final report

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Novel phosphorus removal using lanthanum precipitation

Executive summary

V&V Walsh Meat Processors and Exporters operate a facility in Bunbury, WA, that disposes of treated effluent via irrigation to land. V&V Walsh have taken the initiative to explore chemical dosing with a novel coagulant to reduce effluent phosphorus concentrations so as to be compliant with the allowable loading limits in the DWER Licence for their irrigation areas.

This project aimed to explore the application of a novel rare earth coagulant lanthanum to meat processing wastewater and to evaluate its benefits and challenges compared to the more well-known precipitants (specifically ferric chloride). This involved an initial assessment of the current irrigation system at V&V Walsh, a review of lanthanum ecotoxicity, onsite dosing trials and sludge settling tests.

It is important to make the distinction between the use of lanthanum chloride as a coagulant in this project, and the use of Phoslock, a lanthanum-containing commercially available product. Phoslock is a clay-based material, and studies have shown that it requires doses that are orders of magnitude higher than lanthanum chloride to achieve the same degree of phosphorus removal. The results in this report are not applicable to Phoslock.

An assessment of the wastewater treatment and effluent irrigation system at the V&V Walsh facility identified phosphorus values that can be considered sustainable for two operating options. V&V Walsh indicated that they have a preference for treating the entire wastewater stream, which would require a phosphorus concentration in the irrigated effluent of 10 mgP/L.

A review of scientific and technical literature has shown that lanthanum chloride has similar toxicological impacts on the environment as common coagulants, except for freshwater aquatic systems where the free lanthanum ion appears more impacting. This environmental risk is mitigated by both the properties of lanthanum itself and by applying good irrigation practice.

Onsite dosing trials revealed that both lanthanum chloride and ferric chloride were capable of efficiently precipitating phosphorus from pond-treated effluent, with fairly low dose rates. Both are capable of achieving low phosphorus concentrations (<2 mg/L) if required. To achieve a given phosphorus concentration, more ferric chloride (≈32% by mass) was required than lanthanum. However, the commercially available lanthanum chloride costs $7,000/kL compared to approximately $1,500/kL for ferric chloride, resulting in an estimated annual chemical expenditure of $190,000 for lanthanum chloride, or $60,000 for ferric chloride to reduce the phosphorus concentration from 24 mg/L to 10 mg/L at the site.

Two stage dosing trials were also performed but they did not show any great benefit relative to single stage dosing. When the added operational complexity associated with two stage dosing is considered, it is clear that it is not worthwhile.

Ferric chloride had a more substantial impact on the pH and alkalinity of the effluent, meaning that pH correction may be required to protect downstream treatment processes or meet discharge limits. Lanthanum chloride did not have these effects and would most probably not require pH correction. Both coagulants produced similar quantities of sludge on a mass basis.

Sludge settling trials showed that the sludge produced by lanthanum chloride dosing settled much faster than ferric chloride sludge. This is a critical factor in the design of a chemical phosphorus precipitation system as it determines that size of settler required, which is often the most expensive capital component of such a system. It is estimated that for a settler would need to be

approximately 2.5 times the size to achieve the same solids removal for ferric as lanthanum dosing. This adds substantial capital cost to the installation required for ferric chloride. Correspondingly, coagulant selection for processors becomes a tradeoff between capital and operating expenditure.

The key finding of this project is that for phosphorus precipitation and separation from wastewater, lanthanum chloride is the superior coagulant to ferric chloride on a number of criteria. However, the price premium (operating expenditure) is so substantial that few processors are likely to be able to justify using it. In addition to the price premium, the majority of chemical suppliers do not stock lanthanum chloride, potentially making it difficult for processors to obtain.

Despite this, literature suggests that rare earth elements such as cerium and lanthanum are becoming more sought after for a variety of industrial uses. This is prompting the opening of an increasing number of rare earth mines, which produce lanthanum chloride as a byproduct (USEPA 2012). If the price of lanthanum chloride were to drop substantially over the coming years, it may well find a place amongst common coagulants as a tool for processors to treat phosphorus.

In terms of future research, there is merit in investigating the effectiveness of lanthanum chloride dosing for phosphorus removal in meat processing streams that are rich with suspended solids and organic matter to determine if it is more effective than other coagulants.

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Abbreviations

Bio P	=	biological phosphorus (removal)
BOD_5	=	biochemical oxygen demand (measured in 5 days at 20°C) (mg/L).
CAL	=	Covered Anaerobic Lagoon
CAPEX	=	capital cost
COD	=	chemical oxygen demand (mg/L)
DAF	=	dissolved air flotation
DNEL	=	derived no effect level
DO	=	dissolved oxygen concentration (mg/L)
DS	=	dry solids (usually %)
DWER	=	Department of Water and Environmental Regulation
EBPR	=	Enhanced Biological Phosphorus Removal
EC	=	Electrical conductivity
EC50	=	concentration required to give 50% of the maximal effect over the given time
$FeCl_3$	=	ferric chloride
FRP	=	filtered reactive phosphorus
HDPE	=	High Density Polyethylene
HRT	=	hydraulic retention time (days)
IC50	=	half maximal inhibitory concentration
IMBL	=	immobilisation
JEG	=	Johns Environmental Group Pty Ltd
$LaCl_3$	=	lanthanum chloride
LC50	=	lethal dose for 50% of the population over the given time
MLA	=	Meat & Livestock Australia
MOR	=	mortality
MSDS	=	material safety data sheet
NH_3-N	=	ammonia-nitrogen concentration (mg/L)
NO_2-N	=	nitrite-nitrogen concentration (mg/L)
NO_3-N	=	nitrate-nitrogen concentration (mg/L)
NR-LETH	=	100% mortality of the population over the given time
O&G	=	Oil and Grease (mg/L)
OFR	=	overflow rate (usually m/h, or $m^3/m^2/h$)
Soln	=	solution (of coagulant)
TDS	=	Total Dissolved Solids (mg/L)
TKN	=	Total Kjeldahl nitrogen (mg/L)
TN	=	Total Nitrogen concentration (mg/L)
TP	=	Total Phosphorus concentration (mg/L)
TSS	=	Total Suspended Solids (mg/L)
VFA	=	volatile fatty acids (mg/L as acetic acid)
WWTP	=	wastewater treatment plant

LIST of UNITS

°C	=	degrees Celcius
ha	=	hectare
kg	=	kilogram
kL/d	=	kilolitres (cubic metres) per day
mg/L	=	milligrams per litre = ppm.
m/h	=	metres per hour
ML	=	Megalitres (1,000 kL)

1   Background

1.1   Project context

Meat processing wastewater contains elevated levels of phosphorus (P) and the sustainable disposal of P-rich effluent has increasingly become an issue for the red meat processing industry in Australia. Processors typically dispose of their wastewater to land, sewer or river but these disposal routes often have phosphorus limits that are much lower than the concentration of phosphorus in the wastewater. To sustainably release wastewater to the environment, processors increasingly treat it to remove phosphorus.

Phosphorus removal from meat processing wastewater is typically done using aluminium and iron-based coagulants such as aluminium sulphate, ferric sulphate and ferric chloride. Another option is a crystallisation process to produce a product known as struvite. Struvite crystallisation is still an emerging technology in Australia, however, and is rarely used in the red meat processing industry. A recent report suggests that the technology is too expensive for all but the largest facilities (Butler, 2018). Another option is Enhanced Biological Phosphorus Removal (EBPR or Bio P), whereby a particular type of bacteria are employed to take up phosphorus from the wastewater and store it in their cells for removal as sludge. This is difficult to achieve in meat processing effluent and if achieved, is often unstable in real life situations and prone to phosphorus releases back into the effluent.

For this reason, processors typically use coagulants to precipitate the phosphorus as a solid and separate it from the water using flotation or settling. The aluminium and iron-based coagulants that are currently available to processors unfortunately do not target phosphorus alone and can react with other contaminants in the wastewater, such as alkalinity, suspended solids or organic matter. Since suspended solids and organic matter would otherwise largely settle and/or break down in a pond system, this is a 'waste' of the additional coagulant used. This means that the processor often has to add coagulant in substantial excess of what would be required to react with the phosphorus alone, to account for the 'wasted' coagulant that is consumed in these competing side reactions. The additional chemical usage adds significant operating cost to phosphorus removal. Chemical dosing trials at some meat processing sites have indicated that doses in excess of 400% of the theoretical value may be required, depending on the concentration of these other contaminants.

This project aims to determine the effectiveness of a novel coagulant known as lanthanum chloride as a chemical for precipitation of phosphorus from meat processing wastewater, with comparison to ferric chloride, a coagulant that is already used widely in the industry for this purpose. The necessary dose, sludge produced and sludge settleability were investigated for both chemicals.

1.2   Site description

At the V&V Walsh facility, all of the wastewater produced is combined after screening and treated in a newly installed Dissolved Air Flotation (DAF) system, where a coagulant (typically ferric sulphate or ferric chloride) is added to precipitate contaminants such as organic matter, total suspended solids (TSS), nitrogen (N) and phosphorus (P) from the wastewater. This generates a sludge that is separated and floated from the wastewater by the DAF before it is disposed of off-site.

Effluent from the DAF passes through a system of 7 ponds (anaerobic, aerated and storage) for final treatment prior to irrigation. There is an inline flowmeter and sampling point at the end of Pond 7 to monitor the quantity and quality of the treated effluent that is applied to the land. The typical

concentration of nitrogen and phosphorus have been 60mg/L and 24mg/L respectively, for the first 6 months of 2018. The average effluent flow to irrigation in the last decade has been fairly constant, with an average of 216 ML/year.

There are two available disposal routes for the treated effluent from Pond 7. The first option is irrigation via a 13ha pivot irrigator to an area south of the facility that is operated by a third party contractor as a turf farm. The second option is irrigation to a collection of 3 areas that total 27.8ha and are owned and operated by V&V Walsh as pasture for grazing and/or cropping.

A result of the different operating philosophies for these two areas is that the assimilation of nitrogen and phosphorus into plant material is very different. Consequently, the Department of Water and Environmental Regulation (DWER) has set different allowable loading rates of nitrogen and phosphorus for each area. These are summarised in the table below. The nitrogen and phosphorus loading for the pasture areas is actually listed as inorganic nitrogen and reactive phosphorus respectively, but these make up >90% of total nitrogen and total phosphorus, so for ease of comparison, the loadings for the pasture have been listed as the more conservative total loadings.

Table 1. DWER allowable irrigation loading rates (as per licence L6001/1989/15)

Units	Area (ha)	N loading (kg N/ha/yr)	P loading (kg P/ha/yr)
Turf farm	13	600	180
Pasture	27.8	180	20

Clearly, the turf farm has significantly higher allowable loading rates as the physical removal of turf is a highly effective method of removing nutrients from land. Grazing and/or cropping of pasture achieves lower nutrient removal and the allowable loading rates are accordingly lower.

The objective of V&V Walsh is to remove phosphorus from the wastewater to the point where the effluent is sustainably irrigated to land and maintain compliance with the loading limits in Table 1.

1.3   Lanthanum as a coagulant of interest

Trials conducted under the US Federal Water Quality program in the late 1960s by Recht & Ghassemi (1970) showed that the trivalent ion of the rare earth element, lanthanum was a very effective precipitant of phosphorus from water. The reaction was rapid, lanthanum was effective against a wider range of phosphorus forms, had a broader effective pH range (important where ponds with high algae levels have alkaline pH) and achieved high phosphorus removal at low doses - all properties important for use in real-life situations. However, there appears to have been little application of lanthanum for this purpose in the water industry.

Subsequently, Strileski (2013) working with EPBR waste sidestreams in Canada confirmed these earlier results and investigated the possibility of regenerating the lanthanum from the precipitated sludge.   Both publications suggest that lanthanum chloride has, relative to standard coagulants, a greater tendency to react with phosphorus alone and ignore other components such as suspended solids and organic matter. This specificity to phosphorus is a highly desirable characteristic of a coagulant where phosphorus removal is the primary aim and has the potential to allow processors to reduce the quantity (and therefore the cost) of chemicals dosed for phosphorus removal.

An alternate product that contains lanthanum and is used for sequestering phosphorus is phoslock. This product – originally developed and patented by CSIRO in 1997 – is a lanthanum-modified bentonite clay. Unlike lanthanum itself (which removes phosphorus by reaction), phoslock is an adsorption process and large quantities of product are required. Kurzbaum & Shalom (2016) found that phoslock doses of 300 – 1,200 mg were needed to remove 1 mgP from wastewater. In contrast only 7 mg/mgP of 42% $LaCl_3$ solution is needed. This is important, since sludge production is hugely less with lanthanum solution. This is a major disadvantage of phoslock for industrial application.

The primary issue identified with lanthanum was its high cost. It is expected that lanthanum chloride prices will fall since it is a by-product of rare earth mines (although lanthanum is not rare!) and the increasing demand for rare earths for modern electronic applications (e.g. cell phones, car batteries, etc) should see the supply increase. Nevertheless, it remains expensive at present relative to competing coagulants. Consequently, despite research showing its effectiveness becoming available as early as 1970 (Recht & Ghassemi), lanthanum chloride has only seen limited use for phosphorus removal, with its application typically confined to phosphorus removal in public and residential swimming pools (which has been done for many years).   Domestic and industrial wastewater applications of lanthanum chloride in Australia have been virtually non-existant.

A further downside for lanthanum is that is an element with a high molecular mass, meaning that to dose the same number of lanthanum molecules as iron or aluminium, a greater mass (and volume) of chemical is required. As the precipitated form of phosphorus is $MePO_4$, where Me is the metal such as La^{3+}, Al^{3+} or Fe^{3+}, at least one molecule of metal is required for each molecule of phosphorus that is to be removed. This can make comparison of the various coagulants difficult. Literature often discusses doses required for particular coagulants as a ratio of the molar (molecular) quantity of the metal required to the molar quantity of phosphorus removed. Where the same molar ratio is required for an iron and a lanthanum-based coagulant, significantly more lanthanum will be required on a mass basis, as lanthanum has a molecular mass 150% greater than iron. The bulk densities of chemical solutions also vary greatly, making mass and volume not equivalent when discussing doses. Since these chemicals are sold on both mass and volume bases, performing the appropriate conversions is absolutely critical when making a comparison.

2   Project objectives

This project seeks to explore the use of lanthanum chloride as a means of reducing phosphorus levels in meat processing wastewater and to evaluate its benefits and challenges compared to the more well-known precipitants (specifically ferric chloride).

3   Methodology

3.1 Coagulant dosing trials

The primary objective of this part of the project was to benchmark the performance of lanthanum chloride with respect to phosphorus removal, relative to ferric chloride. For this purpose, Johns Environmental (JEG) shipped the following laboratory equipment to V&V Walsh in Bunbury, WA:

- Lovibond jar tester and glass beakers to determine dosages;
- Hach DR1900 spectrophotometer to measure phosphorus levels on-site;
- Hach HQ40d portable instrument with pH, EC and DO probes;
- Hach TNT845 total/reactive phosphorus test vials for use with the Hach DR1900 unit, and
- Miscellaneous other laboratory equipment.

Mike Johns and Louis Fredheim of JEG visited the V&V Walsh site on the 15th and 16th of August 2018 to perform the dosing trials. They met with Paul Oosthuizen (Chief Engineer) of V&V Walsh and inspected the wastewater treatment system.

For the trials wastewater was collected from the inlet into Pond 5 since this was upstream of lanthanum pilot trial dosing by V&V Walsh and the water quality at this point was excellent and safe access for collection was possible.
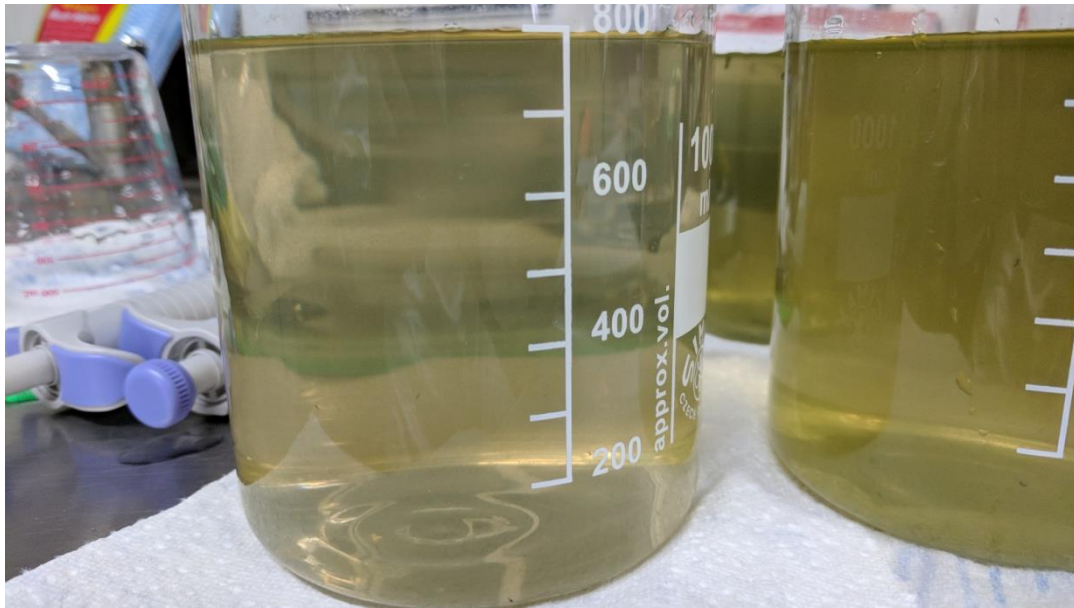
Figure 1. Pond 4 wastewater prior to any chemical dosing

Lanthanum chloride (40% solution of $LaCl_3$) was provided by Redox Pty. Ltd and ferric chloride (42% solution of $FeCl_3$) was obtained from an IBC (Solenis Australia Pty. Ltd) on-site used for dosing into the Dissolved Air Flotation plant. Note that care is needed when calculating lanthanum doses. The commercially available product is termed 60% lanthanum chloride, but since the structure contains 7 H_2O (water) molecules, actual lanthanum chloride content is only 40% by mass. The MSDS supplied by Redox is ambiguous in this regard and it is easy to make a significant error in calculating the lanthanum dose.

A dilution of the Pond 4 wastewater was made up and the reactive phosphorus concentration in the effluent was measured by the Hach DR1900 to determine the baseline phosphorus level present in the untreated effluent at this location. This concentration served as the reference point for calculating the degree of phosphorus removal.

3.1.1   Dosing Trials in Jar Tester

A large volume (800mL) of Pond 4 effluent was added to a glass beaker and dosed with a precise quantity of lanthanum chloride solution using calibrated laboratory pipettes. The solution was mixed using the Lovibond jar tester at a speed of 200rpm for 2 minutes and the solution was allowed to

settle. A sample (10mL) of the supernatant was collected via a syringe and filtered through a 0.45μm mixed cellulose ester syringe filter into a plastic container. From this plastic container, 0.4mL of solution was collected and analysed for reactive phosphorus concentration using the Hach DR1900 spectrophotometer and Hach TNT845 total/reactive phosphorus test vials.
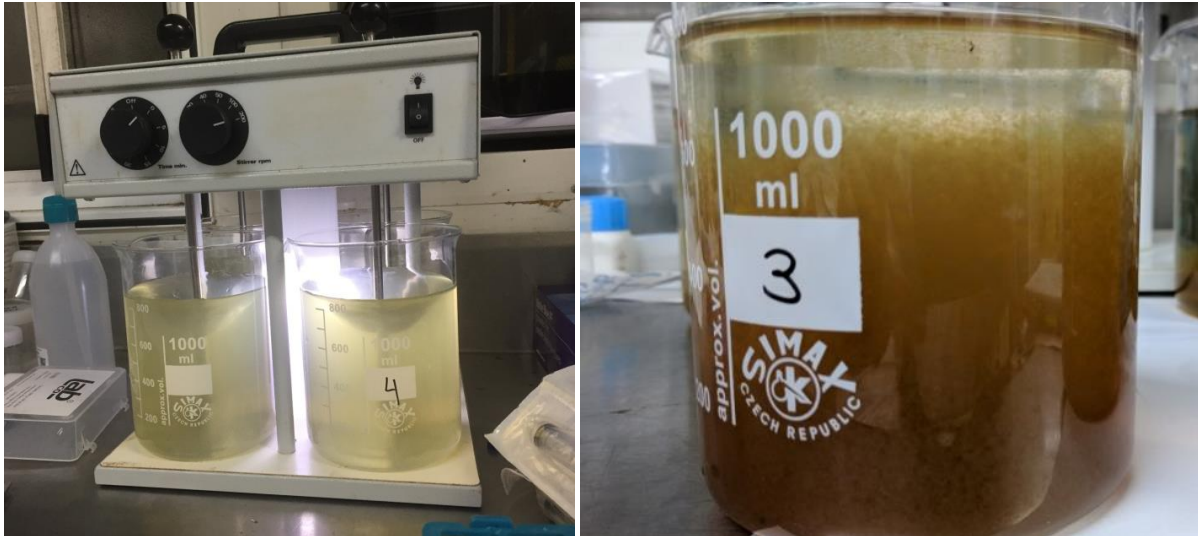
Figure 2. Lanthanum chloride and ferric chloride dosing trials

Reactive phosphorus was measured in lieu of total phosphorus because for the preliminary dosing calculations, only the residual phosphate that remained in solution (ie. unbound to a coagulant) was of interest. For this reason, the reactive phosphorus concentrations measured represent the ideal phosphorus removal, ie. the residual phosphorus concentration if all of the particulate phosphorus sludge settled and was separated from the supernatant (equivalent to the clarified effluent).

This process was repeated a number of times with different lanthanum chloride dosages to develop a plot of coagulant dose against residual filtered reactive phosphorus concentration. Four separate doses were selected and the corresponding treated effluent solutions were bottled for further analysis at an independent laboratory (ALS Environmental) in Perth. Once complete, the same procedure was carried out for the ferric chloride.

Figure 3. Settled sludge produced during dosing trials

Literature suggests that a number of coagulants perform more efficiently if they are dosed in 2 stages, especially where large reductions in phosphorus concentration are required. Due to the

nature of the chemical reaction between the coagulant and the phosphorus, a higher initial concentration of phosphorus should result in a higher fraction of the dosed coagulant reacting with the phosphorus rather than other compounds in the wastewater, such as alkalinity, suspended solids or organic matter.

To test whether this theory applied to the V&V Walsh wastewater, a number of tests were performed where 2 half-doses of coagulant were applied, followed by 2 minutes of mixing at 200rpm after each dose. The treated effluent was again analysed for filtered reactive phosphorus and the results compared to the results for the same dose of coagulant applied in a single stage.

3.2   Sludge settling trials

For the sludge settling trials, 120 litres of V&V Walsh Pond 4 effluent was collected whilst JEG was on-site and freighted back to the JEG premises in Brisbane, QLD.

The objective was to determine the volume of sludge generated by dosing lanthanum chloride or ferric chloride, as well as the settling rate and compactness of the final settled sludge. These are key design parameters for a full scale coagulant dosing system.

To measure settling rates, a purpose-built settling column (Figure 4) was used. The device is designed on the Eckenfelder model (Eckenfelder, 1989) consisting of a 2.65m high by 150mm diameter acrylic tube to minimise edge effects and four sampling ports fitted with ball valves distributed at 600mm intervals up the column. This column allows the settling interface to be measured with time and samples of the settling contents to be withdrawn at various times during the trial.

Ten litres of Pond 4 wastewater was poured into a bucket and mixed using a portable drill with a mixing attachment. The initial reactive phosphorus concentration of the wastewater was measured once again to confirm that it had not changed from the values recorded when onsite. Whilst being mixed, 2.50 mL of lanthanum chloride was added to the bucket. This dosage was calculated from the results of the on-site trials performed earlier, as detailed in the previous section. It was the dosage required to achieve a residual filtered reactive phosphorus concentration of approximately 2 mg/L. After the lanthanum chloride was added, the bucket contents were thoroughly mixed for 2 minutes. The 10L of effluent was then added to the 2.65 metre high settling column. This was repeated a number of times to fill the settling column with 40L of coagulant-dosed effluent.

Upon filling the column, an air stone connected to a small, single phase blower was lowered to the base of the column. The blower was turned on and the column was gently aerated until thoroughly mixed. After turning off the blower, the remaining air in the column dissipated rapidly and a stopwatch was started to measure the length of time that the contents of the column had been settling for.

Figure 4. Settling column full of lanthanum chloride dosed effluent, prior to settling

At multiple time intervals:
- the sludge interface height in the column, and
- the turbidity of the supernatant above the interface was measured and recorded.
- Samples were collected using the 4 sampling points on the column for sending to an external laboratory for analysis of suspended solids, total phosphorus and metals such as lanthanum and iron;

After measuring interfaces, turbidity and collecting effluent samples intensively for an hour, the column was left overnight and the sludge was allowed to further compact. The volume of settled sludge was recorded the following morning and two final samples were collected, the clear supernatant at the top of the column and the sludge at the base.

This procedure was then repeated with ferric chloride, dosing 3.15mL of coagulant per 10L of effluent (slightly more than the quantity of lanthanum chloride that was used). This again was based on the results from the onsite dosing trials.

4 Ecotoxicity of Lanthanum

The project included provision for a review of the literature surrounding the ecotoxicology of lanthanum chloride. A comparison with other common coagulants, such as ferric chloride and aluminium sulphate, has been undertaken.

Fortunately, lanthanum is well known in Western Australia.   Phoslock® – in which lanthanum is bound to a bentonite clay – was developed by CSIRO and the Western Australian Water & Rivers Commmission in the 1990s (patented in 1997) to combat serious algal blooms that were experienced in areas such as Peel Estuary and the Swan & Canning Rivers (CSIRO, 2017; Phoslock Environmental Technologies, 2018).   The product has been widely applied to surface waters in WA and since commercialisation it has been widely accepted world-wide for this application. As a result, significant ecological data has been gathered. To understand the degree of risk posed by lanthanum dosing into effluent with subsequent irrigation to land, a review of the scientific literature was undertaken.

4.1   Context

The use of chemicals in wastewater treatment should consider the potential for adverse environmental impacts both within the treatment system and in the wider environment after the treated effluent is released. Since lanthanum is not widely used in the water and wastewater industry, a review of existing information concerning its eco-toxicity was performed.

The V&V Walsh site is within a relatively sensitive location. To the south-west is a wetland known as Manea Park, while to the east and north, the Preston River borders the irrigation areas. This river runs through Bunbury to discharge into Leschenault Estuary. The site is situated on the coastal sand plain which contains significant quantities of high quality groundwater used for drinking and is becoming more important as the south west dries out due to climate change.

4.2   Literature

The ecotoxicity of lanthanum was reviewed comprehensively by Herrmann *et al.* (2016) covering 187 peer-reviewed publications including documents from the US EPA (2012) and the European Commission (2006). This very recent review provides an excellent foundation for the assessment of lanthanum in the environment, although its primary focus is the aquatic environment. The authors acknowledge that toxicology data is sparse for lanthanum for many environments and species.

In addition, the US EPA (2018) has a useful online resource for looking up the ecotoxicity of various chemicals. It searches available databases and journal articles and draws data from them. This resource along with Hermann *et al.* (2016) were the primary basis for this review.

Table 2 summarises selected information from Hermann *et al.* (2016) concerning toxicity towards freshwater species commonly used in toxicological studies.   Direct comparison between coagulants and research papers is difficult due to the different test species, methodologies and endpoints used, but some generalisations are possible. Lanthanum appears to be substantially more toxic than ferric chloride to freshwater aquatic species, particularly with standard test species such as Daphnia (water flea) and rainbow trout. The 2 day, EC50 dose was 0.05 mg/L lanthanum vs. 8.8 mg/L for ferric chloride. Dissolved concentrations of the lanthanum ion (La^{3+}) are mainly responsible for the adverse effects. Typically, freshwater species are the most vulnerable to chemicals.

The widespread use of Phoslock in freshwater environments is considered safe since the lanthanum ion is bound to the clay and its action in limiting algal blooms is not due to direct toxic effects, but rather through the indirect action of starving the algae of phosphorus – usually the limiting nutrient in aquatic environments.

With respect to marine aquatic animals, however, lanthanum chloride has similar levels of toxicity to other coagulants. In large part, the toxicity of lanthanum (and other coagulants) appears due to the competition of the soluble trivalent cation (La^{3+}, Fe^{3+}, Al^{3+}) with calcium (Ca^{2+}) uptake, which is essential for cellular functions in most organisms. Lanthanum is listed in Table 3.4.1 of the ANZECC Guidelines on Freshwater and Marine Water Quality (2000), but it is noted that there is insufficient data to identify toxicant trigger levels.

Table 2. Aquatic life ecotoxicity by coagulant

Chemical	Animal	Duration	Effect	Endpoint	Concentration (mg/L)
Lanthanum Chloride	Rainbow Trout (eggs)	28 d	LC50	MOR	0.02
	Zebra Danio	4 d	LC50	MOR	>100
	Eastern Narrow-Mouthed Toad	7 d	LC50	MOR	0.29
	Water Flea	2 d	EC50	MOR	0.049
Ferric Chloride	Rainbow Trout (sperm and eggs)	21 d	NR-LETH	MOR	3,400
	Zebra Danio	4 d	LC50	MOR	32
	Asian Common Toad	4 d	LC50	MOR	0.4
	Water Flea	2 d	EC50	IMBL	8.8
Aluminium Sulphate	Water Flea	2 d	IC50	IMBL	3.4
	Asian Common Toad	4 d	LC50	MOR	1.87

Ecotoxicity abbreviations:

DNEL	=	Derived No Effect Level – the level of exposure above which humans should not be exposed.
EC50	=	Concentration required to give 50% of the maximal effect over the given time.
IC50	=	Half maximal inhibitory concentration – this is the potency of a substance inhibiting biological activity.
IMBL	=	Immobilisation.
LC50	=	Lethal dose for 50% of the population over the given time.
MOR	=	Mortality.
NR-LETH	=	100% mortality of the population over the given time.

Relative to the other coagulants, lanthanum chloride exhibits similar levels of toxicity to terrestrial animals (Table 3). For example, oral route LD50 concentrations for lanthanum chloride, ferric chloride and aluminium sulphate in rats are 4.18, 0.32 – 2.9, and 6.2 – >9 g/kg, respectively. Provided appropriate safety precautions are followed, there appears little additional risk to humans working with lanthanum chloride relative to other commonly used coagulants. This recommendation is made in the lanthanum chloride product MSDS (Redox, 2015).

There is negligible data regarding lanthanum toxicity to terrestrial plants (Table 4). This is somewhat unfortunate since the context of this project is treating effluent for a final use by irrigation to plant crops, especially pasture and turf grasses. In one of the few studies available, Zhang *et al.* (1999) found that lanthanum exhibited similar toxic effects on the Australian native plant, Geraldton waxflower (a flower endemic to Western Australia) as aluminium chloride. Exposure to both of these coagulants at doses of 2-3 mg/L resulted in reduced germination frequency and increased frequency of pollen tubes bursting. For aluminium chloride, there was negligible effect at half this concentration. Unfortunately, the equivalent data for lanthanum is not given, but it can be assumed that a similar result could be expected.

Table 3. Animal toxicity by coagulant

Chemical	Animal	Route	Effect	Endpoint	Concentration (mg/kg)
Lanthanum Chloride	Rat	Oral	LD50	MOR	4,184
		Intraperitoneal	LD50	MOR	106
		Intratesticular		Mutagen	5
		Parenteral (10D pregnant)		Reproductive	175
	Mouse	Intraperitoneal	LD50	MOR	121
		Subcutaneous	LD50	MOR	2,424
		Intravenous	LD50	MOR	18
		Intraperitoneal (12D pregnant)			112
Ferric Chloride	Human	Dermal	DNEL		2.8 mg/kg/day
	Rat	Oral	LD50	MOR	316 – 2,900
		Intratesticular	LD0	Reproductive	13
		Intravaginal	LD0	Reproductive	29
	Mouse	Oral	LD50	MOR	440 – 895
Aluminium Sulphate	Mouse	Oral	LD50	MOR	6,207 - >9,000

Table 4. Terrestrial plant ecotoxicity by coagulant (Zhang *et al.*, 1999)

Chemical	Plant	Concentration	Effect	Effect frequency (% - normal is 100%)
Lanthanum Chloride	Geraldton Waxflower	10μM (2.45 mg/L)	Germination Frequency	13
			Pollen Tube Burst Frequency	76
Aluminium Chloride	Geraldton Waxflower	10μM (1.33 mg/L)	Germination Frequency	97
		20μM (2.67 mg/L)	Germination Frequency	22
			Pollen Tube Burst Frequency	65

4.3   Assessment of Ecotoxicological Risks at Meat Processing Facilities

This project studies the use of the rare earth element, lanthanum, to precipitate phosphorus from meat processing effluent to levels which allow compliance with phosphorus loading rates during irrigation to land. Under these circumstances, not all of the dissolved phosphorus in the effluent is removed, since the residual phosphorus is beneficial to the irrigated plants. In fact, excessive phosphorus precipitation increases operating costs due to higher lanthanum consumption and the additional precipitated sludge volume that must be processed and disposed of. In the context of the ecotoxicology of a coagulant this is a vital distinction. The residual phosphorus levels in the treated effluent (5 – 10 mg/L) remain high relative to those normally measured in slightly or moderately disturbed environments (~ 50 µg/l). The reaction between lanthanum and phosphate ions in water is very rapid and ensures that any residual of dissolved lanthanum ion in the final effluent is negligible, since the lanthanum phosphate ($LaPO_4$) precipitate is only sparingly soluble in water having a typical solubility in the order of 4.4×10^{-8} mg/L (Firsching & Brune, 1991). At these levels, lanthanum poses negligible risk to animals, plants or humans.

This conclusion is supported by the widespread use of lanthanum in two particular applications:

1. For use in aquatic environments as Phoslock product to control algal blooms. The sparingly soluble nature of lanthanum in water ensures that any releases are well below levels that have deleterious impact on the flora and fauna in surface waters.

2. The unregulated use of lanthanum chloride as an aid in public and domestic swimming pools to control algal growth. The product is typically sold widely as a 15% solution.

The same conclusion can be applied in the first instance to reuse of the treated effluent for non-potable purposes around the facility. Lanthanum or rare earths are not highlighted as a significant risk in National Recycling Guidelines, although its use where potable reuse was being considered would merit more careful consideration.

In relation to the impact of lanthanum on aquatic environments, well managed irrigation of the effluent should ensure that surface runoff from the irrigated area into adjacent waterways and leaching of the applied effluent below the plant root zone is negligible. This minimises the risk of any residual lanthanum entering the surrounding environment by either of these pathways. This risk is further mitigated by the low residual concentration in the treated effluent.

4.4   Summary

It can be concluded that the use of lanthanum chloride in meat processing plant wastewater treatment systems where the treated effluent is use for crops or pasture irrigation, or non-potable reuse poses little or no additional risk to the environment, animals or humans than that from existing coagulants provided well managed irrigation occurs as required by most normal environmental licences.

5 Results

5.1 Irrigation assessment

V&V Walsh have taken the initiative to explore chemical dosing with lanthanum to reduce the effluent phosphorus concentration so as to be compliant with the allowable loading limits in their DWER Licence for their irrigation areas (Table 1). In conjunction with reducing the P concentration, the distribution of wastewater to each of the disposal points is also important to meet the allowable annual loadings.

5.1.1 Nutrient considerations

Approximately 216 ML of treated effluent is currently produced annually by the wastewater treatment system for irrigation. It contains (without additional reduction in P level) 60 mg/L of nitrogen and 24 mg/L of phosphorus - a N/P ratio of 2.5. Table 1 indicates that the maximum allowable loadings for the turf farm and pasture have quite different N/P ratios of 3.33 and 9, respectively. This means that whereas the currently treated effluent is nicely balanced for irrigation to the turf farm, there is a large excess of phosphorus for irrigation to pasture. Unfortunately, this means that sustainable application of nutrients on the available property is not currently feasible.

This could be solved by purchasing additional land, or using third party irrigation. Bunbury however is one of the fastest growing areas in Australia and additional land suitable for effluent irrigation is not available. The alternative is to reduce phosphorus levels. Through the innovative work of the Chief Engineer, Paul Oosthuizen, lanthanum chloride was identified as a locally available product with potential to be used as a coagulant to reduce phosphorus levels.

5.1.2 Options for Applying Sustainable Nutrient Loads

Two possible strategies for dosing coagulant into the wastewater to lower the P concentration were considered for the facility:
- The first option is to conduct chemical dosing of the total wastewater flow after Pond 5 with a coagulant (lanthanum or ferric) to reduce the P concentration from 20 mg/L to 10 mg/L. This allows the wastewater to be sent to either the turf farm or pasture (with the right flow split). This option maximises nitrogen loading onto the turf farm (the preferred irrigation area) while ensuring that the balance of flow sent to the pasture area remains compliant with allowable loading for phosphorus.

- The second option is to irrigate the turf farm with effluent at the current P level (20 mg/L) and dose only the effluent that will irrigated to the pasture areas, where the lower P loadings are required. The advantage of this option is that much less volume needs dosing – keeping any required physical equipment such as settlers smaller and less expensive. The downside is that the required P level would be lower – approximately 5 mg/L.

This is summarised in the table below which shows the P concentrations that must be achieved in each case and the crude split of annual flow between the two areas for each option. Note that these are only indicative values for the purposes of determining the P levels that need to be obtained through dosing trials with lanthanum and ferric chloride.

Table 5. Phosphorus treatment strategies

	Flow	TN concentration	TP concentration	TN loading	TP loading
	ML/yr	mg/L	mg/L	kg/ha/yr	kg/ha/yr
Option 1 – Single effluent P concentration					
Turf farm	160	60	10	600	123
Pasture	56	60	10	97	20
Option 2 – P concentration adjusted for destination					
Turf farm	117	60	20	437	180
Pasture	99	60	5	173	18

In discussions with Paul Oosthuizen, it was decided to pursue Option 1 largely because irrigation of the turf farm is seasonal and consequently the potential benefits of Option 2 (lower dosed volumes) cannot be realised. In this event, the flexibility offered by Option 1 is of more value.

5.2   Coagulant dosing trials

The results from the dosing trials with lanthanum chloride and ferric chloride are summarised in the tables below. They are a combination of on-site data collected by JEG and laboratory data from ALS.

Table 6. Lanthanum chloride dosing results

		Raw Wastewater		Single Stage Dosing								Double Stage Dosing	
	mL soln/800mL	0	0	0.100	0.150	0.175	0.200	0.225	0.250	0.300	0.400	0.100	0.200
	mg soln/L	0	0	195	293	341	390	439	488	585	780	195	390
Dosage	mol La/mol P	0	0	0.41	0.61	0.71	0.81	0.92	1.02	1.22	1.63	0.41	0.81
	mg La/L	0	0	44	66	77	88	98	109	131	175	44	88
	mg Cl/L	0	0	34	50	59	67	75	84	101	134	34	67
pH (onsite)	---	7.47	7.35	7.45	7.22		7.40	7.00	6.91			7.17	7.00
EC (onsite)	µS/cm	1652	1665	1696			1786	1731	1735			1751	1785
FRP (onsite)	mg/L	24.0		15.7		9.6	7.6	4.7	< 2	< 2	< 2	14.8	4.5
FRP (ALS)	mg/L	21.7	20.9	8.1	4.8		0.9		0.1				
FRP removal	%			62%	77%		96%		100%				
TP	mg/L	21.9	22.4	23.2	22.8		24.0		25.2				
COD	mg/L	66	124	98	118		135		116				
TSS	mg/L	8	47	174	234		306		329				
Total Alkalinity	mg/L	503	474	418	408		393		406				
Na	mg/L	130	136										
K	mg/L	47	52										
Ca	mg/L	29	29										
Mg	mg/L	15	16										
Cl	mg/L	228	235	272	290		317		335				
La (total)	mg/L	0.018	0.004	49	77		92		124				
La (dissolved)	mg/L	0.003	0.002	0.062	0.046		0.008		0.005				
NH_3-N	mg/L	87	88	78	76		87		80				
NO_2-N	mg/L	0.1	0.2	0.1	0.1		0.1		0.1				
NO_3-N	mg/L	0.1	0.1	0.1	0.1		0.1		0.1				
NO_x-N	mg/L	0.2	0.3	0.3	0.3		0.3		0.3				
TKN	mg/L	85	87	85	84		93		86				
TN	mg/L	85	88	85	84		93		86				

Table 7. Ferric chloride dosing results

		Raw Wastewater		Single Stage Dosing								Double Stage Dosing	
Dosage	mL soln/800mL	0	0	0.100	0.150	0.200	0.250	0.250	0.500	0.750	1.000	0.100	0.200
	mg soln/L	0	0	181	272	363	453	453	906	1359	1813	181	363
	mol Fe/mol P	0	0	0.61	0.91	1.21	1.52	1.52	3.03	4.55	6.06	0.61	1.21
	mg Fe/L	0	0	26	39	52	66	66	131	197	262	26	52
	mg Cl/L	0	0	50	75	100	125	125	250	374	499	50	100
pH (onsite)	---	7.47	7.35	6.65	6.48	6.50	6.32	6.60	6.04	5.30	2.80	6.90	6.71
EC (onsite)	µS/cm	1652	1665	1710	1728	1744	1758	1773	1925	2065	2680	1695	1740
FRP (onsite)	mg/L	24.0		15.2	11.1	5.6	< 2	4.3	< 2	< 2	13.4	12.7	5.4
FRP (ALS)	mg/L	21.7	20.9	14.0	7.3	5.5		3.4					
FRP removal	%			34%	66%	74%		84%					
TP	mg/L	21.9	22.4	23.4	24.6	25.2		23.6					
COD	mg/L	66	124	103	120	112		116					
TSS	mg/L	8	47	139	166	185		253					
Total Alkalinity	mg/L	503	474	408	373	348		322					
Na	mg/L	130	136										
K	mg/L	47	52										
Ca	mg/L	29	29										
Mg	mg/L	15	16										
Cl	mg/L	228	235										
Fe (total)	mg/L	0.54	0.64	28	42	52		67					
Fe (dissolved)	mg/L	0.37	0.36	0.27	0.24	0.30		0.21					
NH_3-N	mg/L	87	88	80	90	86		86					
NO_2-N	mg/L	0.1	0.2	0.2	0.2	0.2		0.1					
NO_3-N	mg/L	0.1	0.1	0.1	0.1	0.1		0.1					
NO_x-N	mg/L	0.2	0.3	0.3	0.3	0.3		0.3					
TKN	mg/L	85	87	81	89	91		91					
TN	mg/L	85	88	82	89	91		91					

5.3 Sludge settling trials

The results below are from the sludge settling trials performed in Brisbane, QLD. Table 8 and Table 9 present the sludge interface height and supernatant turbidity results for lanthanum chloride and ferric chloride respectively. These indicate how quickly the sludge was able to settle in the column and the quality of the supernatant above the settled sludge. Note that the top water level (TWL) fell slightly with time due to removal of samples from the column.

The top interface height (%) is the ratio of the height of the settling solid interface to the top water level at that point in time. It took about 1.5 minutes and 6 minutes for a relatively defined top interface between the settling sludge and clear supernatant to form for lanthanum and ferric, respectively. The bottom interface occurred near the base of the settling column and demarked a clear distinction between the bulk settling sludge and the lower, denser compacting settled sludge. The bottom interface height (%) is the ratio of the height of the settled sludge interface to the top water level at that point in time. It took at least 5 minutes to form a distinguishable bottom interface for both coagulants.

Table 10 to Table 13 show the laboratory data from the sludge settling tests. These include suspended solids concentrations at a number of depths in the settling column as well as at a number of time intervals over the trials. These data provide a comprehensive understanding of how the precipitated sludge behaves and settles over an extended period of time. Measurements of total phosphorus and metals (lanthanum and iron) also indicate how well fine precipitated material settles, which may be independent of the bulk sludge.

From these data, key design parameters such as upflow velocity, overflow rates and suspended solids removal rates can be calculated and potentially used to design a settling system to achieve removal of precipitated solids. Total solids concentrations of the settled sludge at the base of the column informs design decisions around the selection of dewatering equipment and chemicals.

Table 8. Lanthanum chloride sludge settling test results

Time	TWL	Interface height (mm)				Supernatant turbidity
		Top		Bottom		
min	mm	mm	%	mm	%	
0.2	2530					
0.3	2530					
0.5	2530					
1	2490					
1.5	2490	2480	100%			
2	2455	2410	98%		0%	Cloudy brown
5	2455	2240	91%	50	2%	Cloudy white, light flocs present (1-1.5mm dia)
8	2455	1960	80%	100	4%	
10	2395	1735	72%	140	6%	Turbidity improving (clearing up). Only a few fine, white flocs at top, larger flocs towards bottom of supernatant
13.5	2395	1480	62%	180	8%	
15	2395	1380	58%	200	8%	Distribution of particle sizes from small at top of supernatant to large at bottom
18	2395	1040	43%	240	10%	
20	2395	900	38%	260	11%	
23.5	2395	750	31%	315	13%	
25	2335	550	24%	315	13%	
28	2335	400	17%	330	14%	
30	2335	315	13%	315	13%	
32	2335	300	13%	300	13%	
34	2335	290	12%	290	12%	
36	2335	280	12%	280	12%	
40	2335	260	11%	260	11%	
45	2285	230	10%	230	10%	
48	2285	225	10%	225	10%	
50	2285	220	10%	220	10%	
60	2285	200	9%	200	9%	
1080	2285	95	4%	95	4%	Clear supernatant, no discernible solid

Table 9. Ferric chloride sludge settling test results

Time	TWL	Interface height (mm)				Supernatant turbidity
		Top		Bottom		
min	mm	mm	%	mm	%	
0.2	2530					
0.3	2530					
0.5	2500					
1	2500					Very fine, small floc present
1.5	2500					
2	2460					
5	2460				0%	Larger flocs starting to form. 2-3mm dia avg.
6	2460	2400	98%	30	1%	
8	2460	2340	95%	30	1%	
9	2460	2380	97%	30	1%	
10	2405	2180	91%	60	2%	Light, stagnant 1mm flocs uniformly present
11	2405	2150	89%	75	3%	
13	2405	2080	86%	90	4%	
15	2405	1980	82%	100	4%	Uniform 1mm flocs present. Supernatant clear but with discernible flocs
17	2405	1915	80%	110	5%	
19	2405	1840	77%	150	6%	
21	2405	1790	74%	160	7%	
23	2405	1730	72%	175	7%	
25	2365	1600	68%	190	8%	Uniform 1mm flocs
27	2365	1550	66%	200	8%	
29	2365	1450	61%	220	9%	
31	2365	1410	60%	235	10%	
33	2365	1330	56%	255	11%	
35	2365	1280	54%	260	11%	
37	2365	1200	51%	275	12%	
39	2365	1150	49%	290	12%	
41	2365	1050	44%	295	12%	
43	2365	1020	43%	315	13%	
45	2325	905	39%	320	14%	Top 300mm very clear. Below that uniform 1mm flocs
52	2325	700	30%	375	16%	
55	2325	610	26%	390	17%	
58	2325	530	23%	400	17%	
60	2325	465	20%	420	18%	Top 600mm clear. Uniform 1mm flocs below that
70	2325	390	17%	390	17%	
1320	2325	110	5%	110	5%	

Table 10. Lanthanum chloride settling column TSS concentrations at 4 depths with time.

Time (min)	0.6 m	1.2 m	1.8 m	2.3 m
0.5	271	254	281	283
2	279	272	273	303
10	88	272	280	1270
25	25	55	105	1910
45	24	10	14	2060
1080	8			5330

Table 11. Ferric chloride settling column TSS concentrations at 4 depths with time.

Time (min)	0.6 m	1.2 m	1.8 m	2.3 m
0.5	270	300	270	286
2	262	260	271	292
10	282	276	271	677
25	107	286	298	1220
45	42	94	296	1520
1080	17			4890

Table 12. Lanthanum chloride settling column TP concentrations at 4 depths with time.

Time (min)	0.6 m	1.2 m	1.8 m	2.3 m
0.5				
2				
10	6.7	21.7	22.2	109
25	2.3	4.1	8.9	165
45				
1080	1.5			512

Table 13. Ferric chloride settling column TP concentrations at 4 depths with time.

Time (min)	0.6 m	1.2 m	1.8 m	2.3 m
0.5				
2				
10	23.1	23.3	23.1	54.7
25	8.7	23.3	24.1	94.1
45				
1080	2.3			465

6   Discussion

6.1   Ecotoxicity of lanthanum

Lanthanum appears to have similar levels of impact on the environment and humans as other commonly used coagulants, although there is less data for comparison. Only in freshwater aquatic environments is lanthanum more toxic and the level of impact is highly dependent on other factors such as water hardness, dissolved organic carbon levels and so on. The toxicity is mediated largely by the soluble form of the lanthanum trivalent ion.

In the context of dosing lanthanum to precipitate phosphorus from meat processing effluents with subsequent irrigation to land of the treated effluent, impacts on the environment should be negligible. This is due to three factors:

1. Lanthanum chloride would be used at doses ensuring finite concentrations of excess phosphorus remain. This ensures that all the lanthanum dosed to the effluent forms lanthanum phosphate.
2. The reaction to form lanthanum phosphate is rapid (< 5s) and the solubility of this material in water is negligible.
3. Irrigation management protocols exist to ensure that appropriate quantities of treated effluent are applied to land to prevent surface runoff or groundwater impacts from the applied effluent.

Under these operating protocols, there appears to be little risk of the free lanthanum ion entering the environment at harmful levels.

6.2   Coagulant dosing trials

The Pond 4 effluent collected at V&V Walsh was well treated and visually clear and free of solids other than some algae. It had a neutral pH (7.4), moderate conductivity (1,650 µS/cm) and low COD (100mg/L). TSS was virtually nonexistent, alkalinity was low (500mg/L) and total nitrogen was about 85mg/L (entirely in the form of ammonium). The total and filtered reactive phosphorus concentrations were both approximately 22 mg/L (see Table 6 and Table 7 for more details) which shows that there had been almost complete conversion of phosphorus into the soluble phosphate ion (PO_4^{3+}) form. Literature and past experience with other dosing trials suggests that this kind of well-treated effluent is ideal for phosphorus dosing as minimal quantities of the coagulant will be lost to competing side reactions.

6.2.1   Effectiveness of Dosing

The onsite dosing trials revealed that both lanthanum chloride and ferric chloride rapidly precipitated phosphorus from Pond 4 effluent. Both coagulants achieved very low residual filtered reactive phosphorus (FRP) concentrations of less than 2 mgP/L. This is excellent and demonstrates the applicability of these coagulants for most phosphorus limits that a processor may have to meet. As expected, dosing the coagulants reduced the FRP but did not impact the total phosphorus of the unsettled wastewater. This means that if the wastewater is dosed with coagulant, but the solid formed is not separated from the effluent, the total phosphorus value will remain unchanged. Total phosphorus is typically the value that environmental authorities are the most interested in, so this highlights the absolute necessity of successful solids separation from the dosed effluent.

For lanthanum chloride, the FRP results from the onsite Hach spectrophotometer differed from the independent laboratory (ALS) results significantly (see Table 6 and Table 7). This may be due to the fact that if the sample is collected and filtered immediately after dosing and mixing the solution, the precipitated $LaPO_4$ is so fine that it seems to pass through the 0.45µm filter paper. After 5-10 minutes have passed, the precipitated solids appear to agglomerate to the point where they are captured by the filter paper. For the FRP analysis, the laboratory filtered the samples themselves. This was more than 24 hours after the collection of the samples, so the precipated solids had sufficient time to agglomerate. As such, the laboratory data is considered more reliable than the onsite measurements from the Hach spectrophotometer.

Table 14 and Table 15 below outline how each of the coagulants performed with respect to phosphorus removal at various doses. Note that the bulk densities of the lanthanum chloride 60% solution and the 42% ferric chloride solution are 1,560 kg/m^3 and 1,450 kg/m^3 respectively.

Table 14. Lanthanum chloride phosphorus removal performance

Dosage		FRP (ALS)	Removal		
mg soln/L	mol La/mol P	mgP/L treated	% P removal	mg P/mL LaCl₃ soln	mg P/g LaCl₃ soln
0	0	21.7	0		
0	0	20.9	0		
195	0.41	8.1	62	106	68
293	0.61	4.8	77	88	56
390	0.81	0.9	96	81	52
488	1.02	0.1	100	68	44

Note: soln = solution of 60% lanthanum chloride

Table 15. Ferric chloride phosphorus removal performance

Dosage		FRP (ALS)	Removal		
mg soln/L	mol Fe/mol P	mgP/L treated	% P removal	mg P/mL FeCl3 soln	mg P/g FeCl3 soln
0	0	21.7	0		
0	0	20.9	0		
181	0.61	14.0	34	58	40
272	0.91	7.3	66	74	51
363	1.21	5.5	74	63	44
453	1.52	3.4	84	57	40

Note: soln = solution of 42% ferric chloride

From the tables above, it is clear that for a given dose of coagulant, the lanthanum chloride was able to achieve a lower FRP concentration. For example, to achieve a residual FRP of 8 mg/L, approximately 200 mg/L of LaCl₃ solution was required, compared to 270 mg/L of FeCl₃ solution. Each millilitre of lanthanum chloride solution can precipitate 68-106 mg of phosphorus, relative to 55-75 mg of phosphorus per millilitre of ferric chloride solution. The graph below shows the dose required to achieve a certain FRP removal for both coagulants.
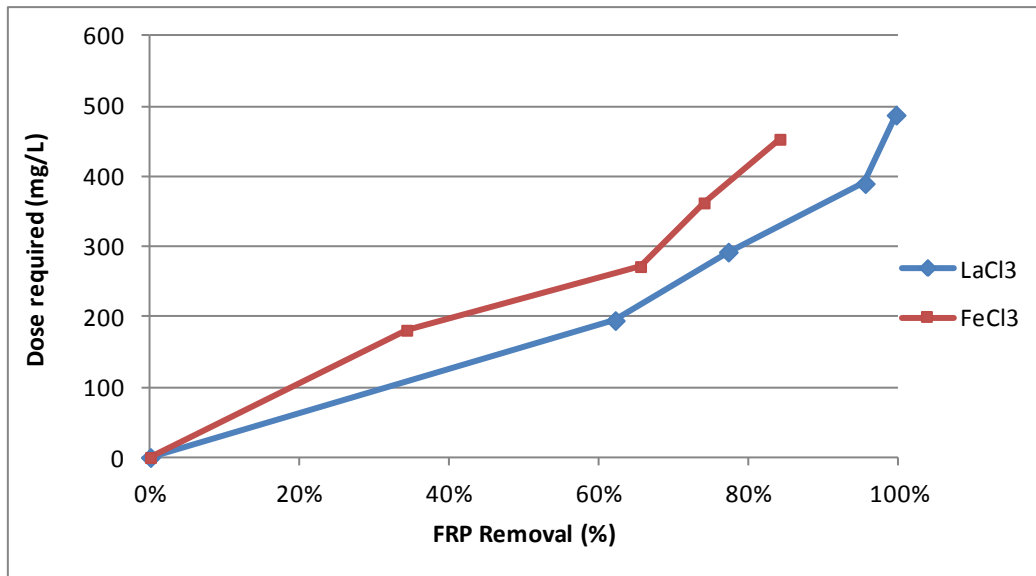
Figure 5. Coagulant dose required to achieve certain FRP removal

For a given removal of FRP, less lanthanum chloride solution is required than ferric chloride solution. However, the dose is not the only consideration when selecting the most suitable coagulant. The graphs below show the impact that each of the coagulants have on pH, EC, TSS and total alkalinity.

6.2.2 Effect on pH

Both coagulant solutions are highly acidic (pH 1-3), so it was expected that coagulant dosing would somewhat depress the pH of the effluent. Depression of the pH can be a negative side effect of a coagulant, as it may severely inhibit downstream biological treatment of the wastewater and it can be expensive to correct the pH to a neutral value if required (via caustic or similar).

As can be seen in Figure 6, the ferric chloride depressed the pH more than lanthanum chloride, however, the impact was not linear. It reduced the pH from a starting point of about pH 7.4 to 6.4 at even low degrees of P removal. A pH less than 7 is detrimental to most aerobic bacterial treatment processes and may favour anaerobic activity at low oxygen levels. Generally for irrigation, a pH greater than 6.5 is required by many licences. In this case, corrective dosing of alkalinity would be potentially needed, which requires an additional dosing system and ongoing purchase of alkalinity solution.

The lanthanum chloride, on the other hand, had virtually no impact on the pH other than the dose that achieved almost 100% FRP removal. This may be due to the fact that once the lanthanum chloride is dosed in excess of the phosphorus, the residual lanthanum reacts with other components in the wastewater which consequently depresses the pH. Consequently, lanthanum is a superior coagulant from this point of view.
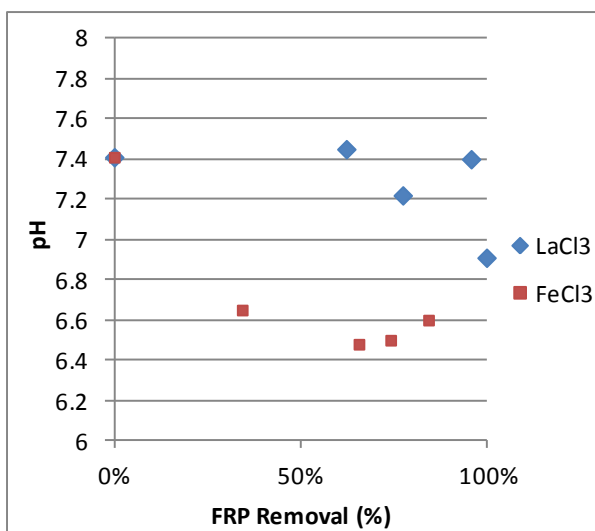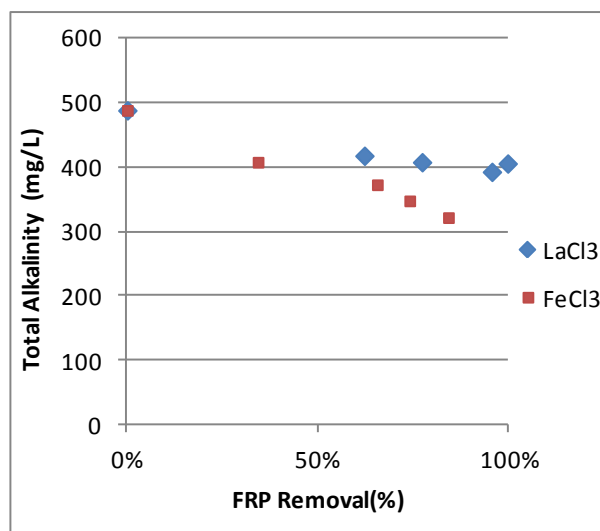
Figure 6. pH vs. FRP removal

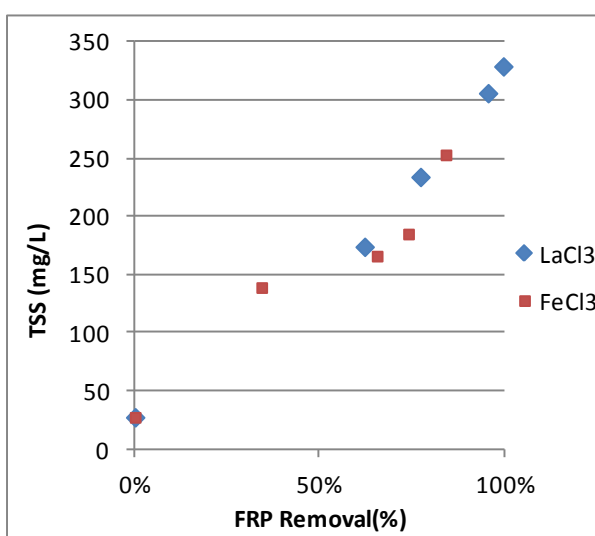**Figure 7.** Total alkalinity vs. FRP removal

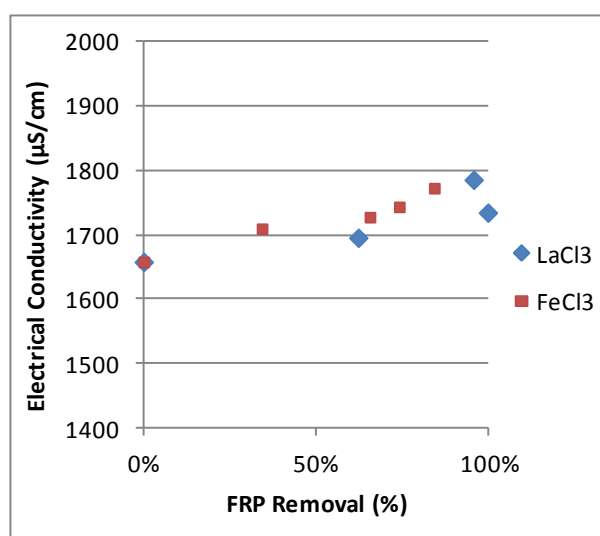**Figure 8.** TSS vs. FRP removal

Figure 9. Electrical conductivity vs. FRP removal

Figure 7 confirms this effect, showing that to achieve 85% FRP removal with ferric chloride, over 33% of the available total alkalinity in the effluent is consumed. This relates to the fact that ferric chloride is a general coagulant and often reacts to form $Fe(OH)_3$ instead of $FePO_4$ when alkalinity is present. This alkalinity consumes coagulant that is no longer able to precipitate phosphorus from the effluent. Lanthanum chloride only consumed about 18% of the alkalinity for the same FRP removal.

6.2.3 Sludge formation

Another important consideration for coagulation processes is the quantity of sludge produced. The coagulants precipitate phosphorus as a solid, which must be disposed of, often at significant expense to the processor. A coagulant that produces excess sludge is undesirable as it adds cost (both capital for sludge separation and dewatering equipment as well as ongoing operational costs for trucking and landfill or similar charges).

Both coagulants generated similar quantities of sludge on a mass basis (Figure 8). For a FRP removal of ≈65%, both coagulants produced approximately 150 mg/L of sludge (the starting TSS was ≈25 mg/L).

6.2.4   Effect on other contaminants

Electrical conductivity can be considered a measure of the total dissolved solids (TDS) in a solution. Some processors may have a TDS limit for their discharge and chemical dosing can increase this substantially. TDS removal from wastewater is not trivial, so it is important that this parameter is monitored closely when new chemicals are introduced to the WWTP. However, both coagulants had minimal impacts on the electrical conductivity (see Figure 9), increasing it by no more than 150 µS/cm (<10%). This should have little effect on irrigation quality.

Neither of the coagulants had any discernible impacts on the ammonia in the effluent. The COD and major cations were similarly unaffected.

As both coagulants are chloride salts, the chloride concentration of the dosed effluent is also a consideration. Excess chloride can promote corrosion and is detrimental for irrigation due to its effect on plant foliage health. At 85% FRP removal with lanthanum chloride, the dosing added approximately 70mg/L of chloride to the effluent. While undesirable, the final level of 300 mg/L chloride is unlikely to be a cause for concern for turf or pasture.

6.2.5   Residual lanthanum concentrations

As discussed previously in the ecotoxicity section, there are concerns about the toxicity of lanthanum to freshwater aquatic life, and particularly if the lanthanum remains as dissolved lanthanum that is unreacted with phosphorus. For this reason, the total and dissolved lanthanum concentration of the undosed and lanthanum chloride-dosed effluent was measured (Table 6). The laboratory results show that residual dissolved lanthanum ion was present at very low concentrations (micrograms/litre) and was low even at high P removal. This result is in accordance with previous work by Recht & Ghassemi (1970) and Strileski (2013). Total lanthanum for the dosed samples was in proportion to the dose, as expected, since this test included the precipitated lanthanum phosphate.

An increase in dissolved lanthanum was also reported for the dosed samples but this may be due to the phenomenon discussed earlier whereby if the sample is filtered immediately after dosing and mixing, the precipitant is so fine that it can pass through the 0.45µm filter paper. This would be picked up by the laboratory as 'dissolved' lanthanum when in fact it is very small molecules of $LaPO_4$ that have reacted but have not yet agglomerated to form larger flocs. The dissolved lanthanum samples were filtered onsite at V&V Walsh, unlike the FRP samples which were filtered by the laboratory. Considering that lanthanum phosphate has a solubility of 4.4×10^{-8} mg/L, it seems unlikely that there could be up 0.062 mg/L dissolved lanthanum remaining in the wastewater, considering that there was still significant excess phosphorus for that sample (8.1 mg/L).

6.2.6   Comparison of Chemical Cost for Ferric and Lanthanum

An important outcome of the dosing trials is the quantity of coagulant required to achieve a certain final phosphorus concentration and the associated chemical cost. The irrigation assessment in Section 5.1 found that for V&V Walsh to be compliant, they would need to either treat the entire wastewater stream down to a phosphorus concentration of 10 mg/L, or treat about 46% of the wastewater down to 5 mg/L of phosphorus (in addition to a modest increase in dosing at the DAF for the entire wastewater stream to reduce phosphorus to 20 mg/L).

The unit price for lanthanum chloride (60% solution) and ferric chloride (42% solution) for V&V Walsh are $7,000/kL and $1,500/kL respectively (excl. GST). The cost for each of the coagulants in the options discussed in the irrigation assessment are outlined in the table below.

Table 16. Coagulant cost summary to reduce phosphorus levels in Pond 4 effluent

	Units	Lanthanum Chloride 60%	Ferric Chloride 42%
Option 1 – treat whole effluent stream			
Flow	ML/yr	216	216
Final P concentration	mg/L	10	10
Coagulant dose required	mg/L	193	262
	kL/yr	27	39
Unit cost	$/kL	$7,000	$1,500
Annual cost	**$/yr**	**$190,000**	**$60,000**
Option 2 – treat only turf farm stream			
Flow	ML/yr	99	99
Final P concentration	mg/L	5	5
Coagulant dose required	mg/L	282	382
	kL/yr	18	26
Unit cost	$/kL	$7,000	$1,500
Annual cost	**$/yr**	**$130,000**	**$40,000**

Table 16 shows there is a large price differential between the two coagulants, with lanthanum chloride being almost 5 times as expensive as ferric chloride on a volume basis. This translates into the operating cost for lanthanum dosing for either option being a multiple of 3 times as expensive as ferric chloride, despite the increased dose required for latter. Few processors are likely to be able to justify paying such a premium on the price for lanthanum chloride when many other, much cheaper alternatives are readily available. It also indicates that the price breakeven point for lanthanum chloride is about $2,250/kL to be competitive with other coagulants such as ferric salts on an operating cost basis.

Of course, capital costs also come into consideration. For V&V Walsh, the intention is to dose coagulant into the inlet of a pond and allow the sludge to settle in the pond over time. This means that expensive sludge separation equipment is not required and capital costs do not outweigh the obvious disadvantage in operating cost. If sludge separation is needed, then the situation changes and lanthanum becomes more interesting as shown in Section 6.4 below.

It is important to note that these calculations assume perfect settling of the produced sludge. The sludge solids capture efficiency of the separation device needs to be factored into the dose required and the annual operating cost would have to be increased proportionally to achieve compliance. There is also likely to be additional cost associated with Option 2 that is not factored into the calculations in Table 16 **Error! Reference source not found.**since there will be additional chemical dosing required into the existing DAF to bring the phosphorus concentration down from its current level of 24 mg/L to 20 mg/L. However, this cost will be the same for both coagulants and change only the absolute, and not the relative cost.

Despite the lower cost of Option 2, it is likely that the difficulty in implementing a more complex operating strategy involving differential treatment of the effluent sent to the turf farm does not justify the benefit of the operating cost savings relative to Option 1, especially if the cheaper ferric chloride coagulant is used. Option 1 permits a high degree of flexibility as to which area is irrigated on any given day.

6.3   Sludge settling trials

In addition to the factors discussed above such as coagulant ecotoxicity, dose required and the impact on physico-chemical parameters of the wastewater, the characteristics of the sludge produced are also of great importance. A sludge that settles quickly, leaves a clear supernatant and compacts to a small volume is highly desired as it reduces the volume required to settle the precipitated sludge from the wastewater and reduces the risk of carryover of precipitated solids. Solids that are carried through to the final discharge point would be picked up by a total phosphorus test and could potentially result in a processor discharging non-compliant effluent.

6.3.1   Interface Heights during Settling

As the onsite dosing trials revealed, both coagulants produced similar quantities of sludge on a mass basis. This was confirmed again in the sludge settling trials. However, these trials showed that the sludge produced by the lanthanum chloride settled much faster than the sludge produced by the ferric chloride. The following two graphs show the position of the top and bottom sludge settling interfaces with respect to time during the settling trials for each coagulant (See Section 5.3 for the definition of these interfaces).
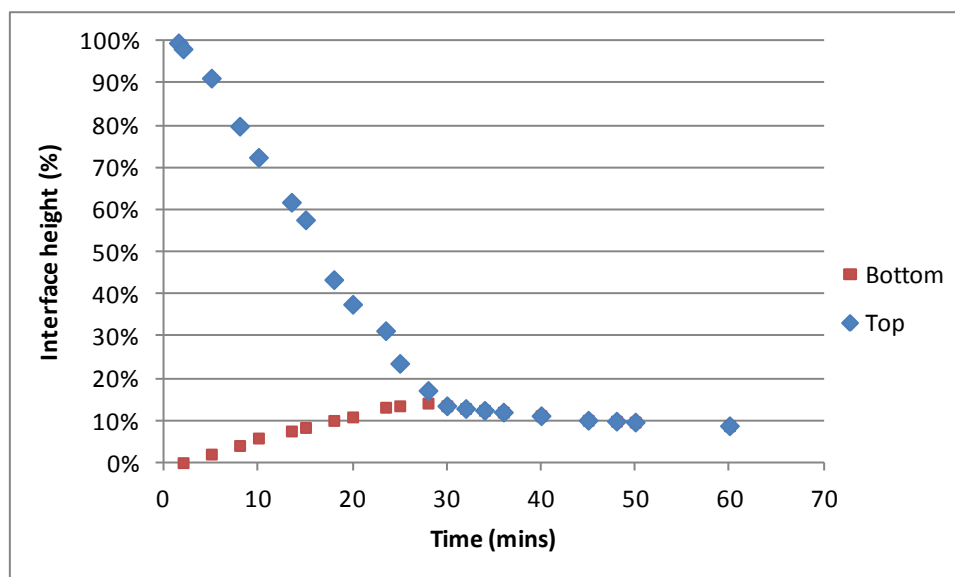

Figure 10. Lanthanum chloride sludge top and bottom interface position vs. time
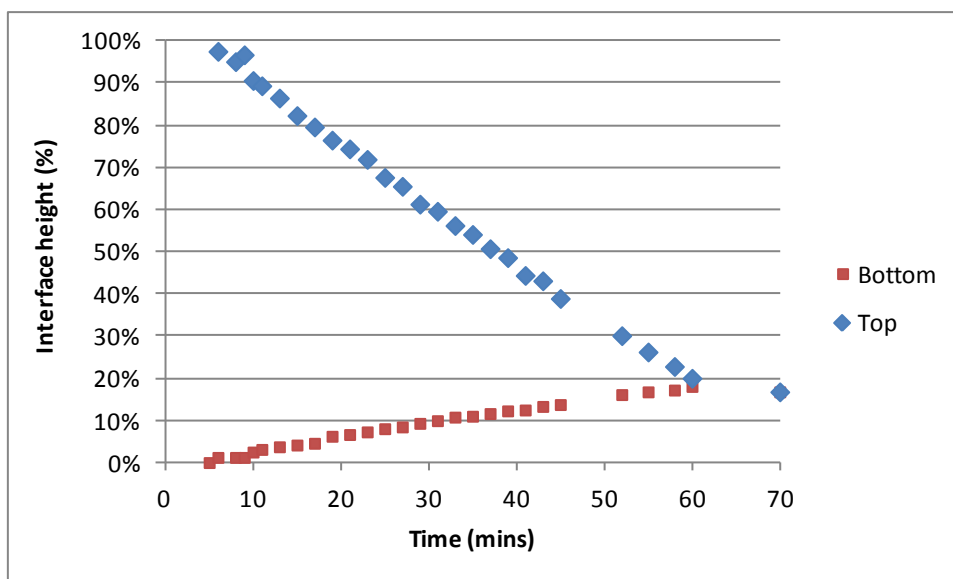
Figure 11. Ferric chloride sludge top and bottom interface position vs. time

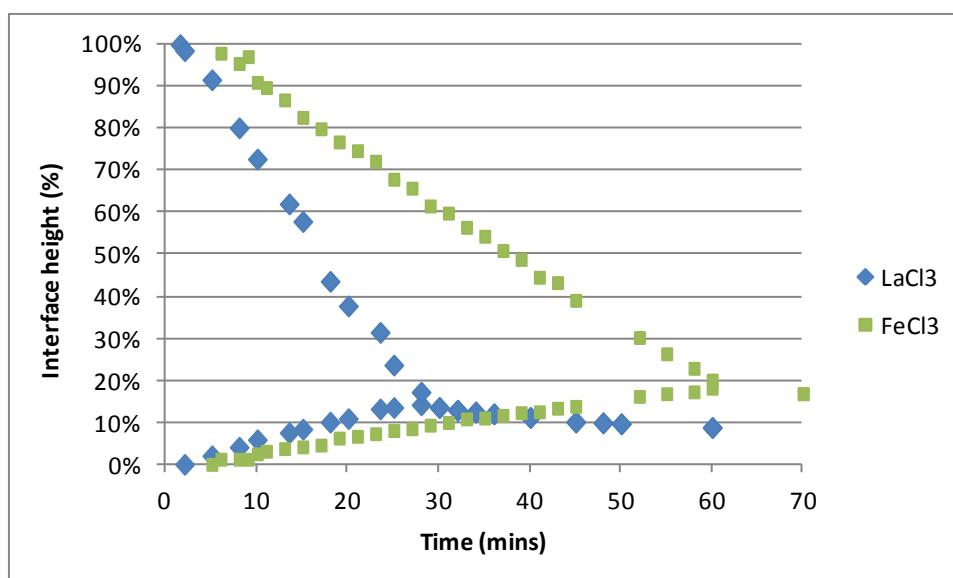Combined onto a single graph, the difference between the two coagulants is clear.

Figure 12. Lanthanum chloride and ferric chloride sludge top and bottom interface position vs. time

The rate of settling of the lanthanum sludge is markedly faster than that of ferric sludges. Within 30 minutes, the top interface of the lanthanum sludge had settled to meet the base compacting sludge layer ("bottom" in Figure 10) compared to 60 minutes for ferric. An alternative way of looking at it, is that for a particular point in time, say 30 minutes, the lanthanum chloride top interface was at 13% of the depth of the standing water level in the column, but the ferric chloride top interface was still at 60% (Figure 12).

Comparison of Table 10 and Table 11 reveal and even more striking difference between the coagulants. After 10 minutes of settling, the 0.6 metre deep sampling port on the column showed a TSS removal of 68% removal for lanthanum chloride, but 0% for ferric chloride. After 25 minutes, the same port had 91% removal for lanthanum chloride and 64% for ferric chloride. After 45 minutes, the 1.8 metre deep port showed 95% TSS removal for lanthanum chloride, but 0% removal for ferric chloride. This was confirmed by the total phosphorus results in the column (Table 12 and Table 13).

In essence, the lanthanum chloride produces a much better settling sludge than ferric chloride.

Dissolved lanthanum concentrations in the settling column were very low and concur with the discussion earlier regarding the apparent fineness of the freshly precipitated $LaPO_4$, to the point that it can pass through 0.45μm filter paper. The dissolved lanthanum concentrations recorded in the column after dosing are comparable to the dissolved lanthanum concentrations in the untreated Pond 4 effluent, indicating that these results are possibly artefacts of the laboratory testing methodology.

6.3.2 Sludge Characteristics

After leaving the precipitated sludge in the settling column overnight for both coagulants, the lanthanum chloride sludge compacted down to 4.2% of the water volume and the ferric chloride sludge down to 4.7% of the water volume. Again, for the same mass of sludge, the lanthanum sludge compacted down to a smaller volume, which is beneficial.

The compacted sludges shared similar characteristics, as seen in the table below. The solids content of both sludges was of the order of 0.5% by mass.

Table 17. Compacted sludge characteristics

Coagulant	TSS mg/L	TP mg/L	Total metal (La/Fe) mg/L
Lanthanum chloride	5,330	512	2,170
Ferric chloride	4,890	465	1,430

6.3.3 Settling Rates and Solids Capture

From the results gathered during the settling trials, suspended solids removal rates and overflow (sludge settling) rates can be calculated for an ideal settler operating on the sludges produced by each of the coagulants. This has been done using the method from Eckenfelder (1989) to generate the graphs below.
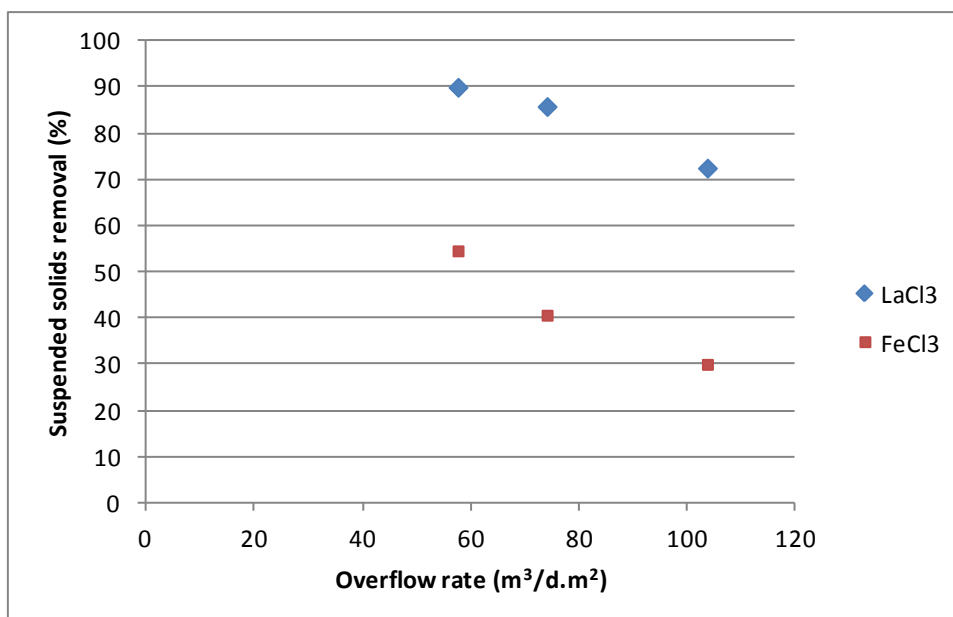
Figure 13. Suspended solids removal rate vs. overflow rate for an ideal settler acting on the precipitated sludges

The difference between the coagulants is quite stark. For a given overflow rate, the suspended solids removal by the settler is superior for lanthanum chloride compared to ferric chloride. An overflow rate of 104 m^3/m^2.d yields a TSS capture rate of 73% for lanthanum chloride but only 30% for ferric chloride. For ferric chloride to achieve a SS removal rate of 73%, it would need to have a settler approximately 2.5 times the size. This represents significant additional upfront CAPEX for a processor. The graph below shows the same data expressed in terms of detention time within the settler.
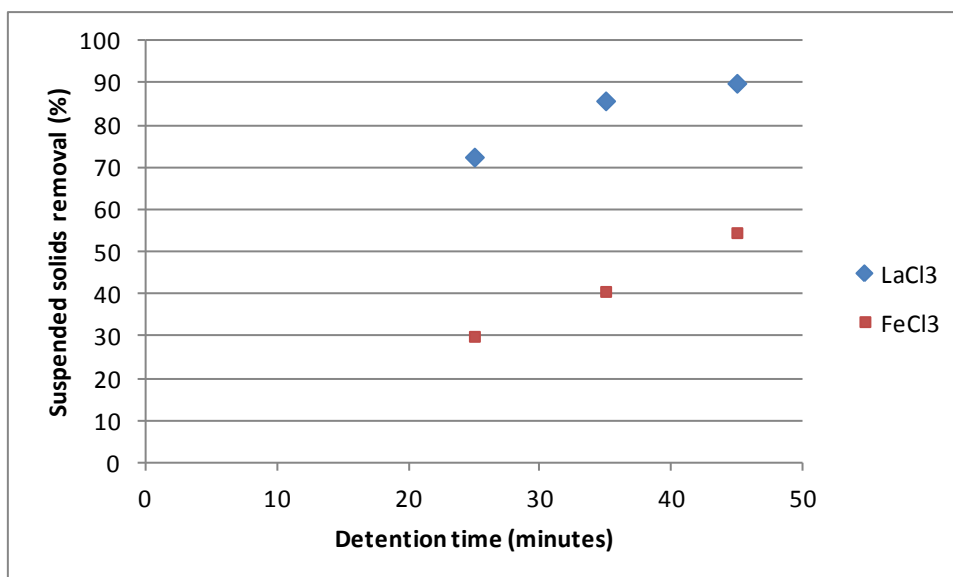

Figure 14. Suspended solids removal rate vs. detention time for an ideal settler acting on the precipitated sludges

Essentially, a ferric chloride precipitated sludge would require a much larger settler (and correspondingly longer detention time) to achieve the same degree of suspended solids removal. In this instance, where a settling device is required, there is a clear trade-off between capital and

operating costs to determine which coagulant returns the best bang for buck. Typically however, the higher capital cost process is more challenging to fund.

6.4   Summary

Considering all of the data and outcomes of the trials undertaken as part of this project, the following table summarises the differences between the two coagulants. Unit costs for each of the coagulants were supplied by V&V Walsh. The cell colours in the table represent good (green), neutral (yellow) and poor (red) outcomes.

Table 18. Summary of coagulant performance at ≈85% FRP removal

Parameter	Lanthanum Chloride	Ferric Chloride
Ecotoxicity	Moderate	Moderate
Dose required	340 mg/L	450 mg/L
Impact on pH	Negligible	1 pH unit
Impact on total alkalinity	Low (18%)	Moderate (33%)
Impact on electrical conductivity	Low (<10%)	Low (<10%)
Impact on chlorides	Low	Low
Sludge produced (mass)	240 mg/L	230 mg/L
Sludge settleability	Good (interface at 13% after 30 mins)	Poor (interface at 60% after 30 mins)
Sludge compactness	4.2%	4.7%
Pond 6 sludge capacity lifetime (approximate)	10 months	8.8 months
Overflow rate to achieve 70% TSS capture	104 m^3/d.m^2	40 m^3/d.m^2
Settling volume required for 70% TSS capture (ideal – not for design)	15 m^3	40 m^3
Coagulant cost	$7,000/kL	$1,500/kL
Annual cost (for Scenario 1 – final P of 10mg/L) assuming pond capture of sludge	$190,000/yr	$60,000/yr

In essence, lanthanum chloride is a superior coagulant to ferric chloride for precipitation and separation of phosphorus from wastewater, but comes with a substantial premium on the price (even when the reduced dose is accounted for). Processors will have to consider whether the increased cost is worthwhile on a case by case basis. Large processors are likely to find that the lanthanum chloride will be far too expensive to be considered, but small processors wishing to delay large capital expenditure may find the lanthanum chloride more attractive.

6.5   Achievement of project objectives

The objective of this project was as follows:

This project seeks to explore the use of lanthanum chloride as a means of reducing phosphorus levels in meat processing wastewater and to evaluate its benefits and challenges compared to the more well-known precipitants (specifically ferric chloride).

This objective has been achieved through an ecotoxicity assessment, comprehensive onsite dosing trials, sludge settling trials in a purpose-built settling column and critical analysis of the data produced by both of these trials in this report.

7 Conclusions/recommendations

7.1 Conclusions

All of the activities undertaken as part of this project were successful. Based on the initial irrigation and ecotoxicity assessment, coagulant dosing trials and sludge settling trials, the following conclusions have been generated:

1. To achieve compliance with the site environmental licence, the TP concentration in the wastewater must be either less than 10 mg/L in the entire treated effluent (option 1), or less than 20mg/L in the effluent irrigated to the turf farm and less than 5 mg/L in the pasture irrigated effluent (option 2).

2. Lanthanum chloride is more toxic to freshwater aquatic life than ferric chloride, but exhibits similar levels of toxicity to marine aquatic life and terrestrial species to commonly used coagulants. There is little data regarding lanthanum toxicity to vegetation, but it will be important to ensure free lanthanum levels are as low as possible.

3. Reaction of lanthanum chloride with phosphate ions in wastewater will generate a sparingly soluble precipitate, $LaPO_4$, that has a solubility of 4.4×10^{-8} mg/L. The negligible solubility of lanthanum phosphate combined with comparably high P levels in the final irrigated effluent should result in free lanthanum ion concentrations that pose little risk to the environment when irrigated to land under well managed conditions Results of the dosing trials confirmed that dissolved lanthanum ion concentrations were very low. With a combination of careful dosing system design and best practice irrigation management protocols, there should be minimal risk of lanthanum impacting the environment.

4. The use of lanthanum chloride as a coagulant for phosphorus removal should not be confused with the commercially available lanthanum-containing product Phoslock. The latter is a clay-based material with active lanthanum sites for reaction with phosphorus, but literature studies show that the doses (and associated costs) required for a given phosphorus removal from wastewater are orders of magnitude higher than for lanthanum chloride solution. The results in this report cannot be applied to Phoslock.

5. The lanthanum chloride and ferric chloride were both able to effectively precipitate phosphorus from the Pond 4 effluent. Both were able to achieve very low residual reactive phosphorus concentrations (<2 mg/L) at reasonable dosing rates. To achieve a particular phosphorus concentration, more ferric chloride was required than lanthanum chloride (≈32% more by mass).

6. Many Australian chemical suppliers do not sell lanthanum chloride, making it more difficult to obtain than ferric chloride. It is also substantially more expensive than ferric chloride (4-5 times the price). Even with the lower dose required, the operating chemical cost associated with lanthanum chloride is still approximately 3 times more than for ferric chloride for a given TP removal.

7. Ferric chloride had a greater impact on the pH and total alkalinity of the effluent than lanthanum chloride, however they both had minimal impact on the electrical conductivity and chloride concentration. In some instances, the use of ferric chloride may require alkalinity dosing to counterbalance the reduction in pH in downstream ponds, biological systems or irrigation areas. It is unlikely that this will be needed for lanthanum dosing.

8. The two stage dosing trials revealed that there is little advantage in doing this relative to single stage dosing for the Pond 4 effluent. The additional cost and complexity of running two separate dosing and mixing tanks likely outweighs the small potential reduction in operating costs from reduced chemical usage. However, other sites with effluent more concentrated in solids and organic matter may find greater benefit in doing two stage dosing.

9. Both coagulants produced similar masses of sludge that settled fairly rapidly. However, the sludge produced by the lanthanum chloride dosing settled much faster than the ferric sludge. Consequently to separate the precipitated sludge from the treated effluent using a settler, the equipment for ferric sludge would need to be approximately 2.5 times the size necessary for lanthanum sludge. Since settlers are highly expensive devices, the lower capital cost for a settler for lanthanum sludge may outweigh the downside of the higher lanthanum cost for a given application.

7.2   Recommendations

The scope of this research was limited to the application of lanthanum to precipitate phosphorus at V&V Walsh's facility. The conclusions presented above satisfactorily define its performance with well-treated meat processing wastewater.

In terms of further investigations, there is merit in performing trials of the effectiveness of lanthanum chloride dosing for phosphorus removal in meat processing streams that are rich with suspended solids and organic matter to determine if it is more effective than other coagulants. A major challenge with these types of waste streams – such as screened wastewater, or anaerobic pond-treated effluent is that competing side reactions often require coagulant doses many times the stoichiometric dose to reduce phosphorus. This is a critical issue for several meat processing plants. Technical literature suggests that lanthanum chloride is more effective at targeting phosphorus than other coagulants, which have a tendency to react with many other contaminants in wastewater.

8   Key messages

1. Both lanthanum chloride and ferric chloride are able to effectively precipitate phosphorus from solution and achieve low levels of residual phosphorus at reasonable doses. However, approximately 32% more ferric chloride than lanthanum chloride is required to achieve the same degree of phosphorus removal.

2. The sludge produced by the lanthanum chloride settled much faster than the ferric chloride sludge. To achieve the same degree of solids separation for ferric chloride as lanthanum chloride, a much larger and more expensive settler would be required.

3. Lanthanum chloride is the superior coagulant to ferric chloride for this application on a number of criteria, but the price premium is so substantial that few processors are likely to be able to justify using lanthanum chloride.

4. Careful design and appropriate management protocols are able to minimise the risk of lanthanum impacting the environment.

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