REMOVAL OF DISSOLVED REACTIVE PHOSPHORUS FROM MUNICIPAL AND DAIRY FACTORY WASTEWATER USING ALLOPHANIC SOIL

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Abstract

Many of New Zealand's sewage treatment plants (STPs) and rural factories discharge treated or partially treated sewage, which is rich in dissolved reactive phosphorus (DRP), into rivers and streams. A large number of these STPs are not able to comply with the current DRP river standards because conventional treatment methods are cost-prohibitive. There is an abundance of Allophanic soils with high phosphorus (P) sorption capacities located in the central North Island of New Zealand that have potential for use as low-cost filter material for removing DRP from wastewaters. For Allophanic soil filters to be a viable treatment option, the soil, in addition to having a high P sorption capacity, should be both accessible and plentiful. The main aims of this study were to assess and improve the effectiveness of Allophanic soil filters at removing DRP from wastewaters and to evaluate the agronomic value of P-enriched soils as a P source for plant growth. It also sought to contribute to a better understanding of the feasibility and important design characteristics of full-scale soil-based treatment systems.

Five quarry sites in the Waikato Region were soil sampled to identify soils with high P retention values. Only the Te Mata Quarry (TQ) soil in the, north-western Waikato Region, had a high P retention value at or close to 100% as assessed using the standard (5 g) anion storage capacity (ASC) test. The modified (1 g) ASC test revealed P retention values of 47 – 91% for samples taken from different soil depths at TQ. All of the soil depths down to 600 cm, except for the 125 – 175 cm depth, had modified (1 g) ASC test values >58%. This indicated that the TQ soil had P sorption capacities that would potentially make it a suitable material for filtering DRP from wastewater and, therefore, it warranted further evaluation using real wastewater.

Wastewater pH has a marked influence on the P sorption capacity of soil filters, with the sorption capacity expected to increase as wastewater pH is decreased, from being alkaline to acidic. The laboratory soil column experiment quantified the effect of the level of acid dosing and the type of acid used on the capacity of soils to remove P from wastewater. Columns of soil, taken from a quarry at Ohakune (OQ), and treated with wastewater adjusted to pH 5.5 removed the greatest amount of DRP. A total of 8.9 mg P/g oven-dried soil was removed at an average removal efficiency of 75%. In comparison, the soil columns treated with wastewater without pH adjustment, removed only 4.5 mg P/g oven-dried soil at the same removal efficiency of 75%. This highlights the merits of lowering wastewater pH to increase DRP removal capacity.

The performance pilot-scale soil filters at the Dannevirke STP and Fonterra Te Rapa WTP were evaluated, under field conditions, for a total operational period of 440 and 376 days, respectively. Each filter contained the OQ soil and had a surface area of 1 m^2. The OQ soil had an overall P removal efficiency of 67% and 71% at the STP and WTP sites, respectively. The OQ soil filters at Dannevirke STP removed a total of 6.4 mg P/g oven-dried soil, while the OQ soil filters at the Fonterra Te Rapa WTP removed a total of 1.87 mg P/g oven-dried soil. This discrepancy in performance was due to the difference in wastewater type and pH adjustment, initial P concentrations, and soil pre-treatment (i.e. the soil used at Dannevirke was sieved).

A cost/benefit analysis suggested that if the STP was 225 km from the soil source then the cost of acid dosing is about ten times greater than the cost of supplying additional soil to achieve the same amount of P removal. Therefore, it is unlikely that acid dosing will be cost competitive for most wastewater treatment sites in the central North Island of New Zealand.

The wastewater treated soil (WTS) obtained from the Dannevirke STP pilot-scale filter experiment was evaluated for its agronomic effectiveness in a glasshouse pot experiment. The ability of WTS to supply P for ryegrass growth (*Lolium multiflorum*) was compared with a soluble phosphorus source (monocalcium phosphate, MCP). The WTS was highly effective at increasing available P in the soil, as measured by the Olsen P soil test, ryegrass yield and ryegrass P uptake. The soluble fertiliser P value of WTS was estimated to be equivalent to 61% of MCP applied at the same rate. Therefore, the results show that WTS is an effective P source for plant growth and its application to soil has the potential to recycle both the soil and the P it contains.

List of Abbreviations

$Al_2(SO_4)_3{\cdot}14H_2O$	Aluminium sulphate or alum
AMD	Acid Mine Drainage
ASC	Anion Storage Capacity
BFS	Blast furnace slag
BOF	Basic Oxygen Steel Furnace
$Ca(OH)_2$	Hydrate lime
COD	Chemical Oxygen Demand
CWS	Constructed Wetland System
d10	First 10% grain size distribution
DO	Dissolved Oxygen
DRP	Dissolved Reactive Phosphorus
EAF	Electric Arc Furnace
EBPR	Enhance Biological Phosphorus Removal
FDE	Farm Dairy Effluent
$FeCl_3$	Ferric chloride
$FeSO_4.7H_2O$	Ferrous sulphate
HAIX	Hybrid Anion Exchanger
HFO	Hydrated Fe^{3+} oxide
HLR	Hydraulic Loading Rate
HRT	Hydraulic Retention Time
IBPs	Industrial by-products
LTS	Land Treatment System

MCP	Monocalcium Phosphate
Olsen P	Bicarbonate-extractable phosphorus
OQ	Ohakune Quarry
PAOs	Phosphate Accumulating Organisms
pH_{PZC}	pH at point of zero charge
STP	Sewage Treatment Plant
TP	Total Phosphorus
TQ	Te Mata Quarry
VFAs	Volatile Fatty Acids
WTP	Wastewater Treatment Plant

Forward

This PhD unknowingly began in the beginning of the monsoon season of the year 2010 in Bangkok, Thailand. I was discussing an employment opportunity with a director of a non-profit children organisation located in the far north of Thailand. He was looking to hire an English teacher with an entrepreneurial mindset. As I told him of my background in Chemical Engineering, he told me about the algal problem in the pond in their backyard, and asked if I know how to get rid of them. I must admit that, during that time, I paid very little concern or attention over the subject matter and merely told him to stall aeration baffles. I was certain that the issue would resolve itself in due time. As expected, I did not seek further opportunity with them and thought very little of it. And mainly because I didn't know what an entrepreneur was.

So fast forward a few years later, where not only did I involve myself in the research but I also felt a great amount of appreciation in his effort to tackle algae pollution. Sadly, this issue will still be a significant global crisis that won't resolve itself anytime soon.

Hence, the fight for clean water continues.

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Chapter 1

Introduction

1.1 Research background

Eutrophication is a seasonal phenomenon that frequently occurs in nutrient-sensitive fresh water systems. It is caused by a shift or deviation in the local ambient nutrient level. Nitrogen (N) and phosphorus (P) are the primary nutrients responsible for eutrophication. In New Zealand streams the availability of P commonly limits eutrophication, with an estimated 76% of tested sites exhibiting P-limiting conditions (McDowell and Larned 2008; McDowell et al. 2009). Therefore, the effect of eutrophication is frequently linked to P concentrations in fresh water systems. Phosphorus is a major plant nutrient (Solovchenko et al. 2016), that if released into surface water via runoff from agricultural land or discharge of municipal or industrial wastewaters (Conley et al. 2009), can cause excessive aquatic weed and algal growth. Algal blooms are not only aesthetically unpleasant, lowering the appeal for recreational use, but also results in dissolved oxygen (DO) depletion in the fresh water receiving environment (Quinn and Gilliland 1989), which degrades water quality of the affected water body, diminishing its ability to sustain aquatic life (McArthur and Clark 2007).

There are various anthropogenic activities that the influence the magnitude and seasonality of P loads influencing the P concentrations of the receiving water bodies (Smith et al. 1999). In the main dairy farming regions of New Zealand, a major source of elevated P concentrations in surface waters, particularly during river low-flow conditions in summer, has historically been the discharge of dairy farm effluent (FDE). Over the last 20 years, the direct discharge of FDE to surface waters has mostly been eliminated in the majority of regions, due to the adoption of land treatment systems (LTS) in combination with adequate effluent storage (Houlbrooke et al. 2004; Roygard et al. 2012). This has markedly reduced these P contributions to receiving surface waters (Houlbrooke 2008). However, there are still numerous direct discharges of P rich wastewaters from towns and industries into surface waters. For example, there are approximately 30 small and medium sized towns within the Manawatu–Wanganui Region that continue to discharge municipal wastewaters into rivers, with the smaller sized communities mainly only using pond treatment prior to discharge. These point-source discharges are high in dissolved reactive phosphorus (DRP) concentrations, typically <25 mg P/L (Tchobanoglous et al. 2014), which are discharged all year-round. The high DRP load of these discharges make them a significant contributor of P into the receiving rivers. The main rivers in the Manawatu-Wanganui Region have sections of poor water quality, particularly during low flow conditions. The P concentrations in the Manawatu River are amongst the highest, exceeding approximately 84 – 88% of the target nutrient loads at all flows (Roygard et al. 2012). In the Manawatu-Wanganui Region, the water quality target for DRP varies in the different catchments from 0.006 – 0.015 mg P/L. Consequently, the Regional Council is are placing greater emphasis on limiting the inputs of P into surface waters.

Another important point-source discharge of P into rivers is from dairy factories located throughout New Zealand. Dairy factories also produce large volumes of nutrient rich wastewater. While a number dairy factories use land treatment as the final treatment stage, not all factories have access to sufficient areas of suitable land that are available for land application, which is particularly a constraint near larger urban centres. Therefore, where land treatment isn't an option, the use of the chemical and biological treatment, including the use of aerated lagoons, is then followed by discharge of treated wastewater to surface water (Brown 2016, 2017), which in some cases can still have high DRP concentrations.

In New Zealand, waste stabilisation lagoons or oxidation ponds are the major treatment of urban wastewaters (Davies-Colley et al. 1995). Solely, these ponds are ineffective at achieving low DRP concentrations (Davies-Colley et al. 1995). To reduce DRP in discharges, add-on chemical dosing treatments are more commonly used. These involve precipitation reactions using lime or coagulation/flocculation reactions with, for example, aluminium sulphate (alum; $Al_2(SO_4)_3$) or ferric sulphate ($Fe_2(SO4)_3$). These forms of treatment are relatively expensive (Morse et al. 1998), particularly when the cost of disposal of the resultant sludge is also accounted for (Aguilar et al. 2002). Therefore, there is a need to develop an alternative method of DRP removal from wastewater to reduce the cost of treatment, particularly for small to medium sized towns where the per capita cost of current treatment methods can be especially high (Keplinger et al. 2004).

Active filters, which utilise reactive media, have shown promise in removing P from wastewater (Shilton et al. 2006). A wide variety of substrates have been used in these filters, including shale, limestone and steel-waste slags (Johansson Westholm 2006; Vohla et al. 2011). Allophanic soils formed from tephra (volcanic ash and lapilli) have also shown potential as relatively low cost substrates for use in active filters. Ryden and Syers (1975) demonstrated that, of the New Zealand Allophanic soils they studied, soils derived from moderately weathered andesitic tephra showed a high level of P removal from wastewater. While previous research has shown that Allophanic soils show promise as potential filter media for removing DRP from wastewaters, further research is required to further evaluate and identify methods of improving the performance characteristics of soil filters prior to their use in full-scale filters. For example, previous research has shown that P sorption processes are influenced by wastewater pH. Therefore, it will be useful to gain a better understanding of how much influence wastewater pH can have on the effectiveness of soil filters. In addition, the cost of sourcing soil for soil filters is can be greatly influenced by the distance that soil needs to be transport, so the feasibility of soil filters will depend on identifying sources of soils close to where the soil filter will be constructed. There is also limited information on the potential uses of the P-enriched soil after it has been used in wastewater treatment filter. Therefore, evaluating its agronomic effectiveness, in particular is the P fertiliser value of the soil, will help to determine how it and the P it contains can be productively re-cycled.

1.2 Research questions

Specific research questions that relate to the gaps in the existing knowledge about soil filters for wastewater DRP removal, include the following:

i. Are there suitable Allophanic soils available in quarries in regions other than the Taranaki region and the Ruapehu district, that also have potential for use in DRP removal filters?
ii. Can wastewater characteristics, in particular pH, be modified to optimise the P removal capacity of Allophanic soil filters?
iii. How well do Allophanic soil filters perform at removing DRP from wastewater when operated with actual wastewater under the field conditions experienced at wastewater treatment plants?
iv. What is the P fertiliser value of the P-enriched soil once its use in wastewater DRP removal filters is completed?

1.3 Research hypothesis

The overarching hypothesis of this study is:

Sources of Allophanic soil can be found to efficiently treat wastewaters in soil filters, for which the performance can be further enhanced by acidification of the wastewater and uniform distribution of soil particle size, and that a portion of the captured phosphorus can be recycled as a soil amendment for plant growth.

1.4 Research objectives

The main research objectives of this study are:

i. To identify and evaluate suitable sources of Allophanic soils in the northern Waikato region that have potential for use in wastewater treatment in the upper central North Island.
ii. Quantify the effect of acid dosing wastewater on the DRP removal capacity and efficiency of Allophanic soils.
iii. Evaluate the performance of pilot-scale soil filters at removing DRP from wastewater under field conditions.
iv. Design a full-scale soil filter for removing DRP from wastewater for a medium sized town.
v. Determine the agronomic effectiveness of P-enriched Allophanic soil after being used as a filter substrate to treat municipal wastewater.

1.5 Thesis outline

This thesis is comprised of seven chapters in total including this first introductory chapter. Chapter 2 is a review of literature of the key areas of research that relate to wastewater DRP treatment methods and the potential of soil filters as a treatment method. Experimental chapters are provided in Chapters 3 – 6, each with its own introduction, methodologies, results and discussion, and conclusions. The experiment presented in Chapter 6 was also published in the Soil Use and Management journal. The last chapter, Chapter 7, provides a summary of the key findings of this study. Figure 1.1 presents the overall aims and hypothesis of the research, including the key objectives of each individual experimental chapter.

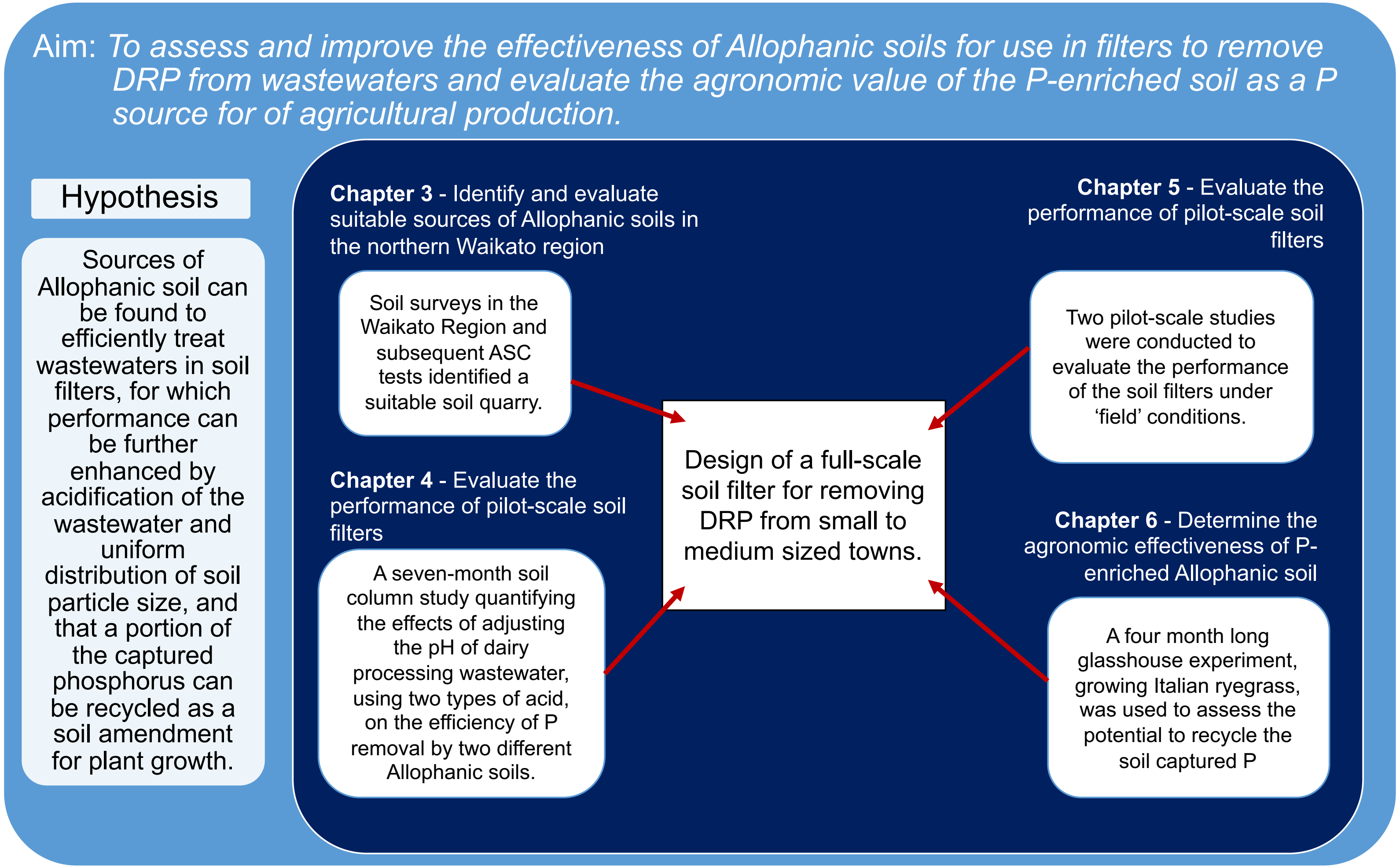

Figure 1.1 An overview of the four main experimental chapters.

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Chapter 2

Literature Review

2.1 Introduction

Ongoing runoff from agricultural land and, municipal and industrial discharges contribute significantly to dissolved reactive phosphorus (DRP) increases in surface waters above the natural background P concentrations (Parfitt et al. 2008). This has put many New Zealand rivers at risk of water quality degradation from eutrophication and unwanted aquatic weed growth. Dissolved reactive phosphorus is the fraction of soluble inorganic P that passes through 0.45 μm filter; a fraction that can be taken up directly by photosynthesising aquatic organisms (Mcdowell et al. 2009). It is often perceived as a limiting nutrient and, therefore, a compound of interest to mitigate algal bloom-sensitive waterways. Hereafter in this review of literature, the term P will be used to describe the soluble inorganic portion of P (i.e. DRP), unless stated otherwise.

Pre-treated municipal and industrial wastewaters generally contain 4 - 25 mg P/L (Hanly et al. 2012; Tchobanoglous et al. 2014), which if discharged to surface waters, can contribute to elevated DRP concentrations. In some of these receiving environments DRP concentrations as low as 0.020 mg DRP/L have been shown to still promote eutrophication (Sharpley 1993; Sharpley et al. 1994). Stricter water quality DRP regulatory limits have been introduced to some regions of New Zealand to address excessive DRP concentrations in surface waters. For example, the Manawatu-Wanganui Region's introduced river DRP standards ranging from 0.006 – 0.015 mg DRP/L, depending on the catchment's sensitivity to DRP (i.e. inland catchment vs coastal catchment).

In order for wastewater treatment plants to achieve wasterwater DRP concentrations low enough to comply with stricter water quality standards, additional treatment after pond treatment is often required. Common treatments for DRP removal include adding chemicals to promote flocculation and or precipitation of P in wastewater. These chemicals are (hydrated) alum or aluminium sulphates ($Al_2(SO_4)_3{\cdot}14H_2O$), iron salts ($FeCl_3$ and $Fe_2(SO_4)_3$), and lime ($Ca(OH)_2$) (Tanada et al. 2003; Tchobanoglous et al. 2014; Wilfert et al. 2015). Another treatment method involves the removal of P biologically, through regulation of oxygen levels and the facilitation of P accumulating organisms to obtain desirable removal (Danesh and Oleszkiewicz 1997). While both treatment types are options for P removal, the costs associated with employing these technologies may not be economical for small to medium sized treatment plants where the per capita cost can many fold higher compared to larger towns and cities (Keplinger et al. 2004). With chemical treatment, the main costs are associated with the chemicals and the disposal of the resultant sludge (Georgantas and Grigoropoulou 2007; U.S. EPA 2008; Tchobanoglous et al. 2014; Guopeng 2015). For biological P removal, specific designs to optimise the environment for bacterial growth, to achieve a desirable level of removal, contributes to the cost of treatment (Minnesota Pollution Control Agency 2006). Additionally, the energy consumption associated with aeration requirements could be a significant limiting factor in biological P removal (Sells et al. 2018). Consequently, there is a need to develop alternative affordable methods for P removal from wastewater for small to medium sized towns. The treatment technology should also not be too complex, and it should also be easy to operate and maintain.

An alternative treatment method involves the use of reactive filter media that have physico-chemical properties that facilitate P removal from wastewater through soption processes. This type of wastewater treatment has been termed ‘active filters’ (Shilton et al. 2013). In the central region of New Zealand’s North Island, Allophanic subsoils of andesitic origin (Lowe 2010) have the potential for use as locally available active filter media. These soils contain significant amounts of allophane minerals, which strongly attract negatively charged phosphate anions present in wastewater (Parfitt 1989). Ryden and Syers (1975) demonstrated using laboratory experiments that some allophanic soils had high capacities to retain P from municipal wastewater and, therefore, have potential as DRP retaining materials in wastewater filtration systems. However, very little subsequent assessments were made on evaluating allophanic soil in New Zealand for use in wastewater treatment until relatively recently (Liesch 2010; Hanly et al. 2011, 2012).

A literature review was conducted to summarise the current knowledge and principles relating to DRP removal methods for wastewater treatment, which is divided into the following sections:

i. Section 2.2 summarises current conventional P removal technologies and compares their advantages and disadvantages.
ii. Section 2.3 provides an overview of the underlying mechanisms of P removal possible with inorganic materials.
iii. Section 2.4 covers the main P sorbents being studied and their corresponding P sorption capacities in different solutions and experimental set-ups.
iv. Section 2.5 provides an introduced the New Zealand’s North Island Allophanic soil characteristics and assesses the feasibility of employing these soils in filtration systems for P removal.
v. Section 2.6 discusses the factors that affect P sorption of soils and how they can be optimised.

2.2 Chemical and biological phosphorus removal technologies – conventional phosphorus removal technologies

There are a range of different technologies used for removing P from wastewaters in practice that are designed to suit various levels of treatment and financial requirements. The type of removal technologies selected for a wastewater treatment plant depends on the size of wastewater treatment plant, the characteristics of the raw wastewater, and the standard of treated wastewater that is required to meet discharge requirements. In New Zealand, waste stabilisation ponds and/or oxidation ponds are the main treatment method for domestic sewage. Davies-Colley et al. (1995) had reported that treated sewage discharged into the nearby stream, following pond treatment, could end up with a median effluent DRP concentration of 5.1 mg P/L, from a range of 2.1 – 6.4 mg P/L. This had shown that there was minimal treatment in terms of P concentration. In order to improve effluent quality in terms of P concentration, the STPs often require upgrading to include additional treatment steps to reduce the impacts on the receiving surface waters. Predominately, P removal technologies is categorised as chemical or biological (Clark et al. 1997; Morse et al. 1998; Tchobanoglous et al. 2014; Wilfert et al. 2015). They are employed as standalone treatments or employed in tandem with other treatments for more effective P removal, particularly for treatment plants with high P loads (Morse et al. 1998; Georgantas and Grigoropoulou 2007; U.S. EPA 2008). Some wastewater treatment methods also offer the opportunity to reuse the P recovered. For example, the use of phosphate precipitation under high pH conditions to form struvite, which can then be used a slow-release fertiliser (Abma et al. 2010).

2.2.1 Chemical precipitation of phosphorus

Precipitation of DRP present in wastewater via chemical addition, is the most common P removal technology used in STPs worldwide (Takács et al. 2011; Tanyi 2013). For instance, in Québec, Canada, chemical P removal methods are used in most STPs to achieve target TP levels of 0.8 – 1 mg P/L (Galarneau and Gehr 1997). This method is widely accepted as it is very flexible, it can be applied at multiple treatment steps (Morse et al., 1998), and the chemicals are widely available. Chemical precipitation relies on the use of chemical coagulants to lower the solubility of dissolved orthophosphates in wastewater, which then settle to the bottom and the resultant solids or precipitates are removed by separation (Tchobanoglous and Burton 1991; Pagilla et al. 2006; Georgantas and Grigoropoulou 2007). In New Zealand, the principle metal salts used in P precipitation are: aluminium sulphate, also known as alum ($Al_2[SO_4]_3 \cdot 14H_2O$; containing 9% soluble Al), ferric chloride ($FeCl_3$) and ferrous sulphate ($FeSO_4 \cdot 7H_2O$), and hydrated lime ($Ca[OH]_2$) (Khan and Irvine 2006). An example of alum dosing rates are 1.2 – 4.0 moles Al/Fe per 1 mole P (0.97 – 2.26 kg Al and 3.55 – 7.10 kg Fe per 1 kg P) to achieve concentrations of 0.3 – 1.0 mg P/L (Minnesota Pollution Control Agency 2006). The P removal rate is dependent on the wastewater alkalinity and initial concentration of inorganic P, and in some cases removal rates as high as 90 – 95% and final DRP concentrations of <0.5 mg P/L can be achieved. In New Zealand, ferric chloride and ferric sulphate are commonly used at average rates of about 5.2 kg per 1 kg P, which equates to approximately 0.19 moles ferric chloride per mole of P, to achieve a final P concentration of ~1 mg P/L (Khan and Irvine 2006). The prevalence of lime usage in treatment plants has declined over time due to the high feed lime requirements needed for effective P removal (Shannon 1980;Khan and Irvine 2006). For instance, the estimated lime requirement to achieve final effluent TP concentration of 1 mg TP/L can be 6.7 kg lime per 1 kg P or lime, or 2.8 moles lime per mole of P (Dunets 2014).

Chemical P removal involves feeding of metal salts at various strategic stages in the treatment process; at the beginning of treatment (primary stage), with or before activated sludge process (secondary stage), or at the final treatment (tertiary stage) (Morse et al. 1998; Minnesota Pollution Control Agency 2006). The stage at which the chemical is introduced can significantly influence the overall removal rates, chemical usage and the quantity of solids formed. The sludge that results from chemical treatment then may undergo additional treatment steps, such as dewatering, before it is disposed of (Crittenden et al. 2012). In some cases, the sludge may be suitable for use as a soil amendment or fertiliser. However, the agronomic benefits of the sludge generated by chemical treatment, such as alum sludge, may be highly variable. Although, the quality of alum sludge has been shown to be improved, for example, by pasteurising the sludge to enhance P availability for plant uptake when applied as a fertiliser (Morse et al. 1998; Pritchard et al. 2010; Rigby et al. 2013)

The use of chemical precipitation treatment methods often requires only a minor investment in capital (Tetra Tech 2013); however, the major drawback of this method is the high operational and maintenance costs (U.S. EPA 2008). The operational cost includes the cost of chemicals, sludge dewatering and proper disposal in a land fill, if land application is not suitable (De-Bashan and Bashan 2004). When chemical treatment is used, a skilled treatment plant operator may also be required, as there are a number of critical factors that affect the performance of chemical precipitation that have to be taken into account and managed. These factors include the species of P present in the wastewater, metal/P ratios, pH, temperature, mixing rate, competing ions and the coagulant itself (Georgantas and Grigoropoulou 2007; U.S. EPA 2008; Tetra Tech 2013). The additional costs and management requirements of chemical treatment can, therefore, be particularly challenging to implement for STPs of smaller towns. Moreover, other drawbacks of chemical precipitation are that this method can limit the recycling potential of P in wastewater due to the unselective removal of P along with other contaminants, which can make it unsuitable for land application (Stratful et al. 1999).

2.2.2 Biological phosphorus removal

Biological P removal treatment methods have been developed as alternatives to chemical treatment, in order to reduce the costs associated with chemical usage and sludge production (van Loosdrecht et al. 1997). Biological P removal is achieved by feeding P-rich wastewater to specific microbes that can intracellularly store P in excess as polyphosphate (i.e. an energy source) (Strickland 1998). Enhanced biological P removal (EBPR) is a process of biological P removal that relies on the uptake of P through selection of organisms that can store high amounts of polyphosphates in their cells (Rittmann et al. 2011).

Commonly in STPs P is removed biologically using bacteria or phosphate accumulating organisms (PAOs), such as Acinetobacter (Cloete & Steyn 1988; Martin et al. 2006), and microalgae (Solovchenko et al. 2016; Sells et al. 2018). In STPs, the luxury uptake of P from PAOs is facilitated by subjecting the PAOs to zones of varying oxygen contents (aerobic, anaerobic, and anoxic zones). These PAOs under anaerobic conditions release phosphate, and upon re-addition of oxygen (aerobic conditions) will take up phosphate in excess (Levin and Shapiro 1965; Morse et al. 1998; Krishnaswamy et al. 2011). During the aerobic stage, PAOs multiply resulting in an increase in the overall biomass, which in turn causes enhanced P uptake (Kaschka and Weyrer 1999). This enhanced P uptake by microbes is known as luxury uptake, where the microbes can store as much as 5 – 30% of P on a dry-weight basis (Minnesota Pollution Control Agency 2006). To supply energy for luxury uptake (i.e. carbon source for the biomass), volatile fatty acids (VFAs) or other biodegradable compounds, such as acetic acid, are provided (Appledoorn et al. 1992; Morse et al. 1998; Stratful et al. 1999; Pagilla et al. 2006). Some studies have also used sugars, such as glucose, starch, lactose and sucrose, as carbon sources for bacterial growth and phosphate removal (Krishnaswamy et al. 2011).

In full-scale operations, the efficiency of EBPR can be as high as 85%, producing treated wastewater with final P concentrations of <0.1 mg P/L (Gebremariam et al. 2011; Gautam et al. 2014). Adding EBPR treatment to systems that also use chemical treatment, can significantly reduce chemical usage and produce a higher quality effluent (Kaschka and Weyrer 1999; Pagilla et al. 2006). For example, the Durham Plant in Oregon, USA, reduced the amount of alum used by 85% when EBPR was also introduced (Baur et al. 2002; Pagilla et al. 2006).

Another advantage of EBPR, compared to chemical treatment, is its potential ability to be modified to remove N in addition to P. However, like chemical treatment, EBPR has high operational and maintenance costs associated with the complex processes involved, such as microbial control and fermentation, that require a specialised operator to manage. In small scale treatment facilities, carbon content in wastewater can be lower, which increases the cost of operating EBPR because an external carbon source is needed to be added to the system for microbial utilisation (He et al. 2015), generating secondary pollution associated with additional carbon source input (Zou and Wang 2016). The table below provides a summary of the advantages and disadvantages of chemical and biological P removal processes previously discussed.

Table 2.1 Advantages and disadvantages of the common chemical and biological phosphorus removal technologies (Tchobanoglous and Burton 1991; Morse et al 1998; Stratful et al. 1999; Pagilla et al. 2006; U.S. EPA 2008; Tchobanoglous et al. 2014; Sells et al. 2018).

Removal Technology	Advantages	Disadvantages
Chemical	• Can be retrofitted to existing treatment systems at various stages in the treatment process. • Can remove a high proportion of inorganic P (up to 95%) • Potential for reuse the P captured in the resultant sludge, as a soil amendment/fertiliser	• The correct chemical requirement ratio to the amount of phosphate in wastewater has to be accounted for • High chemical and polymer costs • The resultant sludge is difficult to dewater, which adds weight and increases transport costs • Higher transport and sludge disposal costs
Biological	• Reduced chemical usage and sludge production • Potential to remove both N and P • Produces a more bioavailable P-enriched sludge, which can be reused as a soil amendment/fertiliser	• May require the addition of a carbon source • Performance influenced by temperature, with reduced effectiveness in cooler conditions • Aeration requirement and careful process control

2.3 Phosphorus sorption technology – a novel approach to phosphorus mitigation in point-source discharges

The use of chemical P precipitation and/or EBPR treatment methods are effective removing P from wastewaters. However, the costs and operational requirements, previously discussed, make them less suited for smaller STPs. Adoption of alternative small-scale treatment for P removal is still limited worldwide (Kholoma et al. 2016). Therefore, there is currently a need for wastewater treatment methods that are more appropriate for smaller communities with centralised treatment systems. The use of filtrations systems that remove P through sorption by low-cost materials have the advantage of having less complex operational requirements, which make them more suited to smaller systems.

2.3.1 Phosphorus removal from wastewater using sorption technology

The ability to remove inorganic P from wastewaters using adsorption processes is highly dependent on the properties of the media used (Crittenden et al. 2012; Tchobanoglous et al. 2014). The use of sorption as a treatment method to selectively remove constituents from a fluid phase (liquid or gas) to a solid phase is not a new concept, and has been studied for over a 100 years (Dąbrowski 2001). Initially, adsorption processes were used in drinking water treatment, focusing on removing colour, odour and for improving taste of contaminated water supplies (Worch 2012). For example, in drinking water treatment activated alumina (AA) has been used to remove arsenic and fluoride (Tchobanoglous et al. 2014). Adsorption processes are also applied to remove organic constituents, such as chlorophenol, heavy metals and for dechlorination (Crittenden et al. 2012). The most commonly used material for water treatment is activated carbon, which is used to remove organic substances, dissolved organic matter (Worch 2012) and micropollutants, such polyaromatic hydrocarbons (PAHs) (Mailler et al. 2015). Over the last few decades, the use of adsorption processes for removing P from wastewaters has been gaining increasing attention, which involves using ‘active’ media in constructed wetland system (CWS) or filters (Johansson Westholm 2006; Vohla et al. 2011; Haynes 2015)

In order for P removal to occur, the material used for treating the wastewater needs to contain specific physiochemical properties. Facilitation of P removal is mainly due to adsorption under the presence of amorphous and crystalline Fe/Al oxides and -hydroxides, aluminosilicates, which are associated with the soil mineral allophane (Parfitt 1989; Oh et al. 1999), or by precipitation reactions with Ca and Mg-rich materials (Vohla et al. 2011). As P-rich wastewater infiltrate through filters containing materials with high P sorption capacities, the phosphate anions are retained via forming complexes with the exposed ligand (-OH) on the surface forming strong bonds. Adsorption of P is considered to be a reversible process, with P desorption also occurring depending on the concentration gradient between the solution and solid phases. After P is adsorbed onto reactive surface sites of the solid phase, then stronger absorption or occlusion of P can also occur, which more permanently retains P and prevents desorption back into solution (Cornforth, n.d.). Both adsorption and absorption can occur simultaneously and can be difficult to distinguish without the use of sequential extraction methods (Dąbrowski 2001; Worch 2012). Therefore, both processes will hereafter be referred to collectively as 'sorption'. The next section covers the specifics of sorption reactions of soils and other inorganic sorbents.

2.4 Phosphorus sorption reactions of soils and other inorganic sorbents

In the review of Loganathan et al. (2014), sorption mechanisms are described as the following five processes:

i. ion exchange (electrostatic attraction resulting in outersphere surface complexation)
ii. ligand exchange (covalent bond formation forming inner sphere surface complexation)
iii. hydrogen bonding (dipole-dipole attractive force)
iv. surface precipitation (metal atoms on material surfaces precipitating with phosphate), and
v. diffusion (intraparticle sorption of phosphate within the micropores).

Sorption of P by inorganic sorbents consisting of Al/Fe oxy-hydroxides (metal oxides) or allophane (soil mineral) has been well documented in a number of studies, for instance Parfitt (1989 and 1990), Gustafsson (2001), and Arai and Sparks (2001). Under natural conditions, soils are made up of diverse constituents (inorganic and organic), therefore, the nature of the interactions within the soil system is complex, being influenced by the physio-chemical and biological dynamics of the soils (Berkheiser et al. 1980). Nonetheless, the basic fundamentals of P sorption reactions primarily involve inorganic constituents of the soil that give the soil its P retention characteristics. These inorganic constituents have an affinity for the phosphate anion, which under favourable conditions can form surface complexes with the anion (Kholoma et al. 2016).

The sorption reaction is also governed by the relative affinities of P anions for sorption. Inorganic P constituents present in wastewater, such as $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}, have high affinities for charged surfaces (Pigna and Violante 2003). In soils, inorganic P anions can be sorbed onto allophanic soil mineral constituents (and metal oxy-hydroxides) through inner-sphere surface complexation (Parfitt 1989; Haynes 2015), which result in the immobilisation of phosphate. This process involves three steps (Tchobanoglous and Burton 1991; Fulazzaky et al. 2013; Tchobanoglous et al. 2014):

i. phosphate ions in wastewater are transported to the mineral or sorbent – solution interface from the bulk solution (mobile phase) via advection and diffusion,
ii. at the diffuse layer, phosphate ions diffused into the micropores and sub-micropores of the soil grains reaching the reactive surface sites by long – range electrostatic forces (Thompson and Goyne 2012), 2012) where,
iii. sorption of phosphate ions occur as illustrated in Figure 2.1.

Sorption can be mainly categorised as either outersphere (Sposito 1984) or innersphere complexeation. Innersphere complexation involves strong, direct bonding between surface functional groups (OH- ligands) and phosphate anions (Apak 2002; Sparks 2003). While outersphere complexation involves weak, electrostatic interaction without sharing ligands (Hiemstra 2010)(Rietra et al. 2001). Phosphorus anions are known to form innersphere complexes with amorphous and crystalline metal oxy-hydroxides and aluminosilicates (Zhou and Haynes 2010) and the reaction is illustrated in Figure 2.1. The ligand exchange (exchange of surface OH^- group) occurs between phosphate anions and surface ligands (Yang et al. 2006) in which OH ligands (of P anions) are shared with one or more metal ions of the mineral or sorbent (Hiemstra 2010), forming complexes of phosphate ions with surface metal (Al/Fe) atoms (Parfitt 1978).

Inner-sphere surface complexation of P anions have an advantage when other potentially competing anions, such as sulphates, are also present in solution. Metal oxy-hydroxides (Al/Fe) or soil minerals present in soils partakes in numerous sorption reactions with many species; they are variable charge surface reactive sites which occasionally become hydroxylated (gain hydroxyl group) in water (Liu et al. 1998). These minerals are pH dependant, so at lower pH (i.e. acidic conditions) they are positively charged (Kaplan, 2003), attracting negatively charged phosphate and sulphate anions. The pH at point of zero charge of pH_{PZC} or pH when the net total particle charge is zero (Appel et al. 2003) is the determinant parameter of surface charge of a soil (Morais et al. 1976). Thus, the pH of soil is inversely proportional to soil surface charge. When the pH of soil is lower than pH_{PZC}, then the soil surface becomes positively charged and vice versa for alkaline conditions (Appel et al. 2003). The pH_{PZC} for Al-rich allophane (Al/Si ~2 or proto-imogolite (Levard et al. 2012) is 6 – 7 (Gustafsson 2001). Therefore, Allophanic soils in acidic conditions will exhibit higher P sorption rates than in alkaline conditions.

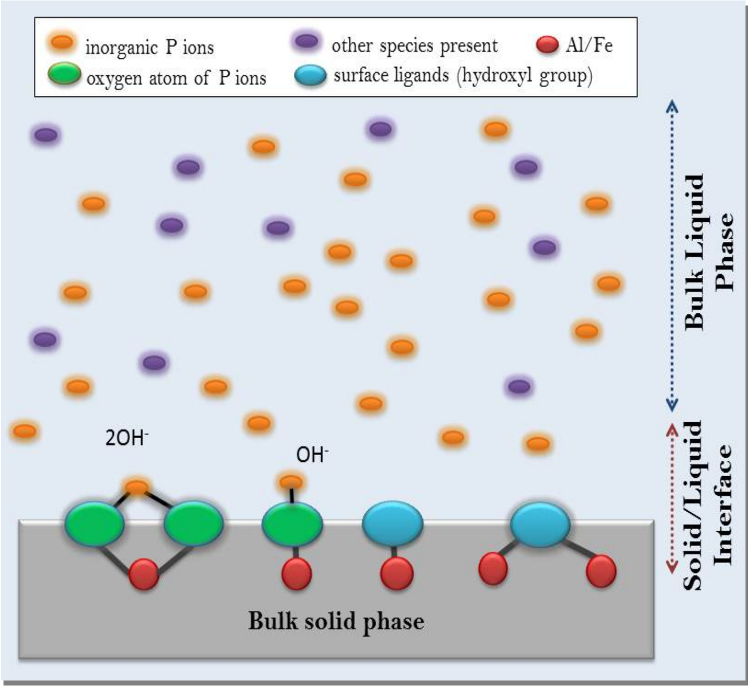

Figure 2.1 Illustration of inner-sphere surface complexation of phosphate ions and surface ligands (adapted from Hiemstra (2010) and Thompson and Goyne (2012)). When phosphate ions present in the aqueous phase comes into close proximity of soil-mineral surface, high sorption affinity of phosphate "attracts" the molecule to the active sites and binds the anion to surface, displacing OH^- and/or water molecules (Cornforth, n.d.).

2.5 Phosphorus sorption capacities of sorbents and their use as filter bed media

Phosphorus removal using chemically reactive materials has been considered as potentially suitable for small-scale treatment systems (Pratt et al. 2012). The use of sorbents can be incorporated into various types of treatment systems, such as in CWS and filter systems (Johansson Westholm 2006; Shilton et al. 2006; Vohla et al. 2011; Loganathan et al. 2014), substituting conventional filter media, such as sand or gravel (Hylander et al. 2006) that are ineffective at P removal (Haynes 2015). Sorption studies provide an assessment of the P removal capacity of potential sorbents. Table 2.2 presents examples of sorbents that had been assessed as potential filter material, along with their corresponding P sorption. The following section discusses the P removal capacities of examples of various types of sorbents from previous studies, which are grouped into by-product, synthetic sorbents or natural sorbents. The particular factors that influence P sorption and/or P removal and limitations of specific sorbents are also discussed.

2.5.1 Industrial by-product sorbents

Many studies have been dedicated to identifying and utilising industrial by-products (IBPs) as sorbents for wastewater treatment. A majority of IBPs studied are slags rich in Ca, Al and Fe oxides. These are waste materials from steel manufacturing or iron ore refining processes (Pratt et al. 2012). Slags have different characteristic depending on the manufacturing process and the type of ore used. Some examples of slags are basic oxygen steel furnace (BOF) slags, blast furnace slags (BFS), smelter slags and electric arc furnace (EAF) slags (Bowden et al. 2009). Many Ca and Al oxide-rich slags have been studied intensively as CWS materials (Johansson Westholm 2006) and as P sorbing material in filtration system. Generally, the dominant P removal mechanism of slags is through Ca phosphate precipitation. This is due to the high Ca content of slags (21 – 38% Ca (Zuo et al. 2018)) and alkaline conditions associated with high wastewater pH (Bowden et al. 2009; Barca et al. 2012) and the slags (Xu et al. 2006)). For instance, Xu et al. (2006) reported the pH of furnace slag used in their study to be 12.3. Shilton et al. (2006) used steel smelter slag as a sorbent in a full-scale filter beds to treat domestic wastewater. The filter beds removed 72% of the TP from the wastewater (average concentration 8.2 mg TP/L, hydraulic retention time (HRT) of ~3 days) for the first five years, after which removal markedly declined. The slag had an overall removal of 1.23 mg TP/g slag and the final P removal efficiency was 37%.

Barca et al. (2013) performed a two-year full-scale subsurface flow filters using EAF and BOF slags to remove P from CWS (HRT of 2 days). They found that the BOF slag filter showed higher P removal efficiency than the EAF slag filter. The BOF slag filter removed 62% of the wastewater inlet TP, achieving wastewater mean outlet TP concentrations of 3.5 mg P/L from a mean inlet TP concentration of 8.5 mg TP/L, while the EAF slag achieved an average outlet wastewater TP concentration of 4.7 mg TP/L. During the two-year span of the study, the BOF slag filter removed approximately 0.60 mg P/g slag and the EAF slag removed 0.32 mg P/g slag. Barca et al. (2013) suggested that the predominant P removal mechanism of slags was likely to be Ca phosphate precipitation, because the wastewaters from the filter outlet TP concentrations decreased with increasing wastewater pH. In a prior study by Barca et al. (2012), the slag-treated wastewater or P solution had the tendency to increase in pH, from a starting pH of 7 to a final pH range of 10.8 – 12.5 for the EAF and BOF treatments. One drawback of employing slag in filtration systems would be the high pH of wastewater that can be unfavourable to the receiving environments. In addition, presence of heavy metals, such as chromium (Cr), in slag materials are a major leaching concern as elevated Cr concentrations were associated with effluent pH ranges of 8 - 13 (Baciocchi et al. 2015). Therefore, the potential for disposing of slags to land may be limited by their heavy metal concentrations, which can be higher than the permitted standard (McDowell et al. 2004).

2.5.2 Manufactured or modified sorbents

Manufactured or modified sorbents are materials that have been engineered or altered specifically for enhanced P-sorption capacity. An example of manufactured sorbents are hydrous zirconium ion-exchange resins (O'Neal and Boyer 2013). Modified sorbents include light-weight aggregates, like heat-modified clay (Filtralite$^{\mathrm{TM}}$; Johansson Westholm, 2006) and modified zeolites

(Yang et al. 2014). The characteristics of P sorption capacities of some of the modified materials are similar to some naturally-occurring minerals, which are also discussed in the next section.

Filtralite^{TM} or light weight expanded clay aggregates is a commercial filter material for wastewater treatment from Norway (Suliman et al. 2006), which is characterised by its high capacity P sorption capacity (Ádám et al. 2007) and high pH (pH 12) (Kirjanova and Rimeika 2012). Heistad et al (2006) investigated the use of Filtralite^{TM} in a compact upflow saturated filter treating domestic wastewater from a single household. The filter's efficiency at reducing TP during the three years of operation was high, reducing the wastewater TP on average by 99%. The filters produced effluent TP concentrations of <0.1 mg P/L until the final two months, after which the effluent TP concentrations gradually increased to 0.2 mg P/L from a range of influent TP concentrations of 2 – 8 mg P/L. From their effluent pH monitoring, they found a decreasing trend in effluent pH from 12.8 (start of experiment) to 10 after three years of operation. The filter HRT and P sorption capacity was not reported here; however, in a lab-scale column study by Kirjanova and Rimeika (2012), the P sorption capacity of Filtralite^{TM} was 0.9 – 1.6 mg P/g Filtralite^{TM} (average synthetic wastewater concentration of 8.4 mg P/L) after 66 days of operation (until saturation). Adam et al. (2005) reported a P sorption capacity of up to 10 mg P/g Filtralite^{TM} from small-scale box experiments, operating at P solution concentration of 15 mg P/L for 150 days (saturation) and an HRT of 5 hours (Ádám et al. 2006). In another study, this material was reported to exhibit P sorption of up to 12 mg P/g sorbent (Vohla et al. 2011). Similar to slags, the primary P removal mechanism of Filtralite^{TM} is precipitation. Filtralite^{TM} has high Ca and Mg oxide contents, which react with water to form Ca and Mg hydroxides and later form Ca and Mg ions. These cations react with phosphate anions in wastewater to form precipitates of Ca and Mg

(Ádám et al. 2005). Wastewater treated with Filtralite^{TM} can also have a high pH, which may require further treatment prior to discharge, such as acid dosing. The manufacturing process of Filtralite^{TM} requires high energy input, which contributes to the high cost of the material (Ádám et al. 2007).

Modified sorbents that are engineered to enhance P sorption and selectivity for P have also been previously studied for use in wastewater treatment. These include anion exchange resins coated with high P retaining minerals that have been shown to increase the P sorption capacity of the ion exchange resin (Martin et al. 2009). For example, when polymeric ion-exchanger resin is coated with hydrated Fe^{3+} oxide (HFO) nanoparticles it has greater selectivity towards P anions (Sengupta and Pandit 2011) due to the high surface area of nano-sized Fe oxides (Loganathan et al. 2014). Martin et al. (2009) reported the overall P sorption capacity of HFO-bound hybrid anion exchanger (HAIX) columns to be 7.8 mg P/g sorbent (initial P solution concentration 15.2 mg P/L) to which the column capacity was used up after 1000 bed volumes. From a subsequent study, Sengupta and Pandit (2011) reported maximum P sorption capacity of this material using an isotherm study to be 23 mg P/g sorbent. The results of ion exchanger resin studies showed promising removal rates, however, they are prone to losing reactive surface sites via detachment or bleeding of the coated Fe oxide particles. Therefore, pilot and full-scale studies are required to allow a life cycle assessment of the material (Martin et al. 2009). In addition, the manufacturing cost for these modified sorbents is high, which can limit its use (Herron et al. 2016). Therefore, sorbents or materials that do not require elaborate modifications are preferable to be more affordable for use in full scale wastewater treatment systems.

2.5.3 Natural sorbents

Naturally-occurring P sorbents include Al, Fe or Ca- rich soils (Singh and Gilkes 1991), peat (Kõiv et al. 2009), and zeolites (Wang and Peng, 2010). The effectiveness of natural sorbents have been widely studied for their application in wastewater treatment and CWS. The first example of natural sorbent commonly associated with P removal is zeolite (Sakadevan and Bavor 1998; Johansson Westholm 2006; Vohla et al. 2011; Haynes 2015). Zeolite is a porous crystalline aluminosilicates (Haynes, 2015) with a high surface area of 200 – 700 m^2/g (Yates 1968; Nakano et al. 2001), which contributes to its sorption capacity (Wang and Peng 2010). Despite its high surface area, Sakadevan and Bavor (1998) showed that zeolites have relatively low P sorption capacities of 2.15 mg P/g zeolite. This is because natural zeolites have low affinity towards anions due to their net negative surface charge, which make them more suited to sorbing cations like ammonium (Loganathan et al. 2014; Wang and Peng 2010).

Another natural material evaluated for their P sorptive capacity is mineralised peat. Kõiv et al. (2009) conducted onsite subsurface filtration experiments treating landfill leachate (mean initial TP concentration of 3.4 mg P/L; range 2.5 – 5.2 mg P/L) for 12 months at a HRT of ~14 days. They found that the P sorption capacity of peat-filled filters was estimated to be only 0.081 mg P/g dry peat. The peat filter had shown good P removal efficiency for the first six months of operation with an average TP reduction of 63%, which declined over the following 6 months.

Bruch et al. (2011) used lava sand or zeolite-containing sand in a constructed wetland study to evaluate these materials' P removal efficiency. This involved installing lava sand filters at a constructed wetland site, used for treating sedimentation pond wastewater (initial TP concentration 5.6 mg P/L). The mean P removal efficiencies achieved after 1.6 years of operation were within the range of 70 – 92%, however, this removal was only equivalent to 0.13 – 0.23 mg TP/g sand. Other examples of natural sorbents investigated are shale and lake sediments. These materials exhibit relatively low P sorption capacities despite the high initial P concentrations used. Drizo et al. (1999) investigated suitability of several materials for constructed wetlands under long term exposure to high P concentrations (up to 42 mg P/L) and found that shale had the highest P sorption capacity of 0.73 mg P/g shale followed by bauxite (0.36 mg P/g bauxite). Jin et al. (2005) performed a P sorption experiment at initial P concentrations between 0 – 15 mg P/L and a reaction time of 10 min on two trophic lake sediments. They reported the P sorption capacities of 0.35 and 0.50 mg P/g sediment. These low P sorption capacities were likely influence both by the characteristics of the sediments and the short reaction time. Also, in many circumstances, these sediments act as P sinks, accumulating P which may influence further capacity of retain P (Sharpley et al. 2014).

Zeolite has been used in advanced filtration systems, known as the multi-soil-layering (MSL) systems, for the removal of nutrients and other wastewater contaminants. The MSL system has proven to be effective at removing P, N, COD, total suspended solids (TSS), and organics, with good hydraulic performance (Sato et al. 2005, 2019; Pattnaik et al. 2008; Latrach et al. 2018). However, the cost associated with aeration, addition of carbon source, such as sucrose, and enhancing the structure of the blocks, may not be a cost-effective solution to small and medium sized communities. The MSL system consists of several materials, for example, zeolites, charcoal, saw dust and soil, which may make it challenging to recycle as a soil amendment for plant growth.

Allophane is a common constituent in soils formed from moderately weathered volcanic tephra, such as found in Allophanic Soil (New Zealand Classification) also known as Andisol Soil (USDA Soil Taxonomy). Allophanic soils generally have relatively high P sorption capacities (i.e. Anion Storage Capacity, ASC) (Saunders 1965; Perrott 1977; Theng 1982). Allophanic soils occur in many parts of the world, but occur mostly in countries around the Pacific Ring of Fire, including Chile, Ecuador, Colombia, Mexico, the Pacific Northwest USA, Japan, Indonesia, a number of pacific islands countries including New Zealand. Allophane is a short-range order (poorly crystalline) hydrous aluminosilicates with varying Al/Si ratios, depending on the parent materials, degree of weathering including tephra origin or mineralogical composition (Wada and Harward 1974; Ryden and Syers 1975). For example, tephra collected from various locations in New Zealand exhibited differing short-range order Al contents ranging from 0.20 – 33.8 mg Al/g tephra (Ryden and Syers 1975) or up to 70 mg Al/g soil. This factor becomes a key determinant in identifying potential source of Allophanic soil for P removal. Allophane has high specific surface area and variable (pH-dependent) surface charge (Uehara 1985), which promotes P sorption. The surface area of allophane can range from 400 – 900 m^2/g (Parfitt and Hemni 1980).

In New Zealand, Allophanic soils are mostly found the central region of the North Island, being particularly concentrated around the Taranaki basin and in the southern Central Plateau (Lowe 2010). The high P sorption capacities of Allophanic soils have been demonstrated in several laboratory studies (Ryden and Syers 1975; Parfitt 1989; Pigna and Violante 2003). Parfitt (1989) compared the reactivity of natural allophane, goethite, and ferrihydrite, and found that allophane retained the highest amount of P (approximately 30 mg P/g mineral). This level of P retention is high compared to many of the P sorbing materials previously discussed. Ryden and Syers (1975) used laboratory experiments to assess the P sorption capacity of Allophanic soils from various sites in the North Island. The P adsorption capacity ranged from 0.8 - 4.85 mg P/g, from an initial P loading of 5 mg P/g soil. Ryden and Syers (1975) concluded that Allophanic soils formed from andesitic tephra and containing high levels of crystalline Fe oxides and short-range order Al (allophane) were able to retain higher amounts of P, compared to soils formed form rhyolitic tephra. These properties create reactive sites on soil or sediments for complexation reactions to occur (Parfitt, 1989).

Liesch (2010) investigated two types of Allophanic soils in laboratory column studies, the Okato subsoil from the Taranaki region and the Papakai subsoil from the Central Plateau. The experiment used a synthetic P influent solution containing 20.5 mg P/L and used HRT in the columns of ~3 hours. Phosphorus adsorption capacity of the Okato soil was a total of 8.0 mg P/g soil with an average removal 97% of the DRP added (Liesch, 2010). The Papakai soil had a P adsorption capacity of 4.0 mg P/g soil and it only removed 52% of the total P added to the columns over the duration of the study. Further laboratory column experiments were conducted on seven Allophanic subsoils, collected from the Taranaki region and Ruapehu District, using inorganic P solutions and town sewage wastewater at concentrations of 20 mg P/L and using HRT of 3 – 4 hours (Hanly et al. 2012). The results showed that the P adsorption capacity of soils varied widely, but both regions had soils with relatively high sorption capacities. One of the andesitic tephra soils from the Ruapehu District, had a P sorption capacity of 8.7 – 8.9 mg P/g tephra at 75% average removal efficiency, using both an inorganic P solution and town wastewater (Hanly et al., 2012). These studies demonstrated that some Allophanic subsoils in the central regions of the North Island of New Zealand have high P sorption capacities and, therefore, have potential as materials that could be used in P removal filters.

Table 2.2 Sorbents used for P removal and their P sorption capacities of various P sorbents

Sorbent	Origin	Sorption capacity (mg P/g sorbent)	Reference
		Natural	
Allophanic soil (Okato)	New Zealand	4.9	Ryden and Syers (1975)
Andisol soil	Italy	43.7	Pigna and Violante (2003)
Polonite	Poland	1.3	Renman and Renman (2010)
Granulated ferric hydroxide (GFH)	Germany	9.2 – 11	Genz et al. (2004)
		Manufactured/Modified	
Hybrid anion exchange resin (HAIX)	USA	7.7	Martin et al. (2009)
Magnetic (Fe_3O_4) nano-particles	Taiwan	0.17 – 2.4	Tu et al. (2015)
Electric arc furnace (EAF) steel slag	Canada	2.2	Drizo et al. (2006)
		Industrial by-product	
Acid mine drainage (AMD) sludge	USA	10	Sibrell and Tucker (2012)
Ferric and alum water treatment residuals (FARs)	China	3.5	Gao et al. (2013)
Acid mine drainage (AMD) sludge	New Zealand	0.52 (10 wt%)	Wang et al. (2013)
Coal fly ash		0.49 (10 wt%)	
Melter slag	New Zealand	1.23 (TP)	Shilton et al. (2013)

2.6 Factors affecting P removal by soil filters

A range of sorbents with varying P sorption capacities have previously been discussed, with Allophanic soils comparing well in terms of having high P removal capacities, even at relatively short HRTs of only a few hours. They also have the advantage of being low cost compared to manufactured or modified sorbents. However, there are factors in addition to P sorption capacity that can influence the effectiveness of soils when used as a filter substrate. For example, soil particle or aggregate size influences infiltration rates and the potential for the soil to cog when used to filter wastewater. Some of the other key factors influencing the performance of soil filters relate to characteristics of the wastewater, such as wastewater pH, ionic strength and DRP concentration. Some of these factors are discussed in the following sections.

2.6.1 Solution pH

Wastewater characteristics can greatly impact on the sorption capacity of Allophanic soils and overall filter performance and longevity. Phosphate ions are known to have a strong affinity for sorption sites, and are preferentially sorbed compared to a number of other anions typically found in wastewater, such as nitrate and sulphate (Zhou and Haynes 2010) (Hingston et al. 1971; Parfitt et al. 1982; Manning and Goldberg 1996; Pigna and Violante 2003). At very low pH, <3, presence of competing ions, particularly sulphate anions can strongly compete and inhibit sorption of phosphate (Geelhoed et al. 1997; Pigna and Violante 2003; Ishiguro and Makino 2011), but at pH 5 sulphate adsorption is negligible (Pigna and Violante 2003) and P sorption is usually assumed to be stronger than sulphate sorption (Barrow and Debnath 2015). In addition, as mentioned earlier in Section 2.3.2, the pH, or more specifically the pH at point of zero (pH_{PZC}), influences the surface charge of inorganic sorbents (Hamdi and Srasra 2012) and the charge on oxide surfaces is highly pH-dependent (Parfitt 1978). Surface charge of metal oxy-hydroxides become positive at pH below pH_{PZC} (Appel et al. 2003; Gao et al. 2013); the pH-dependent surface charges of amorphous aluminosilicates will exhibit positive charges at decreasing pH values (Perrott 1977) with pHPZC for allophane ranging from pH 7 or lower (Wada and Harward 1974).

Ryden and Syers (1975) demonstrated the effects of added H^+ (mmol/g) in batch sorption experiments on the P sorption capacities of Allophanic soils collected from various locations around the North Island of New Zealand. Their study demonstrated that P sorption capacities increased for the soils when H^+ was added to reduce pH of the solution, with the highest P sorption occurring at a final pH of 4.2 – 4.4 .

Figure 2.2 presents the phosphate sorption capacity of three Allophanic soils from South-Central Italy region at different solution pH levels (Pigna and Violante 2003). Here, all soils exhibited an increase in sorption capacities when solution pH was decreased from pH 8 to pH 4. For example, this reduction in solution pH increased the P sorption from approximately 3.9 to 4.8 mg P/g soil for Sample 7, from solution initial phosphate concentration of 0.007 M (equates to approximately 200 mg P/L), which was a 23% increase. Sample 7's high P sorption capacity increase was due to the soil's high allophane content (42%), while Sample 8 exhibited the lowest P sorption due to the soil's low allophane content. In addition, sulphate sorption (results not shown here) markedly decreased by between 50-100% as solution pH increased from 4 to 5.

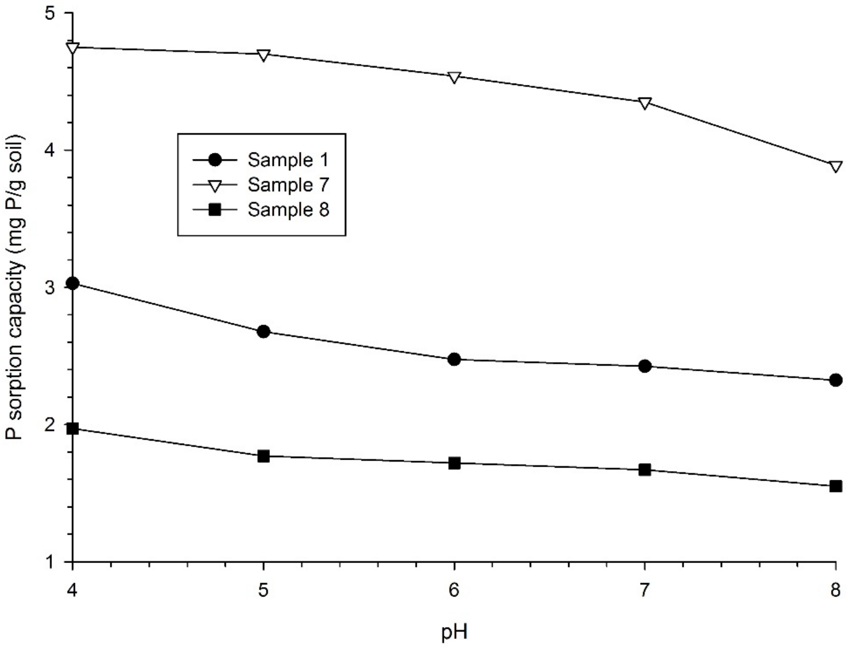

Figure 2.2 The effect of solution pH on P sorption capacities of three Andisol soil samples (adapted from Pigna and Violante (2003)).

2.6.2 Solution ionic strength and phosphorus concentration

It is well established that sorption processes of ions between a solution and sorption sites are dependent on ionic strength or the amount of ions present in solution and, therefore, have a direct effect on the sorption mechanism (Liu et al. 2011). Accordingly, when assessing the P removal performance of a material for suitability as filter media, it is important to test the material under conditions similar to real wastewater. High initial P concentrations, beyond the levels found in wastewater (>20 mg P/L) can give misleadingly high P sorption capacities (Drizo et al. 2002). For example, Sakadevan and Bavor (1998) reported a P sorption capacity of 44 mg P/g slag from an experiment using 8,000 mg P/L initial P concentration. Unnaturally high initial P concentrations can also lead to over-prediction of the material's longevity as shown in Figure 2.3. Thus, a more realistic P sorption capacity under initial P concentrations typically found in effluents (i.e. < 50 mg P/L) is likely to be < 2 mg P/g slag. Therefore, to reduce this over estimation P sorption experiments should be conducted within the range of typical wastewater P concentrations.

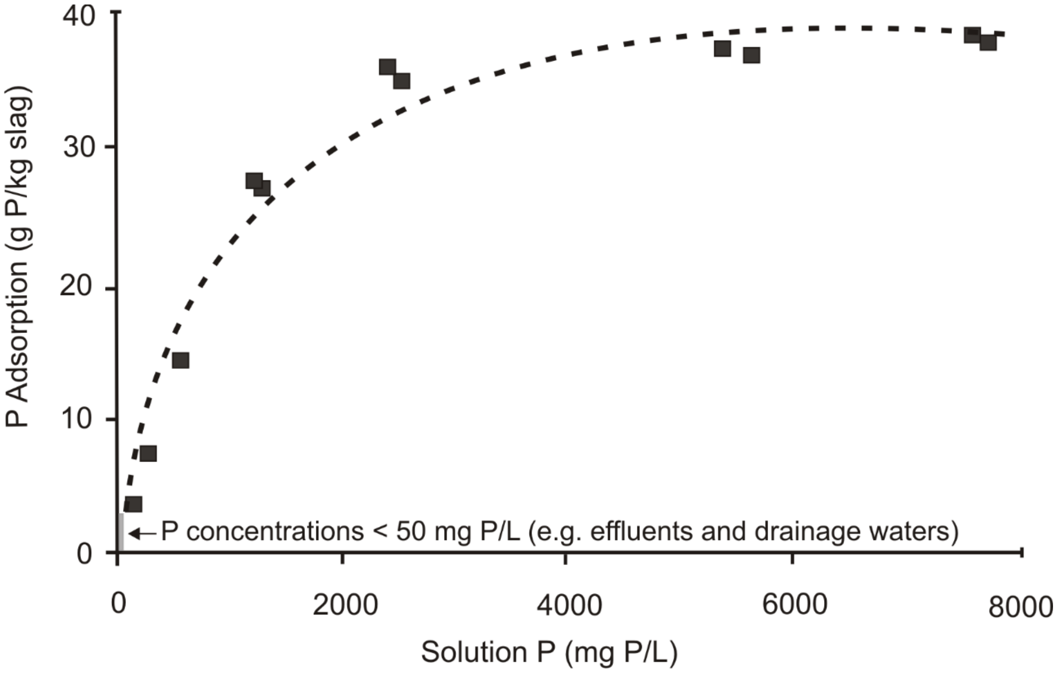

Figure 2.3 Relationship between equilibrium solution P (mg P/L) and adsorbed P (g/kg slag) for blast furnace slag (adapted from Sakadevan & Bavor, 1998).

2.6.3 Wastewater Infiltration of Soil Filters

Another important parameter that needs to be taken into consideration for soil filtration systems is HRT. This is the amount of time the solution, which contains inorganic P, remains in contact with the sorbent. There have been a limited number of studies investigating the effects of HRT on P sorption. For example, the P sorption capacities of acid mine drainage (AMD) sludge, a by-product of coal mine drainage neutralisation rich in Al/Fe hydroxides, investigated by Wei et al. (2008) showed a small improvement in P sorption, increasing from 18.5 to 19 mg P/g, when material contact time is increased from 0.5 to 1.5 hours. Zuo et al. (2018) proposed an optimal HRT for slag materials to be between 4 – 6 hours to achieve high P removal. From their prior batch experiment, using real wastewater, they obtained P removal efficiency of 99% in 4 hours, although initial P concentrations and P sorption capacity were not reported. Shilton et al. (2013) conducted a continuous-flow column experiment containing iron slags to determine P removal efficiencies under variable HRTs using synthetic and real wastewater. They found that the relationship between P removal efficiency and HRT is logarithmic. Using synthetic wastewater (initial P concentration of 7 mg P/L), P removal efficiencies increased with increasing HRT. Efficiencies increased from 20% to approximately 70% as HRTs increased from 17 – 250 hours. For real wastewater, with a P concentration of 3.5 mg P/L, efficiencies increased from 65 to 100% when HRTs increased from 10 to 100 hours. The results showed that the net P removal also depends on the effective contact time between phosphate ions and the reactive sorption sites. Similar logarithmic relationship was also observed in a prior study by Shilton et al. (2005), where efficiencies increased from 27% to 52% between HRTs of 12 to 72 hours in lab-scale column study (initial P concentration = 10 mg P/L). A field column study, which was also run continuously for 6 months at a fixed HRT of 12 hours, showed removal efficiency of 72% (unknown initial P concentration).

These studies showed that longer HRTs can result in improved P removal efficiency, however longer HRTs can also negatively affect filter operation. For example, clogging via chemical precipitation can occur in filters containing Ca-rich hydrated oil shale ash at HRT >12 hours (Liira and Kõiv 2009). In addition, physical clogging can occur from organic compounds and suspended solids from wastewater settling (Shilton et al. 2013). Moreover, increasing the HRT raises the cost of filter construction, as the longer the HRT the larger the filter is required to be to treat a given STP daily discharge volume.

Another co-dependent factor effecting wastewater infiltration of soil filtration system is the hydraulic loading rate (HLR). It is the factor that governs the pore velocity that also influences the surface reaction between phosphorus in wastewater and the material's reactive surface sites (Herrmann et al. 2013). A direct correlation between the optimal hydraulic parameter and P removal efficiency for a given material is a challenge to derive (Vohla et al. 2011). In many aspects, the HRT and HLR are closely related parameters where increasing HLR can result in shorter HRT and vice versa. In some soil filter systems, HRT is the key factor in both hydraulic and P removal efficiency of the system. For instance, in the MSL filters, Latrach et al. (2018) found that, using the same HLR of 0.2 m^3/m^2/day, the modified MSL filter, with higher mean HRT, performed better at removing P from domestic wastewater. The modified MSL filter had a mean removal of 98% at a HRT of 22.1 hr in comparison to the standard MSL filter, which achieved 80% removal at a HRT of 15.8 hr.

2.6.4 Sorbent particle size

Mass transfer is the key factor that influences the sorption of phosphate, removal of P primarily depends on the contact between wastewater and soil surfaces that can be obtained by having good infiltration rates (Sakadevan and Bavor, 1998). Insufficient infiltration caused by preferential flow or bypass flow may lower the overall P removal rates, as residence time is relatively short, resulting in an emergence of “non-flowing” zones. This can affect filter performance, such as lowered redox potential of the soil, resulting in desorption of P anions due to unstable iron hydroxides (Pratt and Shilton, 2010). With filtration systems there can be a trade-off between using a sorbent with a small particle size to increase the surface area of sorption sites, but not too small as there is insufficient wastewater infiltration rates or an increase in the risk of the filter clogging (Bishop et al. 1991; Vohla et al. 2011; Crittenden et al. 2012). The fine-grained materials can reduce the flow rate as the material becomes more compacted over time, causing lowered P sorption if bypass flow occurs (Kadlec and Knight 1996; Zhu et al. 1997; Drizo et al. 1999; Li et al. 2017). Also, clogging of the filtration system may occur, which will also be influenced by the suspended solids content of the wastewater (Vohla et al., 2011). Hence, it is important to determine the appropriate particle size for the quality of wastewater being treated. Secondary clogging from biological growths, occupying the void space, can also occur. For example, biofilms can adhere to soil surfaces, which cause reductions in the P sorption capacity of the studied material (Lahav and Green 2000).

Grain size distribution of filter material is used to determine clogging potential of the system which can limit efficiency of treatment. It was found that the effect of clogging can be reduced if coarser material is used to ensure good flow-through of wastewater (Suliman et al. 2006). For example, soils or other materials with the first 10% grain size distribution (d_{10}) between 0.3 and 1.0 mm are suitable for intermittent operation (operation with breaks in between run) while materials with d_{10} between 1 and 1.5 mm is suitable for continuous long-term operation for CWS (Suliman et al. 2006).

In a column study, a hydraulic conductivity test was carried out using Allophanic soil to determine its infiltration rate (Hanly et al. 2012). The test was conducted at a constant head of 20 cm for seven months in total. Initially the columns exhibited relatively high hydraulic conductivities of > 220 mm/hr. After continuously running for 120 days, the columns exhibit a constant rate of 80 – 100 mm/hr until the end of the experiment. The decline in infiltration over time is likely due, in part, to compaction of the soil over time. As this was assessed using water, rather than wastewater, it provides an estimate of the maximum potential infiltrations over time. However, actual infiltrations may be slower for wastewaters containing varying levels of suspended solids and/or biological materials, all of which may clog the filter over time. One aspect of improvement is to change the wastewater application method by, for instance, changing from down flow to upflow systems (Qi et al. 2013), or by using high quality wastewater that has been through a microfiltration system prior to treatment with soil.

2.7 Summary

Point-source discharges from municipal or industrial origin typically have high DRP concentrations, which contribute to the degradation of receiving water bodies. Wastewater treatment methods that involve chemical dosing to facilitate removal by precipitation of P or biological P removal such as the EBPR are common treatment methods. However, the high costs of these technologies may not be economically viable for small to medium sized communities. For instance, chemical dosing, in addition to on-going chemical requirement, generates sludge that requires proper disposal in landfills. For biological P removal, specific design and operation demand for highly skilled personnel and higher costs. Therefore, on alternative treatment technology is required to provide a sustainable option for small to medium-sized communities that is easy to operate and maintain.

Sorption technologies for P removal, although not an entirely new concept, has more recently focused on modified or manufactured materials. However, these materials are also cost prohibitive for wastewater treatment due to the large quantities required to be effective. The central North Island of New Zealand is abundant in Allophanic soils with high affinity for P. However, there has been minimal evaluations of these soils for use in wastewater treatment until relatively recently. In order to determine whether Allophanic soils have potential was a sorbent for removing DRP from wastewaters further research is required to evaluate their suitability. This includes the following aspects:

i. Determine the longevity of the Allophanic soil filters and P removal capacity and assess how these are influenced by key wastewater characteristics, such as pH.

ii. Assess the effectiveness of Allophanic soil filters at the pilot-scale, to better predict the performance and constraints of these systems at the full-scale.

iii. Assess the agronomic benefit (i.e. P fertiliser equivalent value) of the Allophanic soils after they have been treated with wastewater, to assess how much of the captured P can be re-used productively when applied to land.

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Chapter 3

Quarry soil sample collection and evaluation for phosphate sorption capacity

3.1 Introduction

The use of soil as a reactive filter media for removing dissolved reactive phosphorus (DRP) from wastewaters provides a potential alternative to more conventional treatment methods (i.e. chemical and biological P removal). The ability of soil filters to treat wastewaters to a standard that comply with regional wastewater discharge requirements will depend on the soil's P sorption capacity, which, in turn, influences the level of removal efficiency achieved by the filter system. The removal efficiency is the proportion of the wastewater DRP concentration that is reduced by the soil filter. Soils with higher P sorption capacities have the ability to maintain higher P removal efficiencies at shorter hydraulic retention times (HRT) and remove a greater quantity of P over the life of the filter. For a given volume of wastewater and DRP concentration, a soil with a higher P sorption capacity will require replacing less frequently, reducing the cost of supplying the soil.

If soil filters are to be a viable alternative wastewater treatment method, the cost of supplying the soil must be economically competitive. The cost of supply will include the costs of extraction, processing (e.g. sieving) and transport. These costs can vary greatly, with the variation largely due to differences in transport distance and associated costs. Once the distance between the soil source and the wastewater treatment plant exceeds ~100 km then the transport cost can be greater than 50% of the total supply cost (Hanly et al. 2011). Extraction costs can be minimised if the soil is sourced from an existing quarry and the soil is overburden above material that is used for other purposes (e.g. hard rock used for road construction).

In order for soil filters to be a viable option for wastewater treatment it will be important to identify soil sources that:

- have high P sorption capacities,
- are readily available for extraction,
- are in adequate supply, and
- are located within close proximity to the soil filter installation site.

The central North Island region has an abundance of Allophanic soils around the Taranaki basin and in the southern Central Plateau (Lowe 2010), which are known to have high P sorption capacities as assess by the P retention or Anions Storage Capacitity (ASC) test. A number of studies have assessed the P sorption capacities of Allophanic soils located in the central North Island (Ryden and Syers 1975; Perrott 1977; Hanly et al. 2008; Liesch 2010). Hanly et al. (2011, 2012) also identified suitable sites for potential soil extraction. These studies have shown that quarries in the Taranaki region and the Ruapehu district have potential to provide soil for filters within the lower central North Island (including the Taranaki region, Manawatu-Wanganui region and the lower Waikato region).

Some of the soils in the Waikato Region are also formed from volcanic tephra (Lowe, 2010), but with varying P sorption capacities, depending on the type of tephra that form the parent materials and the degree of weathering (Ryden and Syers 1975). If suitable soils could be located in the Waikato Region, then there is the potential to supply soil for filters in the Northern Waikato and Auckland regions. These regions represent a large population and a high intensity of manufacturing activity that contribute to large volumes of wastewater. In the Waikato Region alone, there are more than 80 point-source discharges with consents to discharge directly into the Waikato River, with approximately 30 of them being classified as large discharges, which include from municipal sewage treatment plants, meatworks, and a major dairy factory (Waikato Regional Council, n.d.).

The objective of this study was to conduct a soil survey of quarries in the Waikato region to identify quarries that have the potential to provide soils with high P sorption capacities for use in soil filters.

3.2 Materials and Methods

3.2.1 Soil collection locations

Five quarry sites in the Waikato Region were selected for soil sampling. Quarries were selected for sampling because they already have a resource consent to extract soil, the machinery for extraction is usually available on site and the soil is often an overburden with minimal commercial value. All of these factors contribute to reducing the cost of supplying these soils for use in filter systems. Soil samples were collected from Osterns Quarry, Andersons Quarry, Taotaoroa Quarry and Hyndsman Quarry and from Te Mata Quarry (Figure 3.1). The soil samples were taken at various depths, depending on changes in profile colour and/or texture, and the overall depth of the soil profile that could be accessed (Table 3.1). The Ohakune Quarry (OQ) soil is an Ohakune silt loam soil (10 – 60 cm soil depth), which was collected from a quarry near the Tohunga Junction, approximately 10 km from the township of Ohakune, in the Ruapehu District (-39.356960° S, 175.319576° E). This soil had previously been shown to have a high P sorption capacity (Hanly et al. 2011) and so it provided a useful comparison with the Waikato soils. It is also the same soil used in the soil column experiment (Chapter 4) and the pilot-scale filter studies (Chapter 5). All of the soil samples collected were evaluated for their P sorption capacities using the ASC test.

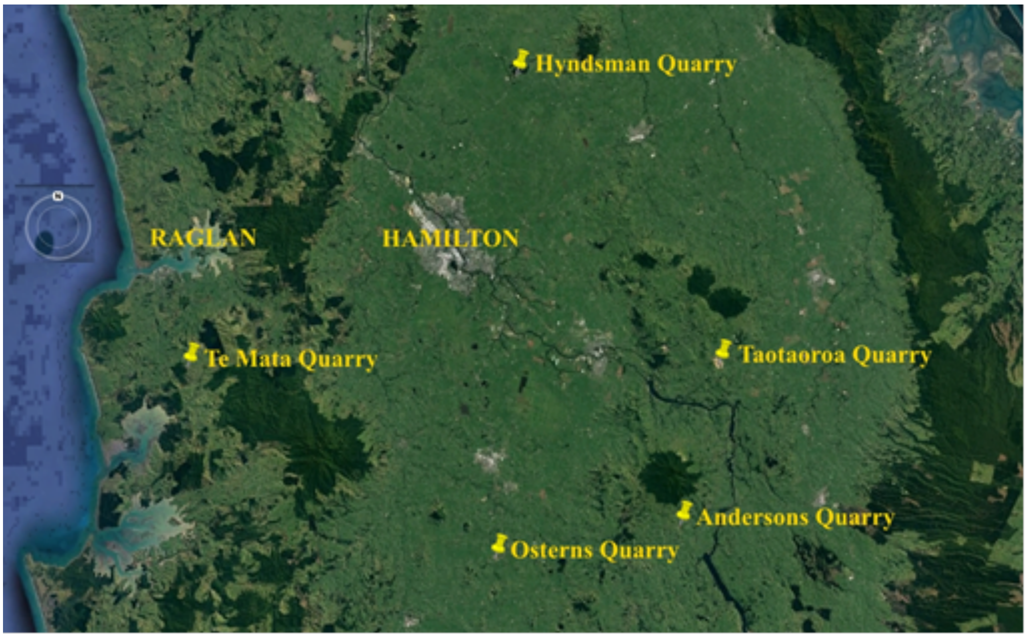

Figure 3.1 Location of the quarries were soil sample were collected (Source: Google Earth).

Table 3.1 Summary of soils sampled.

Soil sampling site	Location in the Waikato region	Soil sampling depths
Ostern Quarry	Otorohanga Road (38° 6'58.24"S; 175°20'2.38"E)	10 – 35 cm 35 – 110 cm
Andersons Quarry	Waimanu Road (38° 4'48.87"S; 175°35'6.25"E)	~10 – 50 cm
Taotaoroa Quarry	Taotaoroa Road (37°54'26.85"S; 175°38'17.77"E)	0 – 300 cm 300 – 600 cm 600 – 900 cm
Hyndsman Quarry	Morrinsville-Walton Road (37°35'26.03"S; 175°21'39.34"E)	0 – 50 cm
Te Mata Quarry (Profile 1, 2013 sampling)	Plateau Road (37°54'24.91"S; 174°54'26.34"E)	20 – 270 cm (50 cm increments)
Te Mata Quarry (Profile 2, 2014 sampling)	Plateau Road (37°54'24.91"S; 174°54'26.34"E)	25 – 625 cm (25 or 50 cm increments)

Figure 3.2 Example of a soil profile at the Te Mata Quarry.

3.2.2 Anion Storage Capacity test evaluation

Anion storage capacity (ASC) tests were performed on all soils to rank their potential P sorption capacities. Soil samples were air-dried and passed through a 2-mm sieve. In addition to the standard ASC test, which consists of using 5 g air-dried soil, modified ASC tests were also performed using 2 and 1 g of air-dried soil. The modified tests were better able to rank the P sorption capacity of soils that achieve values at or close to 100% P retention using the standard method.

Standard and modified ASC tests were performed by adding 5, 2 or 1 g of air-dried soil to 25 ml P solution (1000 mg P/L [0.032 M KH_2PO_4] in acetate buffer, pH 4.6) in polycarbonate centrifuge tubes. Soil samples were replicated three times for each ASC test, unless stated otherwise. The tubes were shaken for approximately 16 hours in an end-over-end shaker, and then the soil suspensions were centrifuged at 8000 rpm for 5 minutes. The supernatant was filtered with an ashless membrane filter (no. 41, MicroScience). After filtration, 2 ml of each supernatant was pipetted into a 50 ml volumetric flask, then 12.5 ml of Vanomolybdate reagent was added and the flask was made to volume (50 ml) with de-ionised water and was well mixed (Saunders, 1965). The solution was given 15 minutes to react. The amount of P remaining in solution was determined spectrophotometrically with a UV-Vis spectrophotometer (Philips PU8625 UV/Vis, Philips Scientific) at a wavelength of 420 nm via optical density (absorbance) measurements in a 1 cm absorbance cell, and calibrated using a standard curve. The results were expressed as the % P retained by the soil from the original 1000 mg P/L solution and retained by the soil.

3.3 Results and Discussion

3.3.1 Anion Storage Capacity test evaluation of soils

The standard ASC (5 g soil) test provides a relatively quick method to rank the ability of soil to retain P (Saunders 1965). The OQ soil achieved an ASC value of 100%, using the standard test, meaning that all of the P was removed from the 25 ml of 1000 mg P/L. Because all the P was removed from solution, this test was not able to show the total removal capacity of the soil. Of the five Waikato soils evaluated, the Ostern, Andersons, Taotaoroa, and Hyndsman Quarries had low to medium ASC test values ranging from 28.4 - 64.4% (Table 3.2). These levels equate to removals of 1.4 - 3.2 mg P/g soil from solution. In contrast, soil from all depths at the Te Mata Quarry (TQ) achieved high P retention values of 99 - 100%, using the standard ASC test. Therefore, of the Waikato quarry soils tested only the TQ soil showed an ability to retain P at levels comparable to the OQ soil and, therefore, this was the only soil collected from the Waikato quarries that was also evaluated using the modified ASC tests.

Table 3.2 The ASC test values for the five Waikato soils and Ohakune soil using 5 g soil (standard test).

Soil sampling site	Soil sampling depths	ASC (% P retention)	P sorbed (mg P/g soil)
Ostern Quarry	10 – 35 cm	39.2	1.96
	35 – 110 cm	24.7	1.24
Anderson's Quarry	1 soil profile	64.4	3.22
Taotaoroa Quarry	0 – 300 cm	33.6	1.68
	300 – 600 cm	33.0	1.65
	600 – 900 cm	46.6	2.33
Hyndsman Quarry	0 – 50 cm	46.6	2.33
Te Mata Quarry (TQ) (Profile 1)	All soil depths (20 – 270 cm)	99 - 100	4.95 - 5.00
Ohakune Quarry (OQ)	10 – 60 cm	100	5.00

The modified ASC tests were able to better discriminate between the P retention values of the soils from different depths at TQ (Figure 3.3). While there was some variation in P retention with depth for the TQ Profile 1 soil, overall values were high. All of the soil samples, apart from the 20 - 70 cm depth, had values similar to or greater than the OQ soil. The TQ (170 - 220 cm) and TQ (220 - 270 cm) soil depths ranked the highest with P retentions of 99 - 100% for both soils using the 2 g soil test, and 89% and 91% for the 1 g soil test, respectively. In comparison, the OQ soil exhibited P retention values of 91% for the 2 g soil test and 70% for the 1 g soil test. TQ soil from other depths in Profile 1 had P retention values ranging from 89 - 95% for the 2 g soil test and 61 - 76% for the 1 g soil test.

For the 2 g soil ASC test, the quantities of P sorbed were similar for the soils tested, ranging from 11.1 - 12.2 mg P/g soil. For the 1 g soil test, there was a greater range in P sorbed values between the soils. The two TQ soils with the highest amount of P sorbed, 1.70 - 2.20 m and 2.20 - 2.70 m soil depths, achieved 22.0 and 22.4 mg P/g soil, respectively. In comparison, the OQ soil sorbed a total of 17.3 mg P/ g soil (Figure 3.3).

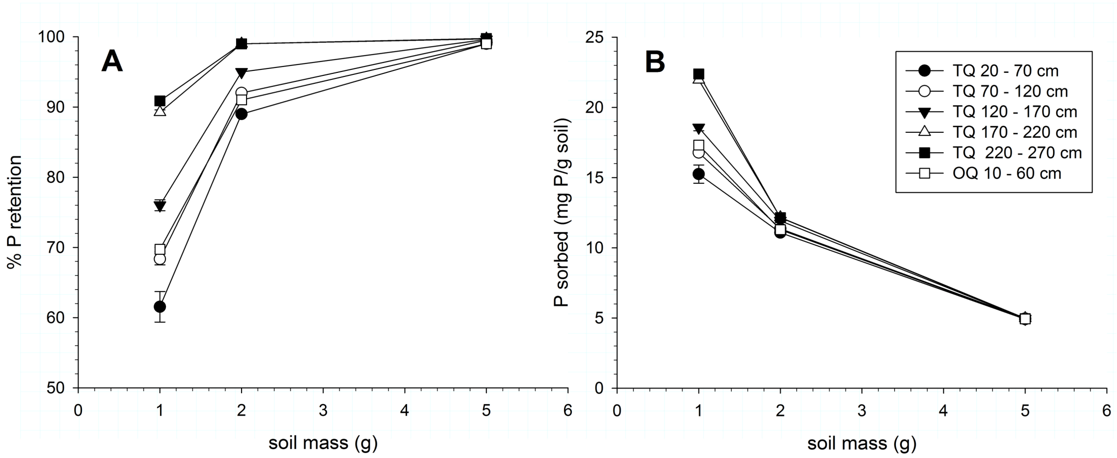

Figure 3.3 Anion Storage Capacity (1, 2 & 5 g soil) test values (A) and the quantity of P sorbed (B) for the Te Mata Quarry (TQ, Profile 1, 2013 sampling) and Ohakune Quarry (OQ) soils.

Due to the high ASC values obtained for the first TQ soil profile to a depth of 2.70 m, a further soil sampling of a deeper soil profile (Profile 2) was conducted at the TQ on the 4th of December 2014. At this later sampling time, the soil profile was sampled to a total depth of 6.25 m (25 - 625 cm) and analysed using the modified (1 g soil) ASC test. The ASC values were compared with the values from the first TQ soil profile (Profile 1) in Figure 3.4. The modified (1 g soil) ASC test values ranged from 47 - 78% for the second TQ soil profile. All soil depths, except the 1.25 - 1.75 m soil depth, had values >58% P retention (modified 1 g soil test), which indicate a high P retention capacity for the majority of the 6 m soil profile. In comparison, the range of values for Profile 1 sampling was 62 – 91%. Apart from the 1.25 - 1.75 m soil depth, the majority of the second TQ soil profile had values similar to the first TQ soil profile at 25 - 125 cm soil depths. Overall, the results of both samplings show that there is a deep soil layer, to at least 600 cm, at the Te Mata Quarry with a high capacity to sorb P. Therefore, this quarry has potential as a source of soil for use in P removal filters in the Waikato region and so warrants further evaluation.

The high standard ASC test values of the TQ and OQ soils were attributed to their high allophane contents of approximately 49% (Chapter 4, Section 4.2). The TQ soil was collected from beneath the Otorohonga silt loam soil from a quarry near Te Mata in the Waikato Region (-37.590025° S, 175.360842°E). The TQ and OQ soils are classified as Typic Orthic Allophanic Soil (NZ Soil Classification; Hewitt 2010) or Andisol Soil (USDA soil taxonomy), formed from andesitic tephra ash (Sparling et al. 2000). As discussed in the literature review, allophane content is closely related to the phosphorus retention properties of soil. It is a clay-sized short-range order mineral containing silica, alumina and water molecules (Parfitt, 1990). Allophane's reactivity is partly attributed to its large specific surface area and the amount of measured short-range order Al. Ryden and Syer (1975) demonstrated that the Allophanic soils they tested sorbed >80% of the added P (P added was 5 mg P/g soil). In another study, by Yuan and Wu (2007), an allophane nanoclay removed 70% of initial P in real effluent simulation, reducing P concentration from 14.2 mg P/L to 4.2 mg P/L. The high P retention capacity of the allophane nanoclay was also attributed to the high concentration of active Al (11.2%).

In the current study, the short-range order Al content of the OQ soil was approximately 7.1% active Al, whereas, the TQ soil (Profile 1; depth profile of 220 – 270 cm) contained 13.6% Al. Therefore, the greater P retention exhibited by the TQ soil (profile 1) in the modified 1 g soil ASC test, reflects the higher

Al content and, thus, higher allophane content. The results from the ASC tests provide a good indication of the soil's suitability as P removal material, which is influenced by the amount of allophane present.

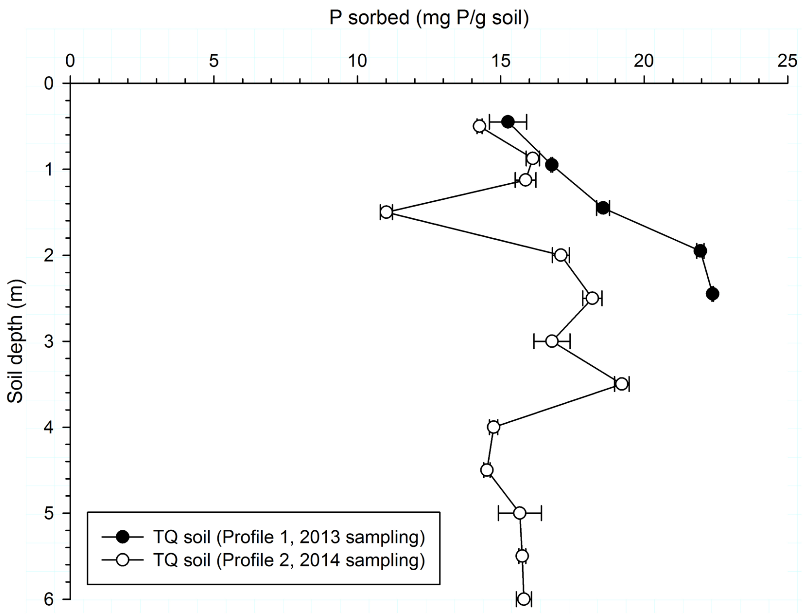

Figure 3.4 The average Anion Storage Capacity (modified 1 g soil) test values for the two TQ soil profiles.

3.4 Conclusions

The ASC test provided an effective means of ranking the soils in terms of their relative P sorption capacity and identified a quarry that may have potential to supply soil with a high P sorption capacity. In particular, the modified ASC tests (2 g and 1 g soil) were effective methods for ranking soils that have high retention values using the standard test. The ASC test results identified that of the five Waikato quarry sites sample, only soils from the TQ in the Waikato region had high P sorption capacities. At this quarry, the majority of soil depths had medium to high values using the modified ASC (1 g soil) test for the two soil profiles tested up a depth of 600 cm. Further evaluation of this soil's suitability as a medium for soil filters to remove DRP from wastewaters is required. The TQ soil depth exhibiting the highest ASC value (Profile 1, 220 - 270 cm) were further evaluated in the long-term column study and the results were presented in Chapter 4.

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Chapter 4

Effects of acid dosing dairy processing wastewater on phosphorus removal using Allophanic soil filtration

4.1 Introduction

Phosphorus is present in many forms in wastewater (total, organic, and inorganic) and the different forms correspond to different mechanisms to control the input of P in surface waters. The primary mechanism that is considered as most effective is to limit the concentrations of plant available dissolved reactive phosphorus (DRP) (Roygard et al. 2012). Accordingly, reducing the DRP load from wastewater discharges at critical times of the year will help improve water quality (Withers et al. 2011).

In Chapter 3, ASC tests (standard and modified) identified an Allophanic soil in the Waikato region to have a high P sorption capacities. Phosphorus adsorption isotherms (e.g. Freundlich isotherm) of allophane has been investigated extensively in other studies (Bache and Williams 1971; Parfitt 1989; Yuan and Wu 2007). These isotherms, similarly to ASC tests, provide an estimation of the degree of saturation of sorption sites and so they are useful in identifying new sorbents. However, they cannot accurately quantify the P removal efficiency achieved by sorbents under field conditions. This is because short-term tests often use P solution concentrations well above the concentration expected in actual wastewaters (Beck et al. 1999; Yuan and Wu 2007). For example, isotherms evaluations can involve agitation of a material in suspension with artificial P solutions of P concentrations ranging from 0 –

100 mg P/L (Nair et al. 1984). This range of initial P concentrations falls outside the typical P concentrations found in wastewater. Moreover artificial P solutions do not have the same characteristics as real wastewater, such as hydraulics and competing ions (Hedström 2006). As a result, there is the potential to overstate the P removal capacity (Brand-Klibanski et al. 2007). Consequently, the corresponding P sorption capacities obtained from rapid shaking experiments cannot be interpreted to field-scale operations (Hedström 2006). Therefore, the evaluation of soils for wastewater treatment should ideally be assessed with solution P concentrations more typical of pre-treated wastewaters (i.e. <25 mg P/L) (Tchobanoglous et al. 2014).

Column studies are useful at providing more realistic approach to predicting soil filters performance and life span. A previous continuous soil column study by Liesch (2010) using synthetic P solution demonstrated that P sorption capacity of the Allophanic soils was as high as 8.0 mg P/kg (52 – 97 % overall P removal efficiency from a 20.5 mg P/L initial P solution). However, the experimental design did not sufficiently replicate field conditions as the length of study was short (52 days) and real wastewater was not used. In addition to solution P concentration, there are other characteristics of wastewater that can also influence the retention of P by soils. One influential wastewater characteristic is pH because the specific sorption sites for P in soils are pH dependent. This is attributed to the tendency of the surface hydrous oxides of iron or aluminium to gain or lose H^+ when in contact with aqueous solution at differing pH levels, contributing to the surface charge of the oxides and P sorption capacity (Barrow and Debnath 2015). The standard test for P retention in New Zealand soils is a rapid method to determine maximum P sorption capacity of soils and it is performed at a low pH of 4.6 (Saunders 1965). Ryden and Syers (1975) evaluated the effect of acidity (in terms of amount of H^+ in mmole added per g of sample) and found that maximum P sorption occurred at pH values of 4.4 for an Allophanic soil from Taranaki region. In comparison to these evaluations, many wastewaters have alkaline pH, typically greater than pH 8. Therefore, lowering the pH of wastewaters is expected to improve the P removal efficiency of Allophanic soil filters (Ryden and Syers 1975). Another influential wastewater characteristic is the chemical oxygen demand (COD). For example, phosphate desorption in soils can be caused by iron oxide reductive dissolution as a result of microbial reduction processes in anaerobic conditions (Hutchison and Hesterberg 2004). To minimise the potential for microbial reduction, it is preferable to pre-treat wastewaters to achieve low levels of COD prior soil treatment.

The objective of this study was to quantify the effect of adjusting the pH of a dairy processing wastewater, using two types of acid, on the efficiency of P removal by two different Allophanic soils.

4.2 Materials and methods

A laboratory soil column experiment was conducted to investigate the effect of wastewater pH and the type of acid used for adjusting wastewater pH on the P sorption capacities of two Allophanic soils sourced from quarries in the central North Island of New Zealand. The first soil was the OQ soil (Ruapehua District) and the second soil was the TQ soil (Waikato Region) with allophane contents of approximately 49%. Allophane content was determined by oxalate extraction of Al and Si and pyrophosphate extraction of Al (Blakemore et al. 1981; Parfitt and Wilson 1985). The soils have a pH (1:2.5 H_2O) of approximately 6.2. The soils were collected from different depths because the objective was to use the soil with the highest ASC at each location, which were present in the soil profiles at different depths. The soils were air-dried and sieved through a 2 mm sieve. The wastewater used in this experiment was supplied by Fonterra's Te Rapa dairy processing plant, Hamilton, New Zealand. The wastewater was collected from the final stage of the wastewater treatment process, following clarifier treatment, and had a low COD of typically <50 mg/L.

The soil columns were constructed by placing soil into polypropylene syringes (60 ml internal volume, Monoject), with dimensions of 2.7 cm diameter and 13 cm height (9 cm soil height). The bottom of each syringe was lined with plastic mesh to contain the soil. On average, 39.4 g air-dried OQ soil (equivalent to 34 g of oven-dried OQ soil) or 52.2 g air-dried TQ soil (equivalent to 41.0 g of oven-dried TQ soil) were packed into the syringes to provide ~50 ml soil columns. There were eight soil columns containing OQ soil and two columns containing TQ soil.

The acids used to adjust wastewater pH were hydrochloric acid (HCl) and sulphuric acid (H_2SO_4). These two acids were selected because they are both commonly used for pH adjustment in wastewater treatment systems. Four different wastewater influent treatments were formulated using the Fonterra's Te Rapa wastewater treatment plant (WTP) wastewater:

i. Treatment 1 (T1): wastewater without acid treatment (average pH of 8.2),
ii. Treatment 2 (T2): wastewater pH adjusted to pH 5.5 with HCl,
iii. Treatment 3 (T3): wastewater pH adjusted to pH 6.5 with HCl, and
iv. Treatment 4 (T4): wastewater pH adjusted to pH 6.5 with H_2SO_4

The OQ soil received all four wastewater treatments and the TQ soil only received the T3 treatment. The pH value of 6.5 was selected as a compromise between the pH levels considered optimum for P sorption (~pH 4.6) and levels sufficiently close to a neutral pH to allow discharge to natural surface waters. The lower pH of 5.5 was selected to determine the additional benefit of further reducing pH on P sorption. This provided a total of five wastewater/soil combination treatments, which were each replicated twice. The requirement for ongoing supplies of wastewater to be delivered from Fonterra's Te Rapa dairy processing plant, limited the volumes of wastewater that could practically be used and, therefore, this was a determinant in the number of treatment replicates used. Individual batches of wastewater were collected in several 20 L containers, which were stored at 4°C. A detailed description of Fonterra's Te Rapa WTP wastewater is provided in Chapter 5.

Wastewater was pumped from reservoirs onto the soil columns at an average rate of 0.175 ml/min per column, which provided a hydraulic retention time (HRT) of ~3 hours. This HRT was based on the results of a previous similar study (Liesch 2010). This brings the hydraulic loading rate of the column to be approximately 0.44 m^3/m^2/day or 18 mm/hr. Column filtrates (hereafter referred to as 'post-filter wastewater') were collected in 2 L containers, which were covered with aluminium foil to minimise light entry. Column pre- and post-filter wastewater samples were initially collected at intervals of 5 hrs, 1, 2, 5, and 7 days after the start of the experiment and then weekly after the first week of operation. Each of the pre- and post-filter wastewater samples were analysed for pH and were passed through a 0.45 µm cellulose-nitrate membrane filter (Millipore) before DRP analysis. The DRP concentrations (mg P/L) were measured following the methods of Murphy and Riley (1962), using an automated continuous segmented flow autoanalyzer (Technicon). The DRP removal capacities of the soil columns (expressed as the quantity of P removed in mg P/g oven-dried soil) were determined using a mass balance approach, which involved calculating the difference between the DRP added to each soil column filter, in the pre-filter wastewater, and the DRP remaining in post-filter wastewater at each sampling time. The results are expressed on an oven-dried soil weight basis because the air-dried samples of the two different soils used in the study had differing initial moisture contents.

The number of days that the wastewater was added to the columns to achieve a similar application of P (~13.3 mg P/g oven-dry soil) across all treatments, ranged from 190 – 208 days; however, the total period of the study was longer due to pauses in operation. The wastewater flow to the columns was stopped at various times mainly due to gaps in the supply of wastewater from the processing plant.

Due to relatively low wastewater DRP concentrations (range 0.17 – 6.7 mg P/L) during the initial stage of the experiment, a P solution (containing potassium dihydrogen phosphate; KH_2PO_4) was added to the wastewater after 80 days of operation in order to ensure the experiment could be completed within a practicable period of time. The aim of this P addition was to achieve concentrations of 15 – 20 mg P/L (Figure 4.1, A-D), which is at the higher end of the typical DRP concentration range of wastewaters discharged to surface waters. Although using higher P concentrations is expected to achieve higher P removal (Brand-Klibanski et al. 2007), the P concentrations used were still representative of levels that could be expected in pre-treated wastewaters (i.e. <25 mg P/L). The observed step changes in influent wastewater DRP concentrations at various times were due to the range of wastewater concentrations supplied in different batches of wastewater from the processing plant, which after 80 days of operation also included the P added as KH_2PO_4.

Prior to the column study, all soils were analysed using ASC tests (Saunders 1965) to rank their P sorption capacities. Soil samples were air-dried and passed through a 2 mm sieve. In addition to the standard ASC test, which consists of using 5 g air-dried soil, a modified ASC tests was also performed using 2 g of air-dried soil. The modified tests were performed to improve comparisons between soils that achieved ASC values of 100% using the standard method.

4.3 Statistical analysis

The results were evaluated using analysis of variance (ANOVA) to identify any significant differences between treatments. Pairwise Multiple Comparisons were performed between each treatment using SigmaPlot graphing and data analysis tool ($P<0.05$).

4.4 Results and discussion

All post-filter wastewater treatments showed low DRP concentrations of <0.1 mg P/L for up to 90 days of operation (Figure 1, A-D). For this initial period, the overall average P removal efficiency for all treatments was >98%. The

T1(OQ) treatment (no acid treatment) started to exhibit increases in post-filter wastewater DRP concentrations after 90 days, which was approximately 10 days after the pre-filter wastewater DRP concentration was increased using the added P solution. The pH adjusted wastewater treatments exhibited increases in post-filter wastewater DRP concentrations after about 120 days of operation. For the OQ soil columns, the T2(OQ) treatment (wastewater adjusted to pH 5.5 with HCl) maintained the lowest post-filter DRP concentrations over the duration of the study. The pH of 5.5 is likely to have increased the reactivity of the soil's specific P sorption sites, compared to the higher wastewater pH treatments.

The post-filter DRP concentrations for the T3 wastewater treatment were lower at most sampling times for the TQ soil compared to the OQ soil, which is likely due to differences in the P sorption capacity of these two soils. Both soils achieved values of 100% using the standard ASC test. With the modified (2 g soil) ASC test, the TQ soil had a test value of 94.9% compared to 90.1% for the OQ soil. This difference, while small, supports that the TQ soil had a higher P sorption capacity.

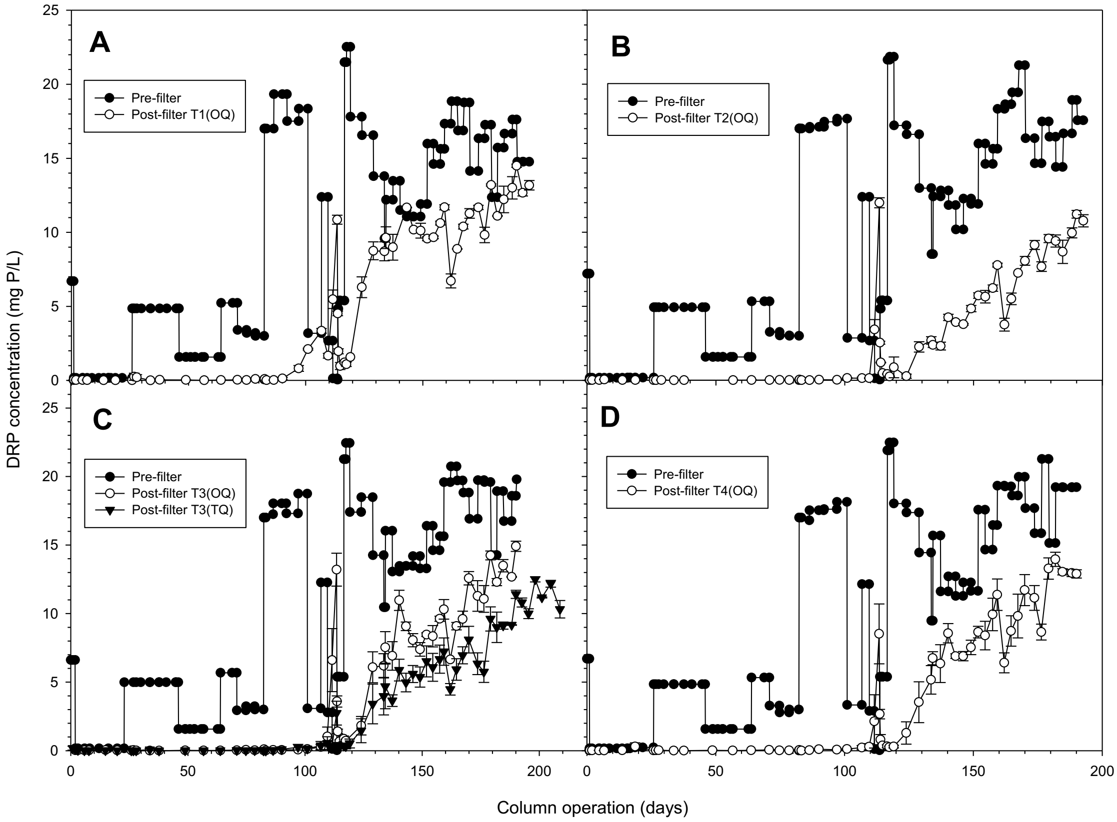

Figure 4.1 Pre- and post-filter wastewater DRP concentrations for each wastewater/soil combination treatment. A) T1(OQ) – without acid addition; B) T2(OQ) – adjusted to pH 5.5 with HCl; C) T3(OQ) and T3(TQ) – adjusted to pH 6.5 with HCl; D) T4(OQ) – adjusted to pH 6.5 with H_2SO_4. OQ represents Ohakune Quarry soil and TQ represents Te Mata Quarry soil. The error bars represent the standard error of the means (where error bars are not visible, symbols are larger than error bars).

At about 110 days after commencement of the experiment, all treatments exhibited a sudden, but short lived, spike in post-filter wastewater DRP concentrations. At this time, a pre-filter solution with a very low P content and ionic strength was inadvertently used, and this is likely to have resulted in P desorption from the soil columns causing the temporary elevations in post-filter wastewater P concentrations. This observation highlights the potential risk of increasing P losses from soil filters during periods when the wastewater has a low P concentration and ionic strength. Solution ionic strength is an important parameter in P sorption, with very low initial P concentrations also having the tendency cause the release of sorbed P (Yang et al. 2014; Tu et al. 2015). Further evaluation needs to be under taken to determine the extent to which P desorption can be used as a method of regenerating the P sorption capacity of the soil used in the present study.

The quantity of DRP removed from each wastewater treatment is compared at a similar quantity of P added, which was 13.3 mg P/g oven-dried soil on average (Table 4.1). At this level of P added from wastewater, the T1(OQ) treatment removed a total of 6.5 mg P/g oven-dried soil, which provided an average P removal efficiency of 49% (Table 4.1). Overall, acid dosing improved the effectiveness of P removal by the soil columns, with a trend of increasing DRP removal capacity with decreasing wastewater pH. The T2(OQ) and T3(TQ) treatments, showed significant increases in DRP removal compared to the T1(OQ) treatment.

The lower pH of the T2(OQ) treatment achieved a removal of 9.4 mg P/g oven-dried soil, at an average removal efficiency 71%. This was a 44.6% increase in DRP removal compared to the soil columns receiving wastewater without acid treatment. As previously discussed, the lower pH would have contributed to greater reactivity of the P sorption sites in the OQ soil (Hanly et al. 2013), which is corroborated in other studies (Ryden and Syers 1975; Pigna and Violante 2003). The T3(TQ) treatment resulted in a total DRP removal of 9.1 mg P/ g oven-dried soil, at an average removal efficiency of 68%. This was a 40% increase in removal capacity compared to the soil columns receiving wastewater without acid treatment. Although the quantity of DRP removed was higher for the T3(TQ) treatment compared to the T3(OQ) treatment, the difference was not large enough to be statistically significant.

These results compare favourably to those obtained in another column study using an Allophanic soil from the Taranaki region, New Zealand, of 8 g P/kg soil removed by the soil from a 20.5 mg P/L solution at HRT of 3 hr and HLR of 0.86 m^3/m^2/day or 36 mm/hr (Liesch 2010). Bowden et al. (Bowden et al. 2009) also achieved a similar level of P removal with basic oxygen steel slag of 8.39 g P/kg slag, using a column experiment. However, the solution P concentrations ranged from 100 – 300 mg P/L, which was well above the levels typically measured in wastewaters. Harouiya et al. (2011) conducted column studies to evaluate P removal capacity of apatite, a material rich in calcium, using synthetic P solutions with more realistic P concentrations ranging from 1 – 16 mg P/L, and achieved final P removal rates of 10 – 13.9 g P/kg apatite at HLR of 0.8 - 1.6 m^3/m^2/day (i.e. 33 - 67 mm/hr) and a hydraulic residence time of 3.3 hr. Although this apatite performed better than the Allophanic soil used in the current study, at similar rates of HRT and HLR, the availability of apatite is more limited, making it a less viable option for use in soil filters.

The T4(OQ) treatment, which received wastewater adjusted to pH 6.5 with H_2SO_4, achieved an estimated DRP removal of 8.7 mg P/g oven-dried soil, with an average P removal efficiency of 65%. This treatment had a higher DRP removal compared to the T3(OQ) treatment (8.0 mg P/g oven-dried soil), which received wastewater adjusted to pH 6.5 with HCl. However, the difference between these treatments was not large enough to be statistically significant. Therefore, choice of acid type (HCl versus H_2SO_4) is unlikely to be an important determinant of DRP removal effectiveness of soil filters.

Table 4.1 Total DRP removed from wastewater treatments by the soil columns (ranked from lowest to highest).

Treatments	DRP removed* (mg P/g oven-dried soil)	Average DRP removal efficiency (%)
T1(OQ) – pH 8.2 (no acid)	6.5^{a}	49
T3(OQ) – pH 6.5 (HCl)	8.0^{a,b}	60
T4(OQ) – pH 6.5 (H_2SO_4)	8.7^{a,b}	65
T3(TQ) – pH 6.5 (HCl)	9.1^{b}	68
T2(OQ) – pH 5.5 (HCl)	9.4^{b}	71

* From an average of 13.3 mg P/g oven-dried soil added in wastewater. The subsets ($\alpha = 0.05$) a and b represent the statistical significant difference between the treatments. The means were compared using Pairwise Multiple Comparison Procedure (Holm-Sidak method) at P = 0.05.

It is also useful to compare the treatments in terms of the quantity of DRP removal achieved at the same average removal efficiency (Figure 4.2, A-D). For this comparison, an average removal efficiency of 75% was used. All of the pH adjusted wastewater treatments removed significantly more DRP at an average of 75% removal efficiency compared with the wastewater treatment without acid, which removed only 4.5 mg P/g oven-dried at the same removal efficiency. In comparison, the T2(OQ) and T3(TQ) exhibited the highest cumulative DRP removals of 8.9 and 8.0 mg P/g oven-dried soil, respectively. At the same removal efficiency, the T3(OQ) treatment removed 5.8 mg P/g oven-dried soil and the T4(OQ) treatment removed 6.9 mg P/g oven-dried soil. The difference between T3(TQ) and T3(OQ) was not statistically significant.

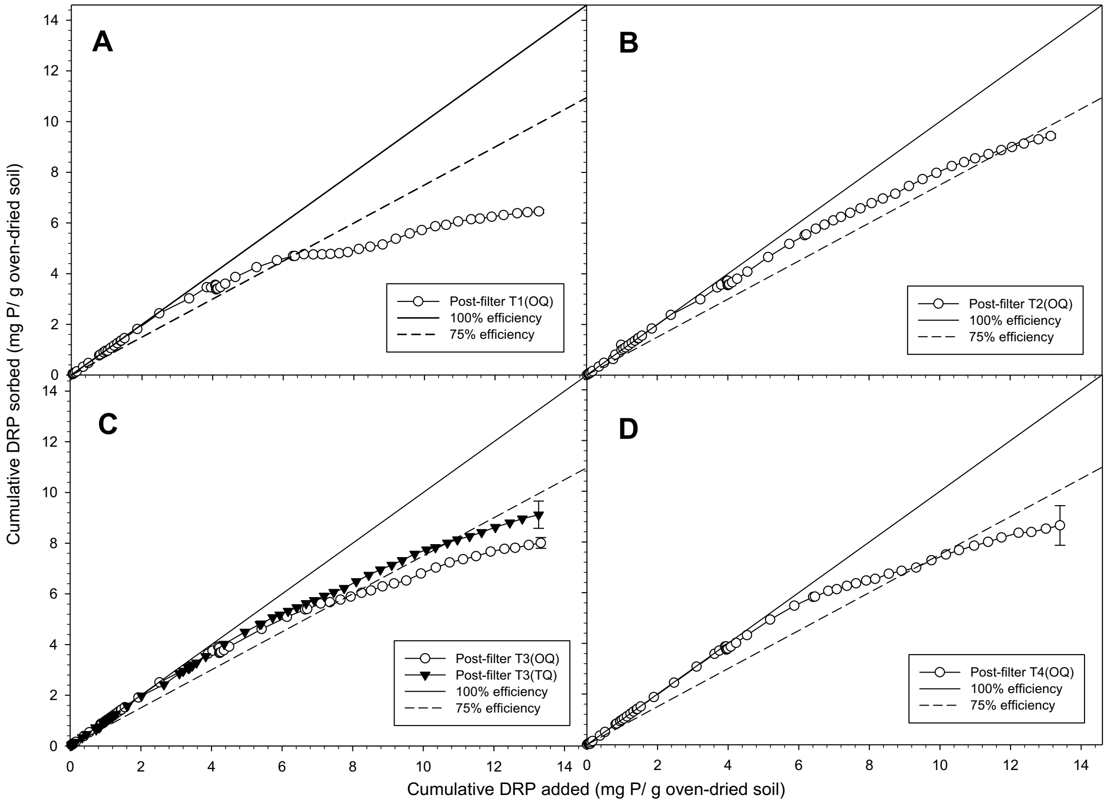

Figure 4.2 Relationship between cumulative DRP added and cumulative DRP removed from wastewater for each treatment. A) T1(OQ) – without acid addition, B) T2(OQ) – adjusted to pH 5.5 with HCl, C) T3(OQ) and T3(TQ) – adjusted to pH 6.5 with HCl, D) T4(OQ) – adjusted to pH 6.5 with H_2SO_4. OQ represents Ohakune Quarry soil and TQ represents Te Mata Quarry soil. The error bars represent the standard errors of the means.

The results from this study were scaled up to provide an indication of the potential influence of using acid dosing with a full-scale soil filter. The longevity of the filter is estimated based on the maximum obtainable P removal capacity for each treatment with the total mass of the Allophanic soil used in full-scale filter. For example, at a medium-sized wastewater treatment plant in the North Island of New Zealand, 3,000 m^3 of wastewater is produced per day with an average DRP concentration of 6 mg P/L (discharge of 18 kg P/day as DRP). At this site, a full-scale soil filter containing 2,000 m^3 soil (equivalent to ~1360 tonnes of oven-dried soil) is used to achieve an average DRP removal efficiency of 75%. Without acid dosing, the OQ soil is estimated to remove

6,120 kg P (i.e. 75%) from a total of 8,160 kg P produced in wastewater over 453 days or 1.24 years. In comparison, if the wastewater is acid dosed with HCl to achieve a pH of 5.5, then the soil filter is estimated to remove 12,104 kg P (i.e. 75%) from a total of 16,139 kg P produced in wastewater over 897 days or 2.46 years. Therefore, acid dosing would enable the soil filter to remove an additional 5984 kg P and extend operational life by 444 days (1.22 years) based on operational capacity. However, if the cost of the soil; including sourcing, installing the soil into the filter containment area and soil disposal, is less than acid dosing, then it would be less costly to use more soil than to use acid dosing. Once the soil filter's P removal capacity is spent, then it is anticipated that it could be applied to pastoral or cropping land as a soil amendment. Further research assessing the proportion of the sorbed P that is potentially plant available (i.e. its P fertiliser equivalent value) is presented in Chapter 6.

4.5 Conclusions

Both of the Allophanic soils evaluated in this study had high capacities to remove DRP from dairy processing plant wastewater. Phosphorus removal was further improved when wastewater pH was lowered using acid dosing. The highest removal of 9.4 mg P/g oven-dried soil was achieved for the OQ soil when wastewater pH was reduced from pH 8.2 to 5.5, resulting in a 45% increase in DRP removal compared to wastewater without acid treatment. The TQ soil, with a higher ASC test value, achieved a similar level of P removal from less acid dosing. There was a minimal difference in DRP removal capacities between the two types of acid (HCl and H_2SO_4) used to dose the wastewater, therefore, choice of acid for dosing is unlikely to be an important consideration with soil filter performance. Overall, acid dosing was an effective method of improving the performance of Allophanic soils at removing DRP from wastewater. However, a comparison of the cost of acid dosing needs to be evaluated for each filter system to determine whether acid dosing is cost effective compared to renewing the soil more frequently. This evaluation should be site specific because the cost of the soil will vary with the distance from the soil source.

4.6 References

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Chapter 5

Phosphorus removal from municipal and dairy factory wastewater using pilot-scale Allophanic soil filters

5.1 Introduction

The column study in Chapter 4 quantified the effectiveness of selected Allophanic soils at removing DRP from a wastewater. It also assessed the additional P removal capacity that could be achieved by acid dosing the wastewater. It is widely accepted that laboratory-based studies are useful for evaluating the potential performance of treatment methods; however the results obtained in these studies do not always translate well through to full-scale systems (Drizo et al. 2002; Hedström 2006). Ideally, laboratory-scale P sorption studies should be coupled with long-term larger-scale experiments to validate the findings (Drizo et al. 2002). Ewing (1996) demonstrated the difficulty associated with prediction of transport behaviour of contaminants in full-scale constructed wetland system based on laboratory column studies, as transport is dependent on scale (Appelo and Postma, 1999). This study highlighted the differences that can occur in performance outcomes with a full-scale system operating at on-site conditions, compared to results obtained in the laboratory operated under more controlled conditions (Bratieres et al. 2008). Therefore, before constructing full-scale treatment systems, it is useful to evaluate the effectiveness at a smaller scale that can better replicate the conditions and operation of a full-scale system (i.e. pilot-scale systems), compared to laboratory assessments. Pilot-scale systems allow testing under field conditions to validate performance of treatment methods and process design constraints from scaling-up process. They are conducted under specific environmental conditions to establish optimised conditions for full-scale operations (Tchobanoglous et al. 2014).

Key aspects of a soil filter design that can be tested at the pilot-scale are the effects of using deeper soil depths on hydraulic conductivity of wastewater through the filter over time. For example, soils have the tendency to compact over time from continuous hydraulic loading, which can cause reductions in hydraulic conductivity, reducing matrix flow, restricting wastewater movement through the soil and lowering the P removal efficiency (Hanly et al. 2012). Other aspects that can be evaluated at the pilot-scale in field conditions, are changes in temperature and the potential for biological growths to influence operation. Efficiency of treatment is not only dependant on the chemical and physical properties of filter material, but can also be influenced by biofilms, algae and weeds (Kauppinen et al. 2014). For example, biofilms can adhere to soil surfaces which cause reductions in the P sorption capacity of the studied material (Lahav and Green 2000).

This study involved the use of pilot-scale soil filters in order to gain a better understanding of the performance of soil filters at removing DRP from wastewater under field conditions and to identify possible constraints to their effectives when used in full-scale systems. The pilot-scale filters were constructed to evaluate the DRP removal from wastewaters at both a municipal sewage and a dairy-processing wastewater treatment plant. The objective of this study was to evaluate the effectiveness of Allophanic soil filters, along with wastewater acid dosing, at removing DRP from wastewaters under field conditions over an extended period of operation.

5.2 Materials and Methods

5.2.1 Sites description

5.2.1.1 Dannevirke Sewage Treatment Plant Site

The first pair of pilot soil filters was set up at the Dannevirke Sewage Treatment Plant (STP), which is located on Makirikiri Road, approximately 3 km from the town centre. The Dannevirke STP receives domestic wastewater primarily from residential, commercial areas and recreational facilities within the town, which has a population size of approximately 5500. Treatment of wastewater at the Dannevirke STP is managed with a 4-pond system and a microfiltration plant, and an additional overspill pond for high flow events (Figure 5.1). The microfiltration plant provides final treatment before the treated wastewater is discharged into the Mangatera Stream, which is a tributary of the Manawatu River. The STP discharges an average wastewater volume of an average discharge of approximately 3082 m^3/day (maximum consent of 6370 m^3/day) (McArthur and Clark, 2007).

Figure 5.1 Aerial map of the Dannevirke STP. Arrow indicates location of the microfiltration plant and pilot-scale soil filters (Source: Google Earth).

5.2.1.2 Fonterra's Te Rapa Wastewater Treatment Plant Site

The second pair of pilot soil filters was set up at Fonterra's Te Rapa dairy-processing plant Wastewater Treatment Plant (WTP), which is located in Te Rapa, Hamilton, adjacent to the Waikato River. The general processing wastewater from cream and milk production is treated on site and passes through the low solid pump well, anoxic tank, aerobic carousel and alum dosing, which is applied prior to anoxic tank (Pene 2016; Wang and Irvine, 2016). Degree of alum dosing is dependent on the seasonal DRP concentrations from cream and milk production. The final treatment stage is the clarifier, after which the treated wastewater is discharged into a mixing pond, along with storm water and cooling water, before entering the Waikato River (Figure 5.2). The WTP discharges a seasonal average wastewater volume of approximately 5900 m^3 per day, based on the 2015 financial year data (Wang and Irvine, 2016).

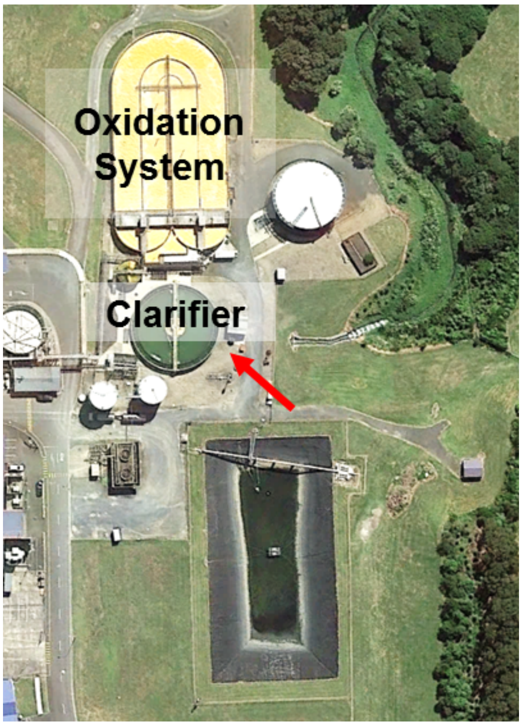

Figure 5.2 Aerial map of the Fonterra Te Rapa WTP. Arrow indicates location of the pilot-scale soil filters (Source: Google Earth).

5.2.2 Pilot-scale soil filter design

At both sites, the two replicate pilot-scale soil filters each had a surface area of 1 m^2 (0.9 x 1.1 m). The soil used for all soil filters was 'as-received' subsoil (0.1-0.6 m soil depth) from the Ohakune Quarry (OQ), located in the Ruapehu District and each replicate was run in parallel. At the Dannevirke STP site, the average soil depth used in the soil filters was 0.26 m, which was installed in the filter containers on top of a 0.28 m deep gravel layer. At the Fonterra WTP site, the average soil depth was 0.60 m, which was installed on top of a 0.10 m deep gravel layer. The two different soil depths used at the two sites provided two examples of potential depths that could be used in full-scale systems.

5.2.3 Soil filter operation

5.2.3.1 Dannevirke STP soil filters

At the Dannevirke STP site, wastewater from a microfiltration plant was gravity-fed onto the soil filters (Figure 5.3 and 5.4). Wastewater was applied to each filter via two micro-spray irrigation nozzles. Initially, the average wastewater flow rate was ~26.0 L/hr/filter resulting in an estimated average wastewater hydraulic retention time (HRT) in the soil filters of ~5.1 hours per filter (HLR ~0.62 m^3/m^2/day or 26 mm/hr). After soil sieving of the filters soil, which occurred after the second period of operation, the average wastewater flow was ~23.0 L/hr/filter resulting in an average HRT of ~4.7 hours per filter (HLR ~0.55 m^3/m^2/day or 23 mm/hr). The shorter HRT following soil sieving was also due to less material being returned to the filter after sieving (Figure 5.4). The microfiltration plant wastewater was dosed with diluted 5% hydrochloric acid (HCl, ~1.4 M) at a rate of 0.15 L/hr (0.075 L/hr/filter) in order to decrease wastewater pH closer to neutral to improve DRP removal efficiency of the soil. Wastewater flow rates from the outflow at the bottom of each filter were monitored using tipping bucket flow meters. A data logger with cellular telemetry was connected to the tipping buckets to record the number of tips every hour to provide a continuous measure of flow rate and volume.

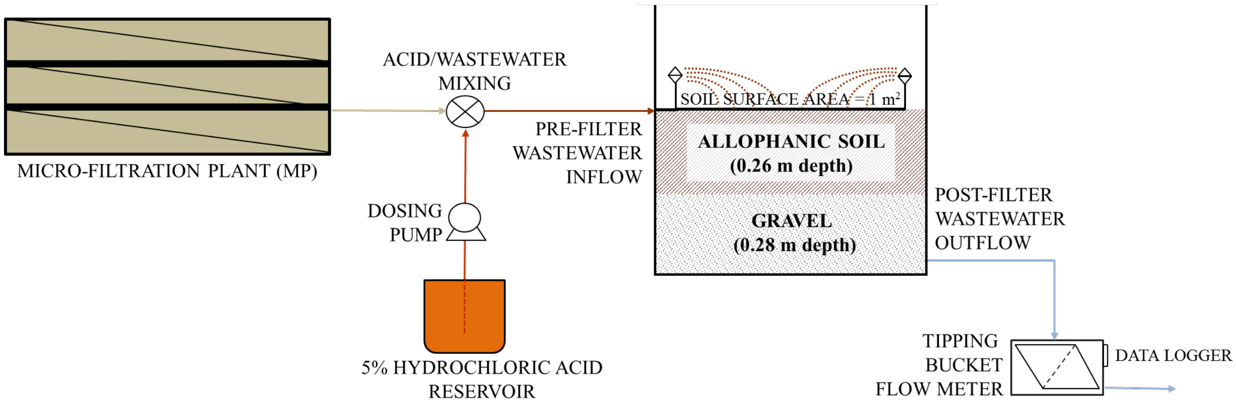

Figure 5.3 Flow diagram of soil filter system at Dannevirke STP.

Figure 5.4 Pilot soil filters at Dannevirke STP (tipping bucket flow meters shown in the bottom right-hand corner).

Soil filter operation started on the 22nd November 2013 and was halted for approximately 3 months, from 31st December 2013 to the 2nd April 2014. This break in filter operation occurred because there was insufficient flow of wastewater from the microfiltration plant, due to maintenance work being conducted on the treatment ponds. The operation of the filters was stopped during a second period, from the 4th June to the 29th June 2104, to allow for the removal of the soil from the filter containers, drying and sieving (<4 mm) of the soil and then reinstallation of the soil (Figure 5.5). This was done to assess whether soil sieving would improve P removal efficiency by enhancing the contact between the wastewater and the soil, which was originally installed in an ‘as-received’ (i.e. not sieved) form. All large cemented aggregated clods, which had low P-retention values, and hard rocks were removed. The soils were then reinstalled into the filter containers with a new average soil depth of 0.21 m, which was less than the original depth of 0.26 m, due to the removal aforementioned material during sieving.

Figure 5.5 The Dannevirke STP pilot filter soil before (left) just prior to passing through a <4 mm sieve and reinstallation into a filter container after sieving (right).

Operation of the filters was paused for a third extended period from the 2nd December 2014 to the 24th March 2015, again due to insufficient wastewater supply. Acid dosing inadvertently stopped on the 19th October 2015 and the operation soil filters was finally completed on the 25th November 2015. Total operation time was 440 days that was conducted over a total period 24-month.

Over the entire experimental period there were a total of 55 sampling times. At each sampling time, four wastewater samples were collected, which were; microfiltration plant wastewater, pH adjusted wastewater, soil filter 1 (post-filter wastewater) and soil filter 2 (post-filter wastewater). The collected samples were kept frozen until analysis.

5.2.3.2 Fonterra WTP soil filters

At the Fonterra WTP site, wastewater from the wastewater discharge sampling well was initially pumped to the soil filters (Figures 5.6 and 5.7). Wastewater was applied to each filter via four micro-spray irrigation nozzles. The average wastewater flow rate was ~36.0 L/hr/filter, resulting in an estimated average wastewater HRT in the soil of ~8.5 hours per filter (HLR ~0.86 m^3/m^2/day or 36 mm/hr). Wastewater flow rates were measured and recorded using the same methods as described for the Dannevirke STP soil filters. In addition, digital counters were connected to the tipping bucket flow meters to provide another record of tipping bucket tips.

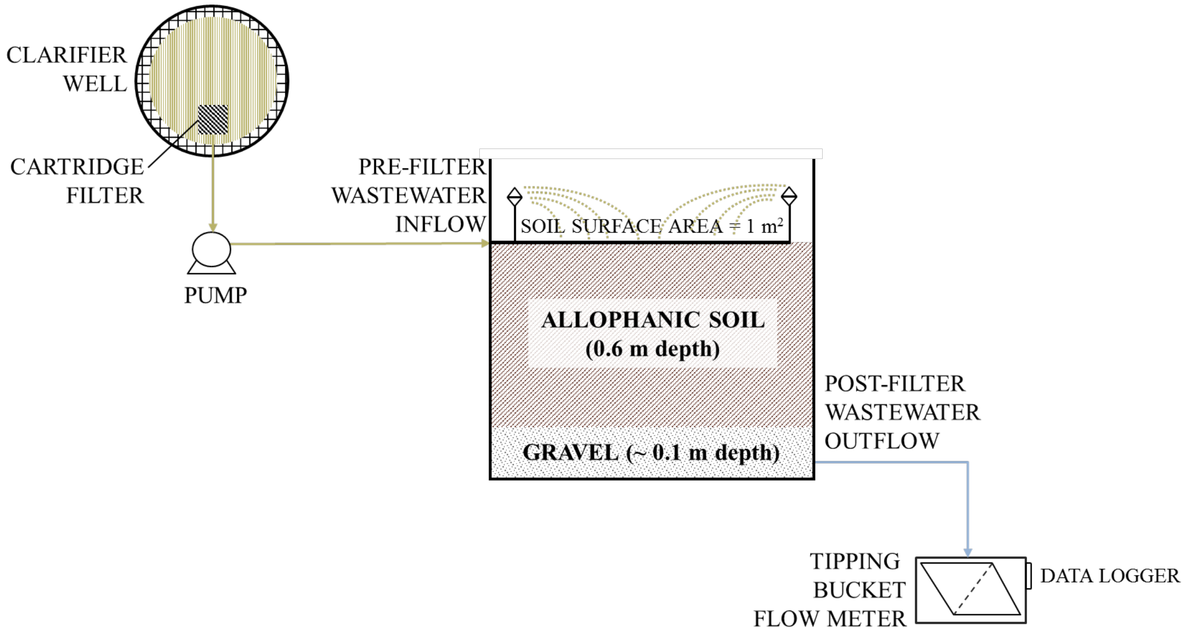

Figure 5.6 Flow diagram of the spray irrigation application method initially used to apply wastewater to the pilot soil filters at Fonterra's Te Rapa WTP.

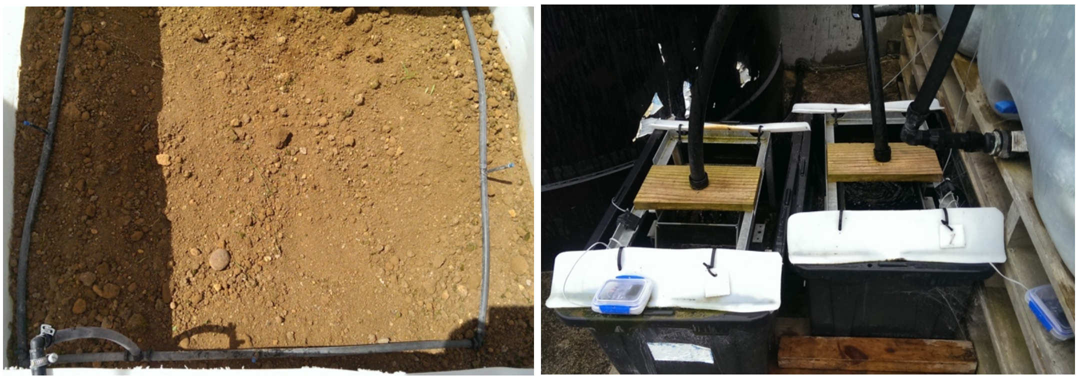

Figure 5.7 Top view of a soil filter (left) and the tipping buckets flow meters (right) used at Fonterra's Te Rapa WTP.

Pilot soil filters began operation in early April 2014, were stopped on the 16th June 2014 for the annual processing plant maintenance and then started again on the 1st August 2014. Filter operation was stopped on 18th December 2014, when blockages of the sprinklers by algae caused highly variable wastewater flow rates. These irregular flow rates prevented the commencement of the acid dosing.

On the 18th January 2015, a cartridge filter was added to the wastewater line, between the pump and the sprinklers, to remove algae material and then the wastewater application to the filters was started again. The cartridge filter reduced the rate at which blockages were forming, however, it was later observed that slime biological growths also developed in the wastewater pipes after the cartridge filter, also contributing to sprinkler blockages. Regular maintenance was required to clear micro sprinkler nozzle blockages. The flow to the filters was turned off on the 29th March 2015 due to these on-going nozzle blockages.

Due to the difficulty in preventing the biological growths, the decision was made to remove the sprinklers. As a replacement to sprinkler irrigation, wastewater was piped on top of each of the two soil filters to maintain a static head (approximately 5 cm depth) of wastewater. This procedure distributed wastewater evenly across the soil filter surface (Figure 5.8). The change of application method occurred on the 16th July 2015, after the processing plant started processing again and producing wastewater following its annual maintenance period. At this time a 200 L tank was installed, which had a wastewater pumped to it continually and the excess wastewater overflowed back to the WTP sampling well. This made it possible to deliver wastewater to the soil filters using a small submersible pump, which was installed in the tank.

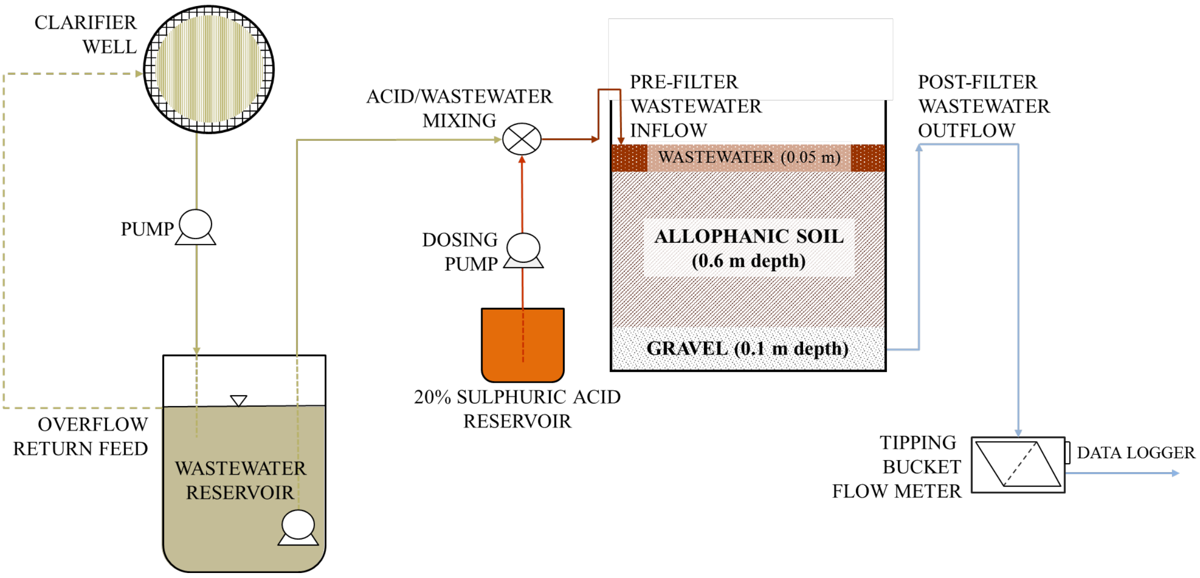

Figure 5.8 Flow diagram of soil filter system at Fonterra's Te Rapa WTP modified wastewater application method.

Acid dosing of the wastewater started on the 29th September 2015. The wastewater flow rate of 120.8 L/hr (60.4 L/hr/filter) was mixed with 20% sulphuric acid (20% H_2SO_4, ~2 M) at an average flow rate of 0.150 L/hr (0.075 L/hr/filter), in order to reduce the wastewater pH closer to neutral. The experiment was ended on 4th December 2015, due to the soil filters starting to clog, which caused reduced infiltration rates. The clogging was also contributed to by excessive algae growths developing in the standing head wastewater on top of the soil filters. Total filter operation time was 376 days spread over a total period of 18 months.

Over the entire experimental period there were a total of 45 sampling times. Prior to the commencement of acid dosing, three wastewater samples were collected at each sampling time, which were; sampling well wastewater, soil filter 1 (post-filter wastewater) and soil filter 2 (post-filter wastewater). Following acid dosing commencement, a sample of acid-dosed wastewater was also collect at each sampling time. The collected samples were kept frozen until analysis.

5.3 Wastewater analysis

All wastewater samples were filtered through 0.45 μm cellulose-acetate/nitrate membrane filters (MF-Millipore^{TM}) and analysed for pH and DRP. The pH of the wastewater sample was measured using the PHM210 standard pH meter (MeterLab) and DRP analysis was determined colormetrically using the phosphomolybdate method (Murphy & Riley, 1962) and a Technicon Auto-analyser.

5.4 Results and Discussion

5.4.1 Dannevirke STP soil filters

Over the total experimental period, the measured volumes of wastewater treated by the soil filters was an average of 251,850 L/filter (Figure 5.9). There was some variation between the volumes of wastewater treated by each of the two filters. This variation was primarily due to the wastewater being supplied to the filters by a single gravity fed hose, with a T-junction used to split the flow between the two filters. Therefore, although the flows were similar between the two filters, they were not exactly even.

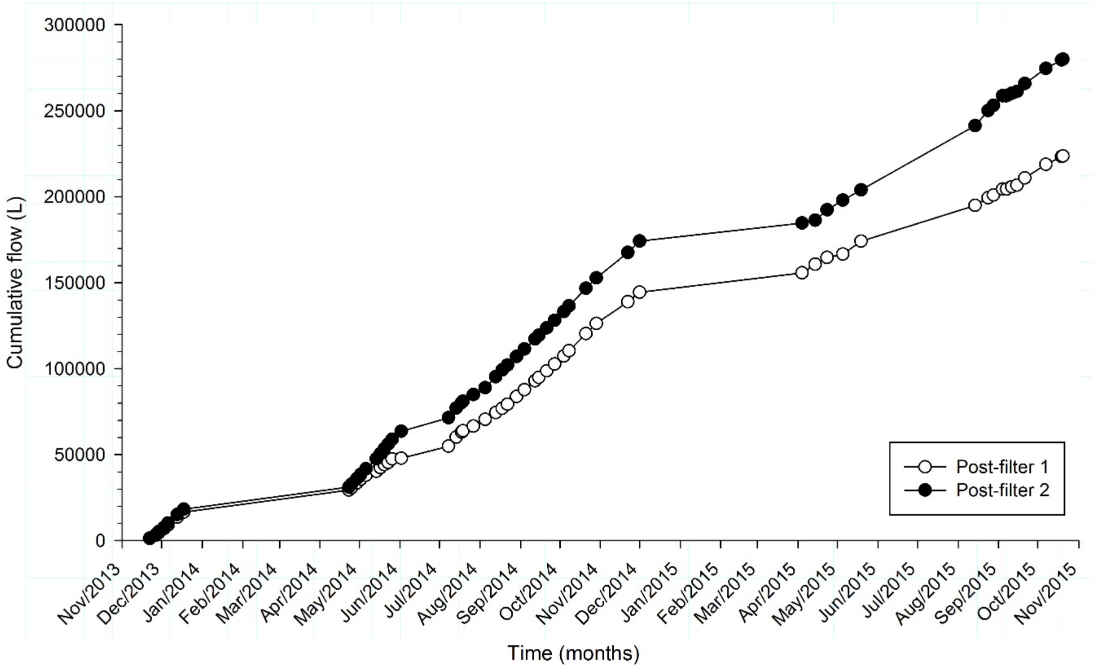

Figure 5.9 Cumulative volume of wastewater applied to each soil filter at the Dannevirke STP.

The soil filters achieved a high DRP removal efficiency of 94% on average during the first month of operation (Figure 5.10). Dissolved reactive P concentrations of pre-filter wastewater ranged between 5–5.8 mg P/L over this initial period. Wastewater pre-filter DRP concentrations were higher and fluctuated more widely during the second period of operation, being within the range of 6.2 – 10.7 mg P/L. At this stage, post-filter wastewaters showed an increasing trend in DRP concentrations, and removal efficiency decreased to an average of approximately 50% by the end of the period. After the second period of operation, the soils were removed and sieved in order to improve contact between the wastewater and the soil's sorption sites. After restarting the filter operation, the filters returned to having a high DRP removal efficiency at the start of the third period of operation. During this period, which had a duration of approximately 5 months, pre-filter wastewater had an average DRP concentration of 4.7 mg P/L (range 3.4 – 5.7 mg P/L), and the average post-filter DRP concentration for the two soil filters was 1 mg P/L (range 0.4 – 2.2 mg P/L), which provided an average removal efficiency for this period of 78 %.

The potential advantage of removing and sieving the soil to improve or regain the soil filter's performance was highlighted by Ádám et al. (2006). In their study, constructed wetland systems were simulated using variable scale box experiments to evaluate the P removal capacities of Filtralite^{TM} (an expanded clay material from Norway). One aspect of assessment from this experiment that emphasised the need to redistribute filter material was the heterogeneity in the spatial distribution of sorbed P by Filtralite^{TM} sampled from various locations within the boxes. In comparison, the soil filters at Dannevirke STP, which had a soil height of 0.26 m and HRT of 5.1 hr/filter, may exhibit similar spatial distribution of sorbed P. Therefore, by mixing the soils at Dannevirke STP, the original flow pathways are changed and decreasing the variation in grain size distribution amongst the soil aggregates, increases the potential for contact between new reactive sites and the wastewater.

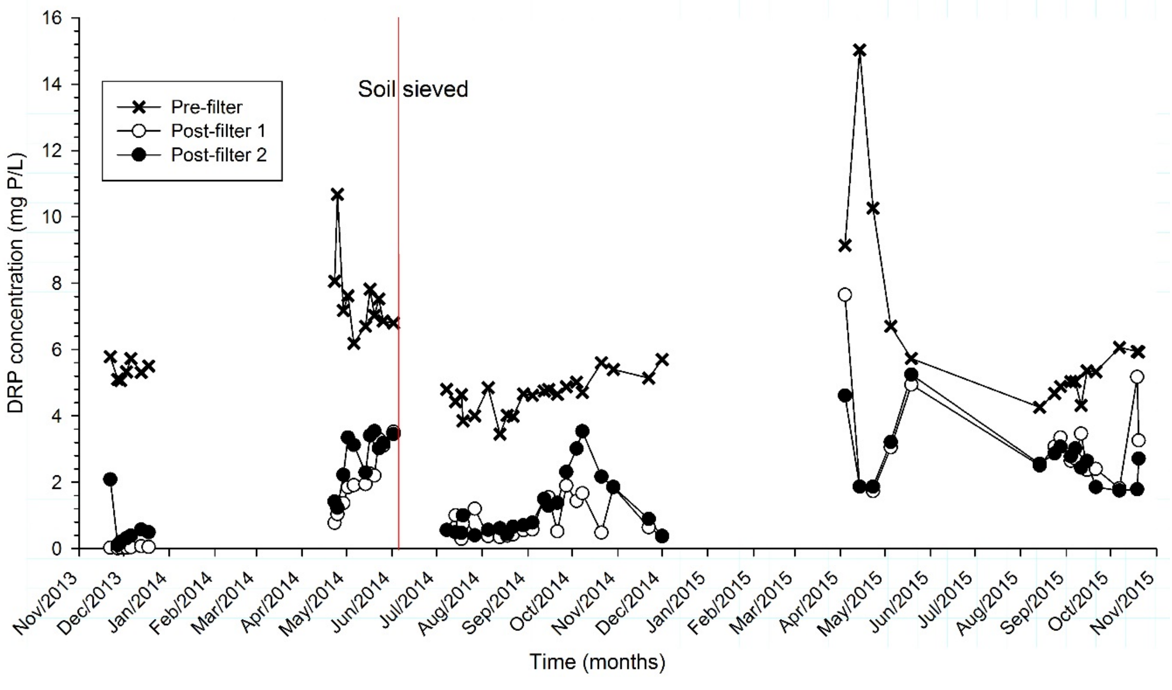

Figure 5.10 Changes in the DRP concentrations of pre and post-filter wastewater over time for the four main periods of operation.

During the final period of operation, which had a duration of approximately 7 months, the average wastewater pre-filter DRP concentration was 6.5 mg P/L (range 4.3 – 15.0 mg P/L). The average post-filter DRP concentration for the two soil filters was 3 mg P/L (range 1.8 – 6.1 mg P/L), which provided an average removal efficiency for this period of 53 %. At the last sampling time, on 20th October, 2015, the removal efficiency was an average of approximately 50%.

The filters maintained an average cumulative DRP removal >95% for the first 0.5 mg P/g oven-dried soil added (Figure 5.11). By the time 2.1 mg P/g oven-dried soil were added, the average cumulative removal efficiency had reduced to 75%. The average cumulative DRP removal remained close to 75% between 2.1 and 7.5 mg P/g oven-dried soil added (i.e. between 1.6 and 5.6 mg P/g oven-dried soil removed). By the end of the experimental period, an average of 6.4 mg P/g oven-dried soil had been removed from an average of 9.6 mg P/g oven-dried soil added in wastewater, which provided an overall average DRP removal efficiency of 67%.

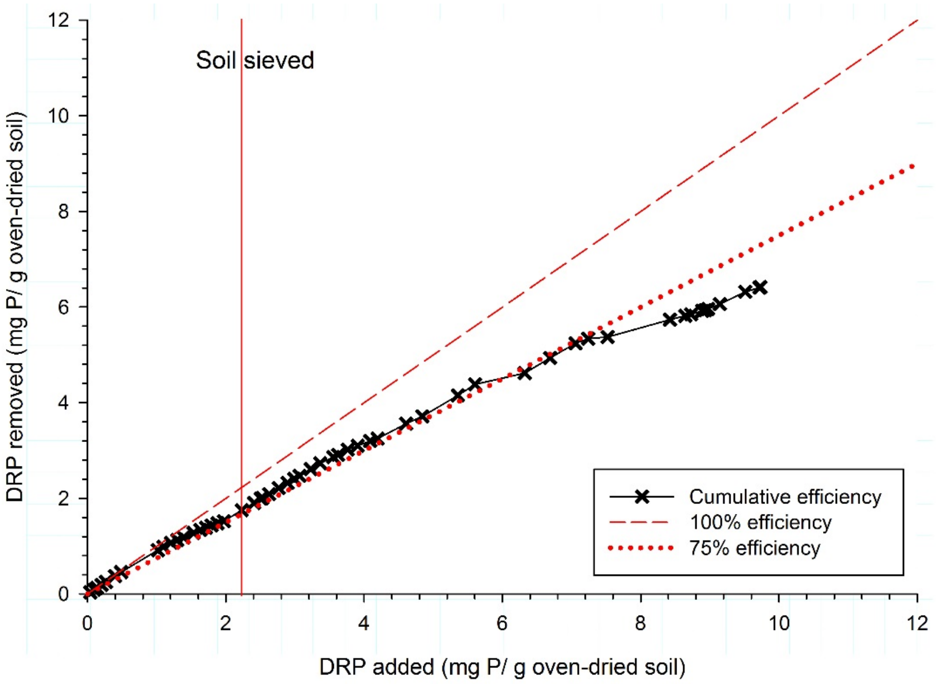

Figure 5.11 Relationship between the averaged cumulative DRP added and the averaged amount of DRP removed on to soils of filter 1 and filter 2.

The pH of the wastewater coming from the micro-filtration plant, prior to the addition of acid, had an average value of 8.3 (range 6.1 – 9.2) over the duration of the experiment. The pH of the acid treated wastewater (pre-filter wastewater) was highly variable ranging from 2.6 to 9.0, having an average value of 7.7. A cause of this variation is likely to be due to variation in wastewater flow from the micro-filtration plant, which varied with the different operation stages that the micro filtration plant was going through. Because the acid dosing was pumped at constant flow rate, and could not be automatically adjusted to the change in wastewater flow rate, this would have caused variation in wastewater pH. The average pH of the post-filter wastewater was 6.5 (range 4.1 – 8.3). The soil filtration resulted in a further reduction in the average pH of the wastewater, with a narrower range in pH, which is likely to be due to processes associated with the soils pH buffering capacity, such as the soil's reserve acidity (Lee 1995). The combination of acid dosing and soil treatment resulted in a final wastewater pH close to neutral, which is preferable for discharging to fresh water systems (Quinn and Gilliland 1989).

In the column study (Chapter 4), at an average DRP removal efficiency from wastewater was of 75%, the OQ soil achieved a P removal of 4.5 mg P/g oven-dried soil when the wastewater was not acid treated (pH 8.2) and 6.9 mg P/g oven-dried soil when the wastewater was adjusted to pH 6.5 with sulphuric acid. The 5.6 mg P/g oven-dried achieved in the pilot study, at the same average DRP removal efficiency of 75%, was in between the two aforementioned values obtained in the column study. The average wastewater (pre-filter wastewater) pH achieved by acid dosing in this pilot study was 7.7, which was also in between the pH levels of the wastewater of the two treatments in the column study, which may help to explain the level of P removal capacity achieved in the pilot study. There were a number of factors that differed in the pilot soil filter study compared to the column study, such as a different type of wastewater with a lower average wastewater DRP concentration. In addition, the soil in the pilot study filters was sieved part way through the experiment rather than at the start, which was the case for the column study. Sieving the soil potentially increases the contact between the wastewater and soil reactive sites, as previously discussed. Another difference between the studies was that the pilot soil filters were operated over a longer duration. This could have allowed more time for the development biological growths in the soil, which is known to reduce sorption capacities of the material (Suliman et al. 2006). Presence of microorganisms, suspended solids, and organic matter in wastewater can lead to biofilm formation followed by attachment onto the active sorption sites of the soil which led to blockage of these sorption sites, ultimately clogging the filters (Stark, 2004).

5.4.2 Fonterra WTP soil filters

Over the total experimental period, the average measured volumes of wastewater treated by the soil filters was 262,800 L/filter (Figure 5.12), which was a similar volume that was treated by the Dannevirke STP pilot soil filters. As with the Dannevirke STP study, there were also variations between the volumes of wastewater treated by each of the two filters. Although the wastewater flow was pumped, a T-junction was also used to split the flow between the two filters, so exact even flows were not achieved to both filters. However, the volumes treatment by each filter were similar.

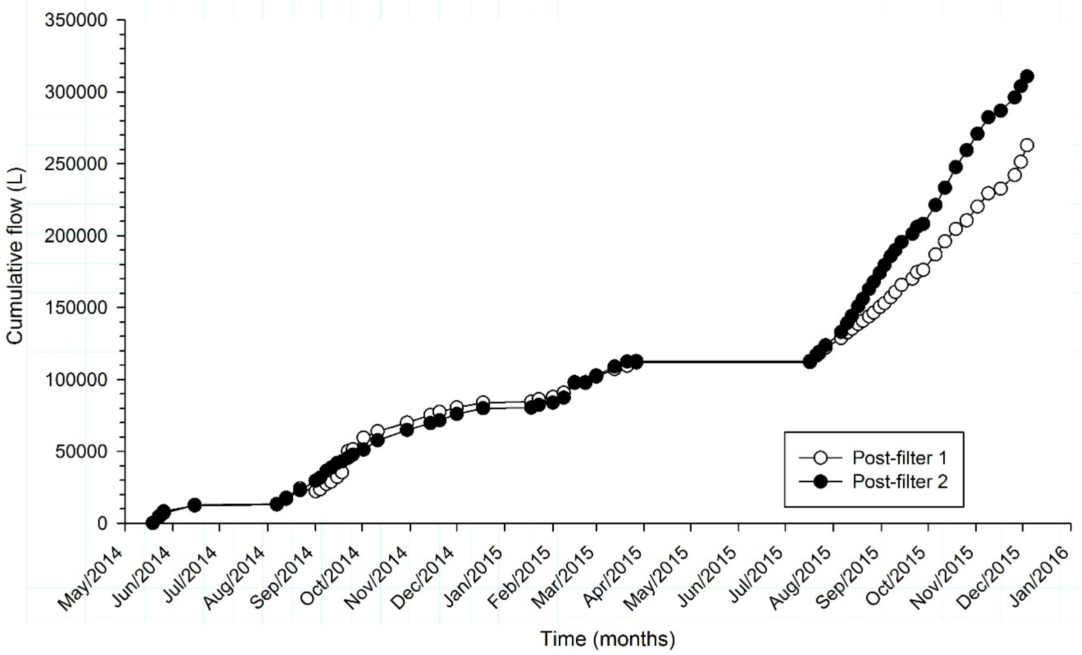

Figure 5.12 Cumulative volume of wastewater applied to each soil filter at the Fonterra WTP.

During the first short period of operation, the pre-filter wastewater DRP concentrations were relatively low, being on average 0.9 mg P/L (range 0.3–1.9 mg P/L, Figure 5.12). During this same period, the post-filter wastewater DRP concentrations were maintained at <0.03 mg P/L. Over the second period of operation, which was a duration of almost three months, the pre-filter DRP concentrations increased and were highly variable, being on average of 3.9 mg P/L (ranging 2.0-5.6 mg P/L). During this period, the DRP concentration of the post-filter wastewater remained at <0.30 mg P/L. The overall average DRP removal efficiency for the first and second periods of operations were 97 and 98%, respectively.

During the third period of filter operation, represented by the diagonal shading section in Figure 5.13, samples were inadvertently not collected. The average pre-filter wastewater DRP concentrations was estimated (3.56 mg P/L), being based on the average of the last two concentrations sampled from period two and the first two concentrations of period four as. While it is not possible to know what actual concentration was, this estimation provides an indication of probable DRP load over this period. The average post-filter wastewater DRP concentration during this period was estimated as the average value (0.38 mg P/L) of the last sampling time from the previous flow period on 20th November 2014, and the first sampling time from the subsequent flow period on 21st July 2015.

During the fourth period of operation, which lasted for a duration of approximately 5 months, the pre-filter DRP concentrations were also highly variable, having an average value of 3.4 mg P/L (ranging from 0.8 – 7.2 mg P/L). Acid dosing was introduced about half way through this last operational period (29th September 2015). During the operational period prior to acid dosing, the post-filter average DRP concentration was 1.0 mg P/L (range 0.5 – 1.5 mg P/L), providing an average removal efficiency of 61%. For the second half of the period, which followed acid dosing commencement, the post-filter average DRP concentration was 0.52 mg P/L (range 0.04 – 0.9 mg P/L), providing an average removal efficiency of 90%. During this period some of the samples were unavailable from Filter 2. The final overall average efficiency for this last period was at 89%.

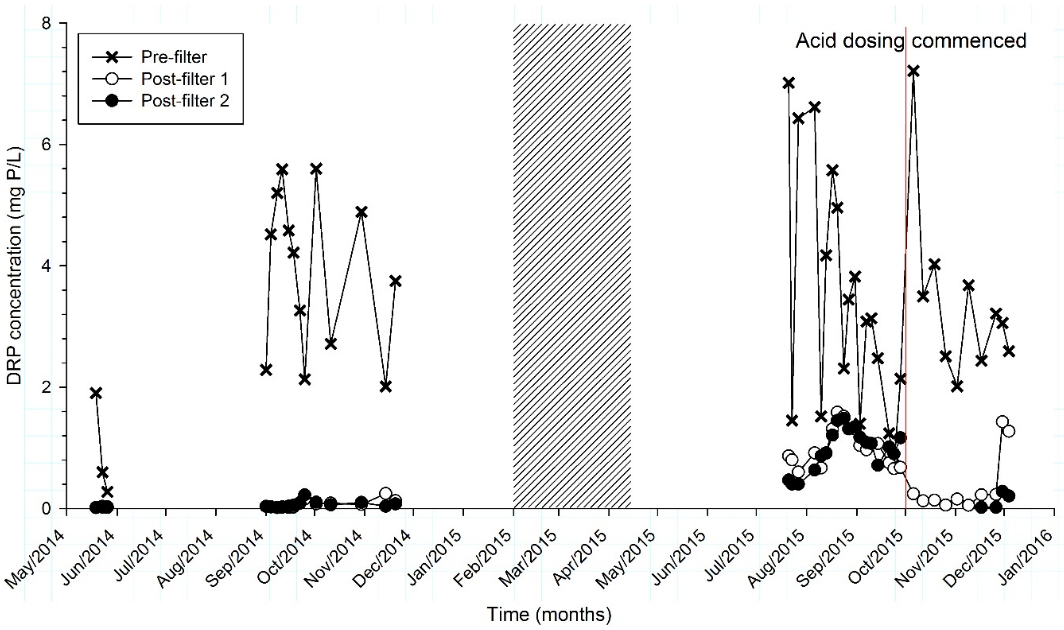

Figure 5.13 Changes in the DRP concentrations of pre- and post-filter wastewaters over time. Area in diagonal shade indicates a period when the filters were operating, but samples were not collected.

The filters maintained an average cumulative DRP removal >95% for the first 0.7 mg P/g oven-dried soil added (Figure 5.14). Over the duration of the study, a total average of 2.13 mg P/g oven-dried soil was added to the soil filters and an average of 1.87 mg P/g oven-dried soil was removed from the wastewater, which provided an overall average removal efficiency of 86% (Figure 5.14). Even though the wastewater volumes added were similar to that added Dannevirke STP, the quantity of DRP added, on a per weight of soil basis, was less due to lower wastewater initial DRP concentrations and because more soil was used in the Fonterra soil filters. In the column study (Chapter 4), when pH was adjusted to 6.5 with sulphuric acid for the entire duration, about 5.6 mg P/g oven-dried soil was removed from the wastewater by the time the average removal efficiency declined to 86%. This represented a higher level of removal compared to the pilot study, which is likely to be due to the column study using acid dosing for the entire duration of the column study and also the use of sieved soil (<2 mm), compared to the 'as-received' soil used in the

Fonterra pilot soil filters. The sieved soil potentially provides increased contact between the wastewater and specific adsorption sites on the soil surfaces, compared to the 'as-received' soil used in the pilot study. In addition, the pilot soil filters were stopped while the P removal efficiency was still high, due to clogging of the filters, which meant the amount of P sorbed by the filters when the average P removal efficiency was 75% could not be obtained.

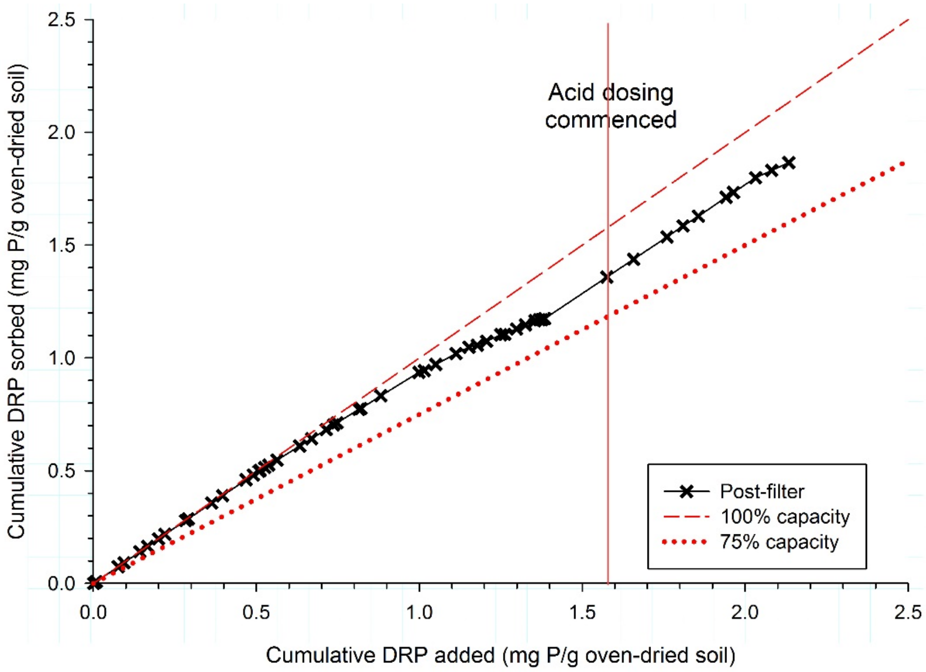

Figure 5.14 Relationship between average cumulative DRP added and removed for both filters.

5.5 Full-scale soil filter design

Results from the pilot-scale soil filters at Dannevirke STP have been scaled up to provide an indication of the design features of a theoretical full-size soil filter (Table 5.1). The filter is designed to treat wastewater for a population of approximately 5500, that are generating an average daily discharge of approximately 3000 m^3 and a maximum daily volume of 4000 m^3. In order to achieve a maximum hourly wastewater application depth of 42 mm, which was based on ensuring the application rate was no more than about half of the soil's initial infiltration rate (Hanly et al. 2012), the soil filter area would need to be 4000 m^2. If the filter soil depth is 0.5 m, then this would achieve a HRT of 6 – 8 hours (6 hours at maximum daily volume and 8 hours at average daily volumes). This would require a total soil volume of 2000 m^3 (equivalent to 1360 tonnes of oven-dried soil).

Table 5.1 Summary of the full-scale soil design parameters.

Soil filter design parameters	
Average daily wastewater discharge volume (m^3)	3000
Maximum daily volume allowed for in the design (m^3)	4000
Application rate (m^3/hour)	167
Target maximum application depth (mm/hour)	42
Average wastewater DRP concentration (mg P/L)	6
Average daily DRP load (kg P/day)	18
Filter surface area/wastewater application area (m^2)	4000
Filter soil depth (m)	0.5
Filter soil volume (m^3)	2000
Target average filter efficiency	75%
Approximate hydraulic retention time (h)	6-8

Based on the results of the pilot-scale study, if the soil filter is operated to achieve an average DRP removal efficiency 75% over its life time, removing 5.6 mg P/g oven-dried, then this would be equivalent to a DRP removal capacity of 7616 kg P from a total of 10,155 kg P added (for a 2000 m^3 soil filter). For a wastewater DRP load of 18 kg/day the longevity of the filter will be 564 days (i.e. ~1.5 years, Figure 5.15), which would treat approximately 1.69 million m^3 of wastewater. This volume of wastewater would require 768 m^3 of 33% HCl. Assuming the acid costs of \$650/m^3, the total acid cost over the life of the filter would be approximately \$500,000. This high cost of acid dosing is likely to make its use prohibitive.

The pilot soil filter study did not include a treatment without acid dosing, therefore, it is not possible to know exactly what the DRP removal capacity of the filters would have been using wastewater with its original pH level. Therefore, an estimation of the marginal benefit of the acid dosing was estimated using results from the column study (Chapter 4). In the column study the treatment with no acid dosing achieved a P removal capacity of 4.5 mg P/g oven-dried soil. Using this value, achieving an average DRP removal efficiency of 75%, the soil filter is estimated to remove approximately 6,120 kg P, from a total of 8,160 kg P produced in wastewater, which provides a longevity of 453 days. Based on this, the assumed additional benefit of acid dosing would be an additional 1,496 kg P removed over an additional 111 days of filter operation. Therefore, the acid dosing equates to approximately a cost of \$334 per additional kg of P removed. In comparison, an additional 490 m^3 of soil would be required to remove an additional 1,496 kg P. Assuming the cost of soil, including excavation and screening costs of \$26/m^3 soil and transport cost of \$0.36/m^3/km (assuming the distance from OQ soil quarry to Dannevirke STP = 225 km), then the additional soil cost is \$52,400 or \$35 per additional kg of P removed. This value is almost a tenth of the acid dosing costs, which supports the conclusion that it will be more cost effective to use more soil rather than use acid dosing. Further assessments at a pilot study scale are required to confirm this. Until this information is available, it is preferable to begin operation at full scale without acid dosing. The cost of supplying 2,000 m^3 of soil, using the costings previously described, is estimated to be approximately \$215,000.

Another option is to use soil filters as a final DRP removal step, after another P removal method, rather than being the primary DRP removal treatment. A number of studies have shown that the quantity of chemical dosing required to remove DRP increases per unit of DRP removed to achieve lower final DRP concentrations (Khan and Irvine 2006; Guopeng 2015). Jiang (2015) investigated the efficiency of ferric sulphate at removing DRP from pond treated municipal wastewater. The wastewater was sourced from an STP in the town of Woodville, in the Tararua District, about 25 km south west of Dannevirke. In this study, there was a near linear decrease in DRP concentration, from 4.2 - 1.1 mg P/L, in relation to the quantity of ferric sulphate added. However, there was a 4-fold increase the in the quantity of ferric sulphate required, relative to the quantity of P removed, to decrease DRP concentration from 1.09 to 0.03 mg P/L. In terms of the quantity of chemical, to reduce wastewater DRP concentration from 4.2 – 1.1 mg P/L, approximately 15.9 mg ferric sulphate was required per 1 mg P. To reduce wastewater DRP from 1.09 – 0.03 mg P/L a further 66.7 mg ferric sulphate was required. Hence, the first 3 mg P/L would require approximately 15.9 kg ferric sulphate/kg P and the remaining 1 mg P/L in wastewater would require 66.7 kg ferric sulphate/kg P. This demonstrates a higher chemical requirement and cost would be involved in achieving wastewater P concentrations below 1 mg P/L. Therefore, a combination of chemical dosing to decrease the DRP concentration closer to 1 mg P/L and then using a soil filter to reduce the concentration further, may be an effective method to achieve the required DRP levels for discharge to the river, with the soil filter reducing the chemical requirements.

Figure 5.15 shows the effect on filter longevity of treatment wastewater at different initial DRP concentrations assuming average removal of 5.6 mg P/g oven-dried soil (i.e. based on Dannevirke STP pilot study). If initial DRP concentration is an average of 1 mg P/L then the predicted longevity of the soil would be up to ~9.3 years, compared to ~1.5 years with a concentration of 6 mg P/L.

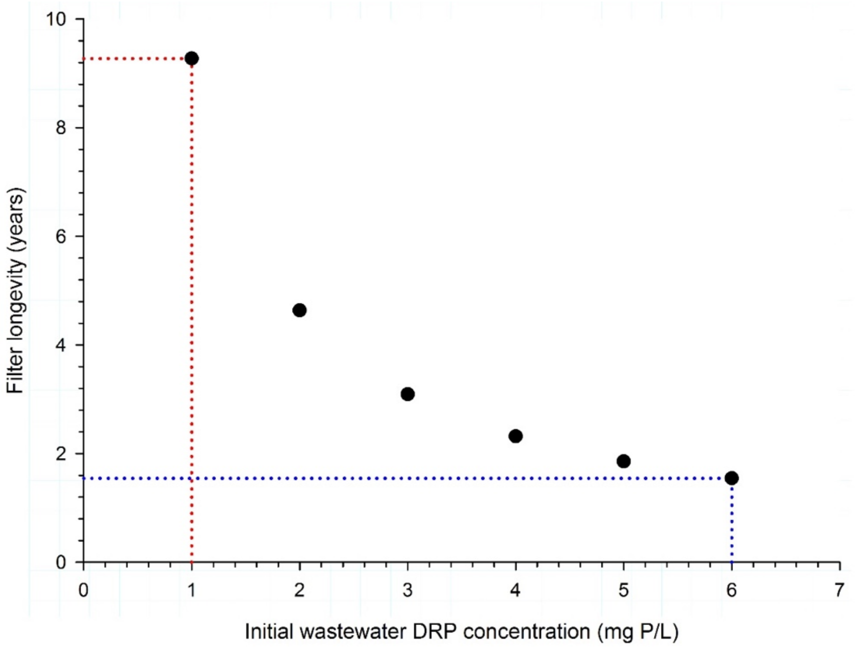

Figure 5.15 Predicted soil longevity in relation to wastewater initial DRP concentration (assuming a removal of 5.6 mg P/g oven-dried soil and a 75% removal efficiency).

Figure 5.16 and 5.17 present examples of the contribution of the Dannevirke STP discharge to DRP concentrations in the Manawatu River at two different existing river DRP concentrations over a one-year period. In this modelling, it was assumed that chemical dosing would be used to achieve a wastewater DRP concentration of 1 mg P/L and if the soil filter was also used (at an average of 75% DRP removal efficiency), as a final treatment step after chemical dosing, then wastewater discharge DRP concentration could be further reduced to 0.25 mg P/L. The effects of the contribution of these wastewater DRP concentrations to river concentrations were modelled using two scenarios. The first scenario (Figure 5.16) demonstrates solely the influence of the STP discharge to river DRP concentrations, therefore, it does not account for the existing river DRP concentrations. The second scenario (Figure 5.17) assumes that the existing river concentrations is at the headwater sub-catchment DRP limit of 0.006 mg P/L (referred to as the upper DRP limit). The modelled values were based on the monthly river flows at the Weber Road monitoring site from 1st June 2017 – 31st May 2018. The modelled values were calculated according to the methods of Keller et al. (2014) and compared with the river DRP standard. The DRP river standard pertains to the resulting concentration after the wastewater discharge is mixed with the river flow. The river DRP standard of 0.010 mg P/L corresponds to the limit at part of the river were the Dannevirke STP discharge is located.

When the river has negligible existing DRP concentrations, chemical dosing to achieve a wastewater discharge DRP concentration of 1 mg P/L, then the contribution to river DRP concentration can be maintained at near or less than 0.010 mg P/L from May to November, and then mostly above 0.010 mg P/L for the remaining months, which coincides with lower river flows during the late spring to early autumn period. During the lowest rivers flows, between mid-December until early April, the river DRP also exceeds 0.015 mg P/L. Therefore, even when the river's existing DRP concentration is not accounted for, a wastewater discharge with a DRP concentration of 1 mg P/L is insufficient to achieve the standard of 0.010 mg P/L all year round. Further treatment is required for about five months, when the rivers flows are the lowest. When the discharge DRP concentration is reduced to 0.25 mg P/L, by using the combination of chemical dosing and soil treatment, then the contribution to the river DRP concentrations remains below 0.006 mg P/L, even during the lower river flow months in summer.

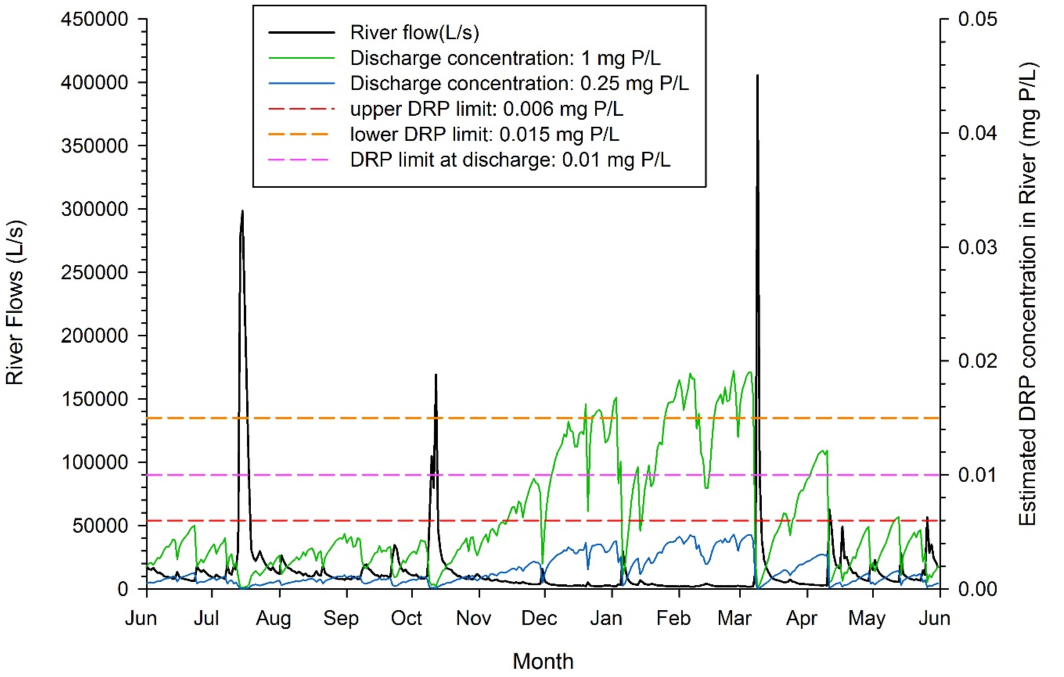

Figure 5.16 Estimation of river DRP concentration in the Manawatu River at Weber Road flow monitoring as influenced only by the STP wastewater DRP discharge (i.e. assuming existing river DRP concentration = 0 mg P/L)

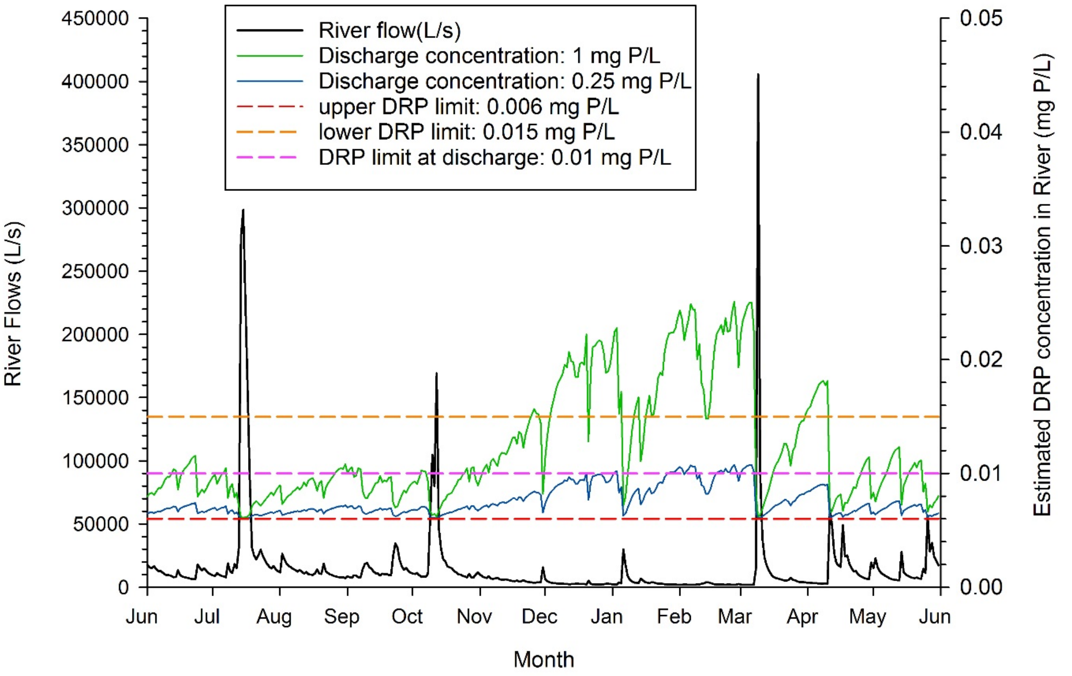

Figure 5.17 Estimation of river DRP concentration in the Manawatu River at Weber Road flow monitoring site as influenced by the STP wastewater DRP discharge also assuming an existing river DRP concentration = 0.006 mg P/L.

When the background river DRP concentration is at 0.006 mg P/L, a wastewater discharge DRP concentration of 1 mg P/L results in an estimated down-stream river DRP concentration above the DRP standard of 0.010 mg P/L for the majority of the time from November to June. If the discharge concertation is reduced to 0.25 mg P/L then the river concentration can be maintained near or below the river standard of 0.010 mg P/L all year round (Figure 5.17). Therefore, it is conceivable, assuming the background river DRP level is below 0.006 mg P/L, that using chemical dosing to achieve a discharge DRP concentration of about 1 mg P/L can maintain river DRP levels close to the river standards for about half of the year with the highest river flows. Then the additional use of soil filtration to produce DRP discharge concentrations close to 0.25 mg P/L will help to maintain to river DRP values near or below to the river standard for the remainder of the year. Therefore, the longevity of the filter when the wastewater DRP concentration is an average of 1 mg P/L, and when only used for about six months each year, would be about 18 years (i.e. double the longevity shown in Figure 5.15). However, a further analysis using actual river background DRP concentrations is needed to assess the exact number of months that the soil filter operation is required each year as a final polishing step for DRP removal. Further research is also required to assess the effectiveness of soil filters when initial DRP concentrations are close to 1 mg P/L, which is higher than the average wastewater concentrations used in this study

5.6 Conclusions

The pilot-scale Allophanic soil filters were conducted to test their performance at removing DRP under field conditions. For the entire filter operation at Dannevirke STP, the quantity of P sorbed by the soil was an estimate of 6.40 mg P/g oven-dried soil; achieving an overall removal efficiency of DRP from the wastewater of 67%. In comparison, the quantity of P sorbed by the soil in the pilot-scale study at Fonterra Te Rapa WTP was 1.85 mg P/g oven-dried soil on average. However, the lower value at this site was in part due filter operation stopping while the average removal efficiency was still high (86%), which was due to clogging of the filters, but were also due to the delay in the use of acid dosing and the use of 'as-received' soil rather than sieved soil. The introduction of acid dosing at Te Rapa WTP, which decreased wastewater pH on average from 8.3 to 6.7, substantially improved the incremental P removal efficiency. However, due to ongoing issues with algal deposition and growths in the ponded wastewater on the filters, the study has ended before the influence of acid dosing could be fully assessed. This highlighted the importance of using wastewater with a low level of suspended solids prior to treatment with soil filters, as was the case with the Dannvirke STP system. Soil removal and sieving may also contribute to further improvements by increasing the contact between wastewater and the soil reactive surfaces and uniform distribution of soil particle size.

A cost/benefit analysis of acid dosing estimated that the cost of dosing is about ten times greater than the cost of supplying additional soil to maintain the same amount of P removal, for a wastewater treatment site that is 225 km away from the soil source. Therefore, it is unlikely that acid dosing will be cost competitive for most wastewater treatment sites in the central North Island. The full-scale soil filter designed for the Dannevirke STP would have a relatively short longevity of less than 2 years, if used as the primary DRP removal method. Therefore, to improve the longevity of soil filters it may be beneficial to use in combination with other DRP removal method, such as chemical dosing. Modelling to predict the contribution of DRP from Dannevirke STP discharge to the river estimated that chemical treatment to achieve a wastewater DRP concentration of 1 mg P/L is insufficient to comply with the Manawatu River DRP standard year-round. Using a soil filter as a final wastewater polishing step, in combination with chemical treatment, to further reduce wastewater DRP concentration from 1 to 0.25 mg P/L in the wastewater, for about 6 months each year (i.e. during the low flow summer months where dilution factor is low) would improve the ability of the STP be achieve compliance and reduce chemical costs. This is also estimated to extend the longevity of the soil filter to about 18 years. Once a soil filter has been exhausted in terms of its P removal capacity, then there is the potential to re-use some of the captured P for plant growth. The following chapter describes a glasshouse experiment use to quantify the fertiliser P value of the P-enriched soil used in the pilot filters at the Dannevirke STP.

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Chapter 6

Assessing the agronomic effectiveness of wastewater- treated Allophanic soil as a phosphorus source for plant growth

Publication arising from this Chapter:

Cheuyglintase S, Hanly JA, Horne DJ (2018) Assessing the agronomic effectiveness of wastewater treated Allophanic soil as a phosphorus source for plant growth. *Soil Use and Management* 34(4): 472-478 .

6.1 Introduction

Key sustainability challenges for phosphorus (P) use include low life cycle P use efficiency and limited recycling of P in food production systems, and the increasing transfers of P to water bodies (Camps-Arbestain & Hanly, 2017). Enrichment of freshwater lakes and rivers with P promotes nuisance weed and periphyton (algal) growth, causing a decline in water quality. Point-source discharges, primarily from domestic sewage treatment plants (STPs), can be a major cause of elevated dissolved reactive phosphorus (DRP) concentrations during low-flow conditions (Jarvie et al., 2006; Neal et al., 2010; Macintosh et al., 2011), examples of which have been evident at many river-monitoring sites within the Manawatu-Wanganui region of New Zealand (Ausseil & Clark, 2007). Reducing the DRP load in STP wastewater discharges at critical times of the year is expected to help improve water quality. The most widely used method of P removal is chemical precipitation using alum (Huang et al., 2000), but this method can be cost-prohibitive (Morse et al., 1998) for small to medium sized STPs, as the cost per capita typically increases as population size decreases (Keplinger et al., 2004). The cost of chemical P treatment includes the disposal of the resulting sludge via enclosed landfill (Aguilar et al., 2002).

Active filters, which are comprised of reactive media, have been shown to remove P from wastewater (Kostura et al., 2005; Shilton et al., 2005, 2006). A wide variety of substrates have been used in these filters, with limestone and steel waste being just a few examples (Johansson Westholm, 2006; Haynes, 2015). Soils and parent materials derived from tephra (volcanic ash and lapilli) have potential as relatively low-cost substrates for use in active filters. The presence of hydrous oxides of iron and aluminium, associated with the mineral allophane, has been shown to influence the P-sorbing capacity of these soils (Parfitt, 1989). Allophanic soils (New Zealand Classification), also known as Andisol soils (USDA Soil Taxonomy), formed from andesitic tephra generally have relatively high P retention values. These soils occur in many parts of the world, but occur mostly in countries around the Pacific Ring of Fire, including Chile, Ecuador, Colombia, Mexico, the Pacific Northwest USA, Japan, Indonesia and a number of Pacific Islands countries, including New Zealand's North Island. The ability of Allophanic soils to act as P filters has been demonstrated in a number of laboratory batch or column studies (Ryden & Syers, 1975; Liesch, 2010; Hanly et al., 2011, 2012). Once the P sorption capacity of the Allophanic soil is exhausted, it has potential for re-use as a soil amendment. The capture of P by a soil filter provides the opportunity to recycle this P by applying it to agricultural land to supply P to meet crop requirements. Knowing the agronomic effectiveness of the P-enriched soil will help to establish its value as a P source and whether this benefit will help to offset disposal costs (Hylander & Sim´an, 2001). Its value as a P source will be influenced by its P fertiliser equivalent value for maintaining plant available P status of land, such as that measured by the Olsen P soil test (Johnston &

Richards, 2003). Grazed perennial ryegrass (*Lolium perenne*) and white clover (*Trifolium repens*) pasture is one of the main land uses in the Manawatu-Wanganui region that requires annual inputs of fertiliser P to maintain soil test levels and, therefore, these farms are potential end users of soil filter P derived from wastewater.

The objective of this study was to evaluate the agronomic effectiveness of soil filter P as a P source for ryegrass growth. The P-enriched soil was obtained from a pilot-scale filter used to treat wastewater from an STP. A glasshouse experiment was conducted to determine the equivalent soluble fertiliser P value of the soil filter P, by comparing it with mono-calcium phosphate (MCP) in terms of its influence on Olsen P soil test levels and on ryegrass dry matter (DM) yield and P uptake.

6.2 Materials and methods

6.2.1 Phosphorus sources

The two phosphorus sources used in this study were soil used to filter wastewater and MCP. The soil was obtained from a pilot-scale filter study evaluating the effectiveness of an Allophanic soil at removing DRP from wastewater sourced from the Dannevirke STP, Tararua District, New Zealand (see Chapter 5 for details). The soil was originally sourced from a quarry located approximately 10 km north-west of the township of Ohakune, Ruapehu District (175°180E, 39°210S). The soil (10–60 cm soil depth) is an Ohakune silt loam soil, which is classified as Typic Orthic Allophanic Soil (NZ Soil Classification; Hewitt, 2010), and is a well-drained, moderately permeable soil formed from andesitic tephra ash with a high allophane content of 49%. Prior to wastewater treatment, the original Ohakune soil had an Anion Storage Capacity (ASC; Saunders, 1965) test value of 100% and contained a total P

(TP) concentration of approximately 533 mg P/kg oven- dried soil. The soil was used to filter STP wastewater (i.e. wastewater-treated soil, hereafter referred to as WTS), which had received prior pond and micro-filtration treatment, for a combined operational period of 440 days. At the end of this period, the WTS contained a TP concentration of 8128 mg TP/kg oven-dried soil (0.81% P), therefore, the wastewater is estimated to have contributed 7595 mg TP/kg oven-dried soil. It was determined that 6397 mg P/kg oven-dried soil was from wastewater DRP and, therefore, an estimated 1198 mg P/kg oven-dried soil is likely to have been from organic P or other forms of non-reactive P in the wastewater. The MCP fertiliser treatment was used to provide a soluble phosphate source as a comparison for the WTS. The WTS soil had a pH of 6.2, an Olsen P value of 435 mg P/kg soil and a total N (TN) of 0.46% N.

6.2.2 Soil for pot trial

The main growth medium soil used for this glasshouse pot experiment was also an Ohakune silt loam sourced from another site near Ohakune (175°230E, 39°240S). This soil was selected as it has low fertility and similar ASC and physical properties to the original WTS. The soil was collected from below the topsoil layer. The soil had a pH of 6.2, an Olsen P value of 4.4 mg P/kg soil, a TP of 0.12% P, a TN of 0.82% N and an ASC test value of 94%.

6.2.3 Glasshouse experiment

Ryegrass was grown in pots of air-dried Ohakune silt loam (sieved to <4 mm) to compare the effects on yield of adding either WTS or MCP as a P source. The WTS treatment was applied at rates of: 347 (WTS1), 486 (WTS2), 686 (WTS3), 914 (WTS4) and 1494 (WTS5) mg TP/kg oven-dried soil (this equated to adding 4.3–18.4% of the total weight of the oven-dried soil in the pot). There were two WTS5 treatments; one received the standard quantity of nitrogen fertiliser (WTS5) described below, while the other received a higher N rate (WTS5-HN). The quantity of the growth medium Ohakune soil was adjusted to provide a total soil weight of 585 g air-dried soil/pot (equivalent to 500 g oven-dried soil), including the weight of the WTS. The MCP treatment was applied at 60 (MCP1), 120 (MCP2), 180 (MCP3), 240 (MCP4) and 300 (MCP5) mg TP/kg oven-dried soil and a Control (no added P) treatment. The proportion of TP that was plant available was originally predicted to be very different between the two materials (MCP and WTS), with the WTS expected to have only a small percentage of its TP being plant available. Therefore, rather than basing the rates of the two materials on their TP content, it was based on their expected influence on Olsen P, with the aim of achieving a similar range of Olsen P levels from below to above optimum (~30 mg P/kg soil) for both treatments. Each treatment was replicated five times and all pots received the same rates of basal potassium (K) sulphate (equivalent to 200 mg K/kg oven-dried soil). The fertiliser quantity required for each pot was individually weighed and mixed with soil for each pot. After mixing, a small quantity of soil was removed from each pot and 40 Italian ryegrass seeds (*Lolium multiflorum*) were evenly distributed on top of the soil and then the removed soil was applied to thinly cover the seeds.

Each pot was randomly allocated to a position within one of the five rows on a table in a glasshouse, with each row having one pot from each treatment. After establishment, the ryegrass plants were thinned to the 15 strongest, well-spaced plants in each pot. Two days after thinning, a standard rate of urea (500 mg N/kg oven-dried soil) was applied as a solution to all of the pots except for the WTS5-HN treatment pots, which received 600 mg N/kg oven-dried soil. The N fertiliser solutions were reapplied after each ryegrass harvest. The pots were initially watered every second day and then daily during periods of higher growth rates, to achieve 80% of pot moisture holding capacity. The average minimum air temperature in the glasshouse during the experimental period was 14 °C and the average maximum temperature was 20 °C.

6.2.4 Plant and soil analysis

Three harvests were made over the total experimental period of 18 weeks. At each harvest, the ryegrass plants were cut 2 cm above the soil layer and air-dried at 70–75 °C. Soil samples were collected from each pot at the end of the experiment; these samples were air-dried, sieved to <2 mm and then analysed for Olsen P using the method of Olsen et al. (1954).

Following air-drying of harvested ryegrass herbage at 70 °C, herbage P concentrations were determined. This involved digesting approximately 0.2 g ground herbage in concentrated nitric acid (HNO3) using a block digester at 130 °C for 20 min followed by a step-up in temperature to 200 °C until approximately 1 mL of concentrate remained (Ni et al., 2018). The P concentrations of the digests were determined using atomic emission spectrometry (MP-AES, Agilent 4200).

6.2.5 Statistical analysis

The results were evaluated using analysis of variance (ANOVA) to identify any significant differences between treatments. Pairwise Multiple Comparisons were performed between each treatment using SigmaPlot graphing and data analysis tool, with significance set to $P < 0.05$ unless stated otherwise.

6.3 Results and discussion

6.3.1 Dry matter yield

The effects of treatments on ryegrass yield were highly significant ($P < 0.001$), with total cumulative ryegrass yields increasing with increasing rates of total

P added (Table 6.1). The total cumulative yield of the Control treatment (no added P) was only 0.28 g DM/pot, which reflects the very low P status of the Ohakune silt loam used as the growth medium. All other treatments significantly ($P < 0.001$) increased DM yield compared to the Control treatment. The highest yields were achieved by the WTS5 and WTS5-HN treatments, which had total cumulative yields of 9.32 and 9.65 g DM/pot, respectively. The yield of the WTS5-HN treatment was not significantly different from the WTS5 treatment, indicating that N availability was unlikely to be limiting yield at the lower rate of N (500 mg N/pot/application) when applied with the highest rate of WTS treatment.

The MCP treatments showed a general trend of increasing yields with increasing P rates. The four higher rates of MCP achieved ryegrass yields significantly higher than the MCP1 treatment. In addition, the highest rate of MCP (MCP5) resulted in a ryegrass yield of 6.53 g DM/pot, which was significantly higher than yields of the three lowest MCP rates. The WTS treatments also showed a trend of increasing yields with increasing P addition. All WTS treatments, except for the WTS3 and WTS4 treatments, resulted in yields that were significantly different from each other. The two highest rates of WTS achieved yields that were higher than all of the MCP treatments.

Table 6.1 Ryegrass cumulative dry matter yields, herbage P concentration and total P uptake over all three harvests.

Treatment	TP application rate (mg P/kg oven-dried soil)	Dry matter yields of individual harvests (g DM/pot)			Cumulative dry matter yield (g DM/pot)	Average herbage P concentration (% P)	Plant total P uptake (mg P/pot)
		Harvest 1	Harvest 2	Harvest 3			
Control	0	0.11	0.08	0.09	0.28^{a**}	0.05^{a**}	0.15^{a**}
MCP1	60	0.55	1.80	1.30	3.65^{b}	$0.13^{b,c}$	4.85^{b}
WTS1	347	0.95	2.26	1.70	4.91^{c}	0.11^{b}	5.56^{b}
MCP2	120	0.94	2.46	1.83	$5.23^{c,d}$	$0.13^{b,c}$	$6.89^{b,c}$
MCP3	180	1.07	2.50	1.72	$5.29^{c,d}$	$0.17^{c,d}$	$8.93^{c,d}$
MCP4	240	1.21	2.81	2.02	$6.04^{d,e}$	$0.20^{d,e}$	12.14^{e}
WTS2	486	1.72	2.44	1.92	$6.08^{d,e}$	$0.17^{c,d}$	$10.9^{d,e}$
MCP5	300	1.38	3.00	2.15	6.53^{e}	$0.19^{d,e}$	13.74^{e}
WTS3	686	2.26	2.72	2.01	$6.99^{e,f}$	$0.19^{d,e}$	13.13^{e}
WTS4	914	2.56	3.13	2.32	8.01^{f}	0.22^{e}	17.70^{f}
WTS5	1494	3.00	3.83	2.49	9.32^{g}	0.29^{f}	27.12^{g}
WTS5-HN*	1494	3.14	3.88	2.63	9.65^{g}	N/A	N/A

*HN = Higher rate of N, which was 600 mg N/kg oven-dried soil/application. All other treatments received 500 mg N/kg oven-dried soil/application. **Means with the same letter are not statistically different ($P<0.05$). N/A = not analysed.

6.3.2 Relationship between total P addition and Olsen P

For the MCP and WTS treatments, there were clear linear relationships between the TP addition and the Olsen P values of the soil sampled at the conclusion of the experiment (Figure 6.1). The Olsen P response per unit of TP addition was higher with MCP, compared to WTS. The response of Olsen P to added MCP was lower than originally predicted, as a result of the soil's very high ASC (94%), with the highest rate achieving an Olsen P of <14.6 mg kg P/kg soil, which was lower than the target of ~30 mg P/kg soil. In addition, the response of Olsen P to added WTS was higher than originally predicted, with the highest rate achieving an Olsen P of 33.0 mg P/kg soil. However, for some of the rates used, there was an overlapping in Olsen P responses for the two materials. Therefore, it was possible to determine that the rate of Olsen P increase from total P addition for the WTS treatments was on average equivalent to 61% of the MCP response.

This value was derived from the ratio of the slopes obtained from the linear relationship between total P added and Olsen P values of MCP and WTS treatments (Figure 6.1; ratio = 0.605). Other studies using P-sorbing materials to remove P from wastewaters have shown that the fertiliser equivalent value of the retained P can vary greatly, from as little as 4% for ochre (Dobbie et al., 2005) to as much as 109% for precipitated phosphates (Johnston & Richards, 2003). The difference in P availability between WTS and MCP can likely be accounted for by the proportion of the TP in the WTS being strongly sorbed by hydrous oxides of iron and aluminium, and, therefore, unavailable to plants. According to Johnston & Richards (2003) and Dobbie et al. (2005), the insoluble portion of sorbed P may become available over time. For example, Dobbie et al. (2005) showed that P-saturated ochre acted as a slow-release P source, where the initially unavailable bound P became available over time owing to conversion of unavailable P into available forms via dissolution of unavailable Ca, Al and Fe phosphates from the secretion of root organic acids (Dakora & Phillips, 2002). The long-term P availability from WTS should be further evaluated in an extended study.

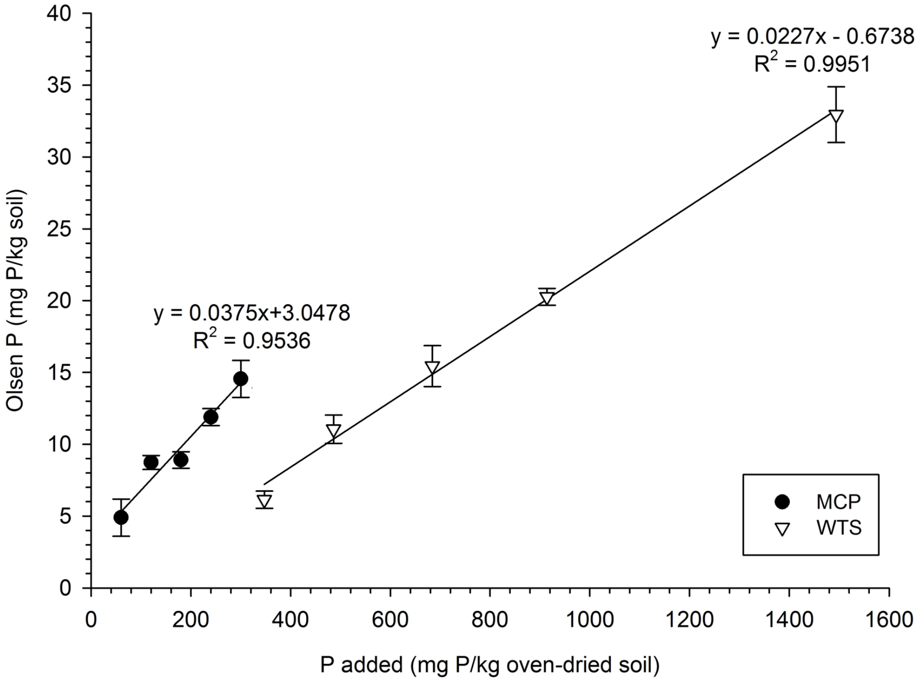

Figure 6.1 Relationship between total P added and Olsen P values of each treatment.

6.3.3 MCP-equivalent value of WTS

The yield response curve for the different rates of MCP and different rates of MCP-equivalent P added in WTS is presented in Figure 6.2. The MCP-equivalent P added in the WTS assumes, based on the Olsen P response, that the P in WTS is equivalent to 61% of the solubility of the P in MCP, which contains 100% citric acid (2%) soluble P. The diminishing marginal yield near the top of the response curve indicates that the highest rate of WTS (a MCP-equivalent rate of 904 mg P/kg soil) provided a near maximum yield response from added P.

The effect of treatments on ryegrass P concentration and uptake was statistically significant ($P < 0.001$). Herbage P concentrations were lowest for the Control treatment (0.05% P) and highest for the WTS5 treatment (0.29% P) and showed a close linear relationship with total cumulative yield ($R_2 = 0.89$). Robinson & Eilers (1996) demonstrated that when ryegrass P concentration was similar to that achieved by the WTS5 treatment, then 95% of maximum yield was achieved. In the current study, higher P concentrations and yields resulted in higher P uptake, which ranged from as little as 0.15 mg P/pot, for the Control treatment, up to 27.12 mg P/pot, for the WTS5 treatment. Saggar et al. (1993) also used a glasshouse study to assess the relative agronomic effectiveness of various P sources, added to soils with low initial P status (Olsen $P < 15$ mg P/kg). They also found that both ryegrass P uptake and yield increased significantly with P addition.

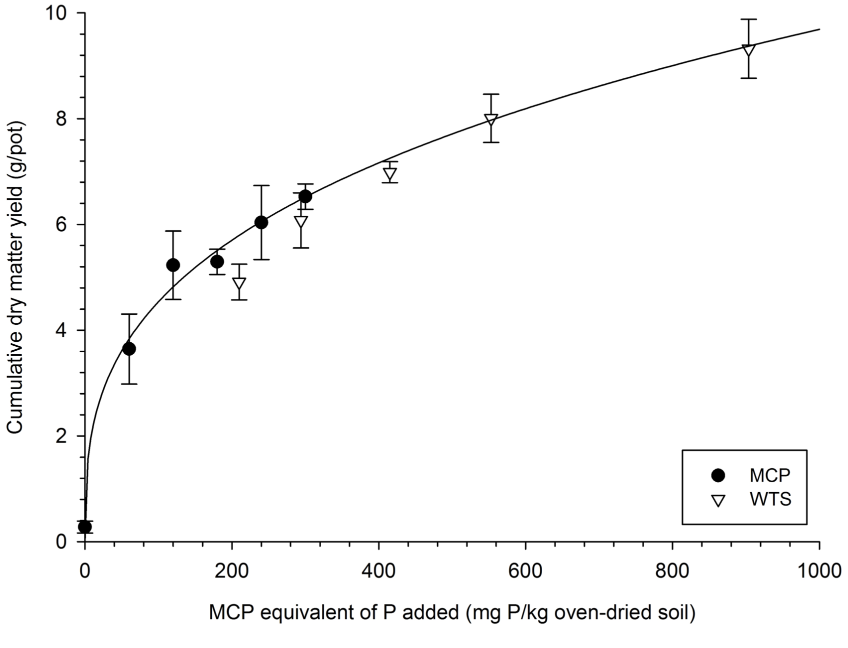

Figure 6.2 Relationship between rates of MCP-equivalent P added and ryegrass cumulative dry matter yield.

6.3.4 Relationship between Olsen P and dry matter yield

The relationship between Olsen P and cumulative dry matter yield (Figure 6.3) exhibited a similar response curve to that presented in Figure 6.2. Near maximum ryegrass yield was achieved at an Olsen P of approximately at 30–35 mg P/kg soil, which is a little higher than the 'optimum range' for Ash soil of 20 – 30 mg P/kg soil (Roberts & Morton, 2016). In glasshouse conditions, where there are very few limitations to growth, there may be further yield benefits from a higher soil P status compared to field conditions (Tillman et al., 2012). The yield response in this study from added P showed that the relationships were similar for both forms of P added when the WTS P was expressed as its MCP-equivalent value (i.e. 61% of TP), which was obtained from the Olsen P response. However, longer studies have shown that the relative agronomic effectiveness of less soluble P sources improved relative to MCP, owing to the decrease in the absolute effectiveness of MCP over time (Saggar et al., 1993). Therefore, it is possible that over a longer growth period the MCP-equivalent value of P in WTS could have improved further. A longer-term study would be required to confirm this.

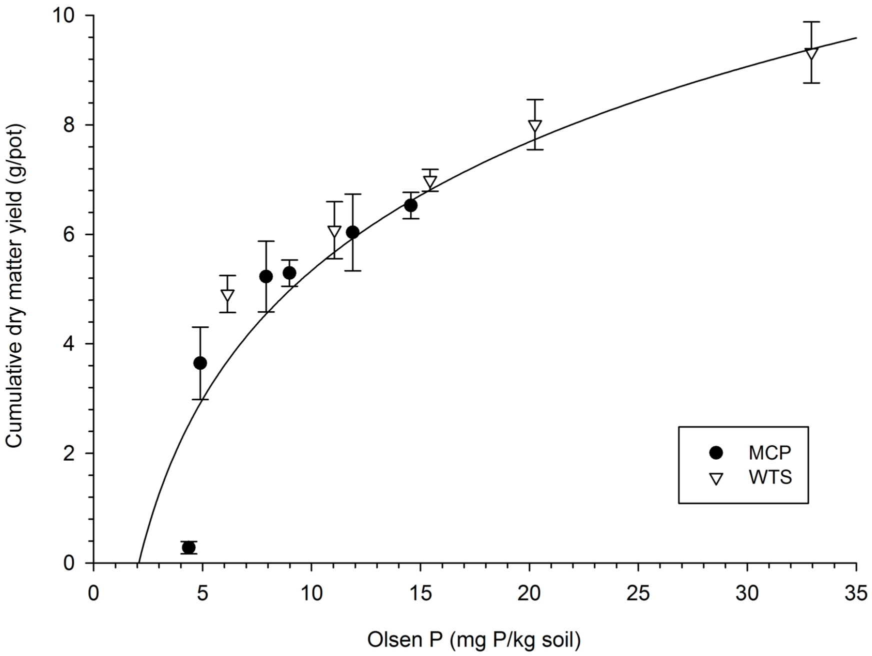

Figure 6.3 Relationship between cumulative dry matter yield and the rate of P uptake.

6.3.5 Use of WTS as a phosphorus source for pastoral farms

The glasshouse pot study allowed the performance of the WTS to be compared with an established P fertiliser, which is a common method used for evaluating fertiliser materials (Mackay et al., 1984; Saggar et al., 1993). This then provides an indication of its likely performance when scaled up to the field level, which can then be confirmed with field trials. The likely usefulness or role of WTS as a P source for pastoral farms is demonstrated with the following example. A town the size of Dannevirke, with a population of approximately 5500, and a soil filter of 2000 m^3, would supply approximately 6688 kg MCP-equivalent P annually (assuming a bulk density of 680 kg oven-dried soil/m3). Using a WTS application depth of 1 mm (10 m^3/ha), this would supply approximately 33.4 kg MCP-equivalent P/ha to an area of 200 hectares. This rate of P addition is similar to the annual maintenance fertiliser P requirements of an average pastoral dairy farm (~12 000 kg DM/ha/yr pasture production) with an Olsen P of 30 mg P/L and a medium ASC (OVERSEER® Nutrient Budgets;

Shepherd & Wheeler, 2012). Assuming that the combined cartage and spreading costs are \$NZ25/T, then the cost of applying 6.8 T/ha (i.e. 10 m^3/ha) of filter soil is estimated to be \$NZ170/ha. In comparison, the cost of supplying the same quantity of soluble P using fertiliser would be ~\$NZ120/ha. Therefore, the net cost of using the filter soil, above the savings in fertiliser costs, would be \$NZ50/ha (\$NZ5/m^3). This represents a relatively small cost of recycling the soil once its use for wastewater treatment is completed, making it a cost- effective alternative to transportation and disposal in a landfill. The cost of removing the soil from the filter containment area was not included in the cost assessment, because this cost would be incurred irrespective of whether the soil was applied to land or landfill.

If the filter soil was replaced once every five years, then the annual maintenance fertiliser P requirements of a ~200 ha farm could be met by application of the filter material in the year of replacement. Higher rates could be used on a cropping farm where the WTS would be incorporated into the soil with cultivation.

Environmental considerations with applying WTS to land include the potential addition of contaminants, such as heavy metals and pathogenic microorganisms, being transferred to land as well as the risk of increasing of P losses to water. Municipal wastes are known to contain heavy metals, such as zinc, cadmium and lead (Kaplan et al., 1987). However, heavy metals accumulate more typically in biosolids, with less being retained in treated wastewaters that would be applied to soil filters. Alternatively, WTS can be applied to forestry land instead of agricultural land as a means to reduce heavy metal cycling in the human food chain (Wolstenholme et al., 1992). Pathogenic organisms present in wastewater, such as enteric viruses, Giardia cyst and Cryptosporidium oocyst (Payment & Franco, 1993), have potential to accumulate in soil filters during treatment. Hence, further research is required to determine which contaminants are likely to accumulate in soil filters when treating town wastewaters, and whether their levels would be considered unsafe for land treatment. Prior to land application, WTS should be tested to ensure that potential containments are quantified to determine whether they pose a risk. One notable advantage of WTS is that it just needs to be tested once for possible contaminants prior to land application. In comparison, land application of wastewater, which is continuously being applied to land, requires regular on-going sampling and analysis.

In order to minimise the risk of P losses to water from land applying WTS, best practices for land application of fertilisers and manures should be followed. The primary transport pathway of P to water is typically from overland flow rather than via leaching in drainage water (McDowell et al., 2004). To mitigate the risk of P losses in overland flow, applications of WTS should avoid times of year when soils are at or near saturation. Typically, this will mean avoiding applications from late autumn to early spring. In addition, applying the WTS to land with flat topography will also reduce the potential for losses via overland flow.

6.4 Conclusions

In the glasshouse evaluation, ryegrass yield was significantly increased by P addition, owing to the very low initial P status of the soil. The WTS was highly effective at increasing available P in the soil, as measured by increases in Olsen P values and ryegrass yield. Based on both the Olsen P test response and the ryegrass yield response, the soluble fertiliser P value of WTS was estimated as being more than half of its total P content, when compared to the response from a soluble P source (MCP). These results support the view that WTS has agronomic value as a P source for agricultural production, and, therefore, provides a way of recycling P that would otherwise be lost from productive use. This provides an advantage over some other more common wastewater treatment methods for DRP removal, such as chemical dosing with alum, which often involve land filling for the resulting sludge and loss of P from the productive cycle.

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DRC 16

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STATEMENT OF CONTRIBUTION
TO DOCTORAL THESIS CONTAINING PUBLICATIONS

(To appear at the end of each thesis chapter/section/appendix submitted as an article/paper or collected as an appendix at the end of the thesis)

We, the candidate and the candidate's Principal Supervisor, certify that all co-authors have consented to their work being included in the thesis and they have accepted the candidate's contribution as indicated below in the *Statement of Originality*.

Name of Candidate: Sasikunya Cheuyglintase

Name/Title of Principal Supervisor: Dr. James Hanly / Senior Lecturer in Soil Science

Name of Published Research Output and full reference:

Cheuyglintase, S., J. A. Hanly, and D. J. Horne. 2018. Assessing the agronomic effectiveness of wastewater treated Allophanic soil as a phosphorus source for plant growth. Soil Use and Manag. 1-7.

In which Chapter is the Published Work: Chapter 6

Please indicate either:

- The percentage of the Published Work that was contributed by the candidate:

  and / or ~70%

- Describe the contribution that the candidate has made to the Published Work:

The candidate was responsible for undertaking the research as described in the Published work as well as data analysis and manuscript preparation. This was conducted under the superision of the Principal Supervisor, who has contributed by providing constructive feedbacks and validated and approved the protocols in the study.

Sasikunya C.
Candidate's Signature

28/11/2018
Date

Principal Supervisor's signature

28/11/2018
Date

GRS Version 3– 16 September 2011

Chapter 7

Conclusions and Recommendations

7.1 Conclusions of research findings

7.1.1 Waikato Region quarry soil sampling and P retention results

The soil survey involved collecting soil samples from five quarries in the Waikato

Region and then the subsequent evaluation of the P retention of these samples by both the standard and modified ASC tests (Chapter 3). This work identified that only soils collected from one of the quarries in the Waikato, the Te Mata Quarry (TQ), had P retention levels that were sufficiently high enough to be suitable for evaluation as a possible P sorbent in soil filters. The soils from this quarry had P retention values near or at 100% using the standard ASC test. Therefore, it was necessary to use a modified (1 g soil) P retention test to be able to rank the soil's ability to sorb P. Using this modified test, all soil depths in one of the soil profiles sampled to a depth of 6 m, except for the 1.25 - 1.75 m soil depth, had values >58% P retention, which indicates a high P retention capacity. Overall, the modified ASC test provided an effective means of ranking the soils according to their potential P sorption capacity. Further evaluation of this soil's ability to remove DRP from wastewaters was quantified in a column study, which is discussed in the next section.

7.1.2 Effects of acid dosing dairy processing wastewater on phosphorus removal using Allophanic soil filtration

The soil column study, described in Chapter 4, evaluated the effect of acid dosing dairy processing wastewater, with two types of acid (HCl and H2SO4), on the P removal capacities of the Ohakune Quarry (OQ) soil. The pH of wastewater significantly influenced P removal capacity of the OQ soil. Soil columns that were used to filter wastewater that was acid dosed showed higher reductions in wastewater DRP compared to soil columns without acid dosing. The treatment that involved wastewater with a pH adjusted to 5.5 ranked the highest in terms of P removal (9.44 mg P/g oven-dried soil). This compares to a removal rate of only 6.50 mg P/g oven-dried soil for the OQ soil without acid dosing. The TQ soil achieved a similar level of P removal to the OQ soil but with less acid dosing (adjusted to pH 6.5), which was likely due to the TQ soil having a higher P retention value. There was no significant difference in the effect that acid type (either hydrochloric or sulphuric acid) had on the quantity of P removed from the wastewater by the OQ soil. Therefore, it is suggested that the type of acid used is not likely to influence P removal capacity of soils. Overall, acid dosing was an effective method of improving the performance of Allophanic soils at removing DRP from wastewater. However, if the benefit gained by acid dosing can be achieve by using additional soil at a lower cost, then it would be more economic to replace the soil more frequently instead of treating the wastewater with acid.

7.1.3 Phosphorus removal from municipal and dairy factory wastewater using pilot-scale Allophanic soil filters

The performance of pilot-scale soil filters containing OQ soil were monitored at the Dannevirke STP and Fonterra Te Rapa dairy processing WTP (Chapter 5). Dissolved reactive phosphorus removal values varied between the two sites. At the end of the study, the soil filters at the Dannevirke STP achieved a higher quantity of P removal than at the Fonterra Te Rapa WTP, removing a total of 6.4 mg P/g oven-dried soil while the latter removed a total of 1.85 mg P/g oven-dried soil. This difference was largely due to the Dannevirke sol filter receiving more DRP in wastewater relative to the quantity of soil in the filters, because the Fonterra filters contained more soil. Due to clogging of the filters, the filter operation at the Fonterra site was stopped when the average removal efficiency was still high (86%). Therefore, it was not possible to evaluate the DRP removal capacity at the same level of average removal efficiency (67%) achieved at the Dannevirke site. The introduction of acid dosing at the Te Rapa WTP, which decreased wastewater pH on average from 8.3 to 6.7, substantially improved the incremental P removal efficiency. However, due to ongoing issues with filter clogging, the study was ended before the influence of acid dosing could be fully assessed.

The soil filters at the Dannevirke STP had less problems with blockages compared to Fonterra Te Rapa WTP. This is likely due to the STP wastewater being treated via a micro-filtration plant prior to application to the filters, which resulted in low suspended solids concentrations. This highlighted the importance of using wastewater with a low level of suspended solids prior to treatment with soil filters. Sieving of the soil from the filters at this site, part way through the study, may have also contributed to improvements in DRP removal by increasing the contact between wastewater and the soil's reactive surfaces.

A cost/benefit analysis of acid dosing showed that the if the soil source is 225 km away from the treatment site then the cost of dosing is about ten times greater than the cost of supplying additional soil to maintain the same amount of P removal. Therefore, it is unlikely that acid dosing will be cost competitive for most wastewater treatment sites in the central North Island.

The full-scale soil filter designed for the Dannevirke STP was estimated to have a longevity of <2 years when used as the primary DRP removal method. Therefore, to improve the longevity of soil filters it may be beneficial to use it in combination with other DRP removal methods, such as chemical dosing. For example, if chemical dosing reduced the wastewater DRP concentration to approximately 1 mg P/L, then the soil filter can be used to remove the remaining DRP up to 0.25 mg P/L. If the soil filters are in use for 6 months each year during the low flow summer months, then it this could potentially extend the longevity of the soil filter up to about 18 years.

7.1.4 Phosphorus availability of P-enriched Allophanic soil and their application to ryegrass

The wastewater treated soil (WTS) was obtained from the pilot study soil filters form the Dannevirke STP, which is described in Chapter 5. In Chapter 6, glasshouse pot study compared the effect of the WTS with monocalcium phosphate (MCP) on Olsen P and ryegrass growth. The rate of Olsen P increase following the addition of WTS was, on average, equivalent to 61% of the corresponding response to MCP. This study demonstrated that a substantial portion of the P removed from wastewater by the WTS can be recycled for maintaining or increasing soil P status and for plant growth. An effective soil filter size of 2000 m^3 might be expected to supply about 6700 kg of MCP equivalent P or 33.4 kg of MCP-equivalent P/ha to a 200 ha farm at 1 mm application depth. This is a similar rate as the annual P fertiliser required to maintain an average pastoral dairy farm with an Olsen P of 30 mg P/L and a medium ASC. Therefore, WTS has an agronomic value as a P source for agricultural production, and, therefore, provides a way of recycling P that would otherwise be lost from productive use.

7.2 Recommendations for future research

Areas of future research include the following:

- Evaluation of the performance of soil filters in combination with other P removal treatments, such as chemical dosing, at pilot- or full-scale. This could include assessing the influence that changing wastewater DRP concentrations have on the potential for desorption of P from soil filters.
- Evaluate the long-term effect of applying WTS to land field conditions, to compare its agronomic value to P fertilisers. Methods to improve the plant availability of the P retained by the WTS, should be examined to enhance plant P uptake. For example, the effects of pH and plant root interactions on P availability. Also, as WTS is an emerging class of soil amendment, assessment of the potential of heavy metal and pathogen contamination from WTS application to crops is needed.
- For optimisation of soil filter performance, other soil configurations should be considered, for example, the use of Multi-Soil-Layering (MSL) technique to reduce preferential flow and remove a range of wastewater contaminants in combination with other materials, such as charcoal and zeolite.
- The dosing of wastewater with very fine soil particles could, as an alternative to soil filters, could potentially eliminate preferential flow and maximise P removal efficiency of the soil. To achieve both higher P sorption by soil and lower final P solution concentrations, the wastewater could be dosed to wastewater in a series of mixing tanks where fresh soil is applied to mixing tank with the lowest wastewater P concentration (i.e. the final stage). The soil used for dosing this final stage, could be reused to dose earlier stages with

higher wastewater P concentrations, thereby, maximising the P sorption by the soil.