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The application of mine waste for the removal of phosphorus from wastewater

Victoria Pinner

The research presented in this thesis aimed to investigate the use of ochre, produced during mine water treatment, for the removal of phosphorus from wastewater. Three methods of ochre application were tested: as part of a filter-based system, dosed directly into wastewater and transformed into a coagulant. Ochre from five sites in North East England were used in the trials; Acomb, Bates, Blenkinsopp, Dawdon and Saltburn.

Prior to the ochre-based filter trials, three binder materials were tested for mixing with Dawdon ochre to produce an adsorbent layer. Based on these trial results, the Dawdon ochre was mixed with sand for the onsite ochre-based filter trials. These trials were completed on two scales: within an IBC and within pond filter units. The filter trial results suggest that ochre-based filters are capable of removing phosphorus as a tertiary treatment, but removal is not consistent. Small-scale growth experiments were completed to determine whether phosphorus-saturated ochre adsorbent from filter systems could be used as a fertiliser. The results from these trials suggested phosphorus-saturated ochre does not improve plant growth.

Phosphorus removal when dosing ochre was investigated at bench-scale. The trial showed that the ochre was capable of removing phosphorus but was not able to equal the removal of ferric sulphate. Phosphorus removal when dosing ochre was found to be affected by ochre dose, source and form as well as flocculation time. All five ochres were trialled.

The coagulant produced from the five ochres (ochre derived ferric; ODF) was trialled as part of bench-scale jar tests which demonstrated the phosphorus removal potential. The results showed that the ODF was not as effective as ferric sulphate and does not have an equivalent iron content. A trial was completed dosing Bates ODF upstream of primary settlement tanks at a sewage treatment works, however, the results were inconclusive.

The application of mine waste for the removal of phosphorus from wastewater

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List of Abbreviations

AMD	Acid Mine Drainage	20
Cm	Centimetre	33
COD	Chemical Oxygen Demand	18
DI	Deionised water	49
FTU	Formazin Turbidity Units	57
G	Grams	23
g/l	Grams per litre	46
HRT	Hydraulic Retention Time	43
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy	50
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy	50
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy	51
L	Litre	20
L/s	Litres per second	28
M	Molar	19
Mg	Milligrams	13
mg PO ₄ /g	Milligrams of phosphate per gram	13
mg/l	Milligrams per litre	18
ml	Millilitre	25
ml/min	Millilitres per minute	28
Mm	Millimetre	25
MWTP	Mine Water Treatment Plant	20
NE	North East	13
ODF	Ochre Derived ferric	24
PE	Population Equivalent	17
PST	Primary Settlement Tank	44
Rpm	Revolutions per minute	20
SRP	Soluble Reactive Phosphorus	53
STW	Sewage Treatment Plant	17
TN	Total Nitrogen	17
TP	Total Phosphorus	18
TSS	Total Suspended Solids	19
μl	Microlitre	46
μm	Micrometre	25

UWWTD	Urban Waste Water Treatment Directive	17
w/w	Weight per weight	23
WFD	Water Framework Directive	17

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1. Introduction

1.1 Background

The removal and recovery of phosphorus from wastewater is an area of interest across the water industry. Phosphorus is a finite resource (Wendling et al., 2013) and excess levels in watercourses can lead to eutrophication (de Bashan and Bashan, 2004). Furthermore, high phosphorus content rock (used to produce fertilisers) is now listed as a critical raw material by the European Commission (Egle, 2016; EC, 2018).

Phosphorus removal at sewage treatment works is primarily achieved by the application of metal salts (Morse et al., 1998). However, new phosphorus removal technologies have been trialled as part of the UK Water Industry's Chemical Investigations Programme (CIP) (UKWIR, 2018).

Previous Durham University research into ochre's capacity for the removal of phosphate has been completed by Jessett (2014) and Pinner (2014). The results of Jessett (2014) showed that Dawdon ochre had a removal capacity of approximately 19 milligrams (mg) of phosphate per gram ochre (mg PO₄/g). The Pinner (2014) study confirmed that ochre within the North East (NE) had a high adsorption capacity for phosphate when tested in both batch and flow-through experiments.

This study sets out to further investigate the potential application of ochre for the removal of phosphorus from wastewater.

1.2 Aims

The overall aim of the study is to investigate the practical application of ochre, fine grained iron oxyhydroxides produced during treatment of coal and metal drainage, for the removal of phosphorus from wastewater where it presents a problem upon discharge. This overall aim is supported by the following specific aims:

- To investigate how sustainable the use of ochre is as an alternative to ferric salts for phosphorus removal from wastewater.
- To investigate the effectiveness of ochre for phosphorus removal as a granular media, as part of a filter-based system.
- To investigate the effectiveness of ochre when directly dosed into waste water for phosphorus removal as an alternative to ferric salts.

1.3 Hypotheses

The hypotheses to be tested are:

1. Ochre can be applied at sewage treatment works for the removal of phosphorus from wastewater.

Bench-scale and full-scale trials of using ochre for phosphorus removal are documented in the literature, for example, Heal et al. (2003; 2004) and Dobbie et al. (2009). As such, it should be expected that ochre can be used to treat waste water. However the specific ochre/waste water combinations in the North East of England have yet to be assessed at scale. Additionally, the way in which the ochre is immobilised for large-scale application needs assessing.

2. Ochre can remove phosphorus as effectively as traditional ferric sulphate

Chemical dosing to remove phosphorus using ferric sulphate is an established method of phosphorus removal in the water industry. Ochre must be as effective as ferric sulphate in order to be considered as an alternative method.

3. Phosphorus-saturated ochre from a filter-based system can be used as a fertiliser

Dobbie et al. (2005) demonstrated that phosphorus-saturated ochre could be used as a fertiliser. This reuse would offer a sustainable alternative to landfill, however, without a low-cost disposal route, the process would be unviable.

1.4 Overview of the study

The study looks at methods to develop a sustainable, practical application of ochre for the removal of phosphorus from wastewater which could be implemented on a sewage treatment works. As a result of this practical focus, the study is split into distinct trials, each with a different method of application. The key stages of the study are shown in Figure 1.1 and summarised in the following text.

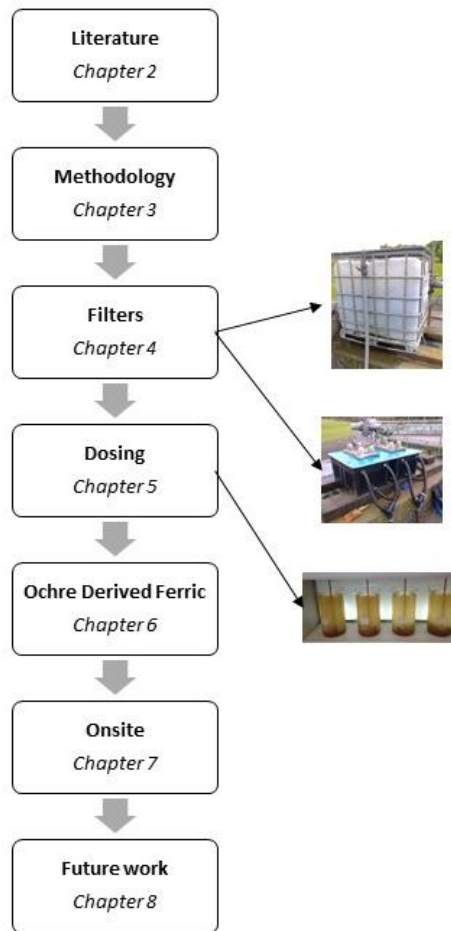


Figure 1.1: Key stages of ochre application development

Chapter 2 will focus on the previous academic literature relevant to the study, including mine water treatment and current chemical removal techniques for the treatment of wastewater.

Chapter 3 will provide a detailed methodology for each completed trial and any associated analysis.

Chapter 4 will focus on the use of ochre in a filter-based system for phosphorus removal from wastewater. The chapter will document the development from determining the optimal ochre-based adsorbent through to a series of filter-based onsite trials. Also included will be small-scale growth trials to determine whether phosphorus-saturated ochre is suitable for application to land as a fertiliser.

Chapter 5 will focus on the direct application of ochre as a slurry and as a solid by direct dosing. The trials completed were bench-scale jar tests investigating the impact of variables on phosphorus removal. Ochre will also be considered as a ferric supplement.

Chapter 6 will document bench-scale trials using a coagulant derived from ochre (ochre derived ferric).

Chapter 7 will focus on applying this coagulant on a sewage treatment works as part of an onsite trial.

Chapter 8 will summarise the key findings and conclusions from the completed work. This chapter will also include recommendations for future work building on these findings.

2. Literature review

2.1 Phosphorus

Phosphorus (P) is an essential element for life (Wendling *et al.*, 2013). However, when it is present in excess in watercourses it can lead to a phenomenon known as eutrophication, where an unusually rapid and significant algal growth occurs (de Bashan and Bashan, 2004). Phosphorus can be present in the form of orthophosphates, polyphosphates and organic phosphate in solutions (Tchobanoglous *et al.*, 2014a). Orthophosphates (such as PO_4^{3-} , H_2PO_4^- , HPO_4^{2-} and H_3PO_4) are biologically available forms of phosphorus whereas polyphosphates are complex molecules of phosphorus, oxygen and sometimes hydrogen which can be transformed into orthophosphates through hydrolysis (Tchobanoglous *et al.*, 2014a).

Depending on the pH of a solution, phosphorus can be present as a monovalent, divalent or trivalent ion (Triantafyllidis *et al.*, 2010). Triantafyllidis *et al.* (2010) calculated the species present depending on the pH of the solution. They calculated that at pH 6.5 phosphate was present predominantly as a monovalent ion (H_2PO_4^-), at pH 7.5 it was present in equal amounts as monovalent and divalent ions (H_2PO_4^- and HPO_4^{2-}) and around pH 9 and up to pH 10, it was present as a divalent ion (HPO_4^{2-}). The trivalent phosphate species is PO_4^{3-} (Triantafyllidis *et al.*, 2010). Jenkins *et al.* (1971) include a figure showing the speciation of phosphate in wastewater according to pH, which suggests that the monovalent PO_4^{3-} is present at pH values of 10 or greater.

The world's supply of phosphorus comes from phosphate rock, a finite resource (Cordell *et al.*, 2011) and some believe that within the next 50 to 120 years the current phosphate rock resources will be exhausted (Wendling *et al.*, 2013). Furthermore, it is estimated that after 2035 the supply of phosphorus will not be able to meet the forecasted demand (Cordell *et al.*, 2011). Globally, around 90 % of the mined phosphorus is used to grow crops for food and therefore phosphorus scarcity will have a knock-on effect on food security, particularly in areas without local phosphate rock reserves (Wendling *et al.*, 2013). To counteract the depletion of phosphate rock reserves, it is important that phosphorus in waste streams is recovered, recycled and reused.

There is a substantial amount of research still needed to establish the most sustainable method of recovering phosphorus from waste streams, as well as converting it into a fertiliser (Cordell *et al.*, 2011). As part of this research, Cordell *et al.* (2011) suggest that a number of factors should

be taken into account, these include life cycle costs as well as the energy requirements of the process and its accessibility and availability to farmers as a fertiliser product and any potential pollution the product could cause.

2.2 Phosphorus removal from wastewater

Phosphorus removal at Sewage Treatment Works (STWs) is driven by legislation such as the Water Framework Directive (WFD) and Urban Waste Water Treatment Directive (UWWTD), among others (Gray, 2017; Melia et al., 2017). The UWWTD applies to all STWs with a population equivalent (PE) of greater than 10000 which discharge into water bodies which are believed to be sensitive and at risk of eutrophication and stipulates the maximum concentration of total nitrogen (TN) and total phosphorus (TP) in the final effluent which is discharged from the works (Gray, 2017). All works covered by the UWWTD must remove at least 80 % of TP across the treatment process and works with a PE of between 10000 and 100000 must have no more than 2 mg TP/l in the final effluent. For works greater than 100000 PE, the limit for TP in the final effluent is 1 milligram per litre (mg/l). The WFD is supported by the UWWTD (as well as other directives) and required water bodies to achieve 'good' status by 2015 (Gray, 2017).

Phosphorus is present in wastewater in a range of forms and concentrations (Melia et al., 2017; Gray, 2017). On average, the total phosphorus concentration of wastewater entering a sewage treatment works is between 5 and 20 mg P/l, of which roughly 20 to 25 % is in an organic form (Gray, 2017). The standard STW process can remove some of this incoming phosphorus without any additional processes. For example, particulate phosphorus will be removed during clarification and settlement processes (Melia et al., 2017) and the secondary, biological process is able to remove between 1 and 2 mg P/l (Gray, 2017). However, when further inorganic phosphorus removal is required, this can usually only be achieved by chemical and biological methods (de Bashan and Bashan, 2004; Melia et al., 2017, Gray, 2017).

Coagulation is a chemical process reducing the charge of particles to allow them to collide (Ebeling *et al.*, 2003; Tchobanoglous *et al.*, 2014a). Metal salts are often employed as coagulants (Tchobanoglous *et al.*, 2014a). During the flocculation process, the particles bind to form larger particles (Ebeling *et al.*, 2003; Tchobanoglous *et al.*, 2014a). These particles can then be removed through settling or filtering (Tchobanoglous *et al.*, 2014a). In wastewater treatment, coagulation and flocculation are employed to remove solids (Ebeling *et al.*, 2003) and phosphorus (Park *et al.*, 2016).

Chemical phosphorus removal was first developed in the 1950s and is achieved by dosing the waste water with metal salts (Morse et al., 1998). These salts may be either di- or trivalent and are usually aluminium, iron or calcium based (Morse et al., 1998; Melia et al., 2017; Tchobanoglous et al., 2014a). The choice of chemical coagulant will be made based upon factors such as incoming wastewater quality and composition as well as the cost, reliability and availability of the chemical; Gray (2017) lists 8 key considerations when choosing a chemical coagulant. Al and Fe are the most commonly used salts for phosphorus removal and may be dosed as sulphates or chlorides (Melia et al., 2017). The exact mechanism of phosphorus removal when dosing Fe salts is not known (Gray, 2017) although it does result in the formation of metal phosphates which are insoluble and can therefore be settled out of the process and into the sludge (Morse et al., 1998) and consequently the solids generation at the STW will increase (Bratby, 2006). It is unclear whether the phosphorus is bound in a bioavailable form within the sludge or not (Morse et al., 1998; Wilfert et al., 2015).

Metal salts can be dosed into wastewater for phosphorus removal at a number of stages within the STW treatment process (Morse et al., 1998; Bratby, 2006). Coagulants can be added before the primary settlement (known as primary coagulation or precipitation), into the secondary biological process (simultaneous coagulation or precipitation) or after the secondary biological process but upstream of the secondary clarification or settlement process (post-coagulation) (Morse et al., 1998; Bratby, 2006; Gray, 2017). Coagulants can also be added after secondary settlement with a further stage of settlement after the dosing point, this is known as post-precipitation (Gray, 2017). There is some discussion over the best stage of wastewater treatment for the addition of these coagulants. For example, Melia et al. (2017) suggest that chemical phosphorus removal is most effective when the phosphorus concentrations are greatest (at the front end of the process), whilst Gray (2017) state that post-coagulation is more efficient. Bratby (2006) notes that the required chemical dose will be higher when dosing at the front end of the process as the wastewater has not yet been biologically treated and therefore the polyphosphates have not yet been converted into orthophosphates.

The addition of metal salts for phosphorus removal can have an impact upon downstream biological processes, particularly with respect to pH (Bratby, 2006). Ferric chloride lowers pH of the wastewater and therefore it may be necessary to increase the pH using another chemical (such as lime) (Gray, 2017; Bratby, 2006). Tchobanoglous et al. (2014a) note that the alkalinity

of the wastewater and the existing treatment processes on site should be considered when implementing chemical dosing.

In order to calculate the required molar (M) ratio for phosphorus removal using metal salts, bench-scale trials are required (Tchobanoglous et al., 2014). Although the stoichiometric equations for the reactions suggest a 1:1 molar ratio, this ratio is often between 1 and 3 instead (Tchobanoglous et al., 2014a) and sometimes higher than this (Thistleton et al., 2002). This is believed to largely be as a result of competing ions in the wastewater (Thistleton et al., 2002; Tchobanoglous et al., 2014a).

The ideal pH for removal of phosphorus using Fe (III) salts is between 4.5 and 5.0 (Thistleton et al., 2002). Szabó et al. (2008) test Al and Fe salts and found that the best removal occurred between pH 5 and 7. Other factors which were found to influence phosphorus removal included the wastewater chemical oxygen demand (COD), alkalinity and total suspended solids (TSS) which all negatively impact phosphorus removal at higher concentrations (Szabó et al., 2008).

Jar tests completed by Szabó et al. (2008) suggested that the removal of phosphorus by metal salts was a two-stage process with the initial removal occurring within 1 minute and a slower reaction occurring on a timescale of hours or even days. They also found that increasing the intensity of mixing will improve the initial removal. The importance of the mixing conditions was also noted by Thistleton et al. (2002).

2.2.1 Jar test procedures

Jar test procedures vary in the literature. Clark and Stephenson (1999) undertook jar tests in order to develop a procedure for phosphorus removal in an activated sludge treatment process. Their methodology consisted of a rapid mix of 1 to 2 minutes at 100 to 400 revolutions per minute (rpm), followed by a 30 minute slow mix at 30 rpm and 45 minutes of settlement. As part of their methodology, they compared their methodology with that already existing in the literature (Clark and Stephenson, 1999).

Thistleton et al. (2002) compared the phosphorus removal of ferric chloride with that of iron hydroxide using a fast mix of 20 seconds at 0-325 rpm, a slow mix of 30 minutes at 30 rpm and then 60 minutes of settlement. All the jar tests were completed with raw sewage. It was found

that a Fe:P molar ratio of 1.48 was required to remove 80 % of phosphorus and that the duration of the fast mix was not important for phosphorus removal.

The jar tests by Park et al. (2016) were completed as shaking experiments and considered both Al and Fe-based coagulants. After the coagulant addition, samples were shaken for 1 minute at 150 rpm then 10 minutes at 30 rpm before being allowed to settle for 30 minutes. The coagulant dose varied from a Fe:P or Al:P molar ratio of 1:1 up to 1:3 and it was found that the greatest removal occurred at the highest molar ratio (Park et al., 2016).

Keeley et al. (2016) focused on recovered coagulants which were derived from water treatment residuals which were dosed at rates of 0 to 50 mg Fe/l. All jar tests were completed with wastewater and samples were mixed at 200 rpm for 1 minute, 15 minutes at 30 rpm and then settled for 30 minutes. A volume of 1 litre (l) was used.

2.3 Mine water treatment and ochre

In the UK, the Coal Authority is responsible for more than 75 Mine Water Treatment Plants (MWTPs) treating mine water from abandoned coal mines (Coal Authority, 2017). MWTPs treat acid mine drainage (AMD) by oxidising the Fe(II) to Fe(III) and then using hydrolysis to produce a ferric hydroxide (Heal et al., 2003; 2004; Brown et al., 2002). The resulting $\text{Fe}(\text{OH})_3$ and FeOOH solids are known as ochre (Heal et al., 2003; 2004). The resulting sludge contains hydrous ferric oxides (Sapsford *et al.*, 2005) and Heal *et al.* (2003; 2004) found that the solids in Minto and Polkemmet ochres were poorly crystalline. X-ray diffraction (XRD) analysis of the ochre from the Minto and Polkemmet sites found that they contained goethite and ferrihydrite (Heal et al., 2003; 2004). Sapsford et al. (2005) also conducted XRD analysis found that ochre from Taff Methyr was primarily goethite with some SiO_2 .

The Coal Authority categorise the treatment processes at mine water treatment plants as passive, semi-passive or active (Moorhouse and Watson, 2015). Passive treatment systems require no man-made energy or chemical input and minimal maintenance (Younger et al., 2002). These treatment systems produce ochre with iron content of approximately 30 % dry weight and a solids content of less than 5 % (Sapsford et al., 2015). Active systems, on the other hand, require energy and/or chemicals (Younger et al., 2002) and the ochre produced has a lower iron content (approximately 15 % dry weight) due to chemical addition but the water content is lower than that produced from passive systems (Sapsford et al., 2015).

In 2015, the 70 coal MWTPs produced approximately 1500 tonnes of iron (as ochre) annually, 640 tonnes of this was produced in the North East (NE) of England, equating to approximately 1220 tonnes of ochre (Moorhouse and Watson, 2015). Sapsford et al. (2015) estimated that the annual production of ochre in the UK was 4500 tonnes as dry weight and that 80 % of the ochre was produced at just 19 sites.

2.3.1 Ochre as an adsorbent

Ochre is well documented as an adsorbent (e.g. Littler et al., 2013, Heal et al., 2004; 2004, Dobbie et al., 2009). The primary focus of research into ochre has been its capacity for the adsorption of phosphate. However, it has been noted that ochre is capable of removing arsenic (e.g. Doi *et al.*, 2005; Olimah *et al.*, 2015), zinc (e.g. Sapsford *et al.*, 2015), lead (e.g. Sahoo *et al.*, 2014) and copper (e.g. Sahoo *et al.*, 2014).

Phosphates can be removed through sorption, which may be physical and reversible or chemical and irreversible (chemisorption) (Holtan *et al.*, 1988). Chemisorption is a combination of two adsorption reactions - ligand exchange followed by incorporation (Holtan *et al.*, 1988). Sorption is the main phosphorus removal mechanism for ochre (Heal *et al.*, 2003; 2004). Ochre has been found to contain goethite (Heal *et al.*, 2003; 2004; Dobbie *et al.*, 2009) which removes phosphate in a two stage mechanism of an initial quick surface ligand exchange followed by a slower ligand exchange reaction (Heal *et al.*, 2003; 2004).

Heal et al. (2004) discussed the kinetics of phosphorus removal using ochre and referenced experiments suggesting that greater than 98 % of phosphorus was removed within 5 minutes of contact, suggesting a rapid reaction rate. They also suggested that pH did not impact phosphorus removal in batch tests using ochre from Minto and Polkemmet. Heal et al. (2004) further noted that different ochres, with different properties, would be suitable for different applications for treating wastewater. For example, it could be packed into a filter (e.g. Heal et al., 2003; 2004, Dobbie et al., 2009) or it may be more suitable for dosing directly into tanks (Heal et al., 2004). Ochre can also be used in constructed wetlands (Heal et al., 2004).

Heal et al. (2003; 2004) suggest that fine grained ochre is not suited to a filter application but would be suitable for dosing applications. Heal et al. (2003) completed batch tests with two

ochres (one fine grained and one coarse grained) and found that it was a fast reaction. Fine grained ochre would be prone to clogging within a filter unit (Heal et al., 2003; 2004).

Dobbie et al. (2009) completed trials using granular and pelletised ochre in trough experiments with flow in both vertical and horizontal directions and treated secondary effluent on two sewage treatment works. The pellets were produced using dried ochre and Portland cement. Although the trials demonstrated that the filters were capable of removing phosphorus, it was found that clogging was a problem and solids capture in the form of a gravel filter may be required before the ochre-based filter or the ochre-based filter would require backwashing (Dobbie et al., 2009).

Mayes et al. (2009) used Portland cement to bind ochre into pellets for zinc removal, although it was found that the pH was increased as a result of this binder. Littler et al. (2013) also produced a cement-based pellet which was then tested in batch and column experiments to determine the mechanism for phosphorus removal. The trials identified that the addition of a cement binder increased the phosphorus removal, which was attributed to a change in adsorption mechanism (Littler *et al.*, 2013). The trials also identified a pH increase as a result of the cement binder, which would require pH correction and therefore increase treatment costs for any application for wastewater treatment (Littler et al., 2013).

Work by Dobbie et al. (2005) focused on the reuse of phosphorus-saturated ochre as a slow-release fertiliser material. They found that the ochre could be applied annually without exceeding the metal limits used for applying traditional sewage sludge to agricultural land.

2.3.2 Producing coagulants from acid mine drainage

Acid mine drainage (AMD) was considered as a coagulant for water treatment as early as 1992 (Rao et al., 1992). Rao et al. (1992) precipitated iron hydroxide ($\text{Fe}(\text{OH})_3$) from AMD at a pH of 3.5 to 3.6 (the pH was corrected using CaO) in the presence of an amine. The amine was used to reduce the co-precipitation of metals. The iron hydroxide was then mixed with sulphuric acid (H_2SO_4) to produce $\text{Fe}_2(\text{SO}_4)_3$ and CaSO_4 which could then be separated. The resultant coagulant was then compared with commercial FeCl_3 . Although Rao et al. (1992) state that the resultant coagulant was “effective”, they do not provide details, instead focusing on using the AMD itself as a coagulant.

Subsequent papers have focused on converting AMD into a coagulant for clean water applications (Menezes et al., 2009; 2010). Menezes et al. (2009) used an AMD with iron present as 70 % Fe^{2+} and 30 % Fe^{3+} . The Fe^{2+} was then converted to Fe^{3+} by aeration at a pH between 2.5 and 3.0 before increasing the pH slightly to 3.8 (± 0.1) by the addition of 4N NaOH. At this pH, iron was precipitated as ferric hydroxide/oxyhydroxide which was then converted to a solution by dissolving the solid in sulphuric acid. The resulting ferric sulphate coagulant (which represented 90.5 % of the solution) was 12.4 % iron. An aluminium sulphate was also produced, which represented 9.5 % of the final coagulant product. Menezes et al. (2009, 2010) suggest that the procedure could be implemented at AMD treatment plants. A similar method of production was used by Menezes et al. (2010) to produce a poly-alumino-iron sulphate coagulant from AMD.

Sapsford et al. (2015) then used ochre (an AMD treatment product) to produce a reagent for removal of phosphorus (P) and zinc (Zn) for water treatment. They also found that the reagent could be used for phosphorus removal from wastewater. Phosphorus was removed to levels below detection at pH between 6.0 and 8.6 (Sapsford et al., 2015). To produce the reagent, dried ochre was dissolved in acid (either sulphuric acid (H_2SO_4) or hydrochloric acid (HCl)) of varying concentrations. The solutions were shaken at 175 rpm for 24 hours before using vacuum filtration to remove any residual solids. These ochre-derived solutions were compared with conventional ferric chloride (FeCl_3) and ferric sulphate ($\text{Fe}(\text{SO}_4)_3$) solutions in a series of jar tests using both real and synthetic wastewaters. Their results showed that increasing the concentration of the acid did not always increase the quantity of ochre which could be dissolved and that a maximum of 100 grams (g) of ochre could be dissolved per litre of hydrochloric acid (HCl) (20 % weight by weight; w/w) and a maximum of 68 g per litre of sulphuric acid (H_2SO_4) (10 % w/w) (Sapsford et al., 2015).

2.3.3. Analysis of the literature

Phosphorus removal from wastewater is traditionally achieved through the use of metal salts. Although methods vary, coagulant dose rates are determined using jar tests ahead of implementation on site. As previously stated, ochre has been explored in the literature as an adsorbent for phosphorus as well as other contaminants. These studies focused on bench-scale trials with only a small number of these progressing to pilot-scale trials at wastewater treatment works. Dobbie et al (2009) trialled ochre-based filters at two wastewater treatment works.

The conversion of ochre and acid mine drainage to produce a coagulant (primarily for clean water applications) has been explored in the literature. Sapsford et al (2015) assessed the use of an ochre derived coagulant for the treatment of wastewater but did not progress the trials beyond laboratory scale.

From the literature reviewed, lab-scale trials have been explored more extensively than on site trials but are still not comprehensive. There are not many documented full-scale trials using ochre for phosphorus removal from wastewater and no studies using ochre derived coagulants in pilot or full-scale trials were found.

3. Methodology

This methodology chapter will first detail the sites from where the five ochres investigated in this thesis were collected, before describing how each of the trials were undertaken and how and associated analysis was completed. The diagram below (Figure 3.1) shows the proposed location for ochre application at a sewage treatment works (STW).

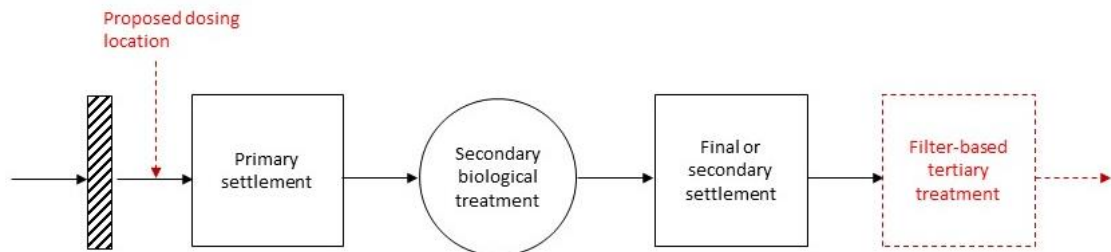


Figure 3.1: Proposed on site location of the trialled ochre application methods

The filter trials detailed in Section 3.2 are proposed to be located at the end of the treatment process as a tertiary treatment. In Figure 3.1, this is shown by the dotted square located after the final or secondary settlement stage.

The ochre and ochre derived ferric (ODF) dosing trials described in Section 3.3 and 3.4 were designed to replicate the conditions when dosing after the preliminary treatment but before the primary settlement. The onsite trial detailed in Section 3.5 was completed at this location in the treatment process at the trial site.

3.1 Ochre sample locations

Ochre was sourced from 5 mine water treatment works across the North East of England: Acomb, Bates, Blenkinsopp, Dawdon and Saltburn. Acomb and Blenkinsopp are pumped/active treatment sites (Coal Authority, 2014). The treatment process at Acomb involves dosing hydrogen peroxide (Wyatt et al., 2013) whilst Blenkinsopp mine water is dosed with caustic soda (Sapsford et al., 2015). Dawdon is an active site using lime as part of the treatment process (Coal Authority, 2014; Sapsford et al., 2015). Bates is a passive treatment site (Coal Authority, 2014; Sapsford et al., 2015), as is Saltburn, however this site treats a non-coal discharge (Coal Authority, 2014). Ochre samples were stored in sealed containers at room temperature.

3.2 Filters

3.2.1 Binder columns

3.2.1.1 Control columns (binders only)

Three binders were tested; resin, cement and sand. The resin was a resin plaster powder which was purchased from the high street.

The cement and resin binders were mixed with sand in a 3:1 ratio (sand:binder, by mass) with water to form a paste. This paste was transferred into a mould and left to dry into cubes. The approximate volume of each cube in the mould was 30 millilitres (ml). The dry cubes were then crushed and sieved using graduated test sieves to produce particles sized between 1.4 millimetres (mm) and 500 micrometres (μm). The sand was not pre-treated.

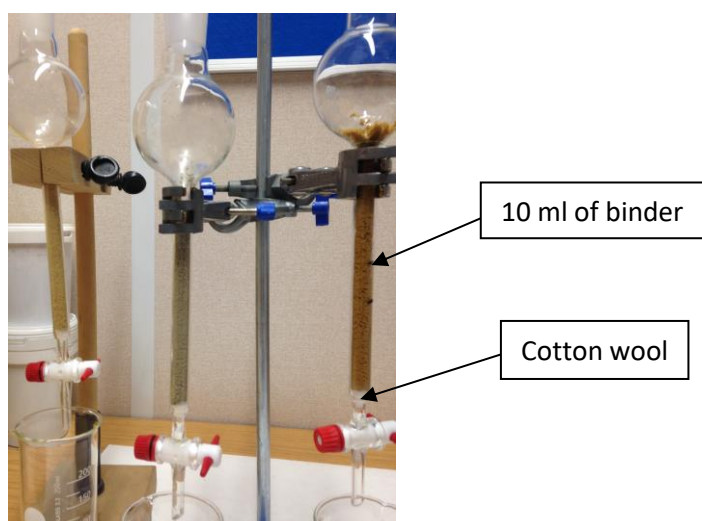


Figure 3.1: Packed binder only columns. From left to right: resin, cement, sand

The bottom of the purpose-made columns was plugged using a small quantity of cotton wool and 10 ml of the binder adsorbent was added on top. The adsorbent was measured out and weighed prior to being added. Figure 3.2 (above) shows the three packed columns, clamped in place with beakers underneath to collect the effluent throughout the trial. A stock 1 molar (M) solution of monopotassium phosphate (KH_2PO_4) was made up from solid potassium phosphate monobasic and then used to produce a solution of 10.50 mg P/L which was used as the initial solution for the columns. This initial concentration was chosen to duplicate the expected total phosphorus entering a works when treating wastewater of average strength (Davis and Cornwall, 1991; Mihelcic et al., 2014).

An initial 100 ml of the diluted phosphorus solution (10.50 mg P/L) was added to the column and allowed to run through the column and collected in the beaker at the outlet. This was repeated with more initial solution and each pass through the column was denoted as a “pass”. The effluent from each pass was analysed for pH, turbidity and P as detailed in Section 3.2.1.5. With the exception of the first pass, the time between the solution being added to the column and collected in the beaker was also monitored. The solution added for the first pass was allowed to drain through overnight and therefore the effluent for that pass was sampled and analysed the following morning.

3.2.1.2 Binder and ochre columns

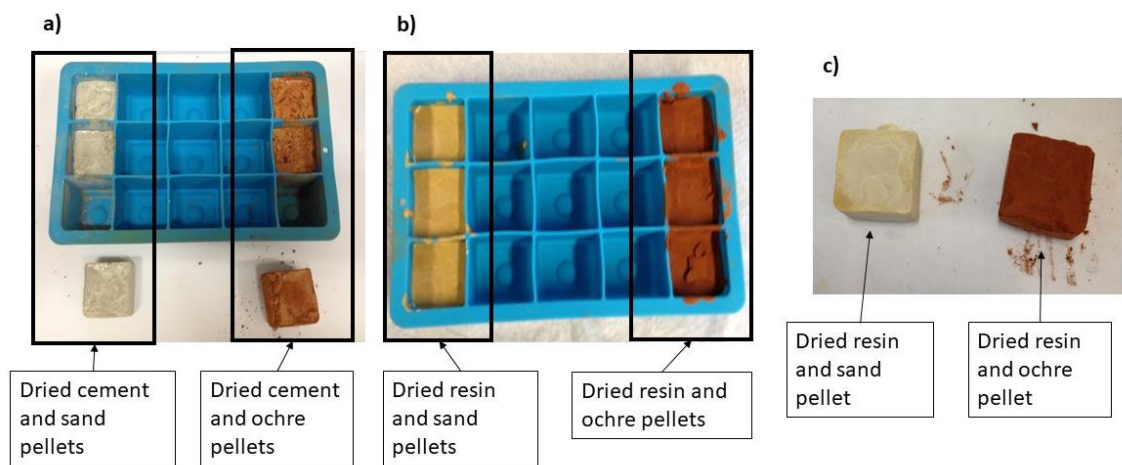


Figure 3.2: Dry cubes of ochre and binders, prior to being crushed and broken up (a) dry cement and sand (L) and cement and ochre (R) pellets, (b) dry resin and sand (L) and resin and ochre (R) pellets, (c) dry resin and sand (L) and resin and ochre (R) pellets, out of the mould.

Dawdon ochre was used for all of the adsorbents and was assumed to have a water content of 36.09 % by weight (based on the results from a previous study, Pinner, 2014). The binder and ochre adsorbents using cement and resin were produced in the same way as the binder and sand control adsorbents. The sand in the cubes was replaced with ochre so that the cubes were prepared with a mass ratio of 3:1 ochre:binder. The dried cubes (shown in Figure 3.3) were crushed and sieved in the way as the control adsorbents. The ochre and sand adsorbent was prepared by mixing the ochre and sand in a 3:1 (ochre:sand) mass ratio. Neither the sand nor the ochre was dried prior to use.

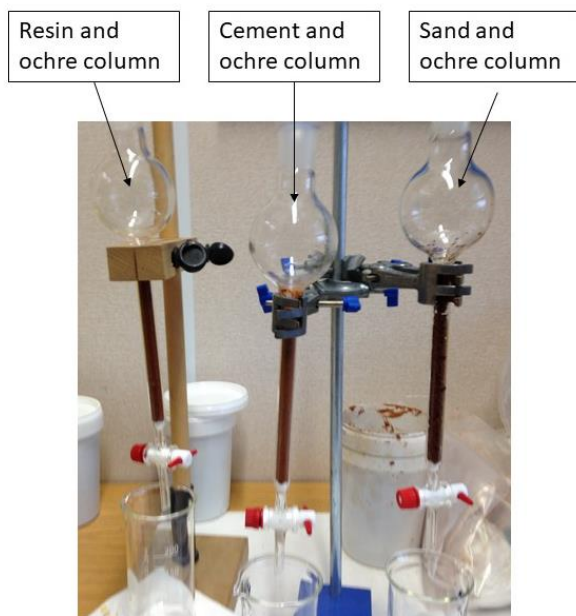


Figure 3.3: Packed binder and ochre columns. From left to right: Resin and ochre, cement and ochre, sand and ochre.

The columns (shown in Figure 3.4) were packed in the same way as the control columns and the 1 M stock solution was diluted to a concentration of 8.90 mg P/L. This initial concentration is representative of a weak to average strength wastewater with a phosphorus concentration of 5 to 10 mg TP/l (Davis and Cornwall, 1991; Mihelcic et al., 2014). The effluent was once again collected and analysed, and the time taken for the solution to pass through the column was noted. Multiple passes were completed for each column.

3.2.1.3 Cement and ochre pH

Following the completion of the ochre and binder columns detailed in Section 3.2.1.3, the cement-based column was run again with water instead of phosphorus solution. The same procedure was followed with 100 ml of tap water added to the column for each pass. The effluent was analysed for pH and turbidity only as detailed in Section 3.2.1.5. For the turbidity analysis, the water was used as the blank. These results were combined with the results from the previous cement and binder column trials (2.1C to 2.5C). The effluent from the final five passes (3.16 to 3.20) were only analysed for pH.

The cement and ochre column was run again, using water instead of phosphate solution. 100 ml of water was added to the column every pass and the effluent collected in a beaker beneath the column. The effluent was analysed for pH and turbidity in the same way as the previous two trials, with the water used as the blank for the turbidity analysis. The data from this analysis

were combined with the data from the first 5 passes (2.1C to 2.5C). The effluent for passes 16 to 20 (3.16 to 3.20) were not analysed for turbidity, only pH.

3.2.1.4 Effect of the ochre/sand ratio

Two further pairs of columns were set up to determine the effect of ochre to sand ratio on flow rate. The first pair of columns consisted of a column packed with a 1:1 ratio (6 g of ochre and 6 g of sand) and a column with a ratio of 1:5 (2 g ochre and 10 g sand). The second pair had columns of 1:10 and 1:15 which were produced by combining 1.5 g ochre with 15 g sand and 0.75 g ochre with 15 g sand, respectively. It was assumed the sand and ochre were completely mixed. The columns were packed in the same manner as the previous trials using 10 ml of the prepared adsorbent and 100 ml of tap water was added to the column. The water was left to run through the column under gravity for a couple of hours (until the flow through the adsorbent appeared to have ceased) and the volume of effluent was then measured.

3.2.1.5 Effluent analysis

The analysis for phosphorus was completed using reagents capable of measuring total phosphorus in the range of 1 to 12 mg P/l; the full analysis method for these reagents can be found online (Palintest Ltd, 2017a). The analysis method for turbidity is also detailed online (Palintest Ltd, 2016). For the analysis of the turbidity, the initial solution (or water) was used as a blank. The range of this method analysis is 5 to 400 turbidity units (Palintest Ltd, 2016). The reader used for both the turbidity and phosphorus analysis was a Palintest Ltd photometer 7100 with an accuracy of $\pm 1\%$ (Palintest Ltd, 2017b).

Fisherbrand pH strips with a range of pH 0 to pH 14 were used to test the effluent pH.

An average flow rate for each pass through the column was calculated from the time taken for the solution or water to pass through the column. This method of calculation assumes that the flow through the column was constant. The flow rate was calculated in millilitres per minute (ml/min) and litres per second (L/s).

3.2.2 Intermediate Bulk Container (IBC) Trial

3.2.2.1 Trial unit design

A tertiary filter was designed within an Intermediate Bulk Container (IBC) unit with a volume of 1 m³. Once the top of the IBC had been removed, a distribution pipe system was affixed where the top had been. The unit was packed with layers of sand and layers of a sand/ochre mix. These layers are illustrated in Figure 3.5. The sand layers were included to trap any larger solids which could block the ochre-based layer and to capture any ochre which may wash out. A membrane material was positioned between each layer to ensure they remained separate but still allow the flow to pass through. Keeping the layers separate would allow the layers to be disposed of separately and the sand to be cleaned, regenerated or replaced in the event of it becoming blocked and flow through the unit drops before the ochre is spent.

The ochre was mixed with sand to improve porosity and therefore flow through the layer as the flow passed through under gravity and was not pumped. This was as a result of the previous column tests and the improvement of gravity flow through the ochre when mixed with sand when compared to ochre alone.



Figure 3.4: Left; empty IBC unit, right; intended layers to be packed within the IBC

3.2.2.2 Onsite implementation

The unit was located on a wastewater treatment site and then packed with the layers. The packing of the unit was not as initially designed as the sand layer and the ochre-based layer depths both had to be decreased. The ratio of sand to ochre in the ochre-based layer was also increased from 1:4 to 1:6 (ochre:sand) as a result of the water content of the ochre creating a

very wet mix and increasing the risk of ochre colour washing out when the unit was in use. The revised layers are shown in Figure 3.6.

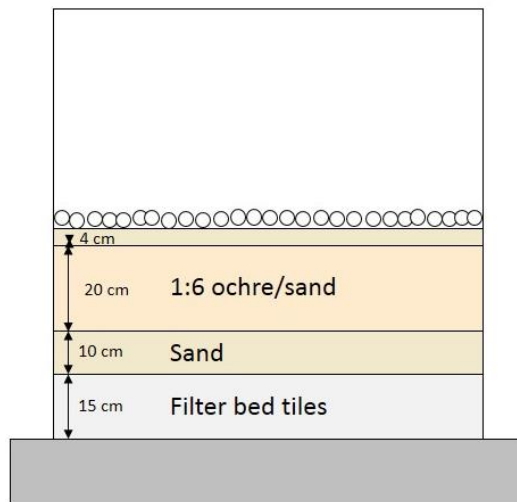


Figure 3.5: Schematic showing the layers as they were packed into the IBC

The unit was fed with final effluent via a submersible pump. The pump was submerged in channel at the outlet of one of the final settlement tanks. The upstream process on the trial site was a secondary activated sludge process. The effluent was initially pumped from the channel into the unit at 0.73 l/s and was controlled by the tap on the unit's distribution pipework. This was subsequently reduced to 0.46 l/s and then 0.19 l/s. The unit was run for two separate periods.

The first run was for a duration of 3 weeks with a total of 9 days of flow through the unit. On the seventh day, the outgoing flow visibly decreased, and the trial was concluded when flow no longer passed through the unit and it was assumed to be blocked.

The unit was covered and left for three weeks before being unpacked. In the period between the trial ending and the unit being unpacked, the effluent had mostly drained through the unit. During the unpacking, the layers were kept separate and the membrane kept for reuse wherever possible. The bottom layer of sand was not removed from the unit but instead sprayed with final effluent in order to ensure flow could pass through as well as to dislodge any solids which may have been present.

Once the above had been completed, the unit was repacked to allow the trial to be run again for comparison with the first trial. This second trial was not run continuously. It was run intermittently on seven separate days with the flow turned off between days and the unit allowed to run dry. The ingoing flow rate was 0.19 l/s throughout the trial. The trial was concluded by the purchase of smaller-scale pond filter units which replaced the IBC unit in order to address the operational issues, including the time necessary to pack and unpack the unit when making changes and maintaining flow. Furthermore, the intermediate units offered flexibility and the ability to test variables, to refine the design and operation of the filter units.

3.2.2.3 Quantity of ochre added to unit

The ochre and sand were combined using a small cement mixer. The materials were added using a shovel and therefore the ratio was based on volume as measured by the number of shovelfuls. The number of shovelfuls of ochre added were noted. In order to estimate the weight of ochre added, a quarter of wet ochre was weighed and multiplied by the number of shovelfuls.

3.2.2.4 Ochre water content

The samples of ochre from Dawdon MWTP were collected and stored in heavy duty rubble bags. Three samples of ochre were taken from these bags for analysis of the water content; a sample of the bag which looked to be visually wettest, visually driest and another randomly selected bag. To determine the water content of each of these samples, a known quantity was added to a beaker and dried in the oven at 100 °C until a constant weight was reached. For each ochre, a percentage weight of water was calculated and from this an average percentage for the Dawdon ochre.

3.2.2.4 Trial sampling

Effluent sampling

Samples were taken upstream of the submersible pump in the final effluent channel and from the outlet of the filter unit. This was completed to determine the impact of the unit on the effluent quality. Initially, 1 litre samples were taken but this was reduced to 250 ml during the sampling period. Samples were collected daily, in the morning and the afternoon, whenever possible. This sampling assumes that the phosphorus content of the final effluent at the time of sampling is representative of the effluent being treated by the unit.

The first 20 litres of effluent treated were collected at the outlet a litre at a time so that the level of colour being flushed out could be monitored.

Ochre layer sampling

During the unpacking of the unit following the first run, the ochre-based layer was sampled from the locations shown in Figure 3.7. No ochre samples were taken following the second run and none of the ochre samples were analysed due to time constraints.



Figure 3.6: Plan view of the sample locations for the ochre layer within the intermediate bulk container (IBC) trial unit. Although collected, these samples were not analysed.

3.2.2.5 Effluent analysis

Total and filtered phosphorus

The phosphorus analysis was completed as for the previous trials using the Palintest colorimetric method with a range of 0 to 12 mg P/l and a Palintest 7100. Full details of the analysis can be found on the Palintest website (Palintest, 2017b; 2017a). The filtered phosphorus analysis was completed using the same method, however, the samples were filtered through a 0.45 µm syringe filter beforehand.

A set of samples taken during the first run of the unit were submitted for analysis at a UKAS accredited commercial laboratory to allow comparison to be made with the above method. Part of the sample was analysed using the Palintest equipment and the remainder of the sample was submitted to the laboratory.

Total suspended solids

For the total suspended solids (TSS) analysis, Whatman glass microfiber filters (GF/C; 55 mm diameter) were dried and weighed. 50 ml of the sample was then passed through the filter paper and put in the oven at 100 °C for two hours and the papers were reweighed, and the weight of solids calculated.

The solids content was calculated using the following equation:

$$TSS (mg/l) = \left(\frac{(w_2 - w_1)}{v} \right) \times 1000000$$

Where;

TSS = Total Suspended Solids

w_1 = dried filter paper (g)

w_2 = filter + sample (g) (after drying)

v = volume of sample used (ml)

Iron analysis

The first litre from the unit (11/7/16 sample 1) and a sample taken after the unit had been running for a week (collected 18/7/16 14:47) were analysed for iron (Fe) content. These samples were also analysed using the Palintest 7100 photometer. A Palintest medium range (0 to 5 mg Fe/l) iron analysis was used. Full details of the analysis method can be found on the Palintest website (Palintest 2017b; 2016).

3.2.2.6 Data analysis

Phosphorus removal estimates

The difference in phosphorus content between the unit inlet and the outlet for each set of samples was used to determine the phosphorus removal. When sampling, the inlet was also sampled before the outlet with a couple of minutes delay between the two samples being collected.

The mean removal for each day of the trial was calculated and then multiplied by the number of litres pumped into the unit each day (3727.8 l) to estimate the phosphorus removal for the day. The removal estimates for the individual days could then be summed to give an estimate of the total removal across the trial period. To estimate the removal of phosphorus per gram of ochre in the unit (mg P/g), this total removal was divided by the estimated ochre quantity as wet weight. It was assumed that no phosphorus was being captured or removed by the sand within the ochre and therefore all observed phosphorus removal was as a result of adsorption by the ochre.

3.2.3 Growth trials

Simple, small-scale growth trials were completed to determine whether P-saturated ochre could be reused as a fertiliser or soil amendment. A ryegrass based lawn seed was applied to the surface of each treatment at the recommended rate of 35 g per m² and a thin layer of sand was applied on top to discourage birds. The ryegrass based lawn seed was chosen as a simple growth system due to needing minimal input and monitoring for the duration of the trial. The pots were then watered well and placed outside. The growth trial was run for a period of 12 weeks.

Three categories of treatment were used; “ochre-based”, “sludge-based” and “compost-based”. The ochre-based treatments were based on Dawdon ochre, the sludge-based were based on sludge collected from a co-treatment reed bed treating mine water and sewage treatment works final effluent and the compost-based treatments were based on a seeding compost.

The sludge was dried slightly in the oven at 100°C to remove excess water. This sludge contained ochre and was also expected to contain extra nutrients which are present in the final effluent. Therefore, this material was used as a proxy for ochre from a filter-based system treating final effluent.

The ochre used in treatments 1 and 5 had not been in contact with effluent and therefore had no additional nutrients. This ochre was used to represent a worst case scenario where short circuiting may occur in a filter and therefore the ochre had no (or very little) contact with the final effluent and did not accumulate the nutrients.

There were, initially, two treatments of each category; one mixed with sand, the other with compost. These treatments were seeded and left to grow for 4 weeks before a further two ochre-based treatments were added. One of the treatments combined the sampled ochre layer from the first run of the IBC trial with compost whilst the other used ochre from the second run. All of the treatments are summarised below (Table 3.1). Each treatment was trialled in duplicate.

Table 3.1: Summary of treatments

	Treatment	Preparation
1	Ochre + sand (1:6)	6 parts sharp sand to 1 part ochre (mixed as part of the preparation for the onsite trial)
2	Sludge + sand (1:6)	6 parts builders sand to 1 part sludge
3	Compost only	None
4	Compost + sand (1:6)	6 parts builders sand to 1 part compost
5	Ochre + compost (1:1)	1 part ochre to 1 part compost (no sand)
6	Sludge + compost (1:1)	1 part sludge to 1 part compost (no sand)
7	Run 1 ochre + compost (1:1)	1 part ochre mix to 1 part compost
8	Run 2 ochre + compost (1:1)	1 part ochre mix to 1 part compost

Treatments containing sand were mixed in a ratio of 6:1 (with sand the largest portion of the treatment) to replicate the ochre mix used within the IBC trial. All other treatments were mixed in a 1:1 ratio. With the exception of treatment 1, all the treatments were mixed by hand. A constant volume of the treatments was added to each pot.

3.2.3.1 Monitoring

The height of the grass was measured weekly and was measured from the soil surface to the tip of the blade. The height was measured at two locations and the tallest blade in each location was taken as the measurement. From these measurements, a mean height was calculated for each pot and each treatment.

3.2.3.2 Analysis

At the end of the growth trials, the grass was cut at the soil surface and weighed. After weighing, the grass was pressed dry in a paper towel. Once dry, it was reweighed and a mean dry weight for each treatment was calculated.

3.2.4 Pond Filters

3.2.4.1 Trial design

Smaller scale ochre-based filters were designed in pond filter units to enable variables to be tested on shorter time scales and with a quicker turnaround between each variable. These variables could then be used to determine an optimum design for an ochre-based filter for phosphorus removal. Two units were used to enable them to be run in parallel and allow a direct comparison. Each “phase” of the trial was designed to test a different variable.

Each of the following phases was run for a minimum of 10 days and, whenever possible, samples were taken daily. The ochre/sand mix from the IBC trial unit was reused for the ochre-based filter units. Each phase was set up with a separate batch of this mix to try and maintain a consistent initial phosphorus within the mix.

The units were packed with a gravel layer at the bottom with an adsorbent layer on top, separated by membrane material.

Figure 3.7 shows the schematic designs for the upflow (Figure 3.7a) and downflow (Figure 3.7c) units used in phases 1 to 4a (inclusive) and identifies the inlet and outlet for the units when configured as upflow (Figure 3.7b and Figure 3.7d). Figure 3.8 shows the schematic design for the phase 4b (Figure 3.8a) and the flow through the pipework between the units (Figure 3.8b). Each of the phase designs are described in more detail in the following section with reference to Figures 3.7 and 3.8.

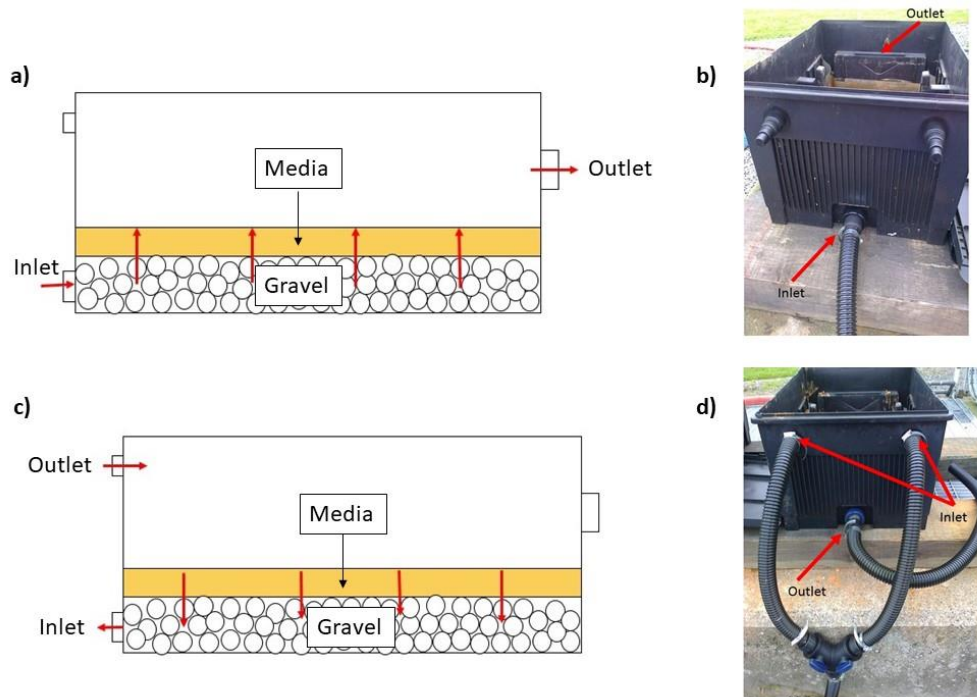


Figure 3.7: Trial unit configurations for Phases 1 to 4a (inclusive); a) Schematic design for an upflow unit with flow through the unit and media shown by the red arrows, b) Photo of an upflow unit with the inlet and outlet to the unit identified, c) Schematic design for a downflow unit with flow through the unit and media shown by the red arrows, d) Photo of a downflow unit with the inlet and outlet to the unit identified.

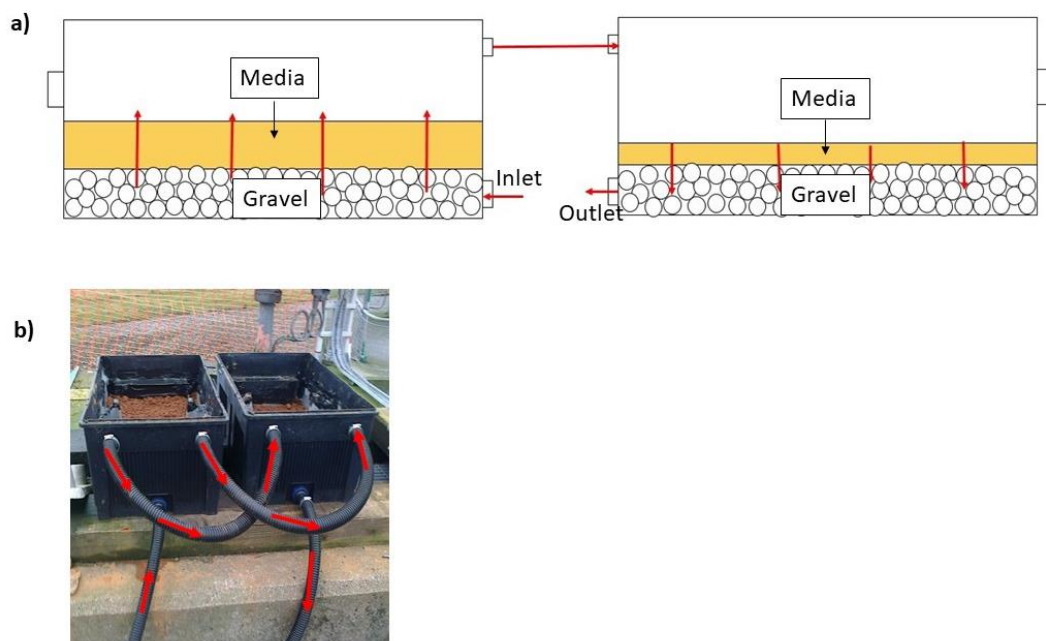


Figure 3.8: Trial unit configurations for Phase 4b; a) Schematic design for the trial system units with flow through the units and media shown by the red arrows, b) Photo of the trial system with flow direction through the pipework identified by the red arrows.

3.2.4.2 Implementation

Phase 1

This phase was designed to determine whether the configuration of the unit impacted upon phosphorus removal. To do this, one unit was designed with an upflow configuration and the other a downflow configuration.

Gravel from the previous IBC trial was washed and placed in the bottom of each unit to cover the drain and encourage free flow into and out of the unit. This drain was used as an inlet for the upflow unit and as an outlet in the downflow unit. Fresh membrane material was then placed on top to prevent ochre entering the gravel layer and washing out. The ochre mix was added to a depth of 10 centimetres (cm) on top of this material. Both units were run with an ingoing flow rate of approximately 0.09 l/s which equated to hydraulic retention time of approximately 6 minutes within the ochre layer (calculated as detailed in Section 3.2.3.4). The pond filter units were not covered.

The configurations for these units is shown in Figure 3.7a for the upflow unit and Figure 3.8c for the downflow unit, which also shows the flow path through the unit (the red arrows). The photos in Figure 3.7b (upflow unit) and 3.7d (downflow unit) show examples of the units after they had been set up with the inlet and outlet of each identified. The trial was run continuously for a period of 5 weeks.

Phase 2

Phase 2 was designed to determine the impact of ochre layer depth (and therefore ochre quantity) on phosphorus removal. To test the depth variable, one unit was packed with an ochre-based layer of 5 cm and the other with 15 cm. Both units were set up in a downflow configuration, with an ingoing flow rate of approximately 0.09 l/s. This flow rate equated to retention times of approximately 3 and 9.5 minutes for the 5 cm and 15 cm unit, respectively. Figures 3.7c show the design schematic and flow paths through the units. An example of an upflow unit is shown in Figure 3.7d. For this phase, the units were covered to prevent algal growth within the units. The trial ran continuously for 4 weeks.

Phase 3

Phase 3 was designed to determine the impact of the sand (which is mixed with the ochre) on phosphorus removal. To test this, one unit was packed with the ochre/sand mix and the other

was packed with sand only. Both media were packed to a depth of 15 cm. The ingoing flow rate was kept consistent with the previous phases (approximately 0.09 l/s) and therefore each unit had an approximate retention time of 9.5 minutes. The units were set up in upflow to minimise clogging or blocking of the media. Both the ingoing and outgoing effluents were sampled.

The diagram in Figure 3.7a shows the flow paths for the two units and Figure 3.7b shows an example of an upflow unit onsite and the inlet and outlet identified. The trial ran for a period of 2 weeks.

Phase 4

Phase 4 was split into two sections. For the first section, the two units were set up in parallel to test the reproducibility of the ochre-based filters whilst for the second section, the units were set up in series to determine whether this set up would improve phosphorus removal.

Phase 4a

As for previous phases, the units were packed with 15 cm of the ochre/sand adsorbent and configured for running in upflow with an ingoing flow rate of 0.09 l/s and retention time of 9.5 minutes for each unit. The design for the units is shown in Figure 3.7a and an example of an upflow unit onsite is shown in Figure 3.7b. The trial lasted 2 weeks.

Phase 4b

The two units were repacked with ochre. Although they were intended to be packed with equal quantities of media, the remaining ochre/sand mix was limited. Therefore, the first, upflow unit was packed with 15 cm of mix, whilst the second, downflow unit was packed with 7 cm. The pipework was reconfigured so that the effluent from the upflow unit flowed into the downflow unit for further treatment.

Figure 3.8a shows the flow schematic through and between the units and Figure 3.8b shows the packed units and the flow of the effluent through the reconfigured pipework. The units were covered once running. Ingoing flow rate into the system was again 0.09 l/s, this resulted in a retention time of 9.5 minutes in the upflow unit and 4.5 minutes in the downflow (assuming the flow rate was consistent). The total retention time for treatment was assumed to be 14 minutes. The trial was run for 2 weeks and sampled on 6 occasions.

3.2.4.2 Trial sampling

Effluent samples were taken from the final effluent channel and the outlet of each unit. At the conclusion of each phase, the media was sampled in three locations and kept in sealed containers in the fridge. Ultimately, these samples were not analysed.

3.2.4.3 Sample analysis

Phosphorus analysis

As for the previous IBC unit, the effluent samples were analysed for total and filtered phosphorus. The filtered samples were filtered using a 0.45 µm syringe filter. They were analysed using Palintest tubetest phosphorus kits and a 7100 photometer. Further details can be found in Section 3.2.2.5.

Total suspended solids

See Section 3.2.2.5.

3.2.3.4 Calculation of Hydraulic Retention Time (HRT)

The hydraulic retention time (HRT) for each phase was calculated using the following equation:

$$HRT (h) = \frac{volume (m^3)}{flow rate (m^3/h)}$$

The hydraulic retention relates to the adsorbent layer not the trial systems or the units. The volume was calculated based on the surface area of the layer multiplied by the depth of ochre mix (or sand). The surface area was based on the width and length of the pond filter units. The surface area of all the layers was calculated to be 0.34 m².

3.2.3.5 Data analysis

The maximum, minimum, mean and median phosphorus removals were calculated based on the ingoing and outgoing phosphorus for each set of samples. A percentage removal was also calculated. These percentage removals were categorised into the following bands:

- <0 %
- 0 - 10 %
- 10 - 20 %
- 20 - 50 %
- ≥ 50 %

Where there is a range, the band is greater than or equal to the lower limit and less than the upper limit. For example, 0 - 10 % are percentage removals of greater than or equal to 0 % removal but less than 10 %.

The percentage of samples in each band was also calculated.

3.3 Ochre dosing

3.3.1 Jar test procedure

The jar test methodology was developed to simulate the addition of ferric sulphate upstream of the primary settlement tanks (PSTs) on an STW. This methodology involved a period of flash mixing followed by a slow mix or flocculation period and, finally, a period without mixing (settlement). The effluent was mixed at 200 rpm before the addition of the ochre. After the addition of the ochre, the mixing was continued for a further minute before the mixing speed was reduced to 20 rpm for a period of 40 minutes. The effluent was then allowed to settle for 30 minutes. The supernatant was sampled using a syringe and analysed for total and filtered phosphorus using Palintest Total Phosphorus Tubetests with a range of 0 - 12 mg/l P (Palintest, 2017a) and a Palintest Photometer 7100 (Palintest, 2017b). Filtered phosphorus samples were filtered through a 0.45 µm syringe filter and analysed using the same method as the total phosphorus samples.

All jar tests were completed using a Lovibond ET750, 6 stirrer jar tester. The table below (Table 3.2) summarises the completed ochre dosing jar test methodologies. Details of these jar tests can be found in the relevant sections of this chapter.

Table 3.2: Summary of jar tests with ochre solids and slurry

	Effluent volume	Ochre source	Ochre form	Standard Jar Test Procedure?	Ferric control?	Duplicates?
Ferric equivalent	500 ml	Dawdon	Solid	Yes	Yes	No
Ochre source	500 ml	Acomb, Bates, Blenkinsopp, Dawdon, Saltburn	Solid, slurry (tap)	Yes	Yes	No
	1 litre	Bates, Dawdon	Slurry (distilled)	Yes	No	Yes
Ochre form	1 litre	Dawdon	Solid, Slurry (distilled)	Yes	No	Yes
Dose rate	500 ml	Dawdon	Slurry (tap)	Yes	No	Yes
	1 litre	Dawdon	Solid, slurry (distilled)	Yes	No	Yes
Effluent volume	500 ml, 1 litre	Dawdon	Slurry (distilled)	Yes	No	Yes
Flocculation time	500 ml	Dawdon	Slurry (distilled)	No – varied 20 rpm mix time	No	Yes
	1 litre	Bates	Slurry (distilled)	No – varied 20 rpm mix time	No	Yes

3.3.2 Ochre Solids

3.3.2.1 Ferric equivalent

Based on the assumption of a ferric sulphate dose rate of 6 milligrams per litre (mg/L) (of ferric sulphate, not iron), an equivalent ochre solid dose rate was calculated. This was calculated on the basis of a ferric sulphate with an iron content of 12.5 % (as iron). Therefore, a 6 mg/L dose rate of ferric sulphate equates to an iron dose of 0.75 mg/L Fe or 0.375 milligrams of iron per litre (mg Fe/l). The ochre used for these initial ochre dosing trials was from Dawdon. The iron content of this ochre was taken as approximately 10 % (based on Moorhouse and Watson, 2015) and the water content was estimated at 50 % (based on analysis from a previous trial). This equated to an approximate iron content of 5 % by wet weight.

The jar tests were completed in jars of 500 ml of raw effluent collected from a sewage treatment works. The effluent was collected downstream of the screens and therefore gross solids were removed. This sample location was chosen to simulate the addition of ferric upstream of a works' primary tanks. A dose rate of 6 mg/L ferric sulphate was the equivalent of 3 µl (microlitre) of ferric sulphate dosed into the 500 ml of effluent. Therefore (based on the above assumptions), the equivalent ochre iron dose rate was calculated to be 7.5 mg (0.0075 g) of Dawdon ochre. The ochre was dosed at rates of 0.0075 g, 0.075 g and 0.75 g. The ochre was not dried prior to addition; therefore, all weights are wet weights. A dilution of 1 in 100 was used for the ferric sulphate and 3 ml of solution was added per 500 ml of effluent (a dose rate of 6 ml/l).

3.3.2.2 Ochre source

The methodology for these jar tests was the same as that used for the ferric equivalent trials, as was the analysis methods. However, these trials compared ochre solids from 5 mine water treatment plants across the North East of England; Acomb, Bates, Blenkinsopp, Dawdon and Saltburn. These five ochres were dosed as solids at a rate of approximately 2 grams per litre (g/l) and compared with the 6 mg/L ferric sulphate dose. It is important to note that the 2 g/l dose rate was a wet weight and that the five ochres have different water contents and iron contents therefore the iron dose rate was not consistent. Each jar contained 500 ml of raw effluent therefore 1 g of ochre was added to each. There were five batches of effluent collected, each with slightly different initial phosphorus concentrations. For the final set of jar tests, ochre was added by mixing 1 g of ochre with 2 ml of tap water to produce a slurry.

3.3.2.3 Bates vs Dawdon

In order to directly compare the removal of the two ochres, the water content of the ochres was used to determine a dose rate of equivalent ochre solids. The approximate water contents were taken from previous analysis and were 64 % and 50 % for Bates and Dawdon, respectively. The ochres were slurried using deionised water and the same jar test procedure was completed as in previous trials. Each jar contained 1 litre of raw, screened effluent. These trials were completed in duplicate.

3.3.3 Ochre Form

Jar tests were completed to determine whether the ochre form impacted upon its phosphorus removal performance. For these trials, a single batch of effluent was collected with initial phosphorus concentrations of 8.50 mg/l total phosphorus and 8.10 mg/l filtered phosphorus and each jar contained 1 litre of effluent. Dawdon ochre was dosed at a rate of 2 g/l (based on the ochre's wet weight) as either a solid, or slurry. The slurry was produced by combining the ochre with distilled water in a ratio of 2:1. This ratio was achieved by combining 2 g of Dawdon ochre with 4 ml of distilled water and mixing by hand to form a smooth slurry. The jar tests were once again completed with a 1 minute flash mix (200 rpm), 40 minutes flocculation (20 rpm) and 30 minutes of settlement. The trials were completed in duplicate.

3.3.4 Ochre Slurry

3.3.4.1 Dose rate

The effect of ochre dose was investigated using Dawdon ochre, which was dosed as a slurry. Dose rates of 2, 4 and 10 g/l were trialled, first dosing into 500 ml of effluent and then 1 litre. For the trials using 500 ml of effluent, the initial phosphorus concentration was 10.20 mg/l P and a filtered phosphorus concentration of 8.20 mg/l P. A single batch of wastewater was used. For the 1 litre trial, 3 batches of wastewater were collected, and the initial concentrations are noted in the results. All the trials were completed in duplicate using the same jar test and analysis methodology as previous trials. The ochre slurry was produced using the same methodology as previously using deionised water.

3.3.4.2 Effluent volume

Based on the results of the dose rate trials, trials were completed to directly compare the effect of effluent volume on phosphorus removal using ochre slurry. A single batch of effluent was collected with an initial concentration of 6.40 mg/l of total phosphorus and 4.15 mg/l filtered

phosphorus. Each jar contained 1 litre of effluent. The dose rate was 2 g (wet weight) of Dawdon ochre per litre in the form of a slurry, which was produced in the same way as previous jar tests and using deionised water. The trial was completed in duplicate and using the same jar test methodology as previous jar tests.

3.3.4.3 Flocculation time (Dawdon)

The effect of flocculation time on phosphorus removal was investigated. Previous trials used flocculation times, at 20 rpm, for 40 minutes. These trials varied this 20 rpm mixing period from 20 minutes up to a maximum of 80 minutes. Apart from the variation in flocculation times, the jar test methodology was unchanged from previous trials with flash mixing for 1 minute and 30 minutes of settlement. The jars each contained 500 ml of effluent and the ochre dose rate was 2 g/l in the form of a slurry. The trial was completed in duplicate.

3.3.4.4 Flocculation time (Bates)

These jar tests were a repeat of those previously completed using Dawdon ochre. The jar test methodology used a flash mix of 1 minute at 200 rpm and a 30 minute settlement period, however the flocculation period was varied from 20 minutes up to 80 minutes. Approximately 2 g (wet weight) of Bates ochre was used to form a slurry and this was dosed into jars of 1 litre raw effluent. The jars were completed in duplicate.

3.3.5 Ochre as a ferric supplement

The use of ochre as a ferric supplement was investigated. These investigations were two-fold. Initially, the use of ochre to correct the pH after the addition of ferric sulphate was tested. This was completed by filling a beaker with 100 ml of distilled water and measuring the pH. An ochre slurry was made using 10 g (wet weight) of Dawdon ochre and made up to 20 ml with distilled water. The pH was monitored using a pH meter.

Ferric was dosed into the distilled water at a rate of 6 mg/L and the pH was once again measured. The slurry was added at doses of 0.1 ml (equating to approximately 0.025 mg ochre) and the pH was measured after each addition. Stirring continued as all additions (including the ferric sulphate) were made and for a period of 1 minute before the pH was measured.

The second part of the ferric supplement trials was the combined phosphorus removal of ferric sulphate and ochre slurry. These jar tests followed the method described for the previously used jar test procedure (1 minute at 200 rpm, 40 minutes at 20 rpm and 30 minutes settlement) and completed in duplicate. Half the jars were dosed with ferric first followed by ochre slurry, half were dosed with ochre slurry and then ferric. The additions were made with as little time between the two additions as possible. The jars were filled with 1 litre of raw, screened effluent.

3.3.6 Primary sludge production estimates when dosing ochre for phosphorus removal

A mass balance calculation was completed to determine the impact of ochre dosing at the front end of a works on the production of primary sludge.

A Northumbrian Water Ltd method was used to estimate litre per day flow from population equivalent (PE) of a sewage treatment works. This calculation assumes a known volume of effluent produced per PE and accounts for infiltration into the sewer network. Primary sludge production without the addition of chemicals (or ochre) was estimated based on 45 g total solids per PE per day, the lower limit of the range stated by Bolzonella et al. (2017) for sludge production at this stage of the treatment process. Ochre dose rate was estimated based on the results of the aforementioned ochre slurry dosing trials, to achieve an 80 % reduction in phosphorus (assuming the site was required to meet UWWTD) and a 50 % reduction in phosphorus (assuming that any further reduction required would be achieved by subsequent treatment stages). These dose rates were 4 g/l and 2 g/l, respectively. These dose rates were then used to calculate the amount of ochre added to the wastewater per day. The ochre solids estimate was added to the unaided primary sludge production to provide an estimated total sludge production when employing ochre for phosphorus removal. This calculation assumes that all the ochre solids dosed, settle into the sludge. The proportion of ochre solids in this sludge was calculated as a percentage for each of the dose rates.

When the proportion of ochre solids in the produced sludge was being assessed, a single population equivalent was chosen. The calculation method means that the proportion of ochre in the sludge is independent of population equivalent and therefore will be constant whether the calculations are for a small or large wastewater treatment works.

3.4 Ochre Derived Ferric (ODF)

Initial trials compared dose rates directly with traditional ferric sulphate doses and dose rate was expressed in terms of milligrams per litre (mg/L) of ferric solution in the effluent rather than the quantity of iron dosed. In later trials, the dose rate is expressed in terms of milligrams (mg) of iron dosed per litre (l) of effluent.

3.4.1 Proof of concept

3.4.1.1 Production

From an initial 12 M hydrochloric acid (HCl), three further concentrations were produced using serial dilutions; 6 M, 3 M and 1.5 M. A 50 ml volume of each was then added to a conical flask and 5 g (wet weight) of Dawdon ochre was added to each. The flasks were sealed using parafilm and transferred to a shaker plate. The solutions were left to shake gently until all of the ochre had dissolved. Once the ochre had dissolved, the solutions were removed from the shaker plate and filtered. The samples were submitted for ICP-MS (inductively coupled plasma mass spectrometry) and ICP-AES (inductively coupled plasma atomic emission spectroscopy) analysis. A full suite of elements was analysed for using the ICP-MS. However, only calcium, iron and magnesium were analysed using the ICP-AES.

3.4.2 Bates and Dawdon

3.4.2.1 Production

For this production of ODF, two ochres were used. These ochres were Bates and Dawdon. The ochres were not dried prior to use and previous analysis showed that the ochres were 64 % and 50 % water, respectively.

A known quantity of each ochre was weighed into a beaker and the ochre was gradually added to a beaker containing 50 ml of 3 M HCl. The beaker contained a stirrer bar which was set to stir the solution gently. The ochre was added until it no longer visually dissolved. The stirring was then ceased and the beaker containing the solution was sealed with parafilm and left to digest at room temperature. The ochre containing beaker was reweighed to assess how much ochre had been dissolved. After digestion, the solutions were filtered to remove any remaining solids from the ochre. The filter papers were left to dry in a fumehood at room temperature.

A total of 12.65 g wet weight of Bates ochre (c. 5.06 g dry weight) and 12.40 g wet weight of Dawdon ochre (c. 6.20 g dry weight) was dissolved in the acid. The two solutions were stored at

room temperature in sealed centrifuge tubes until use, with a small volume submitted for ICP-MS and ICP-OES (inductively coupled plasma optical emission spectrometry) analysis to determine their elemental composition.

These ferric solutions were used in jar tests to compare the phosphorus removal of ODF compared to ochre slurry and traditional ferric sulphate. The methodology for these trials is detailed in section 3.4.2.1.

3.4.2.1 Jar test

Procedure

The ODF solutions were trialled with ochre slurry and traditional ferric sulphate for comparison. The ODF was dosed at three dose rates; 60, 300 and 600 mg/l. These dose rates refer to the volume of ODF solution and not the iron equivalent. The ferric sulphate was only dosed in the first jar test and the ochre slurry only in the first two jar tests. The slurry was produced by combining 2 g (wet weight) of ochre with 4 ml DI water. A slurry made of each Bates and Dawdon ochre was produced.

Beakers were filled with 1 litre of raw, screened effluent and mixed at 200 rpm. The ODF, ferric or ochre slurry was added, and the mixing was continued for 1 minute. The mixing speed was then reduced to 20 rpm for a further 40 minutes. The beakers were settled (with no mixing) for 30 minutes and the supernatant was then sampled for analysis.

Analysis

The settled effluent was analysed for phosphorus using Hach phosphate cuvette tests (LCK 348 and LCK 350) and a Hach Lange DR3900 spectrophotometer. Total phosphorus analysis was completed as detailed on the cuvette tests. For the filtered phosphorus analysis, the samples were filtered using a 0.45 µm syringe filter and analysed in the same way as the total phosphorus, including the digestion stage.

3.4.3 Final Ochre Derived Ferric (ODF)

3.4.3.1 Production

The method of ochre derived ferric (ODF) production was similar to that followed by Sapsford et al. (2015). A known quantity of ochre was weighed out. The ochre was weighed and added wet (unlike Sapsford et al., 2015). The ochre was then gradually added to a conical flask containing

50 ml of 3 M HCl until it no longer dissolved. The ochre was then reweighed to determine the quantity of ochre added. When adding the ochre, some solids adhered to the flask and the spatula and therefore the dissolved quantity of ochre was marginally less than calculated.

Once the ochre had been added the flasks were sealed with parafilm and put onto a shaker plate at 160 mot/min for 24 hours. After 24 hours on the shaker plate, the solutions were vacuum filtered to remove any remaining solids. The filter papers were dried and weighed to determine the quantity of solids which remained in solution. The ochre content of each solution was determined by ICP analysis at a UKAS accredited commercial laboratory.

Five ochres were used, and each ochre was dissolved in triplicate.

Each of the ochres were analysed (in triplicate) using an Ohaus MB90 moisture analyser to determine the water content. From these results, an average percentage moisture content (% MC) was calculated for each ochre.

3.4.3.2 Jar tests

Procedure

Each of the ODF solutions produced was analysed for iron using Hach cuvette tests (LCK 320) and Hach Lange Spectrophotometer to estimate the iron content and therefore calculate an appropriate dose rate. The cuvette tests had a range of 0.2 – 6.0 mg Fe/L and therefore it was necessary to dilute a small portion of the solutions in deionised water for analysis. The results were then corrected according to the dilution factor. Each ODF was dosed at a rate of approximately 10 mg Fe/L. The dose rates were more accurately calculated based on the ICP results from the laboratory. Ferric sulphate was also tested and dosed at a rate of 2.5 mg Fe/l.

The jar test procedure was based on the method used by Keeley et al., 2016. Each beaker was filled with 500 ml of screened effluent and mixed at 200 rpm. The ODF was then dosed and the mixing continued for a further minute at 200 rpm. The speed was then reduced to 30 rpm for 15 minutes which was followed by 30 minutes of settlement.

The jar tests were completed in two phases. The first phase tested each ODF (without repeats) on three separate batches of wastewater. The second batch was completed on a single batch of wastewater and each ochre was tested in triplicate.

Analysis

Phosphorus analysis was completed using Hach cuvette tests and a Hach Lange spectrophotometer. The samples were analysed for total and soluble reactive phosphorus (SRP). For the SRP analysis, the samples were filtered through 0.45 µm syringe filters and the digestion stage of analysis was not undertaken.

3.5 Onsite trial using ochre derived ferric for phosphorus removal

3.5.1 Jar Tests

One of the ODF solutions derived from Bates ochre and produced for the previous jar tests (see Section 3.4.3) was used for the preliminary jar tests ahead of the onsite trial. Raw effluent was collected from the trial site on three consecutive days and jar tests were conducted as described in Section 3.4.3.2.1. The iron dose rate was varied to determine the ideal dose rate for the onsite trial.

Four sets of jar tests were completed. Two sets were completed on the first batch of wastewater. The first set of tests included a wide range of Fe doses at larger increments (from 0 to 100 mg Fe/l) in order to provide a rough curve of removal vs. dose and inform the subsequent jar test dose rates. The second set of tests and all subsequent tests (with the second and third batches of wastewater) were dosed at smaller dose rate increments and up to 50 mg Fe/l. All tests were completed without repeats. A blank was completed in all of the jar tests. This blank was a beaker of effluent which was not dosed with any chemical but subjected to the same procedure of mixing and settlement. This blank was used to represent the phosphorus removal achieved through settling and without chemical aid.

3.5.1.1 Analysis

The supernatant of each beaker was analysed after settlement. The samples were analysed for total phosphorus (TP), soluble reactive phosphorus (SRP), total iron and dissolved iron using Hach cuvette tests and a Hach Lange spectrophotometer. The SRP analysis was completed as described in Section 3.4.3.2. The dissolved iron was analysed by filtering the sample through a 0.45 µm syringe filter and then analysing for total iron.

The alkalinity of the effluent in the beakers was determined using a palintest spectrophotometer and deionised (DI) water as a blank. The pH of the effluent was measured

using a Thermo Scientific pH meter. Some of the pH measurements in the first set of jar tests were taken using pH indicator strips.

3.5.2 Onsite trial

A fresh batch of ochre derived ferric (ODF) was produced from Bates ochre for use in the trial at a small waste water treatment works. A sample of this ODF was submitted to the commercial laboratory to determine the iron content. This ODF was dosed downstream of the “raw” sample point into the raw, screened effluent. The dosing was located at a turbulent point to ensure sufficient mixing. The ODF was dosed at 15.4 l/h, which equated to approximately 16 mg Fe/l (based on the average flow through the site during the dosing). This dose rate was the maximum rate for the pump and dosing lasted for an hour with the available volume of ODF.

Two autosamplers were set up on the trial site. The “raw” sample point was upstream of the primary settlement tanks (PSTs) and the ODF dosing point whilst the “settled” sample point was situated directly after the PSTs. The samplers were programmed to take a sample every 15 minutes and two samples per bottle, resulting in each bottle representing 30 minutes. The samples were submitted to the commercial laboratory for total phosphorus, dissolved phosphorus, total iron and dissolved iron.

3.6 Calculation of Errors

The aim of the study was to find a practical application of ochre for the removal of phosphorus from wastewater and due to time and operational constraints it was not possible to repeat many of the trials and therefore there were not enough data points to accurately calculate the error.

With the exception of the binder column trials, the laboratory-scale trials were conducted using wastewater collected from an operational sewage treatment works rather than ideal solutions. The composition and nature of wastewater at a sewage treatment works is variable. Gray (2017) noted that the nature of wastewater can change hourly as well as daily. Where possible bulk samples of wastewater were collected for the laboratory-scale trials, however, the quantity of wastewater that could be collected and stored was finite and therefore the trials were mostly conducted using multiple batches of wastewater.

Trials completed onsite were also dependent on the wastewater composition at the site. Furthermore, onsite trials were also subject to weather conditions and operational constraints. Repeat trials were undertaken where practicable to demonstrate repeatability as part of the pond filter trials (phase 4a, Chapter 4) and the ochre derived ferric jar tests in chapter 6 (where a set of jar tests were completed in triplicate with a single batch of wastewater).

4. Ochre-based Filters

4.1 Introduction

The work detailed in this chapter considered and investigated how practical using an ochre-based filter as a tertiary treatment or polisher (i.e. treating secondary effluent) at a sewage treatment works might be. The investigations were intended to focus on high level findings at this stage, and therefore the scope was wide rather than specific or in-depth.

Initially, the use of prepared ochre pellets with different binders was assessed. Three different binders were tested using phosphorus solution of a known concentration in a flow through setting, with one of the previously tested ochre sources. The impact of these binders on the effluent quality was monitored. The binders were tested firstly on their own without added ochre (to act as a control), and then combined with the ochre. This design allowed the impact of the binders on effluent quality to be determined.

Following the column experiments, one binder (sand) was selected, and the trial was scaled up to a 1 m³ scale on a STW, using an IBC unit (referred to as the IBC Trial). This trial was subsequently downsized in order to test variables and identify ideal conditions, with different configurations for using ochre-based filter systems for phosphorus removal (Phases 1 to 4). Generally, two units were run in parallel to allow direct comparison. The only exception to this setup was Phase 4b when the two units were run in series with the effluent from the first unit flowing into the second unit for further treatment.

Small-scale growth trials were also undertaken to determine whether the phosphorus-saturated ochre from a filter system could offer secondary benefits by being used as a fertiliser to land and therefore have a potentially commercial end use as a product. These trials were completed as part of the IBC trial.

The stages and overall approach of the trial development and their implementation is summarised in Figure 4.1.

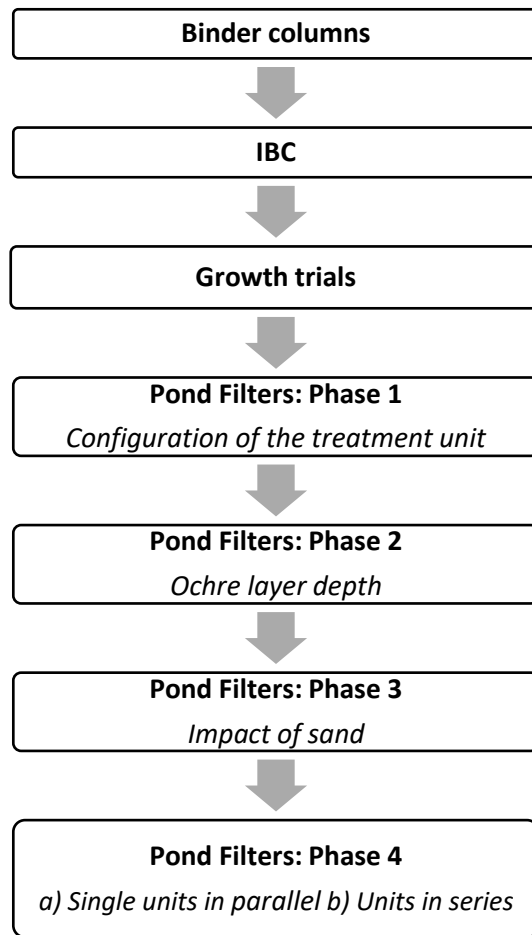


Figure 4.1: Trial stages for ochre-based filter beds

4.2 Methods

The methods used for the following trials are detailed in Section 3.2.

4.3 Binder column trials

4.3.1 Results

The binders all showed phosphorus removal when run as binder only columns, as shown in Table 4.1.

The cement column showed greatest P removal as well as best flow rate as it was the only column to have a flow rate greater than 1 ml/min. Furthermore, P removal remained high throughout the trial.

Table 4.1: Analysis results for the solutions passed through the binder only columns. The solutions were analysed for pH, phosphorus (P) and turbidity. Flow rate of the solutions through the columns and the percentage removal of phosphorus were also calculated.

Pass	Pass ID	Binder	pH	Phosphorus (mg/L)	Turbidity (FTU)	Flow rate (ml/min)	Percentage removal of phosphorus (%)
1	1.1R	Resin	8	4.55	4		56.67
1	1.1C	Cement	12	0.38	6		96.38
1	1.1S	Sand	8	2.14	8		79.62
2	1.2R	Resin	7	8	0	0.4	23.81
2	1.2C	Cement	13	0.35	8	1.87	96.67
2	1.2S	Sand	8	8.1	0	0.65	22.86
3	1.3C	Cement	13	0.52	18	2.27	95.05
4	1.4C	Cement	12	0.28	8	0.87	97.33
	Initial solution		7	10.50			

Resin had the lowest turbidity of the binders tested. The effluent showed an increase in pH from the initial solution (from pH 7 to pH 8) after the first pass (1.1R) but the pH returned to neutral by the second pass. The binder removed over 55 % of the phosphorus in the first pass (1.1R) but less than 25 % in the second (1.2R). The solution took over 4 hours to pass through the column.

Cement showed the best flow through of all the binders tested and was the only column to have flow rates of greater than 1 ml/min. However, the flow rate was not consistent. The pH of the effluent from this column was high (pH 12), with the pH increasing after the second (1.2C) and third (2.3C) passes before returning to pH 12. Turbidity fluctuated but, with the exception of pass 3 (1.3C), remained below 10 FTU (formazin turbidity units). Removal of phosphate by the cement column was consistently about 95 %. The cement column effluent had a visible layer of solids on top, which decreased from pass 1 (1.1C) to pass 4 (1.4C).

The sand column showed turbidity in the first pass (1.1S) but this disappeared by the second pass (1.2S). Although the sand showed removal of almost 80 % phosphate in the first pass (1.1S), this dropped to below 25 % by the second pass (1.2S). The pH of the effluent from this

column was consistently at pH 8, a slight increase from the pH of the initial solution (pH 7). The sand packed into the column compacted down during the first pass (1.1S).

Fluctuating phosphorus removal was observed when the binders were combined with ochre, compared to binders only. The results are shown in Table 4.2.

Table 4.2: Analysis results for the solutions passed through the binder and ochre columns. The solutions were analysed for pH, phosphorus (P) and turbidity. Flow rate of the solutions through the columns and the percentage removal of phosphorus were also calculated.

Pass	Pass ID	Binder	pH	Phosphorus (mg/L)	Turbidity (FTU)	Flow rate through the column (ml/min)	Percentage removal of phosphorus (%)
1	2.1R	Resin	8	0.12	8	2.44	98.65
1	2.1C	Cement	12	2.32	96	25.84	73.93
1	2.1S	Sand	8	n/a	4	n/a	n/a
2	2.2R	Resin	8	n/a	2	0.78	n/a
2	2.2C	Cement	12	0.91	16	10.42	89.78
3	2.3C	Cement	11.5	1	6	8.51	88.76
4	2.4C	Cement	11.5	0.91	10	6.64	89.78
5	2.5C	Cement	11.5	1	6	5.49	88.76
	Initial solution		7	8.90			

The resin and ochre column showed phosphate removal of over 98 % in the first pass (2.1R). Unfortunately, the P in the effluent from the second pass (2.2R) was not analysed due to human error so it cannot be determined whether this level of removal would be consistent and when this may decrease. The turbidity decreased between the first (2.1R) and second passes (2.2R). There was some colour from the columns initially in both passes (2.1R and 2.2R), for the first few millilitres. The colour was visually less in the second pass (2.2R) and it settled to the bottom of the beaker quickly for both passes (2.1R and 2.2R). The pH remained constant for both passes, at pH 8. The flow rate through this column dropped significantly between the first (2.1R) and second (2.2R) passes from 2.44 ml/min to 0.78 ml/min.

The cement and ochre column showed removal of over 70 % in the first pass (2.1C) and then over 88 % from the second (2.2C) to the fifth (2.5C) pass. This column had the best flow through performance. For the 5 passes run, the solution passed through the column in less than 20 minutes. The turbidity was high from the first (2.1C) pass but dropped, although not consistently, by the final pass (2.5C). There was visibly colour leaving the column for the first two passes (for the first few millilitres of each), more than from the resin column and it also settled out quickly. The pH of the effluent was high, initially at pH 12, although this dropped to between pH 11 and pH 12 by the third pass (2.3C) and remained at this level.

The phosphorus solution had not passed through the sand column (packed with 3:1 by mass sand:ochre) after 24 hours (around 50 ml had collected in the beaker underneath), and the adsorbent had compacted down significantly. It was possible to analyse the effluent for turbidity and pH, but it was not analysed for P due to human error. Turbidity was low (4 FTU) and the pH was at pH 8.

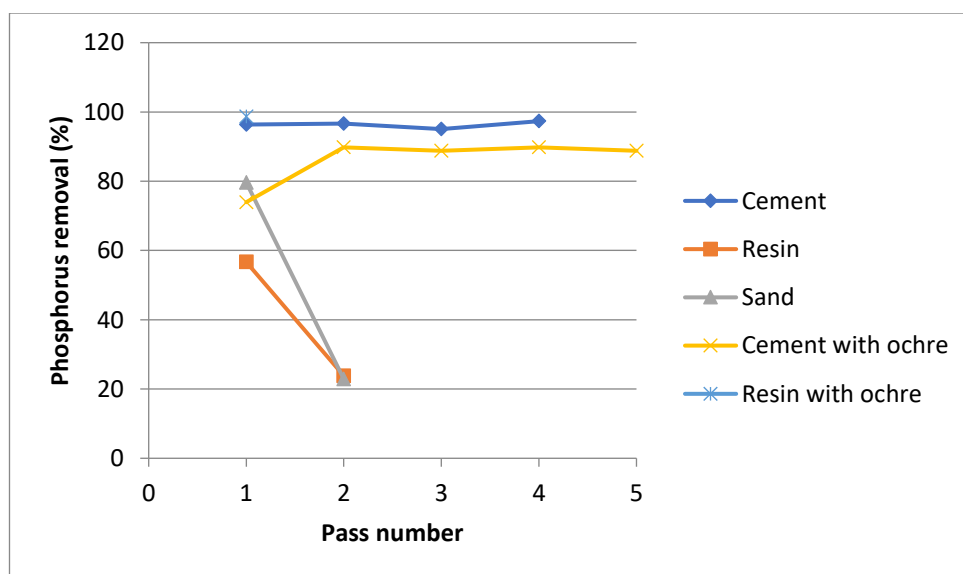


Figure 4.2: Percentage phosphorus removal with respect to pass number for the columns with binder only (cement, resin and sand) and binders with ochre. The percentage removal of phosphorus was calculated for each pass of the solution and fresh solution was used for each pass. Each pass was quantified as 100 ml of solution flowing through the column.

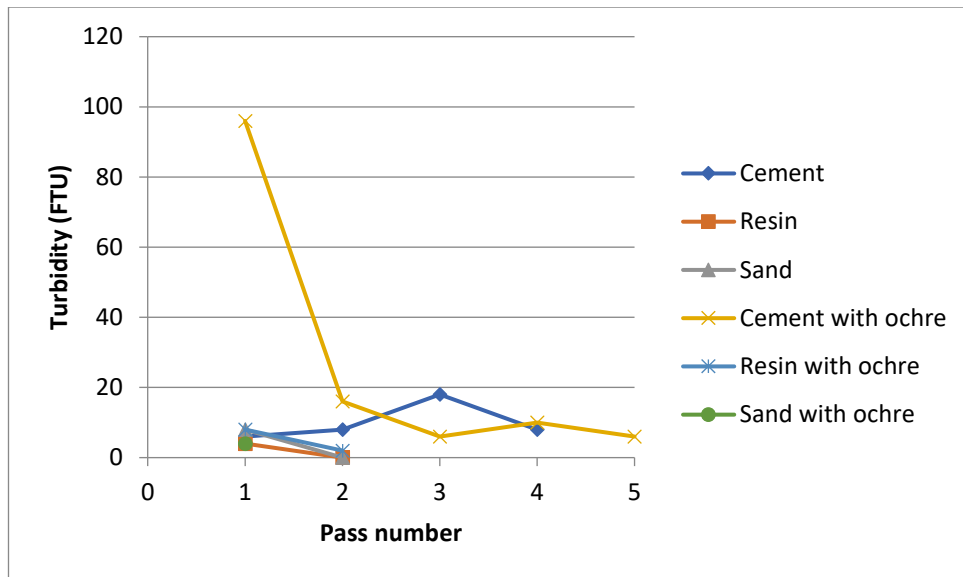


Figure 4.3: Turbidity with respect to pass number for columns packed with binder only (cement, resin and sand) and the binders with ochre. Turbidity was measured after each pass and fresh solution was used for each pass. Each pass was quantified as 100 ml of solution flowing through the column.

Figures 4.2 and 4.3 show the P removal and turbidity of both sets of columns to illustrate the effect of mixing the binders with ochre on these parameters. Figure 4.2 shows that the resin with ochre and the two cement-based columns (with and without ochre) exhibited the best P removal. The cement only column showed better P removal than the cement with ochre column, however (with the exception of cement with ochre pass 1) both columns had a removal of greater than 80 %. Figure 4.4 shows that, with the exception of pass 1 of the cement with ochre column, the turbidity of the effluents of all the columns run were below 20 FTU.

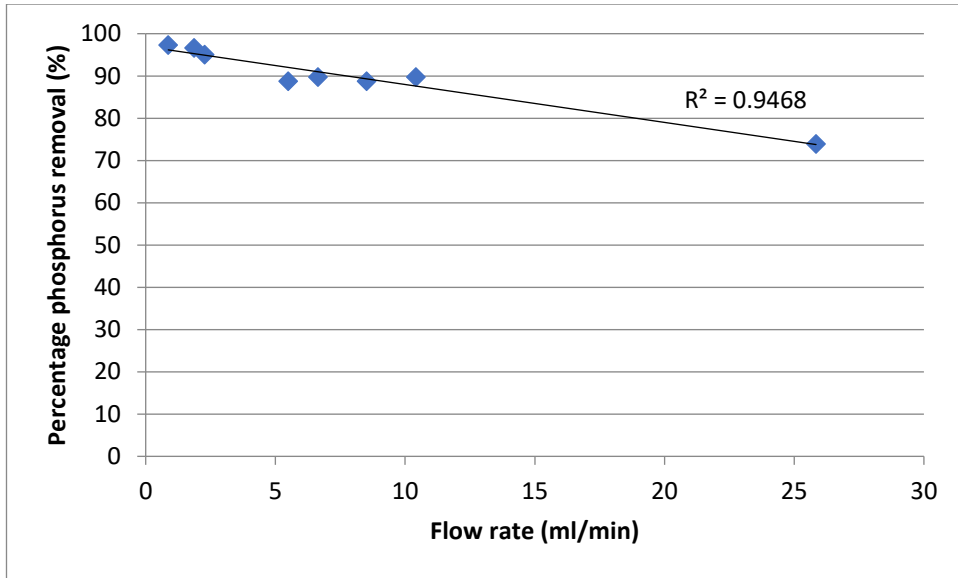


Figure 4.4: Percentage removal of phosphorus plotted against flow rate through the cement with ochre columns. The R^2 value describes the relationship between percentage phosphorus removal and flow rate.

Figure 4.4 shows the relationship between flow rate and P removal for the cement-based columns (both the binder only and cement with ochre columns). It shows a strong negative correlation between flow rate and P removal, with a high flow rate resulting in a lower removal of P.

The pH of the effluent from the cement and ochre has shown a general, although not consistent, decrease, from pH 12 to pH 11, which can be seen in Figure 4.5.

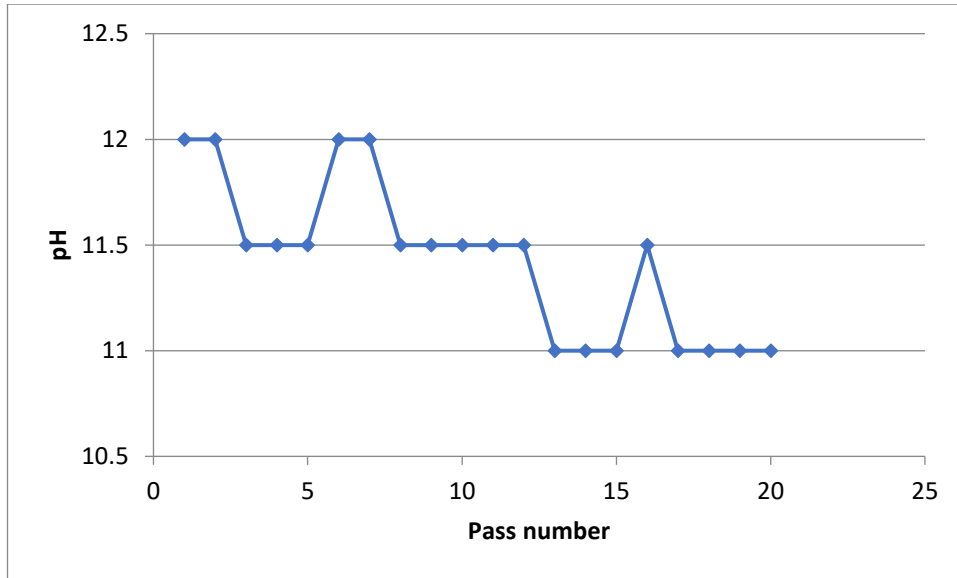


Figure 4.5: pH of the cement and ochre column with respect to pass number. The pH of the solution was measured after each pass and fresh solution was used for each pass. Each pass was quantified as 100 ml of water flowing through the column.

Figure 4.6 shows the average flow rate through the cement and ochre column with increasing passes. From pass 2 to pass 20, the flow rate has remained between 5 and 10 ml/min. From pass 13 to pass 20, the flow rate remained at approximately 5 ml/min. Figure 4.7 shows that the turbidity of the effluent after the third pass was consistently 10 FTU or below.

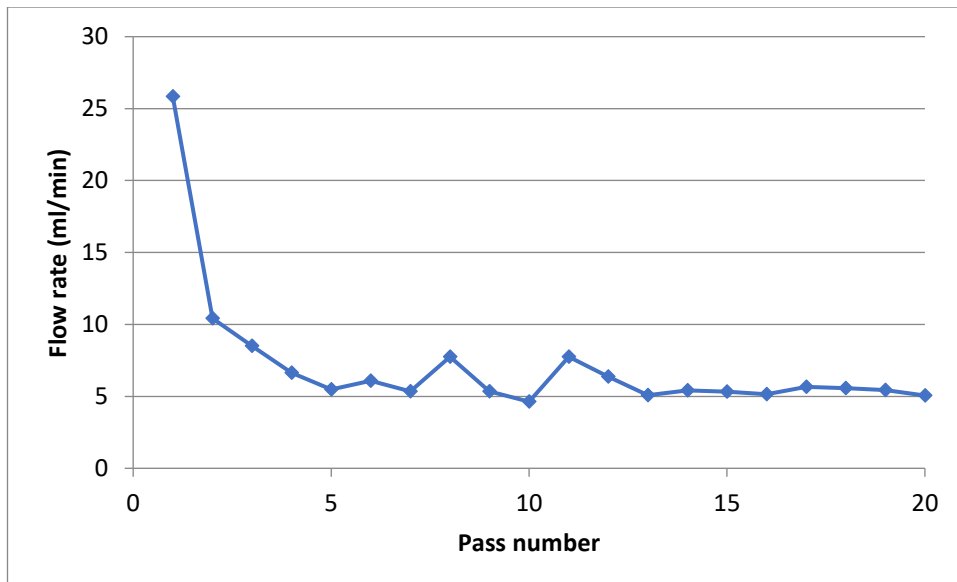


Figure 4.6: Average flow rate through the cement and ochre column with respect to pass number. Each pass was quantified as 100 ml of solution flowing through the column.

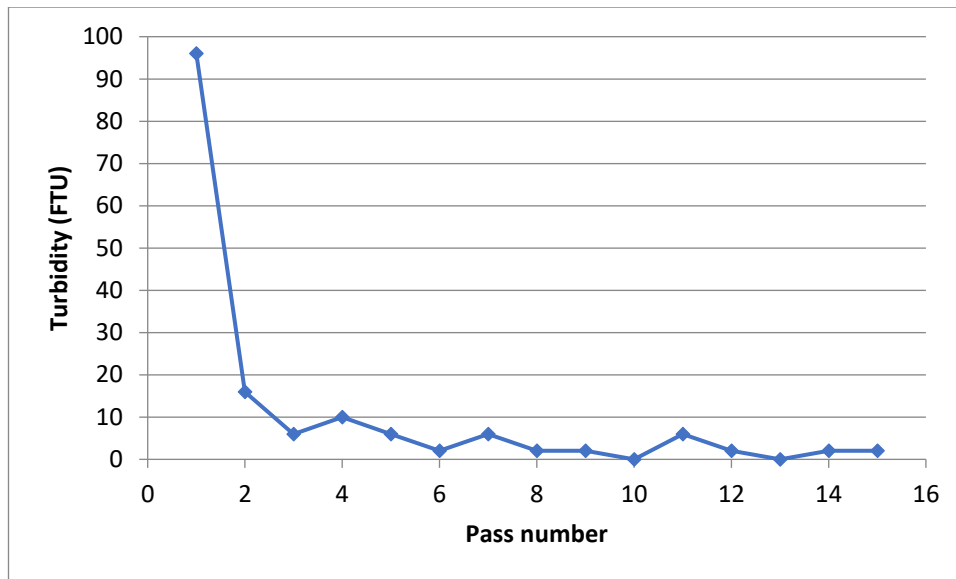


Figure 4.7: Turbidity of the effluent from the cement and sand column with respect to pass number. The turbidity of the solution was measured after each pass with fresh solution used for each pass. Each pass was quantified as 100 ml of solution flowing through the column.

Table 4.3 shows that as the proportion of ochre in the ochre with sand mix decreased, the average flow rate increased. The column packed with a 1:1 ratio of ochre to sand had an average flow rate of 0.074 ml/min, almost 6 times slower than the flow rate of 0.452 ml/min seen in the 1:20 column. The adsorbent in all four columns compacted within the column during the first pass of solution.

Table 4.3: Flow rate results from the ochre and sand columns with varying ratios of ochre to sand.

Ratio (ochre:sand)	Average flow (ml/min)
1:1	0.074
1:5	0.151
1:10	0.376
1:20	0.452

4.3.2 Discussion

The binder only columns showed that the binders themselves remove phosphorus from solution, although this removal decreases quickly for the resin and sand. This may be as a result of partial saturation of the adsorbent. The cement adsorbent showed a consistent removal of

greater than 95 %, this is likely to be due to the high levels of calcium ions present in the cement binder.

The resin column showed improved removal with the addition of ochre to the adsorbent. The first pass through the resin only column showed removal of 56.67 % in comparison to 98.65 % for the first pass of the resin and ochre column. It is not possible to determine whether this level of removal would continue as the phosphorus in the effluent from the second pass was not analysed owing to a process error.

The P removal by the cement column showed a decrease when ochre was added to the adsorbent. However, this was probably due to the increased flow rate (greater than 5.0 ml/min in comparison to less than 2.3 ml/min). The relationship shown in Figure 4.6 suggests that a faster flow rate will result in lower P removal, due to a shorter contact time. Although the percentage removal is lower, the cement column consistently showed removal of greater than 70 %, even with a flow rate of greater than 25.0 ml/min.

The cement columns showed the best P removal, but also showed an increase in pH for both columns, with and without ochre. This is due to the high pH of cement. Further trials using the cement and ochre column showed that the pH dropped to pH 11 (from pH 12) by pass 13 but there was a peak up to pH 11.5 again at pass 16. Each pass represents 100 ml of solution (either phosphate or water) and therefore 1.3 litres had to be passed through the adsorbent before the pH reached pH 11. The spikes in pH of the effluent generally occurred on the first pass of the day, after the column had been sat dry from draining overnight. This may be related to rewetting of fines formed during dehydration of the column. Neither the resin nor sand columns had a significant impact on pH, only ever increasing as far as pH 8.

Further, whilst the relationship between flow rate and P removal for the cement based columns (both the binder only and cement with ochre columns) shows a strong negative correlation, with a high flow rate resulting in a lower removal of P, the flow rates in these trials never exceeded 26 ml/min, which is approximately 0.0004L/s.

The addition of ochre to the cement column improved the flow rate, although it does reduce and appear to plateau. Table 4.1 shows that the cement only column achieved a maximum flow rate of 2.27 ml/min compared to 25.84 ml/min in the cement and ochre column (Table 4.2 and

Figure 4.6). The flow rate through the ochre and cement column was around 5 ml/min from the thirteenth pass to the final pass (pass 20). This could be as a result of the mobilisation of ochre or other fines from the adsorbent. However, it had the opposite effect for the sand column. The sand only column had a flow rate of 0.65 ml/min for its second pass but using ochre and sand in a 3:1 ratio slowed the flow so that only 50 ml had passed through the column after 24 hours. Further investigations showed that reducing the proportion of ochre improved flow rates and that a ratio of 1:20 had a flow rate approaching that of sand alone. These results suggest that ochre is the flow limiting factor when using sand as a base. When using sand and ochre, a balance needs to be struck between flow rate and P removal and use of enough ochre that it doesn't saturate rapidly and require replacement or regeneration. The sand used for these trials was quite fine and therefore may have blocked more readily than coarser sand would have.

The flow rate of the resin column also improved with the addition of ochre. However, the flow rate of the resin and ochre column dropped from 2.44 ml/min in the first pass to 0.78 ml/min in the second. This may be as a result of blocking or blinding and it is not possible to say whether this decrease in flow rate would continue without further trials. The flow rate for the second pass of the resin only column was 0.4 ml/min.

Turbidity for all the columns (with and without ochre) was generally low. With the exception of the cement with ochre column pass 1 (96 FTU) and pass 2 (16 FTU), all effluent turbidity readings were 10 FTU or below. The turbidity of STWs final effluent is monitored as a proxy for site performance. Generally, it would be expected that the turbidity of a site will be below 30 FTU. Therefore, turbidity of 10 FTU as a result of the bound ochre should not have a negative impact on the turbidity of the effluent leaving the STW.

4.4 Intermediate Bulk Container (IBC) Trial

4.4.1 Trial observations

The trial presented a number of operational challenges including optimising the flow rate in order to prevent the filter filling up with effluent and thereby stopping free flow throughout the unit. The second phase of the trial included no-flow periods when flow into the unit was ceased to prevent overflowing when no personnel were available to monitor.

At the conclusion of the first run, a thin layer of sludge was visible coating the top gravel layer and there was algal growth in the outlet pipe (shown in Figure 4.8). This was attributed to light promoting algae growth in the nutrient rich water.



Figure 4.8: Sludge was observed on the gravel layer within the IBC trial unit (left) and algal growth occurred on the outlet pipe of the unit (right).

The unit was covered on completion of the first run and left for three weeks before being unpacked. In the period between the trial ending and the unit being unpacked, the effluent had mostly drained through the unit.

During the unpacking of the unit, the layers were kept separate and the membrane kept for reuse wherever possible. The bottom layer of sand was not removed from the unit but instead sprayed with final effluent in order to ensure flow could pass through as well as to dislodge any solids which may have been present. During the unpacking, it was noted that there was no visible build-up of solids within or between the layers, but the bottom of the ochre layer had been compacted.

Whilst unpacking the units following the second run, it was noted that there was a fining up grading of the sand within the layer with the largest grains located at the bottom of the layer.

4.4.2 Results

The water content of the ochre collected from Dawdon was roughly 48 % at the time it was mixed with sand and added to the unit. The total quantity of ochre added to the unit was

roughly 117.6 kg which, assuming constant water content, is equivalent to approximately 61.15 kg ochre as dry weight.

The first flush of effluent through the unit washed out a lot of ochre colour. After 20 litres had passed through the unit, the colour had mostly disappeared, as demonstrated in Figure 4.9, which shows the first 20 litres (from left to right) alongside the site's final effluent (final bottle on the right). When the unit was left dry and the flow then turned back on there was a small quantity of ochre solids washed out.



Figure 4.9: Samples taken of the first flush of effluent through the IBC unit (taken at the outlet of the unit). There were 20 samples taken in slowly and these are shown in the above image from the first litre on the left to the twentieth on the right. The final sample on the right of the image is a sample of the site's final effluent for comparison.

Figure 4.10 shows the percentage removal of phosphorus throughout the first run of the trial. The phosphorus removal was initially high for both total and filtered phosphorus but reduced quickly. The phosphorus removal continued to drop until day 5 of the trial (19/7/16), when removal began to improve and continued to increase until the trial ceased. The maximum percentage removal of filtered phosphorus was 72.06 % (11/7/16) and 62.80 % for total phosphorus (11/7/16). The minimum percentage removal for filtered phosphorus was 5.85 %, whilst the minimum removal of total phosphorus was 8.63 %.

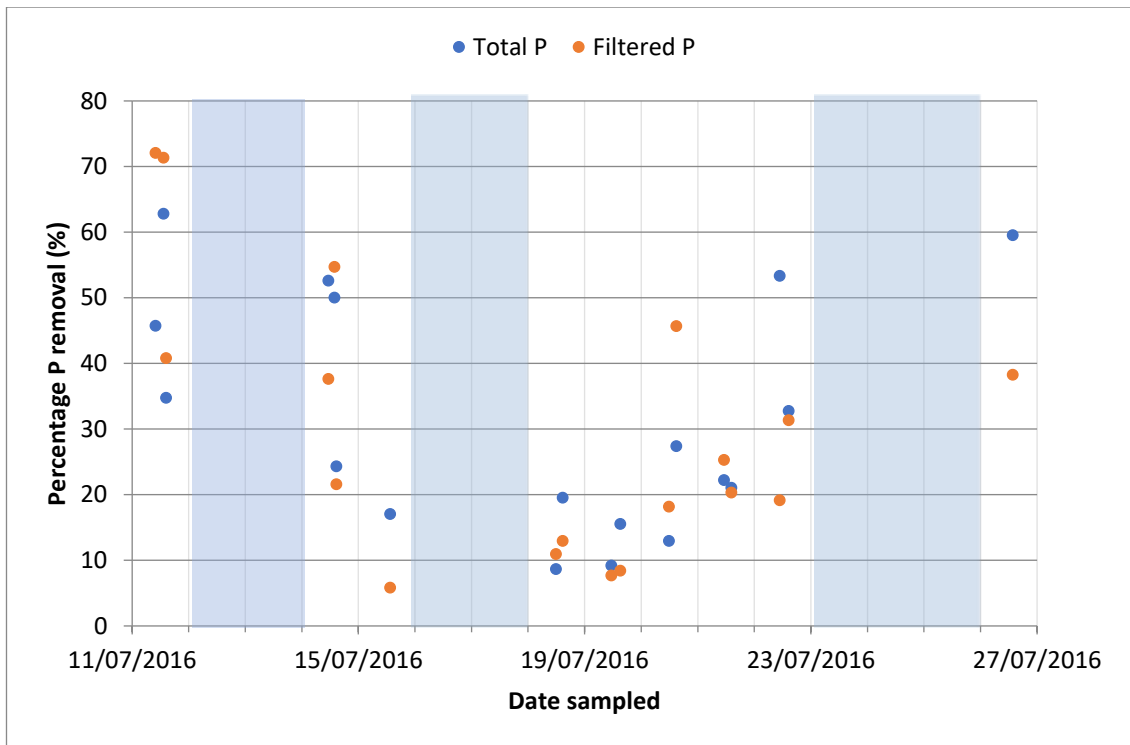


Figure 4.10: Percentage phosphorus removal plotted against the date of sampling for run 1 of the IBC trial. The blue shading shows periods of where there was no flow into the unit.

There were three periods of no flow into the unit (which are shown in Figure 4.10). Following these periods, there was no clear improvement in phosphorus removal.

The ingoing flow rate is identified on Figure 4.11. There is no clear link between the ingoing flow rate and the percentage removal of phosphorus.

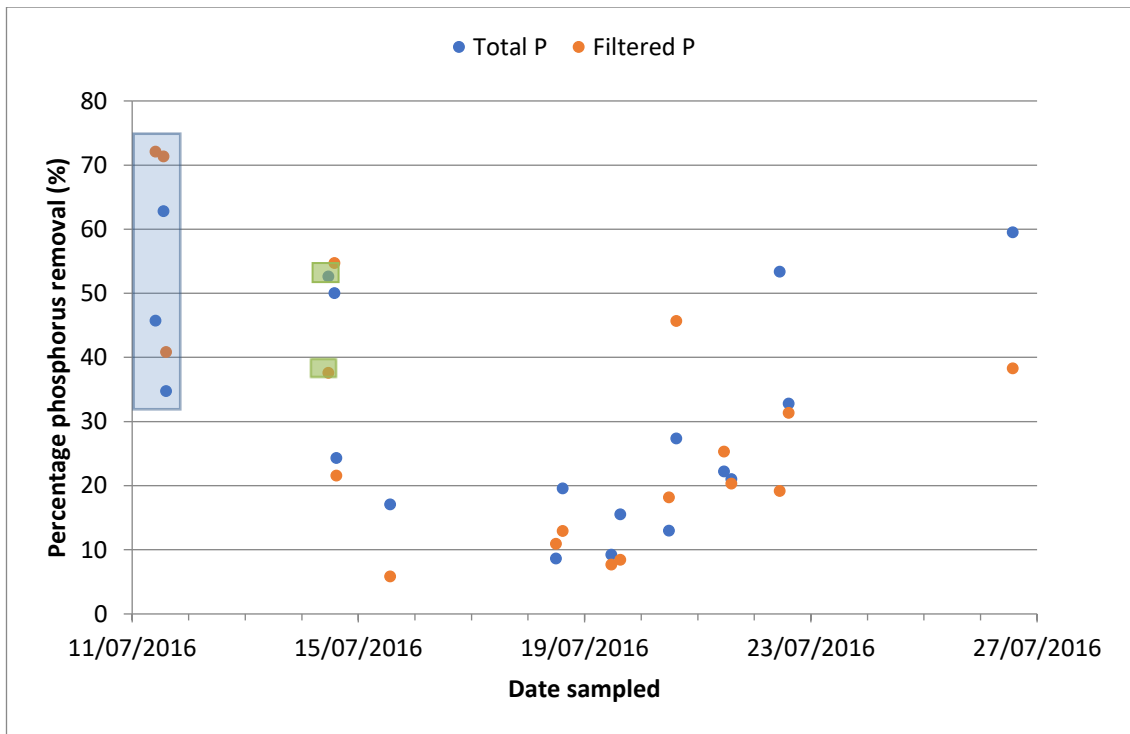


Figure 4.11: Percentage phosphorus removal plotted against the date of sampling with flow rate into the unit indicated. The samples with a blue box around them were sampled when the ingoing flow was 0.73 l/s and the green box indicates samples taken when ingoing flow rate was 0.46 l/s. All other samples were taken when the ingoing flow rate was 0.19 l/s.

Table 4.4 shows the average daily removal of phosphorus, the litres pumped into the unit and the consequential estimate of phosphorus removal for each day of the trial. The unit was allowed to overflow and therefore the litres pumped (as calculated from the flow rate) was a theoretical maximum. The estimated total removal of phosphorus is also shown and was used to estimate the quantity of P removed per gram of ochre. Over the course of the trial, it was estimated that approximately 38596 mg of total phosphorus (almost 39 g) was removed. The data suggests that each gram of ochre removed 0.33 mg TP and 0.15 mg filtered P during the trial period. A total of 30891.4 litres of effluent were pumped into the unit.

Table 4.4: Phosphorus removal estimates for average daily removal of total and filtered phosphorus per litre of effluent and the estimated quantity of total and filtered phosphorus removed in milligrams. Also included is the litres of effluent treated by the unit and the quantity of total and filtered phosphorus removed by the unit across the first IBC trial run in terms of milligrams and per gram of ochre within the unit.

Date	Average daily phosphorus removal (mg P/l)		Litres in the day (l)	Estimate of daily phosphorus removal (mg)	
	Total phosphorus	Filtered phosphorus		Total phosphorus	Filtered phosphorus
11/07/2016	1.57	1.67	1246.4	1956.85	2081.49
14/07/2016	1.17	0.66	2000.0	2340.00	1320.00
15/07/2016	0.36	0.08	3363.0	1210.68	269.04
18/07/2016	0.37	0.45	3727.8	1379.29	1677.51
19/07/2016	0.22	0.09	4742.4	1043.328	426.82
20/07/2016	1.28	0.86	3306.0	4231.68	2843.16
21/07/2016	0.84	0.43	4788.0	4021.92	2058.84
22/07/2016	2.35	0.74	4297.8	10099.83	3180.37
26/07/2016	3.60	1.14	3420.0	12312.00	3898.80
Total phosphorus removal by the trial (mg)				38595.57	17756.03
Phosphorus removal per gram of ochre (mg P/g)				0.33	0.15

Figure 4.12 shows the distribution of percentage removal according to the percentage of samples in each band for Run 1 of the IBC trial. Most of the samples exhibited removal between 20 and 50 % for both total and filtered phosphorus (38.89 and 44.44 % respectively). 27.78 % of samples exhibited greater than (or equal to) 50 % removal of total phosphorus. The percentage of samples with filtered phosphorus removal at this level was 16.67 %.

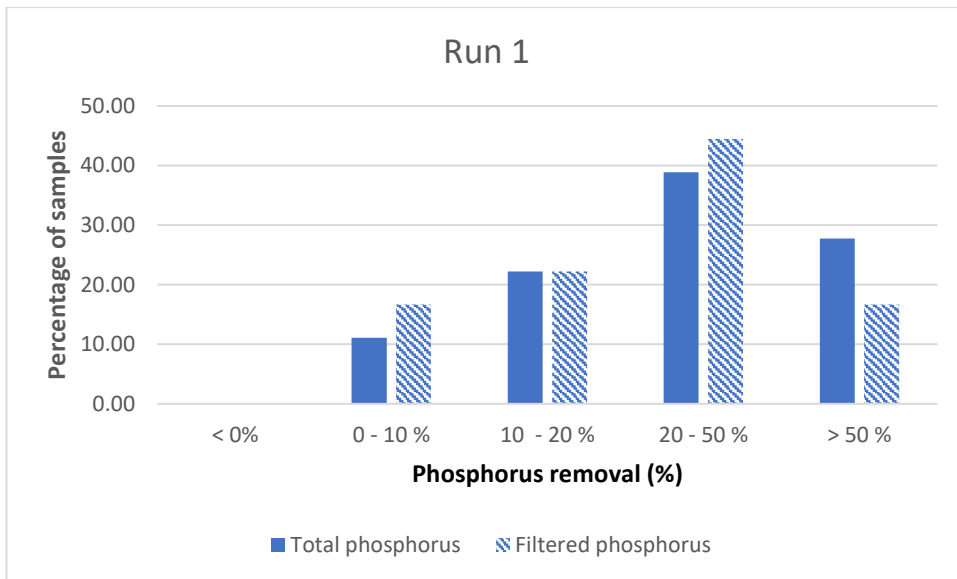


Figure 4.12: Percentage of the Run 1 samples in each removal band for both total and filtered phosphorus.

The analyses of the samples taken on the morning of 22/7/16 shows a difference in results between the Palintest analysis and the analysis completed by the laboratory. Table 4.5 shows the results from both analyses, the results from the laboratory indicate higher phosphorus levels than the Palintest results. The biggest discrepancy can be seen in the filtered phosphorus levels in the inlet sample. The Palintest photometer is calibrated yearly, suggesting that the error is present within the tests themselves. However, the data from the Palintest analyses will be comparative to one another, due to equivalent levels of errors. The analysis for further trials was completed using the Palintest photometer and analysis kits, as the alternative of laboratory ion chromatography was expensive and time consuming.

Table 4.5: Comparison of analysis results of samples taken on 22/7/16. The samples were analysed by a commercial laboratory ion chromatography and using the Palintest tubetest phosphorus kit and photometer

	Laboratory analysis		Palintest analysis	
	Total P mg/l	Filtered P mg/l	Total P mg/l	Filtered P mg/l
Inlet	6.30	2.30	5.55	1.62
Outlet	3.50	1.40	2.59	1.31
Percentage removal (%)	44.44	39.13	53.33	19.14

Figure 4.13 shows the percentage removal of total and filtered phosphorus for the second trial run. The removal of total phosphorus by the unit is consistently above 20 %, with most samples showing a removal of 40 % or greater. Filtered phosphorus removal was generally about 35 % although removal dropped below 20 % on one occasion (9/9/16 PM) and below 30 % on another (5/9/16 AM).

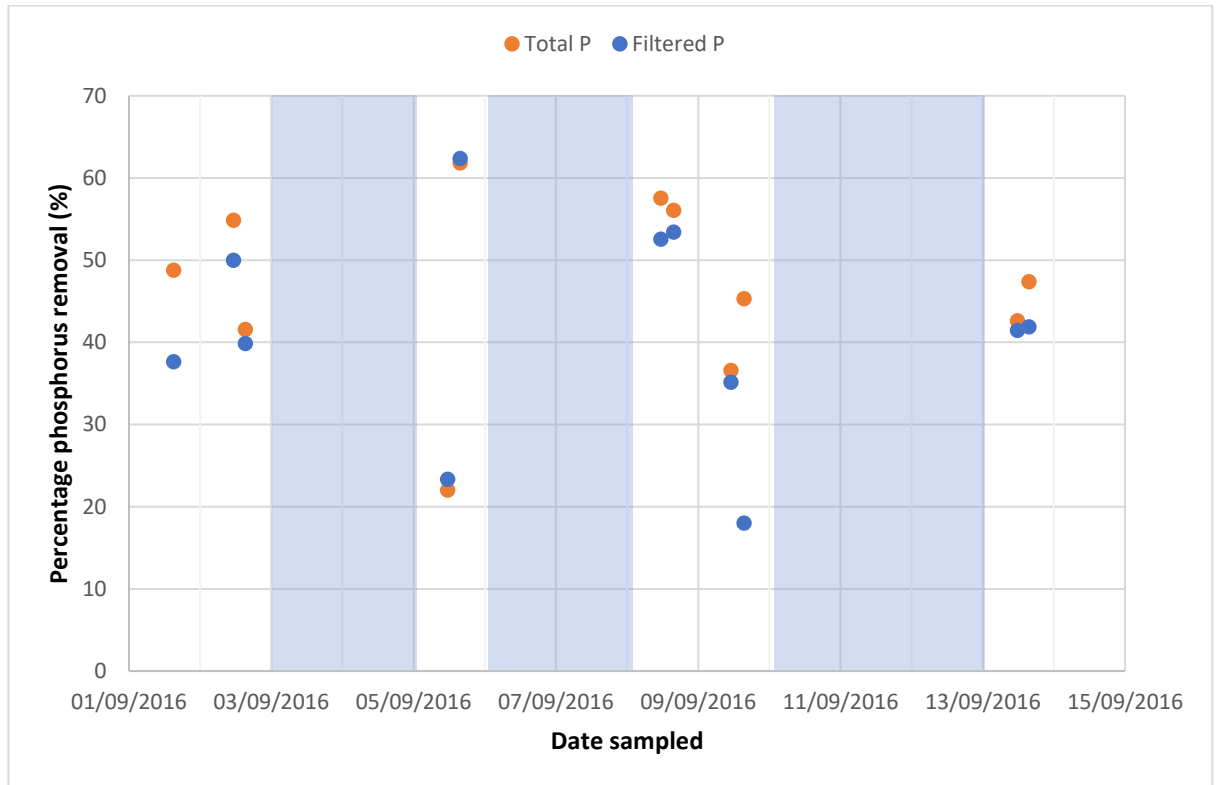


Figure 4.13: Percentage phosphorus removal plotted against the date of sampling for run 2 of the IBC trial. The blue shading shows periods of where there was no flow into the unit.

The periods of no flow (highlighted in Figure 4.13) are not followed by either an increase or a decrease in percentage removal.

Table 4.6: Phosphorus removal estimates for average daily removal of total and filtered phosphorus per litre of effluent and the estimated quantity of total and filtered phosphorus removed in milligrams. Also included is the litres of effluent treated by the unit and the quantity of total and filtered phosphorus removed by the unit across the second IBC trial run in terms of milligrams and per gram of ochre within the unit.

Date	Average daily phosphorus removal (mg/l)		Litres in the day	Estimate of phosphorus removal (mg)	
	Total phosphorus	Filtered phosphorus		Total phosphorus	Filtered phosphorus
01/09/2016	1.21	0.70	1208.4	1462.16	845.88
02/09/2016	0.80	0.53	3841.8	3073.44	2036.15
05/09/2016	0.46	0.35	4069.8	1872.11	1424.43
08/09/2016	1.21	0.88	3887.4	4703.75	3420.91
09/09/2016	0.84	0.44	4218	3522.03	1834.83
13/09/2016	1.58	1.13	3910.2	6158.57	4418.53
19/09/2016	1.17	1.01	3636.6	4254.82	3654.78
Total phosphorus removal (mg)				25046.88	17635.52
Removal mg phosphorus per g ochre				0.21	0.15

Table 4.6 shows that the unit removed a total of 25047 mg of total P during the second run (approximately 25 g) and this equates to around 0.21 mg total P per gram of ochre (compared to 0.33 mg total phosphorus per gram of ochre removed in the first run of the unit). The unit removed more total phosphorus than filtered phosphorus. Theoretically, a maximum of 24772.2 litres of effluent were pumped into the unit.

Figure 4.14 shows that all samples during the second run had removal greater than 20 % for total phosphorus and 92.31 % of samples had greater than 20 % removal of filtered phosphorus (one sample had removal between 10 and 20 %). Most of the removal was between 20 and 50 %.

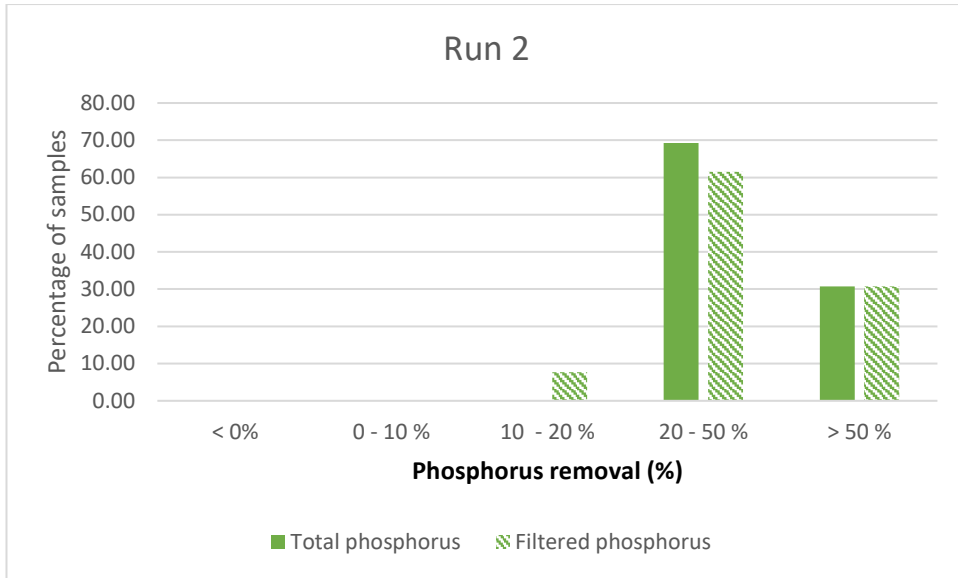


Figure 4.14: Percentage of the Run 2 samples in each removal band for both total and filtered phosphorus.

Table 4.7 shows the estimated removal of phosphorus for the two runs individually as well as the estimated combined total removal of phosphorus.

Table 4.7: Estimated total and filtered phosphorus removal for both runs of the IBC unit in milligrams and per gram of ochre within the trial unit.

	Total litres through unit	Total estimated phosphorus removal (mg)		Estimated phosphorus removal (mg P per g ochre)	
		Total phosphorus	Filtered phosphorus	Total phosphorus	Filtered phosphorus
Run 1	30891.40	38595.57	17756.03	0.33	0.15
Run 2	24772.20	25046.88	17635.52	0.21	0.15
Total	55663.60	63642.46	35391.54	0.54	0.30

The results show that the removal of total phosphorus was greater in the first run than the second run.

The percentage removal in Run 2 was higher than percentage removal in Run 1, for both total and filtered phosphorus, with the exception of the first day's filtered phosphorus (38 % in comparison to 61 %). The data used to produce Figures 4.15 to 4.20 (inclusive) can be found in Appendix A (Table A1).

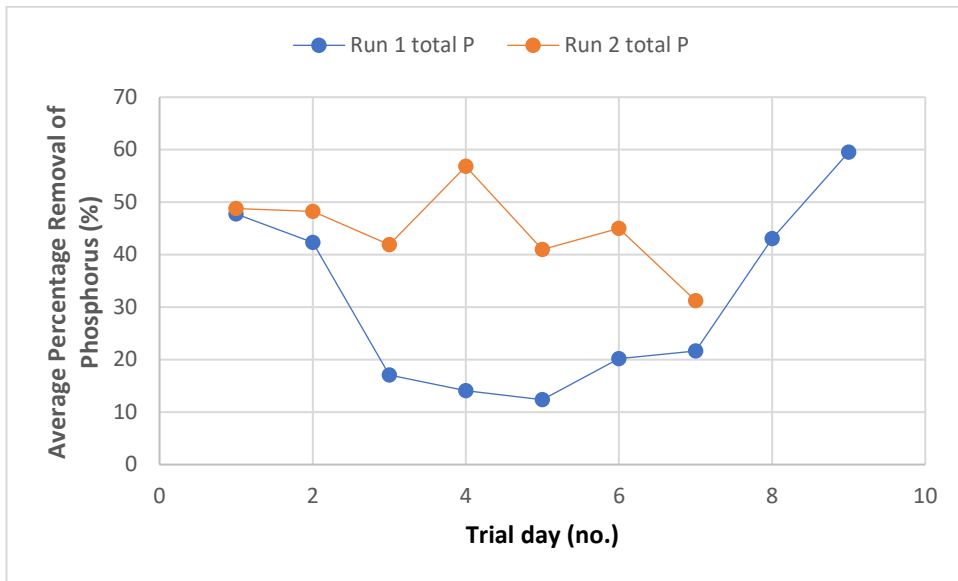


Figure 4.15: Average daily percentage removal of total phosphorus during the two trials. A mean removal was calculated for each day of the trial runs.

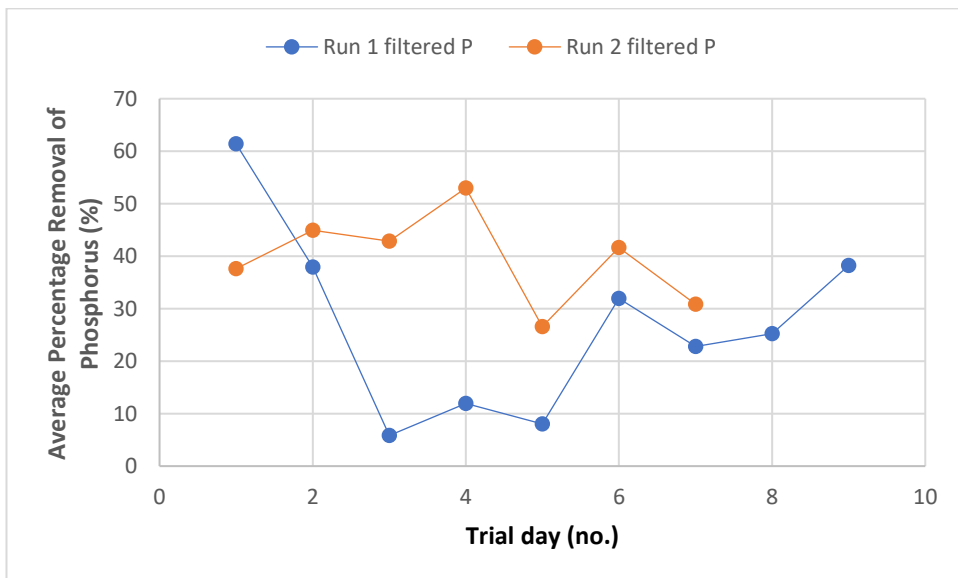


Figure 4.16: Average daily percentage removal of filtered phosphorus during the two trials. A mean removal was calculated for each day of the trial runs.

The first run of the unit exhibited an increase in removal after day 7. For total phosphorus, this was part of an upward trend starting on day 6. The filtered phosphorus in both trial runs appears to follow the same pattern in removal from day 2 onwards.

The removal of phosphorus (both total and filtered) was slightly more consistent during the second run and did not show a large decrease in removal in the first couple of days of running the unit.

Generally, the outlet total phosphorus follows the same pattern as the inlet total phosphorus for both runs. These patterns are shown in Figures 4.17 and 4.18.

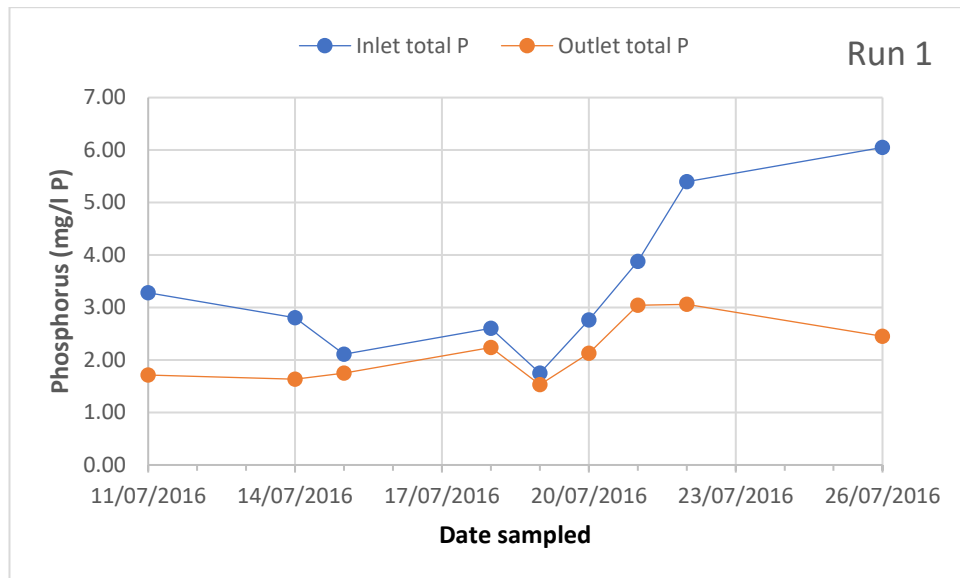


Figure 4.17: The daily average inlet and outlet total phosphorus for Run 1 of the IBC trial.

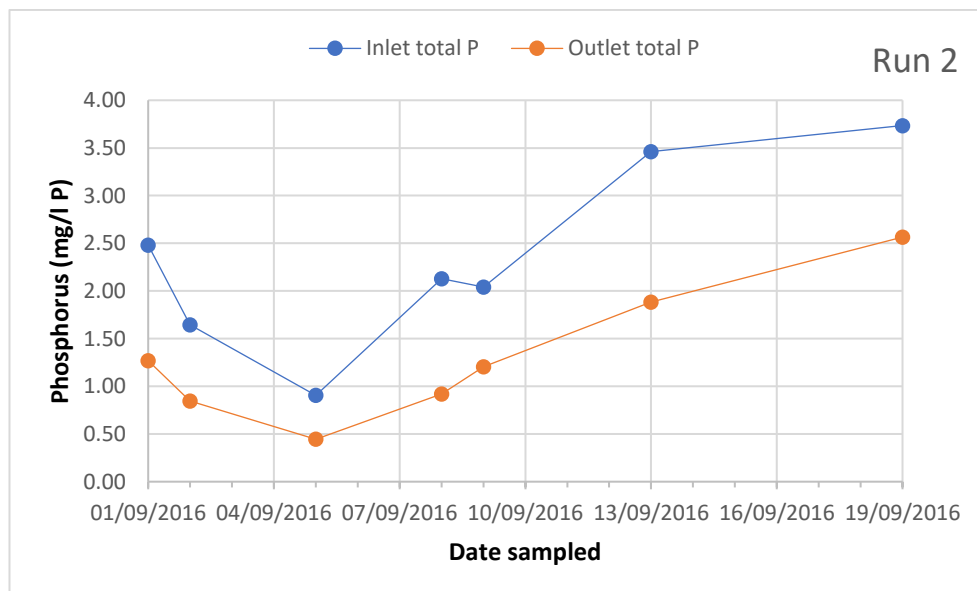


Figure 4.18: The daily average inlet and outlet total phosphorus for Run 2 of the IBC trial.

There is more deviation in the first run than the second. Figures 4.19 and 4.20 show the trends in daily average filtered phosphorus. Again, the inlet and outlet phosphorus concentrations show similar patterns to each other with the first run exhibiting more deviations than the second.

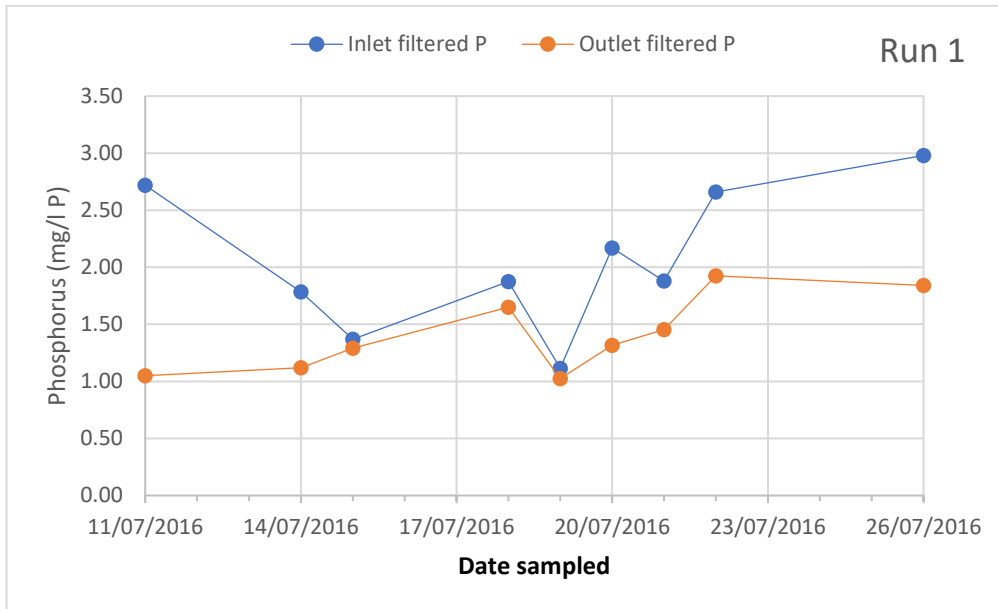


Figure 4.19: The daily average inlet and outlet filtered phosphorus for Run 1 of the IBC trial.

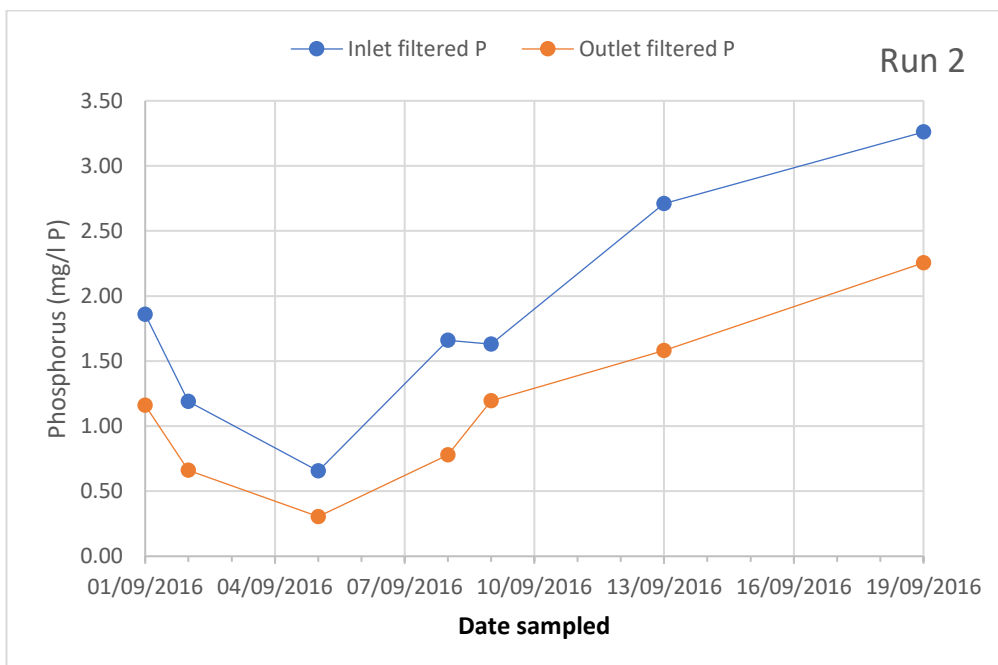


Figure 4.20: The daily average inlet and outlet filtered phosphorus for Run 2 of the IBC trial.

Table 4.8 compares the average inlet and outlet phosphorus of the two trial runs as well as the average removal in mg/l and as a percentage of the inlet concentration.

Table 4.8: Average (mean) inlet and outlet phosphorus (total and filter) and total and filtered phosphorus removal across the duration of the two trial runs.

Average	Inlet phosphorus (mg/l P)		Outlet phosphorus (mg/l P)		Quantity removed (mg/l P)		Percentage phosphorus removal (%)	
	Total	Filtered	Total	Filtered	Total	Filtered	Total	Filtered
Run 1	3.29	2.10	2.12	1.35	1.17	0.72	31.63	30.11
Run 2	2.33	1.85	1.31	1.13	1.02	0.72	44.39	39.80

The two runs both removed an average of 0.72 mg/l of filtered phosphorus. However, the average removal of total phosphorus (in mg/l) was higher in the first run than the second (1.17 mg/l in comparison to 1.02 mg/l). In contrast, average percentage removal of both total and filtered phosphorus was higher in the second run than the first. The average inlet and outlet phosphorus concentrations (both total and filtered) were higher in the first run than the second run. The second run removed, on average, a higher percentage of both total and filtered phosphorus than the first run.

Figure 4.21 shows that, across the two trial runs with the IBC unit, most of the samples exhibited between 20 and 50 % removal of phosphorus (51.61 % of samples for both total and filtered phosphorus). The second largest portion of samples had removal of greater than 50 % (29.03 % of samples for total phosphorus and 22.58 % for filtered phosphorus). The smallest portion of samples had removal between 0 and 10 %, all of which were taken during the first run of the unit (shown in Figure 4.22).

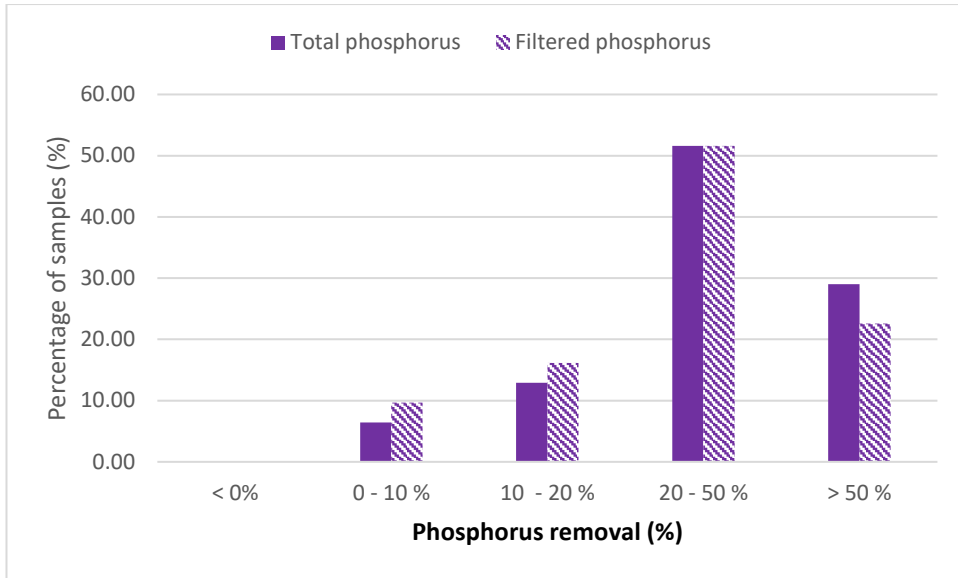


Figure 4.21: Percentage of the samples taken across both runs of the IBC trial in each removal band for both total and filtered phosphorus.

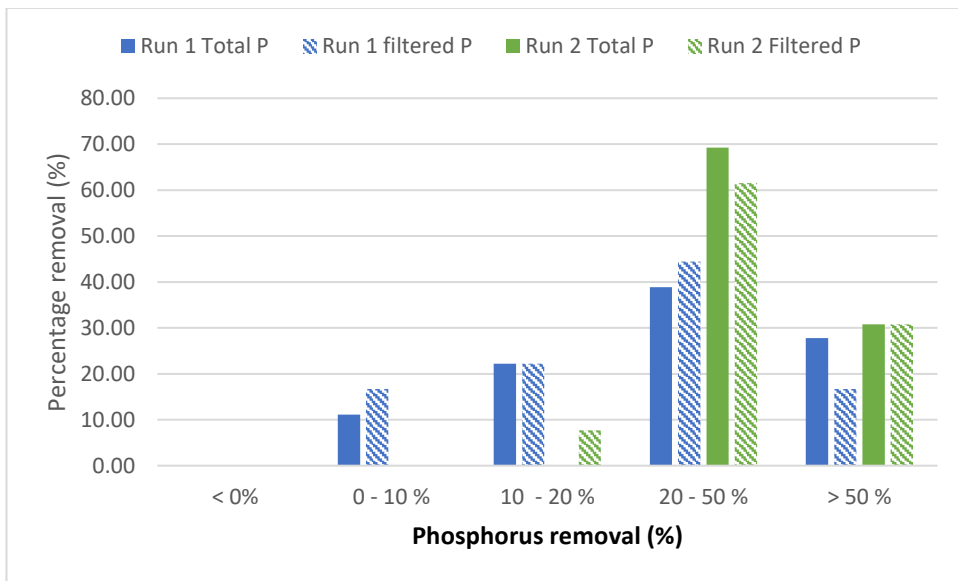


Figure 4.22: Percentage of samples taken in each run of the IBC trial in each removal band for both total and filtered phosphorus.

The data shown in Figure 4.22 suggests that the second run was more effective at removing phosphorus than the first run, with removal of total phosphorus consistently above 20 % for total phosphorus. Almost a third of the samples (30.77 %) had removals greater than 50 % for both total and filtered phosphorus in the second run. The full data used to produce Figures 4.21 and 4.22 can be found in Appendix A (Table A2).

4.4.3 Discussion

The first run of the IBC initially exhibited high percentage removal (72.06 % filtered phosphorus and 62.80 % total phosphorus) before decreasing. Following the second rest period, the removal began to increase again. The reason for the increased uptake of phosphorus in the second half of the trial is not known. When the unit was unpacked after the trial ceased, there was no visual presence of algae or biofilm and therefore nothing to suggest a biological uptake of phosphorus. No studies could be found which investigated the impact of biofilm on the surface of sand filters and whether the presence of a biofilm or algal growth improved phosphorus removal. However, the build-up of biofilm in a filter has been noted to result in clogging of filter media and usually occurs as a result of the organic and total suspended solids in the wastewater (Healy et al., 2011). These solids reduce pore space and encourage the growth of bacteria (Healy et al., 2011). The microalgae in biofilms are capable of removing nutrients from wastewater (Boelee et al., 2011) and fixed film wastewater treatment such as percolating filters and rotating biological contactors (RBCs) use the principle of biofilms attached to media or other surface for the treatment of wastewater, including nutrient removal (Kesaano and Sims, 2014). Therefore, it can be inferred that the presence of a biofilm on the surface of the filter would result in nutrient removal, however, the resultant clogging will impede and eventually prevent flow through the unit.

There is no clear connection between the rest periods and an increase in phosphorus removal, though the removal may appear more consistent after the second rest period. The periods of no flow during the second run of the trial did not result in an increase or decrease in percentage removal. The no flow periods in both the trial runs were only for 2 or 3 days and therefore it cannot be determined if longer periods of no flow would have an impact on phosphorus removal.

During the first run of the trial, variations of the ingoing flow rate did not appear to impact phosphorus removal. It might be expected that a slower flow rate would result in improved removal as a result of the increased contact time with the adsorbent, however, this is not seen in the results. It should be noted that only the ingoing flow rate was controlled, and it was assumed that the flow through the filter was constant, but this may not be true. Additionally, the unit was allowed to overflow and therefore the ingoing flow rate was not equal to the flow passing through the unit or the volume entering the unit.

It is not possible to predict whether the downward trend in removal of both total and filtered P would have continued after day 7 of the second run nor the reason for this trend. It is possible that all (or some) of the ochre within the unit was beginning to saturate but without continuing the trial or analysing the phosphorus content of the ochre it cannot be determined.

The filtered phosphorus in both trial runs appears to follow the same pattern in removal from day 2 onwards and therefore it is possible that the filtered phosphorus removal in the second run may have experienced an increase in phosphorus removal after day 7, which was seen in the first run. The removal of phosphorus (both total and filtered) was slightly more consistent during the second run and did not show a large decrease in removal in the first couple of days of running the unit.

For the two trial runs, the greatest proportion of samples exhibited removal of between 20 and 50 % for both total and filtered phosphorus.

The first run of the IBC treated a larger volume of effluent than the second run (in terms of litres) and removed a greater quantity of total phosphorus. However, the quantities of filtered phosphorus removed by the two runs was similar.

Across the two runs of the trial, it was estimated that 0.54 mg TP per g of ochre was removed. Heal et al. (2004) found that ochre has an adsorption capacity of 26 to 30.5 mg P per g of ochre. For Dawdon ochre (which was used in the IBC trial), Jessett (2014) estimated a maximum adsorption capacity of 19.92 mg PO₄ per g of ochre. These maximum adsorption capacities suggest that the Dawdon ochre is not yet saturated and is still capable of adsorbing and removing phosphorus.

4.5 Plant growth trials using ochre as fertiliser

Growth trials were completed using a ryegrass-based lawn seed to determine whether P-saturated ochre could be reused on agriculture land as a fertiliser. These simple growth trials were designed so that the results could inform any further, large-scale trials should they be undertaken.

4.5.1 Results

Table 4.9 summarises the different treatments and their preparation. It also categorises each treatment as “Dawdon-based” (i.e. ochre), “Sludge-based” or “Compost-based”.

All pots exhibited growth. However, the pattern of growth differed for each treatment.

Table 4.9: Summary of each treatment type tested as part of the growth trials. The colour in the first column indicates the category; orange indicates a Dawdon ochre based treatment, green is sludge-based (mixed with sludge from a co-treatment reed bed) and blue is compost-based.

	Material	Preparation	Category
1	Dawdon ochre:sand (1:6)	6 parts sharp sand to 1 part ochre	Dawdon-based
2	Sludge:sand (1:6)	6 parts builders sand to 1 part sludge	Sludge-based
3	Compost only	None	Compost-based
4	Compost:sand (1:6)	6 parts builders sand to 1 part compost	Compost-based
5	Dawdon ochre:compost (1:1)	1 part ochre to 1 part compost (no sand)	Dawdon-based
6	Sludge:compost (1:1)	1 part sludge to 1 part compost (no sand)	Sludge-based
7	Run 1 ochre:compost (1:1)	1 part ochre mix to 1 part compost	Dawdon-based
8	Run 2 ochre:compost (1:1)	1 part ochre mix to 1 part compost	Dawdon-based

Figure 4.23 shows the average height of grass growth for each treatment type on each day a measurement was taken. The graph shows that initially the only treatments with grass growth were 2, 3, 4 and 6 which were the sludge- and compost-based pots. There was no growth in the two Dawdon-based pots (1 and 5) and pots 7 and 8 were not set up initially and were first measured on 7/10/16.

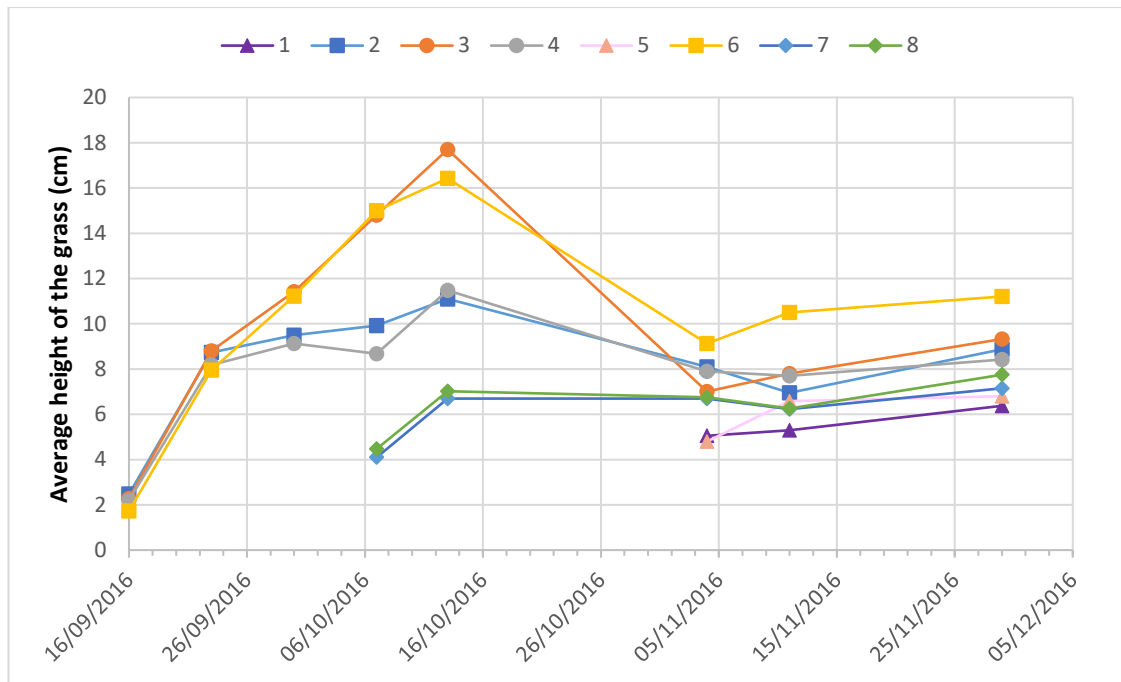


Figure 4.23: Average (mean) height of grass grown on each of the treatment types listed in Table 4.9 as measured weekly.

The initial increase in growth in Treatments 2, 3, 4 and 6 continued until 13/10/16 in pots 3 and 6. However, growth began to slow in Treatments 2 and 4 after 23/9/16. Treatments 7 and 8 showed the same initial growth and growth quickly slowed and levelled. Between 13/10/16 and 4/11/16 there was a decline in grass height, there was no sampling between these dates due to investigator absence and the grass showed signs of breakage, especially in Treatments 3 and 6. Treatments 3, 6, 1 and 5 showed an increase in height between 4/11/16 and 11/11/16, whilst the other pots showed a minor decrease. After 11/11/16, the treatments all showed an increase in grass height up until the final measurement on 29/11/16. At the time of the final measurement, treatment 6 had the tallest growth, on average.

The data shown in Figure 4.23 were averaged to calculate the mean height of the grass for each treatment over the trial period and these are shown in Table 4.10. The grass was harvested on trial completion, pressed dry and the mean weight for each treatment was calculated and is also shown in Table 4.10.

Table 4.10: Average (mean) height of grass for each treatment type over the trial period and mean weight at the end of the trial. The category of each treatment is indicated by the colour in the first column; orange indicates Dawdon-based, green is sludge-based and blue is compost-based

	Treatment	Average height of grass (cm)	Average weight of grass (g)
1	Dawdon ochre:sand	5.58	0.14
2	Sludge:sand	8.21	0.41
3	Compost only	9.89	0.60
4	Compost:sand	7.96	0.31
5	Dawdon ochre:compost	6.06	0.21
6	Sludge:compost	10.39	0.62
7	Run 1:compost	6.18	0.24
8	Run 2:compost	6.45	0.26

Figure 4.24 shows the average dried weight for each treatment and is coloured depending on the base for each treatment. Orange indicates Dawdon-based treatments, green indicates sludge-based treatments and blue indicates compost-based treatment, essentially the control treatments for the trial. The Dawdon-based treatments (on average) had the lowest dry weight at the end of the trial. The treatment with the greatest weight was Treatment 6 (sludge + compost), closely followed by Treatment 3 (compost only).

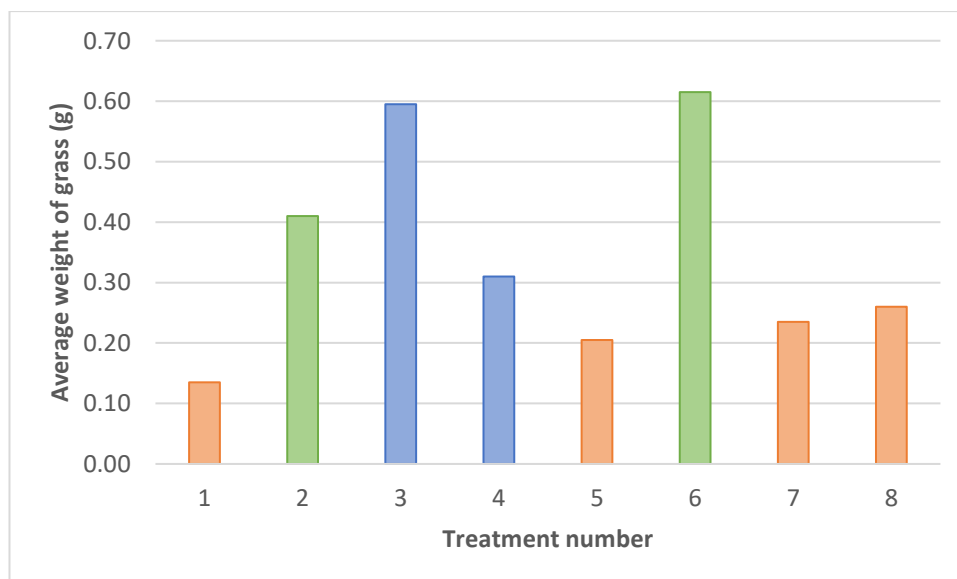


Figure 4.24: Average (mean) dried weight of grass grown with each treatment as sampled and weighed at the end of the trial. The colours of the graph indicate the treatment base type (orange is ochre-based, green is sludge-based and blue is compost-based).

4.5.2 Discussion

The ryegrass planted in the 'sludge and compost' pots (treatment 6) and 'compost only' pots (treatment 3) grew the best. The compost-based pots were included as controls and seeding compost was chosen for these treatments. The seeding compost was expected to have sufficient nutrients to start growth. The results suggest that the addition of the co-treatment sludge (sourced from a reedbed treating STW final effluent and mine water) was sufficient to improve this growth. The sludge is expected to contain further nutrients as a result of the final effluent which is co-treated at the site. The trial results suggest that the co-treatment sludge improves growth and is beneficial to the soil and to plant growth.

The sand-based counterparts (Treatments 2 and 4) exhibited slightly poorer growth than Treatments 6 and 3 but better than the other treatments. Again, the sludge-based pots exhibited better growth than the equivalent compost treatment.

The poorest growth was exhibited by pots treated with Dawdon ochre. The least growth was observed for grass growing in treatments containing ochre which hadn't had contact with final effluent (Treatments 1 and 5). These pots also experienced a delayed start to observed growth. These pots started growing later than the pots with ochre that had had contact with the final effluent (Treatments 7 and 8), despite these being planted over three weeks later. The delayed onset of observed growth in Treatments 1 and 5 suggests that something within the Dawdon ochre is probably inhibitory. Run 1 and 2 Dawdon ochre treatments (Treatments 7 and 8) did not exhibit any delay in growth, suggesting that the flowing of effluent through the material removes the inhibitory effect or component. Dawdon minewater treatment plant is a coastal site, resulting in a saline minewater and therefore an ochre product containing high levels of sodium and calcium (11997 mg/kg and 36 wt. %, respectively), (Moorhouse and Watson, 2015). This salinity is believed to be the inhibitory component.

It should be noted that Treatments 7 and 8 were planted approximately 3 weeks later than the other treatments and therefore the results from these pots are not directly comparable with the earlier plantings. However, these two treatments did exhibit growth before Treatments 1 and 5 which were planted at the commencement of the trial.

Treatment 5 (Dawdon with compost) exhibited better growth than Treatment 1 (Dawdon with sand). Treatment 5 contained seeding compost which contained the necessary nutrients to aid

growth once the salinity had washed out whilst Treatment 1 had no added nutrients other than those within the ochre when collected from source.

The order of growth for the ochre is as expected with the pots containing nutrients from final effluent exhibiting better growth than those without contact with final effluent and therefore with no added nutrients.

The trials completed by Dobbie et al. (2005) suggested that the application of P-saturated ochre to the soil improved crop yields when compared to conventional fertilisers and soils which received no treatment. However, the results of the small-scale trials in this thesis suggest that although the ochre was not toxic it did not improve the grass growth. The Dobbie et al. (2005) study treated all pots with P-saturated ochre and potassium and nitrate were also added. The pots in the current study used a seeding compost which should include additional nutrients compared to soil alone, however, the nutrient levels may not have been as high as in the Dobbie et al. (2005) study. Furthermore, the Dawdon ochre might not have been fully P-saturated.

Dobbie et al. (2005) observed that the Polkemmet ochre did not increase metals (other than Ni) in the soil above accepted limits for sewage sludge application to agriculture land should the P-saturated ochre be applied on an annual basis. The metal content of the soils in the pots was not analysed as part of these trials and therefore cannot be compared with the Dobbie et al. (2005) study. Furthermore, Dawdon ochre was used for these trials (not Polkemmet) and ochres from different sources will have different metals contents. Any further growth trials undertaken should monitor metals limits in the soil to assess whether metal leaching from the P-saturated ochre could negatively impact the soil and therefore restrict the option of reusing as a fertiliser.

4.6 Pond Filter Trials

The pond filter trials were intermediate scale trials following the cessation of the larger scale IBC trials. These trials were designed to allow variables to be investigated with a view to informing and refining the design for a large scale, ochre-based filter system. The pond filter trials were separated into phases with each investigating a different variable.

This Section details the results, discussion and conclusions for each phase of the pond filter trials individually before bringing all the results together in an overview (Section 4.6.5). The literature relevant to these trials is discussed in Section 4.6.5.

4.6.1 Phase 1

The Phase 1 pond filter trials directly compared units with different flow configurations (upflow and downflow) to determine whether flow direction impacted upon P removal when ochre was employed as part of a filter-based system. These trials were conducted in parallel with a common effluent source; the incoming flow split between the two units. Samples were taken of the final effluent entering the units and the treated effluent exiting the units to determine the phosphorus removal achieved by each unit and therefore configuration.

4.6.1.1 Trial observations

It was observed that the downflow unit began to overtop, with flow coming out of the overflow, around a week into the trial. When the two units were unpacked, it was found that there was sludge present in the bottom of the downflow unit, which wasn't present in the upflow unit (see Figure 4.25 below). A dark layer was also present on the underside of the ochre layer (where it was in contact with the membrane) which was not present in the upflow unit.



Figure 4.25: Comparison of the gravel layers in the downflow (left) and upflow (right) units. The downflow unit experienced sludge build up which is visible in the image above. The upflow unit did not experience this sludge build up.

Both units had a build-up of sludge and algae on the top of the ochre layer. The build-up on the upflow unit is shown in Figure 4.26 and the same was present on the downflow unit - although

this is not shown. As this build up was observed on both units, it is not thought to have had a major impact on flow through the units.



Figure 4.26: Sludge and algal build up on the adsorbent layer of upflow unit at the end of the phase 1 trial. Sludge and algal growth were also experienced on the downflow unit (not shown).

4.6.1.2 Results

The data are summarised in Table 4.11, detailing minimum, maximum, mean and median values for the inlet phosphorus concentration, both unit outlets and the percentage removals for the units. It should be noted that the minimum percentage removal is the minimum positive percentage removal, but the mean and median values take any negative removal values into account when calculated.

It should be noted that the depth of the ochre layer within each unit was 10 cm and the ingoing flow rate was approximately 0.09 l/s. These resulted in a retention time of approximately 6 minutes for each unit.

Table 4.11: Summary of data from Phase 1 of the pond filter trials. All data is rounded to two decimal places.

	Inlet phosphorus		Upflow unit outlet phosphorus		Downflow unit outlet phosphorus		Percentage phosphorus removal (%)			
	Total mg/l	Filtered mg/l	Total mg/l	Filtered mg/l	Total mg/l	Filtered mg/l	Upflow unit		Downflow unit	
							Total	Filtered	Total	Filtered
Min.	1.22	0.92	1.18	0.92	1.08	0.82	0.40*	0.69*	1.19*	0.67*
Max.	4.85	4.3	4.75	4.2	4.75	4.15	22.6	18.79	14.2	10.87
Mean	2.47	2.16	2.43	2.1	2.43	2.12	1.48	2.87	1.98	2.51
Median	2.49	2.18	2.48	2.14	2.46	2.09	2.06	1.83	2.76	3.49

* Minimum is the positive percentage removal (i.e. apparent negative removal is discounted)

The average total phosphorus concentration leaving the units was 2.43 mg/l P in comparison to an average of 2.47 mg/l P in the inlet. The average outgoing filtered phosphorus was also similar in both units; 2.10 mg/l P for the upflow unit and 2.12 mg/l P for the downflow unit. The minimum and maximum concentrations for the two units (and for both total and filtered phosphorus) were also similar. Table 4.12 shows the daily percentage removal for each unit and identifies apparent negative removals.

Table 4.12: Daily percentage removal of total and filtered phosphorus for each unit in Phase 1 of the pond filter trials.

Date	Percentage phosphorus removal (%)			
	Upflow unit		Downflow unit	
	Total	Filtered	Total	Filtered
07/10/2016 AM	3.28	0.00	11.48	10.87
07/10/2016 PM	-5.93	0.00	5.93	7.77
10/10/2016 PM	6.28	4.64	8.38	7.95
11/10/2016 AM	7.58	-1.33	10.61	0.67
12/10/2016 PM	-0.31	0.69	2.76	0.69
13/10/2016 PM	8.20	2.96	4.26	3.70
14/10/2016 PM	22.64	18.79	14.15	4.24
17/10/2016 AM	-8.13	10.24	-7.18	4.88
18/10/2016 AM	3.50	-1.87	3.82	-1.87
19/10/2016 AM	-0.40	4.64	-1.98	-2.11
20/10/2016 AM	0.40	1.83	1.21	4.13
25/10/2016 AM	0.00	-1.35	1.19	0.90
26/10/2016 AM	-19.27	-2.09	-26.56	-5.24
27/10/2016 AM	2.25	3.60	-0.37	-2.40
03/11/2016 AM	2.06	2.33	2.06	3.49

Figure 4.27 shows that 33 % of samples exhibited negative total phosphorus removal for the upflow unit and 27 % of samples exhibited negative removal for filtered phosphorus. For the downflow unit, 27 % of samples for both total and filtered phosphorus exhibited negative removal.

For the upflow unit, 60 % of samples exhibited removal between 0 and 10 % for both total and filtered phosphorus. For the downflow unit, 53 % of samples exhibited removal between 0 and 10 % total phosphorus and 66 % for filtered phosphorus. Figure 4.27 illustrates that most of the samples exhibited removal between 0 and 10 % or had a negative removal. There are no samples with any phosphorus removal greater than 50 %. One upflow sample exhibited total phosphorus removal between 20 and 50 %. Both units reduced outgoing total phosphorus to less than 2 mg/l on 5 occasions during the trial (out of the 15 samples taken).

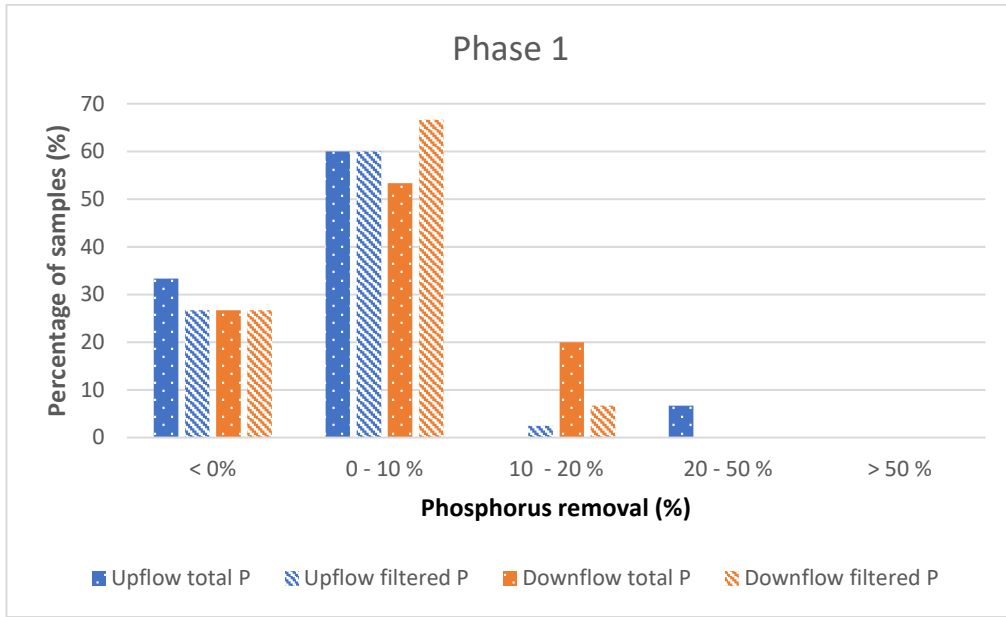


Figure 4.27: Percentage of the samples taken during Phase 1 within each identified removal band for total and filtered phosphorus removal.

There is little difference in phosphorus leaving the two units, either in terms of total or filtered phosphorus as shown in Figures 4.28 and 4.29. Furthermore, neither unit exhibits a large reduction in phosphorus when compared to the inlet (final effluent) concentration with the outlet concentration. The average (mean) inlet concentration is shown in these graphs and therefore the variability of the ingoing phosphorus concentration can be seen.

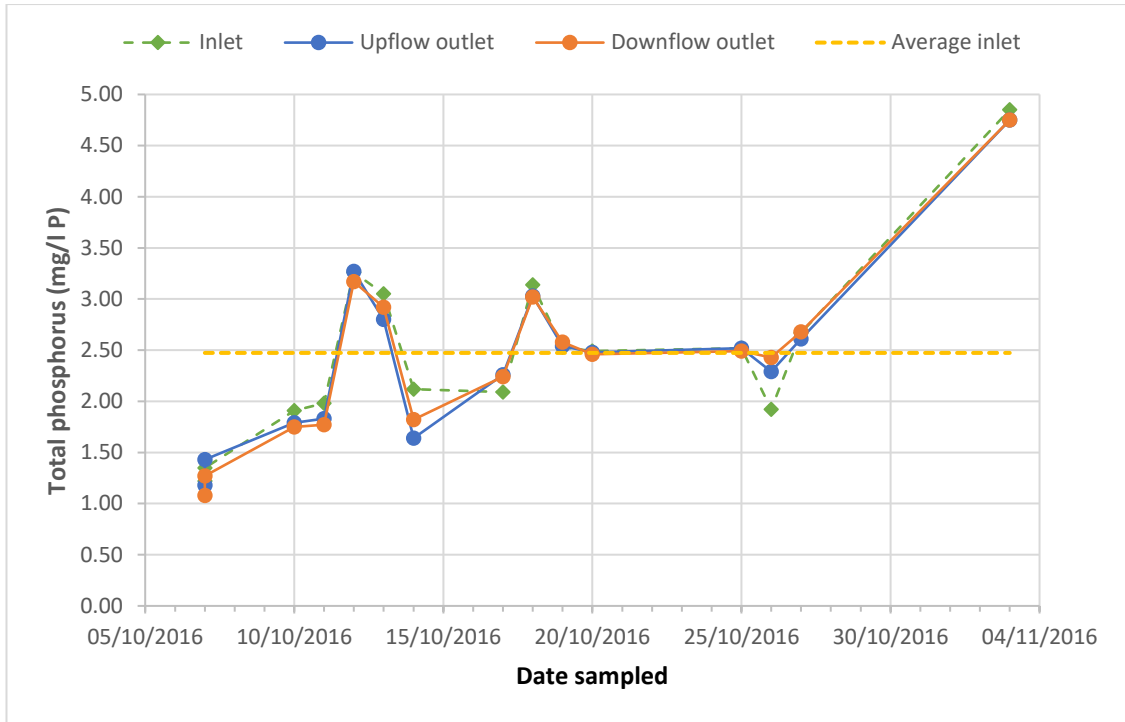


Figure 4.28: Daily inlet and outlet total phosphorus concentrations for each unit in Phase 1 of the pond filter trials. The average inlet total phosphorus concentration across the trial period is plotted for comparison.

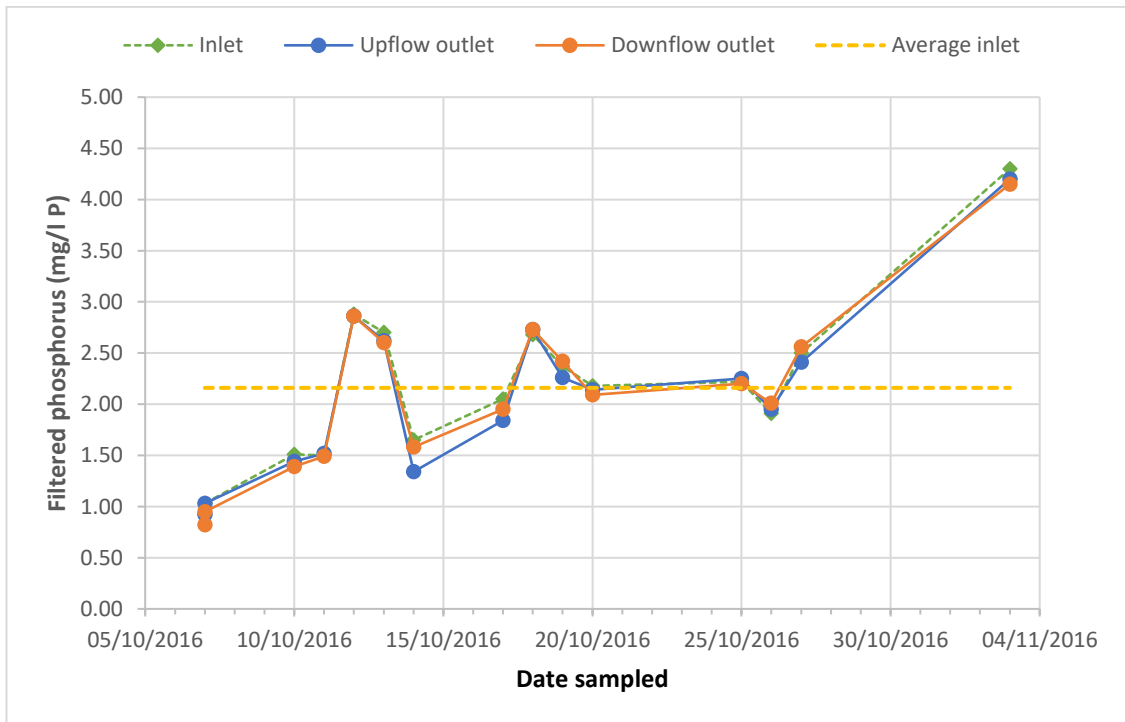


Figure 4.29: Daily inlet and outlet filtered phosphorus concentrations for each unit in Phase 1 of the pond filter trials. The average inlet filtered phosphorus concentration across the trial period is plotted for comparison.

4.6.1.3 Discussion

The accumulation of sludge in the downflow unit but not the upflow unit was not unexpected. The flow through the upflow unit continually flushes the solids from the bottom of the unit and to the surface and therefore most of the solids not captured by the ochre will wash out of the outlet. In the downflow unit this does not happen, and the solids accumulate in the base of the unit. Therefore, any unit set up in a downflow configuration will probably require a desludge or backflush mechanism to remove these solids frequently.

The average (mean) outgoing total phosphorus content for both units was 2.43 mg/l and the average outgoing filtered phosphorus only differed by 0.02 mg/l (2.10 mg/l for the upflow unit and 2.12 mg/l for the downflow unit). The results of these trials suggest that the configuration of the unit does not affect the phosphorus removal by ochre. The maximum percentage removals differ more than these average outgoing concentrations. The maximum removal of total phosphorus was 22.64 % for the upflow unit and 14.15 % for the downflow unit. The filtered phosphorus maximum removals were 18.79 % for the upflow unit and 10.87 % for the downflow unit. These results suggest that the filter units remove more total phosphorus than filtered phosphorus. This is probably as a result of the solids capture by the filters.

The majority of samples across the trial represented removal between 0 and 10 % for both total and filtered phosphorus removal. The upflow unit achieved a removal of greater than 20 % of total phosphorus.

Under the Urban Wastewater Treatment Directive (UWWTD), STWs with PE of between 10000 and 100000 must meet a final effluent total phosphorus permit limit of 2 mg/l (Gray, 2017). The two units were both able to meet this limit on 5 occasions (out of 15 samples). This suggests that the ochre-based filters are capable of meeting a 2 mg TP/l permit limit but that they are not able to meet this permit reliably.

On a number of occasions, the outlet phosphorus concentration is higher than the inlet phosphorus which could be as a result of changes in the phosphorus content of the final effluent. For example, the ingoing final effluent phosphorus concentration might have increased but not been captured when the final effluent was sampled having since reduced. The inlet (final effluent) sample was taken only minutes before the unit outlet samples and therefore the final effluent sample may not be representative of the effluent treated by the unit and now

exiting the unit. The estimated retention time within the unit was 6 minutes but this estimate does not account for the time taken for the effluent to reach the ochre layer through the pipework. Alternatively, the higher concentration in the outgoing, treated effluent could be due to solids in the outlet samples or the effluent bypassing the media within the unit or a combination of these factors. These apparent increases in outgoing phosphorus result in negative percentage removals, making it difficult to accurately quantify the removal by the units.

4.6.2 Phase 2

Phase 2 of the pond filter trials focused on assessing the impact of ochre layer depth on phosphorus removal. The two units were packed with different quantities of ochre and final effluent was pumped into the units and allowed to gravitate through the media. As with the previous phase, the units were fed from a common source. The ingoing final effluent and the effluent leaving the units was analysed to determine phosphorus removal by each unit.

4.6.2.1 Observations

There was a visible layer of solids on the top of both units at the end of the trial (shown in Figure 4.30) and sludge was found to be present in the bottom of the 5 cm unit (shown in Figure 4.31). Both units were completely unpacked and washed out before Phase 3 was set up.



Figure 4.30: Comparison of the sludge build up on the ochre layer of the 5 cm (left) and 15 cm (right) units of Phase 2 of the pond filter trials.



Figure 4.31: Sludge build up within the gravel layer of the 5 cm ochre layer unit is shown in the image above and was visible once the ochre layer was removed at the end of the Phase 2 trial period.

4.6.2.2 Results

The data are summarised in Table 4.13, detailing minimum, maximum, mean and median values for the inlet phosphorus concentration, both unit outlets and the percentage removals for the units.

Table 4.13: Summary of data from Phase 2 of the pond filter trials. All data is rounded to two decimal places.

	Inlet phosphorus		5 cm unit outlet phosphorus		15 cm unit outlet phosphorus		Percentage phosphorus removal (%)			
	Total	Filtered	Total	Filtered	Total	Filtered	5 cm unit		15 cm unit	
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	Total	Filtered	Total	Filtered
Min.	2.05	1.21	2.13	1.37	0.59	0.44	3.41*	0.26*	5.68*	1.87*
Max.	4.5	3.82	4.3	3.78	4.15	3.95	26.46	38.18	74.06	78.64
Mean	3.23	2.64	3.13	2.5	2.51	2.18	1.09	3.92	25.24	23.32
Median	3.25	2.68	2.91	2.47	2.52	2.35	6.34	1.99	17.68	10.7

* Minimum is the positive percentage removal (i.e. apparent negative removal is discounted)

Average total phosphorus concentration leaving the 5 cm unit was 3.13 mg/l, compared to an average ingoing concentration of 3.23 mg/l. The 15 cm unit had an average of 2.51 mg/l total phosphorus leaving it. During the trial period, the 15 cm unit reduced total phosphorus to a minimum of 0.59 mg/l, compared to the 5 cm unit minimum of 2.13 mg/l total phosphorus. The minimum ingoing total phosphorus concentration was 2.05 mg/l. The removal by the 15 cm unit was more consistently positive than the 5 cm unit, with only one sample with negative removal, compared to the three 5 cm unit samples (shown in Table 4.14).

Table 4.14: Daily percentage removal of total and filtered phosphorus for each unit in Phase 2 of the pond filter trials.

Date	Percentage phosphorus removal (%)			
	5 cm unit		15 cm unit	
	Total	Filtered	Total	Filtered
11/11/2016 PM	7.14	4.39	20.07	17.54
14/11/2016 AM	-41.95	-11.64	50.17	69.86
15/11/2016 PM	10.88	6.80	74.06	78.64
16/11/2016 AM	-24.21	1.92	11.58	9.62
18/11/2016 AM	19.51	8.86	17.68	10.70
21/11/2016 AM	26.46	38.18	33.23	30.74
22/11/2016 PM	-9.05	-13.22	40.27	33.06
28/11/2016 PM	8.99	3.73	7.58	1.87
01/12/2016 PM	6.34	1.99	6.25	3.41
02/12/2016 AM	3.41	1.83	5.68	-3.40
05/12/2016 AM	4.44	0.26	11.11	4.49

One of the days exhibiting negative removal was 14/11/16 and Figure 4.32 shows the inlet sample and the outlet samples for each of the units side by side. The image clearly shows visual solids within the 5 cm outlet sample. The 15 cm outlet sample is visibly clearer than the inlet sample.



Figure 4.32: Comparison of effluent quality leaving the 5 cm and 15 cm pond filter units. A sample of the inlet effluent quality is also included. The samples were taken 14/11/16.

Figure 4.33 shows the percentage of samples with percentage phosphorus removal within each of the identified bands. Most of the removal by the 5 cm unit was in the 0 to 10 % removal band, 2 samples in the 10-20% for total phosphorus only and 1 in the 20-50% band (for both total and filtered phosphorus). The 15 cm unit shows a wider range of percentage removals. The unit had a single sample (out of the 11 taken) with a negative percentage removal (for filtered phosphorus only) and a relatively even spread of samples in the other percentage range bands.

The 15 cm unit reduced total phosphorus to less than 2 mg/l on 3 occasions, 2 of which were actually less than 1 mg/l. The 5 cm unit did not reduce outgoing total phosphorus to these levels. This data is shown in Table B1, Appendix B).

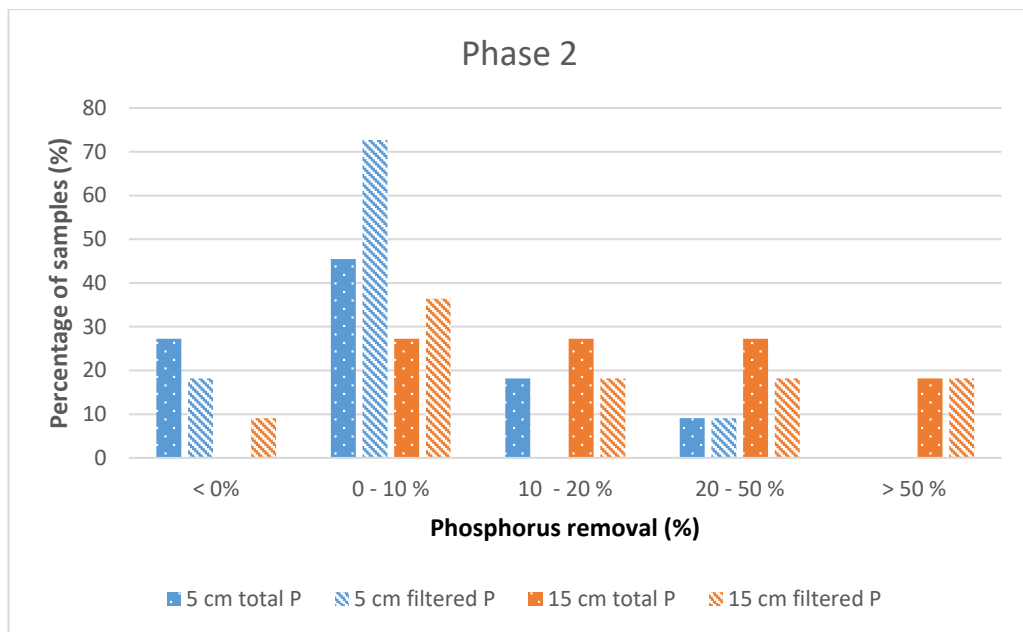


Figure 4.33: Percentage of the samples taken during Phase 2 within each identified removal band for total and filtered phosphorus removal.

There were three occasions when the outgoing total phosphorus concentration from the 5 cm unit was greater than the total phosphorus measured in the ingoing effluent sample, which can be seen in Figure 4.34. The first of these occasions was the day on which the photograph in Figure 4.32 was taken. On the second occasion (16/11/16), only the total phosphorus exhibited an apparent negative removal whilst the filtered phosphorus removal was 1.92 %. The samples taken on 16/11/16 were analysed for total suspended solids (TSS). The results showed an inlet solids concentration of 30 mg/l. The outgoing TSS for the 5 cm unit were 86 mg/l compared to 8 mg/l for the 15 cm unit.

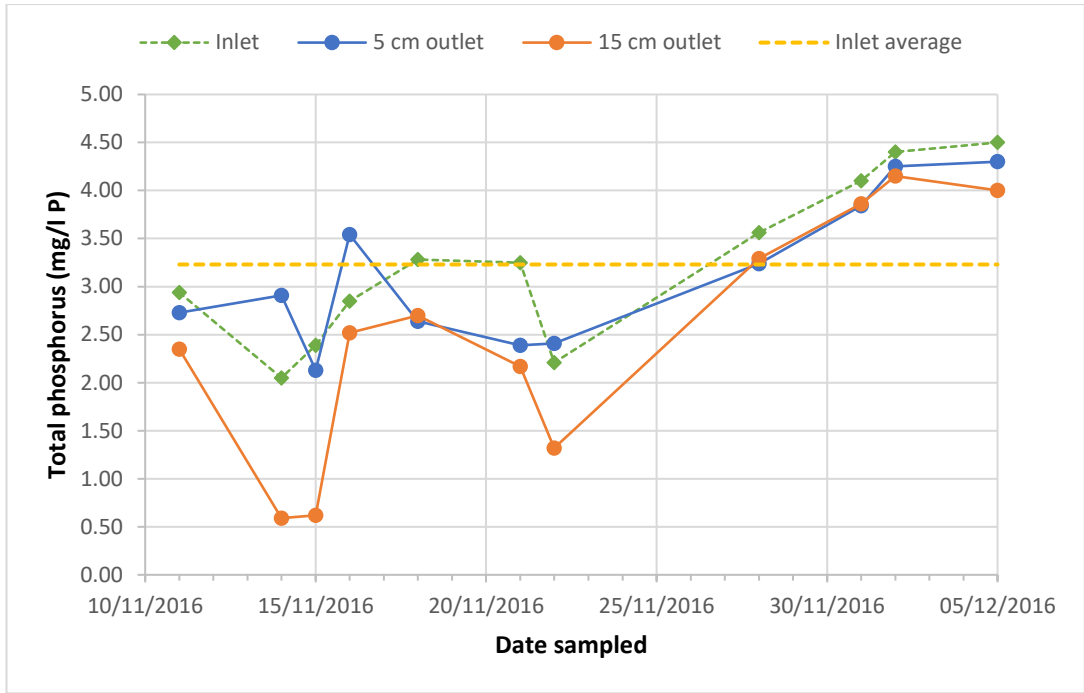


Figure 4.34: Daily inlet and outlet total phosphorus concentrations for each unit in Phase 2 of the pond filter trials. The average inlet total phosphorus concentration across the trial period is plotted for comparison.

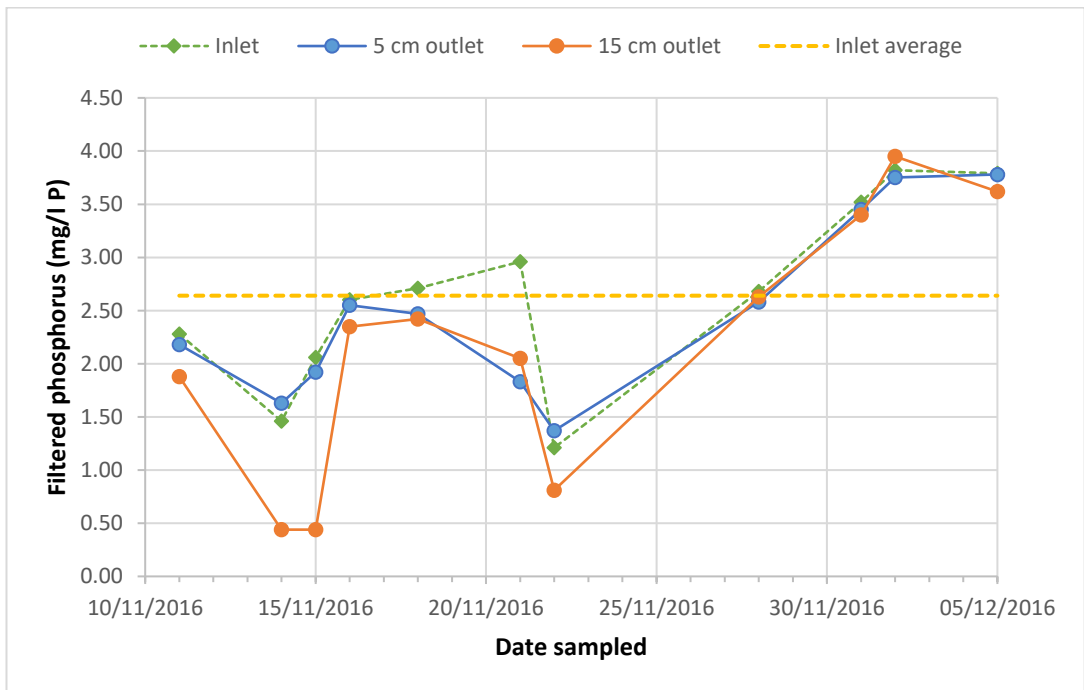


Figure 4.35: Daily inlet and outlet filtered phosphorus concentrations for each unit in Phase 2 of the pond filter trials. The average inlet filtered phosphorus concentration across the trial period is plotted for comparison.

Figure 4.34 and Figure 4.35 show the clear difference between the 5 cm and 15 cm units in terms of outgoing phosphorus concentration and their relationship with the ingoing phosphorus concentrations. The average inlet phosphorus concentration over the duration of the trial is also shown as an indication of the variability of the phosphorus entering the units. Figure 4.34 confirms that the outgoing total phosphorus concentration never exceeded the ingoing concentration during the trials, however the outgoing filtered phosphorus concentrations on 2/12/16 was 3.95 mg/l, which was greater than the ingoing concentration of 3.82 mg/l.

Both of the units had an ingoing flow rate of approximately 0.09 l/s which resulted in a retention time of 3 minutes for the 5 cm unit and 9.5 minutes for the 15 cm unit.

4.6.2.3 Discussion

Following the trials, a visible build-up of solids was observed on the top of the units as well as the bottom of the 5 cm unit. However, flow was still passing through both the units at the end of the trial. These observations suggest that there was no blocking within the ochre layers and that the presence of sludge in the bottom of the unit does not necessarily restrict outgoing flow. Throughout the trial, the inlet pipes had to be flushed due to flow being impeded by a build-up of solids. This solids build up is probably due to the low flow rate through the pipes.

There were occasions where outgoing phosphorus was apparently greater than the ingoing phosphorus and this could be as a result of the sampling method and variations in final effluent phosphorus concentrations. In order to confirm this, sampling the outlet after the period of retention, more detailed or frequent sampling and analysis of the final effluent phosphorus concentration would be necessary.

The photograph of the samples taken on 16/11/16 clearly show the difference in the outgoing effluent from the two units and how they compare to the ingoing effluent. When these samples were analysed, the total phosphorus in the 5cm outlet sample was greater than the ingoing effluent sample. The filtered phosphorus sample was not. The samples were analysed for total suspended solids (TSS) and the 5 cm outlet sample had a TSS content of 86 mg/l compared to the final effluent TSS of 30 mg/l. These results suggest that solids are responsible for the apparent increase in total phosphorus after treatment by the 5 cm unit. The visual difference in outgoing effluents from the 5 cm and 15 cm units, as well as the TSS comparison (8 mg/l and 86

mg/l, respectively) suggests that the removal of solids by the 15 cm unit may be enhancing phosphorus removal on this occasion.

Both the percentage removal data and the phosphorus concentrations leaving the units show that the 15 cm unit is better than the 5 cm unit at removing phosphorus from secondary treated final effluent. This could be as a result of the larger quantity of adsorbent or as the result of a longer retention time, both of which are approximately three times larger in the 15 cm unit than the 5 cm unit. However, the trial methodology does not allow for a determination of which factor is the reason for the increased removal or whether it might be a combination of both. All samples of the 15 cm outlet showed a reduction in total phosphorus and all but one sample had a reduction in filtered phosphorus. The greater depth of material may be capturing more solids and therefore more of the phosphorus associated with those solids, enhancing the total phosphorus removal.

4.6.3 Phase 3

Phase 3 was designed to quantify the impact of combining the ochre with sand. The results of the binder only column trials suggested that sand was quickly saturated with phosphorus and therefore any phosphorus removal experienced once the sand is saturated would be attributed to adsorption by the ochre. One unit was packed with sand only whilst the second unit filled with the ochre and sand mix. The units were packed with equivalent depths and were fed at the same ingoing flow rate and from a common source of final effluent. The ingoing effluent was sampled as well as the effluent leaving the units.

4.6.3.1 Observations

During the trial, it was identified that part of the flow was bypassing the media by travelling up the side of membrane material supporting the media layer. The gaps where the effluent was able to flow up the side of the media can be seen in Figure 4.36, particularly in the ochre unit.

At the end of the trial period, both units were drained before they were unpacked. Figure 4.36 shows the sludge layer present on the top of the media.



Figure 4.36: Comparison of the sludge layer on the sand (left) and ochre (right) units at the end of Phase 3 of the pond filter trials.

4.6.3.2 Results

Table 4.15 data was calculated using only positive percentage removals. However, the majority of the results were negative and therefore the data may not be a true representation of the units' performance.

Table 4.15: Summary of data from Phase 3 of the pond filter trials. All data is rounded to two decimal places.

	Inlet phosphorus		Sand unit outlet phosphorus		Ochre unit outlet phosphorus		Percentage phosphorus removal (%)			
	Total	Filtered	Total	Filtered	Total	Filtered	Sand unit		Ochre unit	
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	Total	Filtered	Total	Filtered
Min.	3.31	3.06	3.28	3.2	3.11	3.06	0.26*	2.68*	3.18*	1.67*
Max.	3.82	3.59	4.05	3.91	4.5	3.82	5.32	3.9	12.89	8.93
Mean	3.56	3.29	3.67	3.52	3.75	3.44	2.76*	3.29*	8.03*	5.30*
Median	3.52	3.27	3.75	3.52	3.83	3.53	2.73*	3.29*	8.03*	5.30*

*All but the maximum values were calculated from the positive percentage removals only.

Table 4.16: Daily percentage removal of total and filtered phosphorus for each unit in Phase 3 of the pond filter trials.

Date	Percentage phosphorus removal (%)			
	Sand unit		Ochre unit	
	Total	Filtered	Total	Filtered
19/12/2016 AM	-13.90	-21.24	-35.95	-15.03
19/12/2016 PM	-17.73	-23.34	-13.08	-20.50
20/12/2016 PM	5.32	2.68	12.89	8.93
21/12/2016 AM	5.20	-3.90	3.18	-1.62
28/12/2016 PM	0.27	3.90	-1.34	1.67
29/12/2016 AM	0.26	-2.87	-1.31	-3.45

Table 4.16 and Figure 4.37 show the percentage removals for the two units over the six sampling days. The ochre unit was the only one to exhibit removal of greater than 10 %, however, it also exhibited more negative removal than the sand unit. There were two samples with positive total phosphorus removal from the ochre unit and two with positive filtered phosphorus removal. However, there was only one sample with positive removal of both total and filtered phosphorus. Most of the samples from phase 3 exhibited negative phosphorus removals.

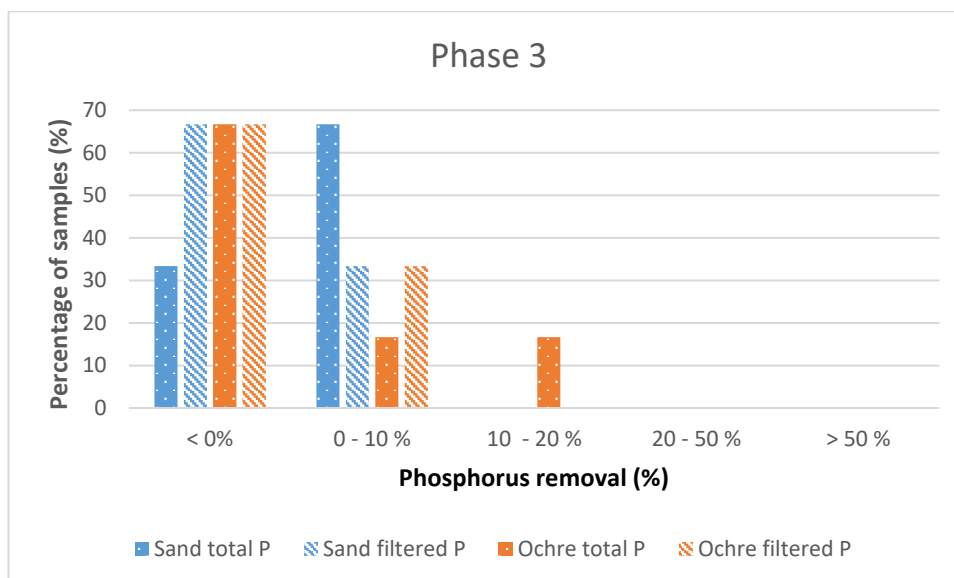


Figure 4.37: Percentage of the samples taken during Phase 3 within each identified removal band for total and filtered phosphorus removal.

Figures 4.38 and 4.39 show the concentrations of total and filtered phosphorus of the inlet and the units' outlets alongside the average inlet concentrations for the trial period. There is a clear increase in concentrations from 21/12/16 to 28/12/16. The minimum outgoing total phosphorus concentration for either unit was 3.11 mg/l leaving the ochre unit (on 20/12/16).

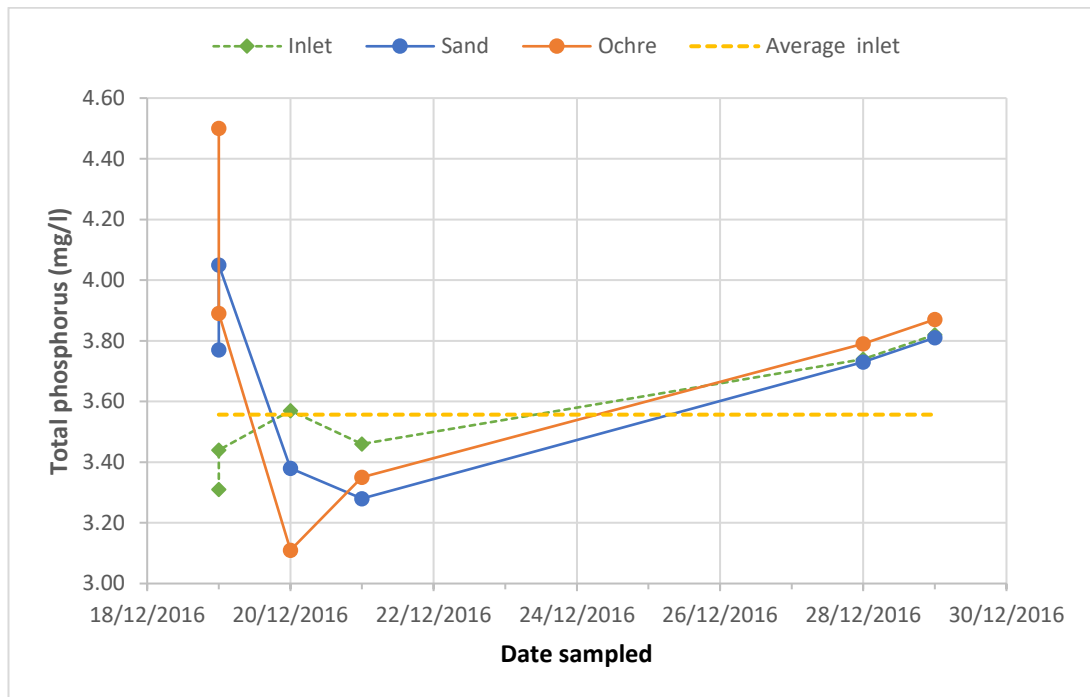


Figure 4.38: Daily inlet and outlet total phosphorus concentrations for each unit in Phase 3 of the pond filter trials. The average inlet total phosphorus concentration across the trial period is plotted for comparison.

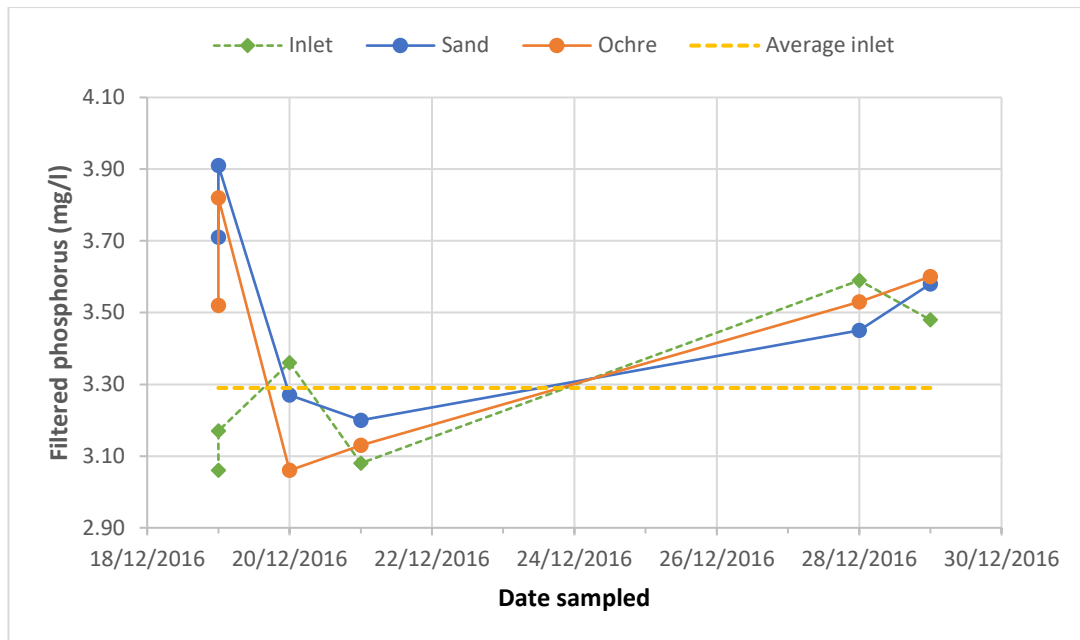


Figure 4.39: Daily inlet and outlet filtered phosphorus concentrations for each unit in Phase 3 of the pond filter trials. The average inlet filtered phosphorus concentration across the trial period is plotted for comparison.

Both units reduced total phosphorus on 20/12/16 and 21/12/16, with ingoing total phosphorus concentrations of 3.57 and 3.46 mg/l, respectively. On 28/12/16 and 29/12/16, the sand unit narrowly reduced total phosphorus from 3.74 and 3.82 mg/l to 3.73 and 3.81 mg/l (0.27 % and 0.27 % reductions), respectively. The ochre unit exhibited slight increases in total phosphorus to 3.79 and 3.87 mg/l (1.34 % and 1.31 % increases).

There were only two dates when both units were able to reduce the filtered phosphorus (20/12/16 and 28/12/16).

4.6.3.3 Discussion

The ingoing phosphorus content during the trial period was between 3.31 and 3.82 mg TP/l (3.06 to 3.59 mg/l filtered phosphorus). Most of the samples taken during the trials had apparent increases in phosphorus after passing through the units. This could be as a result of the effluent picking up phosphorus and/or solids somewhere within the pipework or units, resulting in an increased phosphorus concentration in the outgoing effluent compared to the concentration entering the units. Alternatively, the final effluent quality could have been highly variable within the trial period. Furthermore, some of the flow was found to be bypassing the media in the unit and therefore the effluent may not have been fully treated. The ochre unit exhibited more media bypassing than the sand unit.

Despite the bypassing experienced by the ochre unit, it still exhibited greater maximum removal of both total and filtered phosphorus than the sand unit, as well as a greater average (when considering positive removals only). These results suggest that the presence of ochre enhances the phosphorus removal of a sand-based filter; however, due to the operational issues experienced with these units, further trials will be needed to confirm this finding.

The minimum outgoing total phosphorus concentration throughout the trial was 3.11 mg/l for the ochre-based unit. The results from these trials suggest that the ochre-based unit would not be able to meet a final effluent discharge consent of 2 mg/l if used as a final stage of treatment.

The sand unit removed total phosphorus more consistently than filtered phosphorus. This could be due to the trapping of solids and therefore the solids associated phosphorus. There were only two occasions on which both units were able to reduce filtered phosphorus.

4.6.4 Phase 4

Phase 4 comprised two sections; 4a the two units being run in parallel and 4b with the two units run in series. The trials within this phase were designed to determine whether running a number of units in series will improve phosphorus removal and therefore allow the design of modular units. If the filters were designed as modular units, the site-specific requirements could be easily considered, and the number of units installed on site determined by the required phosphorus removal.

The results and discussion are combined within this section and include a comparison of the results to determine the impact of running the units in series and therefore including a further treatment step.

4.6.4.1 Trial Observations

Throughout the Phase 4a trial, the inlet pipework had to be flushed to maintain flow into the units. This was achieved by increasing the flow rate for a couple of seconds to dislodge any solids build-up. This increase in flow rate resulted in some short-circuiting close to the inlet as the increased flow caused the membrane to come away, allowing effluent to pass up the side of the ochre layer rather than through it.

Figure 4.40 shows the build-up of sludge present on top of both units at the end of the trial.



Figure 4.40: Observed sludge layer on the ochre layer of the Phase 4a units at the end of the trial.

During Phase 4b, the ingoing pipework was flushed once to resolve ingoing flow rate issues. The flushing resulted in the downflow unit overflowing and the trial had to be briefly stopped to allow the water level within the unit to drop before restarting the trial and reaching equilibrium. The flow between the units was slow throughout the trial.

At the end of the trial, there was visual sludge on the top of both units, as shown in Figure 4.41. The units were drained prior to being unpacked. There was visually more sludge on the downflow unit ochre than the upflow unit. The downflow unit took longer to drain and there was still water trapped within the ochre when it was unpacked.



Figure 4.41: Sludge on the ochre layer of the Phase 4b units observed at the end of the trial.

4.6.3.2 Results

The data for Phase 4a are summarised in Table 4.17, detailing the minimum, maximum, mean and median values for inlet and outlet phosphorus concentrations and percentage removal for each unit. The minimum percentage removal for total phosphorus (for both units) is the minimum positive removal.

Table 4.17: Summary of data from Phase 4a of the pond filter trials. All data is rounded to two decimal places.

	Inlet phosphorus		Left unit outlet phosphorus		Right unit outlet phosphorus		Percentage phosphorus removal (%)			
	Total	Filtered	Total	Filtered	Total	Filtered	Left unit		Right unit	
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	Total	Filtered	Total	Filtered
Min.	2.21	2.01	2.08	1.87	2.18	1.98	2.40*	0.66	1.36*	0.57
Max.	3.78	3.49	3.91	3.43	4	3.47	7.54	6.97	7.26	2.91
Mean	3.25	2.91	3.18	2.83	3.22	2.86	2.48	3.14	1.03	1.74
Median	3.34	3.06	3.28	2.99	3.3	3	2.73	2.89	1.58	1.86

*Minimum positive percentage removal only

Although the right unit had lower minimum phosphorus concentrations at the outlet (both total and filtered), the average outlet concentrations (both mean and median) are similar between the two units. For example, the median total phosphorus concentration exiting the left unit was 3.28 mg/l compared to 3.30 mg/l exiting the right unit. However, the percentage removals appear to show far more variation.

Table 4.18 shows the daily percentage removal for each unit. These data show that some days, for example 9/1/17, the units exhibited identical removal (3.07 % total phosphorus removal), other days the percentage removals were similar, for example 0.66 % removal of filtered phosphorus compared to 0.99 % (12/1/17), alternatively the removals could be considerably different (16/1/17, 5.88 % compared to 1.36 % and 6.97 % in comparison to 1.49 %).

Table 4.18: Daily percentage removal of total and filtered phosphorus for each unit in Phase 4a of the pond filter trials.

Date		Percentage phosphorus removal (%)			
		Left unit		Right unit	
		Total	Filtered	Total	Filtered
06/01/2017	AM	7.54	3.70	7.26	2.22
09/01/2017	PM	3.07	3.56	3.07	2.91
10/01/2017	PM	2.40	2.23	1.80	2.23
12/01/2017	AM	-0.60	0.66	-1.49	0.99
13/01/2017	PM	-3.44	1.72	-5.82	0.57
16/01/2017	PM	5.88	6.97	1.36	1.49

Neither unit was capable of removing greater than 10 % of ingoing phosphorus (shown in Figure 4.42). Both units consistently removed between 0 and 10 % of filtered phosphorus but two samples (12/1/17 and 13/1/17) exhibited negative removal of total phosphorus.

Overall, the units exhibited the same patterns of removal, as shown in Figures 4.43 and 4.44.

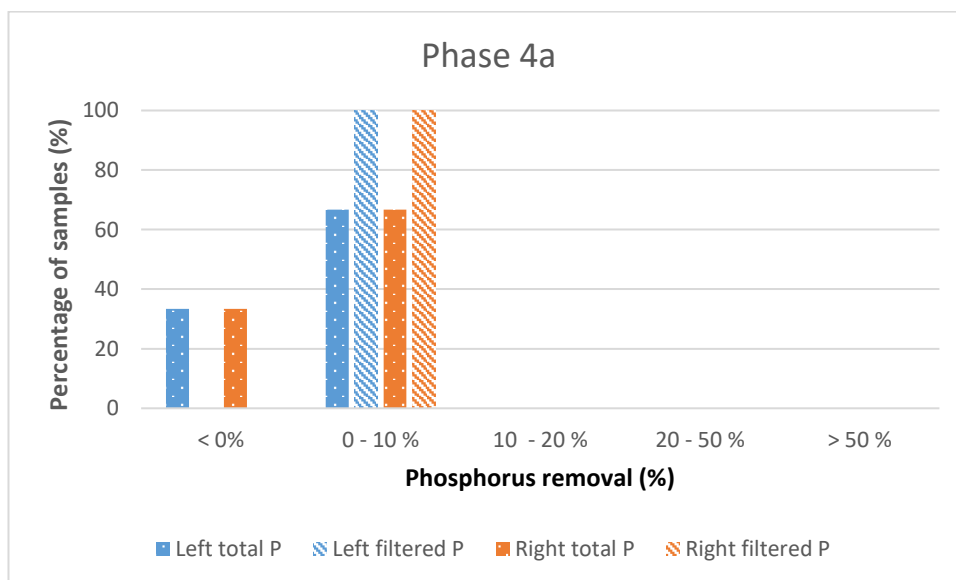


Figure 4.42: Percentage of the samples taken during Phase 4a within each identified removal band for total and filtered phosphorus.

Figures 4.43 and 4.44 show the pattern of phosphorus concentration for the two units. The two units exhibited similar levels of outgoing phosphorus concentrations (following the same trend

as the ingoing phosphorus concentrations). The figures show that there was no significant difference in the outgoing phosphorus concentrations between the two units.

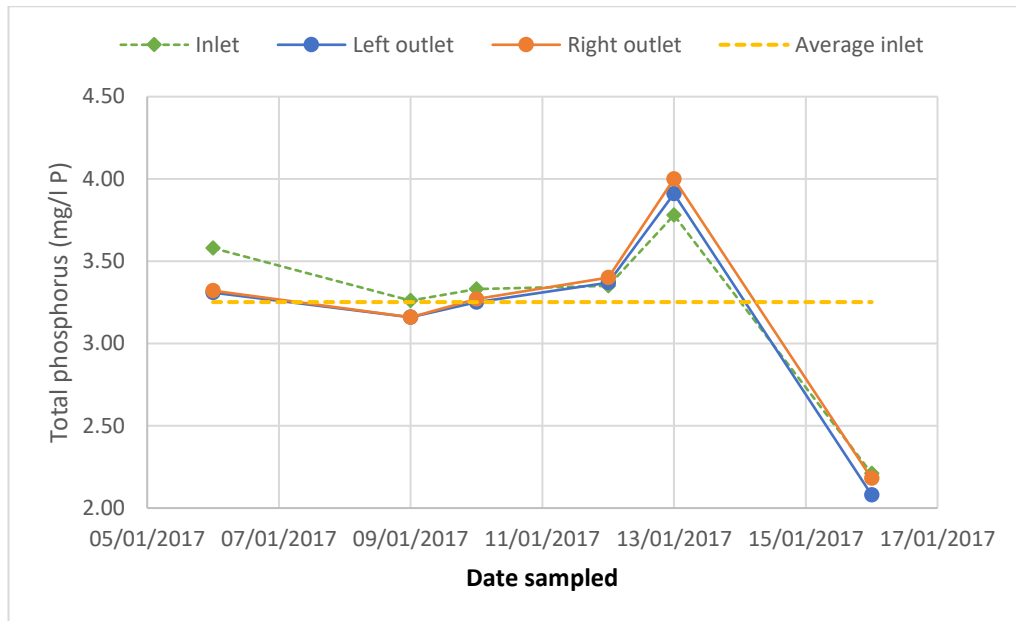


Figure 4.43: Daily inlet and outlet total phosphorus concentrations for each unit in Phase 4a of the pond filter trials. The average inlet total phosphorus concentration across the trial period is plotted for comparison.

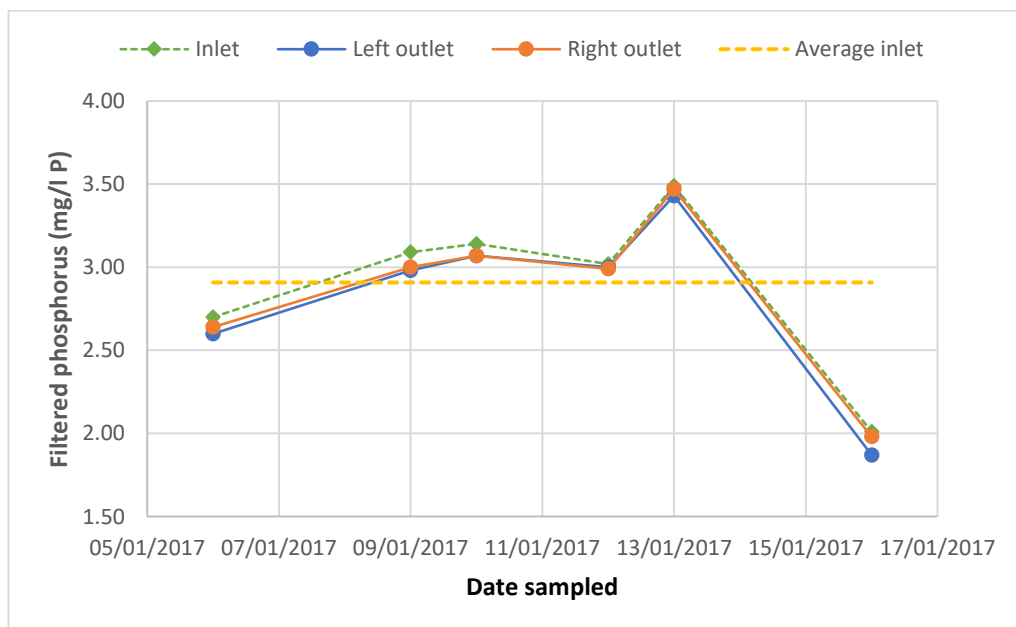


Figure 4.44: Daily inlet and outlet filtered phosphorus concentrations for each unit in Phase 4a of the pond filter trials. The average inlet filtered phosphorus concentration across the trial period is plotted for comparison.

The two units each had a depth of 15 cm of the ochre layer and were fed at an approximate ingoing flow rate of 0.09 l/s, resulting in a retention time of approximately 9.5 minutes.

Phase 4b

The data from the phase 4b units are summarised in Table 4.19, however, the minimum percentage removal is the minimum positive removal as there were some sample dates with negative percentage removals. Table 4.20 summarises the daily percentage removal with negative percentages highlighted in red.

Table 4.19: Summary of data from Phase 4b of the pond filter trials. All data is rounded to two decimal places.

	Inlet phosphorus		Outlet phosphorus		Percentage phosphorus removal (%)	
	Total	Filtered	Total	Filtered	Total	Filtered
	mg/l P	mg/l P	mg/l P	mg/l P		
Minimum	2.97	2.69	2.76	2.56	3.51*	3.65*
Maximum	3.52	3.27	3.62	3.39	13.75	10.80
Mean	3.21	2.91	3.09	2.87	3.66	1.16
Median	3.18	2.89	3.01	2.78	5.02	4.88

*Minimum positive percentage removal

Table 4.20: Daily percentage removal of total and filtered phosphorus for Phase 4b of the pond filter trials.

Date		Percentage phosphorus removal (%)	
		Total	Filtered
20/01/2017	AM	3.51	3.65
23/01/2017	AM	-1.01	-5.58
24/01/2017	PM	13.75	10.80
26/01/2017	AM	-10.37	-14.92
27/01/2017	PM	6.53	6.12
30/01/2017	PM	9.52	6.87

It was found that 50 % of samples exhibited removal of total and filtered phosphorus between 0 and 10 %. One sample had removal between 10 and 20 % but two samples exhibited negative percentage removals as shown in Figure 4.45.

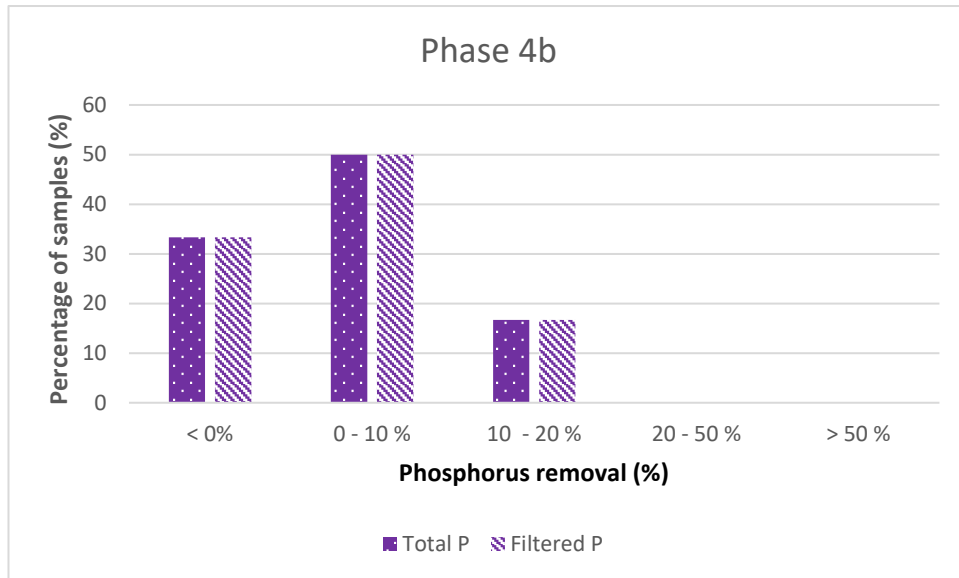


Figure 4.45: Percentage of the samples taken during Phase 4b within each identified removal band for total and filtered phosphorus removal.

Figures 4.46 and 4.47 show little similarity between ingoing and outgoing phosphorus concentration. When the outgoing phosphorus is reduced the maximum reduction is less than 0.5 mg/l (0.44 mg/l total phosphorus and 0.31 mg/l filtered phosphorus on 24/1/17).

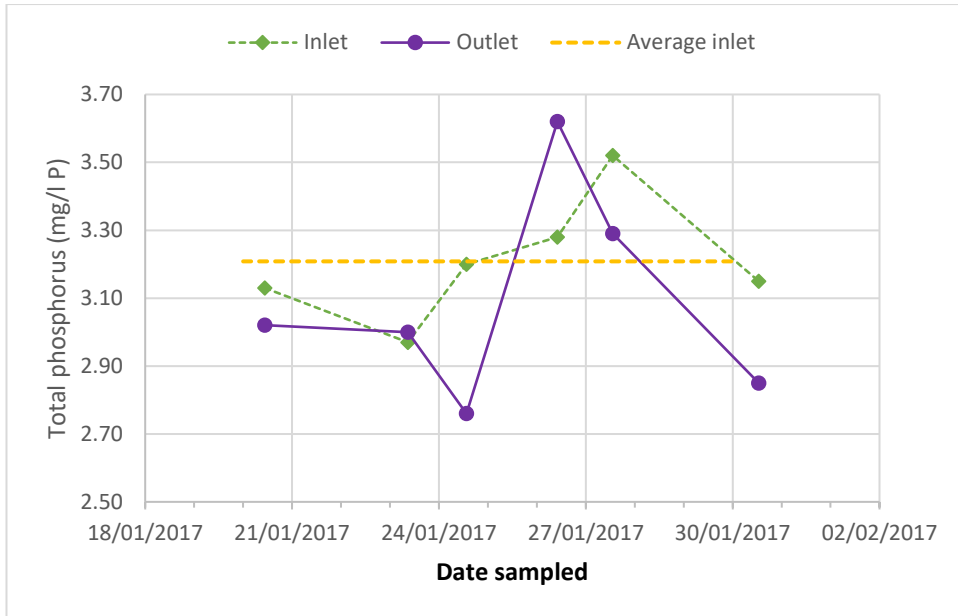


Figure 4.46: Daily inlet and outlet total phosphorus concentrations for the trial system in Phase 4b of the pond filter trials. The average inlet total phosphorus concentration across the trial period is plotted for comparison.

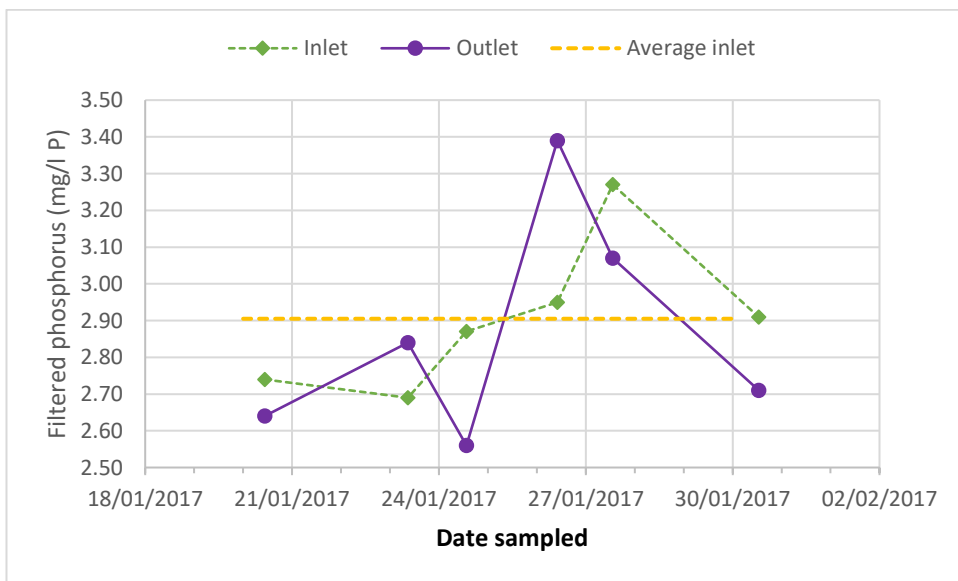


Figure 4.47: Daily inlet and outlet filtered phosphorus concentrations for the trial system in Phase 4b of the pond filter trials. The average inlet filtered phosphorus concentration across the trial period is plotted for comparison.

The two units were fed with a flow rate of 0.09 l/s going into the first of the units. This flow rate was assumed to be constant throughout the filter system for the calculation of the retention time. The retention time of the upflow unit was calculated to be approximately 9.5 minutes and

the downflow unit approximately 4.5 minutes. Therefore, the total retention time was calculated to be 14 minutes.

Comparison of Phase 4a and Phase 4b

Percentage of samples with removal within the identified bands is shown in Figure 4.48 below. The full data can be found in Appendix B, Table B1.

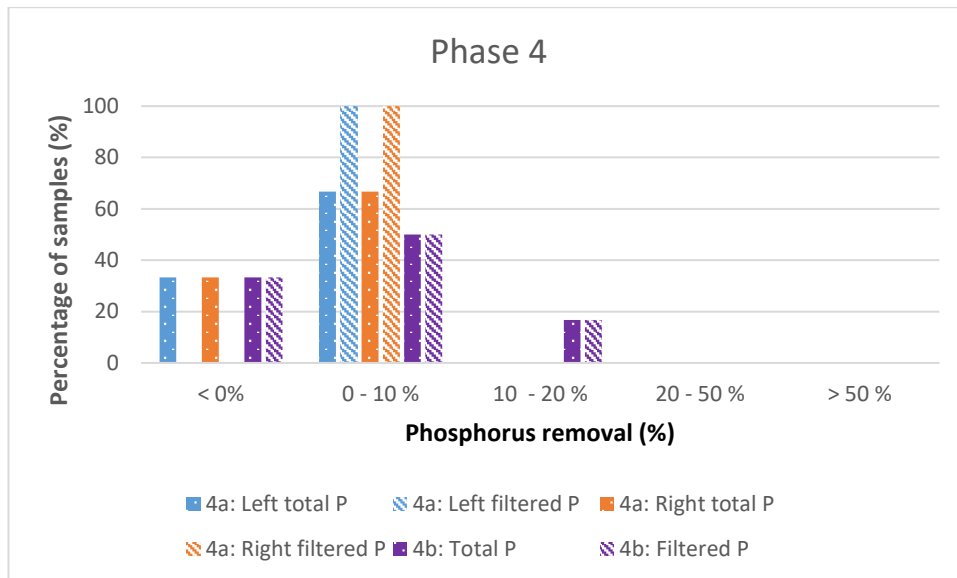


Figure 4.48: Percentage of the samples taken during Phases 4a and 4b within each identified removal band for total and filtered phosphorus.

Figure 4.48 shows that across the Phase 4 trials, the majority of samples exhibited removal of between 0 and 10 % of phosphorus. The only samples with removal between 10 and 20 % were collected during Phase 4b.

Phases 4a and 4b were completed on different dates. Figure 4.49 (a to d) shows phosphorus concentrations plotted against sampling day number rather than date, to allow the data to be overlaid for direct comparison.

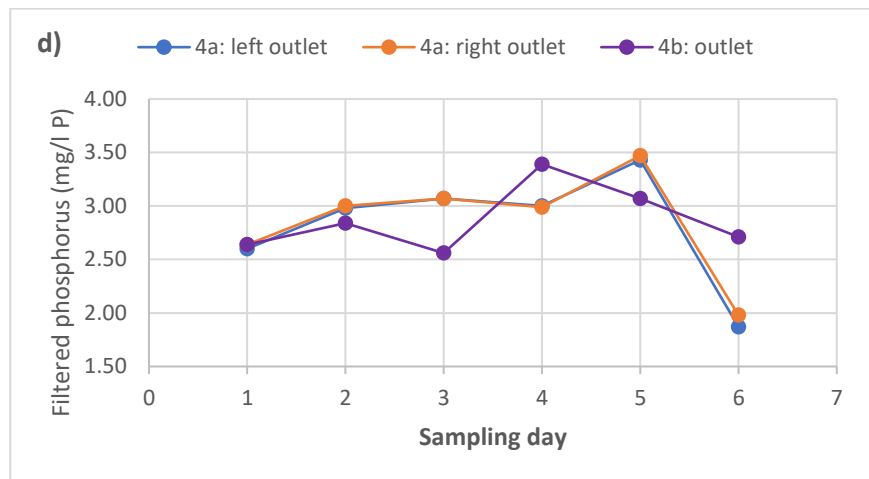
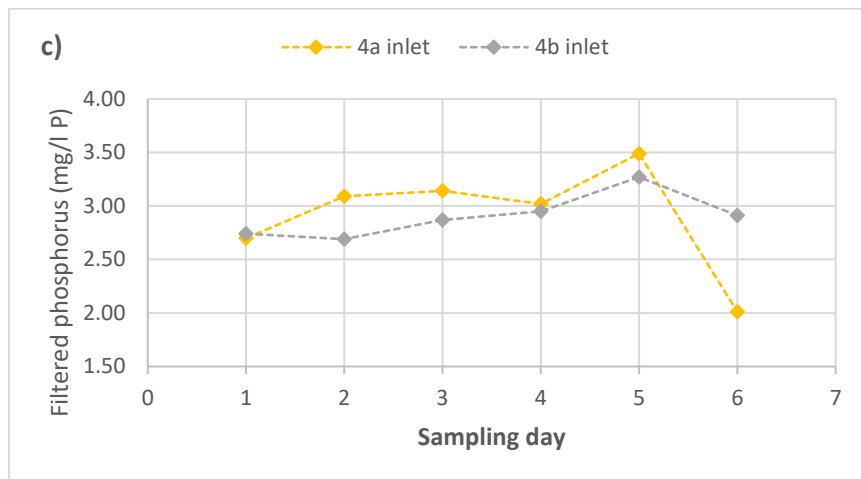
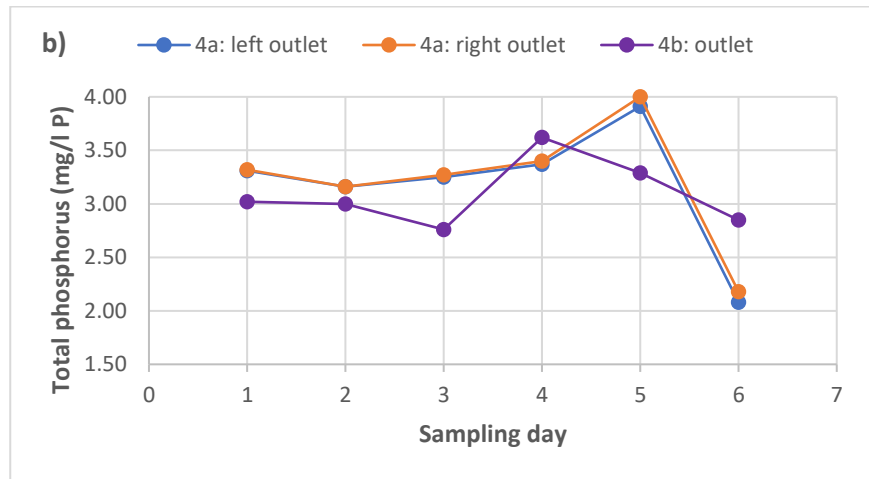
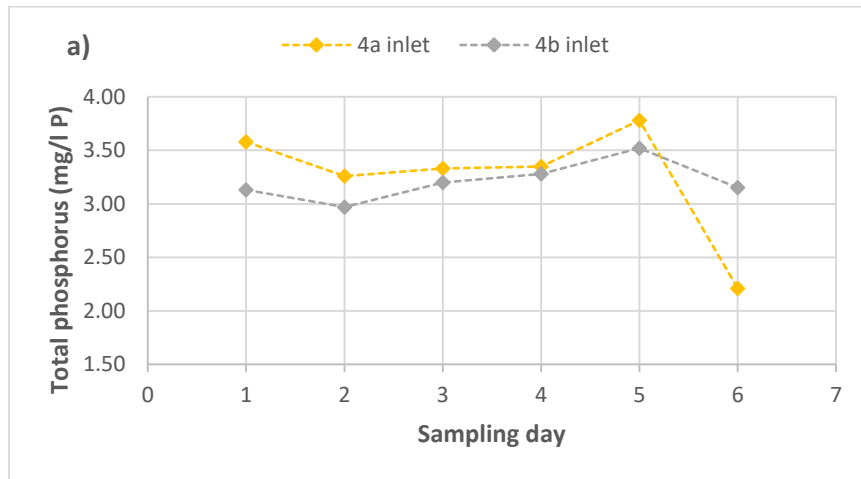


Figure 4.49: a) Inlet total phosphorus for the Phase 4a and 4b trials; b) Outgoing total phosphorus concentrations for the Phase 4a and 4b trial unit outlets; c) Inlet filtered phosphorus for the Phase 4a and 4b trials; d) Outgoing filtered phosphorus concentrations for the Phase 4a and 4b trial unit outlets

On average, the Phase 4b system resulted in lower phosphorus concentrations but the Phase 4a units had a lower minimum phosphorus concentration than 4b (Phase 4a sampling day 6). This was seen for both total and filtered phosphorus concentrations. However, the inlet concentration on that sampling day was much lower than the other days of the trial (shown in Figures 4.49b and 4.49d).

4.6.4.3 Discussion

The results from Phase 4a show that outgoing phosphorus concentrations followed the same trend as the ingoing phosphorus concentration. However, the percentage removals by the two units can vary considerably, particularly for filtered phosphorus. The units were packed identically and fed with the same effluent therefore their percentage removals would be expected to be similar if not identical. A possible reason for this variation in percentage removal is the longer pipe to reach the right unit resulting in different outgoing effluent being sampled but this is not expected to have a significant impact on the results. Alternatively, the percentage removal could be influenced by outside factors or the ochre in one unit could have been more saturated than the other unit following the IBC trial. From the percentage removal data, the right unit appears to perform worse than the left unit.

Both units in Phase 4a expected to apparent negative removals, which could be as a result of solids in the final effluent or being picked up within the pipework

The Phase 4b results show little similarity between the ingoing and outgoing phosphorus concentrations. This could be as a result of variations in the ingoing effluent quality or solids (with associated phosphorus) washing out of the pipes between the units. Alternatively, it may suggest that there is no correlation between ingoing phosphorus removal and the phosphorus removal for the unit set up with the two stage treatment.

The percentage removal of phosphorus by the Phase 4b filter system was variable with 2 samples exhibiting apparent negative removals, 3 samples with removal between 0 and 10 % removal and 1 sample with removal between 10 and 20 %. The cause of this variability is not known but may be due to solids (and associated phosphorus) washing out of the pipework between the two units. The downflow bed had a depth of 7 cm and was possibly insufficient to capture any of these solids or remove the phosphorus. The flow through the pipes between the units would have been less than the pumped ingoing flow rate and without an angle to gravity

aid the flow, the combination of these factors will have increased the deposition of solids in the pipe itself and therefore inhibit flow. Without ceasing the trial, it was not possible to flush this pipe thoroughly.

Previous phases have shown that backflushing is necessary for packed filter systems running in downflow. Dobbie et al. (2009) also noted that an ochre-based filter system would require backwashing. Therefore, a system like that used in Phase 4b, with one upflow and one downflow section, would require a backflush system for the downflow unit and a separate system for the pipework in order to clear any accumulated solids.

As the Phase 4b unit included a further treatment stage and increased the retention time of the filter system (compared to the two single units in Phase 4a), the removal would be expected to be significantly improved. However, this is not reflected in the trial results. When considering the number of samples removing between 0 and 10 % and 10 and 20 %, the two 4a units removed 0 to 10 % of total phosphorus for four samples and 10 to 20 % for no samples. The phase 4b system, on the other hand, removed 0 to 10 % of total phosphorus for three samples and 10 to 20 % for a single sample which, whilst an improvement on a single unit, was not the 50 % improvement that might have been expected by the 50 % increase in bed volume and therefore adsorbent material. When considering filtered phosphorus, all the Phase 4a units exhibited removal of between 0 and 10 %, however, two of the phase 4b samples exhibited negative removal, three removed between 0 and 10 % and one between 10 and 20 %. Again, this is not the improvement that would be expected when comparing the units run in series to those run alone. The reason for this is not known and cannot be determined from the data available.

Neither the phase 4a units nor the phase 4b system were able to achieve outgoing TP concentrations of less than 2 mg/l.

4.6.5 Overview of the Pond Filters

The following results and discussion include all the data produced as part of the pond filter trials.

4.6.5.1 Results

Across the pond filter trials, 82 outlet samples were taken and analysed. A breakdown of the number samples in each phase is shown in Table 4.21.

Table 4.21: Summary of the samples taken in each phase of the pond filter trials.

Phase number	Number of samples from each unit	Number of units	Total samples taken in phase
1	15	2	30
2	11	2	22
3	6	2	12
4a	6	2	12
4b	6	1	6
Total number of samples			82

Over a quarter of the samples exhibited an apparent negative percentage removal for both total and filtered phosphorus.

The following graphs (Figures 4.50 to 4.52) show the percentage of samples exhibiting percentage removal within the intervals marked on the x-axis. Figure 4.50 shows an overview of all the phase results. Figures 4.51 and 4.52 show the breakdown of the results by phase and the units within each phase, with separate graphs for total and filtered phosphorus. The data used to produce Figures 4.50 to 4.52 inclusive can be found in Appendix B, Table B1.

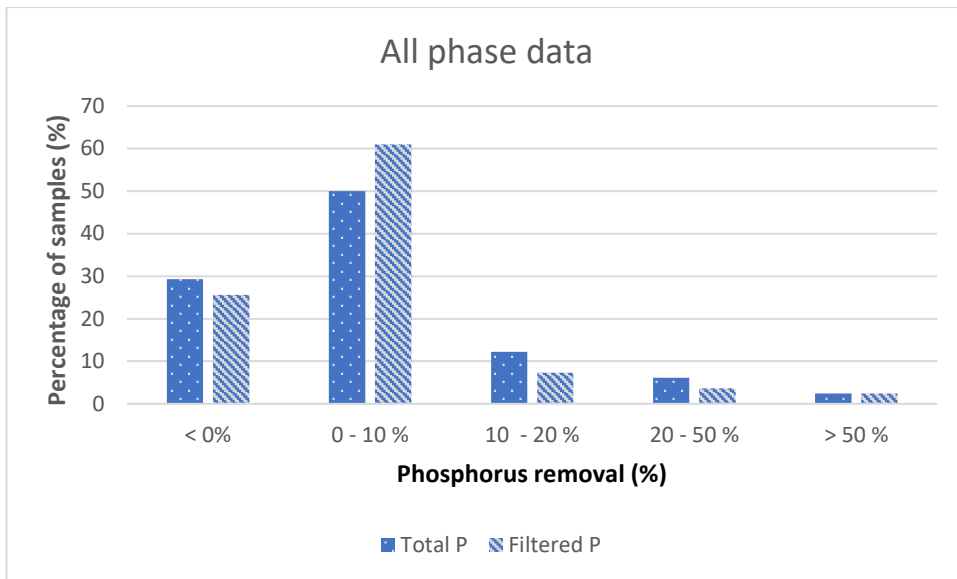


Figure 4.50: Percentage of samples taken during all phases of the pond filter trials within each of the identified removal bands for total and filtered phosphorus removal.

Figure 4.50 shows that the largest portion of samples (for both total and filtered phosphorus) exhibited removal between 0 and 10 % (50 % of samples for total phosphorus and 61 % for filtered phosphorus). The second largest portion were samples with negative percentage removals; 29 % of samples for total phosphorus and 26 % for filtered phosphorus.

Across the pond filter trials, there were a total of 17 samples (out of 82) that exhibited removal of greater than or equal to 10 % removal of total phosphorus and 11 samples for filtered phosphorus. From Figure 4.51, it can be seen that the Phase 2 units had the largest portion of samples with greater than 10 % removal. The 15 cm unit had more samples with greater than 10 % removal than the 5 cm unit. The Phase 1 units, Phase 3 ochre unit and Phase 4b system also managed to remove greater than 10 % total and filtered phosphorus for some samples.

The Phase 2, 15 cm unit was the only unit to exhibit over 50 % removal (maximum removal was 74.06 % total phosphorus and 78.64 % filtered phosphorus). This unit had no samples with apparent negative removals.

The Phase 3 ochre unit had the largest proportion of samples with negative removals for total phosphorus (66.67 %) but had an equal percentage of samples with removal between 0 and 10 %, the same percentage as the two Phase 4a units. In terms of filtered phosphorus, both the sand and ochre Phase 3 units have 66.67 % of samples with negative percentage removals.

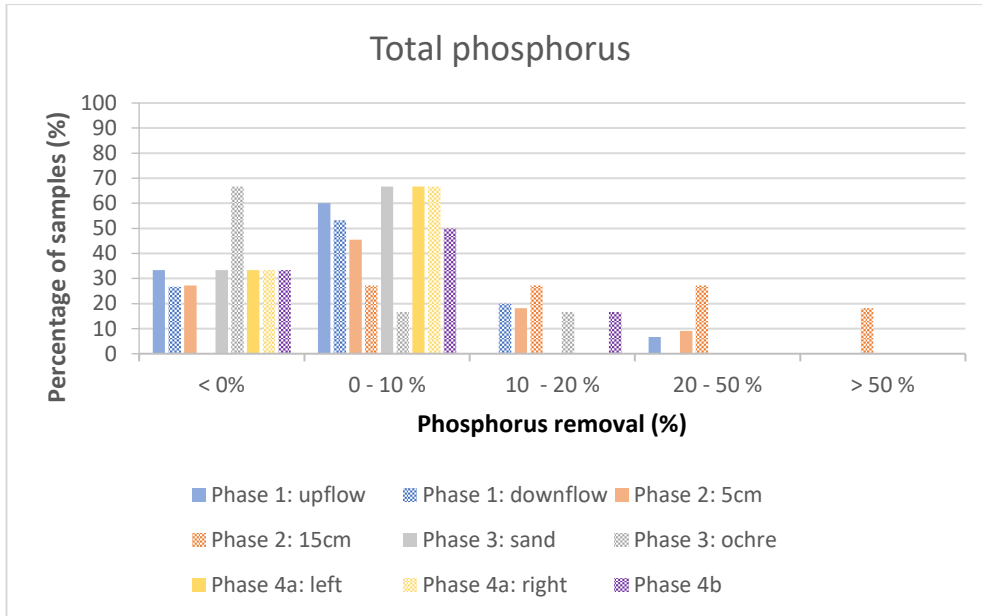


Figure 4.51: Percentage of samples in each phase of the pond filter trials within each of the identified removal bands for total phosphorus removal.

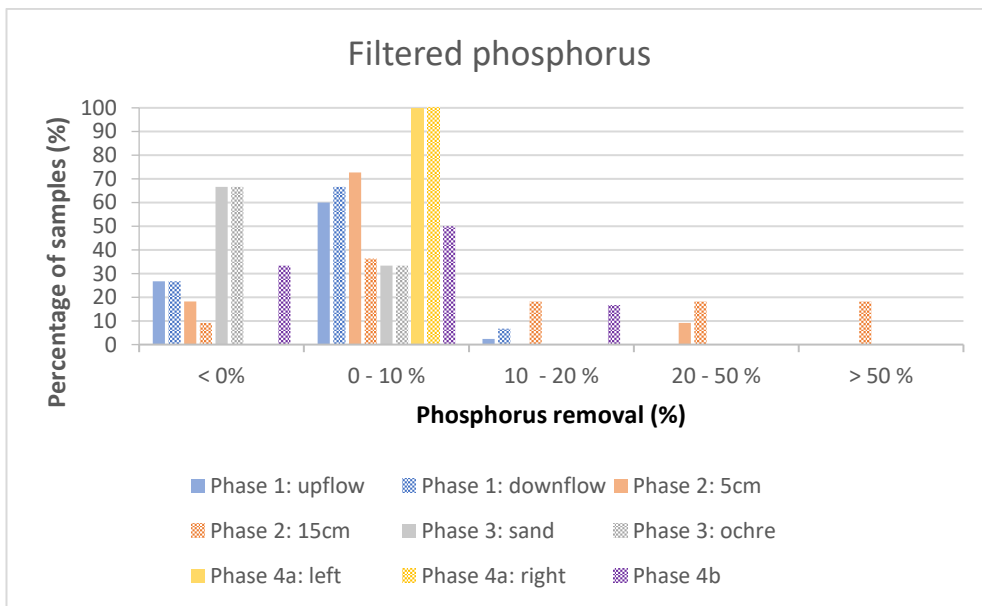


Figure 4.52: Percentage of samples in each phase of the pond filter trials within each of the identified removal bands for filtered phosphorus removal.

The table below shows the calculated retention times for the different ochre depths in the pond filter units. Further details (including flow rate and surface area) can be found in Table B2 (Appendix B). The calculated hydraulic retention time (HRT) for the units ranged from approximately 3 minutes through to 9.5 minutes depending on the depth of media (either sand and ochre or sand only) packed into the unit.

Table 4.22: Hydraulic retention time (HRT) for each ochre depth and the associated pond filter phase. The HRT was calculated as described in the methodology chapter (3.2.3.4).

Media depth	HRT		Pond filter phase
	h	mins	
5	0.05	3.16	2
7	0.07	4.43	4b* (downflow)
10	0.09	5.70	1
15	0.16	9.49	2, 3, 4a, 4b* (upflow)

* Phase 4b included two units, the combined retention time was calculated at 14 minutes

4.6.5.2 Discussion

Comparing the results from all the pond filter trials, shows that the Phase 2 units were the only units that removed greater than 50 % of total and filtered phosphorus. None of the subsequent trials were able to achieve this level of removal. It is not clear whether the variables subsequently tested resulted in lower removal rates or if there were other factors affecting the removal. Without further trials it is not possible to determine the cause.

Many of the phases exhibited apparent negative removals. These apparent increases in phosphorus removal after passing through the treatment units could be as a release or remobilisation of phosphorus and therefore could represent a genuine increase in phosphorus content in the effluent. Alternatively, it could be as a result of the sampling and the lag time between the effluent entering and exiting the units.

Current permit limits for phosphorus are at 2 mg/l total phosphorus. Throughout the pond filter trials, the outgoing total phosphorus was less than or equal to 2 mg/l only 15.85 % (13 samples) of the time. Phase 1 (both upflow and downflow) had outgoing total phosphorus less than or equal to 2 mg/l a third of the time and the Phase 2, 15 cm unit 27.27 % of the time (3 samples out of 11). The Phase 2 15 cm unit was the only unit that reduced outgoing total phosphorus to less than or equal to 1 mg/l (2 samples out of 11 in Phase 2). After Phase 2, there were no outlet samples with total phosphorus less than 2 mg/l. The results suggest that ochre-based filters in this form are not suitable for tertiary treatment at a STW as they would be unable to reliably meet final effluent limits of 2 mg TP/l or less.

The best removal was exhibited by the Phase 2, 15 cm unit. As part of the Phase 2 trials, it was shown that a deeper ochre layer resulted in improved removal of phosphorus. This may be linked to the increased retention time of the unit resulting in a greater contact time between the effluent and adsorbent for removal to occur.

The mechanism of phosphorus sorption is believed to be an initial quick reaction followed by a slower reaction (Habibiandehkordi et al., 2014; Szabó et al., 2008; Heal et al., 2003; 2004). Although Szabó et al. (2008) suggest that initial reaction occurs within a minute, they note that removal can continue for hours or even days. Heal et al. (2003; 2004) found that phosphorus removal by Polkemmet ochre reached equilibrium within 1 hour. The study conducted by Habibiandehkordi et al. (2014) suggested that phosphorus removal by ochre in batch experiments may not reach maximum removal until 5 days after initial contact. These studies suggest that although much of the removal occurs within minutes of contact, a longer contact time (or retention time) will improve phosphorus removal. Therefore, increasing the hydraulic retention time of the units will improve removal, but to significantly improve removal, retention time would have to be on the order of hours or days rather than minutes, which is not practical for a sewage treatment process.

4.7 Chapter Conclusions

This chapter investigated the practicality of ochre-based filters for tertiary treatment at STWs.

First, small-scale binder column trials were undertaken to determine the best binder to improve flow through the ochre-based adsorbent. These trials determined that, of the three binders trialled (resin, cement and sand), sand had the least impact on effluent quality.

Although the first pass of the ochre and resin column showed a removal of greater than 98 % of the P from the initial solution, the flow rate of the column dropped after just one pass (100 ml) of solution. It would have been useful to quantify the removal as part of the second pass, with the slower flow rate and therefore a longer contact time for P removal to occur. The relatively high cost of the resin binders and processing needed for sufficient quantities for large-scale trials, also counted against further progressing studies with resin as a binder.

Although the cement binder offered the best flow-through rate and phosphorus removal, it significantly increased effluent pH. Further investigation would be needed to understand the pH

increase when using cement as a binder and when this may decrease to an acceptable level. It is also necessary to understand when this adsorbent may block, and the flow rate drop off significantly. Both cement columns (with and without ochre) had P removal of greater than 70 %. Cement was discounted as an option for ochre support, despite its removal capacity, as implementing a cement and ochre-based filter onsite would require downstream pH correction.

Combining the ochre with sand, on the other hand, did not negatively impact upon the pH and improved flow-through sufficiently to allow flows to pass through media. Sand was chosen for the following filter-based trials as it is widely available for purchase in large quantities and relatively inexpensive compared to the other binders trialled.

Using sand as a binder will also require further investigation to determine the best ratio of sand to ochre to balance flow rate and phosphorus removal with an acceptable quantity of ochre to prevent saturation occurring too quickly. It also needs to be determined how long this adsorbent will take to block once a suitable flow rate has been attained. However, sand was chosen for the following filter-based trials without further investigation as it is widely available for purchase in large quantities and relatively inexpensive compared to the other binders trialled (cement and resin). Furthermore, the sand required less processing than the other binders and could be combined with the ochre without the need for water or setting.

Based on the results of the binder trials, an ochre-based filter unit was set up onsite at a sewage treatment works. The intermediate bulk container (IBC) unit was situated as a tertiary treatment process, treating effluent after the secondary settlement stage. The trial was run twice. The first run ended when flow through the unit dropped significantly. The unit was not set up with a backwashing mechanism and therefore the trial was ceased, and the unit unpacked. The unit was then repacked and run again. The two runs of the trial showed that ochre-based units were capable of removing phosphorus and treating effluent with variable phosphorus levels but highlighted that the design of the unit was in need of optimisation.

The trial found that ochre-based filter units need to be flushed to remove ochre solids when first set up before the unit is left unsupervised with a continuous flow through it. This is important when using the filter unit as a tertiary treatment as washing ochre solids from the unit will negatively impact the final effluent quality of the site. Furthermore, the nature of ochre

appears to result in a compaction effect of the ochre layer, resulting in the flow no longer being able to freely pass through the unit.

The results of the IBC trial suggested that a decreased flow rate through the unit (and therefore the adsorbent) does not necessarily improve phosphorus removal. Furthermore, the nature of the ochre may result in compaction of the media, as a combined result of the weight of the water and gravity. This compaction may impede flow through the media. The trial also experienced some algal growth, which may have been prevented by reducing light levels within the unit. However, the results suggested that the algal growth did not significantly impact upon flow or phosphorus removal of the unit.

The IBC trial presented further operational challenges when packing and unpacking the unit due to the size and quantity of material required to fill the unit. The unit took several days to pack and unpack requiring multiple people. The unit's size also made it difficult to make changes to the design and investigate issues.

The second run of the IBC trial was concluded in order to implement new, smaller scale trials within pond filters (approx. 70 L volume). These small-scale trials were divided into phases and designed to test variables such as ochre layer depth and the configuration of the filter unit in order to optimise the trial design before potentially scaling up again.

Phase 1 of the pond filter trials were designed to determine whether to configuration of the units impacted phosphorus removal with one unit set up in upflow and the other in downflow. The trials found that the configuration of an ochre-based filter unit does not significantly impact the phosphorus removal in either a positive or negative way. However, the upflow unit did achieve removal of between 20 and 50 % on one occasion, which the downflow unit did not. Furthermore, the results suggested that the units were capable of meeting 2 mg TP/l limits but not reliably.

The phase 1 trials found that units set up in a downflow configuration are more susceptible to solids and sludge building up within the unit and therefore a mechanism would be required for a long-term treatment unit whereby these can be removed to prevent the unit blocking and treatment capacity decreasing. The units also experienced algal growth on the top, ochre layer which could have been prevented by covering the units.

Phase 2 of the pond filter trials investigated the impact of adsorbent depth on phosphorus removal. Two units were set up; one filled with 5 cm of ochre and one with 15 cm. The 15 cm unit was more effective at removing phosphorus than the 5 cm unit. This is likely to be as a result of the increased adsorbent quantity, increased contact time, increased solids capture or a combination of these factors. However, these trials were not sufficiently detailed to assess which factor (or combination of factors) are responsible for this increased performance.

Furthermore, the reason for apparent increases in phosphorus concentration after passing through the treatment units is not fully understood. It could be a result of variations in final effluent phosphorus concentrations which have not been captured during sampling, due to remobilisation of phosphorus within the units. The trials did not allow this discrepancy to be investigated.

Phase 3 of the pond filter trials compared the removal of a filter packed with sand only to one packed with the sand/ochre mix. The trial was designed to determine whether the sand within the ochre/sand mix was responsible for any of the observed phosphorus removal. The results were largely inconclusive, and conclusions cannot be drawn as to the impact of an ochre/sand mix on phosphorus removal when compared to sand alone. Many of the samples exhibited negative percentage removals, i.e. an increase in phosphorus concentrations after treatment by the packed units. From the results of these trials it was not possible to determine why there was increased phosphorus exiting the units, whether solids capture enhanced removal of total phosphorus in the sand unit or if the increased phosphorus was due to the effluent picking up solids and/or phosphorus within the trial equipment. Alternatively, it could have been due to fluctuations in the final effluent phosphorus concentrations or solids content.

The sand filter appeared to capture solids and therefore was more effective at removing total phosphorus than the ochre-based filter was. From the data collected, there appeared to be little difference in removal by sand units and those containing ochre, however this was not considered to be a true representation of the performance of these units due to bypassing of the adsorbent material (particularly within the ochre unit). Following Phase 3 the membrane material was taped down in order to prevent this preferential flow between the material and the walls of the unit.

The final phase (Phase 4) of the pond filter trials was divided into two parts. Phase 4a consisted of two identical units set up to run in parallel to compare phosphorus removal. The general consistency between the two units' outgoing phosphorus concentrations suggested that the variability in percentage removal by the ochre units in this and previous phases may be the result of factors outside the unit (such as temperature, ingoing effluent quality and flow rate). However, there were differences between the units when considering daily removal and daily percentage removal. The reasons for these variations are unclear. The Phase 4a units required flushing in order to maintain ingoing flow rate.

The two units were set up to run in series for Phase 4b to investigate whether additional stages of filter would improve phosphorus removal. The Phase 4b system showed that running the units in series did improve removal (especially with respect to total phosphorus) but not significantly nor to the level which may be expected (i.e. two units would be expected to double removal capabilities). The Phase 4b system was difficult to flush and remove any solids which accumulated. Any downflow section of a system with units running in series would require a separate backflush system, as would any sections of pipe where flow is insufficient to keep solids in suspension and therefore solids are able to accumulate and impede flow.

The pond filter trial results suggested that ochre-based filters were better at removing total phosphorus than filtered phosphorus, which is thought to be as a result of the solids capture by the units. Removal by the pond filter units reached a maximum of almost 80 % (within Phase 2) but not consistently above 10 %. Most of the removal was between 0 and 10 % (for both total and filtered phosphorus), however there were a larger portion of samples with seemingly negative percentage removals. There is no way of determining which samples genuinely experienced an increase in phosphorus and those where there is an apparent increase (possibly as a result of the sampling technique).

There were operational issues throughout the pond filter trials. The units suffered from blocking and solids build up and therefore would require a backwash system to maintain flow through the system. There were also problems with flow bypassing the adsorbent as a result of how the units were packed. Ochre-based units require further engineering and design to fully assess the potential of ochre-based filters, but these trials suggest that tertiary filters are probably not the best application for ochre for phosphorus removal from wastewater. Packed filters may be relevant to applications with greater ingoing phosphorus content and/or a longer contact time

and may need to be much larger in size. The removal of ochre within units of this smaller size was not consistent but this is thought to be as a result of wider operational factors and not due to the ochre itself. The pond filters trialled would struggle to meet a total phosphorus discharge permit of 2 mg TP/l consistently and would be unable to meet more stringent limits.

The results from the trials completed in this chapter suggest that filter-based systems are not effective for phosphorus removal from secondary treated effluent. It is recommended that alternative applications of ochre are investigated, and the following chapters describe such methods.

Growth trials were conducted to investigate a potential use for the phosphorus saturated ochre from an ochre-based filter system. The trials used treatments with three bases; Dawdon ochre, sludge from a co-treatment reedbed and compost. It was found that pots containing nutrients from final effluent exhibiting better growth than those without contact with final effluent and no added nutrients.

The growth trials suggest that following use as part of a filter system, the phosphorus-saturated ochre is not toxic to grass growth, but it does not improve growth. The trials did show that sludge collected from a mine water and final effluent co-treatment reedbed did improve plant growth. The results of these trials would need to be confirmed with more in-depth growth trials before phosphorus-saturated ochre from a filter-based system could be applied to land. The continuation of these trials would be dependent on the method of application for ochre. For example, applying ochre within a filter will require growth trials to justify a possible application to land as a fertiliser or similar, however, dosing ochre for phosphorus removal will not require these trials.

5. Ochre Dosing

5.1 Introduction

The literature suggests that the phosphorus removal kinetics for ochre are quick and therefore should be suitable for directly dosing into wastewater (Heal et al., 2003; 2004). The sorption of P by ochre is believed to occur as a two-stage reaction with the first stage occurring within minutes (Habibiandehkordi et al., 2014; Heal et al., 2003;2004; Szabo et al., 2008). Heal et al. (2003; 2004) suggest that fine grained ochre is better suited to dosing applications than to applications such as wetlands or as part of a filter.

A direct dosing application was tested through a series of jar tests. Initially, the ochre was dosed as a solid then as a slurry. Ochre was also dosed as a ferric supplement to examine whether it would enhance chemical removal, and therefore potentially reduce chemical usage.

The trials were completed using methodology designed to simulate processes at STWs and therefore consisted of high intensity mixing followed by a period of slow mixing or flocculation, and finally settlement. The jar test methodology is detailed in Section 3.3. Short trials were conducted in quick succession to test a number of variables when dosing ochre for phosphorus removal. The trials are summarised below in Figure 5.1.

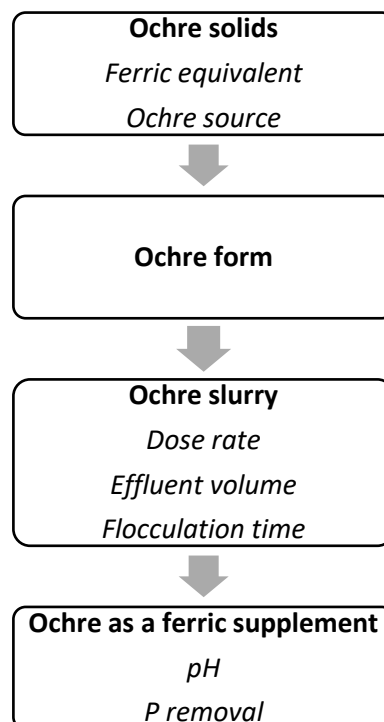


Figure 5.1: Summary of jar tests and the variables tested as part of the ochre dosing trials.

5.2 Methods

The methods used for the following trials are detailed in Section 3.3.

5.3 Ochre solid dosing trials

5.3.1 Ferric equivalent

5.3.1.1 Results

Table 5.1 details the dose rate added to the wastewater, the initial phosphorus concentration and the percentage removal of total and filtered phosphorus. The ochre dose of 0.015g/l was equivalent to the 6 mg/L ferric sulphate typically used in WWTWs in terms of iron content.

Table 5.1: Results from initial phosphorus removal jar testing

	Initial phosphorus (mg/l)		Percentage removal (%)	
	Total phosphorus	Filtered phosphorus	Total phosphorus	Filtered phosphorus
6 mg/L ferric sulphate	7.50	5.65	69.87	69.20
0.015 g ochre/l	7.50	5.65	10.00	1.77
0.15 g ochre/l	8.50	6.65	16.47	6.02
1.5 g ochre/l	8.50	6.65	50.59	59.40

Figure 5.2 shows the ochre dose plotted against percentage removal. The total and filtered phosphorus removal observed in the ferric dosed jars is included in the figure for reference.

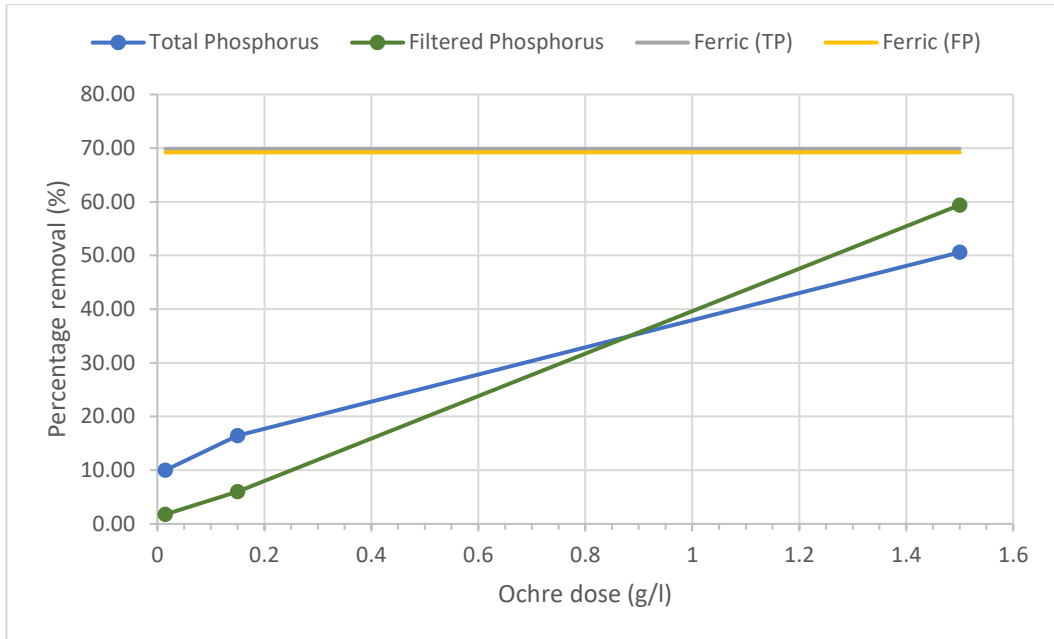


Figure 5.2: Percentage removal of total and filtered phosphorus compared to the ochre dose

Figure 5.2 shows the expected relationship that increasing the dose of ochre increases the removal of phosphorus. The maximum observed removal of filtered phosphorus by ochre was 59.40 % (50.59 % for total phosphorus) when ochre was dosed at 1.5 g/l (0.75 g in 500 ml). The ferric exhibited removal of 69.20 % filtered phosphorus and 69.87 % total phosphorus.

5.3.1.2 Discussion

The results show that phosphorus removal increases as ochre dose rate increases. This may be as a result of the iron dose increasing with increasing ochre dose. When dosing ochre at the lower dose rates (0.015 g/l and 0.15 g/l) the percentage removal of total phosphorus was greater than the percentage removal of filtered phosphorus.

At the greatest ochre dose (1.5 g/l) this relationship was reversed with a greater percentage removal of filtered phosphorus (59.40 %) than total phosphorus (50.59 %). The point at which percentage removal of filtered phosphorus overtakes percentage removal of total phosphorus is not known beyond occurring between ochre doses of 0.15 and 1.5 g/l. Further trials with ochre doses at smaller increments would be required to determine when filtered phosphorus removal becomes greater than total phosphorus removal.

The lowest ochre dose rate (0.015 g/l) was equivalent to the 6 mg/L ferric sulphate dose rate in terms of iron content. The percentage removal by the ochre was 10 % for total phosphorus and

1.77 % for filtered phosphorus compared to 69.87 % total phosphorus and 69.20 % filtered phosphorus removal by the ferric sulphate.

The greatest removal by ochre was at a dose rate of 1.5 g/l (50.59 % removal of total phosphorus and 59.40 % filtered phosphorus). This dose rate is 100 times that of the ferric in terms of iron content (assuming the ochre has a constant iron content) but the removal is not as high. Therefore, these results suggest that a greater dose of iron is required in the form of ochre than as ferric sulphate. This may be as a result of the iron form in the ochre or the way this is bound within the ochre. Without further trials and further analysis of the ochre, it is not possible to determine the reason for the discrepancy based on these results.

5.3.2 Ochre source

The previous dosing trial was completed using a single ochre source (Dawdon). This led to the following trials being designed to compare ochres from different sources to determine whether the ochre source impacts phosphorus removal and, if it does, which source was most effective at removing phosphorus. Ochres from different sources have different characteristics that may impact upon phosphorus removal efficiency, for example, surface area and chemical composition.

5.3.2.1 Results

Figure 5.3 shows the results of the jar tests dosed with 2 g/l of ochre solids and ferric sulphate dosed at 6 mg/L. The columns have been patterned to distinguish between the different ochre sources. The ferric sulphate exhibited percentage removals of 96.44 % total phosphorus and 98.74 % filtered phosphorus. The maximum removal by an ochre was 51.39 % total phosphorus and 57.01 % filtered phosphorus removal by Dawdon ochre. Bates ochre exhibited the lowest removal of total phosphorus (8.24 %) whilst the lowest removal of filtered phosphorus was by Blenkinsopp (19.59 %).

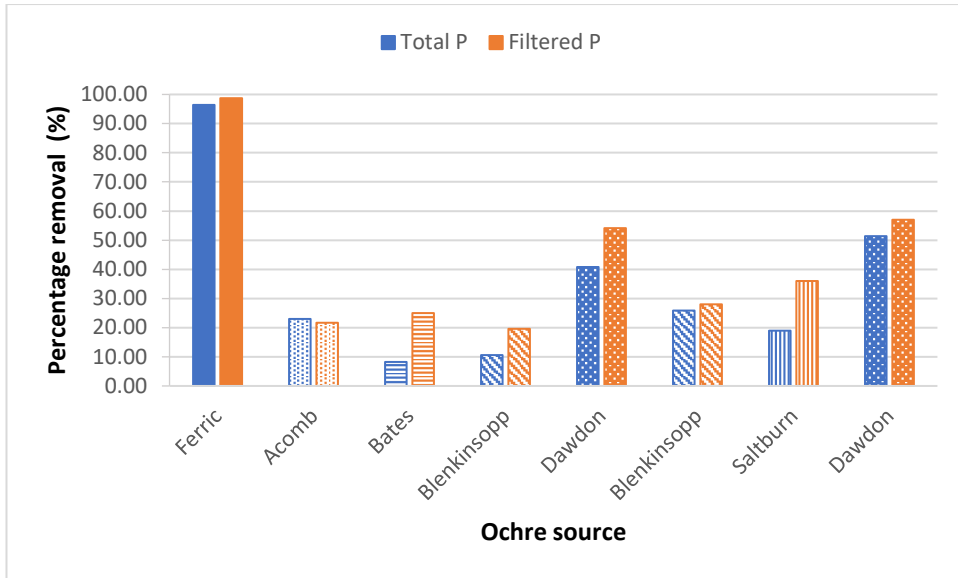


Figure 5.3: Percentage removal of phosphorus when dosing ochre solids into 500 ml of raw effluent (not completed in duplicate)

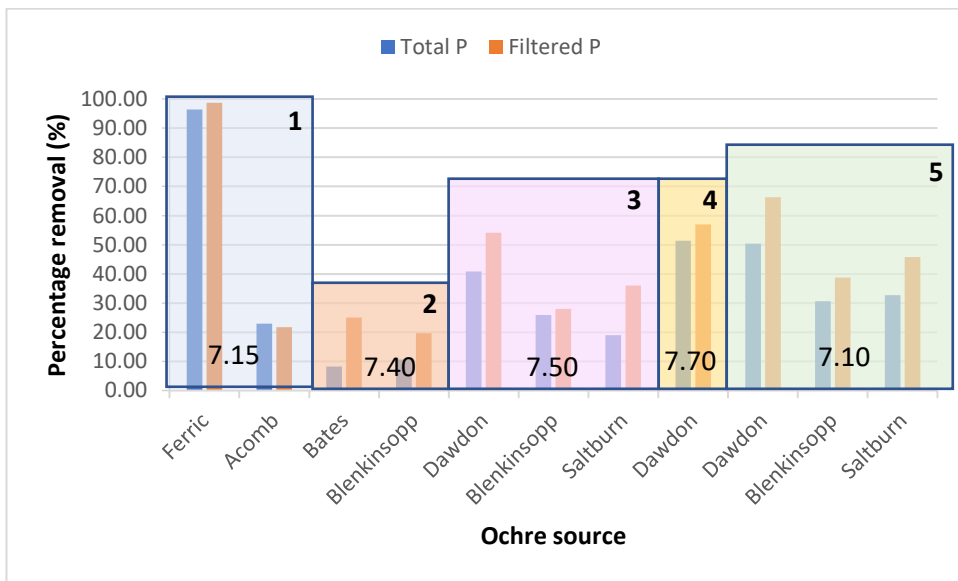


Figure 5.4: Percentage removals for the five ochres with initial filtered phosphorus concentrations labelled

Figure 5.4 shows the percentage removals with effluent batch numbers identified (the numbers at the top of the coloured boxes) and the initial filtered phosphorus concentration detailed at the base of each section of columns. An extra set of jar tests (dosed into raw number 5) have been included. These jars were dosed with ochre as a slurry. The initial phosphorus concentrations are shown in Table 5.2. Figure 5.3 shows that the maximum removal by Dawdon occurred when the initial phosphorus removal was 10.80 mg TP/l. Although the initial total

phosphorus is variable (ranging from 7.50 to 10.80 mg/l P), the filtered phosphorus was between 7.10 and 7.70 mg/l P.

Table 5.2: Initial phosphorus concentrations for each batch of effluent

Raw	Initial (mg/l)	
	Total P	Filtered P
1	8.70	7.15
2	8.50	7.40
3	8.70	7.50
4	10.80	7.70
5	7.50	7.10

The removal of phosphorus by Dawdon and Bates ochre slurry was directly compared in subsequent jar tests. These were dosed at an equivalent dry solids rate rather than based on wet weight as the previous trials. Duplicates were completed, and an average percentage removal was calculated. The results are summarised in Table 5.3 below.

Table 5.3: Average percentage removal when dosing ochre as a slurry

	Average percentage removal (%)	
	TP	FP
Bates	51.20	59.14
Dawdon	56.51	70.20

The results in Table 5.3 show that Dawdon removed more phosphorus than Bates ochre. Dawdon was able to remove over 10 % extra filtered phosphorus and 5 % extra total phosphorus.

5.3.2.2 Discussion

In the jars dosed with ochre solids, Dawdon demonstrated the best removal of the five ochres, for both total and filtered phosphorus removal. Dawdon also had the greatest removal when dosing a slurry in comparison to Blenkinsopp and Saltburn as well as when trialled directly against Bates (with duplicates). It should be noted that all the ochres have different water contents as well as different iron contents. The final slurry trials (comparing Dawdon and Bates)

were dosed according to equivalent dry solids and Dawdon still removed 10 % greater filtered phosphorus compared to Bates. Furthermore, the surface area of Dawdon was previously determined to be approximately 44 m²/g compared to Bates ochre surface area of 137 m²/g (Pinner, 2014). When considering the ochres surface areas, it would be expected that Bates ochre would remove more phosphorus as a result of its greater surface area. Sapsford et al. (2015) noted that Dawdon ochre contained less iron than Bates and Blenkinsopp (6.38 % compared to 31.19 % and 35.67 %, respectively), however, it contained more calcium. Dawdon ochre was found to contain 28.34 % calcium compared to 4.3 % and 5.45 % in the ochre from Bates and Blenkinsopp, respectively (Sapsford *et al.*, 2015). This calcium content may be the reason that the phosphorus removal by Dawdon exceeds that of other ochres despite having the lower iron content and smaller surface area.

There is insufficient data to determine the impact of initial phosphorus concentration on percentage removal by the five ochres. The Dawdon ochre solids removed more phosphorus with an initial phosphorus concentration of 10.80 mg TP/l (7.70 mg/l filtered P) and Blenkinsopp filtered phosphorus removal increased from 19.59 % to 28.00 % when the initial filtered P increased from 7.40 mg/l to 7.50 mg/l. The removal by Saltburn ochre solids decreased from 45.77 % to 36.00 % filtered phosphorus removal as initial filtered phosphorus concentration increased from 7.10 to 7.50 mg/l (7.50 to 8.70 mg TP/l). Without duplicates at these initial concentrations and further trials, the relationship between initial concentration and percentage removal of phosphorus cannot be defined.

These initial results suggest that dosing ochre as a slurry may improve phosphorus removal as Blenkinsopp removal increased to 38.73 % removal of filtered phosphorus (30.67 % TP) from a maximum of 28.00 % filtered phosphorus (25.86 % TP) when dosed as a solid. Dawdon also increased in removal from a maximum of 57.01 % filtered phosphorus removal when dosed as a solid to a removal of 66.34 % filtered phosphorus removal when dosed as a slurry. The total phosphorus removal of Dawdon when dosed as a slurry was 50.40 % which was a slight decrease compared to the previous maximum of 51.39 %.

5.4 Ochre form

5.4.1 Results

The trials were completed using a single batch of effluent with initial concentrations of 8.50 mg/l total phosphorus and 8.10 mg/l filtered phosphorus and the results are shown in Table 5.4.

The average removal of phosphorus when dosing ochre as a solid was 52.65 % total phosphorus and 69.69 % filtered compared to removal of 63.18 % total phosphorus and 80.31 % filtered phosphorus when dosing ochre as a slurry.

Table 5.4: Ochre form trial results

Ochre form	g	Percentage removal (%)		Average percentage removal (%)	
		Total P	Filtered P	Total P	Filtered P
Solid	2.0111	47.65	64.57	52.65	69.69
	2.0093	57.65	74.81		
Slurry	2.0105	61.65	78.64	63.18	80.31
	2.0063	64.71	81.98		

5.4.2 Discussion

The results suggest that dosing ochre as a slurry improves the removal of both total and filtered phosphorus. This may be due to a better dispersal of the ochre particle which consequently increases ochre contact with the effluent and its associated phosphorus. These trials were completed with duplicates but only used a single ochre (sourced from Dawdon MWTP).

5.5 Ochre slurry dosing trials

5.5.1 Ochre dose

5.5.1.1 Results

Jar tests were completed by dosing into both 500 ml and 1 litre of wastewater. The ochre was dosed as a solid at dose rates of less than 1.5 g/l, for dose rates of equal to or greater than 1.5 g/l, the ochre was dosed as a slurry. Each dose rate was completed in duplicate and an average percentage removal was calculated. The results of these trials are shown in Figure 5.5 and summarised in Table 5.5.

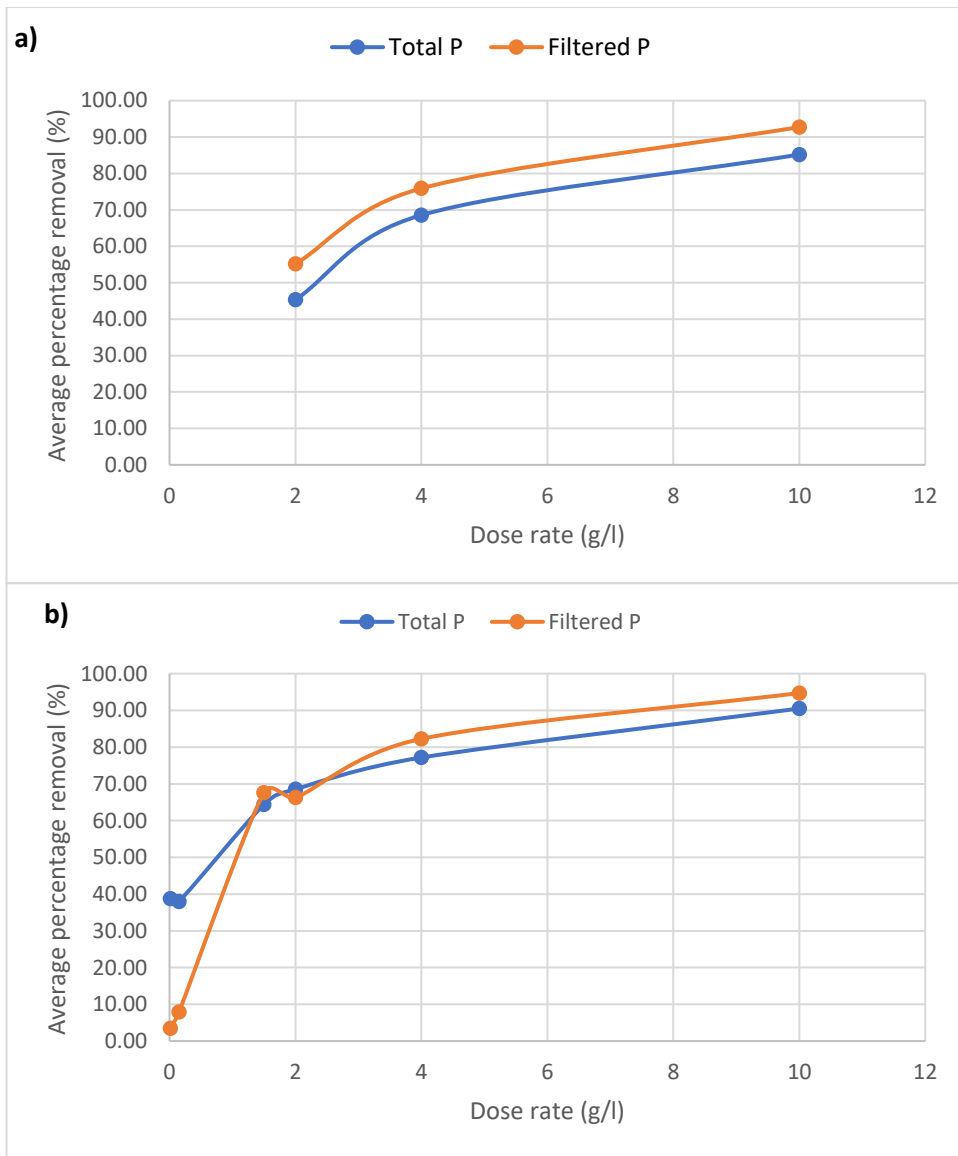


Figure 5.5: Relationship between average percentage removal and ochre dose rate when dosing into a) 500 ml and b) 1 litre of wastewater

The results show that a maximum removal of 92.74 % filtered phosphorus removal and 85.20 % total phosphorus was found when dosing into 500 ml. When dosing into 1 litre, the maximum removal of filtered phosphorus was 94.72 % and 90.52 % of total phosphorus was removed. Both Figures 5.5a and 5.5b show an increase in phosphorus removal as dose rate increases, although there is a slight decrease in filtered phosphorus removal when dose rate increased from 1.5 to 2 mg/l in a volume of 1 litre.

Table 5.5 shows a summary of the average percentage removals at each dose rate according to the wastewater volume. The results show that the average removal of phosphorus (both filtered and total) was greater in 1 litre of wastewater than in 500 ml.

Table 5.5: Summary of the results when dosing ochre as a slurry

Ochre dose (g/l)	Dosed into 500 ml		Dosed into 1 litre	
	Average percentage removal (%)			
	Total P	Filtered P	Total P	Filtered P
0.015			38.80	3.45
0.15			38.00	7.93
1.5			64.38	67.65
2	45.34	55.18	68.54	66.27
4	68.58	75.91	77.17	82.26
10	85.20	92.74	90.51	94.72

5.5.1.2 Discussion

The results show that phosphorus removal increases as ochre dose rate increases, which confirms the findings of previous jar tests.

The results of the trials dosed into 500 ml of effluent show that the percentage removal of filtered phosphorus is greater than the percentage removal of total phosphorus. In the trials conducted with 1 litre of effluent, the lowest dose rates (0.015 g/l and 0.15 g/l) have a greater removal of total phosphorus removal than filtered phosphorus. The total phosphorus removal may, in part, be due to the settlement of solids (and associated phosphorus) rather than as a result of the addition of the ochre but without a control the effect of the settlement stage of the jar tests on phosphorus concentrations cannot be quantified. The results in these trials suggest that effective settlement is key for phosphorus removal.

The results suggest that phosphorus removal when dosing into 1 litre of effluent is greater than when dosing into 500 ml. The slurry for the 500 ml trials was produced using tap water whilst the slurry for the 1 litre used de-ionised (DI) water and therefore the results cannot be directly compared. To determine the impact of effluent volume to be treated on phosphorus removal, further trials should be completed using a single batch of effluent (and therefore a single initial phosphorus concentration) and ochre slurry prepared in the same way to allow a direct comparison. All the trials were completed using Dawdon ochre and other ochre sources should also be trialled.

5.5.2 Effluent volume

5.5.2.1 Results

The effect of volume was investigated using effluent with an initial phosphorus concentration of 6.40 mg/l of total phosphorus and 4.15 mg/l filtered phosphorus. This effluent was dosed with ochre slurry produced with DI water.

Table 5.6 summarises the trial and the average percentage removals for each effluent volume.

Table 5.6: Percentage removal of phosphorus when dosing into 500 ml and 1 L of effluent

Effluent volume	Percentage removal (%)		Average percentage removal (%)	
	Total P	Filtered P	Total P	Filtered P
500 ml	65.78	68.92	66.41	69.76
	67.03	70.60		
1 L	67.34	72.05	67.42	71.81
	67.50	71.57		

The results set out in Table 5.6 show that removal was greater in 1 litre of effluent with the maximum removal of filtered phosphorus 71.81 % compared to the maximum removal of 69.76 % filtered phosphorus in 500 ml.

5.5.2.2 Discussion

The results suggest that the removal of phosphorus is marginally better in 1 litre of effluent than in 500 ml when ochre is dosed at the same rate. The removal of filtered phosphorus was consistently greater than the removal of total phosphorus, regardless of the effluent volume. These results support the findings of the previous trials which also observed better removal of filtered phosphorus than total phosphorus.

5.5.3 Flocculation time

5.5.3.1 Results

The effect of flocculation time on phosphorus removal was investigated. The dose rate was kept at a constant 2 g/l (wet weight) but the flocculation period was varied, and two ochres were trialled; first Dawdon and then Bates.

The average percentage removal for each mix time (flocculation time) was calculated from the duplicates and is plotted in Figure 5.6. The initial phosphorus concentration for the Dawdon trial was 7.00 mg/l total phosphorus and 6.20 mg/l filtered phosphorus.

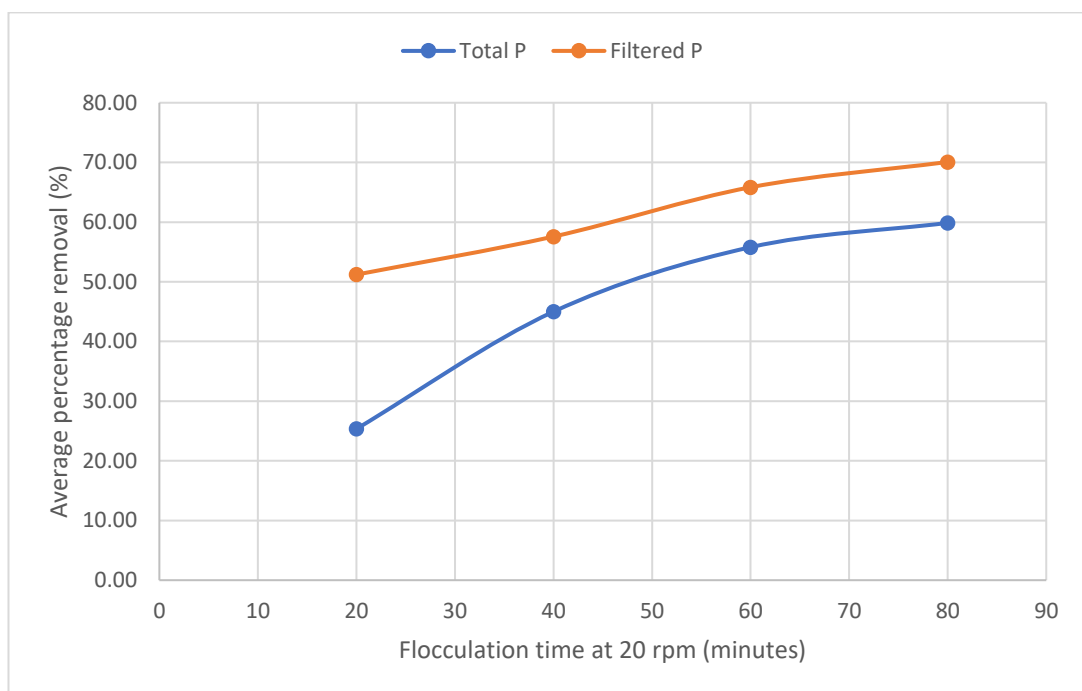


Figure 5.6: Average percentage removal plotted against flocculation time when dosing Dawdon ochre

Figure 5.6 shows that increased mixing time at 20 rpm results in increased phosphorus removal for both total and filtered phosphorus. Increasing the flocculation period from 20 to 80 minutes increases the removal of total phosphorus by 34.51 % whereas filtered phosphorus removal improves 18.87 %. As seen in previous trials, the percentage removal of filtered phosphorus is greater than the percentage removal of total phosphorus.

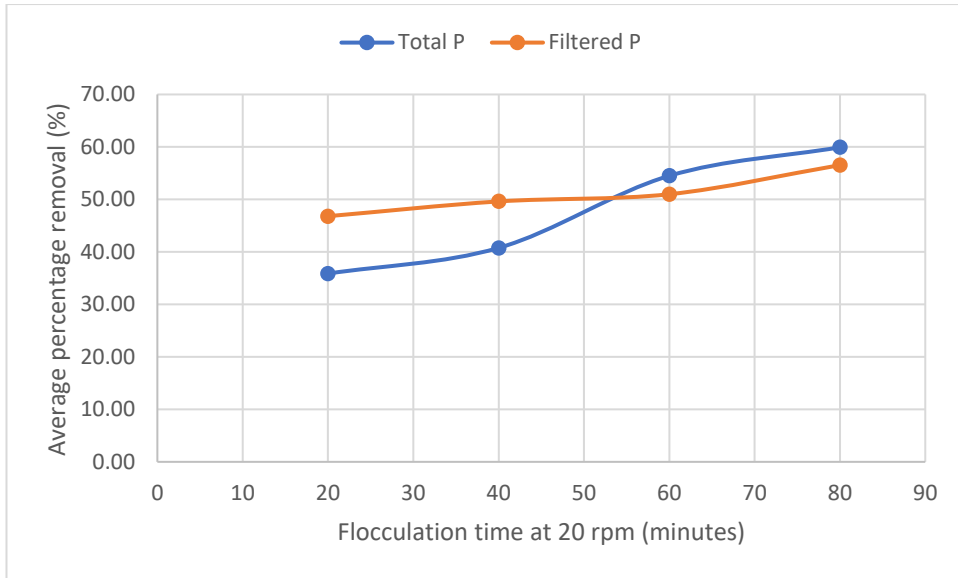


Figure 5.7: Graph showing the impact of flocculation time at 20 rpm on phosphorus removal when dosing Bates ochre

Figure 5.7 shows that percentage removal of phosphorus increases with increased flocculation time. The percentage removal of total phosphorus increases from 35.87 % to 59.93 % when flocculation time increases from 20 to 80 minutes, whilst filtered phosphorus removal increases from 46.80 % to 56.53 %. The increase in total phosphorus removal is greatest between 40 and 60 minutes of flocculation time.

5.5.3.2 Discussion

The Dawdon trial results show that percentage removal of phosphorus increases as flocculation time increases.

The greatest increase in removal occurred when flocculation time was increased from 20 to 40 minutes whilst the smallest increase was between 60 and 80 minutes. The trend suggests that the increasing flocculation time beyond 80 minutes would have a minimal impact upon phosphorus removal. The results suggest that flocculation time has a greater impact upon total phosphorus removal than filtered phosphorus removal. Total phosphorus removal improves by 34.51 % when flocculation time increases from 20 to 80 minutes whereas filtered phosphorus removal improves by 18.87 %. These results suggest that the increased flocculation results in more solids removal and therefore greater particulate P removal. As observed in previous jar tests, the ochre was better at removing filtered phosphorus than total phosphorus.

The results from the trials dosed with Bates ochre also show increased phosphorus removal with increasing flocculation time and that the impact was greater on total phosphorus removal than filtered phosphorus removal. The increase in total phosphorus removal was 24.08 % and filtered phosphorus removal increased by 9.73 %. Unlike the Dawdon trials, the biggest increase in total phosphorus removal was observed when the flocculation time was increased from 40 to 60 minutes. For filtered phosphorus, the greatest increase was between 60 and 80 minutes. Increasing the flocculation time from 60 to 80 minutes resulted in very similar increases in both filtered and total phosphorus; 5.54 % and 5.43 % for filter and total phosphorus, respectively. When the flocculation time was 60 minutes or greater, the removal of total phosphorus was greater than the percentage removal of filtered phosphorus, however this was not observed in the Dawdon trials.

Both trials suggest that flocculation time impacts total phosphorus removal more than filtered phosphorus removal. These results suggest that the enhanced removal of total phosphorus may be as a result of increased solids settlement and the removal of particulate phosphorus. The lesser impact on filtered phosphorus may suggest that the removal of filtered phosphorus is a quicker reaction. Szabó et al. (2008) noted that phosphorus removal with metal salts was a quick reaction first which is followed by a slow reaction. This finding supports the results of these trials.

Furthermore, the results of these jar tests suggest that the Bates and Dawdon ochres are impacted by flocculation time in different ways. The ochres are different in elemental composition with Sapsford et al. (2015) results showing that Bates has a greater iron content than Dawdon; and Dawdon ochre contains more calcium. Furthermore, the Dawdon ochre is produced from an active treatment process with the addition of lime, whilst the Bates ochre is produced at a passive site without chemical addition (Coal Authority, 2014; Sapsford et al., 2015). These processes will impact the chemical composition of the ochres. The different behaviour observed with respect to the flocculation time may be as a result of these variations in chemical compositions and possibly relate to different mechanisms of iron and calcium for phosphorus removal. In order to further investigate the impact of flocculation time on phosphorus removal, trials should be completed with Bates and Dawdon ochre as well as other ochres, alongside an investigation into the removal mechanisms of the ochres.

5.6 Ochre as a ferric supplement

5.6.1 Results

The impact of the ochre upon pH was studied under ideal conditions using DI water dosed with ferric sulphate at 6 mg/L. Dawdon ochre slurry was gradually added and the pH monitored. Figure 5.8 shows the pH curve of the solution with cumulative ochre addition.

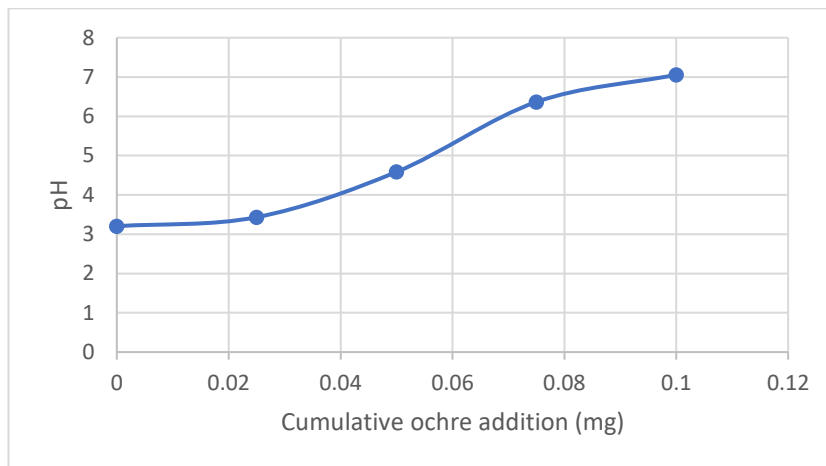


Figure 5.8: Graph showing the impact of ochre addition on pH (after the addition of ferric sulphate)

The pH of the DI water was 6.077 prior to the addition of ferric. The starting pH value on the graph above (Figure 5.8) is after the addition of ferric, which reduced the pH to 3.203. Approximately 0.1 mg of Dawdon ochre (as a slurry) was required to adjust the pH to neutral.

Phosphorus removal was then investigated when ferric sulphate and ochre slurry were dosed one after another with minimal time between the doses. For the trial, half the jars were dosed with ferric then ochre, the other half were dosed first with ochre then with ferric.

An average removal was calculated from the duplicate results and these are shown in Table 5.7. The maximum phosphorus removal is observed when ferric is dosed first at a rate of 3 ml/l, resulting in a 60.17 % removal of total phosphorus and 64.46 % removal of filtered phosphorus. The minimum observed removal was when dosing ochre first and ferric was dosed at 0.3 ml/l when total phosphorus removal was 40.63 % and total phosphorus removal was 28.44 %.

Table 5.7: Average percentage removal when using ochre as a ferric supplement

	Ferric dose (ml/l)	Average percentage removal (%)	
		TP	FP
Ferric first	0.3	46.67	33.75
	3	60.17	64.46
Ochre first	0.3	40.63	28.44
	3	59.57	63.91

5.6.2 Discussion

The results show a slight improvement in removal when ferric is dosed before the ochre slurry is added and this improvement is most obvious when the ferric is dosed at 0.3 ml/l. The addition of ferric first will decrease the pH of the effluent, however, Heal et al. (2004) found that pH did not impact phosphorus removal, which was attributed to the ochre's buffering capacity. The Heal et al. (2004) study focused on Polkemmet and Minto ochres (Heal et al., 2004), in comparison this current study used Dawdon ochre, therefore further studies would be needed to determine whether Dawdon ochre phosphorus removal is improved at lower pH.

The results of these trials suggest that ochre and ferric could be used in combination to improve the removal of phosphorus from wastewater and adjust the pH. Further trials would be required to determine the ideal dose of each ferric and ochre slurry and whether delaying the addition of the ochre after the ferric addition would enhance phosphorus removal further.

5.7 Primary sludge production estimates when dosing ochre for phosphorus removal

5.7.1 Results

The calculated flow rate for the selected population equivalent was 2145000 litres per day which resulted in an unaided primary sludge production of 450000 g per day (450 kg per day). When dosing at 4 g of ochre per litre of effluent (to achieve 80 % removal) the total quantity of ochre sludge per day was 8580 kg and therefore ochre solids would make up 95 % of the total sludge produced at this stage of the treatment process. When dosing to achieve 50 % phosphorus removal (2 g of ochre per litre) the ochre sludge produced would be 4290 kg per day and account for over 90 % of the total sludge solids.

5.7.2 Discussion

The results of the sludge production calculation suggest that the dosing of ochre into raw wastewater (upstream of the primary tanks) will result in a primary sludge which is 90 to 95 % ochre solids. This sludge would therefore no longer be classified as sewage sludge and would be disposed of via landfill. This input of solids would greatly increase the quantity of sludge produced at the sewage treatment works on a daily basis. This increase in sludge would then require increased tankering from the site and increase operating costs for the site.

5.8 Chapter Conclusions

The tested variables and the factors they impacted are summarised in the diagram below (Figure 5.9) alongside the characteristics of wastewater which were affected by these variables and factors.

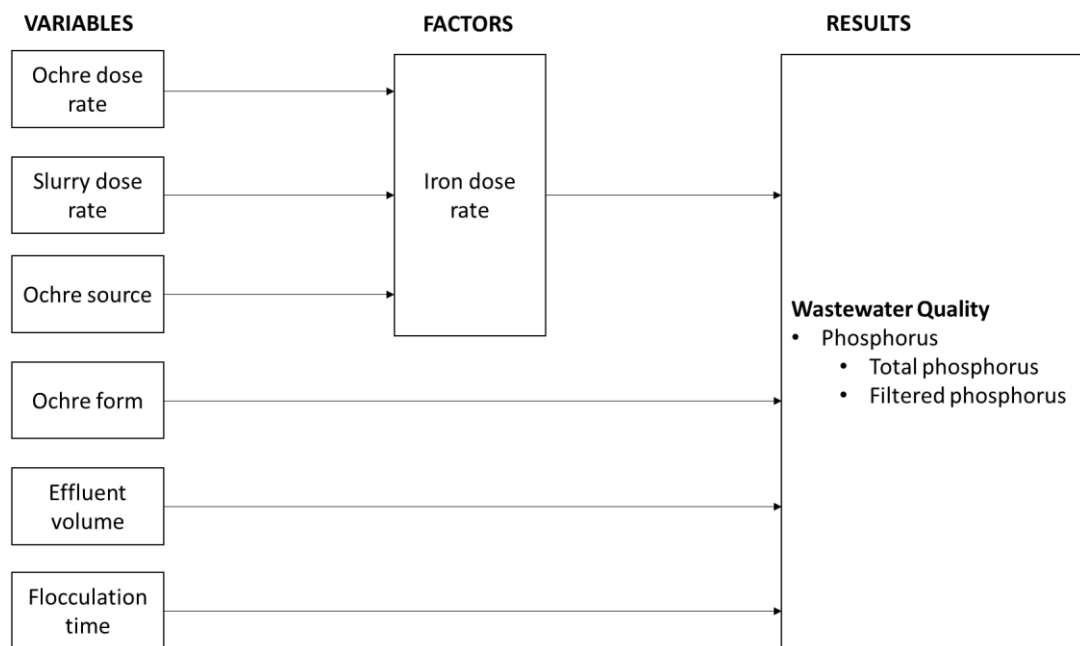


Figure 5.9: Model summarising the tested variables, factors (uncontrolled variables) and results considered in the ochre dosing trials.

The results show that ochre removes a greater percentage of filtered phosphorus than total phosphorus, suggesting that ochre is better at removing soluble phosphorus than phosphorus which is associated with solids.

The results suggest that Dawdon ochre is more effective at removing phosphorus than the other ochres trialled and dosing with equivalent wet weight quantities, this may be due to its lower

water content. Alternatively, it could be due to the elemental composition of the ochre or other factors which cannot be determined from the results of these trials. Further trials would be required to investigate this.

The results show that dosing ochre as a slurry rather than dosing as a solid will improve the percentage removal of phosphorus. Dosing into a larger volume of effluent may also improve percentage removal.

A longer flocculation time (and thus increased contact time) results in increased removal of phosphorus. The flocculation time has a greater impact on the removal of total phosphorus than the removal of filtered phosphorus. Furthermore, the flocculation time appeared to impact Bates and Dawdon ochre phosphorus removals differently.

The use of ochre as a ferric supplement was trialed; however, it was not investigated in detail. The results do suggest that ferric and ochre can be dosed together and that dosing ferric before the addition of ochre improves removal compared to dosing ochre first. These results were not sufficient to determine whether chemical savings could be achieved by dosing ochre and ferric concurrently. Further, more detailed trials would be required to determine if these savings could be made.

The initial sludge production calculation suggests that dosing ochre into wastewater for phosphorus removal will greatly increase the quantity of sludge produced and that the sludge will mostly consist of ochre solids rather than conventional sewage material. Further calculations and studies would need to be completed to quantify this impact more exactly, however, this first look suggests that the sludge production would be prohibitive to the addition of ochre solids for phosphorus removal in the primary treatment stage.

In order to apply ochre dosing for wastewater treatment, further trials would be required. It is recommended that:

- Further trials are completed to investigate the effect of the ochre source on phosphorus removal and the reason for improved removal by some ochres compared to others.
- Trials should be completed to further investigate the dosing of ferric and ochre together to improve phosphorus removal and whether chemical savings can be made.

- The impact of dosing ochre directly into wastewater on the treatment process and potential sludge production needs to be further investigated and fully understood before the approach is implemented onsite.

6. Ochre-Derived Ferric (ODF)

6.1 Introduction

The previous trials in this thesis have focussed on ochre-based filters and the direct dosing of ochre into wastewater. These trials progressed from using ochre solids to converting the ochre into a ferric replacement product, therefore eliminating the need to find a disposal route for the ochre once it has been exhausted and is P-saturated.

This chapter documents the stages of production of ochre-derived ferric (ODF) and the associated trials. These stages are illustrated in Figure 6.1. The methodology relating to the production of ODF and the jar tests completed can be found in Section 3.4 of the Methodology chapter.

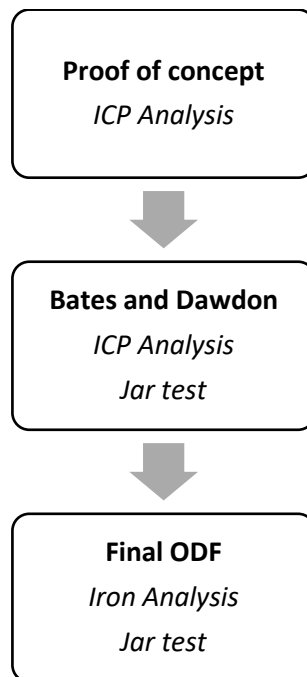


Figure 6.1: Stages of ODF production and their associated analysis and trials

6.2 Methods

The methods used for the following trials are detailed in Section 3.4

6.3 Proof of concept

6.3.1 Results of ochre dissolution experiments with varied acid concentration

The results of the ICP analysis on the produced ODF is shown in Figures 6.2 and 6.3. Although a full suite of elements was analysed using the ICP-MS method, the ICP-AES focused on calcium

(Ca), magnesium (Mg) and iron (Fe). Figures 6.2 and 6.3 both show that (of these elements), Fe is present in the largest concentration, followed by Ca and finally Mg.

Both sets of analysis show a sharp increase in Fe concentration when the acid concentration is increased from 1.5 M to 3 M and a slight decrease when the concentration increases to 6 M. The ICP-MS analysis shows a continuing decrease at 12 M HCl, however, the ICP-AES analysis shows a slight increase in Fe content.

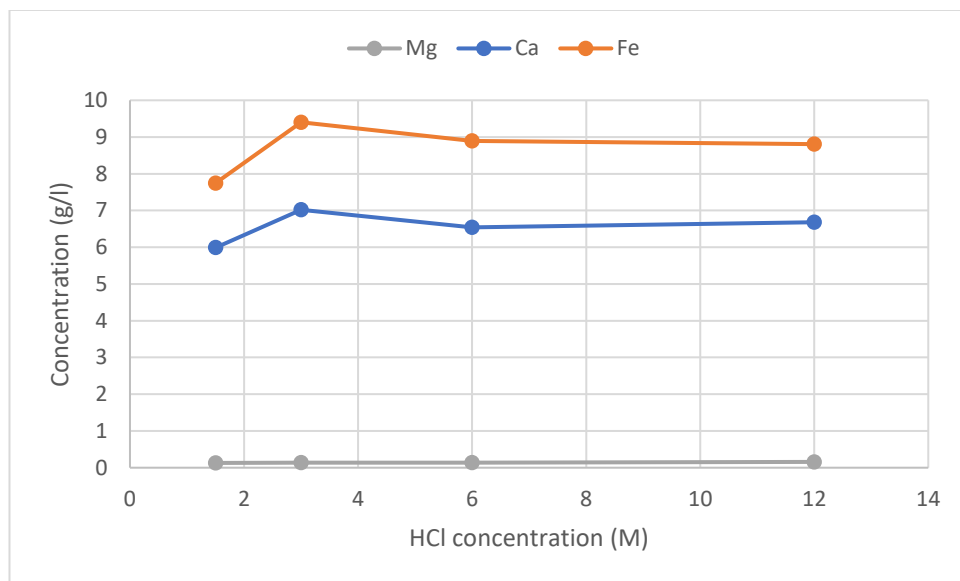


Figure 6.2: Magnesium, calcium and iron concentrations in ochre derived ferric produced using 1.5 M, 3 M and 6 M hydrochloric acid as determined by ICP-MS analysis.

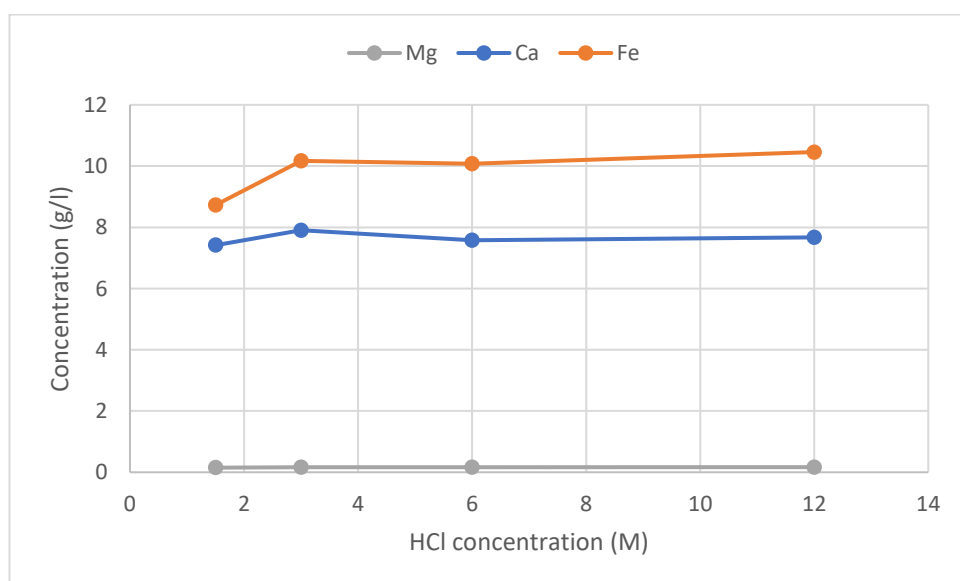


Figure 6.3: Magnesium, calcium and iron concentrations in ochre derived ferric produced using 1.5 M, 3 M and 6 M hydrochloric acid as determined by ICP-AES analysis.

When the Dawdon ochre was dissolved in 3 M HCl, it produced an ODF with an Fe concentration of between 9.4 and 10.2 g/l (for ICP-MS and ICP-AES, respectively). The Ca concentration of this ODF was between 7.0 and 7.9 g/l. The Mg content is less than 0.2 g/l.

6.3.2 Discussion

The ICP analysis results suggest that increasing the acid concentration beyond 3 M does not have a significant impact upon the Fe content of the resulting ODF. This is also seen in the Ca concentration of the ODF. The Mg concentration remains consistent regardless of acid concentration.

According to analysis completed by both Moorhouse and Watson (2015) and Sapsford et al. (2015), the elements present in the largest quantities are iron, calcium and sodium (Na). This was also observed in all of the ODF produced, regardless of acid concentration.

6.4 Bates and Dawdon

6.4.1 ODF Production

6.4.1.1 Results

The results of the ICP-MS analysis show that the elements present in the greatest concentration for both the Bates and the Dawdon ODF solutions were (in order of decreasing concentration) iron, calcium and sodium. These were also the elements present in the greatest concentrations in the proof of concept ODF (Section 6.3.1).

The ICP-MS analysis results for sodium, calcium and iron are shown in Figure 6.4 alongside the ICP-OES results for Fe. From this data, it can be seen that the Bates ODF has a greater iron content than ochre but a lower calcium and sodium content. The ICP-MS results for sodium show a higher concentration in the Dawdon ODF than the Bates ODF; 1177 mg/l compared to 475 mg/l.

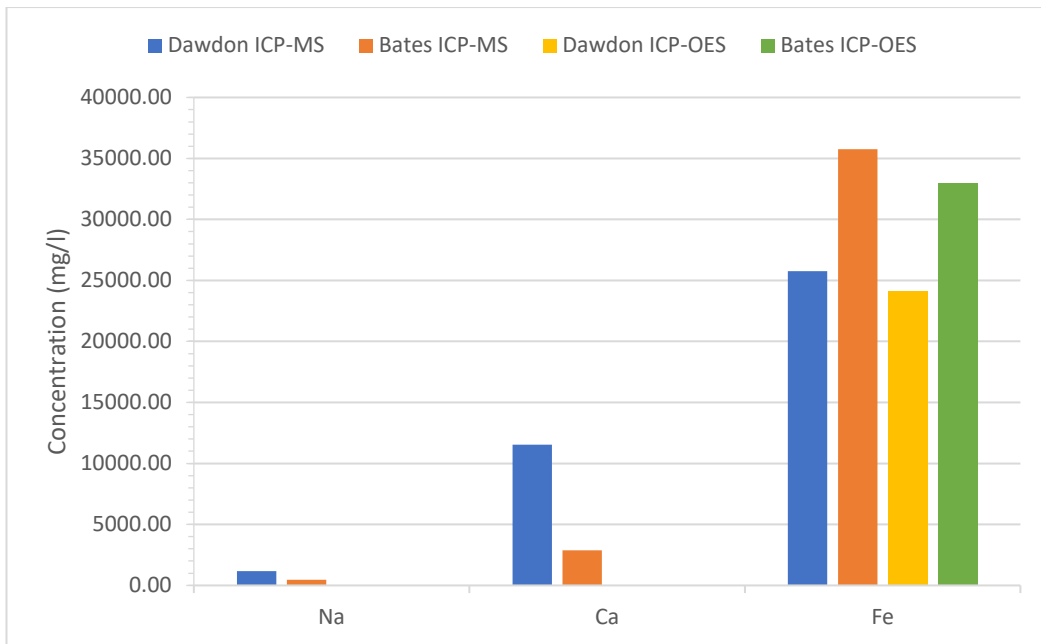


Figure 6.4: Highest concentration elements from ICP-MS analysis with Fe data (from ICP-MS and ICP-OES analysis)

Table 6.1 shows the ICP iron analysis results expressed as a percentage. This allowed a comparison to be made with supplied ferric sulphate. The ferric chloride solutions had approximate Fe contents of 2.5 % and 3.4 % (Dawdon and Bates, respectively). The ferric sulphate supplied for wastewater treatment and used for the jar tests was approximately 12.5 % Fe and therefore the ochre ferric solutions contain approximately one third of the iron found in supplied ferric.

Table 6.1: Iron ICP analysis results

	Average (mg Fe/ml)	Percentage iron (%)
ICP-MS		
Dawdon	25.75	2.575
Bates	35.75	3.575
ICP-OES		
Dawdon	24.15	2.415
Bates	32.95	3.295
Average		
Dawdon	24.95	2.495
Bates	34.35	3.435

6.4.1.2 Discussion

The comparative quantities of iron and calcium of the ODF agree with ochre analysis completed by Moorhouse and Watson (2015) and Sapsford et al. (2015). The low iron concentration of Dawdon ochre is thought to be as a result of the active treatment process at this mine water treatment plant (Sapsford et al., 2015). In the Sapsford et al. (2015) study, Dawdon ochre had an Fe content of approximately a fifth of the Fe content of Bates ochre (6.38 % Fe compared to 31.19 % Fe) and their ochre-derived reagents had similar relative quantities. The ODF produced for this study had Fe contents of approximately 25 g/l and 35 g/l for Dawdon and Bates derived ODF, respectively. To produce these ODF solutions, 6.20 g (dry solids) of Dawdon ochre was dissolved and 5.06 g (DS) of Bates ochre was dissolved and therefore the Fe content of Bates ODF might be expected to be significantly higher than the Dawdon ODF, which is not seen in these results.

The Dawdon ODF had a higher concentration of sodium than the Bates ODF. Moorhouse and Watson (2015) found that the ochre from these sites mirrored this relationship, however, Sapsford et al. (2015) found that Bates ochre had marginally greater concentrations. Both Dawdon and Bates MWTPs treat mine waters which are saline (Moorhouse and Watson, 2015), which could be the reason for the high concentrations of sodium in both the ochre and the ODF produced from the ochre.

6.4.2 Jar tests

The data in this section were produced from the jar tests dosing ochre slurry and ochre derived ferric produced from Bates and Dawdon ochre and ferric sulphate dosed at varying dose rates (60, 300 and 600 mg/L) into raw, screened sewage.

6.4.2.1 Results

Initially, the jar tests were dosed at rates of 60, 300 and 600 mg/L, relating to the volume of ferric or quantity of ochre added and not the iron content. Ferric sulphate was also dosed in the first set of jar tests (at 60 mg/L) to allow a comparison between the supplied ferric and ODF phosphorus removal performance. Figure 6.5 shows the results of these trials. Figures 6.5a and 6.5b show the percentage removal of the four adsorbents.

These results show that the Bates ODF consistently removes a greater percentage of phosphorus (both total and filtered phosphorus) than the Dawdon ODF. However, the Dawdon ochre removes a greater percentage than the Bates ochre.

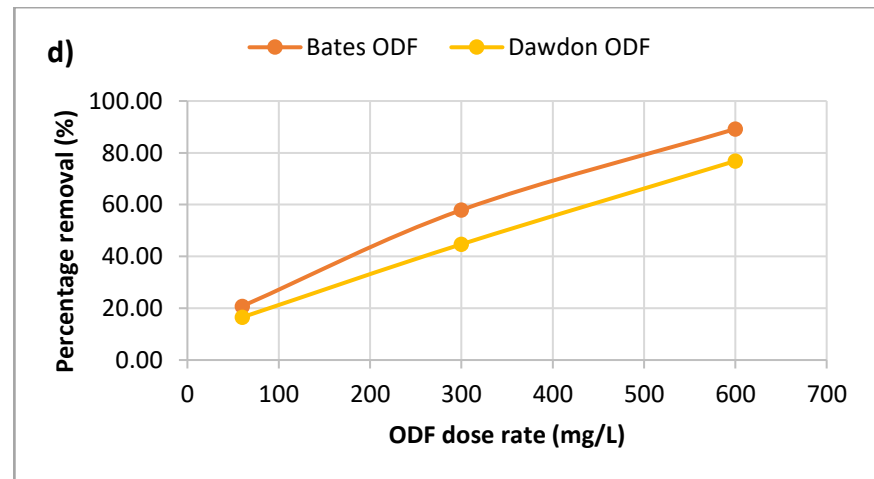
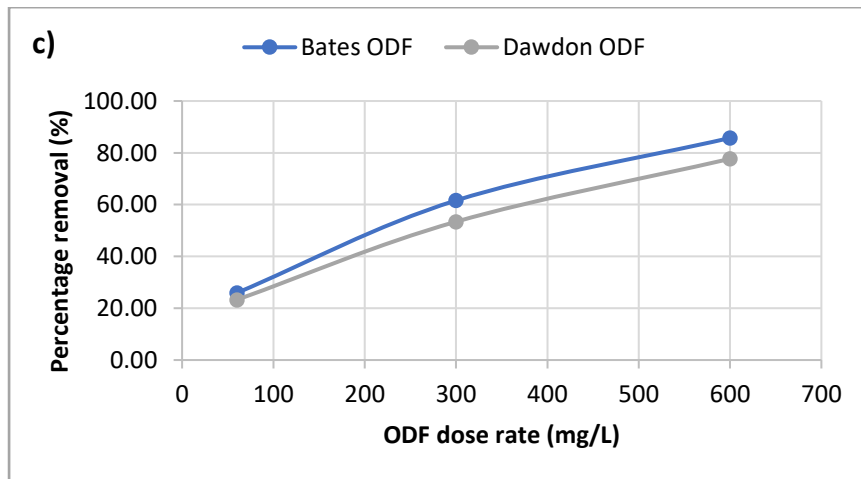
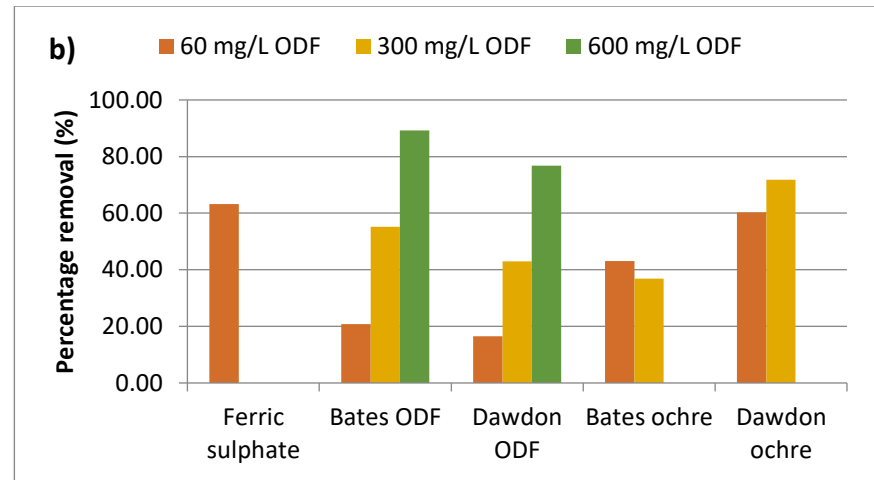
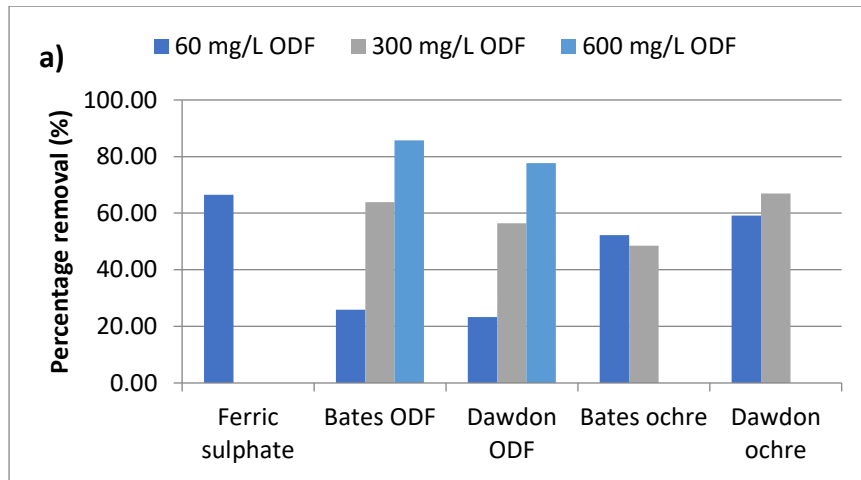


Figure 6.5: Graphs showing (a) percentage removal of total phosphorus; (b) percentage removal of filtered phosphorus; (c) the effect of dose rate on percentage removal of total phosphorus by ODF; (d) the effect of dose rate on percentage removal of filtered phosphorus by ODF

Further trials were completed with an ODF dose rate of 300 mg/L and these were completed in duplicate to determine repeatability.

The results of these trials are shown in Table 6.2 alongside the results for the 300 mg/L dosing in the previous set of jar tests. The initial concentration for these further trials was 9.90 mg/l total P and 5.87 mg/l filtered P, compared to 10.50 mg/l and 6.78 mg/l for the previous trial. The results show that percentage removal was similar on the duplicates but slightly decreased with the lower initial phosphorus concentration.

Table 6.2: Results from trials with 300 mg/L dose rate of ochre derived ferric (ODF)

	A		B		Previous trial	
	Percentage removal		Percentage removal		Percentage removal	
	Total P	Filtered P	Total P	Filtered P	Total P	Filtered P
Bates ferric	60.00	59.63	60.91	58.94	63.90	55.16
Dawdon ferric	51.92	45.14	51.82	46.00	56.48	42.92

The dose rates for the ferric sulphate and ODF solutions were converted from mg of ochre derived ferric per litre to mg Fe/l and plotted against percentage removal of phosphorus (Figures 6.6a and 6.6b). These graphs show that as dose rate increases, so does the percentage removal of phosphorus by the ODF solutions and that this is true for both total and filtered phosphorus. The graphs also show that when the Dawdon ODF is dosed at approximately the same rate as the ferric sulphate (between 7 and 7.5 mg Fe/l), the Dawdon ODF does not remove as much total or filtered phosphorus as the ferric sulphate.

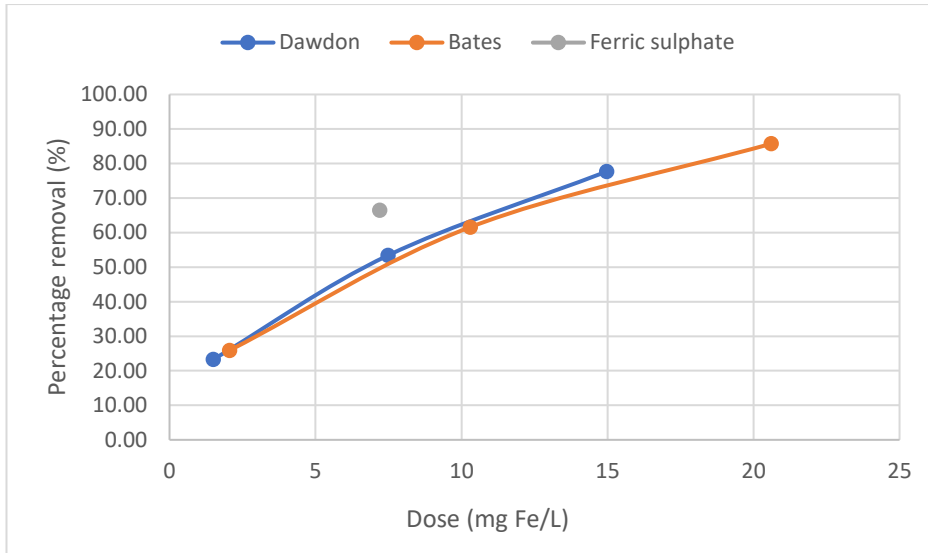


Figure 6.6a: Graph showing percentage removal of total P against mg Fe/l dose of ferric solution

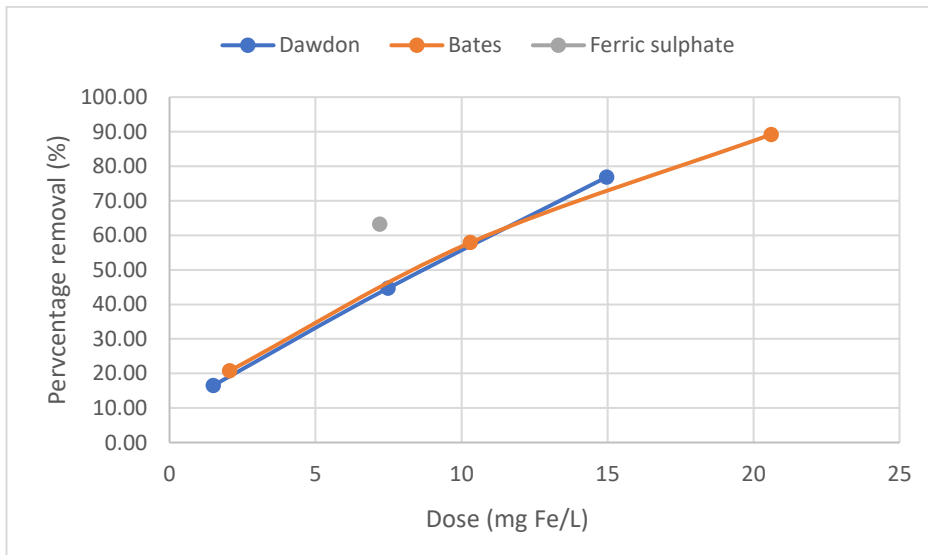


Figure 6.6b: Graph showing percentage removal of filtered P against mg Fe/l dose of ferric solution

Figure 6.7a and 6.7b show the percentage removal of phosphorus per mg of iron dosed, this is again plotted against dose rate expressed as mg Fe per litre. The results show that for both total and filtered phosphorus, the percentage removal per milligram of iron decreases as dose rate increases and that this is not a linear relationship.

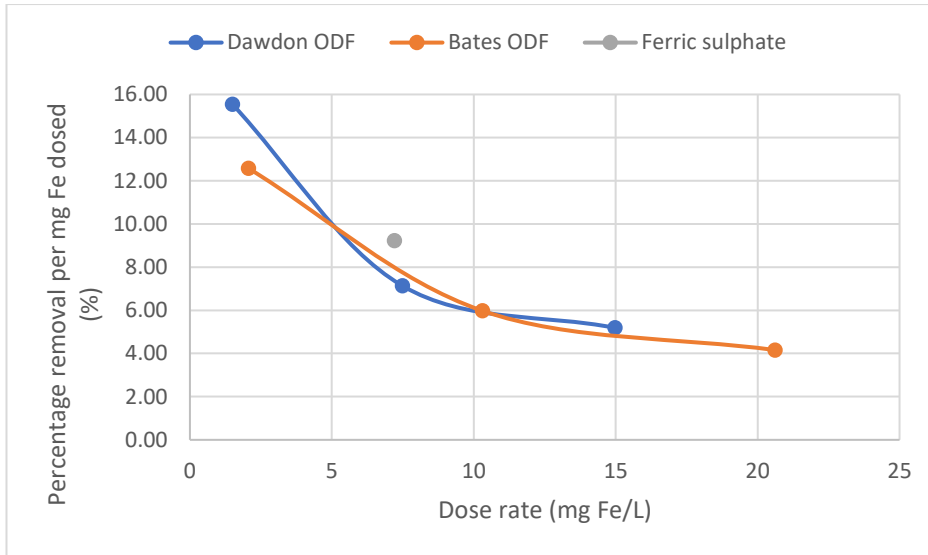


Figure 6.7a: Total P removal per mg Fe dosed per litre

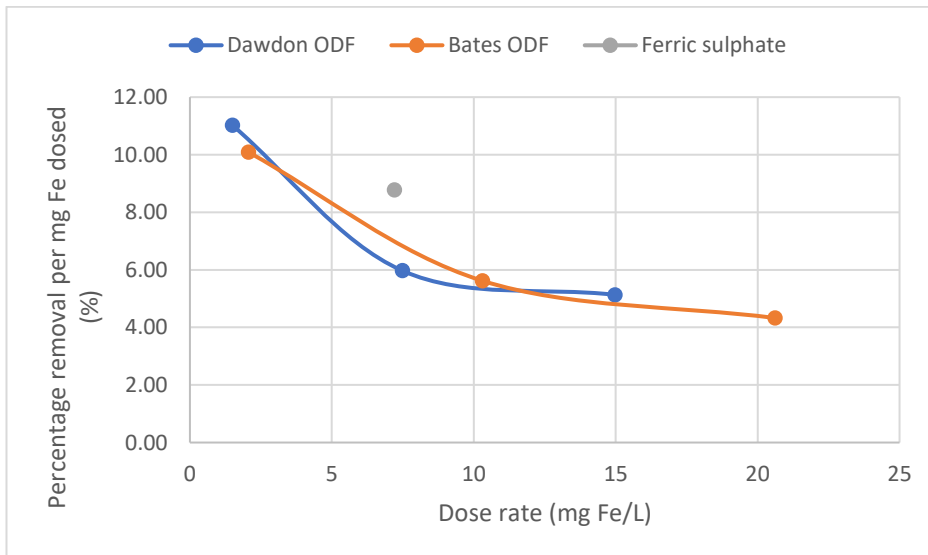


Figure 6.7b: Filtered P removal per mg Fe dosed per litre

6.4.2.2 Discussion

The jar test results suggest that the Bates ODF is more efficient at removal phosphorus than the Dawdon ODF, whilst the Dawdon ochre is more efficient than the Bates ochre. The ICP results show that the Bates ODF had a greater iron content and therefore it may be expected to have improved phosphorus removal in comparison to the Dawdon ODF. The Dawdon ochre, on the other hand, has a lower iron content than Bates ochre but it has a much greater concentration of calcium, which may improve phosphorus removal. Both ochres and both ODF solutions exhibited higher percentage removal of filtered phosphorus than total phosphorus.

The percentage removal by the two ODF solutions was less than half of the removal by the ferric sulphate (Figures 6.5a and 6.5b) when dosed at the same rate (60 mg/L). However, this may be as a result of the much lower iron content of the ODF compared to the ferric sulphate.

Figures 6.5c and 6.5d show the relationship between dose rate (mg/L) and percentage removal of phosphorus. As expected, the percentage removal of both total and phosphorus increases with increasing dose rate.

The results of the jar test suggest a much greater dose will be needed to achieve greater percentage removal and therefore meet the tightest effluent phosphorus limits. This is shown in Figures 6.7a and 6.7b which show a decrease in removal per milligram of iron dosed as iron dose rate increases. This relationship between coagulant dose and removal efficiency has previously been noted by Szabó et al. (2008) and Keeley et al. (2016).

6.5 Final Ochre Derived Ferric (ODF)

6.5.1 ODF Production

6.5.1.1 Results

The iron content of the ODF solutions was analysed using two techniques. First the Fe content was estimated by diluting and analysing the solutions using bench-top analysis kits and a spectrophotometer. This analysis was completed in triplicate and a mean iron content was calculated. The solutions were also submitted to a commercial laboratory for ICP analysis. For each ochre source, there were 3 ODF solutions and therefore there were 15 solutions analysed.

Figure 6.8 shows the results for each of these solutions. The graphs show that the two techniques generally agree although there is more discrepancy between the two techniques on Saltburn ODF solutions. However, the bench-scale also shows much more variation between the three Saltburn ODF solutions than seen in the laboratory analysis.

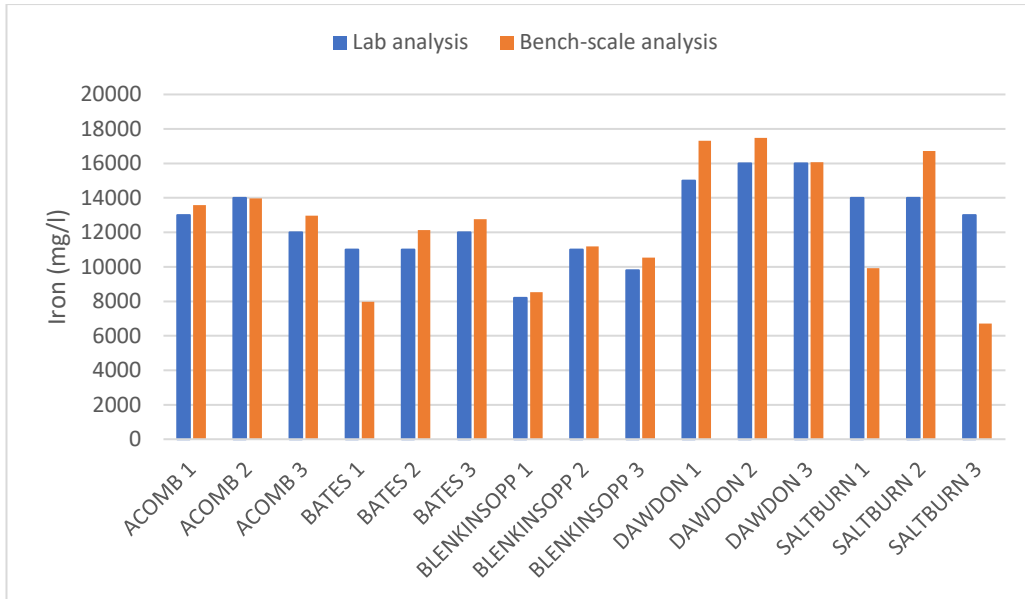


Figure 6.8: Fe analysis results for the 15 ODF solutions

An average (mean) Fe content was calculated for each ODF source and these are shown in Figure 6.9.

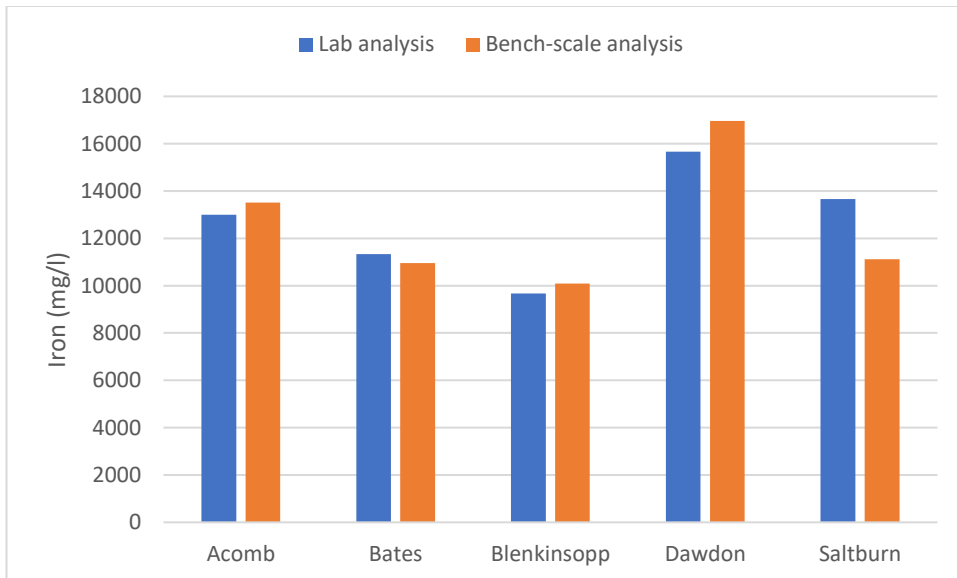


Figure 6.9: Average Fe for each ochre source (MWTP)

The two analysis methods again show similar results with more discrepancy between the results for the Saltburn ODF. The ODF with the greatest Fe content is that derived from Dawdon ochre, whilst the Blenkinsopp ODF had the lowest Fe content.

Figure 6.10 shows the relationship between the ochre dry solids dissolved into the acid and the iron content of the ODF produced. The dry solids were calculated based on the quantity of ochre added and dissolved to produce the ODF along with the moisture content of the ochre. These data are shown in Table 6.3. Figure 6.10 suggests that there is a positive correlation between dry solids dissolved and the Fe concentration of the ODF. However, the Dawdon ochre and ODF does not fit the same trend, potentially due to the presence of carbonate.

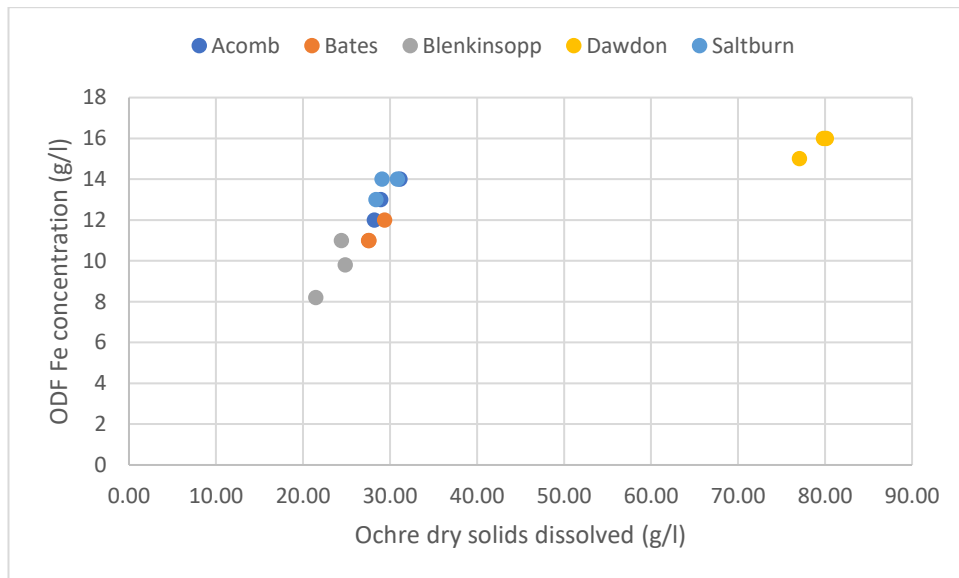


Figure 6.10: The relationship between ochre dry solids dissolved and the Fe content of the resulting ODF solution

The maximum dry solids (DS) equivalent of ochre to be dissolved in 3M HCl was 80.14 g/l of Dawdon ochre (see Table 6.3). The minimum was 12.46 g/l for Blenkinsopp ochre.

Table 6.3: The quantity of ochre added to produce each ODF solution.

ODF	Ochre solids added	Ave. %MC	DS equivalent
	(g/l)	(%)	(g/l)
Acomb 1	97.22	70.24	28.93
Acomb 2	104.59	70.24	31.13
Acomb 3	94.75	70.24	28.20
Bates 1	82.41	66.60	27.52
Bates 2	82.51	66.60	27.56
Bates 3	87.99	66.60	29.39
Blenkinsopp 1	72.95	70.58	21.46
Blenkinsopp 2	83.02	70.58	24.42
Blenkinsopp 3	84.50	70.58	24.86
Dawdon 1	141.29	45.47	77.05
Dawdon 2	146.38	45.47	79.82
Dawdon 3	146.96	45.47	80.14
Saltburn 1	78.75	63.05	29.10
Saltburn 2	83.49	63.05	30.85
Saltburn 3	76.77	63.05	28.37

6.5.1.2 Discussion

The two analysis methods show some discrepancies in results for the Saltburn ODF. As the ODF solutions were diluted to within the range of the analysis kits, the results had to be adjusted to account for the dilution, and therefore there could have been some error in the dilution and/or calculation. Alternatively, the Saltburn ODF may be more heterogeneous than the other ODF solutions. Without further analysis, it is not possible to determine the cause of these discrepancies.

The results show a positive correlation between the ochre solids dissolved and the resulting ODF Fe content. The Dawdon ochre and ODF does not fit the same trend, which may be as a result of the low iron content of the ochre and therefore more ochre solids need to be dissolved to produce an ODF with an Fe content equivalent to an ODF from an ochre with a higher

content. The low iron of Dawdon ochre was noted as part of the work completed by Sapsford et al (2015).

The maximum dry solids dissolved as part of the ODF production was 80.14 g/l of Dawdon ochre in 3M HCl. Sapsford et al. (2015) determined a maximum solubility of 100 g/l and therefore it may be possible to dissolve more ochre solids and consequently increase the Fe content of the ODF solutions.

6.5.2 Jar tests

6.5.2.1 Results

Four sets of jar tests were completed with repeats using six coagulants (five ODF solutions and a ferric sulphate solution). The percentage removal for each of these coagulants and each of these sets are shown in Figures 6.11 and 6.12. The raw effluent analysis results for each set of jar tests are detailed in Table 6.4. This analysis shows that the three batches of raw effluent collected were all similar in composition and therefore the initial conditions were similar for all of the jar tests.

Table 6.4: Analysis results of the raw effluent samples which were used in each of the jar test sets. The raw effluent was analysed for pH, total iron, total phosphorus (TP) and soluble reactive phosphorus (SRP).

Jar test set(s)	pH	Total Fe	TP	SRP
		mg/l	mg/l	mg/l
1 and 2	7.922	2.19	6.28	2.62
3	7.825	1.73	5.83	3.01
4	7.797	1.8	5.66	2.57

It was found that the ODF solutions are capable of removing similar levels of phosphorus as the ferric sulphate as shown in Figures 6.11 and 6.12. However, it should be noted that the ferric sulphate was dosed at approximately a quarter of the rate of the ODF solutions (in terms of Fe). These dose rates are detailed in Table 6.5.

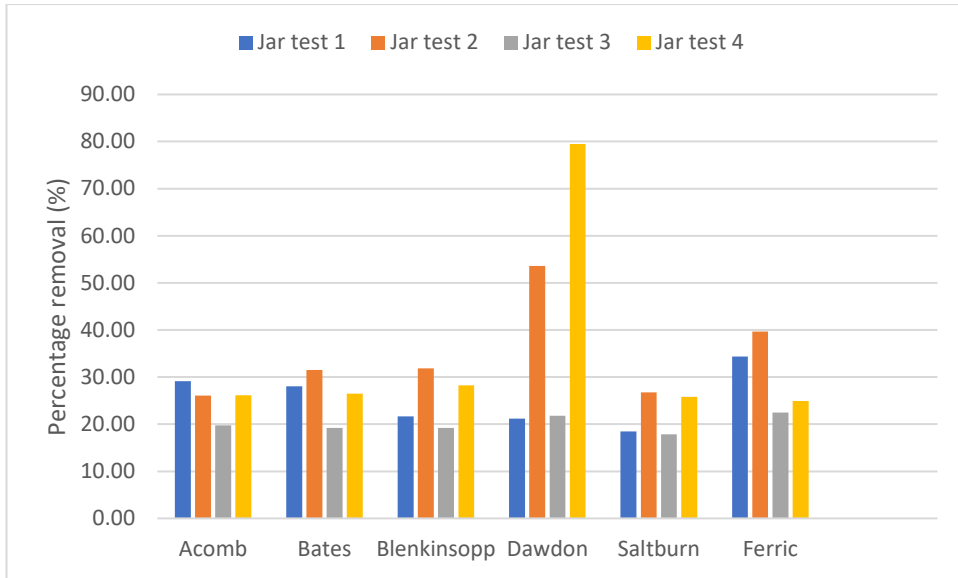


Figure 6.11: Percentage removal of total phosphorus (TP) by the five final ochre derived ferric (ODF) solutions and ferric sulphate.

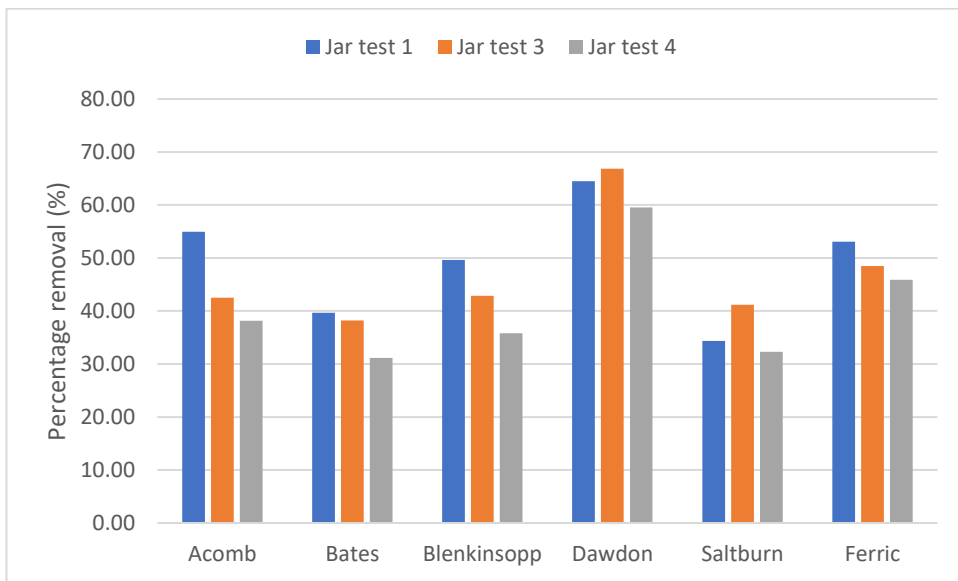


Figure 6.12: Percentage removal of soluble reactive phosphorus (SRP) by the five final ochre derived ferric (ODF) solutions and ferric sulphate.

Table 6.5: Dose rates of each coagulant for the jar tests

	Iron dose rate (mg/l)
Acomb ODF	9.94
Bates ODF	9.96
Blenkinsopp ODF	10.01
Dawdon ODF	9.44
Saltburn ODF	8.26
Ferric sulphate	2.5

The ODF solutions demonstrated greater removal of soluble reactive phosphorus (SRP) than total phosphorus (TP), for all the ochre sources.

The total phosphorus removal exhibited by the Dawdon ODF was highly variable. However, the SRP removal by this ODF was much more consistent across the three trial sets. The average percentage removals (shown in Table 6.6) show that Dawdon had the greatest average removal (44 % TP and 64 % SRP) despite the variability in removal. The ODF with the lowest average percentage removal was Saltburn (22 % TP, 36 % SRP), followed by Bates (26 % TP, 45 % SRP).

Table 6.6: Percentage phosphorus removal averaged across all four sets of jar tests

	Average percentage removals (%)	
	Total phosphorus	Soluble reactive phosphorus
Acomb ODF	25.28	45.21
Bates ODF	26.30	36.34
Blenkinsopp ODF	23.05	42.76
Dawdon ODF	44.01	63.64
Saltburn ODF	22.22	35.95
Ferric sulphate	30.36	49.16

No apparent correlation was found between pH and average percentage phosphorus removal for either TP or SRP (Figures 6.13 and 6.14). The results demonstrate that ferric sulphate had the least impact upon pH of all the coagulants with the pH after the trials remaining between 7 and 8. The ODF solutions reduced pH to between pH 6 and 7. Of these ODF solutions, Blenkinsopp reduced pH the most (to a minimum of approximately pH 6.2).

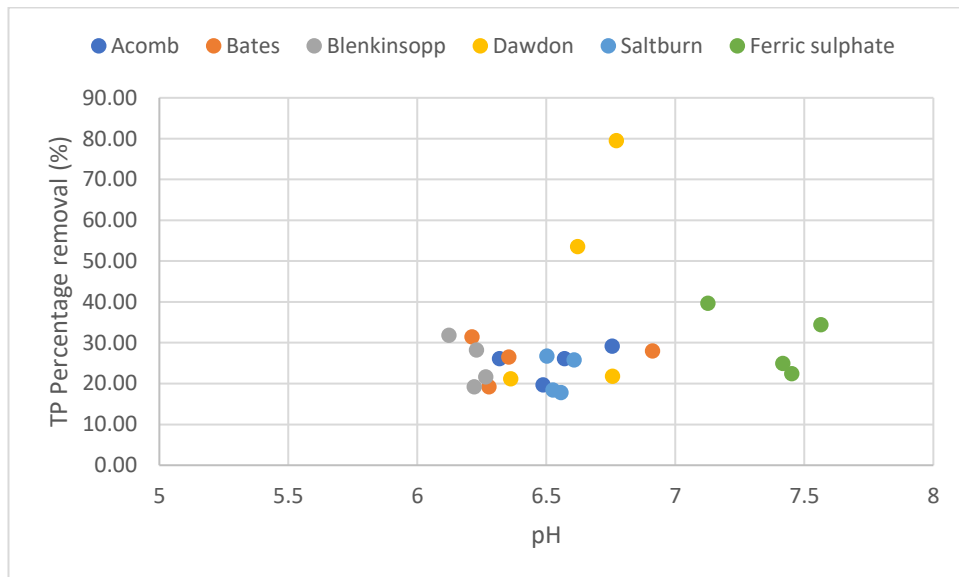


Figure 6.13: Relationship between total phosphorus removal and pH when dosing ODF solutions (initial effluent pH was between 7.1 and 7.9)

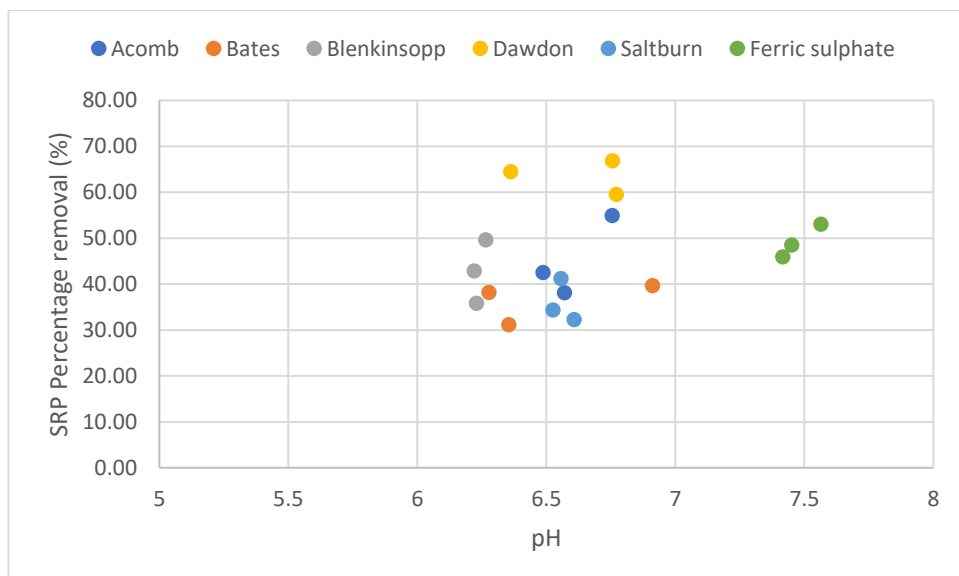


Figure 6.14: Relationship between soluble reactive phosphorus removal and pH when dosing ODF solutions (initial effluent pH was between 7.1 and 7.9)

Table 6.7 details the residual iron after the jar tests for each coagulant. The raw effluent iron content is also included for comparison. The raw iron was approximately 2 mg Fe/l and this was increased to a maximum of approximately 11 mg/l after contact with the Blenkinsopp ODF (when discounting the above detection reading for the Acomb ODF jar). Blenkinsopp ODF was also dosed at the highest rate (10.01 mg Fe/l). The ferric sulphate resulted in a residual to a maximum of 6.65 mg Fe/l whilst the ODF coagulants increase effluent Fe to between 9.35 and 10.8 mg Fe/l, however, the ferric sulphate dose rate was almost a quarter of the ODF doses.

Table 6.7: Iron content of the raw effluent, which represents the initial iron concentration prior to each of the jar tests (1, 3 and 4). The residual iron is the iron concentration of the effluent after the jar tests with Acomb, Bates and Blenkinsopp ochre derived ferric (ODF) at the dose rate stated.

	1	3	4	Iron dose rate (mg/l)
Raw effluent iron (mg/l)	2.19	1.73	1.8	
	Residual iron (mg/L)			
Acomb ODF	above detection	10.5	10.1	9.94
Bates ODF	9.93	9.74	9.43	9.96
Blenkinsopp ODF	10.8	9.9	10.2	10.01
Dawdon ODF	10.4	10.26	10.3	9.44
Saltburn ODF	9.59	9.34	9.35	8.26
Ferric sulphate	6.65	6.4	6.45	2.5

The percentage removals from the trials completed in triplicate are shown in Figures 6.15 and 6.16 and are plotted against pH. The dose rates were the same as those previously trialled and therefore the ferric sulphate dose rate was approximately a quarter of the ODF dose rates. No iron analysis was completed as part of these trials.

From Figures 6.15 and 6.16, it can be seen that the ODF and ferric solutions removed a greater percentage of SRP than TP. It also shows that the removal of each ODF is consistent and each ODF is distinctive in terms of removal, with the results grouped together on the graph. The Blenkinsopp ODF resulted in the lowest pH (approximately 5.5) and the highest percentage removal of both TP and SRP.

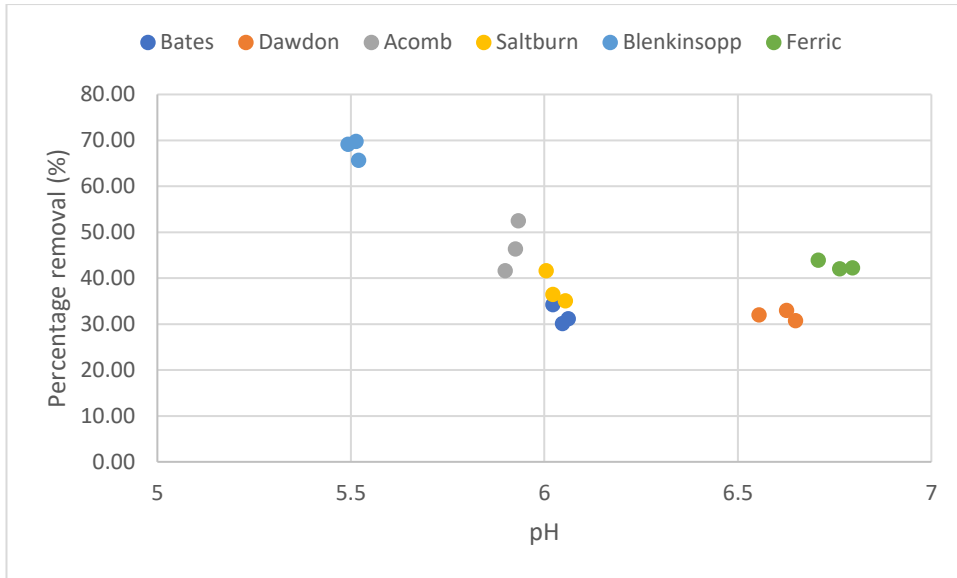


Figure 6.15: Relationship between total phosphorus removal and pH when dosing ODF solutions in triplicate (initial effluent pH was between 6.9 and 7.7)

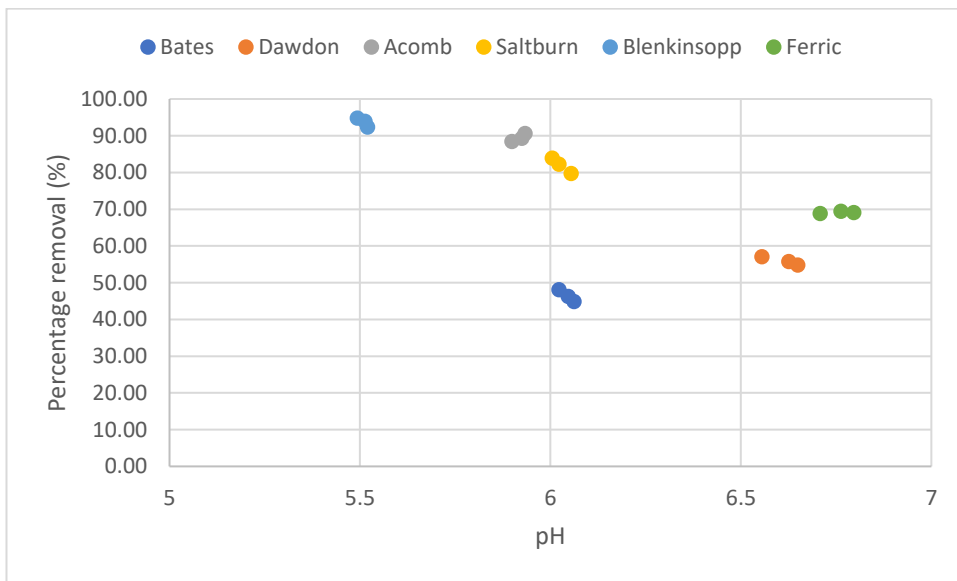


Figure 6.16: Relationship between soluble reactive phosphorus removal and pH when dosing ODF solutions in triplicate (initial effluent pH was between 6.9 and 7.7)

The average percentage removal for each coagulant can be seen in Table 6.8. On average, the Blenkinsopp ODF removed 68 % TP and 94 % SRP. Blenkinsopp and Acomb ODF solutions both exhibited removals greater than the ferric sulphate, however, it should be noted that the ferric sulphate was dosed at approximately a quarter of the iron dose. Three ODF solutions reduced the pH to approximately 6, however, the removal of these solutions ranged from 46 % TP (89 % SRP) to 32 % TP (46 % SRP).

Table 6.8: Average percentage removal of total phosphorus (TP) and soluble reactive phosphorus (SRP) and iron dose rate of each coagulant in jar test set 4. Five ochre derived ferric (ODF) solutions were trialled alongside ferric sulphate. These jar tests were completed in triplicate and the average (mean) removal was calculated.

	Average percentage removal (%)		Iron dose
	TP	SRP	mg/l
Acomb ODF	46.83	89.47	9.94
Bates ODF	31.84	46.42	9.96
Blenkinsopp ODF	68.18	93.70	10.01
Dawdon ODF	31.91	55.90	9.44
Saltburn ODF	37.71	81.96	8.26
Ferric sulphate	42.72	69.11	2.5

Table 6.9 details the average milligram removal of phosphorus per milligram of iron dosed for each coagulant. This was calculated to allow a direct comparison between the performance of the ODF and the ferric sulphate solutions. The results show that ferric sulphate, on average, removed 0.825 mg TP per mg Fe dosed and 0.478 mg SRP per mg Fe dosed. Of the ODF solutions trialled, Blenkinsopp exhibited the best total phosphorus removal per milligram of iron, removing 0.329 mg and Saltburn removed the most soluble reactive phosphorus (0.174 mg SRP/mg Fe). Bates ODF removed the least phosphorus per milligram of iron (0.157 mg TP/mg Fe and 0.081 mg SRP/mg Fe).

Table 6.9: Average removal of total phosphorus (TP) and soluble reactive phosphorus (SRP) (in milligrams) per milligram of Fe dosed. The iron was dosed in the form of ochre derived ferric (ODF) or ferric sulphate. The jar tests (jar test set 4) was completed in triplicate and the average (mean) removal was calculated.

	Average mg phosphorus removed per mg of iron dosed	
	TP	SRP
Acomb ODF	0.208	0.158
Bates ODF	0.157	0.081
Blenkinsopp ODF	0.329	0.162
Dawdon ODF	0.166	0.102
Saltburn ODF	0.202	0.174
Ferric sulphate	0.825	0.478

The residual TP shows a positive correlation with pH (Figure 6.17) but the relationship is not as strong between residual SRP and pH (Figure 6.18). The results in Figure 6.17 show that Blenkinsopp ODF consistently reduced TP concentrations to less than 2 mg/l.

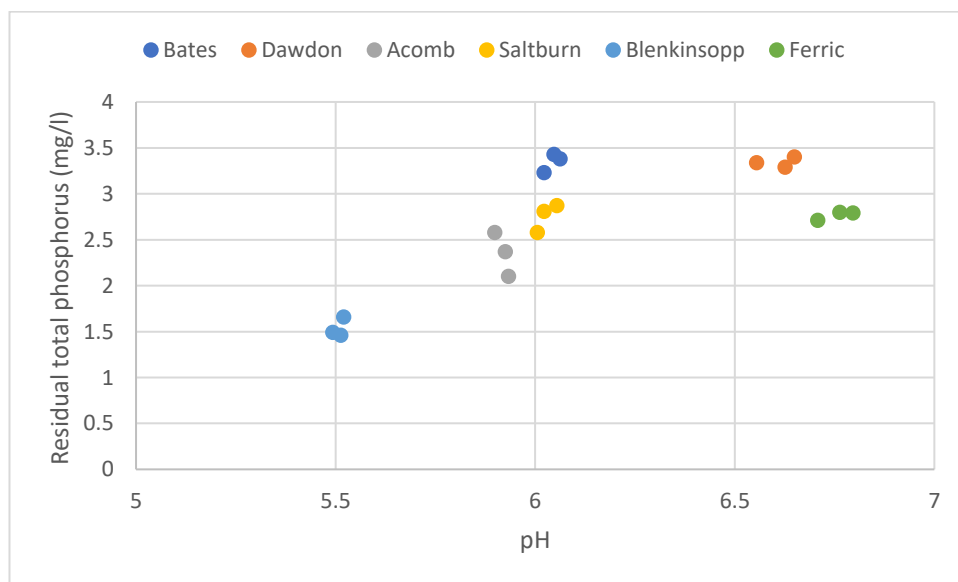


Figure 6.17: Relationship between residual total phosphorus and pH (initial effluent pH was between 6.9 and 7.7)

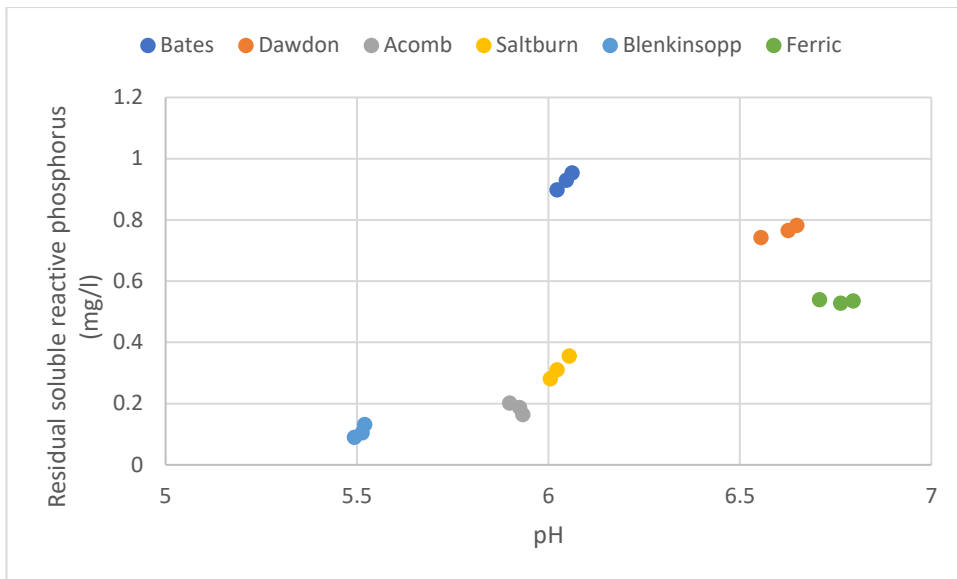


Figure 6.18: Relationship between residual soluble reactive phosphorus and pH (initial effluent pH was between 6.9 and 7.7)

The triplicate trials did not include any residual iron analysis.

6.5.2.1 Discussion

Increasing the Fe dose increases the residual Fe in the effluent, as would be expected. Further treatment of the effluent may be required to remove this additional Fe, depending on the dosing location in the treatment process, any impact this may have on other treatment processes and the site specific permit. If the ODF solution is dosed at the front end of the site, it would be expected that some of the iron (particularly that present as particulates) would be removed by the subsequent treatment processes before reaching the final effluent discharge point.

The results of the triplicate results do not agree with the previous jar tests investigating these ODF solutions (without repeats) as the Dawdon ODF results are also more consistent. The reason for this change in consistency cannot be determined from these trials and their results but may be as a consequence of the wastewater composition or other conditions which have not been recognised in these trials.

In the triplicate trials, the ODF solutions did not remove as much phosphorus as ferric sulphate based on the milligrams of phosphorus removed per milligram of iron dosed. The ferric sulphate removed over twice as much total phosphorus and soluble reactive phosphorus per milligram of iron dosed than the ODF solutions. The results also suggest that the removal of total

phosphorus per milligram of iron dosed is greater than the removal of soluble reactive phosphorus when dosing ferric sulphate and ODF solutions. This suggests that that more iron would have to be dosed in the form of ODF than ferric sulphate in order to achieve the same phosphorus removal.

Based on the triplicate trial results, the Blenkinsopp ODF may be suitable for application on a sewage treatment works (STW) with a 2 mg/l total phosphorus permit when dosed at approximately 10 mg Fe/l, however, pH correction may be required. In these trials, Blenkinsopp reduced pH to approximately 5.5. Further trials with all the ODF solutions would be required to determine if any of the other ODF solutions are also capable of meeting a 2 mg/l phosphorus limit and whether any would be suitable for meeting tighter limits (such as 1 mg/l or below). These trials would also need to monitor the pH of the effluent to determine if pH correction would be required.

The triplicate trials did not include any residual iron analysis and therefore the impact of the ODF solutions on effluent iron concentrations is not known. This would need to be considered prior to application at a STW.

The initial pH of the effluent used in the triplicate experiments fell between 6.9 and 7.7 and the addition of the ODF solution reduced this pH to between 6.8 and 5.5 with greater phosphorus removal at lower pH. Fytianos et al. (1998) found that a pH of 4.5 resulted in the greatest phosphorus removal and the trial results in this study show that the greatest phosphorus removal occurred between pH 5.5 and pH 4. This suggests that the removal of phosphorus when using the ODF solutions could be further improved if pH was lowered to within this range.

6.6 Chapter Conclusions and Recommendations

Figure 6.19 summarises the variables tested in this chapter. Two variables were tested as part of the ochre derived ferric (ODF) production, which then affected the characteristics of the ODF solutions. The ODF dosing trials were then based upon these ODF characteristics. These variables and factors impacted on the wastewater quality in terms of phosphorus, pH and iron content.

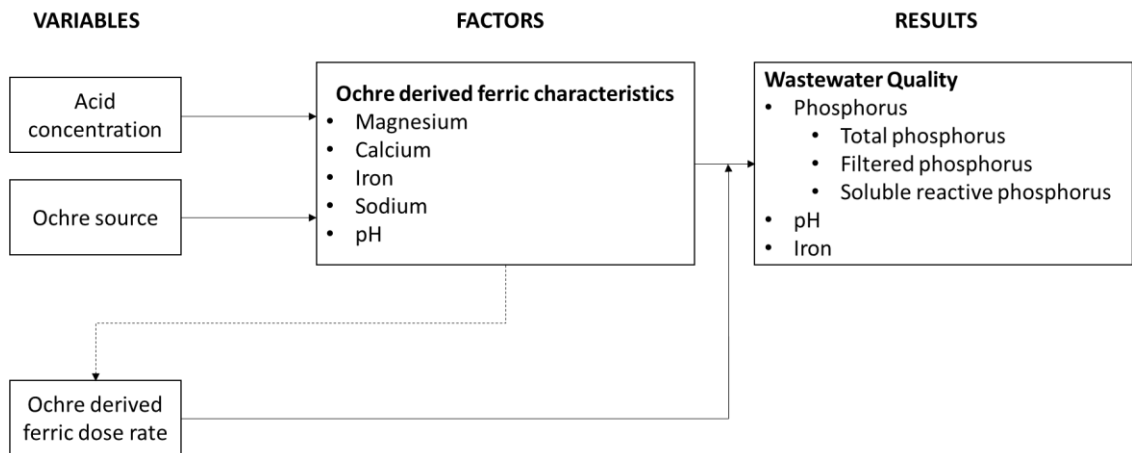


Figure 19.19: Model summarising the tested variables, factors (uncontrolled variables) and results considered in the ochre derived ferric (ODF) dosing trials.

The proof of concept trials were completed to identify the concentration of hydrochloric acid (HCl) required to produce an ODF with the greatest iron content. The ODF solutions were produced using a constant wet weight of ochre and a constant volume of acid. The results of this production trial suggested that increasing the HCl concentration above 3M does not significantly increase the iron content of the ODF solution. However, this was completed on a single ochre sourced from Dawdon MWTP and without repeats. Therefore further trials would be required to verify these results and ochre from other sites should also be considered.

Based on the results of the proof of concept trials, ODF was produced using 3M HCl and ochre from Bates and Dawdon MWTPs. A constant volume of acid was used. However, ochre was added until it no longer dissolved, and the solution was believed to be saturated. These ODF solutions were then trialled against ferric sulphate. When dosed at an equivalent dose rate it was found that ODF solutions were not as effective as the ferric sulphate. However, the results from ICP analysis of the ODF suggests this may be as a result of the lower iron content of these solutions (2.5 – 3.5 % Fe compared to 12 % Fe). The iron equivalent dose (mg Fe dosed per l) suggests that the percentage removal by the two ODF solutions is similar, however, the iron content of the Dawdon ODF is lower and therefore a larger volume of Dawdon ODF would be required to achieve the percentage removal exhibited by the Bates ODF. When comparing the ODF solutions with ferric sulphate on an iron dose, the ODF solution removes slightly less phosphorus (both TP and SRP).

Further ODF solutions were produced using ochre from five MWTPs across the North East. These ODF solutions were produced in the same way as the previous Bates and Dawdon ODF

solutions. The results suggest that there is a positive correlation between dry solids dissolved and the ODF Fe content, however the low iron content of Dawdon ochre results in a greater quantity of dry solids required to achieve equivalent iron contents with other sources. The jar tests completed suggest the ODF solutions have a greater impact on the pH of the wastewater than the supplied ferric sulphate. This impact needs to be further investigated and considered prior to application on a STW. The pH will need to be monitored during any onsite application to avoid negatively impacting downstream biological processes and the final effluent quality. It may be necessary to implement pH adjustment.

The jar tests completed without repeats suggest that removal efficiency of the ODF solutions can be variable, particularly for ODF solutions produced using Dawdon ochre. However, the removal of SRP was consistently greater than TP for all of the ODF solutions and the ferric sulphate. The trials showed a positive correlation between residual iron and the iron dose of the ODF solutions. This iron may be removed by subsequent treatment processes if dosed at the front end of a works. However, the iron content of the wastewater would need to be monitored across the treatment process to avoid high levels of iron being released into the environment via the final effluent potentially resulting in a breach of permit conditions, should there be an iron limit in place.

The jar tests completed in triplicate suggest that the removal efficiency is more consistent than suggested in the previous trials, although it is not possible to account for this discrepancy based on the analysis completed as part of this study. The results of these jar tests suggest that the Blenkinsopp ODF may be suitable for meeting a 2 mg/l TP permit. However, the ODF reduced the pH to 5.5 and pH adjustment may be required at any site implementing this ODF. No iron analysis was completed as part of these trials; however, the residual iron would also be an important factor to consider prior to any onsite application as the previous trials suggest that the application of ODF will increase the Fe content of the wastewater.

The removal of phosphorus per milligram of iron dosed suggests that ODF is not as effective as ferric sulphate and therefore it would be necessary to dose more ODF on an iron basis to achieve the same removal.

The work completed in this study has provided an initial investigation into the production of ochre-derived ferric (ODF) solutions and their potential for the removal of phosphorus from wastewater.

Based on the results of the trials in this chapter, it is recommended that:

- The impact of acid concentration on ODF Fe content is further investigated for Dawdon ochre and other ochres within the region to determine if the iron content of the ODF solutions could be increased with a more concentrated acid.
- The relationship between dry solids of ochre dissolved and the ODF Fe concentration should be further investigated and the maximum solubility for each ochre should also be determined for both dried and undried ochre solids. The impact of ochre water content could also be determined.
- Jar tests with ODF solutions are completed with different initial phosphorus concentrations. Other constituents within the wastewater and any potential competing ions should be monitored.
- Jar tests should be completed to determine what P permit limit could be met using ODF solutions, the potential dose of ODF which would be required to meet this limit and the impact of these solutions on effluent quality with particular focus on pH, iron and heavy metals.

7. Onsite trial using ochre derived ferric for phosphorus removal

7.1 Introduction

This chapter focuses on further testing the efficiency of phosphorus removal using ochre derived ferric (ODF) solutions by conducting a preliminary trial onsite at a sewage treatment works (STW) ahead of more extensive testing later in 2018. Previous onsite trials using ochre have focused on using ochre solids as part of filter systems. There have been no previous trials using an ochre derived coagulant at a STW.

Prior to the onsite trial, further jar tests were undertaken using raw effluent collected from the trial site. The jar tests were designed to determine an ideal dose rate for the onsite trial as well as identify any potential impact dosing the ODF solution may have on wastewater quality. The jar test methodology is described in Section 3.5.1.

The site chosen for the trial was a filter works with two square primary tanks (PSTs), each with a retention time of between 1.3 and 7.8 hours, depending on the flow rate into the works. The site does not currently have a phosphorus limit for its final effluent discharge. The methodology used for this onsite trial can be found in Section 3.5.2.

7.2 Methods

The methods used for the following trials are detailed Section 3.5.

7.3 Jar Tests

7.3.1 Results

The graphs in Figure 7.1 illustrate the relationship between Fe dose and pH and residual phosphorus for the four sets of jar tests completed.

All the completed jar tests showed that the pH of the effluent decreased as the ODF dose increased. The relationship appears to be almost linear in Figure 7.1a, where the increments between the dose rates was much larger than the following jar tests. Figures 7.1b, 7.1c and 7.1d show the relationship between ODF dose and pH in more detail.

During these tests, dosing at a rate of 40 mg Fe/l achieved a residual TP of 2.44 mg/l and 0.419 mg SRP/l. These trials produced a general curve of phosphorus removal (as shown in Figure 1a) and suggested that dose rates above 40 mg Fe/l, the residual phosphorus begins to increase

again. The following jar tests (Figure 7.1b to 7.1d) were dosed at smaller increments and give a more detailed view of the phosphorus removal curve up to a maximum dose rate of 50 mg Fe/l.

Figures 7.1b and 7.1d generally exhibit maximum removal of both TP and SRP at a dose rate of 31.68 mg Fe/l. At this dose rate, the percentage removal was 94.03 to 95.78 % for TP and 98.37 to 99.69 % for SRP, resulting in residual TP and SRP of less than 1 mg/l. When dosing at 31.68 mg Fe/l, the pH of the effluent was reduced to between 3.218 and 3.9968.

Although the trial in Figure 7.1b exhibited the best SRP removal at this dose rate, there was a minor improvement in TP removal when ODF was dosed at 35.68 mg Fe/l with percentage removal increasing from 94.03 % to 94.8 %. Increasing the dose rate from to 35.68 mg Fe/l resulted in a pH reduction from 3.968 to 3.317.

There is no alkalinity data for the first jar test but Figures 7.2a to 7.2c shows the relationship between increasing Fe dose, pH and alkalinity. These results show that the alkalinity decreases as pH decreases and dose rate increases. When the pH of the effluent is between 3 and 5, the alkalinity can be reduced to as little as 0 mg/l CaCO₃ (as seen in Figure 7.2d).

Figure 7.3 shows residual Fe and P against increasing Fe dose. At doses of less than 25 mg Fe/l the residual iron fluctuates, whereas it increases at dose rates of greater than 35 mg Fe/l. The graphs presented in Figures 7.3b to 7.3d show that minimum residual iron concentrations and minimum residual phosphorus coincide. As Fe dose rate increases beyond 35 mg Fe/l the residual Fe increases rapidly, however, the residual TP does not.

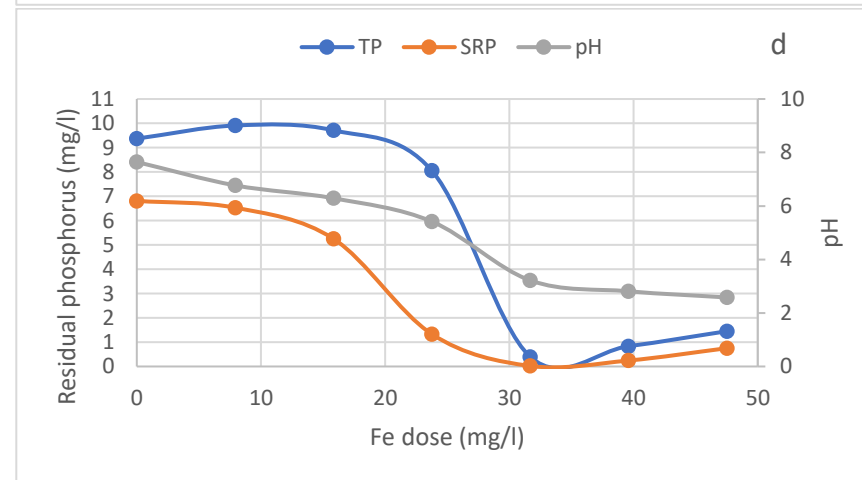
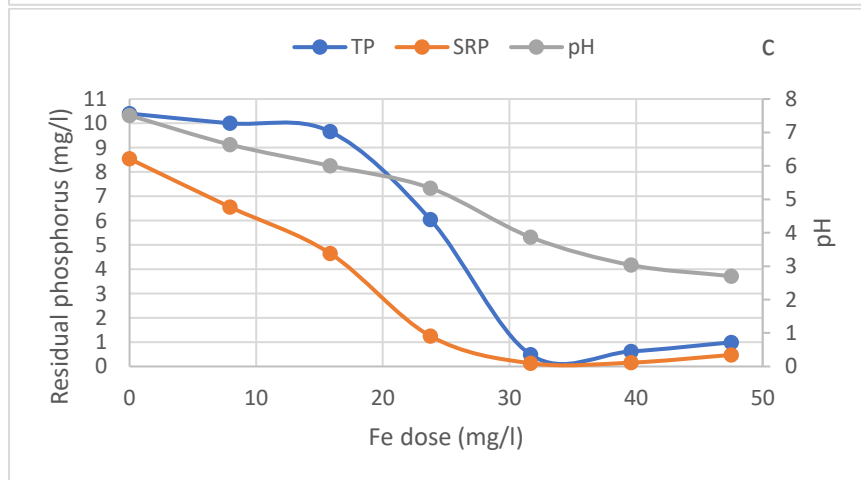
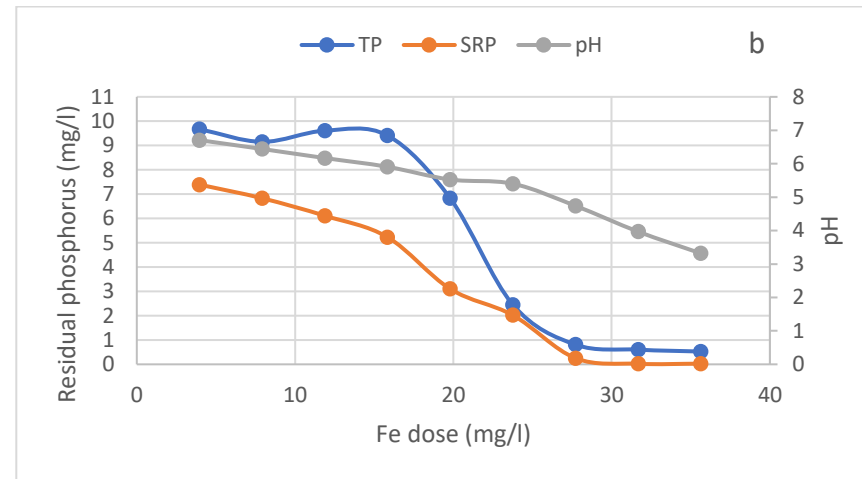
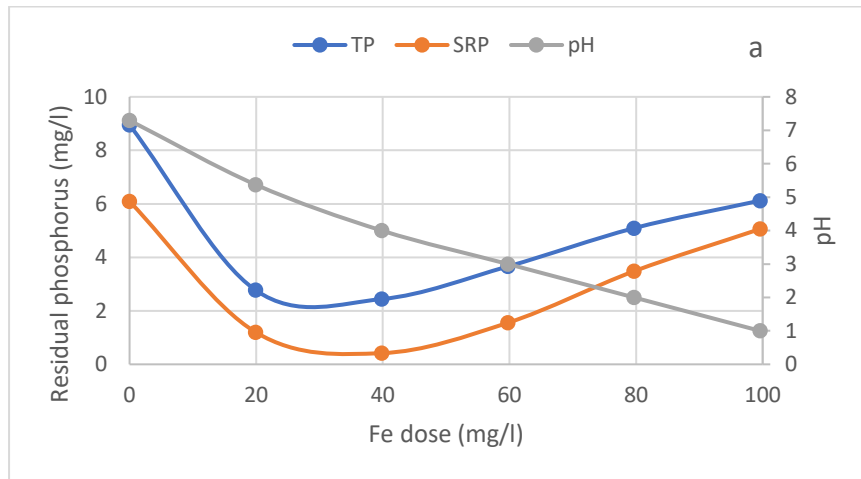


Figure 7.1: The effect of Fe dose on residual phosphorus and effluent pH for jar tests completed on influent sampled on 6/11/17 (a and b), 7/11/17 (c) and 8/11/17 (d) from the proposed trial site.

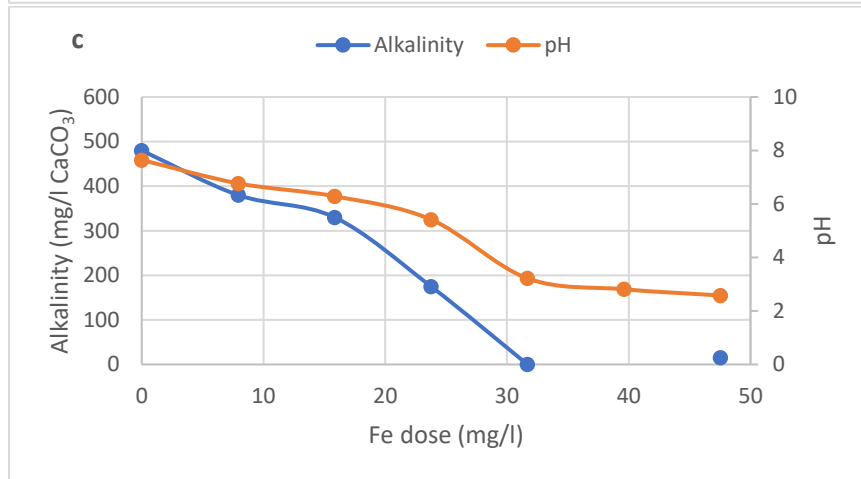
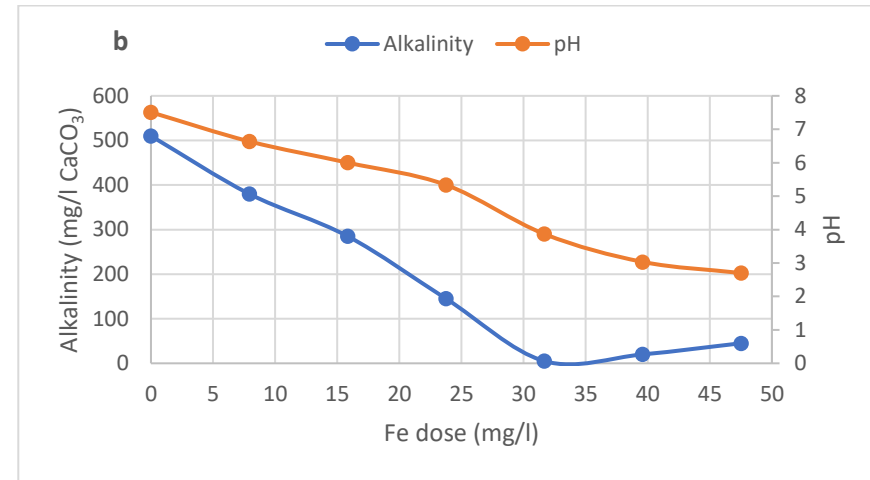
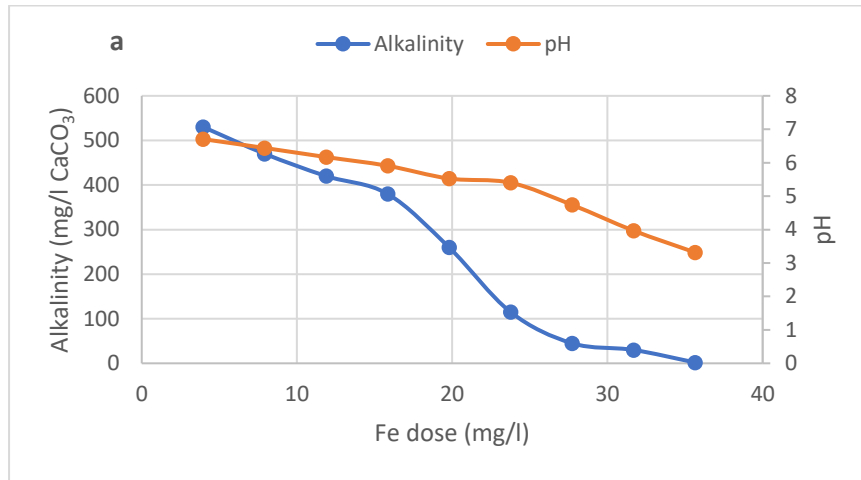


Figure 7.2: The effect of Fe dose on effluent alkalinity and pH for jar tests completed on influent sampled on 6/11/17 (a), 7/11/17 (b) and 8/11/17 (c) from the proposed trial site.

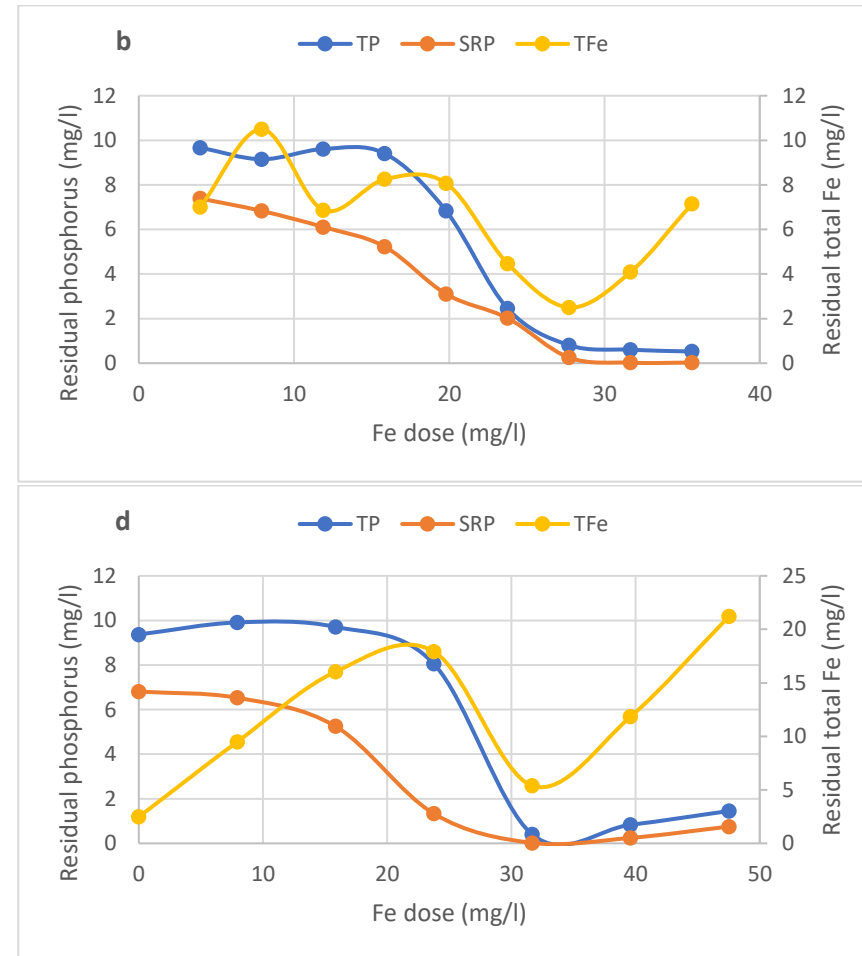
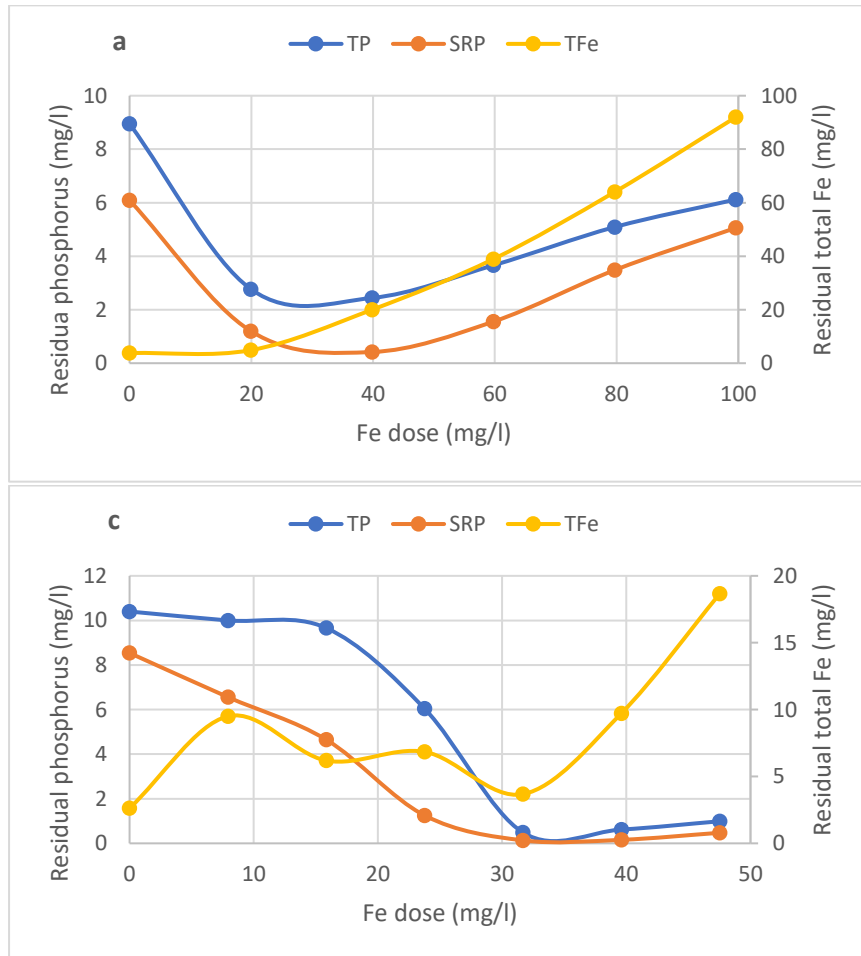


Figure 7.3: The effect of Fe dose on residual phosphorus and residual iron for jar tests completed on influent sampled on 6/11/17 (a and b), 7/11/17 (c) and 8/11/17 (d) from the proposed trial site.

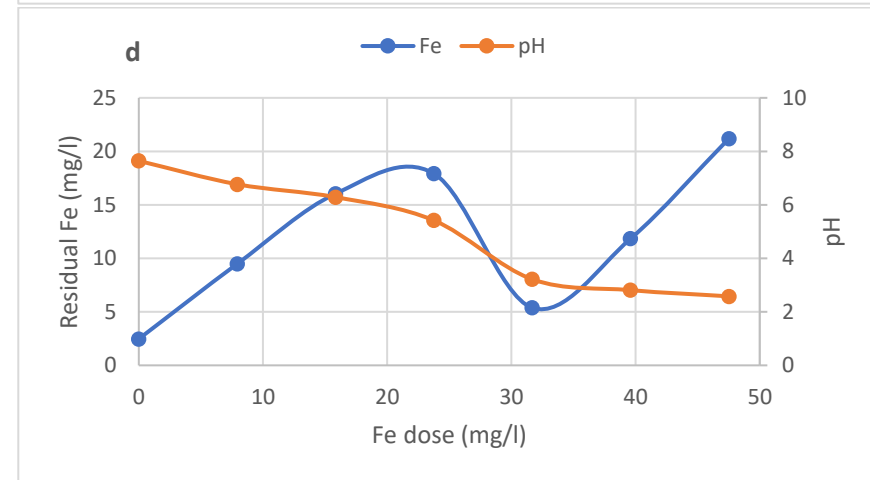
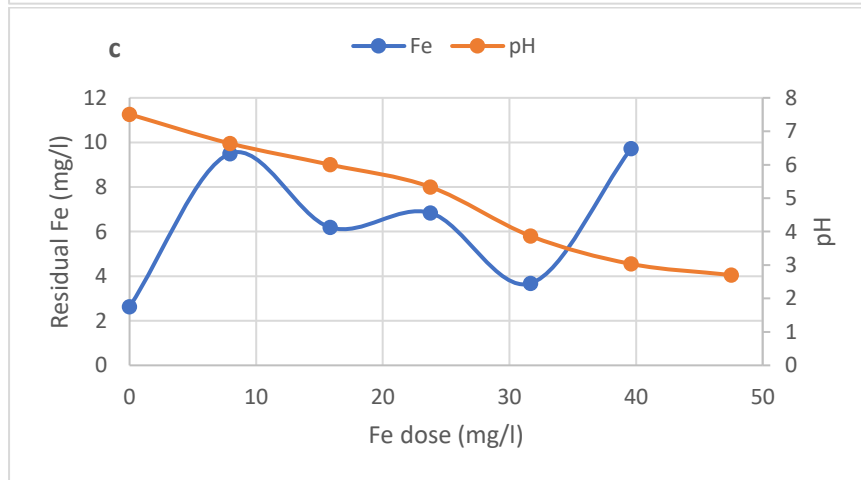
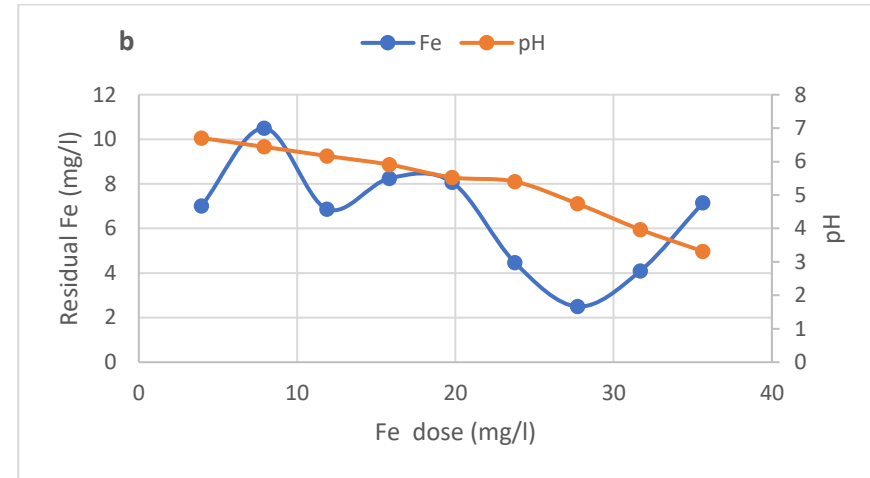
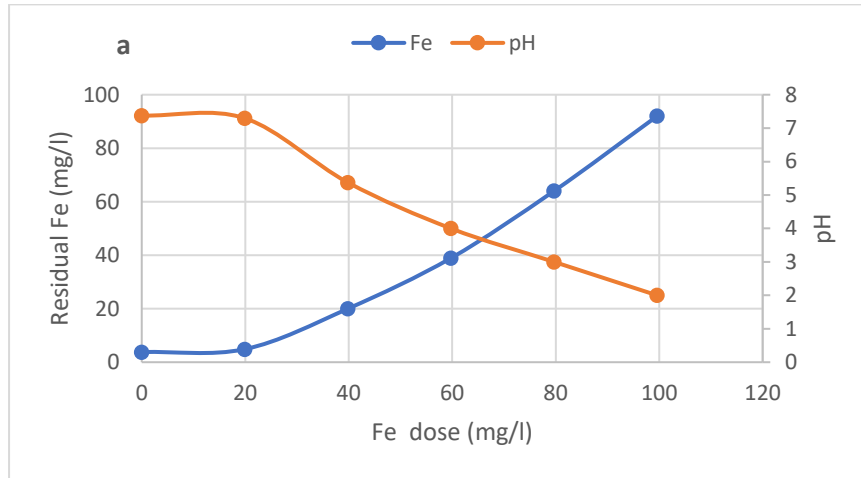


Figure 7.4: The effect of Fe dose on residual iron and effluent pH for jar tests completed on influent sampled on 6/11/17 (a and b), 7/11/17 (c) and 8/11/17 (d) from the proposed trial site.

Figure 7.5 combines data from all the completed jar tests to produce an averaged curve of phosphorus removal against Fe dose. To produce this curve, a mean percentage phosphorus removal was created from all the jar tests for each of the dose rates. The square markers indicate that the mean was calculated using three jar tests results whilst the triangle markers are based on two jar tests. Across the jar tests, the average percentage removal at a dose rate of 31.68 mg Fe/l was 95 % TP and 99% SRP.

The Fe to TP molar ratio for the maximum phosphorus removal in each jar test was calculated to be approximately 2:1.

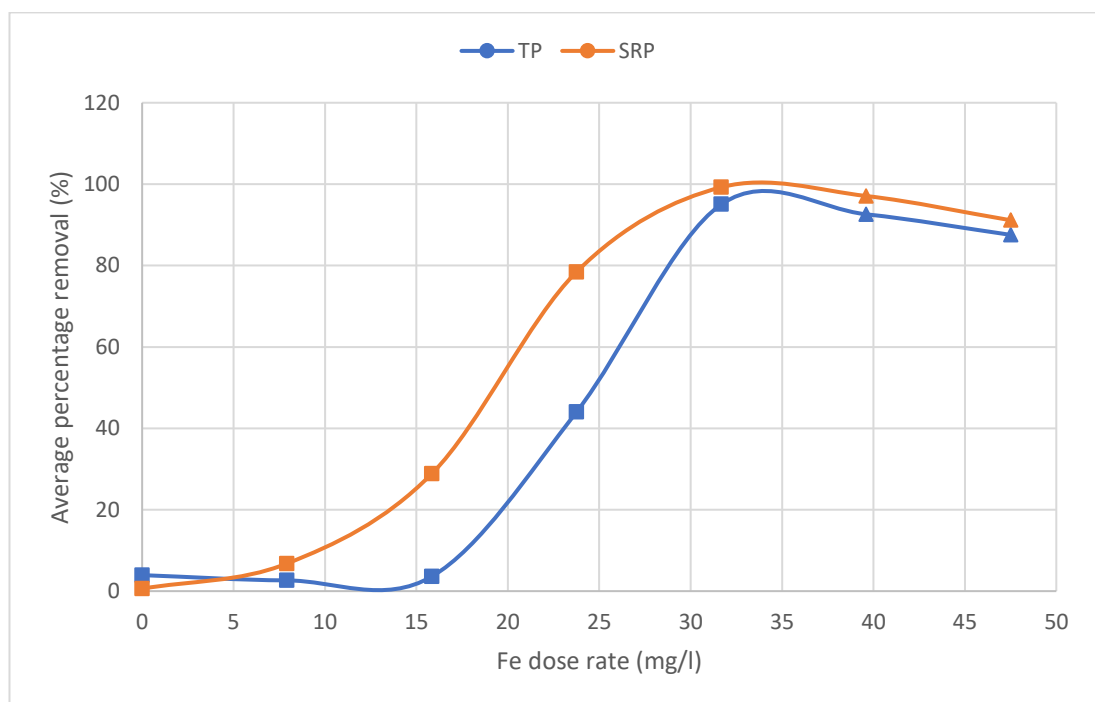


Figure 7.5: Average percentage removal of phosphorus plotted against Fe dose rate

7.3.2 Discussion

The results of the first set of jar tests suggest that a dose rate of approximately 40 mg Fe/l was required to achieve the lowest residual P concentration, but that at dose rates above 40 mg Fe/l, the residual phosphorus begins to increase again (Figure 7.1). Subsequent jar tests with smaller dose rate increments shown that the ideal dose rate is between 30 and 35 mg/l for maximum phosphorus removal. Dosing at 30 –35 mg Fe/l resulting in a residual iron between 3 and 6 mg/l. The results from all the jar tests completed suggest that the ODF trialled is more effective at removing SRP than TP.

The pH of the effluent impacts upon alkalinity, with a pH between 3 and 5 potentially reducing to as little as 0 mg/l CaCO₃. If the alkalinity is significantly reduced at a sewage treatment works (STW) it can negatively impact any biological process following the dosing and therefore alkalinity dosing or some form of pH correction may be required downstream of any ODF dosing point. This is particularly important if nitrification is required as this process uses alkalinity, however, denitrification can recover some alkalinity (Tchobanoglous et al., 2014b).

The results suggest that residual iron is lowest when phosphorus removal is greatest (and consequently residual phosphorus is lowest) suggesting that the iron and phosphorus combine and are removed in the settlement stage of the jar tests. At Fe dose rates above 35 mg Fe/l the residual Fe increases rapidly, yet the residual TP does not, therefore suggesting that the Fe is now in excess and so remaining in solution.

The Fe to TP molar ratio for the maximum phosphorus removal in the jar tests was calculated to be approximately 2:1 and is consistent with the findings of others. The stoichiometric equations stated in both Tchobanoglous et al. (2014a) and Gray (2017) suggest that a 1:1 ratio is required for phosphorus removal using iron. However, Tchobanoglous et al. (2014a) recommend iron dose is calculated based on bench-scale or full-scale trials and the required Fe:TP molar ratios can be up to 3:1.

7.4 Onsite Trial

7.4.1 Results

The final effluent flow at the trial site is monitored by instrumentation at 15-minute intervals and this flow data was used as a proxy for the flow entering the site. Based on this data, an average flow during the hour of dosing was calculated. This average flow was used to calculate that the single primary tank in use at the time of the trial had a retention time of 5.25 hours.

Figures 7.6 and 7.7 show the results of the trial, which have been offset by this retention time to compensate for the time between the effluent being dosed and being sampled after the PST's.

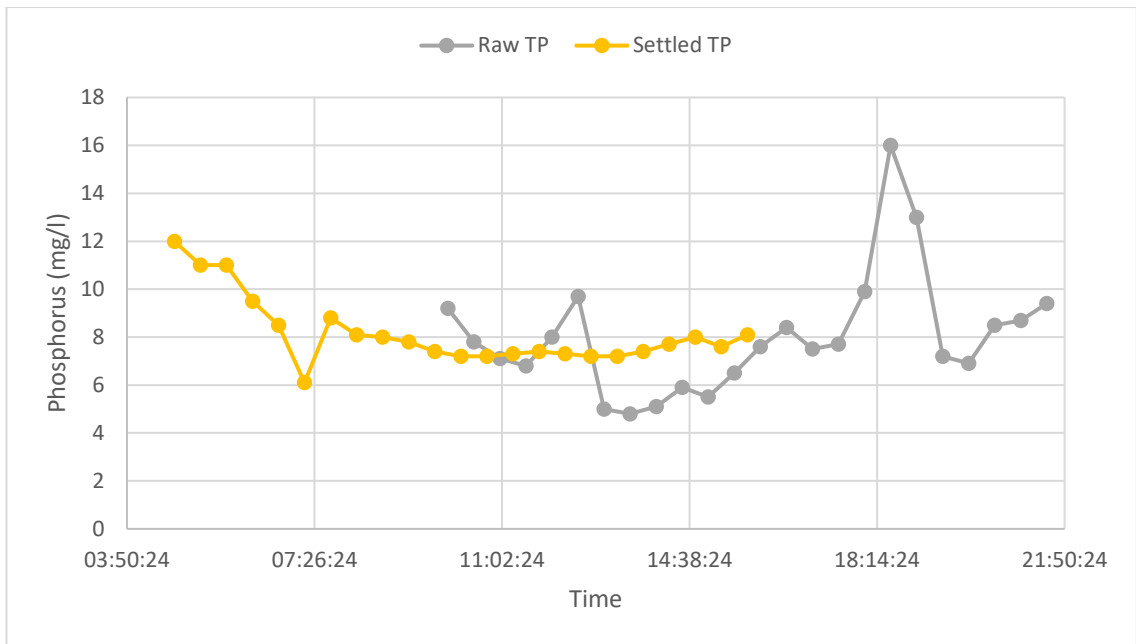


Figure 7.6: Total phosphorus (TP) in the raw and settled effluent samples taken during the onsite trial dosing ochre derived ferric (ODF).

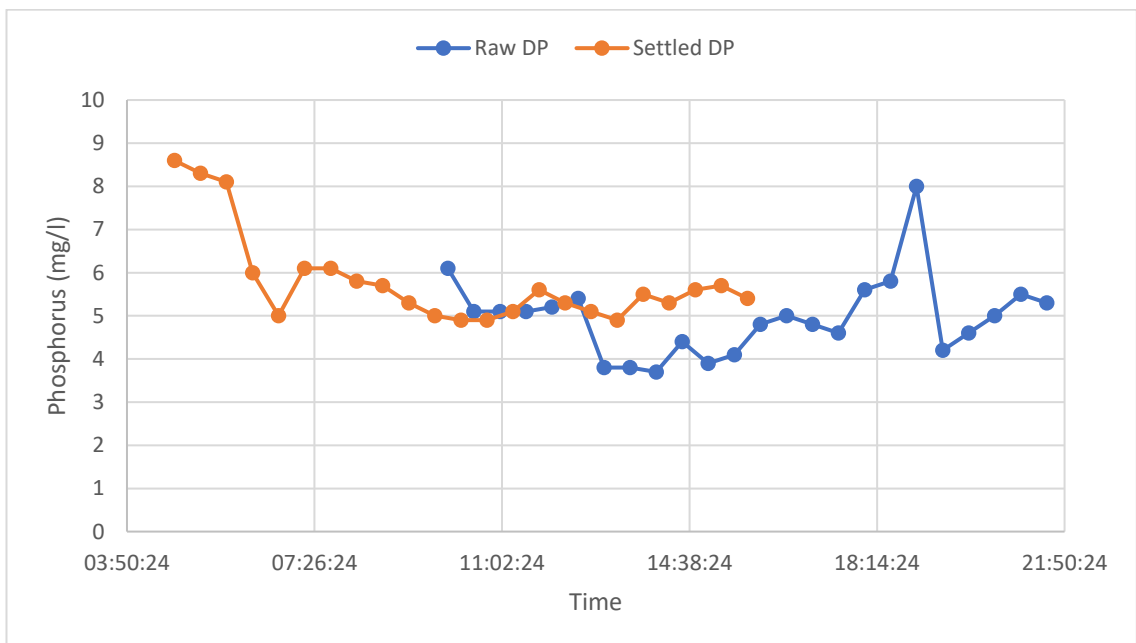


Figure 7.7: Dissolved phosphorus (DP) in the raw and settled effluent samples taken during the onsite trial dosing ochre derived ferric (ODF).

The results from the trial (shown in Figures 7.6 and 7.7) do not show clear reductions in phosphorus as a result of dosing ODF. There is a slight, apparent reduction in total and dissolved phosphorus removal at 10:45. For much of the trial period, the settled phosphorus (sampled after the PSTs) was greater than the raw phosphorus (sampled before the ODF addition).

It should be noted that there was visible flocculation as the ODF was dosed.

7.4.2 Discussion

The results suggest that phosphorus in the wastewater was greater after the primary settlement tanks (PSTs) than before the addition of the ODF (upstream of the PSTs). This apparent increase could be as a result of the sampling method or an input of phosphorus somewhere in the process between the dosing and the settled sample point, however, this cannot be determined based on the samples taken during the trial or the associated results. It is unlikely that phosphorus is being added anywhere during the treatment process between the two sampling locations. The site does have recirculation, but these returns enter upstream of the dosing point but were confirmed not in use at the time of the trial (Northumbrian Water, personal communication).

The slight reduction in total and dissolved phosphorus removal at 10:45 is inconclusive, as it cannot be verified whether this is linked to the ODF dosing or due to a change in flow rate.

Whilst flocculation was observed as the ODF was dosed, the results from the trial are inconclusive and there was no clear removal of phosphorus. Based on the average flow rate of the final effluent during the trial period and the pump rate, the iron dose rate into the wastewater was approximately 16 mg Fe/l and the results suggest that this is insufficient for significant phosphorus removal. This is supported by the results of the jar tests (Section 7.3) which suggested that the ideal dose rate was between 30 and 35 mg Fe/l, approximately twice the trial dose rate.

A further contributor to the inconclusive results from the site trial is the sampling regime. Sampling was not completed for a sufficient period before and after the trial to establish any impact upon phosphorus as a result of the dosing, in comparison with any phosphorus removal occurring across the primary settlement tanks (PSTs) as normal treatment settling. The sampling regime was also found to be overly complex to perform, with the time between samples considered too long.

Furthermore, dosing the ODF for a period of an hour was found to be insufficient when the retention time in a single PST was 5.25 hours. Any reduction in phosphorus content would have been diluted and obscured by the wastewater already held in the tank.

7.5 Chapter Conclusions and Recommendations

The trials in this chapter were in two parts with the jar test trial results informing the onsite trial. One variable was tested in each trial; ochre derived ferric (ODF) dose rate. In both trials, the dose rate impacted on the iron dose rate. However, the results in the onsite trial were also dependent on the primary settlement tank (PST) retention time which, in turn, was affected by the inlet flow rate at the site. The jar test and onsite trial results demonstrated an impact phosphorus in wastewater.

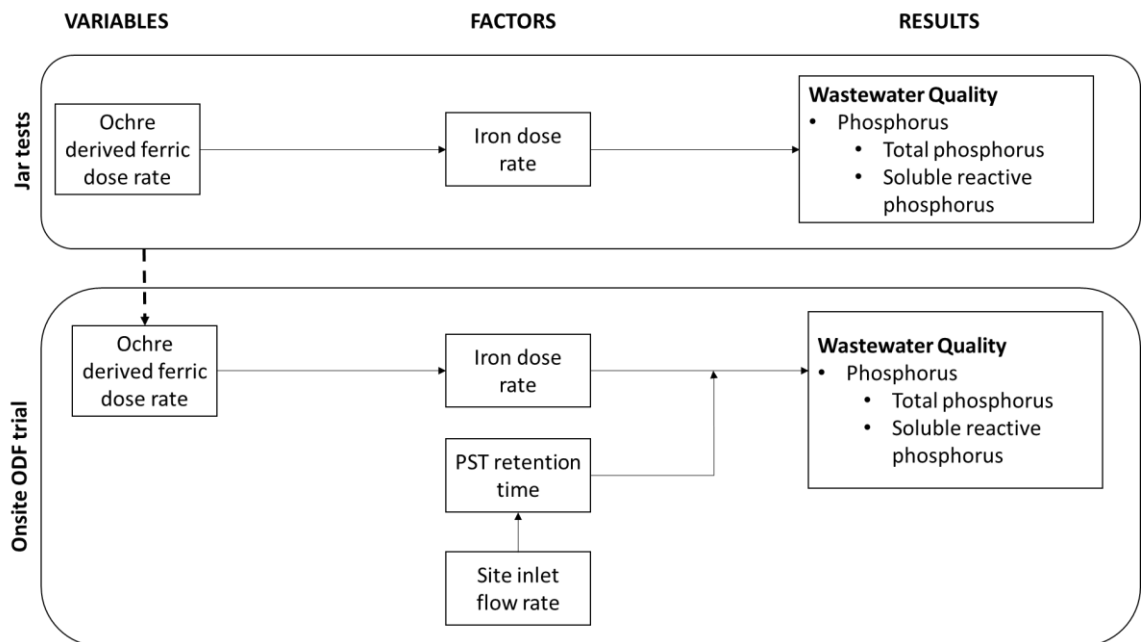


Figure 7.8: Model summarising the tested variables, factors (uncontrolled variables) and results considered in the onsite trial.

The completed jar tests showed that ochre derived ferric (ODF) is more effective at soluble reactive phosphorus (SRP) removal than total phosphorus (TP) when treating wastewater and suggest that the ideal dose rate is between 30 and 35 mg Fe/l. Furthermore, the results showed that (under ideal solutions) ODF is capable of reducing total phosphorus to less than 1 mg/l. Therefore, ODF could be applied to meet a discharge limit of 1 mg TP/l. However, dosing ODF at the required dose rate significantly reduces the effluent pH and alkalinity would could negatively impact any biological downstream process.

Although the jar tests were completed in order to inform the onsite trial, the dose rate was limited by the dose rate of the pump and the volume of ODF available. As a result, ODF was dosed at approximately half the ideal rate and the onsite trial results were inconclusive. A simpler sampling regime, with more frequent samples and for a longer period would have improved the available data. The dosing period was not sufficient given the long retention time of the PSTs. The observed floc at the dosing location was promising, suggesting that the solids and associated phosphorus were being bound by the ODF.

Based on the results of the jar tests and the onsite trial, it is recommended that another, more comprehensive onsite trial is undertaken and should include a longer term, simpler sampling regime. The sampling should be undertaken prior to any dosing, through the dosing and for a period after dosing in order to fully assess the impact of the ochre derived ferric and any associated phosphorus removal. Prior to the trial, the site flows and inputs which may impact upon phosphorus concentrations should be identified and accounted for. The dose rate should be determined using jar tests with wastewater from the trial site and the chosen coagulant and should be dosed for a sufficient period that the effects of the dosing are not lost in the downstream process.

8. Conclusions and future work

The aim of the research was to investigate the application of ochre for phosphorus removal from wastewater. To explore the possibility of applying ochre at a sewage treatment works, filter-based systems were trialled as well as direct application of the ochre through dosing. Finally, ochre was transformed into a coagulant.

The three hypotheses to be tested were:

1. Ochre can be applied a sewage treatment works for the removal of phosphorus from wastewater
2. Ochre can remove phosphorus as effectively as traditional ferric sulphate
3. Phosphorus-saturated ochre from a filter-based system can be used as a fertiliser

The variables test as part of the dosing of ochre and the coagulant (ochre derived ferric; ODF) are summarised in Figure 8.1. Also detailed are factors impacted on by these variables and wastewater characteristics impacted as part of the trials as observed in the trial results.

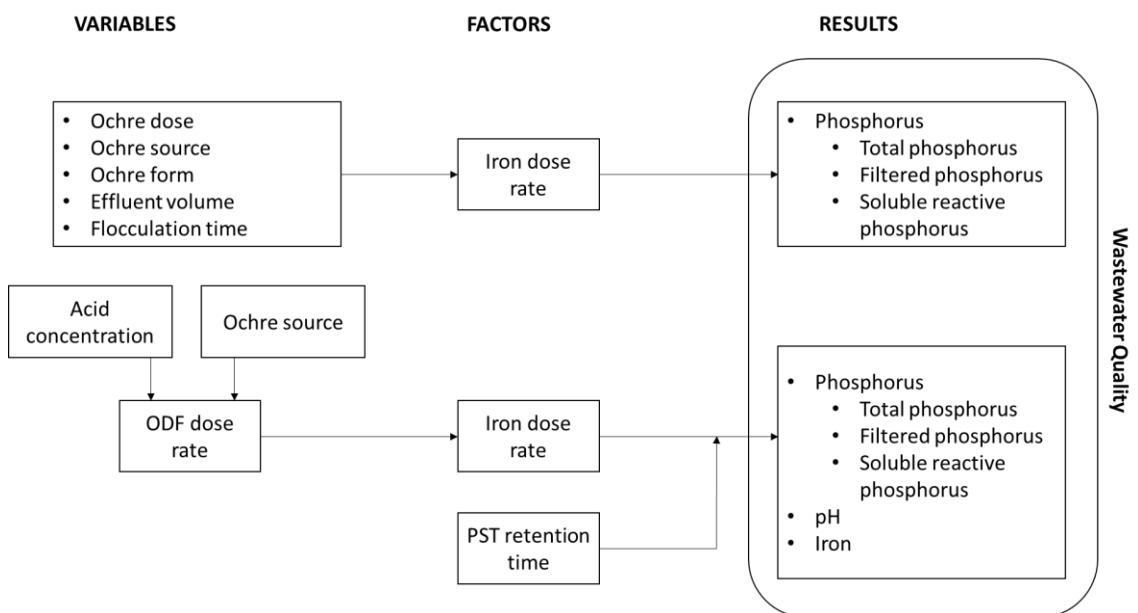


Figure 8.1: Model summarising the tested variables, factors (uncontrolled variables) and results considered in the ochre dosing, ODF dosing and onsite trial.

Hypothesis 1: Ochre can be applied a sewage treatment works for the removal of phosphorus from wastewater

Hypothesis 1 is partially supported by the research and results within this study. The ochre was trialled on sewage treatment works as part of a filter and as a coagulant derived from the ochre solids (ODF).

The ochre-based filters were trialled as a tertiary treatment process treating secondary treated effluent. The filters demonstrated some removal of phosphorus; however, the removal was highly variable and encountered operational difficulties. The percentage removal of total phosphorus was greater than that of filtered phosphorus. To implement ochre-based filters, the design would need to be refined and include a backwash system to keep the media clear of solids and maintain flow through the filter.

The dosing of ochre solids was only trialled as part of bench-scale tests using screened effluent but was not applied onsite. The results from these trials suggest that ochre could be applied at sewage treatment works in this form. However, these trials were conducted under ideal conditions with complete mixing. Without an onsite trial of ochre solids dosing, it is not possible to determine whether this application method could be used on a sewage treatment works.

The ochre-derived ferric (ODF) was trialled first in bench-scale tests and then trialled onsite. The bench-scale tests demonstrated that ODF was capable of removing phosphorus from screened effluent. The results of the subsequent onsite trial were inconclusive and therefore cannot be used to determine whether this hypothesis is supported or not when applying ochre as an ODF solution.

Hypothesis 2: Ochre can remove phosphorus as effectively as traditional ferric sulphate

Hypothesis 2 is partially supported by the results of the trials in this study. The filter trials did not include ferric sulphate for direct comparison, however, the filter-based systems were not able to reliably achieve an outgoing phosphorus concentration of 2 mg TP/l or below. Ferric sulphate is currently used to meet UWWTD limits of 1 and 2 mg TP/l.

Ferric sulphate was included in the bench-scale trials for both ochre and ODF dosing. When dosing ochre as either a solid or as a slurry, a greater iron equivalent was needed when dosing

in the form of ochre than in the form of ferric sulphate to approach an equivalent phosphorus removal. An equivalent removal was not achieved as part of these trials.

The ODF solution trials found that a larger volume of ODF would be required to achieve percentage removal of phosphorus equivalent to the removal by ferric sulphate. The removal of phosphorus per mg of iron in the ODF solutions was less than half of that for the ferric sulphate. As the ODF solutions are not as effective as the ferric when considering removal per mg of iron and the solutions have a lower iron content, a larger volume of ODF solution would be required than when dosing ferric sulphate. Despite, the lower iron content of the ODF solutions and under ideal solutions, the ODF solutions were shown to be able to meet the current UWWTD limits of 2 and 1 mg TP/l. Therefore, in theory ODF could replace ferric sulphate for phosphorus removal at STWs but not on a like for like volumetric basis. The onsite trial of ODF solutions was not sufficient to determine if this theory would transfer into practice under onsite, non-ideal conditions.

Hypothesis 3: Phosphorus-saturated ochre from a filter-based system can be used as a fertiliser

Hypothesis 3 was tested as part of the growth trials. The results of these trials suggest that Dawdon ochre is not detrimental to plant growth, however the growth was impeded slightly by the addition of Dawdon ochre. These results suggest that Dawdon ochre is not beneficial as a fertiliser for the improvement of crop growth. However, it may be beneficial as a soil amendment, for example, to adjust soil pH. These potential applications were not considered as part of the growth trials. Other ochres were not trialled. The results of this trial do not support the hypothesis, but further trials are required.

Recommendations for future work

The results of this study have highlighted areas requiring further study before ochre can be applied at sewage treatment works. Recommendations for further work are:

- To investigate the impact of ochre water content on dissolution when producing ODF solutions
- To investigate the impact of acid concentration on ODF elemental composition
- To investigate the impact of ochre source on ODF composition and removal efficiency
- To further refine the ODF production method to maximise phosphorus removal efficiency

- To complete further onsite trials using the ODF solutions with a suitable dose rate and sampling regime to determine the potential for ochre application and any impact of this application upon downstream processes
- To further investigate the use of ochre as a ferric supplement and explore possible chemical savings as a result
- If an ochre-based filter is to be implemented, the filter design needs to be re-engineered and fitted with a backwash capability

Further to the above recommendations, the regulations relevant to the application of ochre at STWs for the removal of phosphorus need to be fully understood. To determine the economic and commercial viability of ochre application, a full life cost assessment should be undertaken considering the ochre pre-treatment requirements, transportation from production site to application and any additional STW processes which may be required or any onsite adjustments which may be necessary to accommodate the application of ochre. Key stakeholders, such as the regulator and ochre producer, should be consulted prior to implementing ochre as phosphorus removal process.

Appendices

Appendix A: IBC filter trial data

Table A1: Daily average phosphorus removal for the two IBC trial runs

	Run day no.	Date	Average daily P removal (mg/l)		Average daily percentage removal	
			Total	Filtered	Total	Filtered
Run 1	1	11/07/2016	1.57	1.67	47.76	61.40
	2	14/07/2016	1.17	0.66	42.31	37.95
	3	15/07/2016	0.36	0.08	17.06	5.84
	4	18/07/2016	0.37	0.23	14.09	11.93
	5	19/07/2016	0.22	0.09	12.36	8.05
	6	20/07/2016	0.64	0.86	20.16	31.93
	7	21/07/2016	0.84	0.43	21.62	22.79
	8	22/07/2016	2.34	0.74	43.05	25.24
	9	26/07/2016	3.60	1.14	59.50	38.26
Run 2	1	01/09/2016	1.21	0.70	48.79	37.63
	2	02/09/2016	0.80	0.53	48.21	44.92
	3	05/09/2016	0.46	0.35	41.92	42.85
	4	08/09/2016	1.21	0.88	56.81	52.99
	5	09/09/2016	0.84	0.44	40.95	26.58
	6	13/09/2016	1.58	1.13	45.01	41.66
	7	19/09/2016	1.17	1.01	31.24	30.86

Table A2: Summary of percentage removals in the IBC filter trial (No. = number of samples; % = percentage of samples)

		Number of samples	Percentage removal					Outgoing total phosphorus								
			< 0%		0 - 10 %		10 - 20 %		20 - 50 %		> 50 %		<2 mg/l TP		<1 mg/l TP	
			No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%
All data	Total P	31	0	0.00	2	6.45	4	12.90	16	51.61	9	29.03	18	58.06	6	19.35
	Filtered P		0	0.00	3	9.68	5	16.13	16	51.61	7	22.58	n/a	n/a	n/a	n/a
Run 1	Total P	18	0	0.00	2	11.11	4	22.22	7	38.89	5	27.78	8	44.44	0	0.00
	Filtered P		0	0.00	3	16.67	4	22.22	8	44.44	3	16.67	n/a	n/a	n/a	n/a
Run 2	Total P	13	0	0.00	0	0.00	0	0.00	9	69.23	4	30.77	10	76.92	6	46.15
	Filtered P		0	0.00	0	0.00	1	7.69	8	61.54	4	30.77	n/a	n/a	n/a	n/a

Appendix B: Pond filter trials data

Table B1: Summary of percentage removals in each phase and the units (No. = number of samples; % = percentage of samples)

		No. of samples	Percentage removal										Outgoing total phosphorus			
			< 0 %		0 - 10 %		10 - 20 %		20 - 50 %		> 50 %		<2 mg/l TP		<1 mg/l TP	
			No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%
All phases	Total P	82	24	29.27	41	50.00	10	12.20	5	6.10	2	2.44	13	15.85	2	2.44
	Filtered P		21	25.61	50	60.98	6	7.32	3	3.66	2	2.44	n/a	n/a	n/a	n/a
Phase 1: upflow	Total P	15	5	33.33	9	60.00	0	0.00	1	6.67	0	0.00	5	33.33	0	0.00
	Filtered P		4	26.67	9	60.00	2	2.44	0	0.00	0	0.00	n/a	n/a	n/a	n/a
Phase 1: downflow	Total P	15	4	26.67	8	53.33	3	20.00	0	0.00	0	0.00	5	33.33	0	0.00
	Filtered P		4	26.67	10	66.67	1	6.67	0	0.00	0	0.00	n/a	n/a	n/a	n/a
Phase 2: 5 cm	Total P	11	3	27.27	5	45.45	2	18.18	1	9.09	0	0.00	0	0.00	0	0.00
	Filtered P		2	18.18	8	72.73	0	0.00	1	9.09	0	0.00	n/a	n/a	n/a	n/a
Phase 2: 15 cm	Total P	11	0	0.00	3	27.27	3	27.27	3	27.27	2	18.18	3	27.27	2	18.18
	Filtered P		1	9.09	4	36.36	2	18.18	2	18.18	2	18.18	n/a	n/a	n/a	n/a
Phase 3: sand	Total P	6	2	33.33	4	66.67	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00
	Filtered P		4	66.67	2	33.33	0	0.00	0	0.00	0	0.00	n/a	n/a	n/a	n/a
Phase 3: ochre	Total P	6	4	66.67	1	16.67	1	16.67	0	0.00	0	0.00	0	0.00	0	0.00
	Filtered P		4	66.67	2	33.33	0	0.00	0	0.00	0	0.00	n/a	n/a	n/a	n/a
Phase 4a: left	Total P	6	2	33.33	4	66.67	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00
	Filtered P		0	0.00	6	100.00	0	0.00	0	0.00	0	0.00	n/a	n/a	n/a	n/a

Phase 4a: right	Total P	6	2	33.33	4	66.67	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00
	Filtered P		0	0.00	6	100.00	0	0.00	0	0.00	0	0.00	n/a	n/a	n/a	n/a
Phase 4b	Total P	6	2	33.33	3	50.00	1	16.67	0	0.00	0	0.00	0	0.00	0	0.00
	Filtered P		2	33.33	3	50.00	1	16.67	0	0.00	0	0.00	n/a	n/a	n/a	n/a

Table B2: Calculated retention times for the pond filter units

Ochre depth	Surface area		Ochre layer volume		Flowrate		HRT		Phase
	cm²	m²	cm³	m³	l/s	m³/h	h	mins	
5	3417	0.34	17085	0.02	0.09	0.32	0.05	3.16	2
7	3417	0.34	23919	0.02	0.09	0.32	0.07	4.43	4b* (downflow)
10	3417	0.34	34170	0.03	0.1	0.36	0.09	5.70	1
15	3417	0.34	51255	0.05	0.09	0.32	0.16	9.49	2, 3, 4a, 4b* (upflow)

* Phase 4b included two units, the combined retention time was calculated at 14 minutes

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