditions that also effect sorption are pH. Important cations in the immobilization of phosphate are Ca, Al and Fe, (Prochaska & Zouboulis, 2006; Jordan et al., 2005, and Pant, Reddy and Lemon, 2001). Materials with high amounts of calcium cations will sorb phosphorus under alkaline pH conditions. Materials with more iron or aluminum will sorb phosphorus under slightly acidic pH conditions.

<i>Authors & year</i>	<i>Shale</i>	<i>Properties</i>	<i>Langmuir</i>	
			Q_{\max} mg g ⁻¹	R ²
	Cations Impacting PO ₄ ³⁻ immobilization	Particle Size & pH		
<i>Coulibaly et al., 2015</i>	Al>Fe>Mg>Ca	≥ 0.08mm pH 6.0-7.0	0.273	0.960
<i>Jiang et al., 2014</i>	Al , Fe	≥0.85mm pH 7.0	1.395 (0.455)	0.994
<i>Pant, Reddy and Lemon, 2001</i>	Fe>Al >Ca >Mg	pH 8.9	0.588 0.192	0.940

Table 1.6.1: Comparison of properties and values of sorption studies on shale. Physical properties of particle size and pH are displayed. Q_{\max} , the maximum sorption capacity of shale for phosphate in mg g⁻¹ values below these are P. The R_L values give whether sorption is favorable and the R^2 is the correlation coefficient. NDA (No Data Available).

<i>Authors & year</i>	<i>Dolomite</i>	<i>Properties</i>	<i>Langmuir</i>		
	Cations Impacting PO ₄ ³⁻ immobilization	Particle Size & pH	Q _{max} mg g ⁻¹	R _L	R ²
<i>Prochaska & Zouboulis, (2006)</i>	Ca Mg Fe Al Si	1.2-2.4mm pH 7.8	0.515 (0.168)	0.431	0.974
<i>Pant, Reddy and Lemon, (2001)</i>	Ca Mg Fe Al Si	pH 9.3	0.929 (0.303)	NDA	0.950
<i>Yuan et al., (2015)</i>	Ca Mg Si	≥0.15mm pH 9.5	4.76	NDA	0.996

Table 1.6.2: Comparison of properties and values of sorption studies on dolomite. Physical properties of particle size and pH are displayed. Q_{max}, the maximum sorption capacity of dolomite for phosphate in mg g⁻¹ values below these are P. The R_L values give whether sorption is favorable and the R² is the correlation coefficient. NDA (No Data Available).

<i>Authors & year</i>	<i>Soil</i>	<i>Properties</i>	<i>Langmuir</i>	
<i>Characteristic or parameter</i>	Soil type	Particle Size & pH	Q _{max} mg g ⁻¹	R ²
<i>Jordan et al., 2005 Clarnianna</i>	Brown Earth %OM 7.5 Ca > Al > Fe	0-2mm pH 6.7	1.021 (0.333)	Stated that R ² fit
<i>Daly et al., 2015 Roscommon</i>	Loam, %OM 5.9-15.5 Ca > Al > Fe Calcareous glacial till	0-2mm pH 4.6-6.9	0.929 - 1.333 (3.03 - 435)	R ² > 0.95
<i>Daly et al., 2015 Meath</i>	Loam, %OM 7.5-14.7 Ca > Al > Fe Ordovician shale, glacial till	0-2mm pH 4.7-6.4	1.094 – 1.704 (0.357-0.556)	R ² > 0.95

Table 1.6.3: Physical properties of particle size, pH, cations, particle size and clay content. Q_{max}, the maximum sorption capacity of shale for phosphate in mg g⁻¹ values below these are P.

1.7 Sorption Isotherm Mathematical description

P removal and reduction takes place in sediments and soils through chemical/physical processes and in aquatic systems through biological assimilation. The geochemical makeup of the soil and stone used in the various layers of the bioswale may play an important role in the sorption and precipitation of P. Before selecting materials to be used, first it must be determined, if the material is a suitable sorbent and what is the maximum amount of P a material will retain before saturation occurs. There are several different sorption isotherm models that may be used to analyse the data. Various models include Langmuir, Freundlich, BET and Temkin. The Langmuir model has been used in several studies to model the sorption of phosphate to a solid, Coulibaly et al., (2015) used the Langmuir model in the sorption of phosphate to shale as did Jiang et al., (2014), Yuan et al., (2015) and Prochaska & Zouboulis, (2006) who applied the model to sorption of phosphate by dolomite. The following section describes the Langmuir isotherm model, this is a mathematical model that has been used in previous studies to describe the maximum amount of P sorbed in mg per gram of material.

The mass of material in solution sorbed onto a given surface is a function of the sorbate at a given concentration and at a constant temperature. The collective function is called a sorption isotherm. Sorption isotherm models require the following conditions: predetermined mass of adsorbent, varying concentration of adsorbate in a fixed volume of solution and sufficient contact time to allow equilibrium to occur between the sorbate and sorbent. Equation 1.1 describes the sorbent phase concentration after equilibrium has been achieved.

Equation 1.1
$$Q_e = \frac{(C_0 - C_e)V}{m}$$

Where

- q_e = sorbent phase concentration after equilibrium in mg sorbate/ grams sorbent.
- C_0 = sorbate initial concentration in mg
- C_e = sorbate final equilibrium concentration in mg
- V = volume of liquid in litres
- m = mass of sorbent

Langmuir model

The Langmuir isotherm model considers sorption as a chemical phenomenon. Developed to first examine the adsorption of gasses to solids, it was later applied to the sorption of solutes in the liquid phase to sorbents. The Langmuir model provides information as to the uptake capabilities of a material from solution, (Volesky 2013). The assumptions of Langmuir model are:

1. There are a fixed number of sorption sites on the material available, all of which have the same energy.
2. Equilibrium is reached when the rate of sorption is equal to the rate of desorption.
3. All sorption sites are uniform and only one sorbet molecule may react with one site.
4. There is no interaction between absorbent species.

Equation 1.2
$$\frac{1}{q_e} = \frac{1}{b \cdot q_{max}} + \frac{1}{q_{max}} + \frac{1}{C_e}$$

A linear plot of the data $1/q_e$ versus $1/C_e$ shows how good a fit the data is through the R^2 value. The $1/q_{max}$ or the maximum sorption capacity of the material in $mg\ g^{-1}$ is calculated from the $1/\text{intercept}$. The Langmuir constant b is calculated from $1/(\text{slope})(\text{intercept})$, the constant b may then be used to determine the R_L separation factor.

The separation factor (R_L) is a dimensionless constant which is expressed in the following equation, (Hall et al., 1966).

Equation 1.3
$$R_L = \frac{1}{(1+b \cdot C_i)}$$

The value of R_L indicates the type of Langmuir isotherm, irreversible $R_L = 0$, unfavourable $R_L > 1$ and favourable R_L greater than 0 but less than 1 (McKay, Blair and Gardner, 1982). The C_i in the above equation refers to the initial concentration.

1.8 Feasibility Study (Merriman, Arnabat, Germaine & Dowling unpublished report 2015)

The Bioswale uses a reed bed system in the bioremediation of dirty water similar to that of Integrated Constructed Wetlands (ICW) but with innovative design features. Unlike ICW the Bioswale has a relatively small footprint of 30m x 20m. Farmyard dirty water flows from a 5000-liter storage tank into a sediment area before passing through a gabion wall of 1m high and 0.5-0.6m wide. Here large material is removed before entering the Bioswale. Organic material and N and P compounds are reduced by the reed plants and microorganisms. The soil and stone layer beneath the planted wetland provide a filtration system. Diverse microorganisms remove contaminants from the wastewater as it passes through the layered system. Effective removal of nutrients may be achieved by recirculation of water back through the system via pumps and sprinklers. This water can be collected in large underground cisterns with a storage capacity of 3000 gallons and discharged or reused.

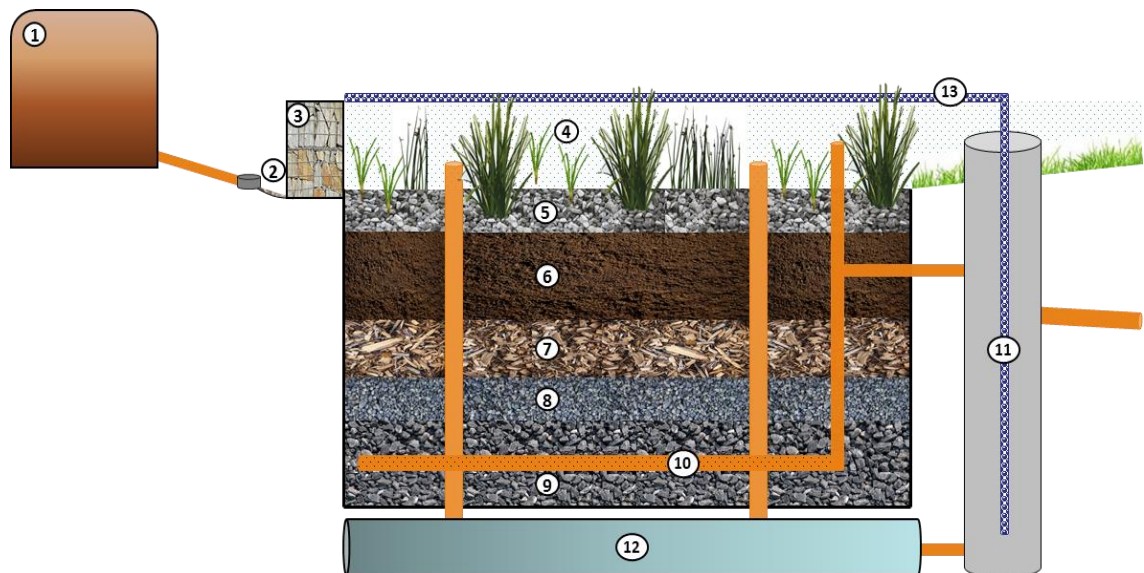


Figure 1.5: Schematic representation of the Novel Bioswale System. 1. 5000 litre storage tank; 2 Sediment basin, 3 Gabion stone wall, 4 Typical wetland plants, 5 Number 57 stone (10cm), 6 Engineered soil (40cm), 7 Willow wood chips (10cm); 8 Pea gravel (5cm), 9 Number 57 stone (40cm), 10 Perforated pipe, 11 Outflow concrete sump, 12 Three large underground interconnected cisterns, 13 Irrigation system (pump & sprinklers).

The top layer of number 57 stone aids aeration of the water by diffusion and protects the underlying soil from erosion. The soil layer performs several functions, acting as a media for the reed plant and much the same as a sewage tank soak hole. It performs nutrient reduction through immobilisation of compounds of N and P allowing microbial assimilation. Available nutrients in the soil may be taken up by the plant. A layer of willow bark beneath the soil provides a carbon source for bacteria. The bottom layer of stone acts as a drainage layer.

Post construction problems not associated with the general design meant postponement of the main project focus which turned to two prototypes small scale Bioswales made to replicate on a smaller scale the Novel Bioswale.

Attention were then focused on developing and testing three small scale prototype bioswales. In 2015 two small prototypes novel bioswale systems were constructed the layers of which were 0.8 ratio depth compared to the large bioswale. These prototype Bioswales were constructed and monitored over a three-month period to determine their ability to reduce waste parameters from farmyard dirty water. Dilute volumes of farmyard wastewater were passed through the system and analysed every few days for the following parameters: ammonia, COD, nitrate, total and reactive phosphate, (Feasibility Study, 2015).

The feasibility study concluded that there were significant reductions in COD removal of 74-67%, a nitrate removal of 85%-83%, an ammonium removal of 69-65%. The report also states levels of total and reactive phosphate was erratic with continuous fluctuations. Levels of TP were between 10-15 mg l⁻¹ and ortho-P were between 7-15 mg l⁻¹ at the end of the 3 month period, , (Feasibility Study, unpublished, (2015)). The feasibility study provided useful information on the pollution reduction of several parameters. While there was a reduction of P over the three month period of the study (Figures 1.6 and 1.7) the amount of P remaining in the systems after 3 months is still in excess of discharge limits for SI 419/1994 MAC limits TP levels to 2mg/l (10000-100000p.e) and 1mg/l P (more than 100000 p.e) in treated urban wastewater discharges. , (Merriman, Arnabat, Germaine & Dowling unpublished report (2015)).

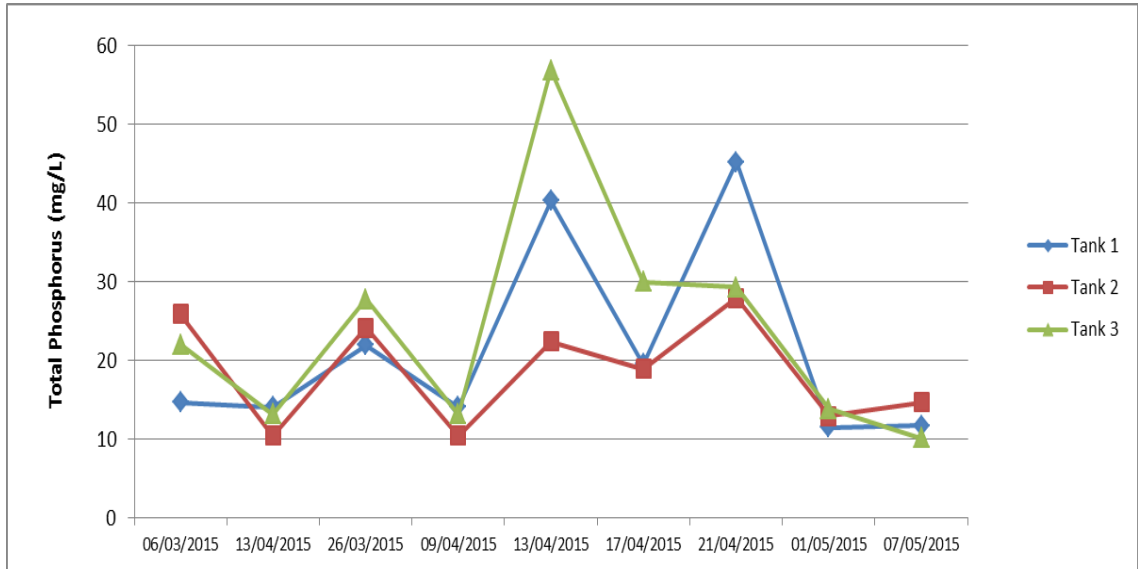


Figure 1.6: Total phosphorous values monitored over a three-month period. Each line is an individual tank and each point (n=3). The tanks had addition of sewage at dates 06/03/2015 and 13/04/2015.

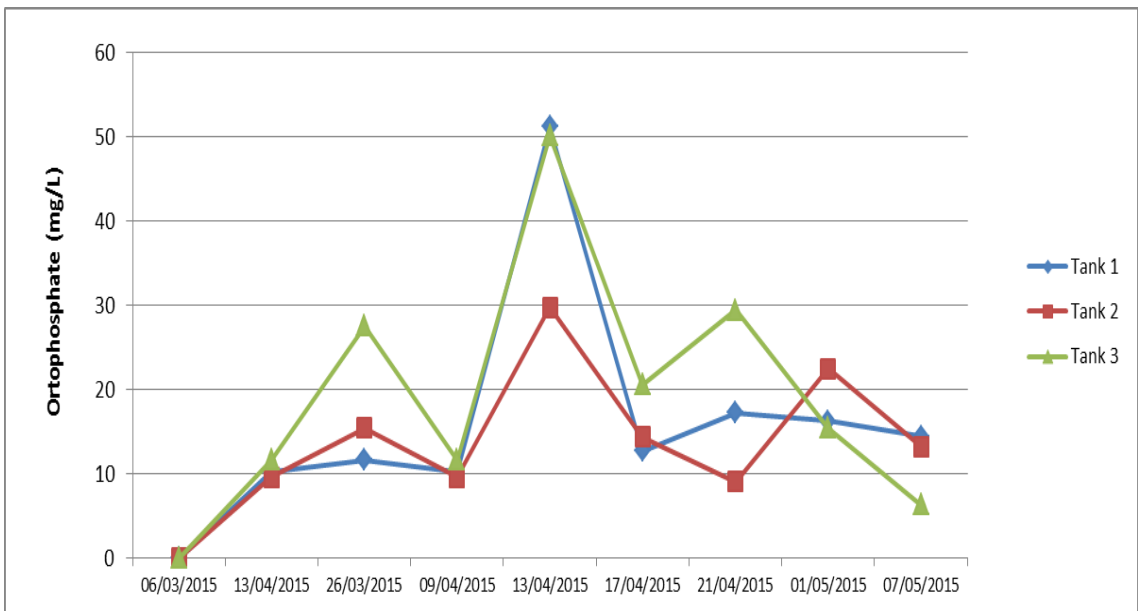


Figure 1.7: Orthophosphate values monitored over a three-month period. Each line is an individual tank and each point (n=3). The tanks had addition of sewage at dates 06/03/2015 and 13/04/2015.

As P is the rate limiting nutrient for eutrophication of natural waters, (Correll, 1999) it was made the focus of this current study. It was thought that the smaller stone of the choke layer could perhaps have a secondary function in reduction of phosphate, through the physiochemical properties of the stone acting as a sink for phosphate.

1.9 Aims and objectives of this study

This study will focus primarily on materials that will reduce concentration of Ortho-phosphates.

The objectives of the study were to:

- The first experiment will be the screening of several materials with respect to their ability to remove phosphate from solution, these materials must also act as a choke layer (this is a layer that will prevent the soil above from washing down through the system) in the Novel Bioswale System. The material will be examined with respect to the P removal to determine the optimal flow rate for phosphate removal.
- The second experiment will use the Langmuir sorption isotherms to find the maximum sorption capacity of the materials chosen from the screening process in the first experiment to determine the amount of phosphorous these materials can sorb in milligram per gram of material. The types of sorption will also be examined.
- The final part of the study will see the construction and analysis of a multi-layered Novel Bioswale System for total and reactive phosphate reduction capacity with the secondary objective of ammonium and nitrate removal.

Other considerations were that the material be relatively cheap, would not negatively impact on the environment and would not require any chemical amendment as this would introduce extra cost.

2.0 Materials and methods

2.1 Chemical and Physical Analysis

Total phosphate digestion method was followed accordance with sections 4500 PB acid digestion method (Rice et al., 2012).

Reactive phosphate was analysed in accordance with section 4500 PE ascorbic acid method (Rice et al., 2012).

Equipment and Reagents

1. Prewashed glassware in 1:1 HCl:DI water.
2. 5.0 N sulphuric acid solution
3. Potassium antimonyl tartrate 0.686g in 100ml of deionized water
4. Ammonium molybdate 10.0 grams in 250ml of deionized water
5. Ascorbic acid 0.1M 1.76 grams in 100ml of deionized water
6. Phenolphthalein indicator
7. Potassium persulfate ($K_2S_2O_8$).
8. Potassium di hydrogen phosphate (1000ppm stock P solution/100ppm intermediate solution)

Procedure

TP persulphate digestion method

1. Pipette 50cm³ of the water sample (or diluted wastewater sample) into a clean 100cm³ conical flask.
2. Add 1cm³ of concentrated H₂SO₄ and 0.5g of potassium persulphate to the water sample.
3. Sample was autoclaved at 120 degrees Celsius for 30 minutes and then allowed cool before been analysed as per reactive P method (please ensure both temperature and pressure has dropped below 40 degrees Celsius before removing samples from autoclave with a heat resistant glove).

Reactive P ascorbic acid method

1. From 100ppm intermediate stock solution a series of standards 0.1 to 1.0 ppm P were prepared.
2. 100 ml of a combined solution was prepared as follows;
3. 50 ml 5.0 N sulphuric acid solution
4. 5 ml of Potassium antimonyl tartrate (0.686g in 100ml of DI water)
5. 15 ml of ammonium molybdate (10.0 grams in 250ml of DI water)
6. 30 ml of ascorbic acid 0.1M (1.76 grams in 100ml)

7. Allow to stand for 1 hour before use.
8. To 5ml of each standard 0.8 ml of combined reagent was added with a calibrated pipette (Standards were analysed on the HACH after 10 minutes but before 30 minutes).
9. When a blue colour had developed the lambda max was read on the HACH and a calibration curve was created from the standards
10. Samples were analysed as per step 8.

Analysis of ammonium was followed in accordance with section 4500 NH₃ F Phenate method for the determination of ammonia-nitrogen (Rice et al., 2012).

Equipment and reagents

1. Samples were collected and kept refrigerated until analysis on the same day as collection.
2. 100ppm stock solution of ammonium stock solution was prepared from ammonium chloride salt.
3. Phenol solution: 555µl phenol and 5ml of ethanol.
4. Sodium nitroprusside: 50mg sodium nitroprusside and 10ml of deionised water stored in an amber bottle.
5. Alkaline citrate: 20g of sodium citrate and 1g of NaOH made up to 1000ml with deionised water.
6. Oxidising solution: 2ml of solution 3 and 0.5ml of concentrated bleach.

Procedure:

1. Calibration curve standards (0.25 – 2.0 ppm) were prepared from the 100ppm ammonium stock solution.
2. 2ml of each standard was pipetted into a glass test tube along with 80 µl of solution 3, 80 µl of solution 4 and 200 µl of solution 6. The test tube was mixed with a table vortex mixer and the colour developed.
3. The lambda max was determined to be 630nm and a calibration curve was determined on the HACH
4. All samples were analysed as per step 2 after appropriate dilutions of the samples.

To ensure the integrity of sampling analysis a 1ppm phosphate solution was prepared and analysed every time a new set of samples were analysed, the same was followed for ammonium analysis, Standard methods for the examination of water and wastewater were used (Rice et al., 2012).

Nitrate by cadmium reduction method reagent HACH powder pillows (Rice et al., 2012).

Equipment and reagents

1. 2 matching HACH sample cells 2495402 for 10ml of sample.
2. NitraVer® 5 Nitrate Reagent Powder Pillow, 10-mL, range 0.3 to 30.0 mg/L NO₃ –N

Procedure

1. Select program 355 N, Nitrate HR PP on the Hach.
2. Place 10ml of sample into HACH sample cell 2495402.
3. Empty the contents of a reagent powder pillow, wait 1 minute stopped and shake well.
4. After 5 minutes an amber colour will develop if nitrate is present.
5. A blank is prepared using deionized water. Both are analysed on the HACH.

Probe Analysis: Redox potential, ORP probe, TDS, Salinity, Conductivity and pH.

Water samples for redox potential were collected and analysed immediately with a Jenway ORP probe. pH was determined with a Hanna probe (HI (98103) and conductivity, Total Dissolved Solids (TDS) and salinity were analysed using a Mettler Toledo probe. All probes were calibrated prior to analysis per manufacturing instructions.

2.3 Preliminary column trial and optimal flow rates for removal of phosphates by dolomite and shale.

Dolomite, milled dolomite, limestone from two sites, potting grit, soil, shale and zeolite were chosen for the initial trial. Columns were constructed from polyvinyl chloride (PVC) pipes. PVC funnels were fixed inside the columns, glass wool was placed at the base of the column to stop leaching of the media and taps were located at the outlet of the funnel to control the flow rate. Each media was prewashed (except for the soil) in tap water before washing in deionised water. All materials were dried in an oven at 70 °C for 24 hours, and $2.5 \times 10^{-3} \text{ m}^3$ by volume of each material was transferred into each column.

Material sizes for the preliminary column trial were as follows; limestone 0.5 – 6.0 mm, sandstone 0.5-6.0 mm, potting grit 0.0-6.0 mm, dolomite 3.0-25.0 mm, milled dolomite 0.0-3.0 mm, zeolite 0.25-6mm, tire crumb 0.5-3mm, soil 0-5mm, shale 0.25-6mm.

The optimal flow rates for phosphate removal using dolomite and shale were examined at 5 and 10 ml min⁻¹. The performance of each material was visualised as a plot of the normalized concentration of solute remaining in solution (C_{eff}/C_0) versus time. Normalization allows the dataset to a common scale without distorting the differences in range of values. Information that may be gained from application of the data include effect of flow rates (Q), on percentage removal (%_R), phosphate retained by the column in mg Kg⁻¹ (q_{total}).

KH₂PO₄ was pre-dried at 70 degrees Celsius for 24 hours. A 1000 mg PO₄³⁻ L⁻¹ stock solution was prepared. The standards for the calibration curve were prepared from the stock solution. The 20mg PO₄³⁻ L⁻¹ (equivalent to 6.52 mg P L⁻¹) solutions were also prepared from the same stock solution. These were applied to each column; flow rates were set at 1ml⁻¹. Experimental set up for statistical analysis consisted of five 1 litre batches for each column and tested in triplicate. Data analysis consisted of graphical representation of phosphate remaining in solution through dot plots and mean values remaining in the solution and standard errors.

Dolomite and shale were selected for the flow rate column studies. Each material was prewashed in deionised water and dried as described in section 2.1. Material was sieved to obtain a material size of shale 150µm-6mm and dolomite 150µm-6mm and then washed in deionised water. The dried material was weighted out and transferred into the columns, $2.5 \times 10^{-3} \text{ m}^3$ by volume.



Figure 2.1: PVC columns, feed vessels and mild steel frame.

Columns were set up for both the shale and the dolomite in triplicate. 1 litre of $20 \text{ mg PO}_4^{3-} \text{ L}^{-1}$ solution was prepared and passed through the columns. Samples were collected every 9 minutes after the first sample was collected, (flow rate 10 ml min^{-1}) and every 18 minutes for the flow rate of 5 ml min^{-1} . Primary analysis focused on determining the optimal flow rate, normalised P concentration versus time and the percentage reductions of phosphate from the test solutions.

2.4 Langmuir batch studies soil, shale and dolomite, to determine the sorption capacity of each material

For the batch studies soil, shale and dolomite were dried at 70°C for 24 hours and were sieved to the following sizes: soil 0-2mm, shale 150µm-3mm, dolomite 150µm-3mm. As the experiment was concerned with investigating the geochemical properties of each material with relation to phosphate sorption, the dolomite, shale and soil were then

autoclaved to eliminate microorganisms that could possibly assimilate phosphate. High density polyethylene (HDPE) containers 125ml volume were acid washed (1 DI: 1 HCl) rinsed with deionised water and dried.

100 mg $\text{PO}_4^{3-} \text{L}^{-1}$ intermediate solution was prepared from the stock phosphate solution. Nine concentrations ranging from 4 -22 mg $\text{PO}_4^{3-} \text{L}^{-1}$ were prepared; two grams of each material was transferred to the HDPE containers along with 50 ml of various concentrations of phosphate. Each material was prepared in triplicate at each concentration.

The solutions were placed on an orbital bench shaker. The solutions were shaken for 24 hours at 350 rpm and ambient room temperature of 20.2⁰C. Before being analysed for total phosphate the solutions were centrifuged at 2750 rpm for 5 minutes. Reactive phosphate samples were centrifuged and filtered with a 0.45 μm cellulose acetate filter before analysis. Data was fitted to Langmuir sorption isotherms to give maximum sorption capacity of each material (mg P g⁻¹) and the correlation coefficient value, a value close to 1 indicates that the data fits the model well. Other objectives were to find whether sorption was favourable R_L and the type of sorption that occurred physical or chemical process.

The geochemical composition of shale soil and dolomite were determined by X-ray fluorescence (XRF). Pellet preparation: composite samples were taken from the sieved stockpile of each material. Samples were oven dried at 70^oC. Samples were milled $\geq 75\mu\text{m}$, 9.1g of sample and 0.9g XRF pellet binder were homogenised using a motor and pestle. Pellets were prepared in a pellet press. Pellets were sent to Irish Cement Ltd, Platin Rd, Drogheda, Co. Louth for XRF analysis.

2.5 Multi horizon packed bed filtration system. The objective of the system to reduce/remove contaminants in FYDW

Pipe scale bioswales were constructed from black polyvinyl chloride pipes. The bottom of the pipes had wood inserts screwed in to take the weight of the media layers. The wood insets were further sealed inside and out using plastic caps with industrial sealant. The outlet tube was constructed from armoured garden hose. Perforated holes in the hose at

the base of the pipe Figure 2.2. This perforated pipe allowed water to flow from the base into the collection vessels. Taps located at the base of the feed vessel (Figure 2.3) allowed for controlled flow rate of 5 ml min^{-1} .

Layers from top to bottom by depth of the system consisted of the following: Limestone 2cm to provide aeration and disperse solution and to stop erosion of soil. Soil layer of 25cm, to allow ammonia reduction through nitrifying bacteria and to act as a sink for phosphate. Willow bark layer 5cm acts as a carbon source for microorganisms. Shale or dolomite layer particle size $150\mu\text{m}$ -6mm to act as stratum to prevent soil particles from reaching the drainage layer. These stones may also aid reduction of phosphate through physiochemical interactions. The bottom layer was 17cm depth of number 57 limestone. This acts as a drainage layer for the effluent and allows the perforated tube to remain clear of obstruction from smaller particles. The choke layer level is slightly above the exit point of the lower tubing (Figure 2.4). It took 2.5 ± 0.02 litres of deionised water to fill up to this point.

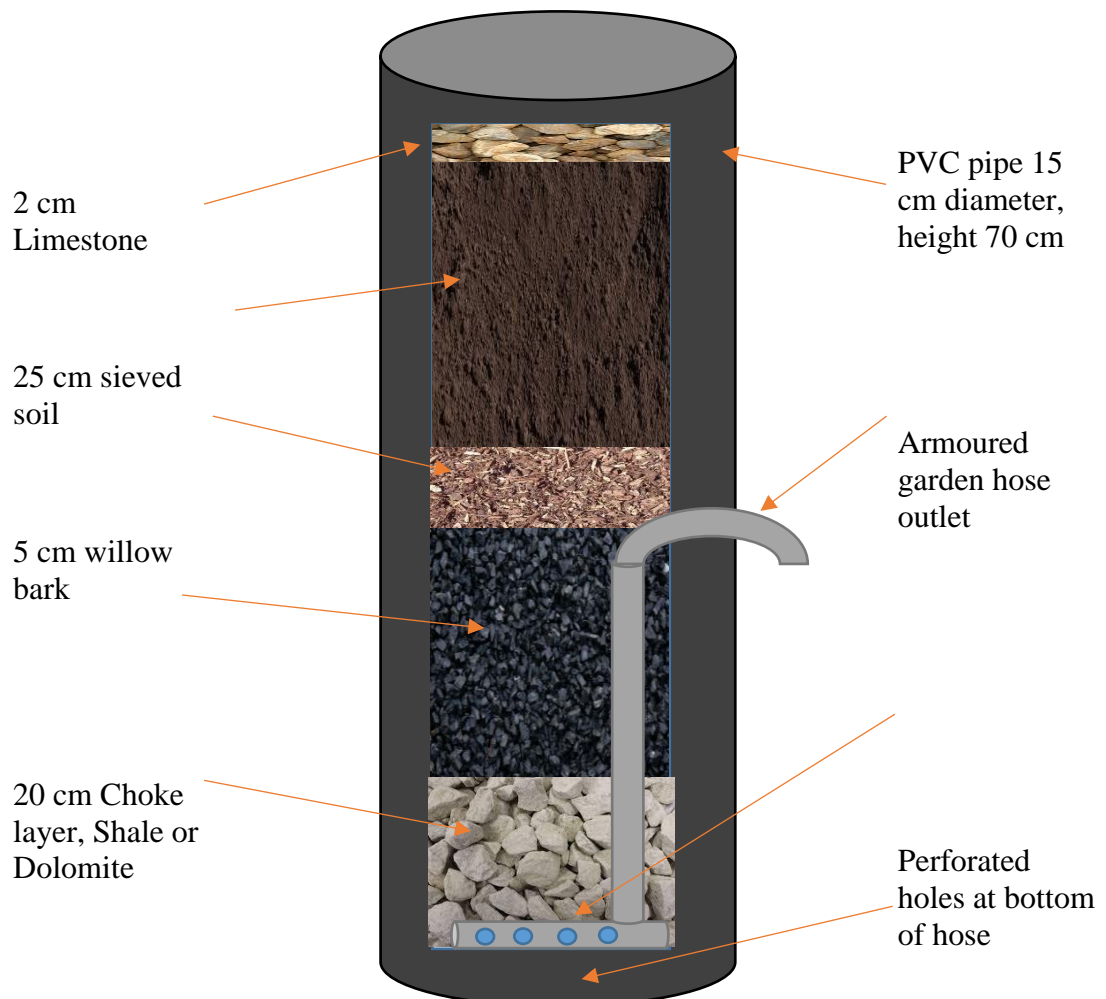


Fig. 2.2: Schematic representation the small scale Bioswales



Fig. 2.3: Columns after the addition of all media.



Fig. 2.4: Inside of pipe prior to addition of willow bark.



Fig. 2.5: Set up of the two different bioswale systems in triplicate, steel supporting structure, feed vessels and 5 litre collection tanks. Location outside greenhouse at Institute of Technology Carlow.

To create an anaerobic environment the choke layer and drainage layer were constantly submerged in solution. In the bioswales there was a total of 2.5 litres of solution below the height of the hose that extends out of the bioswales into the tanks with a further 5 litres of solution in the collection tanks (Figure 2.5). The layer below the level of the hose remained under water until negative redox potential readings were observed. The

displacement of aqueous solution in the system is caused by additional water that percolates through the soil and willow bark layers causing a head pressure on the system water entering the perforated holes and exits through the outlet and into the collection tanks. Mean temperature for April and May were 9.0 and 12.4 degrees celsius. Rainfall was not considered as the bioswale setup was covered in plastic for the duration of the experiment.

Baseline nutrient values were determined by passing 10 litres of deionised water was passed through each of the systems and analysing the resulting effluent. Five litres of synthetic nutrient solutions were prepared for each column. This solution consisted of 30ppm of phosphate (from potassium dihydrogen phosphate) and 60ppm ammonium (from ammonium chloride) (these are standard reagents used in OECD synthetic sewage) (Klein et al., 1981). After dilution of this solution in the water already present in the pipes, the final concentration was estimated to be 20 mg l⁻¹ phosphate and 40 mg l⁻¹ ammonium (the actual concentrations were analysed). These concentrations were consistent with previous reports for influent characteristics of agricultural waste water entering several constructed wetlands in the Annetstown-Dunhill catchment area (ICW number 5, 6, 8, 9, 10, 11 and 13 were receiving waste water from dairy, beef, tillage, sheep and a mixed of agricultural activities. Mean influent values from the listed ICW for NH₄⁺-N was 36.06 mg l⁻¹ and MRP PO₄³⁻- P mg l⁻¹ 8.05, (Scholz et al., 2007). These values represent 43.27 mg l⁻¹ of ammonium and 24.67 mg l⁻¹ of phosphate, values similar to those used in this study).

The synthetic nutrient solutions were passed through the column once with an unrestricted flow to allow the 5 litres solution to mix with the 2.5 litres of deionised water (total volume 7.5 litres), after this the flow was set at 5ml min⁻¹. Each time the solution was circulated through the column once, three well mixed samples were taken from the collection tanks and analysed. This same solution was circulated through the column 4 times.

This procedure was repeated with fresh phosphate ammonium/phosphate nutrient rich solution. Each circulation on the graphs in chapter 5 will be called a cycle and the separate phosphate ammonium solutions are referred to as series A and B. The parameters examined were total phosphate, reactive phosphate, ammonium, and nitrate. Data was analysed for total and reactive phosphate and ammonium through statistical analysis using Mann-Whitney U-test and percentage removal efficiencies. Nitrate was not examined

statically because it was neither the focus of the experiment nor was it possible as it entered the system as ammonium. The progression of ammonium was examined and the correlation between the levels of ammonium and nitrate were examined graphically. Mechanism of phosphate removal were examined by comparing the total and reactive phosphate.

Chapter 3:

Preliminary analysis of several materials and optimal flow rate: Removal of phosphate from aqueous solution.

3.0 Introduction: Preliminary trial of several materials

Following on from the feasibility study in 2014, the focus of the opening chapter was to examine materials that could:

- a) Act as a sink to reduce phosphate from farmyard dirty water, and
- b) Act as a choke layer in the bioswale. The function of this layer is to stop smaller particles percolating down through the system and blocking the perforated pipes at the bottom of the bioswale.

The first part of the chapter focuses on the preliminary examination of several materials for their ability to reduce total and reactive phosphate from solution. In this experiment columns were set up which contained $1.9 \times 10^{-3} \text{ m}^3$ of the test material with a bed depth of 0.2 meters. All materials except for soil were washed with deionized water. A flow rate of 1 ml min^{-1} was applied at the base of the PVC pipes via a burette tap. Samples were collected in triplicate once all the 20 mg L^{-1} phosphate solution had passed through the system. Passing of a 1 litre solution through the columns was repeated 5 times. Samples were analysed for total and reactive phosphate. Results are displayed as mean and standard error (Table 3.1) and graphically through dot plots (Figures 3.1 and 3.2).

This preliminary column experiment was a qualitative screening process aimed at identifying the best materials for removing soluble phosphates and as a choke layer in the bioswale. Soil was examined for phosphate reduction as it would be included in the bioswale as the top layer and later examined through sorption isotherms.

3.1 Results

The column trial showed that Milled dolomite (MD) had the lowest total and reactive phosphate remaining in the effluent, 0.43 mg $\text{TPO}_4^{3-} \text{ l}^{-1}$ and 0.08 mg $\text{RPO}_4^{3-} \text{ l}^{-1}$. Dolomite stone had values of 3.29 mg $\text{TPO}_4^{3-} \text{ l}^{-1}$ and 2.24 mg $\text{RPO}_4^{3-} \text{ l}^{-1}$. Both the milled dolomite and dolomite stone came from the same quarry. The only difference between the two being particle size (milled dolomite 0– 3mm and dolomite stone 3mm-25mm). Figures 3.1 and 3.2 show the distribution of the data for the milled dolomite and dolomite stone, the data points are distributed around the mean, the percentage difference between the two may be seen in Tables 3.1 and 3.2. **all raw data for chapter 3 is contained in the appendices on page i-ii.*

Table 3.1. Shows the reactive phosphate levels remaining in the effluent after a 1L of a 20 mg PO_4^{3-} solution of reactive phosphate were passed through the columns. The values shown in Table 3.1 represent the average (n=5) total, error values are presented as standard error.

Abbreviations: S.S (sandstone), L.S (limestone from Castletown quarry), D.S (Dolomite), M.D (milled dolomite), L.S* (limestone from Clogrennane quarry), S (shale), soil (soil from site at Teagasc Carlow), T.C (tyre crumb) and Z (zeolite clinoptilolite).

<i>Reactive phosphate remaining in solution (mg L⁻¹) (initial concentration 20 mg L⁻¹)</i>									
	S.S	L.S	D.S	M.D	L.S*	S	SOIL	T.C	Z
<i>S.E</i>	0.31	0.25	0.71	0.05	0.56	0.11	0.07	0.47	0.95
<i>MEAN</i>	2.75	3.42	2.24	0.08	3.07	0.38	0.30	1.48	3.69

Table 3.2 shows the Total phosphate levels remaining in the effluent after a 1L of a 20 mg PO₄³⁻ solution of reactive phosphate were passed through the columns. The values shown in Table 3.2 represent the average (n=5) total, error values are presented as standard error.

Abbreviations: S.S (sandstone), L.S (limestone from Castletown quarry), D (Dolomite), M.D (milled dolomite), L.S* (limestone from Clogrennane quarry), S (shale), soil (soil from site at Teagasc Carlow), T.C (tyre crumb) and Z (zeolite clinoptilolite).

Total phosphate remaining from initial concentration 20 mg L ⁻¹									
	S.S	L.S	D	M.D	L.S*	S	SOIL	T.C	Z
<i>S.E</i>	0.24	0.24	0.26	0.08	0.61	0.27	0.11	0.60	0.99
<i>MEAN</i>	3.60	3.66	3.29	0.43	4.05	0.70	0.51	3.66	4.69

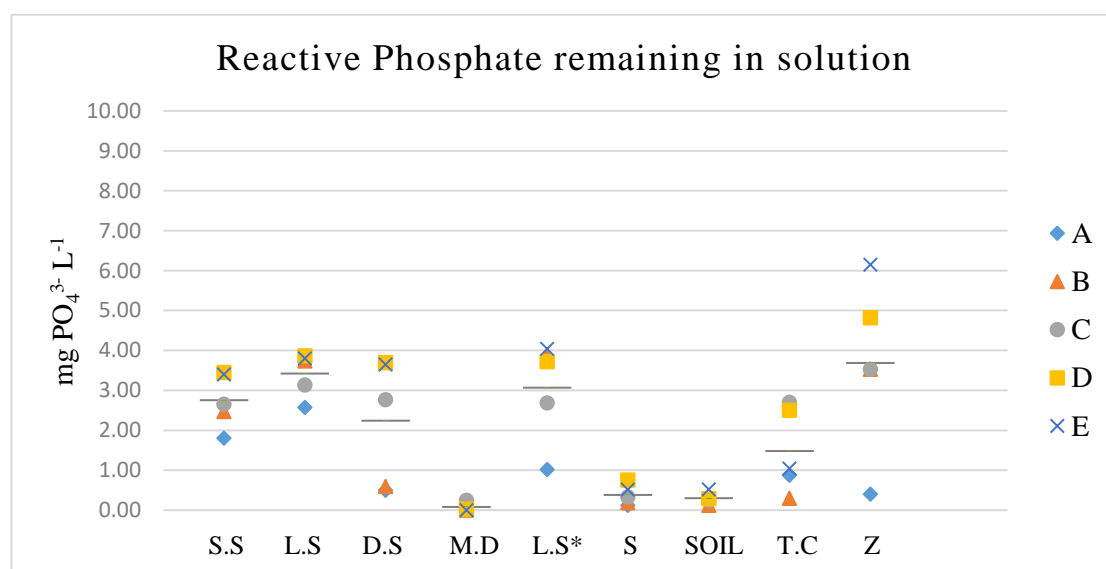


Figure 3.1: Reactive phosphate remaining in column effluent. The mean value shown as a line. Each point on the graph (n=3) represents a 1 litre 20 mg PO₄³⁻ l⁻¹ solution passed through at a flow rate of 1 ml min⁻¹. The experiment was repeated 5 times (A-E).

Abbreviations: S.S (sandstone), L.S (limestone from Castletown quarry), D (Dolomite), M.D (milled dolomite), L.S* (limestone from Clogrennane quarry), S (shale), soil (soil from site at Teagasc Carlow), T.C (tyre crumb) and Z (zeolite clinoptilolite).

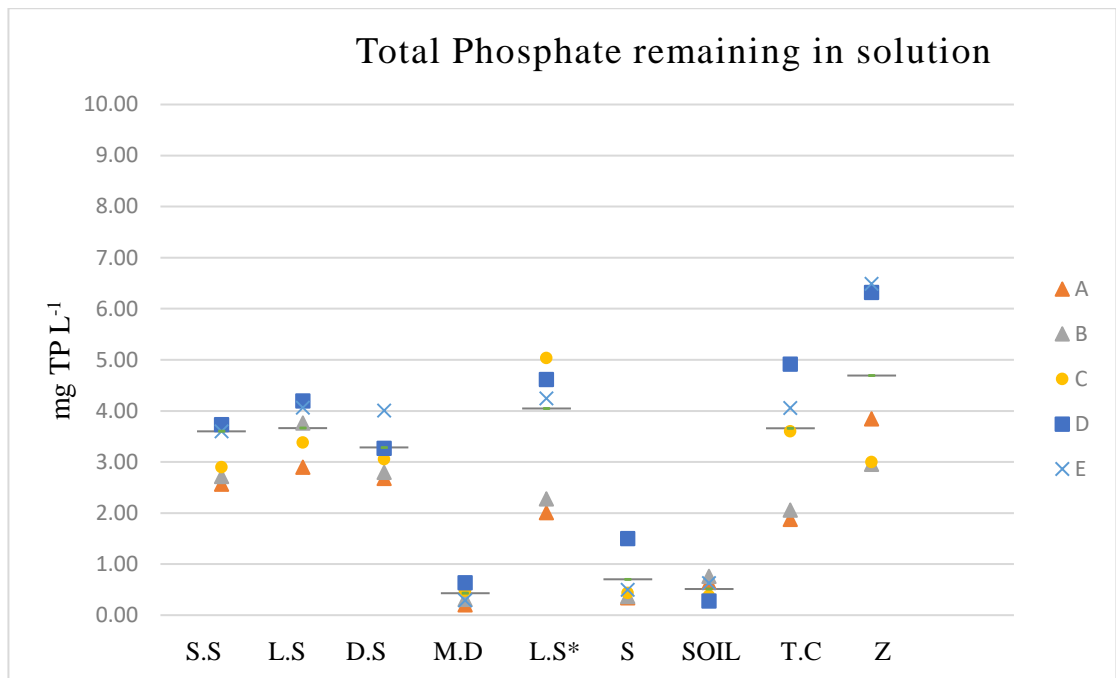


Figure 3.2: Reactive phosphate Total phosphate remaining in column effluent. The mean value shown as a line. Each point on the graph (n=3) represents a 1 litre 20 mg PO₄³⁻ L⁻¹ solution passed through at a flow rate of 1 ml min⁻¹. The experiment was repeated 5 times (A-E).

Abbreviations: S.S (sandstone), L.S (limestone from Castletown quarry), D (Dolomite), M.D (milled dolomite), L.S* (limestone from Clogrennane quarry), S (shale), soil (soil from site at Teagasc Carlow), T.C (tyre crumb) and Z (zeolite clinoptilolite).

Surface area is one of the main characteristics for sorption materials. The smaller the particle size the larger the surface area. The material sizes for this trial were limestone 0.5 - 6mm, sandstone 0.5-6 mm, zeolite 0.25-6mm and tire crumb 0.5-3mm.

Comparison of particle size of a stone is useful when comparing other materials that may be used as a choke layer. Milled dolomite had the lowest values of total and reactive phosphate remaining in solution but may not be suitable as a choke layer, rather than percolating down through the system at a steady rate of 5 to 10 ml⁻¹ it was observed that the flow through the system took days rather than a few hours like the material with bigger particle sizes. . Of the materials suitable as a choke layer. Shale had the lowest mean phosphate values in the column effluent (0.70 mg TPO₄³⁻ l⁻¹ and 0.38 mg RPO₄³⁻l⁻¹). It had a similar particle size to several of the other materials making ‘like for like’ comparison possible.

Soil effluent values were among the lowest 0.51 mg TPO₄³⁻ l⁻¹ and 0.30 mg RPO₄³⁻l⁻¹. Standard error of the mean for TPO₄³⁻ l⁻¹ and RPO₄³⁻l⁻¹ was 0.11 and 0.07. As can be seen from Figure 3.2 the data is distributed around the mean.

Table 3.3: Data summarizing the phosphate removal capacity of all the tested materials.

Material	Mean ± SE TPO ₄ ³⁻ l ⁻¹	% TPO ₄ ³⁻ removal	Mean± SE RPO ₄ ³⁻ l ⁻¹	% RPO ₄ ³⁻ removal
Sandstone	3.60 ± 0.24	82.00	2.75 ± 0.31	86.25
Limestone (Castletown)	3.66 ± 0.24	81.7	3.42 ± 0.24	82.9
Dolomite	3.29 ± 0.26	83.55	2.24 ± 0.71	87.8
Milled Dolomite	0.43 ± 0.08	97.85	0.08 ± 0.05	99.6
Limestone (Clogrennane)	3.07 ± 0.61	84.65	4.05± 0.56	79.95
Shale	0.70 ± 0.27	96.5	0.38 ± 0.11	98.10
Soil	0.51 ± 0.11	97.45	0.30 ± 0.07	98.5
Tyre crumb	3.66 ± 0.47	81.70	1.48 ± 0.60	92.6
Zeolite	4.69 ± 0.99	76.55	3.69 ± 0.95	81.55

3.2 Optimal flow rate for the retention of phosphate by dolomite and shale

Soil, shale and dolomite were best at the removal of phosphate from solution. While shale and dolomite were examined further in column studies, soil was not. The main reasons for this was that A) the material being compared were to be used as a choke layer and soil was unsuitable as such and 2) the materials should allow the flow of solution at similar rates. Flow rates for the removal of phosphate from solution by dolomite and shale were examined. The primary research question was what flow rate would provide optimal sorption of phosphate from solution. This experiment was set up to allow for comparison of dolomite and shale sorption properties, at flow rates of either 5 ml min⁻¹ or 10ml min⁻¹.

For each material, columns were set up in triplicate. The initial concentration of phosphate in solution was 20 mg PO₄³⁻ L⁻¹. Column effluents for flow rates of 5 and 10 ml min⁻¹ were collected at regular time intervals; 18 minutes for a flow rate of 10ml min⁻¹; and 9 minutes for a flow rate of 5 ml min⁻¹. Each effluent sample was analysed for total and reactive phosphate. Figures 3.3 and 3.4 compares the effect of flow rates on normalized concentrations defined as the ratio of phosphate concentration in the effluent (C) divided by initial concentration of phosphate in the influent (C₀).

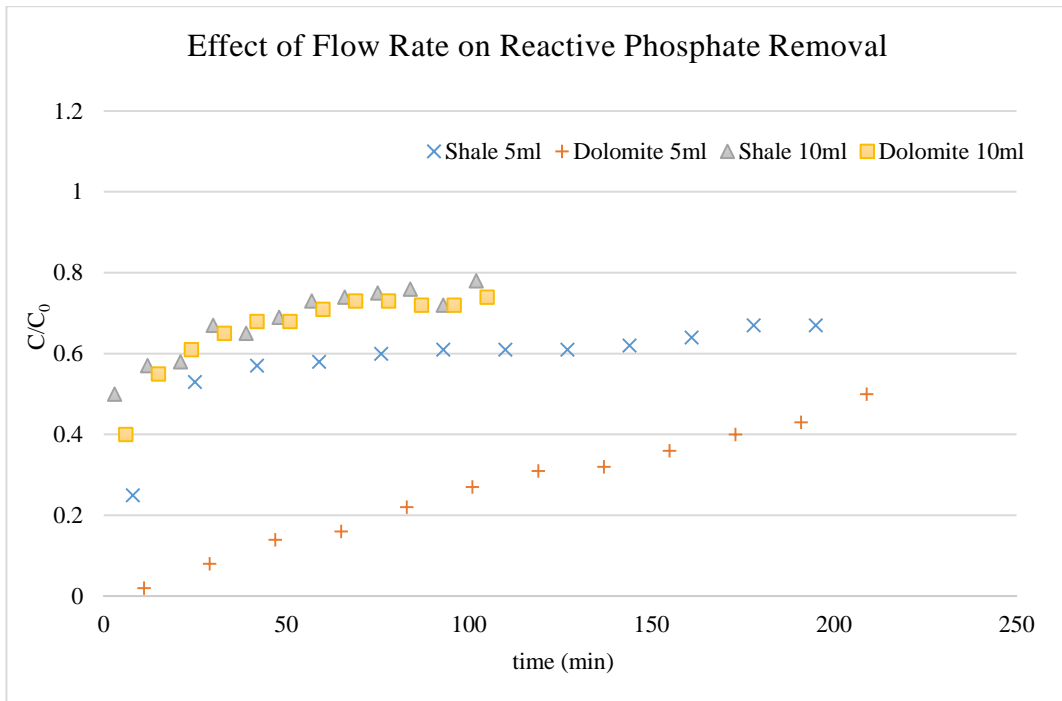


Figure 3.3: Breakthrough curve showing the effect of flow rates on the normalized concentration of reactive phosphate defined as the ratio of phosphate concentration of the effluent (C), to phosphate concentration of the influent (C₀). Each point on the graph represents (n=3) at a given time.

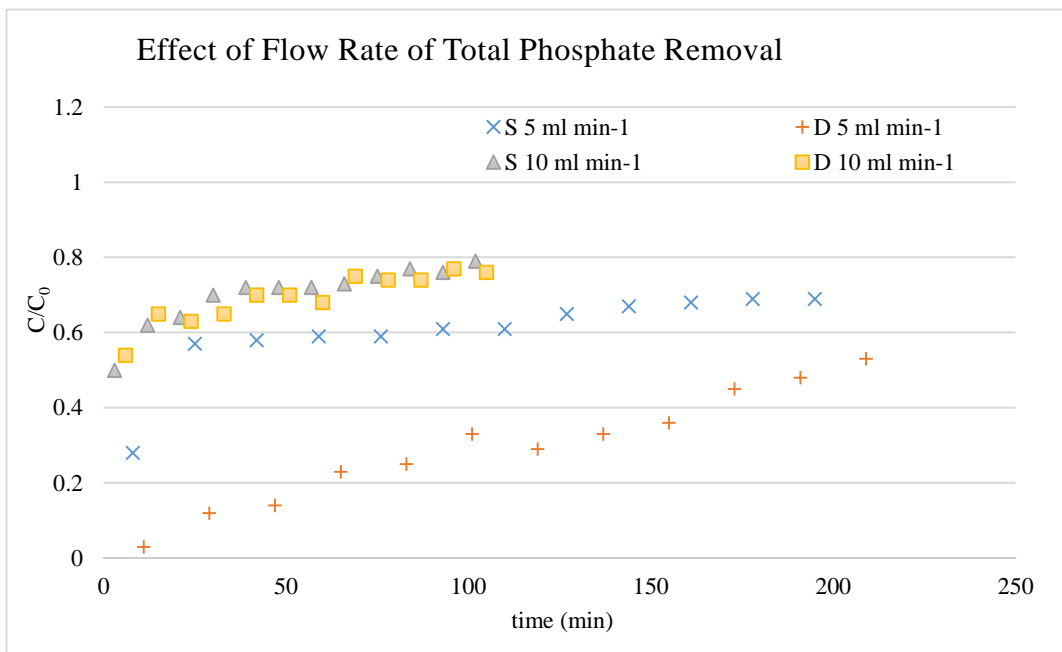


Figure 3.4: Breakthrough curve showing the effect of flow rate on the normalized concentration of total phosphate defined as the ratio of phosphate concentration of the effluent (C), to phosphate concentration of the influent (C₀). Each point on the graph represents (n=3) at a given time. D = Dolomite and S = Shale.

plots of the normalized concentration are given in Figures 3.3 and 3.4. Both reactive and total phosphate follow a similar profile. Changing flow rates is a parameter that may affect the sorption of phosphate onto the dolomite and shale. As indicated on the graphs, the effluent from dolomite columns with a flow rate of 5ml min⁻¹ initially had a low concentration of phosphate remaining. However, over time the phosphate remaining in effluent gradually increased. The increased flow rate of 10ml min⁻¹ for the dolomite resulted in a significantly higher concentration of phosphate when compared to the flow rate of 5 ml min⁻¹. Again, over time there was a gradual increase in phosphate in the 10 ml min⁻¹ dolomite effluent. The shale columns at a flow rate of 5 ml min⁻¹ showed an initial sharp rise in concentrations of phosphate followed by a gradual rise of phosphate concentrations remaining in solution. The flow rate of 10ml min⁻¹ for shale columns had a gradual rise in concentrations over time. Dolomite had a greater removal capacity of both reactive and total phosphate at both flow rates compared to shale.

Table 3.4 Retention of phosphate by dolomite and shale.

<i>Material</i>	<i>Reactive Phosphate</i>			<i>Total Phosphate</i>	
	Q ml min ⁻¹	q _{total} mg PO ₄ Kg ⁻¹	% _R	q _{total} mg PO ₄ Kg ⁻¹	% _R
<i>Dolomite</i>	5	14.42	72.1	13.59	67.93
<i>Dolomite</i>	10	6.33	31.64	5.84	29.19
<i>Shale</i>	5	7.39	36.95	6.64	33.18
<i>Shale</i>	10	6.19	30.93	5.64	28.22

Results of the effects of flow rate on reduction of reactive and total phosphate by dolomite and shale. Q donates flow rate, phosphate percentage removed by the column is given by %_R. q_{total} represents the amount of phosphate in mg retained by 1kg of test material in the column. The values of reactive phosphate include all phosphate removed from solution, values for total phosphate exclude the phosphate removed as a result of precipitate formation.

The percentage removal for reactive phosphate and total phosphate for dolomite 5 ml min⁻¹ was 72.1% and 67.93% respectively. This represents over twice the amount of phosphate taken up by dolomite and shale at 10 ml min⁻¹ and nearly twice the amount taken up by the shale column at 5ml min⁻¹ as can be seen from Table 3.4.

3.3 Discussion

The main goal of this preliminary experiment was to identify a suitable material for the choke layer of the bioswale system that has the capacity to remove phosphate from the farmyard effluent. A secondary aim was to find the optimal flow rate for removal of phosphate from solution. This would only give an indication which flow rate would be best suited for phosphate removal. Quantification of a given amount of phosphate removed from solution by the materials will be examined in detail in the proceeding chapter.

In total, 9 materials were examined, through a simple yet effective screening process. Eight of the materials examined, were studied with the intention of using them as a possible candidate for a choke layer. Although soil was not intended for use as a choke layer, it was analysed on the basis that it was to be used as the upper layer. Other considerations of a suitable material were environmentally friendly and non-toxic, readily available, and relatively inexpensive. The most effective of these 9 at removing phosphate from solution were identified as soil, milled dolomite, and shale.

Tire crumb has been used in several studies in conjunction with other materials to remove phosphate from water. Hood et al., (2013) used a combination of expanded clay 75% and tire crumb 25% to achieve a 60% reduction of PO_4^{3-} . Tire crumb contains 1/3 carbon black which functions like activated carbon. The surface charge is largely affected by the pH of the solution. If the pH of the solution is between pH7-8, this favours a more negatively charged surface (Hood et al, 2013). This means higher adsorption of PO_4^{3-} on the surface can only be achieved through chemical amendment of the solution. In the current study tire crumb achieved reductions of reactive phosphate of 92.6%. However, tire crumb may contain carcinogenic compounds such as polycyclic aromatic hydrocarbons (PAH's) and many heavy metals (Marsili 2014). Considering this, it was decided not to continue investigating this material.

Zeolite was found to be the least effective of the materials tested in removing phosphate. It removed 76.6% of the total phosphate and 81.6% reactive phosphate from the influent. Previous studies have found that zeolite will slowly retain phosphate and must be modified with inorganic salts such as Mg, Al or Fe, (Wn et al., 2006), to increase the rate at which it binds phosphate. This material is also expensive and so it too was eliminated from further investigations.

Limestone has been used in several studies for phosphate removal. Hanna, Sherief and Abo elenin, (2008) found that as pH was increased, the sorption capacity of the material increased due in part to the high content of calcium. Removal efficiency was examined at a constant pH 12, over different times, with different concentrations of phosphate. Equilibrium between phosphate sorption/desorption was reached after 15 minutes and over 50 percent removal efficacy was achieved at a concentration of 176ppm phosphate.

In this qualitative study the removal efficiency for total phosphate of the limestone sourced from Clogrennane quarry was 84.65% compare to 81.7% removal efficiency of Castletown quarry. Clogrennane limestone had a lower removal rate for reactive phosphate, 79.95% compared to 82.9% for Castletown quarry.

In the feasibility study the use of sandstone for phosphate removal was also investigated. Every effort was made to obtain the geological information of the stone from the suppliers Kilsaran of Brownstown Kilcullen Co. Kildare; however, no information was available. The sandstone showed percentage reductions for total and reactive phosphate of 82% and 86%, respectively. Although these results were reasonably good it was decided not to investigate sandstone any further as other materials had a much greater removal capacity.

Milled dolomite, shale and soil had the most significant reductions of both reactive and total phosphate from the influent solution. Effluent from columns containing soil had the lowest phosphate levels. Phosphate uptake in soil will only be inhibited if the concentration is lower in solution than in the soil porewater. From the preliminary experiment the mean percentage phosphate reductions by soil (from initial concentrations of 20ppm) for total and reactive phosphate were 97.45% and 99.45% respectively. Soils are an important sink for phosphate in constructed wetlands. The reduction in this study are reasonable when compared to uptake values of phosphate in the soils of wetlands. Sample soils tested from constructed wetland sites at Johnstown Castle and Dunhill (Dunne et al., 2005) had TP content of $450 \pm 29 \text{ mg kg}^{-1}$ and $867 \pm 33 \text{ mg kg}^{-1}$. The greater capacity of the Dunhill substrate to retain P was due to higher clay and silt content. The Dunhill soil had a high content of aluminium $2079 \pm 194 \text{ mg kg}^{-1}$ and $8013 \pm 341 \text{ mg kg}^{-1}$ of iron). These cations enable retention of P as Al and iron (Fe) oxide, (Dunne et al., 2005).

Shale had mean percentage removal efficiencies of 98.1% reactive phosphate and 96.5% total phosphate. Similar experimental values were achieved during an 11 month pilot scale study using shale as a substrate (Drizo et Al., 2000). In their study, reductions of 95% at a concentration of 20 mg ortho-P L⁻¹ with a hydraulic load rate of 0.02m⁻³ m⁻² d⁻¹ were achieved.

Dolomite is a sedimentary rock and is composed mainly of magnesium calcium carbonate. The column trial showed that milled dolomite could remove more total and reactive phosphate (97.85% and 99.6% respectively) than dolomite stone (83.55% and 88.8%). Milled dolomite was found to be unsuitable a choke layer as it retards the retention time causing clogging and the fine particles may block the perforated holes at the base of the bioswale. It was necessary to increase the particle size of the dolomite to mitigate against this clogging effect; surface area plays a major role in phosphate retention on the materials, therefore only a small increase in particle size was applied. Dolomite stone if reduced in size from 3mm-25mm to 250µ- 5mm should be small enough to increase surface area without causing clogging. Comparisons have been carried out between dolomite of different particle sizes with the same chemical composition. Žibienė et al., (2015) used dolomite powder 1-2mm and dolomite chippings 2-5mm as substrates in pilot scale vertical flow constructed wetlands. They found removal efficiencies for total phosphate from domestic wastewater effluent of 99.9 - 98.9% when dolomite powder was used as a substrate and 98.2 – 93.6% with dolomite chippings.

To date there are no previous studies examining the effect of flow rate on the retention of phosphate by shale. In the current study, the effect of two different flow rates through the shale and dolomite, on phosphate removal from a 20 mg ortho-P L⁻¹ was investigated. The two flow rates investigated were 5 and 10 ml min⁻¹, and were the only parameter changed in this experiment. Other parameters that were kept constant throughout the experiment were the height of the column bed 200mm, pH 7 of the nutrient rich solution and phosphate concentration of the influent (20 mg PO₄³⁻ L⁻¹).

The removal of P at varying flow rates from solution by dolomite was examined at 5 and 10 ml min⁻¹. The qualitative column trial demonstrates that as the flow rate decreases, the phosphate remaining in solution decreases, the percentage reduction is summarized in Table 3.2. Flow rate directly affects contact time between the phosphate and dolomite. Samples of the phosphate solution were regular intervals at a flow rate of 5ml min⁻¹. Initially low concentrations of phosphate were observed. However due to the gradual

movement of the phosphate through the column a gradual increase of phosphate in solution was observed. The average removal of reactive phosphate removed due to adsorption and precipitation was 72.1%. The percentage removed as a precipitate was 4.17% (the difference between the total and reactive phosphate), precipitates may be in the form of $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Mg}_3(\text{PO}_4)_2$.

3.4 Conclusions

The main aim of this chapter was to investigate several materials that would remove phosphate from solution and act as a choke layer in the bioswale system. Secondary to this, optimal flow rates for phosphate removal were examined.

The most effect materials in the preliminary trial were shale, soil, and milled dolomite. All of the materials screened were found to reduce phosphate, consistent with the literature. Phosphate remaining in solution was significantly reduced by milled dolomite. However, it took on average 2 days for the solution to flow through this material, making it unsuitable for the bioswale system. Due to the large phosphate reductions and the good reductions of the larger dolomite stone, it was investigated further in the flow rate experiments (with a particle size of 250 μm - 5mm). Shale had the third lowest reductions of phosphate from solution after milled dolomite and soil. The shale was also investigated further during flow rate experiments. Flow rates for both materials were better at 5 ml min^{-1} , the dolomite had better phosphate reductions of 72.1% compared to the shale 36.95% at 5 ml min^{-1} . The flow rate of 5 ml min^{-1} was used in the bioswale system, investigated in chapter 5.

The following chapter examines dolomite shale and soil in more detail applying Langmuir sorption isotherms. Sorption isotherms gives experimental values for phosphate sorption in mg g^{-1} of material. This give an indication of how much a given amount of material will retain before it becomes saturated.

Chapter 4.0:

**Langmuir adsorption isotherm; Batch study of phosphate adsorption on soil, shale
and dolomite**

4.0 Introduction

In this chapter the sorption of phosphate onto soil, shale and dolomite were examined using through sorption isotherm studies. The Langmuir linear equation was fitted to the experimental data.

Batch studies were carried out, at ambient temperatures 20.2 °C, for 24 hours on a bench top shaker at 300rpm, 50 ml of phosphate solution (n=3), nine concentrations ranging from 4 to 22 mg PO₄³⁻ L⁻¹. The pH of the phosphate solutions was adjusted to pH 7.1. The pH of the soil, shale and dolomite samples were determined. Samples were analysed for total and reactive phosphate.

The main aims and objectives of the sorption isotherms were to;

- I. Determine the maximum sorption capacity Q_{\max} to determine the amount of phosphate in mg g⁻¹ a test material will remove from solution.
- II. To determine if the sorption is favourable or not use the Langmuir dimensionless constant separation factor R_L .
- III. Use the correlation coefficient (R^2) value (this should be close to 1) to determine if the data obtained fits the Langmuir model.
- IV. Use the Langmuir values that are obtained to give an indication of how long a given amount of material will last before phosphate saturation will occur.

4.1 Total and reactive phosphate comparison of results

As discussed in section 1.7, Langmuir isotherms will give information on the amount of phosphate removed from solutions. These models do not shed any light of the type of sorption that has occurred. The purpose of analysing for total phosphates was to determine the amount of phosphate removed from the solution due to ion exchange precipitation reactions. This was the secondary objective of this chapter. The results are displayed in Figures 4.1.1, 4.1.2 and 4.1.3. **all raw data for chapter 4 is contained in the appendices on page iii-vi*

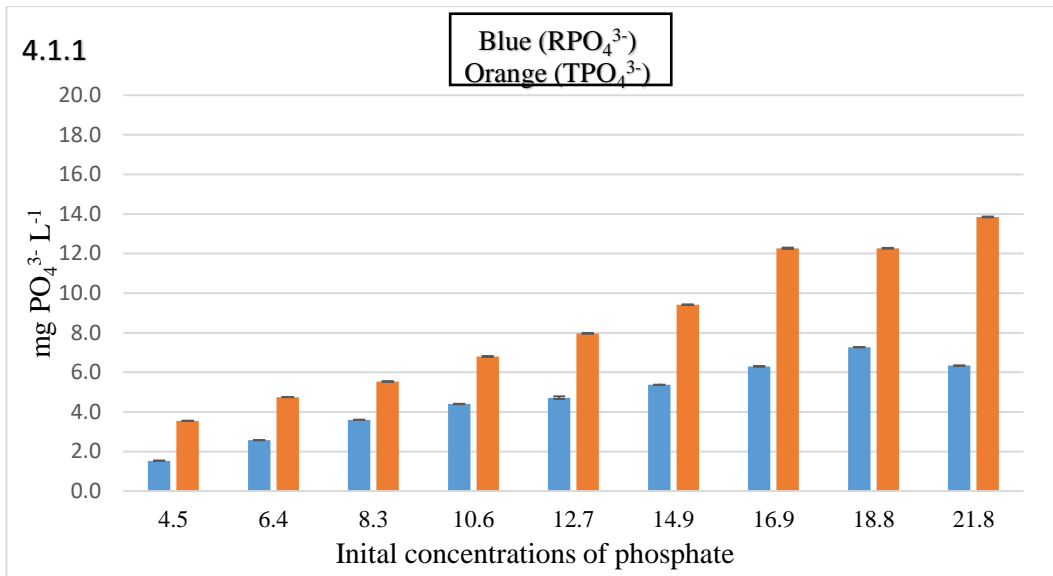


Figure 4.1.1: Dolomite reactive & total phosphate remaining in solution. Describe the relationship between the reactive and total phosphate remaining in solution. Each bar = (n=3). The horizontal numbered legend displays the initial concentration for each set of bars. Reactive phosphate (series 1) and total phosphate (series 2).

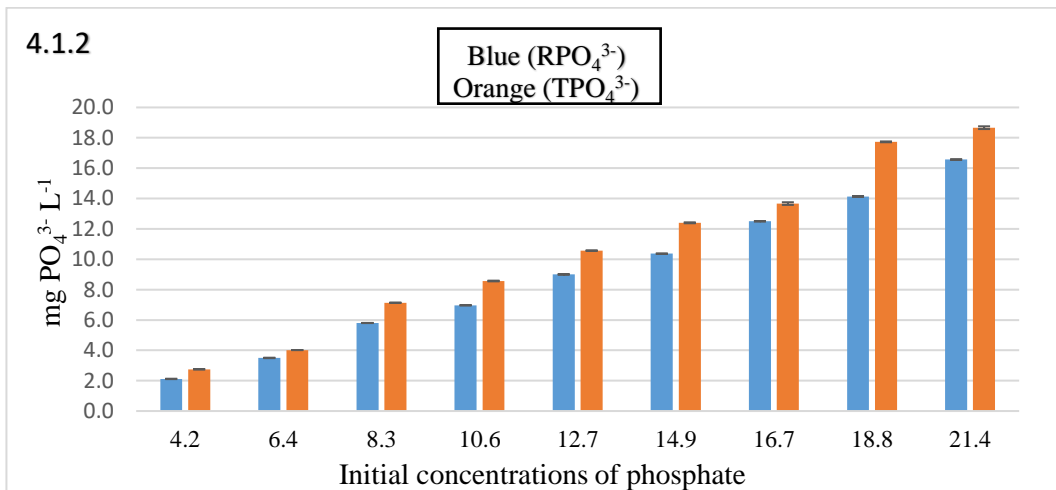
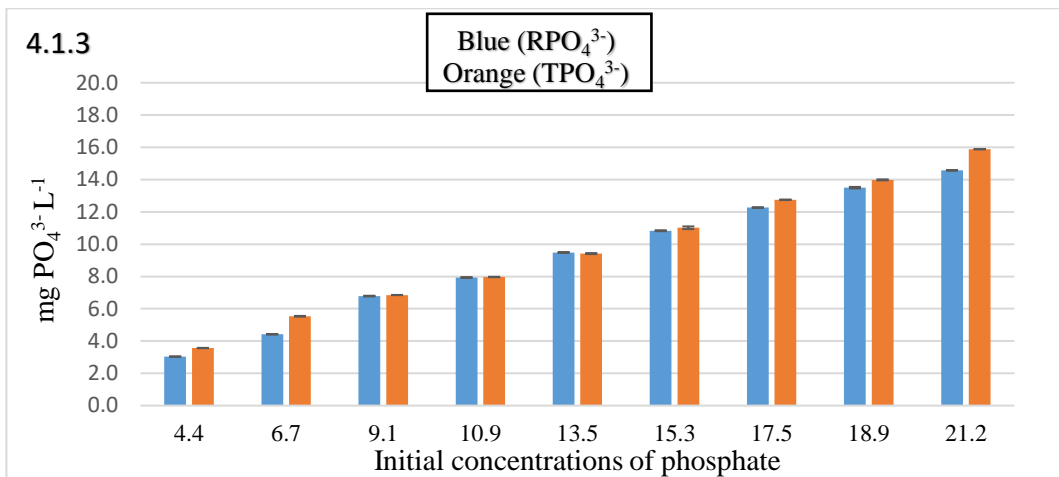


Figure 4.1.2: Shale reactive and total phosphate remaining in solution. Describes the relationship between the reactive and total phosphate remaining in solution. Each bar = (n=3). The horizontal numbered legend displays the initial concentration for each set of bars. Reactive phosphate (series 1) and total phosphate (series 2).



Figures 4.1.3: Soil reactive & total phosphate remaining in solution. Describes the relationship between the reactive and total phosphate remaining in solution. Each bar = (n=3). The horizontal numbered legend displays the initial concentration for each set of bars. Reactive phosphate (series 1) and total phosphate (series 2).

Data from the dolomite batch study (Table 4.1.) shows that 62.5 % ± 1.4 of phosphate in all forms was removed from solution. The amount removed because of ion exchange precipitation was 29.6%.

Data from the shale batch study in Table 4.1. shows an average of 32.5 % ± 3.1 of phosphate in all forms was removed from solution. Ion exchange precipitation reaction accounts for 12.93%.

Data from the soil batch study Table 4.1. shows that 29.6 % ± 0.8 of phosphate in all forms was removed from solution. Only 4.15% was removed because of ion exchange precipitation reactions.

Table 4.1: Total average % phosphate removed from solution, percentage reactive and total phosphate removed from solution.

<i>Material</i>	<i>Percentage Phosphate Removed</i>	
	% Phosphate removed	% phosphate as Precipitate
<i>Dolomite</i>	62.8± S.E 1.4	29.6
<i>Shale</i>	32.5± S.E 3.1	12.93
<i>Soil</i>	29.6± S.E 0.8	4.15

4.2 Results of sorption isotherms and XRF

The primary purpose of the batch studies was to apply the experimental data to the linear form of Langmuir, to compare the sorption capacity of each material to relevant literature values.

Data was plotted to the linear form of the Langmuir type 2 pseudo second order equation $1/q_e$ v $1/C_e$ for dolomite, shale, and soil. As can be seen from figures 4.2.1, 4.2.2 and 4.2.3. it was necessary to describe the goodness of the fit in terms of the correlation coefficient. The closer the R^2 value to 1 the better the fit of the data to the isotherm. R^2 values from the shale batch studies show that the models fit the data well with a value of 0.972. The correlation coefficient R^2 values for soil of 0.971 and dolomite of 0.947 exhibit a good fit for the experimental data.

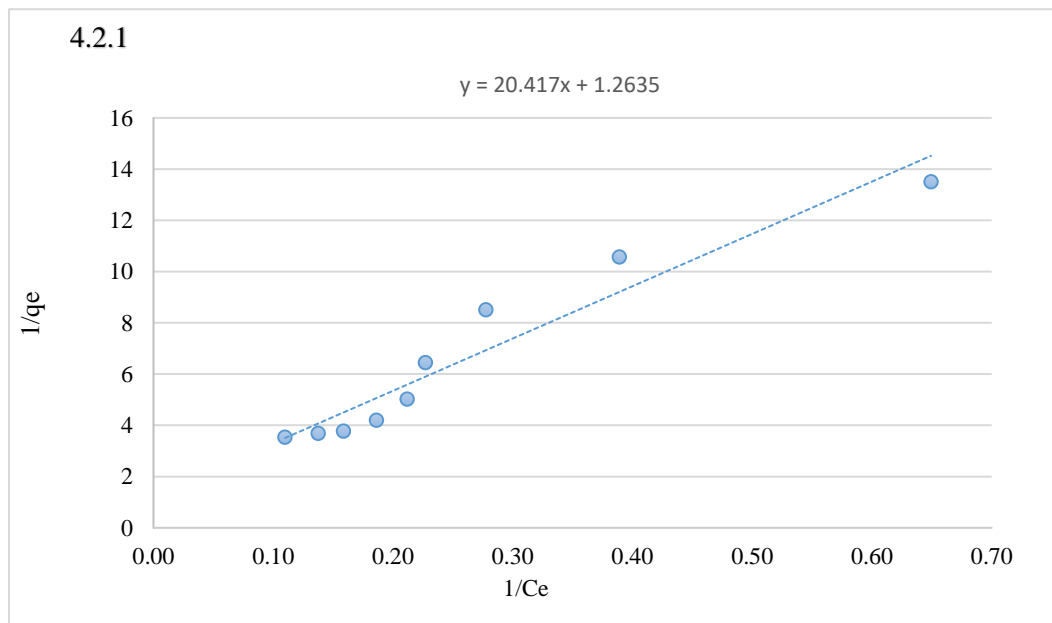


Figure 4.2.1: Dolomite Langmuir isotherm. Linear form of Langmuir sorption isotherms for dolomite.

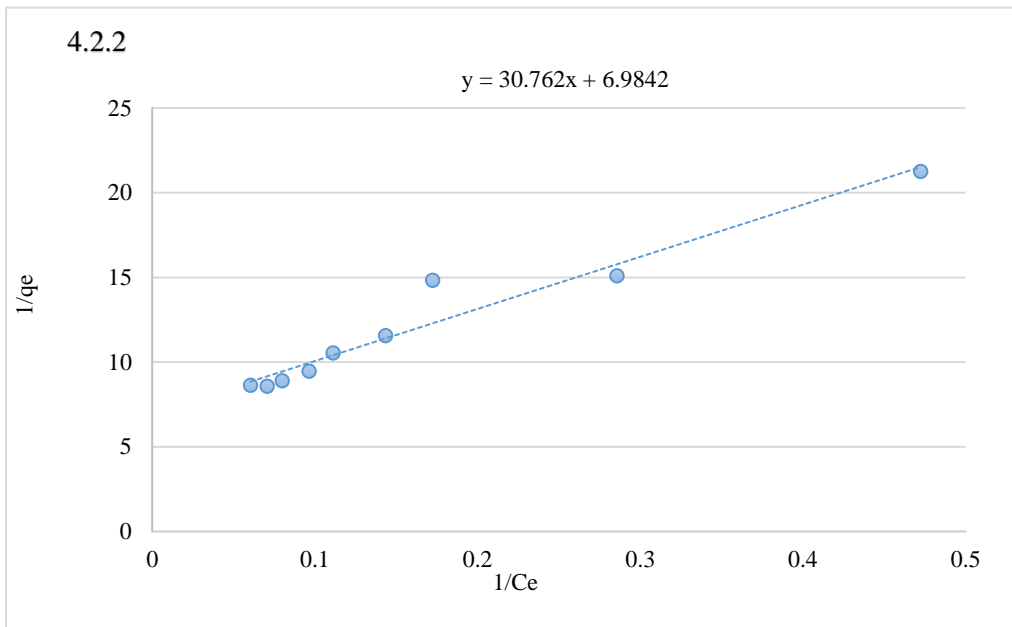


Figure 4.2.2: Shale Langmuir isotherm. Linear form of Langmuir sorption isotherm for shale.

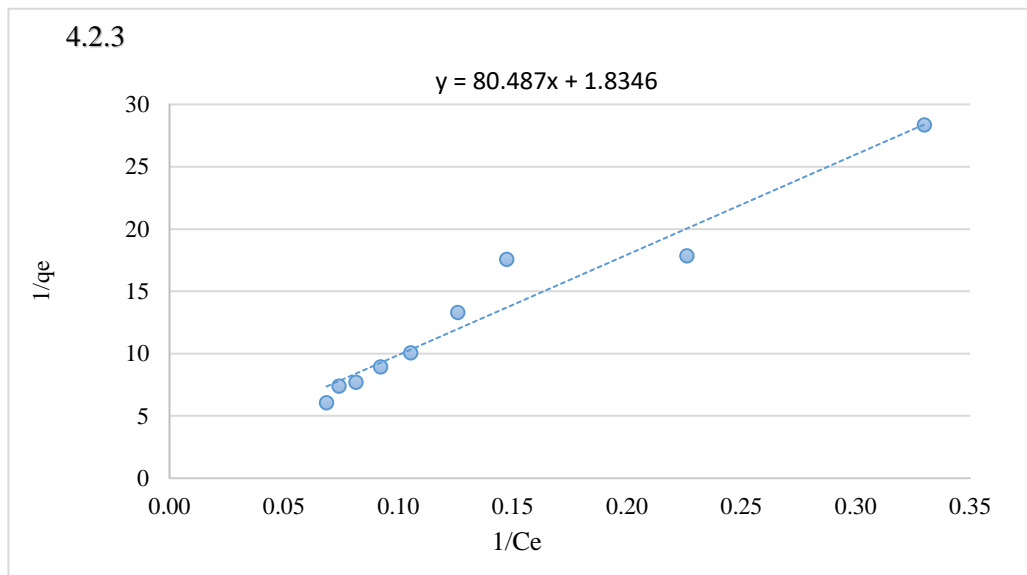


Figure 4.2.3: Soil Langmuir isotherm. Linear form of Langmuir isotherm for soil

Table 4.2.1 shows a comparison of the Langmuir maximum sorption capacity q_{\max} of phosphate for the materials dolomite, shale and soil were found to be 0.587, 0.143 and 0.545 mg PO₄³⁻ g⁻¹ respectively.

The Langmuir dimensionless constant R_L value is used to indicate whether sorption was favourable. The R_L values for dolomite, shale and soil (Table 4.2.1) of 0.134, 0.592 and 0.792 are all under 1, suggest than sorption was favourable.

The average pH of the test materials was taken after batch experiments concluded. The results showed the following: soil pH 6.9, shale pH 7.4 and dolomite pH 8.3. The temperature of the solutions increased slightly during the experiment from 20.2 ± 0.5 to 22.6 ± 0.3 °C.

Table 4.2.1: Sorption isotherm parameters for shale soil and dolomite. Langmuir, maximum sorption capacity of material Q_{\max} in mg g⁻¹, the separation factor R_L and the correlation coefficient R^2 .

<i>Material</i>	<i>Parameters Langmuir Isotherm</i>		
	Q_{\max} (mg g ⁻¹)	R_L	R^2
<i>Shale</i>	0.143	0.592	0.972
<i>Soil</i>	0.545	0.792	0.971
<i>Dolomite</i>	0.587	0.134	0.947

Table 4.2.2: XRF Chemical Analysis Laboratory report by Irish Cement Ltd, Platin Rd, Drogheda, Co. Louth. The table displays the % w/w of the major compounds of shale soil and dolomite.

<i>Sample</i>	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Na	TiO ₂	P ₂ O ₅	Total
<i>Dolomite</i>	1.83	0.3x8	1.13	40.31	16.82	0.06	NDA	NDA	NDA	NDA	60.53
<i>Shale</i>	65.09	13.93	5.43	0.50	1.38	2.48	1.21	2.84	0.88	0.73	94.47
<i>Soil</i>	62.13	5.85	3.19	14.45	0.82	1.21	0.38	1.18	0.37	0.00	89.58

Special Note: XRF analysis give the percentages w/w of each compound in the sample. The XRF will only analyse major and trace element it was calibrated for, namely the compounds in Table 4.2.2. For this reason, the total percentages do not add up to 100%. NDA (No Data Available).

XRF spectrometry allows for the non-destructive chemical analysis of minerals, sediments and rocks. XRF is used to analyze the relative abundance of major and trace elements. Applications include the petrology of rock types and soil analysis (Techniques, 2018). The bulk chemical analysis of interest here were compounds of Al, Fe, Ca and Mg. These elements play a critical role in the sorption/precipitation of phosphate and therefore their relative amounts in the dolomite, shale and soil were of interest.

The major compound in shale (65.09%) and soil (62.13%) was silicon dioxide. Compounds that directly affect the immobilization of phosphate through sorption/precipitate reactions are aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3) or hematite, calcium oxide (CaO) and magnesium oxide (MgO) magnesia, these compounds along with silicon dioxide are typical of shale stone, (Yaalon 1961). In several sorption isotherms studies these compounds are referred to almost exclusively when it comes to phosphate immobilization using soil, shale and dolomite, (Pant, Reddy & Lemon, 2001 and Jordan et al., 2005 and Prochaska & Zouboulis, 2006 and Jiang et al., 2014 and Coulibaly et al., 2015 and Daly et al., 2015).

The most abundant compound in dolomite stone associated with phosphate immobilization was CaO (40.31%), followed by MgO (16.82%). Other elements in smaller amounts were (1.13%) Fe_2O_3 and (0.38%) Al_2O_3 was the most plentiful compound in shale, associated with phosphate immobilization. Compounds in descending order are Al_2O_3 (13.93%), (Fe_2O_3 5.43%) MgO (1.38%) and CaO (0.5%).

Calcareous soils have a calcium carbonate (CaCO_3) content of more than 15%, (Fao.org, 2017). The calcium oxide in the soil was (14.45%), much of this will be in the form of calcium carbonate, classifying the soil as calcareous. Important phosphate immobilization compound in lesser fractions in the soil sample were Al_2O_3 (5.85%), Fe_2O_3 (3.19%) and MgO (0.82%).

4.3 General discussion

The primary purpose of this experiment was to determine the choke layer material that would be best suited to the removal of phosphate from solution through sorption and precipitate mechanisms. Assimilation due to bacteria was not investigated as all materials were autoclaved prior to batch studies. This experiment was concerned with the physical/chemical reactions that cause the removal of phosphate from solution.

Parameters that effect sorption that were monitored for both dolomite and shale were pH, temperature and particle size. Differences between the two materials that may affect sorption was their composition.

The r^2 value of 0.947 for dolomite demonstrations that the data fits well with the Langmuir model this correlation may be seen in figure 4.2.1 (the closer the r^2 value to 1 the better the data is considered to fit). The value for the dimensionless constant R_L of 0.134 indicates favourable adsorption as R_L was greater than 0 but less than 1.

The experimental values for the Q_{max} for dolomite, determined through the Langmuir sorption isotherms were similar to the values in other studies. Prochaska and Zouboulis (2006), obtained values for the Q_{max} of $0.515 \text{ mg PO}_4^{3-} \text{ g}^{-1}$, while Pant, Reddy and Lemon (2001), determined the Q_{max} to be $0.929 \text{ mg PO}_4^{3-}$. These values were nearer to the Q_{max} attained in this study than the values achieved by Yuan et al., (2015), of $4.76 \text{ mg PO}_4^{3-}$. There are two primary reasons for the different Q_{max} achieved in this study and other studies, these are differences in pH and particle size. Yuan et al., (2015) found that the % phosphate removal increased up to a pH of 9.5, beyond this pH phosphate removal by dolomite decreased.

Table 4.3.1: Comparison of properties and values between the current studies and studies in the literature. Cations are the main cations reported for dolomite in each study. Physical properties of particle size and pH. Q_{max} , the maximum sorption capacity of dolomite for phosphate in $mg\ g^{-1}$ values below these are P. The R_L values indicates whether sorption is favorable and the R^2 is the coefficient of determination. NDA (no data available).

<i>Authors & year</i>	<i>Dolomite</i>	<i>Properties</i>	<i>Langmuir</i>		
			Q_{max} mg g ⁻¹	R_L	R^2
<i>Current Study</i>	NDA	0.25-5mm pH 8.8	0.587	0.134	0.947
<i>Prochaska & Zouboulis, (2006)</i>	Ca Mg Fe Al Si	1.2-2.4mm pH 7.8	0.515 (0.168)	0.431	0.974
<i>Pant, Reddy and Lemon, (2001)</i>	Ca Mg Fe Al Si	pH 9.3	0.929 (0.303)	NDA	0.950
<i>Yuan et al., (2015)</i>	Ca Mg Si	$\geq 0.15mm$ pH 9.5	4.76	NDA	0.996

Calcium is the predominant (21.2 to 28.68 % w/w) cation in dolomite (Yuan et al., (2015) and Prochaska and Zouboulis, (2006)) and increases in alkaline conditions favor the formation of calcium precipitates. This may explain the increase of the Q_{max} as the pH increases. The calcium content of dolomite as determined by XRF was in keeping with other studies (Table 4.3.1) with values of 28.79% Ca (40.31% as CaO).

Particle size is another factor that may affect phosphate uptake. The dolomite used in the study by Yuan et al., (2015), had the smallest particle size $\geq 0.15mm$. Small particle size increases surface area thereby increasing the number of sites available for the binding of phosphate. The Q_{max} values for this study closely resemble the values obtained by (Prochaska and Zouboulis, (2006), that had values of pH and particle size that were similar (Table 4.5).

Reactive phosphate remaining in solution is the initial concentration of phosphate in solution minus amount adsorbed by the media. , (Prochaska and Zouboulis, (2006). The uptake of phosphate by dolomite was the difference between initial concentration and the amount of reactive phosphate remaining in solution. The phosphate removed from solution was 62.5%, the difference between total and reactive phosphate was 29.6%. This

value may indicate that removal by precipitation accounts for nearly half of all phosphate removed from solution. This is backed up by Yan et al., (2007). They observed that the formation of calcium phosphates precipitates is the predominate mechanism of phosphate removal from solution at higher alkaline conditions. The above values for the Q_{\max} in each study were carried out at approximately 20°C. It should be noted that temperature effects sorption of phosphate onto dolomite. Thermodynamic experiments by Yuan et al., (2015) found that over a temperature range of 20 – 80°C there was a decrease in phosphate sorption to dolomite as temperature increased, due to the exothermic nature of the reaction. This may mean that cooler climates would suit sorption using dolomite as a substrate in the bioswale. They concluded, from negative entropy values, that the sorption process was probably a chemical reaction (Yuan et al., 2015).

Shale had an R^2 value of 0.972. That demonstrates that the data fits well with the linear Langmuir model, this correlation may be seen in figure 4.1.2. The dimensionless constant R_L of 0.592 indicates favourable adsorption.

Shale had an experimental Q_{\max} value of 0.143 mg $\text{PO}_4^{3-} \text{g}^{-1}$ (Table 4.3.2). The Q_{\max} value in this study for Langmuir sorption isotherms was lower than other studies. Thermodynamics was not a contributing factor for changes in the experimental Q_{\max} values, as all experiments were examined at the same temperature. Differences in values may be attributed to three factors: pH, composition of the shales or changes in surface area due to particle size. It has been found in other studies that the maximum sorption capacity of shale increases with decreasing particle size, grain sizes 0.5-1.0mm gave a Langmuir Q_{\max} of 1.897 mg $\text{PO}_4^{3-} \text{g}^{-1}$ (0.619 mg P g^{-1}), (Tang, Huang and Scholz, (2009).

Aluminum oxide was the most plentiful compound in shale this is associated with phosphate immobilization. Compounds in descending order are Al_2O_3 (13.93%), Fe_2O_3 (5.43%) MgO (1.38%) and CaO (0.5%).

The two most abundant elements, that affect phosphate immobilization, found in this and other shale batch studies in various forms are Al and Fe, (Pant, Reddy & Lemon, (2001) and Jiang et al., (2014) and Coulibaly et al., (2015). Al_2O_3 and Fe_2O_3 were present in substantial amounts, while other cations such as Mg and Ca, were found in much smaller amounts (Coulibaly et al., (2015). The results for the Q_{\max} 0.143 mg g^{-1} for the current study were closer to the Q_{\max} 0.273 achieved by Coulibaly et al., (2015) than any of the other studies. There were differences and similarities between the two studies. One of the

differences between the two studies was particle size. The much smaller particle size used in the study by Coulibaly et al., (2015), increases the availability of sites for sorption of phosphate, thereby increasing phosphate sorption. The geochemical composition of both shales was similar; therefore, particle size may have attributed to differences in Q_{\max} values. Coulibaly et al., (2015), had Al_2O_3 (15.46% w/w) and Fe_2O_3 (9.21 % w/w), whereas the current study had Al_2O_3 values of (13.93%) w/w and Fe_2O_3 (5.43%) w/w. Another reason for a difference between the two may be the slightly acidic conditions of the Coulibaly study.

In wetland soils that are slightly acidic, the cations Fe and Al are responsible for the immobilization of phosphate (Dunne and Reddy, 2005). The pH conditions were slightly alkaline in the current study and a larger Q_{\max} may be possible in a slightly acidic solution. As discussed previously the predominant cation Ca is responsible for immobilization of phosphate from solution in alkaline conditions. It may be that the larger Q_{\max} value for dolomite was a result of more favorable conditions of pH. Batch experiments conducted by Drizo (1999), found shale had a good combination of properties to be used in wetlands and found high Q_{\max} P values between 1.992 – 2.146 mg PO_4^{3-} g⁻¹ (0.650 – 0.730 mg P g⁻¹). This study was conducted at pH 4.5, favourable conditions for phosphate sorption onto shale.

Table 4.3.2: Comparison of properties and values between the current studies and studies in the literature. Physical properties of particle size and pH. Q_{max} , the maximum sorption capacity of shale for phosphate in $mg\ g^{-1}$ values below these are P. The R_L values give whether sorption is favorable and the R^2 is the correlation coefficient. NDA (No Data Available).

<i>Authors & year</i>	<i>Shale</i>	<i>Properties</i>	<i>Langmuir</i>		
			Q_{max} $mg\ g^{-1}$	R_L or K	R^2
<i>Current Study</i>	Al>Fe>Mg>Ca	0.25-5mm pH 7.4	0.143	R_L 0.592	0.972
<i>Coulibaly et al., 2015</i>	Al>Fe>Mg>Ca	$\geq 0.08mm$ pH 6.0-7.0	0.273	NDA	0.960
<i>Jiang et al., 2014</i>	Al , Fe	$\geq 0.85mm$ pH 7.0	1.395 (0.455)	NDA	0.994
<i>Pant, Reddy and Lemon, 2001</i>	Fe>Al >Ca >Mg	pH 8.9	0.588 0.192	NDA	0.940

Comparisons on the effect of pH may only be made if the compositions are known. Jiang et al., (2014) give the percentages w/w of Al and Fe compounds. That study had the highest Q_{max} in Table 4.3.2, at neutral pH suggest that Al and Fe oxides are forming compounds with phosphate.

The R^2 value of 0.971 and the correlation demonstrated in Figure 4.2.1, shows that the data fit well for the Langmuir sorption isotherms. Langmuir model is deemed to be appropriate if the R^2 value greater than 0.95 for phosphate sorption to soil, (Daly et al., 2015). Sorption was found to be favorable with the dimensionless constant R_L of 0.792.

Table 4.3.3: Comparison of properties and values between the current studies and studies in the literature. Physical properties of particle size compared to other studies include pH, cations, particle size and clay content. Q_{max} , the maximum sorption capacity of shale for phosphate in $mg\ g^{-1}$ values below these are P. The R_L values give whether sorption is favorable and the R^2 is the correlation coefficient. NDA (No Data Available).

<i>Authors & year</i>	<i>Soil</i>	<i>Properties</i>	<i>Langmuir</i>		
<i>Characteristic or parameter</i>	Soil type	Particle Size & pH	Q_{max} mg g ⁻¹	R_L or K	R^2
<i>Current Study</i>	Loam (8% Clay) %OM 9.6	0-2mm pH 6.9	0.545	R_L 0.792	0.971
<i>Jordan et al., 2005 Clarnianna</i>	Brown Earth %OM 7.5 Ca > Al > Fe	0-2mm pH 6.7	1.021 (0.333)	NDA	Stated that R^2 fit
<i>Daly et al., 2015 Roscommon</i>	Loam, %OM 5.9-15.5 Ca > Al > Fe Calcareous glacial till	0-2mm pH 4.6-6.9	0.929 - 1.333 (3.03 - 435)	NDA	$R^2 > 0.95$
<i>Daly et al., 2015 Meath</i>	Loam, %OM 7.5-14.7 Ca > Al > Fe Ordovician shale, glacial till	0-2mm pH 4.7-6.4	1.094 – 1.704 (0.357-0.556)	NDA	$R^2 > 0.95$

There were no comparisons between the Q_{max} of the soil against the materials dolomite and shale, as soil will be used in the bioswale along with either dolomite or shale. Langmuir sorption isotherms Q_{max} in this study was compared to the Q_{max} of other studies Table 4.3.3. Q_{max} values for soil in other studies were larger than the Q_{max} values determined in the present study. The reason for differences in Q_{max} values are likely to be a result of differences in the experimental conditions. The present study had some similar parameters to previous studies including particle size 0-2mm, temperature 20°C and contact time 24hour. Characteristics that may affect the Q_{max} of soil studies that were dissimilar to the studies identified in Table 4.3.3 were changes in pH, geochemical composition features of mineral content Al, Fe and calcium and the percentage organic matter.

In the current study the pH of the influent was close to neutral at pH 6.9. Slightly alkaline conditions favor calcium phosphate precipitates and acidic conditions favor formation of

Al and Fe phosphates. The soil in this study may be considered as calcareous soil due to the high content of calcium. Formation of precipitates hydroxyapatite ($\text{Ca}_5(\text{PO}_4)\text{OH}$) and beta tricalcium phosphate ($\text{B-Ca}_3(\text{PO}_4)_2$) may have been the main mechanisms of phosphate removal. Amorphous forms of Al and Fe were present in lesser quantities. These may have, to a lesser extent immobilized phosphate by forming compounds such as variscite (AlPO_4), strengite (FePO_4) and vivianite ($\text{Fe}_3(\text{PO}_4)_2$) on clay particles.

Batch results from the study are only sufficient to gain an initial estimate of phosphate removal using shale. To predict how long a shale substrate will last with respect to phosphate immobilization, full scale trials are necessary to determine this with some degree of accuracy, (Drizo et al., (1999). The same may be applied to the capacity of soil and dolomite.

4.4 Conclusion

Physical conditions of particle size, pH and the geochemical composition of the material were the characteristics that effected immobilization of phosphate from solution during the batch studies.

Batch studies of dolomite, shale and soil and application of the Langmuir sorption isotherm mathematical model demonstrated that all three materials had favourable sorption and were a good fit, with high R^2 values. The R^2 value were 0.972 for shale 0.971 for soil and 0.947 for dolomite all these values are close to 1 demonstrating that the data fits the regression line.

Dolomite Q_{\max} value of $0.587 \text{ mg PO}_4^{3-} \text{ g}^{-1}$ was comparable to similar studies discussed in this chapter. The alkaline conditions pH 8.8 and the high calcium content 28.79% of the dolomite played a critical part in the immobilization of phosphate from solution in the batch study. Immobilization of phosphate was responsible for 62.5% removal of phosphate and is likely due to a combination of sorption/precipitate mechanisms. While the remaining 29.6 % of the removal of phosphate was due to precipitate formation.

Shale Q_{\max} values of $0.143 \text{ mg PO}_4^{3-} \text{ g}^{-1}$ was lower than other studies discussed in this chapter. Coulibaly et al (2015) was the closest study by comparison, in terms of Q_{\max} (0.273 mg g^{-1}). The study had similar particle size and mineral composition in terms of Al_2O_3 and Fe_2O_3 . The pH was also lower in Coulibaly et al (2015) than in the present study and, as has been stated, acidic conditions are more favourable for immobilization by Fe and Al oxides. In the present study a total 32.5% phosphate was removed from the solution, 12.93% of phosphate was removed as a precipitate.

The Q_{\max} of the soil used in the current study was 0.545 mg g^{-1} . This compared well with Jordan et al., (2005) and Daly et al., (2015). The soil was primarily calcareous in composition, with moderate levels of Fe and Al oxides. In cannot be stated with certainty what are the mechanisms of removal. The pH of 6.9 allows for both calcium precipitate formation and sorption onto the aluminium contained in the soil. The main compounds involved in phosphate immobilization from solution are Ca, Al and Fe oxides. These materials based on the Q_{\max} values and their composition were found to be suitable to be used in the bioswale system.

Although dolomite had a better Q_{\max} value than shale, both will be examined further in the next section. Shale based wetlands have already been examined and found to be good sinks for phosphate removal, to date there are no long-term studies of dolomite in wetland systems.

Chapter 5

Reduction of Nutrients in synthetic wastewater by multi horizon packed bed bioswale filtration system.

5.1 Introduction

The previous chapter provided information solely on materials that reduce phosphate through sorption/precipitate mechanisms. The primary aim of this chapter was to examine the reduction capabilities of small scale bioswale systems (mini bioswales) to reduce phosphate from solution. A secondary objective of this chapter was to examine ammonium and nitrate reduction as these are two of the main forms of N found in agricultural wastewater.

The non-parametric test used to determine significant differences between final effluent values of the different bioswales was the Mann-Whitney. Standard error bars or data which overlap indicates no significant difference between two groups and error bars that don't overlap may indicate that there is a significant difference between two groups but this is not always the case therefore it is necessary to carry out further statistical analysis, (Cumming, Fidler and Vaux, 2007).

The parameters monitored throughout included: pH, conductivity, and redox potential. pH affects sorption reactions that reduce phosphate, while a negative redox potential affects the mechanisms by which ammonium is reduced. pH and conductivity are important water quality parameters that affect water bodies productivity.

5.2 Results

The experimental set-up is described in detail in section 2.5. Briefly, it consisted of six PVC pipes with 5 layers of material limestone gravel, soil, willow bark, shale or dolomite and limestone drainage stones. Three pipes had a layer of dolomite and three had a layer of shale.

Analysis of the physical properties of the soil, shale and dolomite were performed, prior to the experiment being undertaken and during the trial (Table 5.1). Additional physical analysis of soil included cation exchange capacity (C.E.C), percentage organic matter and soil texture. These three parameters are linked, as the clay and organic content of soils increase, the C.E.C increases. Soils with high C.E.C retain nutrients better than soils with low C.E.C. Phosphate becomes immobilized through ion exchange precipitation reactions with cations in soil, ammonium is also retained by the organic and clay fractions.

Table 5.1: Physical analysis of pH, conductivity, TDS and Salinity for soil shale and dolomite. Extra physical parameters examined in soil were the cation exchange capacity, percentage organic matter and soil texture (n=3) (ND= not determined).

<i>Sample</i>	<i>pH</i>	<i>Conductivity</i> <i>μs/cm</i>	<i>Salinity</i> <i>PSU (ppt)</i>	<i>meq 100g⁻¹</i>	<i>% Organic</i>	<i>Soil Texture</i>
<i>Soil</i>	6.88	663.3	0.33	14.05 ± 0.11	9.59 ± 0.05	Loam
<i>Shale</i>	7.46	320.0	0.15	ND	ND	ND
<i>Dolomite</i>	8.80	126.2	0.06	ND	ND	ND

Probe analysis for each material included pH, conductivity, TDS and salinity. The redox potential was monitored throughout the experiment. The soil texture was determined to be loam, with a percentage organic matter of 9.59% ±0.05% and a C.E.C of 14.05 ± 0.11 meq per 100grams.

Deionised water was passed through the system and analysed to measure the level of phosphate, ammonium, and nitrate prior to the addition of artificial wastewater. These baseline values are in Table 5.2. An artificial nutrient rich wastewater solution containing ammonium and phosphate was prepared and analysed prior to application on the bioswales, the concentrations of which can be seen in (Table 5.2). The first 7.5L batches

of this solution (series A) were passed through the column once unrestricted, collected and then fed through the columns again at a flow rate of 5ml min⁻¹. Effluent samples were collected in triplicate once all the 7.5 L had passed through the system and each sample was analysed for total and reactive phosphate, ammonium, nitrate, pH, redox potential, salinity, TDS and conductivity. The same solution was recycled through the column at 5 ml min⁻¹ three more times and after each cycle the above parameters were measured. The entire experiment was repeated once more with a fresh batch of artificial wastewater (series B).

Table 5.2 Baseline concentrations of phosphate, nitrate and ammonium after deionised water was flushed through the systems (n=3), prior to any addition of phosphate ammonium solution. Series A give the concentrations of phosphate and ammonium added to the system before analysis (n=3). Series B gives the concentrations of phosphate and ammonium in the system before analysis of series B (n=3).

	<i>Dolomite</i>						<i>Shale</i>					
	NH ₄ ⁺	SD	NO ₃ ⁻	SD	PO ₄ ³⁻	SD	NH ₄ ⁺	SD	NO ₃ ⁻	SD	PO ₄ ³⁻	SD
<i>Baseline</i>	0.03		17.00		0.01		0.03		16.50		0.03	
<i>Series A</i>	41.24		0.00		19.16		41.16		0.00		19.96	
<i>Series B</i>	39.33		0.00		20.56		39.67		0.00		20.67	

Conductivity, TDS and salinity are all an indirect measure of the levels of impurities in water, the mass of dissolved solids and an estimate of the salt concentrations in the water. These three parameters are all related. This experiment will examine conductivity when dealing with water quality. The conductivity of the test materials was measured individually. Soil had the highest 663.3 µs/cm followed by shale 320.0 µs/cm and dolomite 126.2 µs/cm. Soil had a nearly neutral pH of 6.88, shale was very slightly alkaline at 7.46 and dolomite was alkaline at 8.80.

The pH of the effluent from the dolomite columns increased slightly from 8.05 to 8.50, throughout the experiment. The effluent from the shale columns experienced a slightly larger increase in pH from 7.77 to 8.73. Conductivity measurements of the dolomite effluent rose steadily from 780 to 1110 µs/cm before falling to 1000 µs/cm. Effluent from

the shale columns experienced a similar trend with initial measurements of 780 to 916 $\mu\text{s/cm}$ before falling below the initial value to 760 $\mu\text{s/cm}$.

The redox potential for the effluent from both systems was monitored throughout the experiment. The redox potential for both systems was initially positive. The systems were left submerged for two weeks before addition of the artificial wastewater. The redox potential of the effluent from dolomite columns fluctuated between -89.0 mV to -101.0 mV before reaching the lowest point of -120.0 mV at the final reading. Shale effluent redox potential fluctuated between -78.8 mV to -96.8 mV before reaching the lowest point at the final reading of -139.6 mV.

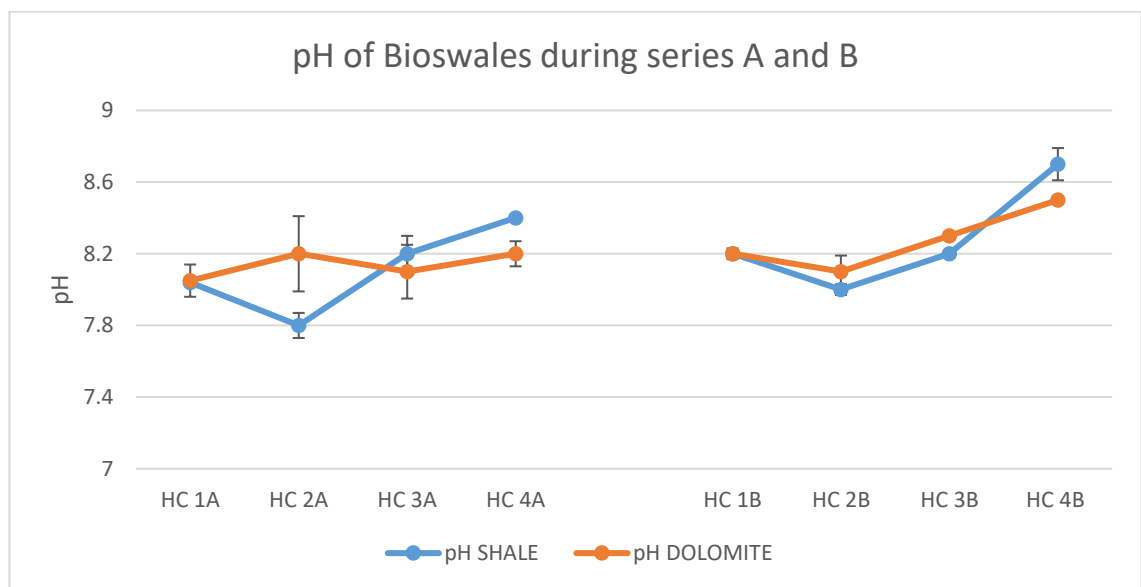


Figure 5.1: Progression of the pH series A and B dolomite and shale bioswales. A and B have a broken line between them. The error bars (n=3) standard error.

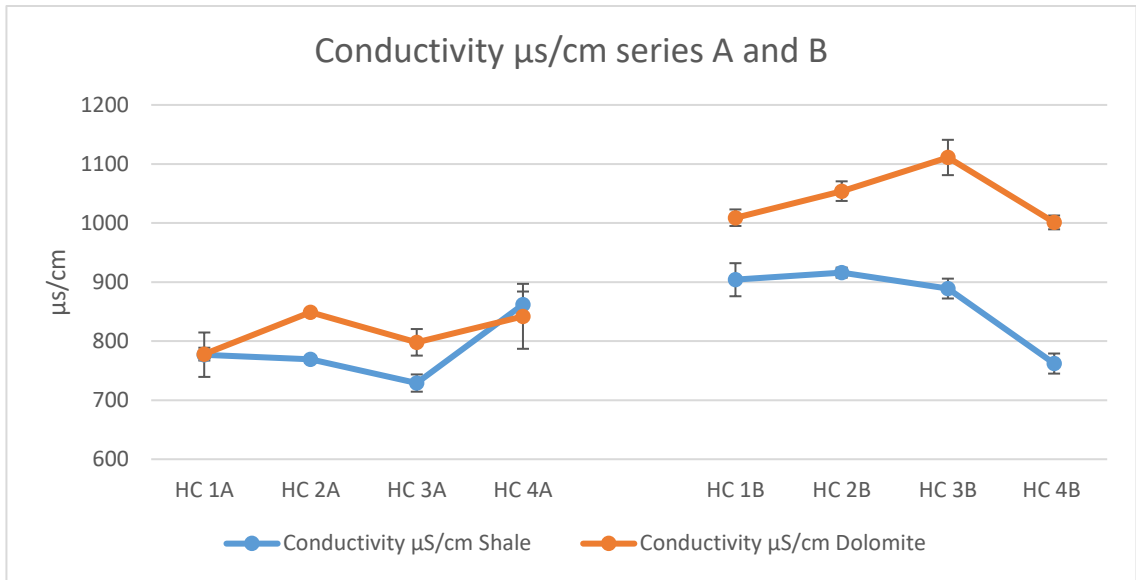


Figure 5.2: Progression of the conductivity series A and B dolomite and shale bioswales. A and B have a broken line between them. The error bars (n=3) standard error.

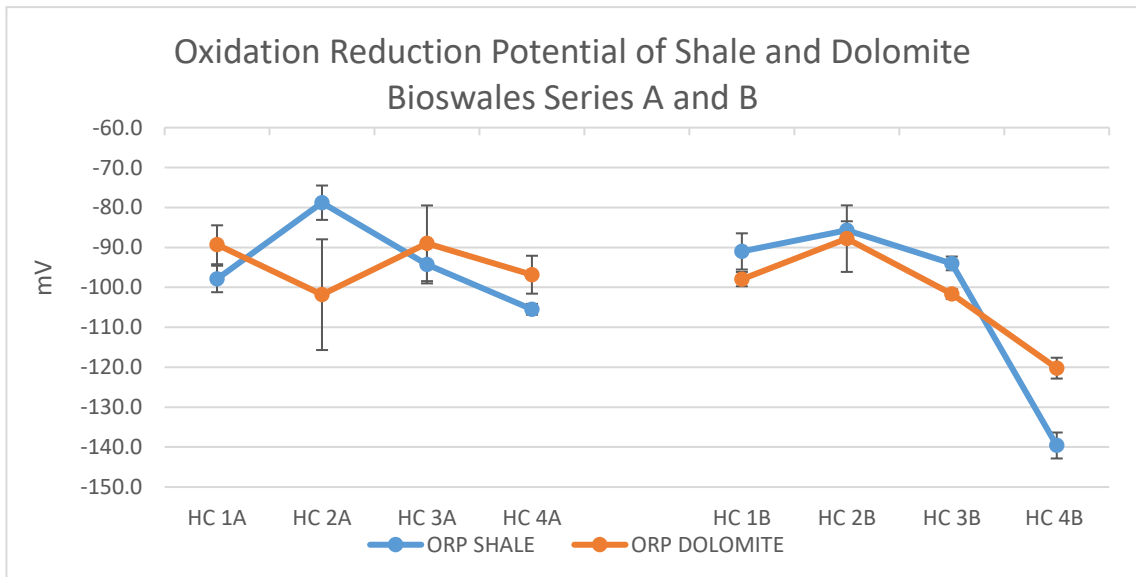


Figure 5.3: Redox potential series A and B. Redox potential each point (n=3), for the dolomite and shale columns. Series A and B have a broken line between them.

5.3 Reactive Phosphate removal efficiency of the mini-bioswales

Both reactive and total phosphate remaining in the effluents for the dolomite and shale mini bioswales was determined (Figures 5.3 A and B). Figure 5.3 A and B shows the reactive phosphate remaining in the effluent in series A and B. Statistical analysis of the data was carried out for the difference between the means of two independent groups using the Mann-Whitney U-test. The null hypothesis was that there is no significant difference between the means ($H_0 = \mu_1 = \mu_2$) when $U\text{-stat} \geq U\text{-crit}$.

**all raw data for chapter 5 is contained in the appendices on page vii-xiv.*

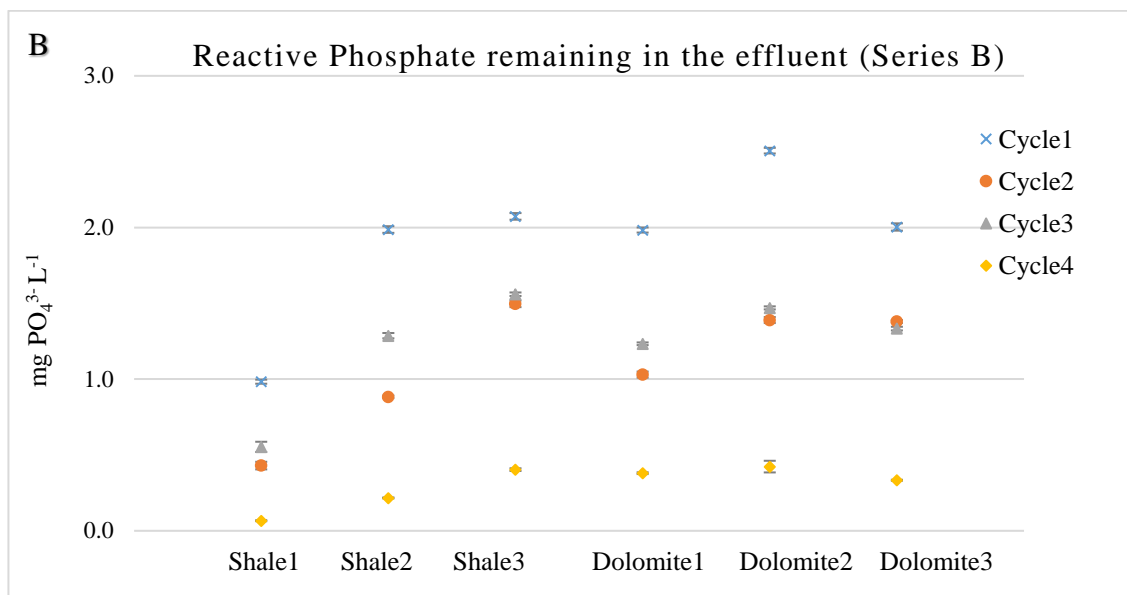
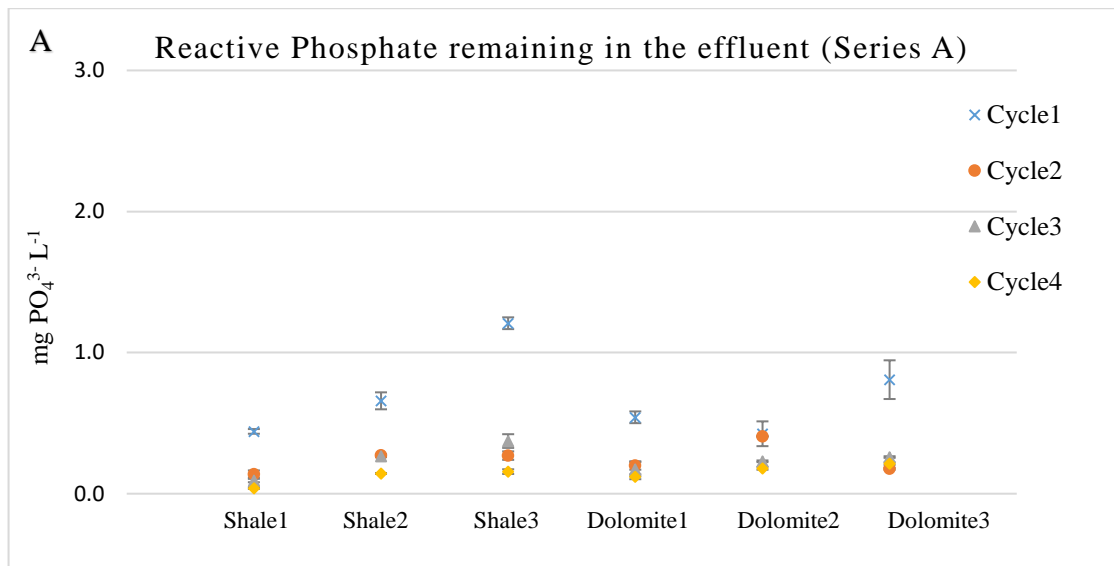


Figure 5.3 A & B: Initial concentration of 20 mg PO₄³⁻ L⁻¹ was passed through each column. Each point on the graph (n=3) signifies remaining reactive phosphate in solution of each individual column. Cycle 1-4 denotes the number of times the effluent had been cycled through the columns. Shale 1-3 & Dolomite 1-3 represent the column number. Error bars represents the standard error across triplicate samples.

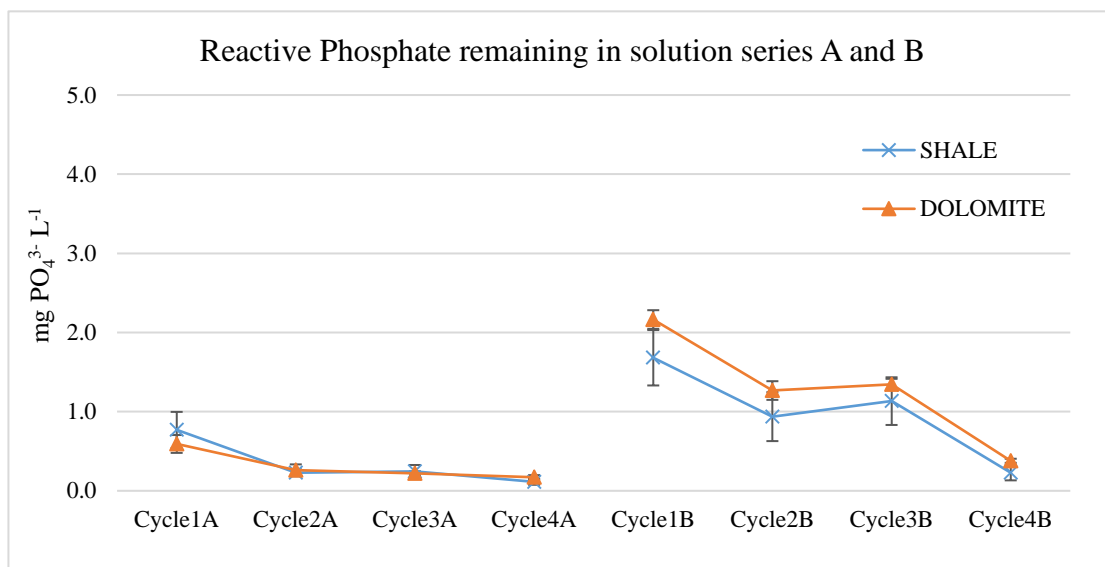


Figure 5.4 Comparison of the mean (n=3 columns) reactive phosphate remaining in the effluent in Series A and Series B. The initial concentration of PO₄³⁻ in the influent was 20 mg PO₄³⁻ L⁻¹. Each point on the graph (n=3) represents the average effluent of phosphate remaining in solution of three columns. Error bars represents the standard error across the three column means.

Table 5.2: Statistical analysis of reactive phosphate series A and B, Mann-Whitney U-test two tailed alpha value of 0.05. The percentage removal of shale and dolomite columns at series A and B ± standard error.

<i>μ comparison</i>	<i>Mann Whitney U test</i>				
	U stat	Ucrit	H ₀	<i>μ</i> columns	% Removal
<i>Shale A, B</i>	18	17	accept	Shale A	99.43 ± 0.59
<i>Dolomite A, B</i>	0	17	reject	Shale B	98.89 ± 1.63
<i>Shale A Dolomite A</i>	18	17	accept	Dolomite A	99.11 ± 0.49
<i>Shale B Dolomite B</i>	22	17	accept	Dolomite B	98.16 ± 0.41

The reduction of phosphate from a 7.5 litre 20 mg PO₄³⁻ l⁻¹ artificial wastewater solution is detailed in figures 5.3 a and b, for series A and B. It was observed from figure 5.3 a and b, that the amount of phosphate remaining in solution decreased with each cycle for both the shale and dolomite columns. In Figure 5.4 each point describes the mean values (n=3) at a specific cycle and series. The phosphate was dramatically reduced in series A from

cycle 1 to 4 for both the shale and dolomite. In the shale columns the initial values of reactive phosphate in the influent was $19.96 \text{ mg PO}_4^{3-} \text{ l}^{-1}$ for was reduced immediately to $0.77 \text{ mg PO}_4^{3-} \text{ l}^{-1}$ after cycle 1 to a final effluent value of $0.11 \text{ mg PO}_4^{3-} \text{ l}^{-1}$ after cycle 4. In the dolomite columns, a similarly dramatic reduction of $0.59 \text{ mg PO}_4^{3-} \text{ l}^{-1}$ after cycle 1 to a final effluent value of $0.17 \text{ mg PO}_4^{3-} \text{ l}^{-1}$ was observed.

Phosphate reduction in series B was slower to begin with for both the shale and dolomite columns. Initial concentrations of $20.67 \text{ mg PO}_4^{3-} \text{ l}^{-1}$ in the shale columns over the cycles 1 to 4 were reduced to 1.68 and finally to $0.23 \text{ mg PO}_4^{3-} \text{ l}^{-1}$. While in the Dolomite columns, reactive phosphate was reduced to 2.16 after just one cycle and finally to $0.38 \text{ mg PO}_4^{3-} \text{ l}^{-1}$ after four cycles (from initial concentration of $20.56 \text{ mg PO}_4^{3-} \text{ l}^{-1}$).

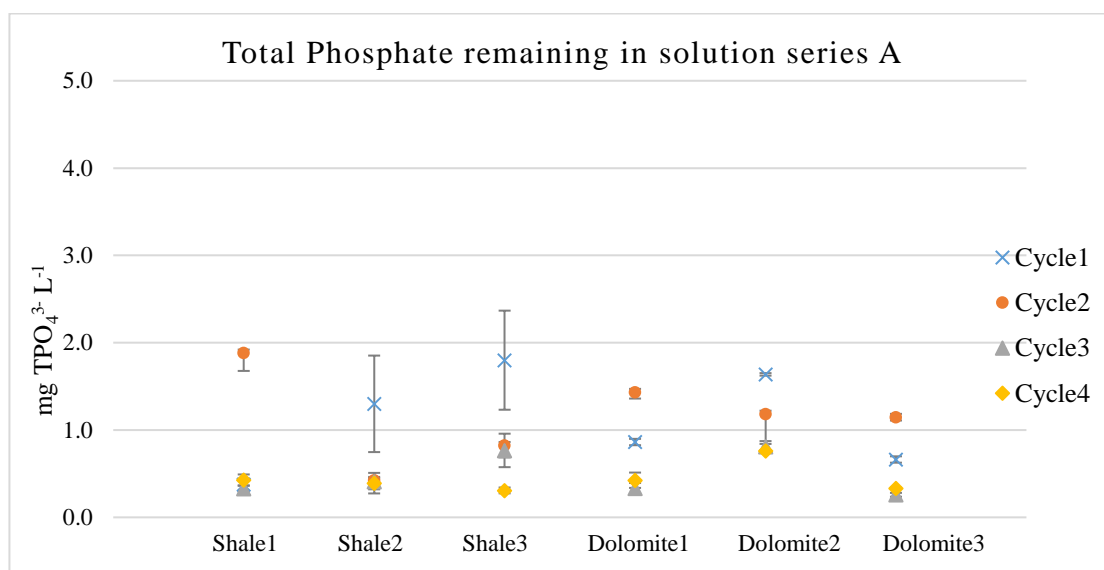
Mann Whitney U-test were applied to determine if there was a significant difference at cycle 4 between the mean final effluent values of the different groups (series, column type). Percentage reductions are given along with standard error values. There was no significant difference found between shale series A and B. The percentage reductions for these two series were $99.43\% \pm 0.59$ and $98.89\% \pm 1.63$, this describes a percentage difference between the means of 0.54%. There was a significant difference found between dolomite series A and B. Percentage reductions for these two series was $99.11\% \pm 0.49$ and $98.16\% \pm 0.41$, a 0.95% difference between the means of the two series.

The variations in the mean final effluent values between the dolomite and shale columns was examined. There was only a significant difference found between Dolomite Series A and B for reactive phosphate.

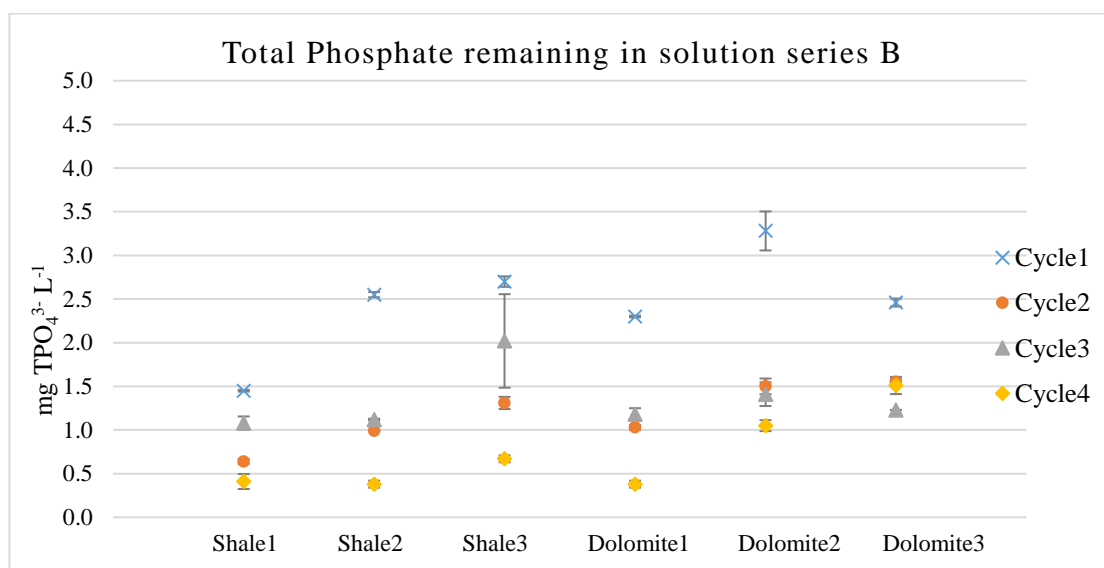
5.4 Total Phosphate removal efficiency of the mini-bioswales

The previous section focused on the reactive phosphate remaining in solution. The focus of this section was to determine the levels of total phosphate. Figures 5.5 a and b display the results of the individual columns after each of the four cycles (cycle 1-4). Figure 5.6 displays the mean of the three columns in series A and B to compare the efficiency of the dolomite and shale columns. Figures 5.7 and 5.8 show the difference between the amount of total and reactive phosphate remaining in solution. Statistical analysis of the data was carried out for the difference between the means of two groups using the Mann-Whitney

U-test. The average percentage removal and standard error (n=3) columns for dolomite and shale series A and B



Figures 5.5 A: Initial concentration of 20 mg PO₄³⁻ L⁻¹ was passed through each column. Each point on the graph (n=3) signifies remaining total phosphate in solution. Cycle 1-4 denotes the number of times the effluent had been cycled through the columns. Shale 1-3 & Dolomite 1-3 represent Shale and Dolomite columns, respectively. Error bars represents the standard error across triplicate samples.



Figures 5.5 B: Initial concentration of 20 mg PO₄³⁻ L⁻¹ was passed through each column. Each point on the graph (n=3) signifies remaining total phosphate in solution. Cycle 1-4 denotes the number of times the effluent had been cycled through the columns. Shale 1-3 & Dolomite 1-3 represent Shale and Dolomite columns, respectively. Error bars represents the standard error across triplicate samples.

The reduction of total phosphate from a 7.5 litre 20 mg l⁻¹ solution is detailed in figures 5.5 A and B, for series A and B. It was observed that the amount of total phosphate remaining in solution decreased with each cycle for both the shale and dolomite columns. The dolomite columns appear to have a slightly higher amount of total phosphate remaining in the effluent after 4 cycles.

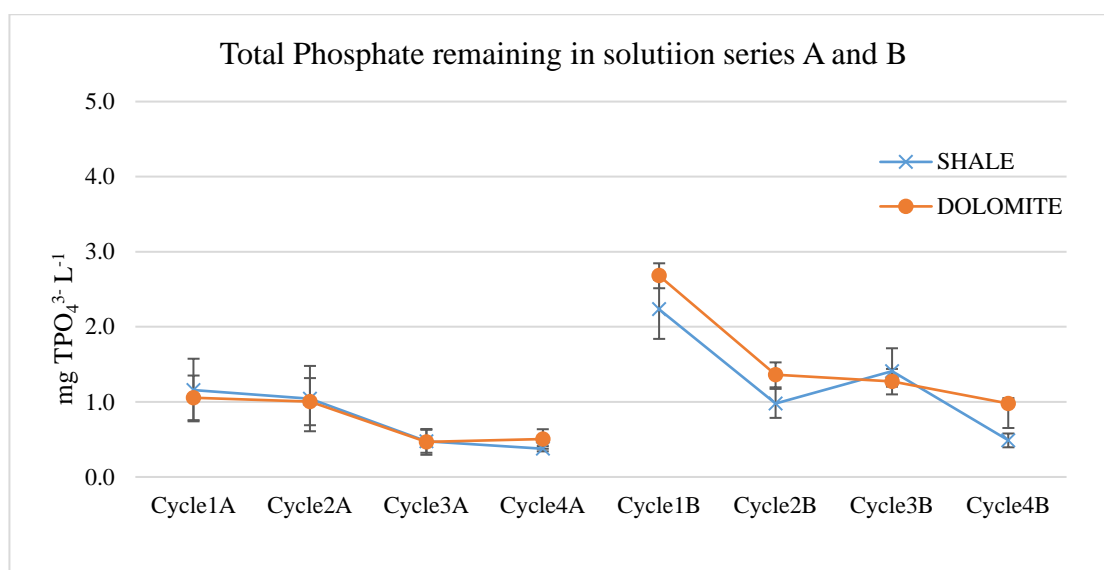


Figure 5.6: Each point on the graph (n=3) signifies the average of three columns. Cycle 1-4 A and B denotes the average remaining Total phosphate in solution. Error bars represents the standard error across the three columns. Initial concentration of 20 mg TP L⁻¹.

In Figure 5.6 each point describes the mean values (n=3) at a specific cycle and series. Total phosphate was dramatically reduced in series A from cycle 1 to 4 for both the shale and dolomite. Initial values of 19.96 mg PO₄³⁻ l⁻¹ for shale was reduced initially to 1.16 mg PO₄³⁻ l⁻¹ to a final effluent value of 0.38 mg PO₄³⁻ l⁻¹ and the dolomite columns seen a similarly reduction of 1.05 mg PO₄³⁻ l⁻¹ to a final effluent value of 0.51 mg PO₄³⁻ l⁻¹ with an initial concentration of 19.16 mg PO₄³⁻ l⁻¹.

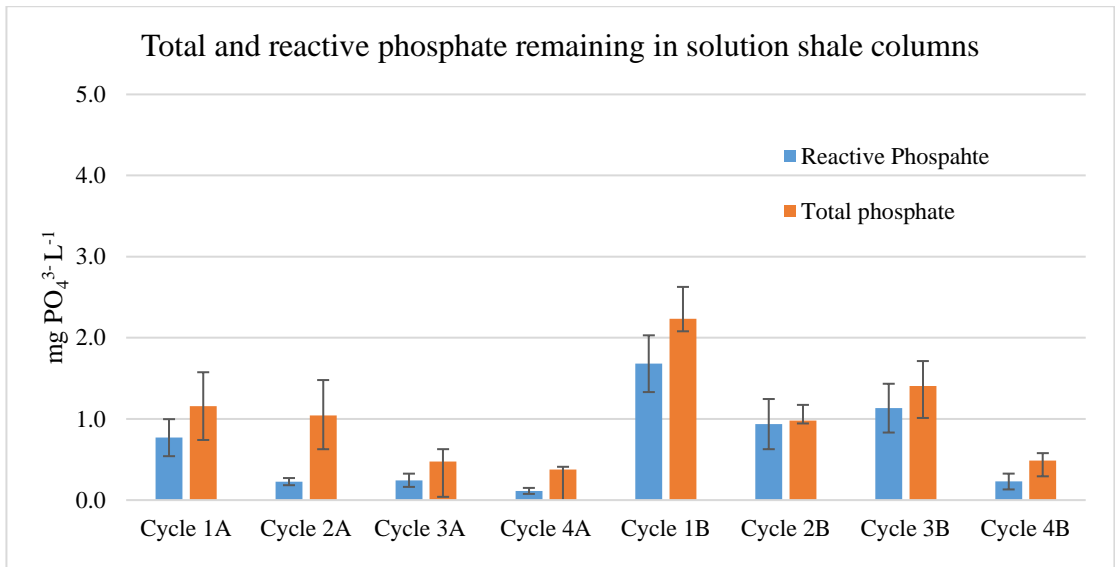


Figure 5.7: Each bar on the graph (n=3) signifies the average of three columns. Blue bars and orange bars denote RP and TP of the shale columns. Cycle 1 A to cycle 4 A represents the recirculation of a 20 mg PO₄³⁻ l⁻¹ through the column four times, Series B denotes the same.

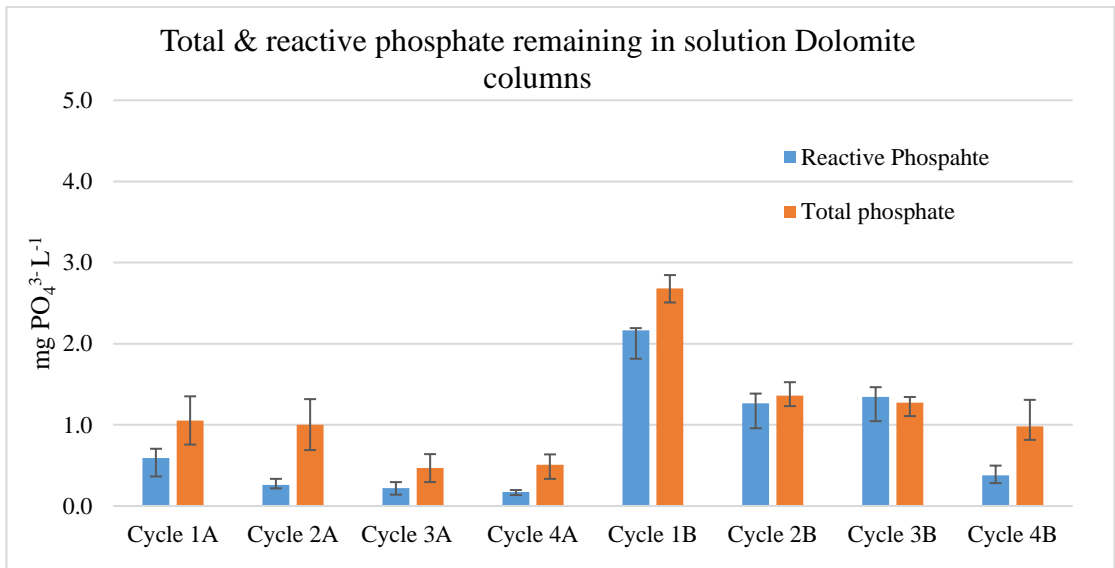


Figure 5.8: Each bar on the graph (n=3) signifies the average of three columns. Blue bars and orange bars denote RP and TP of the dolomite columns. Cycle 1 A to cycle 4 A represents the recirculation of a 20 mg PO₄³⁻ l⁻¹ through the column four times, Series B denotes the same.

Total phosphate reduction in series B, figures 5.7 and 5.8, was like the reactive phosphate, slower to begin with for both the shale and dolomite columns. Initial concentrations of 20.67 mg PO₄³⁻ L⁻¹ in the shale columns over the cycles 1 to 4 were reduced from 2.23 to 0.49 mg TPO₄³⁻ L⁻¹. Dolomite columns from initial concentration of 20.56 mg PO₄³⁻ L⁻¹ over the cycles 1 to 4, were reduced initially to 2.68 mg TPO₄³⁻ L⁻¹ with a final value of 0.98 mg TPO₄³⁻ L⁻¹.

Table 5.3: Statistical analysis of total phosphate series A and B, Mann-Whitney U-test two tailed alpha value of 0.05. The percentage removal of shale and dolomite columns at series A and B ± standard error.

<i>μ comparison</i>	<i>Mann-Whitney U test</i>			<i>μ columns</i>	<i>% Removal</i>
	U stat	Ucrit	H ₀		
<i>Shale A, B</i>	25	17	accept	Shale A	98.12 ±0.30
<i>Dolomite A, B</i>	18	17	accept	Shale B	97.65 ±0.77
<i>Shale A, Dolomite A</i>	24	17	accept	Dolomite A	97.36 ±1.17
<i>Shale B, Dolomite B</i>	17	17	reject	Dolomite B	95.23 ±2.76

Total phosphate final effluent values were statically analysed using Mann Whitney U-tests to determine if there was a significant difference at cycle 4 between the mean final effluent values of the different groups (series A - B, column type dolomite or shale). Percentage reductions are given along with standard error values. No significant difference was found between shale series A and B, percentage reductions for these two series were 98.12% ± 0.30 and 97.65% ±0.77, and this expresses a percentage difference between the means of 0.47%. No significant difference was established between dolomite series A and B, percentage decreases for these two series was 97.36% ± 1.17 and 95.23% ± 2.76, this is a percentage difference between the means of 2.13%.

Variations in the mean final effluent values between the dolomite and shale columns was examined. While there was a no significant difference found between the mean of series A dolomite and shale columns, there was a significant difference found between shale and dolomite columns series B. The percentage difference between the two being 2.42%.

5.5 Results of ammonium and nitrate reductions in the mini bioswales

The fate of the ammonium introduced into the mini-bioswale was determined. The influent was an artificial nutrient rich solution containing phosphate ($20 \text{ mg PO}_4^{3-} \text{ L}^{-1}$) and ammonium ($40 \text{ mg NH}_4^+ \text{ L}^{-1}$). Ammonium and nitrate concentrations were monitored to determine the capacity of the bioswales to remove these nutrients from the introduced wastewater.

The concentration of ammonium remaining in solution during series A and B may be seen in Figures 5.9 A and Figure 5.9 B, these figures shows the results of the individual columns after each cycle (cycle 1 to 4). Figure 5.10 shows the mean ammonium concentrations of all three columns in series A and B. Figure 5.11 shows the mean nitrate concentrations of all three columns in series A and B Figures 5,12 and 5.13 display the correlation between the amount of ammonium and nitrate remaining in solution. Statistical analysis of the ammonium data was carried out for the difference between the means of two groups using the Mann-Whitney U-test. The average percentage removal (using the influent concentration as a baseline) and standard error (n=3) columns for dolomite and shale series A and B were determined.

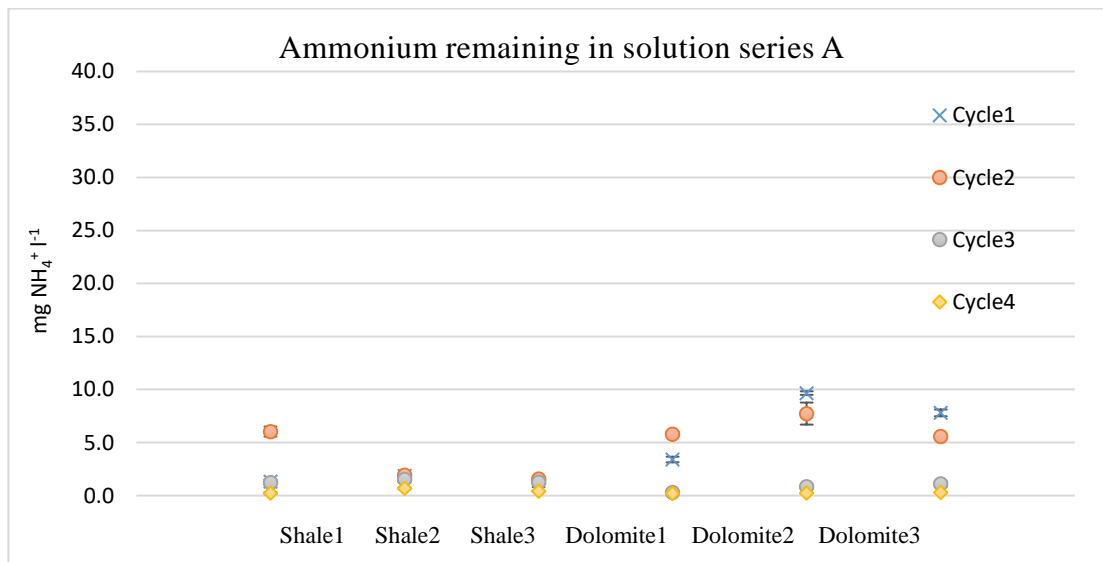


Figure 5.9 A: Concentration of ammonium remaining in the effluent after each cycle in individual columns (n=3). Error bars represents the standard error across triplicate samples. The initial concentration in the influent during the first cycle was $40 \text{ mg NH}_4^+ \text{ L}^{-1}$.

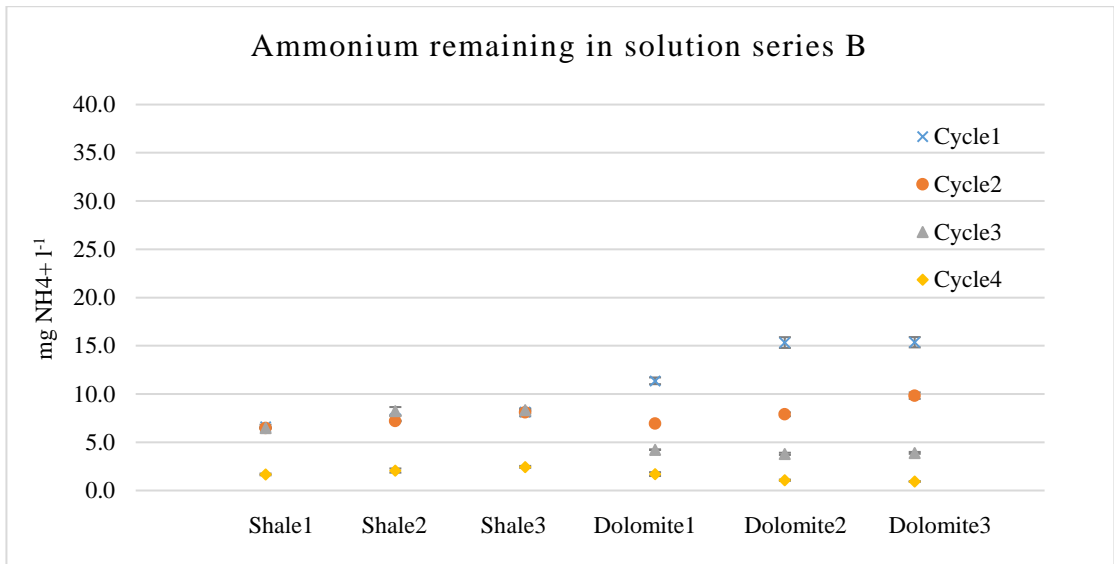


Figure 5.9 B: Concentration of ammonium remaining in the effluent after each cycle in individual columns (n=3). Error bars represents the standard error across triplicate samples. The initial concentration in the influent during the first cycle was 40 mg NH₄⁺ L⁻¹.

Variations regarding the mean final effluent values between the dolomite and shale columns were examined. The difference found between the mean values from series A and B in both the dolomite and shale columns. Dolomite series A removal efficiency was 0.49% greater than shale series A. The same trend was noted in series B where dolomite columns removed 2.06% more than shale columns. Correspondingly it was observed that the ability of both sets of columns to reduce ammonium was reduced from series A to B.

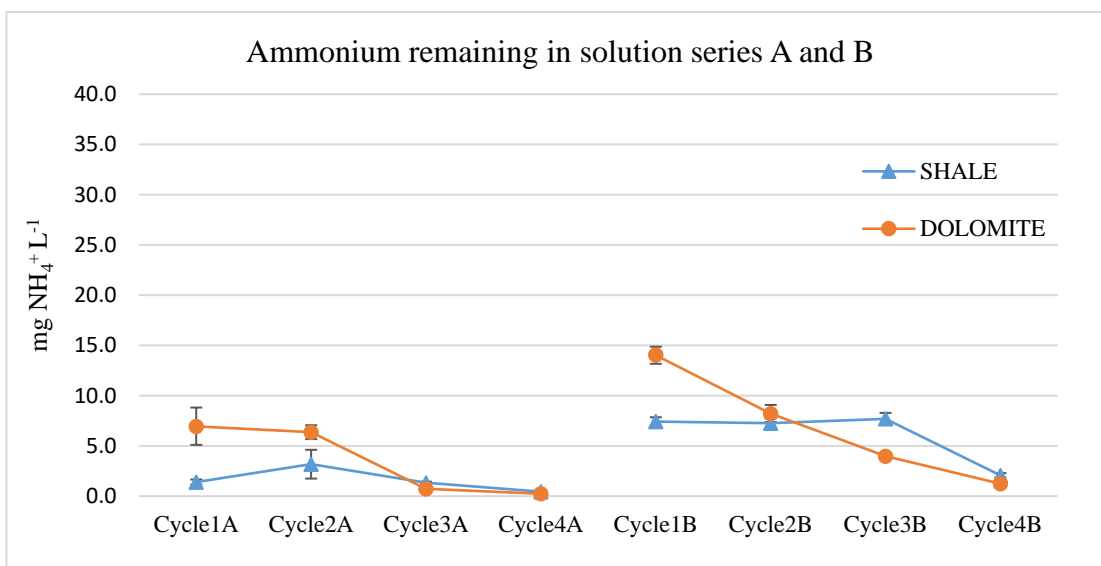


Figure 5.10: The mean ammonium concentrations remaining in the effluent after each cycle (n=3). Error bars represents the standard error across triplicate samples. The initial concentration in the influent during the first cycle was 40 mg NH₄⁺ L⁻¹.

Ammonium final effluent values were statically analysed using Mann Whitney U-tests to determine if there was a significant difference at cycle 4 between the mean final effluent values of the different groups (series, column type). Percentage reductions are given along with standard error values. There was a significant difference was found between shale series A and B, percentage reductions for these two series were 98.93% ± 0.56 and 94.80% ± 0.99. This represents a percentage difference between the means of 4.13%.

Table 5.4: Statistical analysis of ammonium series A and B, Mann-Whitney U-test two tailed alpha value of 0.05. The percentage removal of shale and dolomite columns at series A and B ± standard error.

μ comparison	Mann-Whitney U test			Removal percentages	
	U stat	U crit	H ₀	μ columns	% Removal
Shale A, B	13.5	17	reject	Shale A	98.93±0.56
Dolomite A, B	7	17	reject	Shale B	94.80±0.99
Shale A, Dolomite A	0	17	reject	Dolomite A	99.42±0.11
Shale B Dolomite B	0	17	reject	Dolomite B	96.86±1.04

There was a significant difference found between the means of dolomite series A and B. Percentage removal for these two series was $99.42\% \pm 0.11$ and $96.86\% \pm 1.04$, this depicts a percentage difference between the means of 2.56%. Over time the system should improve in the removal of ammonia as discussed in the section on ICW. The bacteria in the system responsible for nitrification/denitrification need time to mature in order to maintain ammonia conversion and reduction. Assimilation by plants will also play a role in the reduction of ammonia in any future system.

The levels of nitrate were monitored to better understand the fate of ammonium entering the bioswale systems. Nitrate levels series A for the dolomite columns fluctuated, with no clear trend evident figure 5.11. The nitrate levels for series A, for both the dolomite and shale columns, were higher than series B. This may have been a result of the residual Nitrate levels in the system prior to the addition of the artificial wastewater. Nitrate levels in both systems was reduced over the cycles. Dolomite nitrate levels decreased from a high point of 19.78 to $7.36 \text{ mg NO}_3^- \text{ L}^{-1}$. Concentrations of nitrate remaining in solution from the shale columns were lower 12.67 to $2.20 \text{ NO}_3^- \text{ L}^{-1}$.

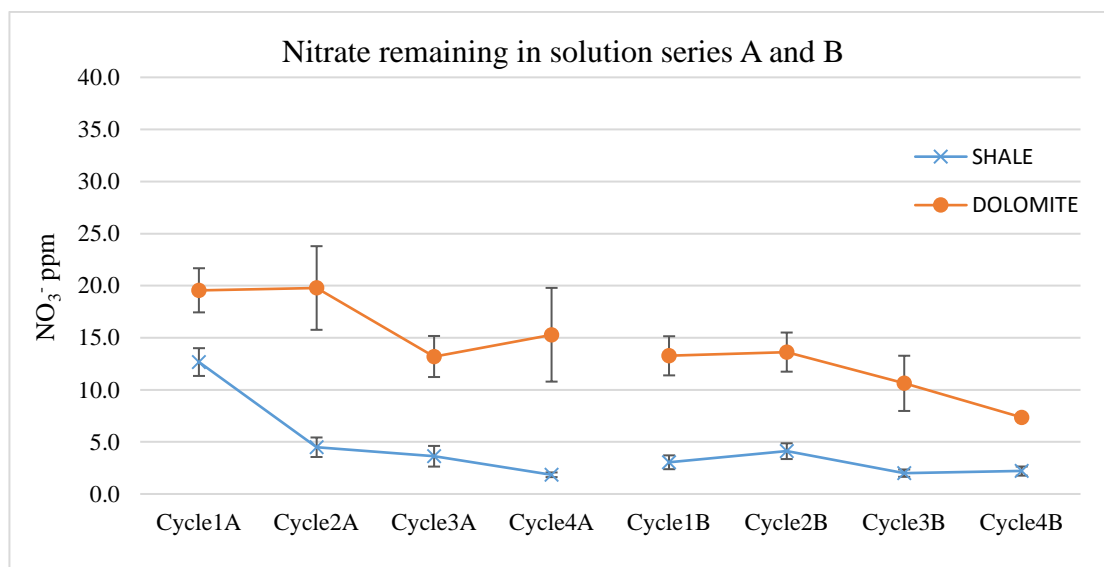


Figure 5.11: Each point on the graph (n=3) signifies the average of three columns. (cycles 1-4) denotes the average remaining NO_3^- in solution. Each point is the average of three columns. Error bars represents the standard error across the three columns. Series A represents concentration of $40 \text{ mg NO}_3^- \text{ L}^{-1}$ recirculated through the column four times, Series B denotes the same.

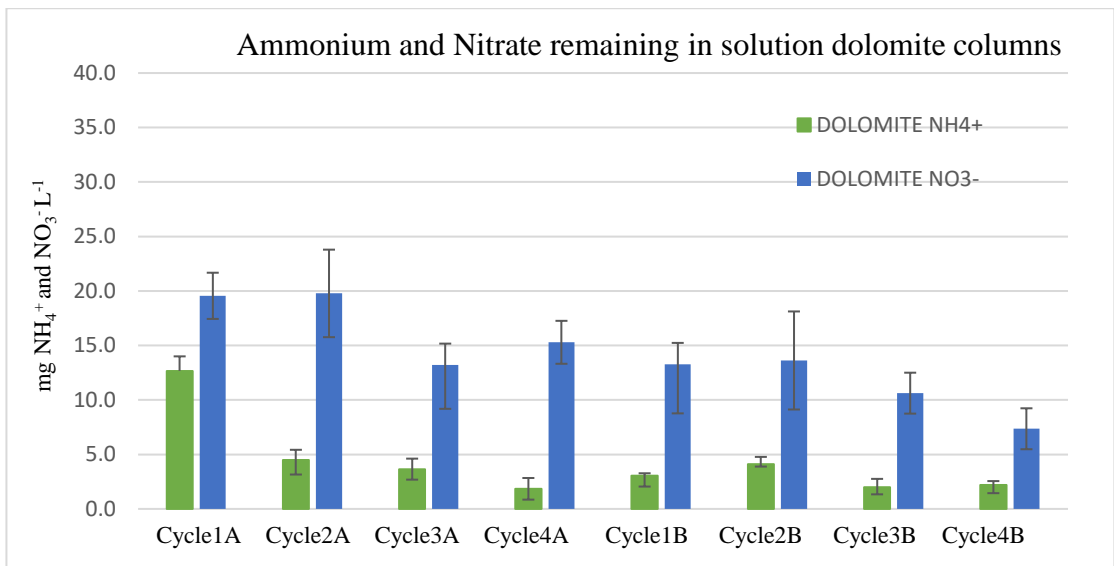


Figure 5.12: Concentration of nitrate and ammonium detected in the effluent after each cycle in individual columns (n=3). Error bars represents the standard error across triplicate samples.

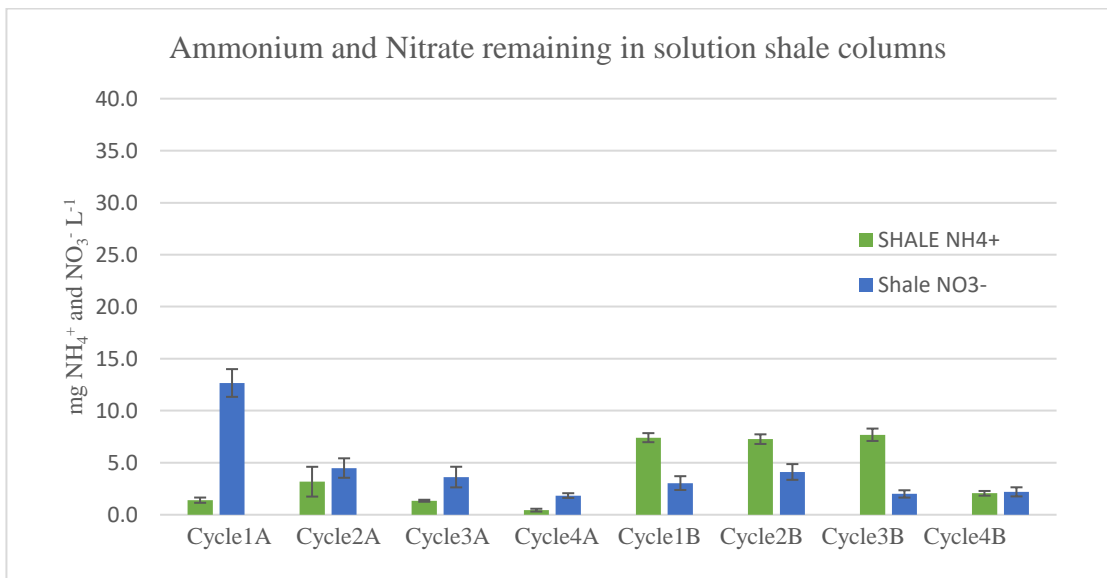


Figure 5.13: Concentration of nitrate and ammonium detected in the effluent after each cycle in individual columns (n=3). Error bars represents the standard error across triplicate samples

5.6 Discussion

The objective of this study was to provide insight into the nutrient reduction capacity of two different novel bioswale (each type performed in triplicate) systems and determine which of these systems should be investigated further in a field scale trial. The primary focus of this chapter was to monitor total and reactive phosphate removal from the small scale bioswales. Two different novel bioswale systems were set up in triplicate, one set with a dolomite stone layer and the other set with a shale stone layer. In this initial trial P and ammonium reductions were monitored throughout, to observe if nitrification or denitrification was occurring. As discussed previously ammonium reduction was considered a secondary objective of the study. The previous feasibility study on a similar small scale bioswale had found substantial reductions of ammonium and nitrate, (Merriman, Arnabat, Germaine & Dowling unpublished report 2015). It was demonstrated that a lower flow rate of 5 ml min^{-1} was noticeably better than a flow rate of 10 ml min^{-1} for phosphate removal using shale and dolomite. This makes sense as decreased flow rate means increased contact time with the material. In the previous chapter, through application of Langmuir sorption isotherms, the experimental amount of phosphate removed from solution was found to be much better in dolomite 0.578 mg g^{-1} than in shale 0.143 mg g^{-1} . Physical conditions of pH, conductivity, salinity and redox potential were monitored. These conditions were observed throughout the experiment as physical conditions, may affect the quality of the effluent while other parameters may affect the sorption/precipitation of nutrients and microbial assimilation of nutrients. The measurements of conductivity and salinity are related. Conductivity measures the concentration of dissolved ions in the water or dissolved salt content of the water in $\mu\text{S/cm}$. The conductivity in both bioswale systems saw a gradual rise and decline, a possible explanation would be the loss of ions associated the nitrification process. Final effluent values of conductivity in the shale and dolomite systems were 0.76 mS ($761 \mu\text{S}$) and 1.00 mS ($1001 \mu\text{S}$) respectively. These values when converted to parts per thousand (ppt) salinity are similar (0.38 ppt and 0.50 ppt), when compared to typical river water values of 0.50 ppt or less, (EPA 2018).

However, values only slightly higher would have negative effects on aquatic life. Adverse biological effects will occur to macroinvertebrates, river plants and micro-algae should salinity rise to 1.00 ppt (1000 mg l^{-1}) (Qomariyah et al., 2017). High salinity concentration in effluents can affect the water treatment process. Wu et al (2008),

conducted a pilot scale study of constructed mangrove wetland systems for the treatment of domestic wastewater and concluded that N removal was negatively affected by high salinity as high salinity affects bacteria associated with nitrification. In the current study dissociated ions from the materials in the system should not negatively affect microbial activity thereby allowing nitrification to occur and effluent of such low salinity could also be discharged to surface water as higher salinity levels would affect aquatic life.

Any treatment system discharging effluent into natural water bodies must be monitored as extremes of pH will negatively affect aquatic life. Fish populations will decrease at pHs below pH 5. Problems will occur in the female fish reproductive cycle and dissociated Al^{3+} from river muds will cause increase in mucus production causing clogging of gills leading to asphyxiation, (Lenntech.com, 2017). Alkaline conditions above pH 9.6, impair disposal of metabolic waste and damages the outer surface of fish causing death (Lenntech.com, 2017). The effluent draining from the bioswale in the current study had pH values between 7.8 and 8.8, and so are predicted to have little or no effect on fish physiology

The effluent values for pH increased slightly over the duration of the experiment, a steady rise of pH was observed, and any future experiments would have to monitor the pH values. Acidic and alkaline conditions can be harmful to the aquatic life of receiving water bodies, depending on the pH buffering capacity of the natural water. Therefore, in any long-term follow-on studies pH must be monitored. Another reason for monitoring the pH is the effect it has on nutrient sorption. As discussed in chapter 4 pH values less than 7 would favor sorption to shale due to the presence of the cations iron and aluminum whereas pH values greater than 7 positively affect the sorption of phosphate to dolomite due to the high presence of calcium ions. The pH of farmyard dirty water varies from season to season but ranges between 6.4 and 7.4 (Martínez-Suller, 2010).

P is considered a macronutrient and will only be available to plants in water soluble forms. The organic form requires mineralization through phosphatase enzymes to become available. Properties of the soil that effect phosphate sorption are cation exchange capacity, soil texture, pH and the percentage organic matter. Soils that have a high clay and organic matter content have a high CEC. One of the main cations that binds phosphate is calcium. The soil used in the mini bioswales contains a high percentage of calcium and is considered a calcareous soil. The CEC value of $14 \text{ meq } 100\text{g}^{-1}$ is considered typical value for a loam soil which are generally between 5 and $15 \text{ meq } 100\text{g}^{-1}$

¹. Increases in pH during the experiment will positively affect the CEC of the soil. This increases cation retention and therefore will positively affect phosphate sorption.

The Langmuir sorption experiments in chapter 4 concluded that phosphate had a much greater affinity for dolomite than shale. Based on that, the expected outcome from this experiment was that the dolomite columns would perform better in the removal of phosphate from solution than the shale columns. This was not the case as there was a significant difference found between total phosphate remaining in solution between the shale and dolomite columns series B. The shale columns resulted in lower total phosphate in the effluent than the dolomite columns. An explanation for this may be that conditions were more favourable to sorption of phosphate in the shale columns, as under negative redox conditions phosphate sorption to Al becomes more favourable (Dunne and Reddy 2005) whereas negative redox conditions of $> -100\text{mV}$ are unfavorable conditions for phosphate sorption to Fe (Braskerud et al., 2005). In chapter 4 the shale was found to have high concentrations Fe and Al cations in their oxide forms. There were no significant differences between the reactive phosphate for the shale columns. There was a significant difference found between the dolomite columns from series A to series B, this may indicate that the system is losing the ability to retain phosphate, although the percentage difference between the two was slightly under one percent.

The influent concentrations of P entering the bioswales from the current study was $6.525 \text{ mg P l}^{-1}$ ($20 \text{ mg PO}_4^{3-} \text{ l}^{-1}$). This value was used as it compares well with levels entering ICWs. Twelve ICW's were constructed in the Anne valley watershed, Waterford Ireland to reduce pollution from farmyards into the Annestown watercourse (Harrington et al., 2013). Three of these had similar P levels to that in this study but slightly higher concentrations of P influent and similar reductions with regards to the effluent. ICWs 6, 9 and 11 had influent values of P of 10.5, 11.0 and 12.8 mg P l^{-1} respectively, with treated effluent values of 0.1, 0.5 and 1 mg P l^{-1} . This represents percentage reductions of 99.05%, 95.45 and 92.19% and compared well with the mini-bioswales in our study which had percentage reductions 97.65% for shale columns and 95.23% for dolomite columns.

The influent initial concentration of 20 mg P L^{-1} was reduced to $0.159 \text{ mg P L}^{-1}$ for dolomite and $0.320 \text{ mg P L}^{-1}$ for shale for series B. These values are much lower than the effluent values allowed for treated urban water for the population equivalent (p.e). SI 419/1994 MAC limits TP levels to 2mg/l (10000-100000p.e) and 1mg/l P (more than

100000 p.e) in treated urban wastewater discharges. The values achieved compare favorably with the MAC limits for surface waters for P which are set in S.I 2014. These limits are 0.5 mg RP l⁻¹ (for high quality rivers) and 0.7 mg RP l⁻¹ for good status rivers. Meaning discharges from either mini-bioswale system would not negatively affect even high-status rivers. Further investigation is required through a long-term study. However, the system has demonstrated the potential to remove phosphate from dirty water.

Ammonium removal was also monitored in the two mini-bioswale systems. The phenate method measures all forms of ammonia in the ionised form. The study found substantial reductions in ammonia. Ammonia percentage reductions from initial values of 40 mg NH₄⁺ l⁻¹ were considerable for both shale and dolomite systems. Mean removal rates for shale series b were 94.8% and 96.96% for dolomite series b. The removal rates were high, however, there were significant differences found between shale series a and b and the dolomite series a and b with a decline in the reduction of ammonium from series a to b. This may indicate a steady decline in ammonium reduction over time. Other treatment systems such as ICWs have plants which play a vital role in the nitrification/denitrification of ammonia. Influent of ammonia from farms into the 12 ICWs located at Annetstown watercourse with similar ammonia levels had effluent values that were better than the ones achieved in our current study (Harrington et al., 2013). In the Annetstown system ICWs 6, 9 and 11 had ammonia levels of 43-47 mg NH₄⁺ l⁻¹ in the influent. This decreased to 0.3-0.6 mg NH₄⁺ l⁻¹, representing reductions of 98-99.3% (Scholz et al., 2007). These ICWs are well matured both for aquatic plants and microorganisms that use N, unlike the current study in which plants have not been used and micro-organisms have only had a short period of time to establish themselves.

Gersberg et al., (1986) investigated the role of higher aquatic plants *Scirpus validus* (bulrush), *Phragmites communis* (common reed) and *Typha latifolia* (cattail) in the reduction of N from artificial wetlands from primary municipal wastewaters. Influent values in these three wetlands had values of 27.7 mg NH₃ l⁻¹ (29.3 NH₄⁺). The Bulrush wetlands had effluent values of 1.4 mg NH₃ l⁻¹ (1.5 NH₄⁺). Wetlands with common reeds had reductions of 5.3 mg NH₃ l⁻¹ (5.6 NH₄⁺) and the wetlands with cattail aquatic plants had effluent values of 17.7 mg NH₃ l⁻¹ (18.7 NH₄⁺). The control wetland (contained no aquatic plants) had effluent values of 22.1 mg NH₃ l⁻¹ (23.4 NH₄⁺). The mini-bioswales, like the control in the above-mentioned study, had no plants but unlike the above mentioned study there was a good rate of ammonia reduction. This reduction may be

down to the denitrification of ammonium to nitrate. Ammonia reduction occurs through denitrification when a system has a negative redox potential.

In the case of ammonium reduction there was a significant difference between the dolomite system and the shale system, with the dolomite systems showing a higher reduction than the shale system. There is currently no similar systems comparing the ammonia reduction of dolomite and shale.

Redox potential gives an indication of whether a system is anaerobic or aerobic. Negative ORP usually means anaerobic conditions while positive ORP usually means an aerobic conditions. Song et al., (2003) conducted a small-scale experiment to see the effects of low level of ORP on a denitrification by the denitrifying bacteria *Ochrobactrum anthropic*. They found that as the ORP decreased from -70 to -225 mV, the nitrate removal efficiency increased by approximately 300% and the time taken for the reduction to occur also decreased significantly. The redox potential of both mini-bioswale systems steadily became more negative during the experiment and the ammonium and nitrate was reduced progressively, possible due to increase microbial activity.

5.7 Conclusions

Based on results from chapter 3 and 4, it was anticipated that the bioswale columns in this experiment containing the dolomite layer would out-perform the shale columns in the removal of phosphate. Total phosphate removal in the shale columns was significantly better than the dolomite columns although the percentage difference was small. The redox conditions may have enhanced the removal of P by the shale columns, while the TP removal in the dolomite columns could be associated with sorption and a small portion of the P removal as a precipitate. There was no significant difference found between the dolomite and shale columns series b for reactive phosphate. However, there was a significant difference found between the shale and dolomite bioswales series b for total phosphate removal meaning, under conditions negative redox conditions it would be better to use shale as the choke layer.

The other nutrient introduced into the bioswale systems was ammonium. For both systems the removal rates of ammonium were above 94.0%, with the dolomite bioswale systems having a higher percentage removal rate than the shale systems. The negative redox conditions favors denitrification. There was a steady decline in both nitrate and ammonium. However, for both systems there was found to be a significant difference between series a and b. This may indicate that the bioswale systems ability to convert ammonia to nitrous gases in the short term would decline. However, over time as the system matures and denitrifying bacteria increase in the system ammonia reduction may increase. Any future field scale bioswale system will have wetland plants, and this as discussed during the literature review should increase N removal through plant assimilation. Discharges of ammonium and nitrate from either system as it stands would not negatively affect aquatic environments.

Chapter 6

Overall Discussion

The project's main objective was to examine suitable cheap and locally available materials that could be used in a novel bioswale system to reduce the impact of nutrients in FYDW to aquatic bodies. The main nutrient of interest was phosphate as during a feasibility study undertaken on site at the Institute of Technology Carlow of several pollutants monitored in mini-bioswale systems phosphate was not reduced sufficiently (Merriman, Arnabat, Germaine & Dowling unpublished report 2015).

The project was divided into three sections. The first section examined several materials that according to the literature were shown to be good materials for phosphate reduction in wastewater, zeolite (Ju et al., 2014), shale (Coulibaly et al., 2015), dolomite (Yuan et al., (2015) and Prochaska & Zouboulis, (2006)), tire crumb (Hood et al., 2013), and limestone (Price et al., 2010). Soil has good sorption properties depending on content of calcium, iron and aluminum, (Jordan et al., 2005 and Daly et al., 2015). Dissolved P forms are removed from waters through chemical precipitation forming Al, Fe or Ca oxides (Spivakov, Maryutina and Muntau, 1999).

The screening process was a qualitative approach and three of these materials showed good removal of phosphate from water. Shale, soil and dolomite were tested. Shale and dolomite were examined further to determine the difference in reduction at different flow rates of 5 and 10 ml min⁻¹. The lower flow rate was found to be much better and concurred with the literature (Ballantine and Tanner, 2010) and (Gao and Xie, 2014) as increased contact time between the substrate and phosphate in solution increased the sorption onto the material.

In chapter four a more quantitative approach was required to find the amount of phosphate (mg per kg) shale/soil/dolomite could sorb before saturation occurred. This was achieved through Langmuir sorption isotherms. The amount of phosphate in mg per kg that each material could hold was as follows; shale 143, soil 545 and dolomite 587. The full scale bioswale will cover an area of 20 by 30 meters, with a soil layer 25cm deep and a choke layer 20cm deep. This suggests that the choke layer material has the potential to hold over 150m³ (150000 L) of material and the soil layer nearly 190m³ (190000 L) of soil. Given that each kg of soil can retain 545mg of phosphate with a soil density of 1.8 kg L⁻¹, this means the soil layer alone would be capable of holding 186.39 kg of phosphate. Using the mean concentrations of 44mg PO₄³⁻ L⁻¹, in FYDW (Carroll et al., 2005) this means that the soil layer alone could treat 4,236,136 litres of FYDW. Shale has a higher

density of 2.6 kg L^{-1} , it has a smaller sorption ability than soil for phosphate and will take up a lesser volume than the soil. This suggests the shale layer would be capable of holding 60.06 kg of phosphate. Using the mean concentrations of $44 \text{ mg PO}_4^{3-} \text{ L}^{-1}$ in FYDW this means that the shale layer can treat up to 1,365,000 litres of FYDW. The dolomite has a sorption ability of 587 mg of phosphate per kg. The density of the dolomite was 2.75 kg L^{-1} , it has a greater affinity for phosphate than both the soil and shale based on the mean concentrations of $44 \text{ mg PO}_4^{3-} \text{ L}^{-1}$ in FYDW, the dolomite in the full scale bioswale should hold 242.14 kg of phosphate. At mean concentrations of $44 \text{ mg PO}_4^{3-} \text{ L}^{-1}$ in FYDW, the dolomite layer could treat 5,503,125 litres of FYDW before becoming saturated.

In chapter five, lab-scale bioswale systems were constructed. Three of these mini-bioswales had a dolomite choke layer and three had a shale layer. Artificial wastewater containing phosphate and ammonia was passed through both types of bioswales under the same physical conditions.

The final effluent values for phosphate in both systems compared well with both ICW's final effluent values, (Carroll et al., 2005) and MAC limit values in good ecological class rivers. Both the shale and dolomite columns experienced high reductions in reactive phosphate. There was a significant difference between the shale and dolomite columns for total phosphate in favor of the shale columns. Even though the dolomite columns were expected to achieve better removal of phosphate, as this was the case in the sorption studies. This was not the case and it was likely due to negative redox conditions favoring the shale columns. Considering this, any future bioswale should incorporate both the shale and dolomite stone layers, with the dolomite above the submerged level in the bioswale and the shale layer below the submerged layer. The combination of all three layers would give the bioswale the capacity to treat approximately 11.1 million liters of FYDW at an average concentration of $44 \text{ mg PO}_4^{3-} \text{ L}^{-1}$. This conservative estimate does not consider other mechanisms of phosphate removal, assimilation by plants, fungi and bacteria.

In both bioswale systems ammonium was introduced at a concentration of 40 mg l^{-1} . The shale bioswales had a percentage reduction of $98.93\% \pm 0.56$ for series A and $94.80\% \pm 0.99$ for series B, even though the removal rate was high there was a significant difference between series A and B suggesting that the bioswales effectiveness would

decline after each application of nutrient rich water. The dolomite bioswales had removal rate that was higher of 99.42% \pm 0.11 for series A and 96.86% \pm 1.04 for series B. There was also a significant difference between dolomite columns series A and B suggesting that the bioswales effectiveness would decline after each application of nutrient rich water. It seems that in the short term at least, both bioswale systems would decrease in their effectiveness of ammonium reduction. In any future bioswale system wetland plants such as *Scirpus validus* (bulrush), *Phragmites communis* (common reed) and *Typha latifolia* (cattail) would be introduced to increase both N removal and P assimilation (Gersberg et al., 1986). The nature of such a system should see ammonia reduction through nitrification/denitrification bacteria that should improve as the system matures.

In a large-scale novel bioswale it may be best to apply the FYDW in short periods of time but often as this would allow good contact time between the materials in the bioswale and the nutrients in the FYDW, for example 10 minutes every two hours.

Wetland plants will play an important role in the removal of P and N compounds (Gersberg et al., 1986). Maintenance of the bioswale system should include trimming and pruning of wetland plants. Removal of biomass will allow wetland plants to regrow causing assimilation of P and N (Kim and Geary, 2001).

Prior to the construction of the full field scale bioswale considerations such as the water table should be undertaken. Ideally the water table will be well below the storage pipes at the bottom of the bioswale. The level of the bioswale could be raised to overcome any potential problems of a high-water table. Rain gauges should be set up onsite as the rainfall will dilute the FYDW entering the bioswale and this dilution needs to be considered when analyzing the effluent. In periods of extremely heavy rainfall it may be best to turn off the system, the system could not be protected from the rainfall as a canopy of the size required would not be workable. The substrate is the only parts of the bioswale that would need replacement once the system become saturated with P. The pipework, impermeable barrier and wetland plants could all be reused. The substrate could be considered as a potential future source of P with its high calcium content it would also act as a soil amendment in acidic soils (Taha Jawad et al., 2014). The amount of phosphate accumulated in the system through sorption/precipitation reactions could be increased by increasing the overall depth of both the soil and dolomite choke layer.

Only a full field scale bioswale trial monitored over an extended period will determine whether such a system would be financially viable. Should the system prove a success in the future, applications for grants for farmers to have such systems built may be in the form of a REPS grant. Although such systems are not specifically covered improvement of the environment and water quality are included as the objective of REPS in the use of agricultural land.

Chapter 7

Concluding remarks and future research

The primary aim of the project to determine materials best suited in a novel bioswale system to remove P from FYWD. The most important finding in the project was the sorption isotherm values. These gave important information with regards to the affinity of phosphate for the materials soil shale and dolomite and allowed experimental values for how much phosphate a material can sorb before saturation occurs.

The first objective of the project was to find a suitable material that would both remove phosphate and act as a choke layer in any future bioswale and to examine the materials under certain flow rates of several materials dolomite and shale were found to be suitable. The next section examined the sorption ability of the choke layer materials, dolomite and shale to remove P from solution using Langmuir sorption isotherms with both materials exhibiting good sorption properties for P. In the final section of the project bioswale systems were constructed and it was found that both systems had good removal rates of P from solution.

The bioswale system containing the dolomite choke layer should be the one used in the full-scale trial. Once the bioswale has been constructed the monitoring of the working system should be carried over a period of a minimum of 12 months. Parameters monitored should include reactive phosphate, ammonia, nitrate, COD and total faecal coliforms. Physical analysis should include pH, dissolved oxygen and conductivity.

Removal of solubilized phosphates from artificial wastewater has been studied by Usharani et al.,(2013). A consortium of heterotrophic bacteria had removal rates between 63.4% and 92.5% soluble phosphate were converted to insoluble polyphosphates forms by the heterotrophic bacteria. Pretreatment of the FYDW with a consortia to reduce phosphate in the header tank prior to discharge to the bioswale should be considered in any future research.

Pesticides and antibiotics, (Robertson and MacCormack, 1977 & Hooda et al., 2000) are two pollutants found in FYDW. The monitoring of these pollutants in FYDW before entering the bioswale and in the effluent from the bioswale would be a valuable inclusion in any future work.

8.0

References

Amery, F. and O.F. Schoumans, 2014. Agricultural P legislation in Europe. Merelbeke, ILVO, 45 p.[online] Available at: http://pure.ilvo.vlaanderen.be/portal/files/2640562/P_legislation_Europe.pdf [Accessed 29 Jan. 2018].

Artiola, J., Pepper, I. and Brusseau, M. (2007). *Environmental monitoring and characterization*. Amsterdam: Elsevier Academic Press, pp. 242-243.

Ballantine, D. and Tanner, C. (2010). Substrate and filter materials to enhance P removal in constructed wetlands treating diffuse farm runoff: a review. *New Zealand Journal of Agricultural Research*, 53(1), pp.71-95.

Bartley P, Johnston P (2006) Eutrophication from agriculture sources, final report, nitrate leaching – groundwater (2000-LS-2.3.1.3-M2) (prepared for the Environmental Protection Agency by Department of Civil, Structural and Environmental Engineering, Trinity College Dublin). Environmental Protection Agency, Wexford, pp. 103-138.

Bastin, O., Janssens, F., Dufey, J. and Peeters, A. (1999). P removal by a synthetic iron oxide–gypsum compound. *Ecological Engineering*, 12(3-4), pp.339-351.

Bradley, C., Byrne, C., Craig, M., Free, G., Gallagher, T., Kennedy, B., Little, R., Lucey, J., Mannix, A., McCreesh, P., McDermott, G., McGarrigle, M., Ní Longphuirt, S., O’Boyle, S., Plant, C., Tierney, D., Trodd, W., Webster, P., Wilkes, R. and Wynne, C., 2015. Water Quality in Ireland 2010–2012. Byrne, B. and Fanning, A. (eds). Environmental Protection Agency, Johnstown Castle, Ireland.

Braskerud, B.C., Dunne, E., Reddy, K. and Carton, O., 2005. Retention of soil particles and P in small constructed wetlands in agricultural watersheds. *Nutrient Management in Agricultural Watersheds: A Wetlands Solution*. Wageningen Academic Publishers. Wageningen, The Netherlands. pp, pp.121-131.

CSO - Central Statistics Office., 2020. [online] Available at: <https://www.cso.ie/en/releasesandpublications/ep/psyi/statisticalyearbookofireland2019/agri/cl/> [Accessed 18 November 2020].

Childers, D., Corman, J., Edwards, M. and Elser, J. (2011). Sustainability Challenges of P and Food: Solutions from Closing the Human P Cycle. *BioScience*, 61(2), pp.117-124.

Carroll, P., Harrington, R., Keohane, J. and Ryder, C., 2005. Water treatment performance and environmental impact of integrated constructed wetlands in the Anne valley watershed. *Nutrient Management in Agricultural Watersheds: A Wetlands Solution*. Wageningen Academic Publishers. Wageningen, The Netherlands. pp, pp. 211.

Correll, D. (1998). The Role of P in the Eutrophication of Receiving Waters: A Review. *Journal of Environment Quality*, 27(2), p.261.

- Coulibaly L.S., Yvon J., Coulibaly L., (2015). Physicochemical Characterization of Lomo Black Shale and Application as Low Cost Material for Phosphate Adsorption in Aqueous Solution. *Journal of Environmental Earth Sciences*, 5(9), 42-60.
- Clenaghan, C., Clinton, F. and Crowe, M., 2005. *P Regulations National Implementation Report*. [online] epa.ie. Available at: https://www.epa.ie/pubs/reports/water/P/EPA_P_report_2005.pdf [Accessed 2 June 2020].
- Cumming, G., Fidler, F. and Vaux, D. (2007). Error bars in experimental biology. *The Journal of Cell Biology*, 177(1), pp.7-11.
- Cyrus, J. and Reddy, G. (2010). Sorption and desorption of P by shale: batch and column studies. *Water Science & Technology*, 61(3), p.599.
- Drizo, A., Frost, C., Grace, J. and Smith, K. (1999). Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Water Research*, 33(17), pp.3595-3602. Ak, M. and Gunduz, O. (2013). Fate of Nutrients in Secondary Treated Municipal Wastewater during Percolation through the Soil Media. *CLEAN - Soil, Air, Water*, 42(8), pp.1036-1043.
- Dunne, E.J., Culleton, N., Donovan G.O and Harrington., (2005). Constructed wetlands to retain contaminants and nutrients, specifically P from farmyard dirty water in Southeast Ireland. *Nutrient Management in Agricultural Watersheds. A Wetlands Solution*, ISBN 9076998612, pp 152.
- Dunne, E.J and Reddy K.R. (2005). P biogeochemistry of wetlands in agricultural watersheds. *Nutrient Management in Agricultural Watersheds. A Wetlands Solution*, ISBN 9076998612, pp 105-111.
- Edwards, A., Kay, D., McDonald, A., Francis, C., Watkins, J., Wilkinson, J. and Wyer, M. (2008). Farmyards, an overlooked source for highly contaminated runoff. *Journal of Environmental Management*, 87(4), pp.551-559.
- EPA (Environmental Protection Agency) 2016. *Classification: Environmental Protection Agency, Ireland*. [online] Available at: <https://www.epa.ie/water/watmg/wfd/classification/> [Accessed 3 May 2020].
- EPA (Environmental Protection Agency), 2016. Irelands Environment, An Assessment 2016. EPA. [Online] Available at: http://www.epa.ie/pubs/reports/indicators/SoE_Report_2016.pdf [Accessed on Dec 12th 2017].
- EPA (2019) Water Quality Assessment 2013-2018. [online] Available at: [http://epa.ie/pubs/reports/water/waterqua/Water%20Quality%20in%20Ireland%202013-2018%20\(web\).pdf](http://epa.ie/pubs/reports/water/waterqua/Water%20Quality%20in%20Ireland%202013-2018%20(web).pdf). [Accessed 5 May 2020].
- FAO.org. (2017). *Calcareous soils / FAO SOILS PORTAL / Food and Agriculture Organization of the United Nations*. [online] Available at: <http://www.fao.org/soils-portal/soil-management/management-of-some-problem-soils/calcareous-soils/en/> [Accessed 7 Sep. 2017].

- Han, G. and Park, J. (2014). Water Quality, Flora and Fauna of 7 Wetlands in Donghae City. *Journal of Wetlands Research*, 16(4), pp.335-352.
- Hart, B., Bailey, P., Edwards, R., Hortle, K., James, K., McMahon, A., Meredith, C. and Swadling, K. (1991). A review of the salt sensitivity of the Australian freshwater biota. *Hydrobiologia*, 210(1-2), pp.105-144.
- Hoagland, C., Gentry, L., David, M. and Kovacic, D. (2001). Plant Nutrient Uptake and Biomass Accumulation in a Constructed Wetland. *Journal of Freshwater Ecology*, 16(4), pp.527-540.
- Gao, L. and Xie, L. (2014). Modelling P Removal in Horizontal Subsurface Flow Constructed Wetlands. *Journal of Clean Energy Technologies*, pp.104-107.
- Gersberg, R., Elkins, B., Lyon, S. and Goldman, C. (1986). Role of aquatic plants in wastewater treatment by artificial wetlands. *Water Research*, 20(3), pp.363-368.
- Gorzal, M., Kornijów, R. and Buczyńska, E., 2018. Quality of Rivers: Comparison of Hydro-Morphological, Physical-Chemical and Biological Methods. *Ecological Chemistry and Engineering S*, [online] 25(1), pp.101-122. Available at: <https://doi.org/10.1515/eces-2018-0007> [Accessed 17 October 2020].
- Grant, C., Flaten, D., Tomaszewicz, D. and Sheppard, S. (2001). The importance of early season P nutrition. *Canadian Journal of Plant Science*, 81(2), pp.211-224.
- Gray, N. (2005). *Water Technology*. Burlington: Elsevier. Table 7.2 pp. 118-119, Table 8.9 pp.163.
- Hall, K., Eagleton, L., Acrivos, A. and Vermeulen, T. (1966). Pore- and Solid-Diffusion Kinetics in Fixed-Bed Adsorption under Constant-Pattern Conditions. *Industrial & Engineering Chemistry Fundamentals*, 5(2), pp.212-223.
- Hanna, A., Sherief, M. and Abo Elenin, R. (2008). Phosphate Removal from Wastewater by Calcite and Dolomite Ores. *P Research Bulletin*, 22(0), pp.7-12.
- Harrington, R., O'Donovan, G. and McGrath, G. (2013). Integrated Constructed Wetlands (ICW) working at the landscape scale: The Anne Valley project, Ireland. *Ecological Informatics*, 14, pp.104-107.
- Hood, A., Chopra, M. and Wanielista, M. (2013). Assessment of Biosorption Activated Media Under Roadside Swales for the Removal of P from Stormwater. *Water*, 5(1), pp.53-66.
- Hooda, P., Edwards, A., Anderson, H. and Miller, A. (2000). A review of water quality concerns in livestock farming areas. *Science of The Total Environment*, 250(1-3), pp.143-167.
- Ireland - European Commission. 2020. *Agriculture - Ireland - European Commission*. [online] Available at: https://ec.europa.eu/ireland/news/key-eu-policy-areas/agriculture_en [Accessed 14 November 2020].
- Jiang, C., Jia, L., Zhang, B., He, Y. and Kirumba, G. (2014). Comparison of quartz sand, anthracite, shale and biological ceramsite for adsorptive removal of P from aqueous solution. *Journal of Environmental Sciences*, 26(2), pp.466-477.

- Jordan, P., Menary, W., Daly, K., Kiely, G., Morgan, G., Byrne, P. and Moles, R. (2005). Patterns and processes of P transfer from Irish grassland soils to rivers—integration of laboratory and catchment studies. *Journal of Hydrology*, 304(1-4), pp.20-34.
- Ju, X., Wu, S., Zhang, Y. and Dong, R. (2014). Intensified nitrogen and P removal in a novel electrolysis-integrated tidal flow constructed wetland system. *Water Research*, 59, pp.37-45.
- Klein, A., Harnisch, M., Poremski, H. and Schmidt-Bleek, F. (1981). OECD Chemicals Testing Programme physico-chemical test. *Chemosphere*, 10(2), pp.153-207.
- Kim, S. and Geary, P. (2001). The impact of biomass harvesting on P uptake by wetland plants. *Water Science and Technology*, 44(11-12), pp.61-67.
- Kioussis, D., Wheaton, F. and Kofinas, P. (1999). Phosphate binding polymeric hydrogels for aquaculture wastewater remediation. *Aquacultural Engineering*, 19(3), pp.163-178.
- Laidler, K., Meiser, J. and Sanctuary, B. (2003). *Physical chemistry*. Boston: Houghton Mifflin.
- Leip, A., Billen, G., Garnier, J., Grizzetti, B., Lassaletta, L., Reis, S., Simpson, D., Sutton, M., de Vries, W., Weiss, F. and Westhoek, H. (2015). Impacts of European livestock production: nitrogen, sulphur, P and greenhouse gas emissions, land-use, water eutrophication and biodiversity. *Environmental Research Letters*, 10(11), p.115004.
- Lenntech.com. (2017). *Effects of acids and alkalis on aquatic life*. [online] Available at: <https://www.lenntech.com/aquatic/acids-alkalis.htm> [Accessed 29 Sep. 2017].
- Lucey, J., Bowman, J.J., Clabby, K.J., Cunningham, P., Lehane, M., MacCarthaigh, M., McGarrigle, M.L., Toner, P.F. 1999. Water Quality in Ireland (1995–1997). EPA Wexford, Ireland.
- Marsili, Letizia & Coppola, Daniele & Bianchi, Nicola & Maltese, Silvia & Bianchi, Massimo & Fossi, Maria. (2014). Release of Polycyclic Aromatic Hydrocarbons and Heavy Metals from Rubber Crump in Synthetic Turf Fields: Preliminary Assessment for Athletes. *Journal of Environmental and Analytical Toxicology*. 5, pp.1-8
- Martínez-Suller L, Provolo G, Carton O.T, Brennan D, Kirwan L and Richards K.G. The composition of dirty water on dairy farms in Ireland. (2010). *Irish Journal of Agricultural and Food Research*, 49(1), pp.67-80.
- McDonald, N. (2019). Nutrient SOURCES in Agricultural Catchments. Agricultural Catchment programme. Teagasc Website. <https://www.teagasc.ie/environment/water-quality/agricultural-catchments/research/source/> . [Accessed 21 December 2019].
- Merriman, R., Arnabat, C., Germaine, K and Dowling, DN. (2015) Feasibility study to test the efficiency reliability and commercial potential of Microbial Enhanced BioSwale (MEBS) systems for the treatment of farmyard dirty water. Unpublished technical report.

- McKay, G., Blair, H. and Gardner, J. (1982). Adsorption of dyes on chitin. I. Equilibrium studies. *Journal of Applied Polymer Science*, 27(8), pp.3043-3057.
- McLaughlin, A. and Mineau, P. (1995). The impact of agricultural practices on biodiversity. *Agriculture, Ecosystems & Environment*, 55(3), pp.201-212.
- Minogue, D., French, P., Bolger, T. and Murphy, P., 2015. Characterisation of dairy soiled water in a survey of 60 Irish dairy farms. *Irish Journal of Agricultural and Food Research*, [online] 54(1), pp.1-16. Available at: https://www.researchgate.net/publication/290623920_Characterisation_of_dairy_soiled_water_in_a_survey_of_60_Irish_dairy_farms [Accessed 18 November 2020].
- Montgomery, D. (2007). Soil erosion and agricultural sustainability. *Proceedings of the National Academy of Sciences*, 104(33), pp.13268-13272.
- Montenegro, C.T. (2013). *Evaluation of the sustainability of controlling diffuse water pollution in urban areas on a life cycle basis*. Environmental Science. <https://www.semanticscholar.org/paper/Evaluation-of-the-sustainability-of-controlling-in-Montenegro/6d5cc7977c2c8bafef059cef26d6946b9211cde1d#references>>. [Accessed on 13/10/20]
- Mustafa, A., Scholz, M., Harrington, R. and Carroll, P. (2009). Long-term performance of a representative integrated constructed wetland treating farmyard runoff. *Ecological Engineering*, 35(5), pp.779-790. Table 2.
- Nitrates Explanatory Handbook for Good Agricultural Practices For The Protection Of Water Regulation 2017*. [online] Available at: <https://www.agriculture.gov.ie/media/migration/ruralenvironment/environment/nitrates/2018Nitratesexplanatoryhandbook03042018.pdf> [Accessed 31 May 2020].
- NOAA (2017). *Where is all the Earth's water?* [online] Available at : <https://oceanservice.noaa.gov/facts/eutrophication.html>. [Accessed] on 13/10/20.
- Ilyas, H. and Masih, I., 2017. Intensification of constructed wetlands for land area reduction: a review. *Environmental Science and Pollution Research*, [online] 24(13), pp.12081-12091. Available at: <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5410209/> [Accessed 12 December 2020].
- Ireland - European Commission. 2020. *Agriculture - Ireland - European Commission*. [online] Available at: https://ec.europa.eu/ireland/news/key-eu-policy-areas/agriculture_en [Accessed 14 November 2020].
- Panagos, P., Standardi, G., Borrelli, P., Lugato, E., Montanarella, L. and Bosello, F., 2018. Cost of agricultural productivity loss due to soil erosion in the European Union: From direct cost evaluation approaches to the use of macroeconomic models. *Land Degradation & Development*, [online] 29(3), pp.471-484. Available at: <https://doi.org/10.1002/ldr.2879> .
- Pant, H., Reddy, K. and Lemon, E. (2001). P retention capacity of root bed media of sub-surface flow constructed wetlands. *Ecological Engineering*, 17(4), pp.345-355.

- Park, M., Blitzer, E., Gibbs, J., Losey, J. and Danforth, B. (2015). Negative effects of pesticides on wild bee communities can be buffered by landscape context. *Proceedings of the Royal Society B: Biological Sciences*, 282(1809), p.20150299.
- Parmar, T., Rawtani, D. and Agrawal, Y., 2016. Bioindicators: the natural indicator of environmental pollution. *Frontiers in Life Science*, [online] 9(2), pp.110-118. Available at: <http://tpps://doi.org/10.1080/21553769.2016.1162753> [Accessed 17 October 2020].
- Price, R., Savabi, M., Jolicoeur, J. and Roy, S. (2010). Adsorption and desorption of phosphate on limestone in experiments simulating seawater intrusion. *Applied Geochemistry*, 25(7), pp.1085-1091.
- Prochaska, C. and Zouboulis, A. (2006). Removal of phosphates by pilot vertical-flow constructed wetlands using a mixture of sand and dolomite as substrate. *Ecological Engineering*, 26(3), pp.293-303.
- Rajput (2014). Influence of Incubation Period, Temperature and Different Phosphate levels on Phosphate Adsorption in Soil. *American Journal of Agricultural and Biological Sciences*, 9(2), pp.251-260.
- Rice E.W, Baird R.B, Eaton AD, Clesceri L.S (2012). *Standard methods for examination of water and wastewater*. ISBN: 9780875530130 American Public Health Association, American Water Works Association, Water Environment Federation 2012.
- Robertson, A. and MacCormack, J. (1977). *Farm wastes handbook*. Bucksburn: Scottish Farm Buildings Investigation Unit, pp. 23.
- Schaechter, M. (2009). *Encyclopedia of microbiology*. Amsterdam [Netherlands]: Elsevier/Academic Press, pp 299-321.
- Schindler, D., Carpenter, S., Chapra, S., Hecky, R. and Orihel, D. (2016). Reducing P to Curb Lake Eutrophication is a Success. *Environmental Science & Technology*, 50(17), pp.8923-8929.
- Scholz, M., Harrington, R., Carroll, P. and Mustafa, A. (2007). The Integrated Constructed Wetlands (ICW) concept. *Wetlands*, 27(2), pp.337-354.
- Scholz, M., Sadowski, A., Harrington, R. and Carroll, P. (2007). Integrated Constructed Wetlands assessment and design for phosphate removal. *Biosystems Engineering*, 97(3), pp.415-423.
- Schriever, C. and Liess, M. (2007). Mapping ecological risk of agricultural pesticide runoff. *Science of The Total Environment*, 384(1-3), pp.264-279. (265)
- Schröder, J. (2005). Revisiting the agronomic benefits of manure: a correct assessment and exploitation of its fertilizer value spares the environment. *Bioresource Technology*, 96(2), pp.253-261.
- Song, S., Yeom, S., Choi, S. and Yoo, Y. (2002). Effect of aeration on denitrification by *Ochrobactrum anthropi* SY509. *Biotechnology and Bioprocess Engineering*, 7(6), pp.352-356.
- Spivakov, B., Maryutina, T. and Muntau, H. (1999). P Speciation in Water and Sediments. *Pure and Applied Chemistry*, 71(11).

Statutory Instruments. S.I. No. 31 of 2014. European Union (Good Agricultural Practices for the protections of water) Regulations 2014.
<http://www.irishstatutebook.ie/eli/2014/si/31/made/en/pdf>. *J. Microbiol. Biotechnol.* (2003), **13**(3), 473–476.

Taha Jawad, I., Raihan Taha, M., Hameed Majeed, Z. and A. Khan, T. (2014). Soil Stabilization Using Lime: Advantages, Disadvantages and Proposing a Potential Alternative. *Research Journal of Applied Sciences, Engineering and Technology*, **8**(4), pp.510-520.

Tang, X., Huang, S. and Scholz, M. (2009). Comparison of P removal between vertical subsurface flow constructed wetlands with different substrates. *Water and Environment Journal*, **23**(3), pp.180-188.

Tchobanoglous, G., Burton, F. and Stensel, H. (2003) Wastewater engineering. McGraw-Hill Series in Civil and Environmental Engineering

Teagasc.ie. (2017). *Source - Teagasc / Agriculture and Food Development Authority*. [online] Available at: <https://www.teagasc.ie/environment/water-quality/agricultural-catchments/research/source/> [Accessed 5 Dec. 2017].

Teagasc.ie, (2015). *Teagasc - Agriculture in Ireland*. [online] Available at: <http://www.teagasc.ie/agrifood/> [Accessed 22 Sep. 2015].

Techniques. (2018). *X-Ray Fluorescence (XRF)*. [online] Available at: https://serc.carleton.edu/research_education/geochemsheets/techniques/XRF.html [Accessed 25 Apr. 2018].

Toner, P., Bowman, J., Clabby, K., Lucey, J., McGarrigle, M., Concannon, C., Clenaghan, C., Cunningham, P., Delaney, J., O’Boyle, S., MacCárthaigh, Craig, M. 71 and Quinn, R. 2005. Water Quality in Ireland 2001-2003. EPA, Wexford, Ireland.

Thiébaud, G. (2008). P and aquatic plants. *Plant Ecophysiology*, pp.31-49.

Tubiello, F., Biancalani, R., Salvatore, M., Rossi, S. and Conchedda, G. (2016). A Worldwide Assessment of Greenhouse Gas Emissions from Drained Organic Soils. *Sustainability*, **8**(4), p.371.

Usharani, K., Lakshmanaperumalsamy, P. and Muthukumar, M. (2013). Optimization of Phosphate Removal from Synthetic Wastewater by Bacterial Consortium Using Box-Behnken Design. *Environmental Engineering and Management Journal*, **12**(12), pp.2371-2383.

Volesky, B. (2003). *Sorption and biosorption*. St. Lambert, Québec: BV Sorbex. Chapter 6.1 pp. 104

Vymazal, J. (2010). Constructed Wetlands for Wastewater Treatment. *Water*, **2**(3), pp.530-549.

Wallace, D., 2001. *S.I. No. 254/2001 - Urban Waste-Water Treatment Regulations*. [online] Irishstatutebook.ie. Available at: <http://www.irishstatutebook.ie/eli/2001/si/254/made/en/print> [Accessed 2 June 2020].

- Water.epa.gov, (2015). *5.11 Fecal Bacteria | Monitoring & Assessment | US EPA*. [online] Available at: <http://water.epa.gov/type/rsl/monitoring/vms511.cfm> [Accessed 17 Sep. 2015].
- Wen, Y., Chen, Y., Zheng, N., Yang, D. and Zhou, Q. (2010). Effects of plant biomass on nitrate removal and transformation of carbon sources in subsurface flow constructed wetlands. *Bioresource Technology*, 101(19), pp.7286-7292.
- WHO. Health hazards from nitrate in drinking water. Environmental Health 1. Copenhagen: World Health Organisation, 1985.
- Wu, D., Zhang, B., Li, C., Zhang, Z. and Kong, H. (2006). Simultaneous removal of ammonium and phosphate by zeolite synthesized from fly ash as influenced by salt treatment. *Journal of Colloid and Interface Science*, 304(2), pp.300-306
- Wu, Y., Tam, N. and Wong, M. (2008). Effects of salinity on treatment of municipal wastewater by constructed mangrove wetland microcosms. *Marine Pollution Bulletin*, 57(6-12), pp.727-734.
- Yaalon D.H (1961), Mineral Composition of the Average Shale. Department of Geology, The Hebrew University, Jerusalem. pp.31
- Yan, J., Kirk, D., Jia, C. and Liu, X. (2007). Sorption of aqueous P onto bituminous and lignitous coal ashes. *Journal of Hazardous Materials*, 148(1-2), pp.395-401.
- Y. Xiao, X. Zhu, H. Cheng, K. Li, Q. Lu, D. Iang (2013). Characteristics of P adsorption by sediment mineral matrices with different particle sizes. *Water Science and Engineering*, 6(3). pp. 262-271.
- Yang, X., Wu, X., Hao, H. and He, Z. (2008). Mechanisms and assessment of water eutrophication. *Journal of Zhejiang University SCIENCE B*, 9(3), pp.197-209.
- Yuan, X., Xia, W., An, J., Yin, J., Zhou, X. and Yang, W. (2015). Kinetic and Thermodynamic Studies on the Phosphate Adsorption Removal by Dolomite Mineral. *Journal of Chemistry*, 2015, pp.1-8.
- Zhang, C., Feng, W., Chen, H., Zhu, Y., Wu, F., Giesy, G.P., He, Z., Wang H., and Sun, F. (2019). Characterization and sources of dissolved and particulate P in 10 freshwater lakes with different trophic statuses in China by solution ³¹P nuclear magnetic resonance spectroscopy. *Ecological Research*, 34: 106-118, DOI: (10.1111/1440-1703.1006).
- Žibienė, G., Dapkienė, M., Kazakevičienė, J. and Radzevičius, A. (2015). P removal in a vertical flow constructed wetland using dolomite powder and chippings as filter media. *Journal of Water Security*, 1(1), pp.46-52.