Department of Civil and Natural Resources Engineering
University of Canterbury

Research Master Thesis

Anaerobic pond treatment of pig farm manure slurry in Aotearoa New Zealand: A case study

Exploring opportunities for enhanced performance

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ENCI 690

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Abstract

Pork production is a relatively small part of Aotearoa New Zealand's important agricultural sector, but manure slurry from pork production gives rise to several environmental challenges, such as odour, eutrophication from wastewater discharges containing high nutrient loading, and the release of greenhouse gases. One way to mitigate the environmental effects is to treat the manure slurry in anaerobic digestion pond systems. Although a functioning pond, together with collection and combustion of the produced methane, does reduce the environmental impact, there are many cases where systems fail. One possible cause of system failure is fats in the manure slurry from the pigs, which in turn is dependent on the pig feed. Fat in anaerobic digestion systems is known to cause issues, such as foaming and uneven methane production. The main objective of this research was to, in the field, measure the performance of the waste treatment system on a pig farm in Aotearoa New Zealand and, in the laboratory, investigate the effect of dairy by-product on methane potential. Fieldwork was carried out to characterise the pond system of the farm and explore possible seasonal variations. Several important parameters, such as Total Kjeldahl Nitrogen (TKN), volatile solids (VS) and phosphate were measured for the manure slurry and pond digestate. Laboratory experiments, using bench-scale reactors, were carried out to measure the methane potential of solutions of manure slurry to inoculum ratios (g VS) of 1:1 and 0.5:1 and first pond digestate to inoculum ratio (g VS) of 1:1. Another laboratory experiment, also using bench-scale reactors and a solution of manure slurry to inoculum ratio (g VS) of 0.5:1, was carried out to measure the effect of concentrations of 5 %, 10 % and 15 % dairy by-product on methane potential. From the seasonal study it could be seen that the concentrations of most parameters analysed in the manure slurry varied widely between sampling occasions, whereas the concentrations were more consistent in the two ponds. The only parameter that showed significant difference between summer and winter months was phosphate with increased concentration in manure slurry and decreased concentration in digestate from the second pond during the summer months. A possible explanation for increased phosphate concentrations in manure slurry is the use of phosphate rich dairy by-product in the pigs' feed during the summer months. For the digestate from the second pond, a possible explanation for the decreased concentration of phosphate could be struvite formation during the summer months. The laboratory experiments investigating two different ratios of manure slurry showed that the methane concentration and cumulative methane produced varied more between samples for manure slurry of the inoculum ratio 1:1 (g VS) solution than for the 0.5:1 solution, probably due to higher heterogeneity of the material. The laboratory experiments of co-digestion of manure slurry and three different concentrations of dairy by-product showed a longer lag phase for methane production, more build-up of crust and less degradation of organic material for higher concentrations of dairy by-product. The overarching conclusion of the study is that there are indications of overload issues in the waste system and one way to address this could be to increase hydraulic retention time by changing flow order of the ponds, and to discard leftover dairy by-product elsewhere.

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1. Introduction

Agriculture, forestry, and fishing are activities of great economic importance to Aotearoa New Zealand. These primary industries collectively represent 5.5 % of the country's Gross Domestic Product (The World Bank, 2019) and employ about 6.6 % of the population (Trading economics, 2019). One important branch of agriculture is pork production. All food production poses environmental challenges, and the pork industry is not the exception. There are about 280,000 pigs in Aotearoa New Zealand (Stats NZ, 2019). Although this number is far exceeded by the approximately 10 million cows, of which 6.5 million are dairy cows (Stats NZ, 2017), the pork industry still has a large impact on the environment. More specifically, pig farms can have a high local impact because large nutrients loads are generated within small areas and odour, specifically from the storage of effluent, is often a significant issue for the surrounding communities. Although all animal production produces odours, pig farms are often the most common cause of complaints (Trabue et al., 2019; Madsen et al., 2009).

The sustainable management of piggery effluent is becoming increasingly important globally due to a need for reducing the environmental impacts of pig farming (USDA, 2019). It is necessary to regularly collect and store the effluent in impermeable storage facilities to prevent runoff and subsequent discharge of nutrients, mainly nitrogen and phosphorous, which can cause eutrophication of water bodies (FAO, 2019). Where effluent is collected and stored, it can be used as a fertiliser for land application and, if the fertiliser is applied appropriately, runoff to water bodies can be kept at a minimum (Hashemi et al., 2019). However, improper storage of effluent is responsible for much of the local environmental impact of pig farms, mostly as air pollution in the form of emission of gases, e.g., ammonia, methane, hydrogen sulphide, and other odorous compounds (Petersen et al., 2009; Petersen et al., 2013). Some of these gases have an especially prominent environmental impact, and local environmental problems increase as animal production facilities get larger and more people live closer to such facilities.

The management and treatment of the effluent and slurry is dependent on the animal production system (both what kind of animal, but also production type and chosen management system etc.) and location. A common approach is to use anaerobic digestion. Anaerobic digestion systems around the world vary. In Aotearoa New Zealand the most common practice is to use two connected uncovered ponds; one anaerobic and one facultative pond. The two ponds differ in size and depth. The aim of this system is mainly to remove a substantial quantity of suspended solids, thus, reducing the insoluble biochemical oxygen demand. This treatment does not significantly reduce nutrient levels nor does it reduce the soluble biochemical oxygen demand (Wang et al., 2004). As such, most pond systems in Aotearoa New Zealand were not designed to optimise the conversion of organic carbon to methane (Park and Craggs, 2007). The focus has been directed towards waste and odour management, and to a lesser extent to the production of renewable energy (Heubeck and Craggs 2010). Nevertheless, in the last 15 years some farms have started to cover their anaerobic ponds and collect the methane generated from the anaerobic respiration of organic material. This system of covered anaerobic ponds for capturing methane is the main system used for wastewater low in solids and in systems in temperate regions such as Aotearoa New Zealand (Figure 1). The main reasons for using this approach are practical implementation and economics. However, in Aotearoa New Zealand more water is used in washing down the slurry from the animal sheds to the storage, than in most other countries. Because of this, the concentration of solids in the pond is relatively low but volumes of wastewater are high, leading to a design that is suboptimal at producing methane (Rennie, 2014).

The amount of methane produced per unit mass of waste treated indicates how well the anaerobic system is functioning and acts as an indicator of the degradability of the organic material (Mottet et al., 2010). There are many factors affecting the biodegradability of pig slurry, such as the composition and amount of the solids in the effluent released to the anaerobic pond, the regularity of the supply of effluent to the pond, the retention time in the pond, and agitation of the pond. As described by Venkiteshwaran et al. (2015), the microbial community responsible for the biodegradation is sensitive to changes, especially the archaea responsible for the methane production (Alves et al., 2009). Consequently, the performance of different anaerobic pond systems vary and depend on local conditions, such as temperature, feedstock, pH, management, and the precise configuration of the pond (Chen and Neibling 2014; Venkiteshwaran, 2015). It is therefore necessary to examine the specifics of each waste treatment system in terms of odour management, methane production, and digestate quality.

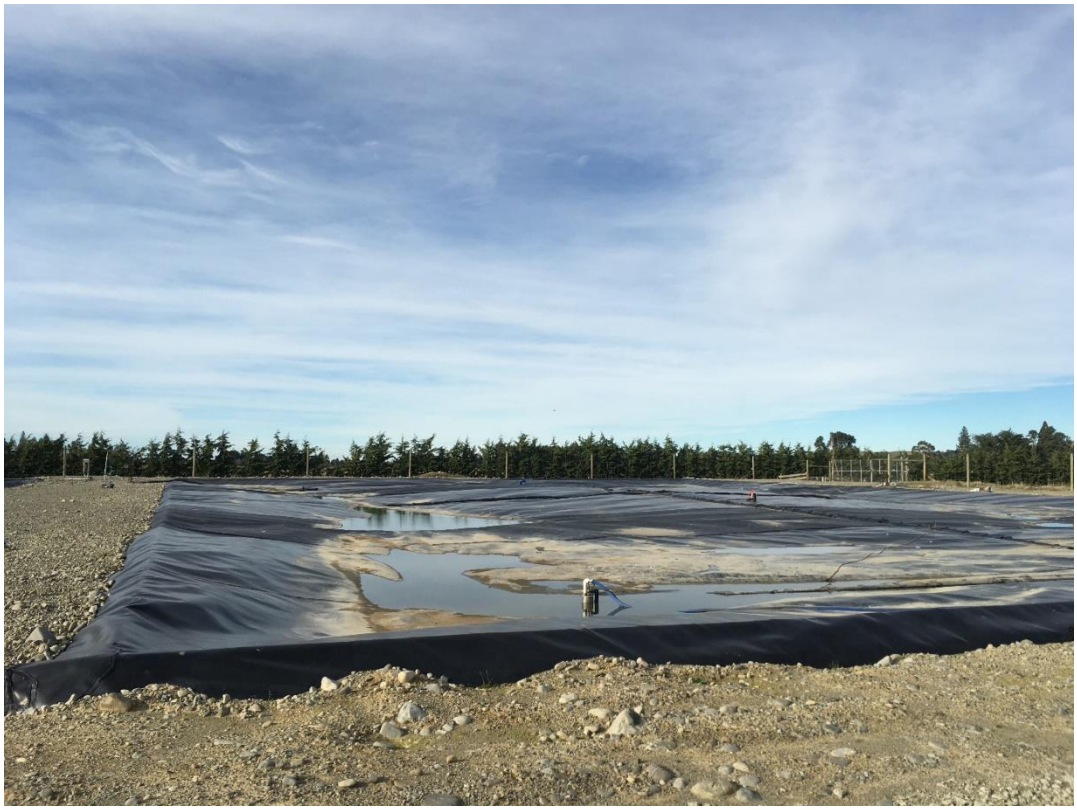

Figure 1: Photo of covered anaerobic pond for capturing methane in Aotearoa New Zealand

The current dominance of the dairy industry in Aotearoa New Zealand means that large volumes of dairy by-products are produced and some of these low-value by-products are given as complimentary feed to pigs. One of these dairy by-products is generated when dairy wastewater, as part of its treatment process, undergoes dissolved air flotation (DAF), a process which separates fats and solids from the rest of the wastewater. The fats and solids are then skimmed off the wastewater surface, which can serve as a cost-effective supplement to pig diets. Past studies on how fats affect anaerobic digestion, such as the co-digestion of cooking oil or similar substrates in wastewater treatment or in co-digestion with manure and slurry, shows that oil and grease, in sufficient volumes, can disturb the process. Several issues have been identified. These include irregular or low methane production, malodours, foaming of wastewater, and aggregation of solids in the anaerobic pond (Alves et al., 2009, Vaidya et al., 2018). However, little research has been undertaken to examine possible effects on anaerobic digestion of pig waste originating from pigs given feed supplemented with fatty dairy by-products. If the anaerobic digestion system is malfunctioning, resulting in malodours, this can result in complaints from the surrounding community. If the functionality of the specific treatment system, and the effects of dairy by-product on the anaerobic digestion process, is known, there might be opportunities to mitigate the negative impact of dairy by-product in pig feed while concurrently generating and capturing more methane.

2. Literature review

In this chapter the general concept of anaerobic digestion, and in what context it is used are first examined. Hereafter follows an outline of different anaerobic pond systems and treatment of pig effluent in anaerobic ponds, with a focus on the Aotearoa New Zealand practice. The chapter finishes with a description of some challenges and limitations of treating pig farm effluents using anaerobic pond systems, focusing on how animal diets affect anaerobic digestion of slurry and how fats from dairy by-products may affect the anaerobic digestion and the resulting methane potential.

2.1. Anaerobic digestion

Anaerobic digestion is a process in which microbial metabolism breaks down (i.e., digests) organic matter to predominately methane (CH_4), carbon dioxide (CO_2) and inorganic and insoluble compounds in an oxygen-free (i.e., anaerobic) environment (see Figure 2). This happens in four main steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. During the hydrolysis step, hydrolytic bacteria break down carbohydrates, proteins and fats to smaller and soluble sugars, amino acids and fatty acids. In the acidogenesis step, the products from hydrolysis are converted by acidogenic (fermentative) microorganisms to predominantly volatile fatty acids (VFAs), carbon dioxide and hydrogen (H_2). During the acetogenesis stage, the VFAs are transformed into acetate, carbon dioxide and hydrogen. In the fourth and last step, methanogenesis, microorganisms belonging to the domain archaea, called methanogens, produce methane and carbon dioxide from acetate and hydrogen (Chen and Neibling, 2014; Venkiteshwaran, 2015).

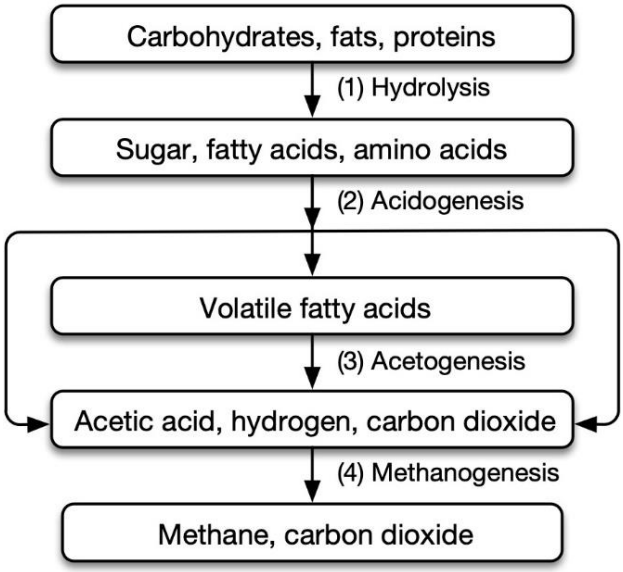

Figure 2: The four-step anaerobic digestion process (based on Chen and Neibling, 2014)

The entire process, involving all four steps, is affected mainly by the feedstock composition and pre-treatment (if any), temperature, hydraulic retention time, organic and hydraulic loading rate and pH. While the hydrolytic and acidogenic bacteria can survive and be productive in a wide range of conditions (Chen and Neibling 2014), the optimal pH range for methanogenesis is relatively narrow at 6.5-8.0 (Anderson et al., 2003). According to Chen and Neibling (2014), acidogenesis is usually the fastest step and hence there is a risk of accumulation of VFAs. Normally the wastewater buffering capacity is maintained by bicarbonate (HCO_3^-)/carbonate (CO_3^{2-}) equilibrium, but if the acid concentration gets too high or the concentrations of carbonate/bicarbonate are too low, the system's buffering capacity is exceeded and the pH drops. This creates an unfavourable environment for the methane-forming organisms, the system collapses and methanogenesis stops completely. This can happen when acid utilization is inhibited or too slow due to organic overload, presence of toxic substances, or quick changes in temperature (Chen and Neibling, 2014).

Anaerobic digestion can take place to various extents under different temperatures. Psychrophilic conditions exists from about 20°C and below (Chua et al., 2018); however, methane production decreases below 20°C (Wang et al., 2019). Mesophilic conditions exists around 32-43°C and thermophilic conditions exists around 49-60°C (Chen and Neibling 2014; Venkiteshwaran, 2015). Depending on the temperature in the pond, different organic loading rates can be applied. The higher temperature provided in a heated digester (mesophilic or thermophilic conditions) enables a higher organic loading rate. In an unheated anaerobic pond on a farm in a temperate climate like Aotearoa New Zealand, the temperature conditions will oscillate between psychrophilic and mesophilic. Therefore, ponds in Aotearoa New Zealand are designed for lower volatile solid (VS) loading rates (0.02–0.46 kg VS/m^3/d) than heated digesters (2.7 to 17.7 kg VS/m^3/d) (Park and Craggs, 2007).

The purpose of the piggery waste treatment varies to some extent depending on source and circumstances. With regard to wastewater treatment, it is largely to reduce the amount of solids and to make it sufficiently clean to safely discharge to waterways or to convert nutrients in the manure and slurry into a more accessible form for plants when applied on land as fertiliser. Depending on how much methane is produced, the methane produced during the process might be flared or combusted to generate electricity and heat or used as biofuels for vehicles (Costa et al., 2015, Jarvie, 2019).

2.2. Pig manure slurry management and anaerobic digestion

In the four subsections below the housing systems of pigs and pig manure slurry treatment in Aotearoa New Zealand are briefly looked into, as well as anaerobic digestion of manure slurry around the world and finally the pros and cons of anaerobic digestion in ponds in Aotearoa New Zealand is shortly reviewed.

2.2.1. Housing systems of pigs in Aotearoa New Zealand

There are different housing systems for pigs in Aotearoa New Zealand. In outdoor pig farming, the pigs are maintained in fenced areas and provided with small sheds or huts for weather protection. The pigs defecate on the ground, which is where the manure is left. The pigs may be moved in a crop rotation cycle to allow the droppings to be used as on-site fertiliser. This system is used predominately in some parts of the South Island, where there are the right soil conditions and lower precipitation rates. The housing in indoor pig farming varies. When deep litter housing of pigs is used, the spent litter is collected and applied directly to land, or is accumulated for composting. However, most pig manure is handled as a slurry. The floors in the pens can either be solid, where the waste is scraped or hosed out, or consist of slats, where the waste falls or is washed into drains which can be hosed or flushed on a regular basis. In another system with slats, the waste falls into a pit under the slats and is stored and flushed out when the pigs are moved from the pen. Alternatively, a dry scraper system can be used to scrape out the waste instead of hosing it out. When the slurry leaves the building, it is flushed to a sump, tank or pond. The way the slurry is stored outside the buildings varies and storage space can be constructed of earth, concrete or glass lined steel. Size, shape and depth of the storage varies and the storage can be above, below or partly below ground. Anaerobic and shallow, often unstirred, aerobic ponds are a common way of storage in Aotearoa New Zealand (New Zealand Pork, 2017).

2.2.2. Pig manure slurry treatment in Aotearoa New Zealand

According to New Zealand Pork (2017), some sort of screening device is often used to separate large solids and hair prior to pumping the slurry from the sump to the storage tank or pond, or directly to land. Also, according to New Zealand Pork (2017), in the sump, there may be some form of agitation device as well to prevent settling of solids and to produce a homogenous slurry. If the effluent is pumped to a deep pond, anaerobic digestion of the organic material will take place. The most common system is an anaerobic pond followed by an aerobic or facultative pond or series of ponds (Figure 1). The anaerobic pond is deep (4-5 meters) with a small surface area to keep the environment low in oxygen and to encourage the anaerobic breakdown of the organic material in the slurry. Most of the settling of suspended solids takes place in the deep anaerobic pond. The facultative pond is instead shallow (about 1 meter), with a large surface area to allow as much oxygen transfer as possible to enable aerobic bacteria to break down the remaining organic material. In this pond, there is some additional settling of suspended solids. The large surface area supports

more sun exposure, algal growth and oxygen transfer. Ultraviolet light from the sun reduces the concentration of pathogens. Sometimes there is an agitator in the pond to provide stirring and to mechanically add oxygen (New Zealand Pork, 2017). The digestate is then mostly applied to land in a process frequently referred to as 'fertigation' (fertiliser-irrigation) by Irrigation New Zealand (2021).

2.2.3. Anaerobic digestion of manure slurry around the world

When manure slurry is anaerobically treated methane is formed from the (anaerobic) microbial breakdown of organic matter and this methane can be collected. In Europe, the use of digesters, i.e., closed vessels in which anaerobic digestion takes place, is most commonly used. Digesters can be used on farms for slurry and crop residues, or in large centralised plants for co-digestion of slurry, crop residues, waste from food processing plants, and other organic materials (Milet, 2015). The main purposes for the anaerobic digestion of slurry in Europe are the generation of methane, the reduction of greenhouse gases emitted from slurry storage and the production of a good biofertiliser for crop cultivation, thereby reducing the need for chemical fertiliser (Scarlat et al. 2018). In the USA, the most common techniques used to treat manure slurries on farms are plug-flow digesters, complete mix digesters, and covered lagoons. The type of digester varies depending on the manure slurry management. The main purposes are to generate electricity, to fuel boilers or furnaces, or to provide combined heat and power (EPA, 2019). In Australia, covered lagoons or heated and stirred-tank digesters are used for anaerobic digestion of slurry only or for co-digestion of slurry with other waste products. The methane that is generated is used mainly to heat the digester and to generate electricity for on-farm use. The digestate is applied to land as fertiliser (Tait, 2017; Dairy Australia, 2017).

2.2.4. Anaerobic digestion in ponds in Aotearoa New Zealand – pros and cons

In Aotearoa New Zealand, ponds are commonly used to store and treat animal waste. Pond systems were originally designed to remove solids rather than to optimise the production of methane (Heubeck and Craggs, 2010; Park and Craggs, 2007). Recently farms have started to cover their anaerobic ponds to collect methane, originally as a result of environmental stewardship led by the National Institute of Water and Atmospheric Research (NIWA) (Rennie, 2014). The methane can then be flared or used to produce heat and electricity on-site (New Zealand Pork, 2017).

The best technique for anaerobic digestion depends on several factors, such as what feedstock is going to be used, the intended goal (e.g. waste reduction or energy production) and how many work hours the operator is willing to put in. The advantages of using ponds for anaerobic digestion as opposed to using heated digesters are that the ponds function at lower temperatures (psychrophile), with no mixing and can treat materials low in solids. Therefore, they are more passive digesters. Most digesters need a higher percentage of solids, a higher temperature (mesophile) and mixing of the material to work optimally. Since the manure slurry management systems in Aotearoa New Zealand use much water and the climate is temperate, ponds are less expensive to construct, operate and manage than digesters. Covered anaerobic ponds have low maintenance requirements, which also decreases the cost (Rennie, 2014). Studies such as those of Heubeck and Craggs (2010), have shown that in spite of lower process temperatures, anaerobic covered ponds can produce similar amounts of methane as heated digesters if long wastewater treatment hydraulic retention times are used. This way, the pond system is much less expensive to operate since no heating or mixing is required.

Disadvantages of using ponds for anaerobic digestion as opposed to using heated digesters can be the long retention time, and hence, the large space required for wastewater treatment. Since the process is unheated and temperature therefore varies over the day and year, the production of methane also varies accordingly (Heubeck and Craggs, 2010). The onsite use of the electricity and/or heat generated from the methane can offset the high capital cost of the pond system (Heubeck, 2012).

There has been very few studies carried out on anaerobic ponds on farms in Aotearoa New Zealand and very few parameters, mostly biogas composition, TS, VS, TKN and BOD_5 was analysed (Heubeck and Craggs, 2010; Park and Craggs, 2007; Craggs et al. 2008).

2.3. Some challenges and limitations of treating pig farm effluents using anaerobic pond systems

Previous research concerning the effects of the pigs' diets on anaerobic digestion has mainly focused on the effects of different levels of crude protein and fibre as in Kerr et al. (2006), and high fibre diets as in Jarret et al. (2012). In the study by Kerr et al. (2006), it was shown that crude protein and cellulose in different amounts in the pigs' diets had an impact on levels of VFA, indoles and phenols in the treated effluent. They did not find a significant effect of diet on methane production, but they did find a correlation between the C:N ratio of the waste and methane potential. Jarret et al. (2012) found that a higher fibre content in the diet could lead to increased methane production potential. The study suggests that pigs fed high fibre diets excrete more organic matter due to lower digestibility, and this results in higher potential methane production. Also, to compensate for the low energy content in the high fibre diet, the diet was complemented with additional fat resulting in more fat in excretions and this could also be part of the explanation to the higher potential methane production. It seems that higher fat content in combination with higher fibre intake is favourable for methane potential. However, research on the effects of fat content in pigs' diets and its consequent effects on anaerobic digestion has not yet been reported.

Studies of anaerobic co-digestion with fats have been made. Vaidya et al. (2018) performed a study with different fatty products, one of them being DAF solids. DAF solids are fats and solids removed from dairy wastewater by dissolved air flotation (DAF). Co-digestion of DAF and dairy wastewater showed high potential for methane production. Although fats can increase methane production under favourable conditions, fats in anaerobic digestion have also been linked to several issues, such as irregular or low methane production, malodours, foaming, sludge flotation and washout of the anaerobic pond (Alves et al., 2009; Vaidya et al., 2018; Salama et al., 2019). Alves et al. (2009) review how fat affects anaerobic digestion in co-digestion and states that overloading and inhibition is common when fats are co-digested with other substrates and that it is still a challenge to manage this co-digestion.

3. Objectives

The objective of this research was to measure the seasonal performance of a pond system used for waste treatment on a pig farm in Aotearoa New Zealand and investigate the effect of dairy by–product used in pig feed on methane potential. This was achieved using a field study and laboratory experiments with the following specific objectives:

(A) Field study – Determine the seasonal variations of physicochemical water quality parameters and biogas composition of an anaerobic pond used to treat pig manure slurry where the pigs are fed feed containing dairy by-product, namely to explore seasonal variations in the performance of the farm's anaerobic digestion waste treatment system.

(B) Laboratory experiments – Determine the effect of the amount of dairy by-products in pig slurry on methane production rates.
   1. Measure the methane potential of manure slurry and first pond digestate, and
   2. Quantify and characterise the effects of dairy by-product on methane potential of the slurry.

4. Materials and methods

Field and laboratory work was carried out to study seasonal variations in the performance of the waste treatment system at the farm. A laboratory study on methane potential of two different concentrations of slurry and on the first anaerobic pond digestate was also carried out, as was a study to investigate the impact of different amounts of dairy by-product on methane potential.

This chapter describes the research approach followed. First, the farm and its waste treatment system are described (Section 4.1), this is followed by a description of the effluent sampling and analysis methods for the seasonal study (Section 4.2). Finally, in section 4.3 the design and methods of the laboratory study of methane potential from two different concentrations of slurry and from the first anaerobic pond digestate are described and the design and methods of the laboratory study investigating the effect of different concentrations of dairy by-product on the methane potential are described.

The part of the study involving collecting farm data from the farmer has been granted authorisation by the University of Canterbury's Human Ethics Committee (see Appendix A). Possible safety hazards and mitigation strategies associated with the field research are listed in Appendix B (Table B1). The form "Field Activity Participant Declaration & Consent" is presented in Appendix C.

4.1. Study site

The farm is located about 50 km North West of Christchurch in the Canterbury region of Aotearoa New Zealand's South Island (see Figure 3 for placement of region). The site experiences a temperate oceanic climate (annual average air temperature: 11.4°C; annual average rainfall: 270 mm) (World Weather Online, 2020).

Figure 3: Location of the farm in Aotearoa New Zealand.

The farm was chosen due to its proximity to the University, the farmer's willingness to participate and because the farmer had reported issues with malodours and incomplete effluent biodegradation as denoted by poor methane production and crust formation on the surface of the first pond. At the time of the study, the farm housed about 400 sows, 70 gilts, 1140 weaners, and about 570 each of porkers, growers and finishers. This results in slightly more than 3,500 Standard Pig Units (SPU) in total. There were no seasonal changes in the pig production, which is a cyclic process, where all the stages occur simultaneously at the farm in different batches (see Figure 4). The pigs' diet constituted of mainly different premixes depending on production stage and an addition of barley, wheat, soya meal, linseed oil, and a by-product from milk processing plants, namely the fat-rich substance generated by dissolved air flotation (DAF) of wastewater from a nearby milk processing plant (containing approximately 76 g/L (76,000 mg/L) of fat). The dairy by-product is included in the pigs' diet from September to May.

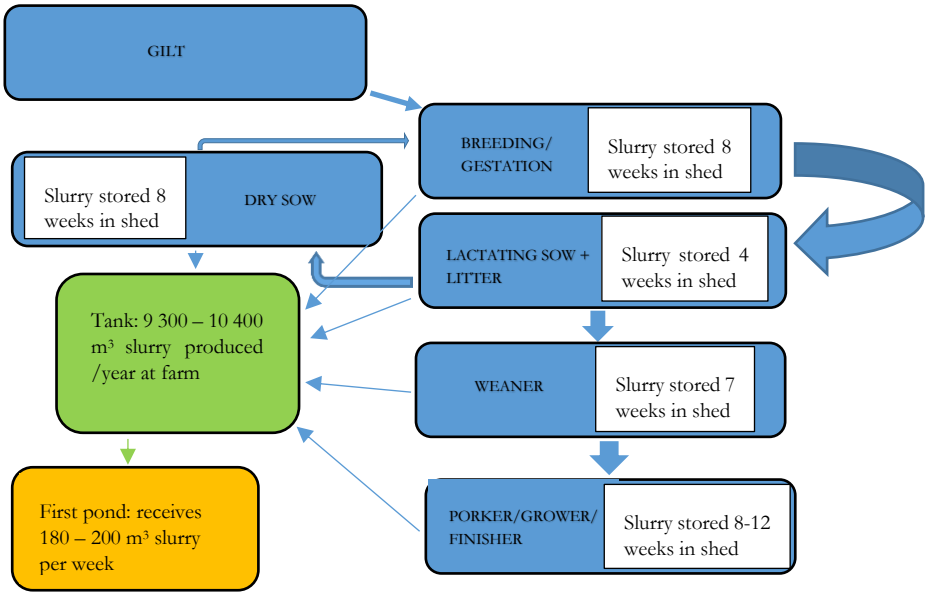

Figure 4: Pig production cycle/production stages and flow of manure slurry (blue arrows)

The pigs are housed indoors, all effluent is managed as manure slurry and is stored in different drains/holding tanks below where the animals are housed in each shed. The effluent from each shed is then sluiced to a central collection tank where it is temporarily stored and then pumped to the first pond for treatment. Before the manure slurry is transferred to the central collection tank, it is stored under the different sheds for different periods of time depending on whether it is dry sows, lactating sows and litters, weaners, porkers, growers or finishers (Figure 4). Effluent from dry sows is stored for about eight weeks. Effluent from lactating sows and litters is stored for four weeks. Effluent from weaners is stored for seven weeks and effluent from porkers, growers and finishers is stored for between eight and 12 weeks. Approximately 9 300 - 10 400 m^3/year of pig effluent is produced at the farm. Once a week, approximately 180 - 200 m^3 manure slurry is pumped from the central collection tank into the first pond. Sometimes this pumping takes two days. The feedstock for the pond is pig manure slurry and periodically small amounts of dairy by-product from cleaning out storage tanks, or spoiled dairy by-product. The pigs drink treated water from the county domestic supply. Wash down water is untreated river water from a storage dam.

4.1.1. Pond system characteristics

The pig effluent is treated in a two-pond in-series system. Effluent from the first pond is transferred by gravity to the second pond at the same time as the raw manure slurry is pumped to the first pond. The effluent from the second pond is used as crop fertiliser during spring, summer and autumn. Both ponds are covered (Figures 5). Figure 6 shows a schematic of the manure slurry collection and waste treatment system at the farm (where liquid refers to the manure slurry). Maximum and minimum daily temperatures

over the duration of the seasonal study were collected from a NIWA weather station (the closest weather station, approximately 40 km from the farm) via the National Climate Database (NIWA, 2021).

Figure 5: First (left) and second (right) covered pond

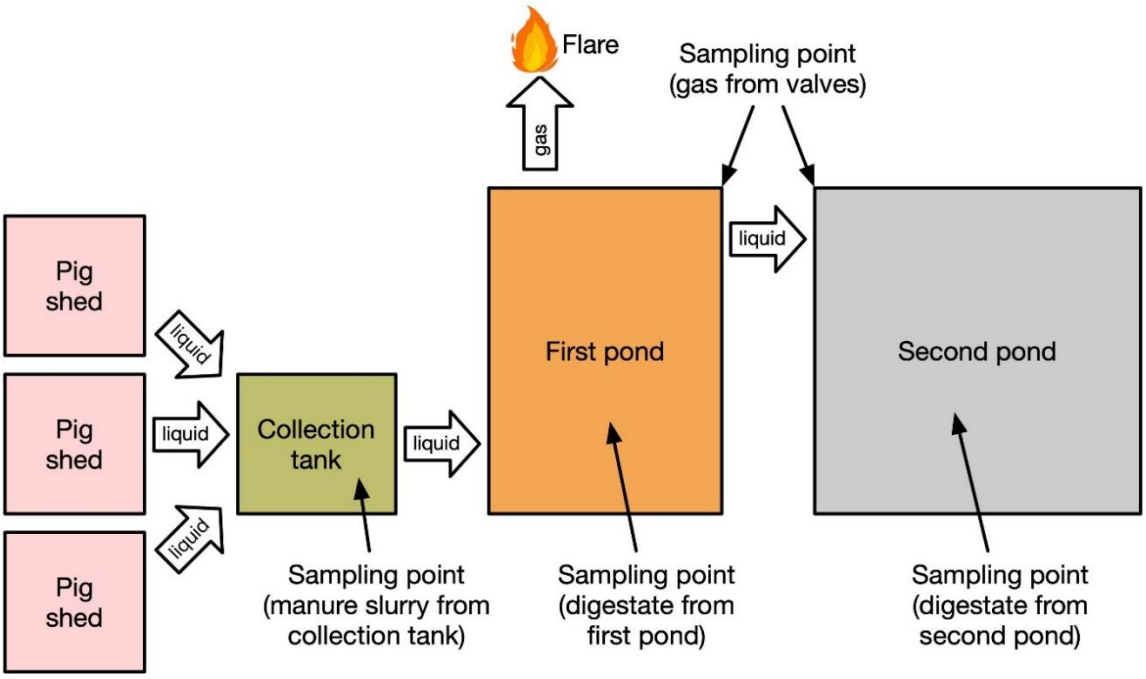

Figure 6: Schematic of farm, the waste treatment system and sampling points

The maximum depth of the first pond is five meters and its surface area is 1 500 m^2 (30 m wide x 50 m long). The pond has a bund slope of approximately 2:1 (vertical: horizontal), with a pond bottom area of 300 m^2, giving a total pond volume of 4 500 m^3. The bottom lining is made of high-density polyethylene (HDPE). The cover material is low-density polyethylene (LDPE). Biogas is collected using a ring pipeline made from perforated pipe (100 mm PVC or PE) under the cover around the perimeter of the pond. A biogas transfer pipeline connects to the solar powered biogas flare (Figure 7). The inlet and outlet structures of the pond are installed below the pond water surface. Tubing of 150 mm in diameter is used for the inlet and outlet structure pipes. The inlet pipe supplies the influent wastewater through the sludge port at the very bottom of the pond (see Figures 8 and 9). The outlet pipe is an in-line double T pipe at a depth of about one meter below the pond surface (see Figures 8). The pond system is based on a biogas system implementation plan by Heubeck (2016). At present, biogas is removed with a vacuum pump and flared. A general schematic of the main features and dimensions of the first pond are shown in Figures 8 and 9.

Figure 7: Flare

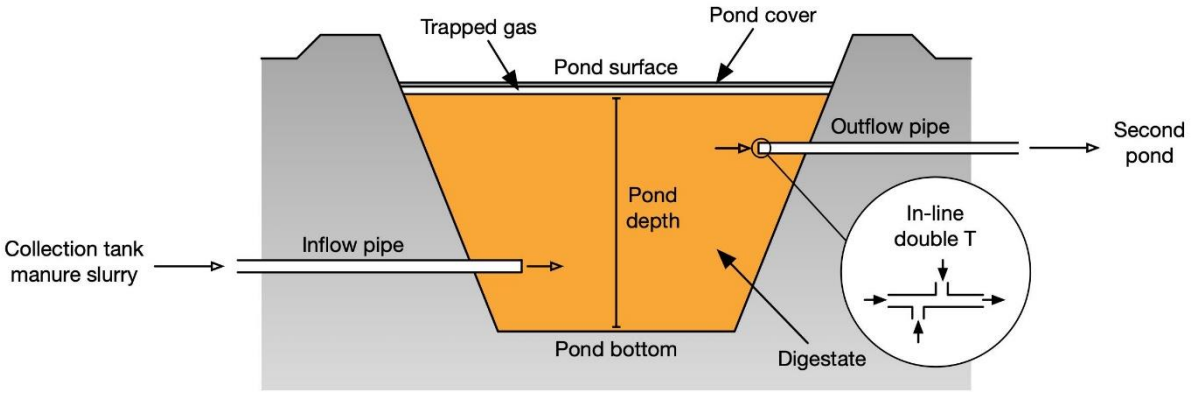

Figure 8: Pond structure and in-line double T appearance (based on Heubeck, 2016)

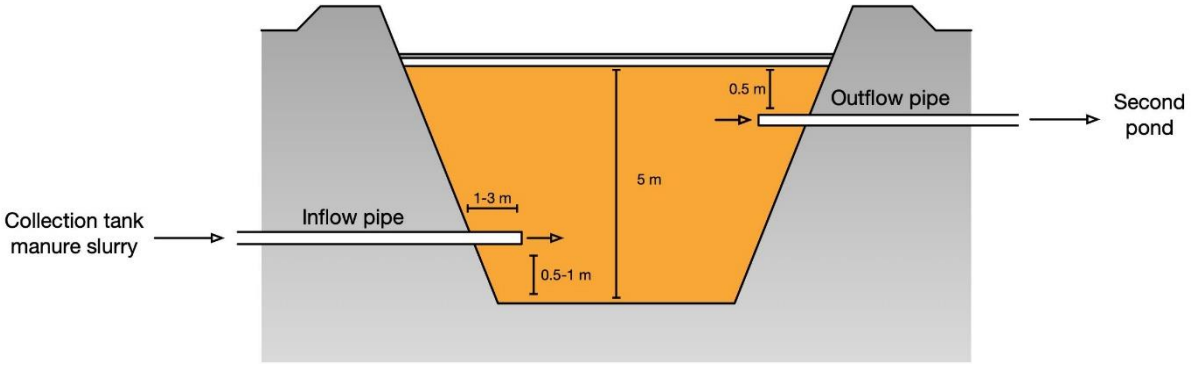

Figure 9: Dimensions of placements of in- and outlet (based on Heubeck, 2016)

The maximum depth of the second pond is 5.5 meters and the pond surface area is 2 500 m^2 (50 m wide x 50 m long). The pond has a bund slope of approximately 2:1 (vertical: horizontal), with a pond bottom area of 1 225 m^2 giving a total pond volume of 10 244 m^3. However, the working depth typically varies between 0.5 to 2 meters, resulting in an actual working volume of between 930 and 3700 m^3. However, when samples were collected in this study the depth was always at least 1.5 m and the sampling device never reached the bottom. The bottom lining is made of high-density polyethylene (HDPE) and the cover material is low-density polyethylene (LDPE). There is no discharge point from the storage pond. The effluent is pumped from the pond to a slurry tanker and used as fertiliser on the fields.

Hydraulic Retention Time (HRT), flow rate (Q) and Organic Loading Rates (OLR) are important factors affecting the anaerobic process and they are defined by equations 1, 2 and 3 below. These factors were used to calculate the waste treatment system's design and operational conditions. HRT [day] is calculated from equation 1. Using the equations below and putting in the values for the working volumes of the two ponds, as mentioned in subsection 4.1.2., the volume of feedstock added during each time interval, as mentioned in subsection 4.1.1. and the mean VS of the manure slurry, as mentioned in Table 5 in subsection 5.1.3., this results for the first pond in the Organic Loading Rate (OLR) of 0.130-0.144 kg VS/m^3/d and the HRT of 158 - 175 days. For the second pond the OLR would be 0.06 kg VS/m^3/d and the HRT would be 359 – 399 days.

$$HRT = V_{pond} / Q \quad \text{(equation 1)}$$

where V_{pond} is the working volume of the pond [m^3] and Q is the inlet flow rate [m^3/day]. In turn, the flow, Q [m^3/day], is calculated according to the following equation:

$$Q = V_{fill} / t_{interval} \quad \text{(equation 2)}$$

where $t_{interval}$ is the time interval of feedstock addition [days] and V_{fill} is the volume of feedstock [m^3] added during each time interval. Subsequently, the Organic Loading Rate, OLR [kg VS/m^3/day], can be calculated using the following equation:

$$OLR = VS \cdot Q/V_{pond} \quad \text{(equation 3)}$$

where VS is Volatile Solids [kg VS/m^3] (derived from sampling). VS is used to quantify the amount of organic material in wastewater and is a measure for water quality.

4.2. Field study: Sampling and physicochemical analyses

This section describes the field sampling procedure, the in-situ analyses, and the laboratory analysis methods for the characterisation of the raw manure slurry, and the digestate from the two ponds.

4.2.1. Field sampling

Grab samples of pig manure slurry and digestate from the two ponds were collected at monthly intervals over ten months. The sampling points are shown in Figure 6. The sampling period began in August 2020 and ended in May 2021. Three litres of liquid were collected per sampling point and event to ensure sufficient quantities to analyse all water quality parameters. Raw manure slurry samples were taken from the slurry central collection tank at a depth of about 1 m. Digestate samples from the first pond were obtained from a sampling port in the pond cover (see Figure 10) at a depth of about 1.2 m. Digestate samples from the second pond were obtained from a sampling port in the pond cover at a depth of about 1.2 m. All the samples were taken using a pump and hose, and collected in one-litre plastic jars with caps. Collection jars and pump hose were flushed with the sample fluid before collection of the sample. After the collection of samples, the sample jars were capped and kept in a chilly bin with cold packs during transport to the laboratory. All samples were then stored in a fridge at 3°C for a maximum of 5 hours before analyses started for total solids (TS), volatile solids (VS), alkalinity and settleable solids and a maximum of

28 hours before analyses started for ammonia nitrogen and phosphate, and preservation started by digestion for Total Kjeldahl Nitrogen (TKN) and by acidification for volatile fatty acids (VFAs).

Figure 10: Sampling port in pond cover, marked with red circle in the picture to the right

4.2.2. In-situ analyses

The following parameters were measured on-site using calibrated field meters: pH using an EDT Instruments FE 257 Micro pH meter, electric conductivity (EC) using a Thermo Electron Corporation Conductivity Orion 130A meter, oxidation-reduction potential (ORP) using a YSI pH 100 portable pH, mV and Temperature Instrument from YSI Environmental Inc. and temperature using a Traceable® Calibration, Lollipop waterproof thermometer. Measurements of all parameters were done immediately after collecting samples of raw manure slurry and digestate from the two ponds.

Biogas composition (methane (CH_4), carbon dioxide (CO_2), oxygen (O_2), carbon monoxide (CO) and hydrogen sulphide (H_2S)) were measured at the site using a portable gas analyser (GA5000 Geotechnical Instruments UK). The gas analyser was checked occasionally with certified standard gases and was calibrated by the manufacturer once during the study period. The biogas was sampled and measured from valves installed in the end caps in the pipes surrounding the two ponds collecting the gas.

4.2.3. Characterisation of raw manure slurry, and pond digestate

The physicochemical characteristics of the pig manure slurry and digestate were analysed (for methods see Table 1) for TS, VS, phosphate, and alkalinity. Ammonia Nitrogen was analysed using a Gerhardt Vapodest 45s and TKN was analysed using a Gerhardt TZ-Controller for the digestion and a Gerhardt Vapodest 45s for the titration (Figure 11).

VFAs were analysed using a gas chromatograph fitted with a flame ionisation detector (GC-FID, Shimadzu Nexis GC-2030, equipped with Shimadzu AOC-20i Plus auto injector, for more details, see Table 1). Before injection in the GC, the samples were centrifuged for 40 minutes (at 4,400 rpm) to produce a supernatant. The supernatant was diluted (dilution factor of 20) and then vacuum filtered through a 0.45µm filter and acidified with phosphoric acid to pH less than 2. Thereafter the prepared samples were stored in a refrigerator at 3°C until GC analysis the next day.

Figure 11: TKN was analysed using a Gerhardt TZ-Controller for the digestion (left) and a Gerhardt Vapodest 45s for the titration (right)

The samples from the March sampling event were frozen two days after collection, treatment and preservation. The reason for this was that the GC broke down and had to be repaired. Two months later, the samples were thawed at room temperature and filtered through 0.2 µm syringe filter before analysed. Since the GC was broken for two months, the samples from April also had to be frozen two days after collection, treatment and preservation, stay frozen for one month and then thawed in room temperature and filtered through 0.2 µm filter, before analysed. The samples from the final month, i.e., May, were analysed two days after being sampled and the day after being preserved and were not frozen. Only the samples from March, April and May were filtered the extra time through the 0.2 µm syringe filter before analyses, to make sure the GC would not break down again. This extra step was introduced to further clean the samples in order to protect the sensitive injection port of the GC. Worth noting is that, a manure slurry sample from March was analysed fresh in March, before the machine broke down and then again after being frozen for two months, see subsection 5.1.6.

Total oil and grease content from samples of manure slurry and digestate from both ponds was analysed once (from the August sampling) using one sample from each tank/pond. The analysis was done by Flinders Cook Laboratory using standard method APHA 5520C. Sulphate was analysed using an ion chromatograph (IonPac AS19 Guard plus Analytical Column, Dionex Corporation) after the samples were centrifuged for 40 minutes (at 4,400 rpm) to produce a supernatant. The supernatant was vacuum filtered through a 0.45µm filter and then stored in a freezer. Before analysis, the supernatant was thawed at room temperature and diluted using a dilution factor of 20 and 10. Settleable solids in the manure slurry, and the digestate from the two ponds (Figure 12) were analysed. However, because of the manure slurry's dark colour it was not possible to take readings, so the analysis of settleable solids for manure slurry was stopped in December. The analyses were carried out for the digestate from the two ponds during the whole study.

Table 1: Parameters analysed, preservation procedure and analysis methods

Parameter	Preservation	Method	Reference
Total Solids (TS)	Chilly bin with ice packs during transport, then immediate processing	APHA 2540 B	Clesceri et al. 1989
Volatile Solids (VS)	Processed immediately from TS analysis	APHA 2540 E	Clesceri et al. 1989
Total Kjeldahl Nitrogen (TKN)	Chilly bin with ice packs during transport, refrigerated at 3°C for less than 24h, before processing	APHA 4500-N_{org} B using Gerhardt TZ-Controller and Gerhardt Vapodest 45s	Eaton et al. 2005
Ammonia nitrogen (NH_3-N)	Processed immediately from Ammonia Nitrogen analysis	APHA 4500-NH_3 B and C using Gerhardt Vapodest 45s	Eaton et al. 2005
Soluble Phosphorous	Chilly bin with ice packs during transport, refrigerated at 3°C for 24h, then centrifuged (40 minutes at 4,400 rpm), diluted (dilution factor of 20) filtered (vacuum filtered through a 0.45µm filter) and analysed	8114 Phosphorous, reactive (ortophosphate). Molybdovanadate Method (0.3-45.0mg/L PO_4^{3-}). Adapted from Standard Methods for the Examination of Water and Wastewater.	Hach Company /Hach Lange GmbH, 1989–2014, 2019
Alkalinity	Chilly bin with ice packs during transport, then immediate processing	APHA 2320	Clesceri et al. 1989
Volatile Fatty Acids (VFA): Acetic acid Propionic acid Butyric acid	Chilly bin with ice packs during transport, refrigerated at 3°C for 24h, then centrifuged (40 minutes at 4,400 rpm), diluted (dilution factor of 20) filtered (vacuum filtered through a 0.45µm filter) and acidified with phosphoric acid before analysing	Gas chromatograph fitted with a flame ionisation detector (GC-FID, Shimadzu Nexis GC-2030) and equipped with Shimadzu AOC-20i Plus auto injector Carrier gas: Helium Injector temp.: 200°C, column temp.: 120°C, detector (FID) temp.: 300°C Carrier gas flow rate: 1.65ml/min Column specifications: HP-INNOWAX, diameter 0.25mm, Film 0.25um, length 30m. Temp limits 40°C to 260°C Split ratio 40.1:1	
Oil and grease	Chilly bin with ice packs during transport, then immediate processing within 24h	APHA 5520C	

Table 1: Parameters analysed, preservation procedure and analysis methods (continued)

Parameter	Preservation	Method	Reference
Sulphate	Chilly bin with ice packs during transport, refrigerated at 3°C for 24h, then centrifuged (40 minutes at 4,400 rpm), filtered (vacuum filtered through a 0.45µm filter) and kept in freezer for six days, thawed, diluted (dilution factor of 20 and 10) and analysed.	Dionex ICS-2100 Ion Chromatography System. Column: AS19 + Guard column. Eluent: KOH – multi gradient method between 10 to 45mM. Flow rate: 1mL/min. Injection loop: 25 microL. Suppressor: Anion Self-regenerating ASRS300, 4mm. Calibrations standards were lab prepared and external lab standards were also used as check calibrations.	
Settleable solids	Chilly bin with ice packs during transport, then immediate processing	APHA 2540 F	Clesceri et al. 1989

All the analyses were only carried out once on each sample due to time constraints. The only exception was the TKN tests that were run in duplicates for all samples for all months, except September and October. The reason for why the TKN tests where run in duplicates was because the digestion of the samples requires a whole day and in high temperatures, and if one test tube would break in the process, the digestion would need to be repeated. Therefore, running a duplicate ensured that at least one sample would be analysed should an accident occur.

Figure 12: Analysis of settleable solids using Imhoff cones

4.3. Biochemical methane potential studies

Laboratory studies were performed to investigate the biochemical methane potential (BMP) of the manure slurry and digestate from the first pond. The first part of the study consisted of exploring the methane potential using two different concentrations of VS in the manure slurry and the original concentration of VS in the digestate. The second part consisted of examining how two different concentrations of dairy by-product affected the BMP of the manure slurry and the digestate from the first pond, see Table 2 for experiment set-up. The results of these studies addressed **objectives B1 and B2.**

Table 2: Objectives B1 and B2 and their associated experiments

Objective	Experiment	Relevant sections	Duration	Number of bottles	Size & type of bench-scale reactor
B1	Methane potential of pig manure slurry and digestate from first pond	4.4.1 and 4.4.2	8.5 weeks until methane production is negligible	Manure slurry: Triplicate of 1:1 (g VS), triplicate of 0.5:1 (g VS), 2 blanks and 2 controls = 10 bottles in total Digestate from first pond: 1:1 (g VS) in triplicate, 2 blanks and 2 controls = 7 bottles in total	1-litre Shott glass bottles for manure slurry and 125 ml serum glass bottles for digestate from first pond
B2	Effect of dairy by-product on methane potential of pig manure slurry	4.4.3	6 weeks until methane production is negligible/ study had to be completed	Manure slurry: Duplicate of high dose dairy by-product, duplicate of medium dose dairy by-product, duplicate of low dose dairy by-product 2 blanks and 2 controls = 10 bottles in total	1-litre Shott glass bottles for manure slurry

4.3.1. Biochemical methane potential of manure slurry

The manure slurry was collected from the farm as previously described in section 4.2.1 and the VS was determined as described in section 4.2.3. Two different concentrations of the pig manure slurry were investigated. In one test, manure slurry was mixed with inoculum in a 1:1 ratio (g VS). The inoculum used was digested sludge from Christchurch WWTP, located in the suburb of Bromley. Before use, the inoculum was degassed by incubation at 37°C for a week in order minimise the methane production from the inoculum (i.e. endogenous methane production). In a second test, the manure slurry was diluted with deionised water to produce a 0.5:1 (g VS) substrate to inoculum ratio. The original VS concentration in the manure slurry was 12,814 mg/L and the original VS concentration in the inoculum was 21,740 mg/L. One-litre Schott bottles were used as digesters and both tests were run in triplicate. After sealing the bottles, the headspace was flushed with nitrogen gas to produce oxygen-free conditions. The bottles were then placed in a shaker box on slow continuous stirring and placed in a temperature-controlled room at 37°C for 8.5 weeks. The substrate bottles were attached to microflow meters (bioprocess control μFlow, Bioprocess Control Sweden AB) that registered produced gas volume. See Figure 13 for study set-up.

Boiled rice mixed with inoculum and deionised water was used as positive control (in duplicate). The controls were used to confirm that the inoculum had an adequate microbial activity, which could be concluded from the analysed gas production and composition. The blanks (in duplicate) consisted of deionised water and inoculum in the same ratio as the samples and were used to subtract the endogenic

methane production from the inoculum from the total methane production of the sample bottles. The blanks and the positive controls were attached to Tedlar® bags to monitor biogas production. Biogas composition (methane and carbon dioxide) was analysed by taking samples using a pressure-lock syringe and analysed in a GC (Agilent Technologies 7820A GC, carrier gas: Helium; carrier gas flow rate: 10ml/min; injector temp.: 70°C, split ratio is 20 to 1, column temp.: 30°C, detector (TCD) temp.: 155°C; Column specifications: HP-Plot/Q, 30m x0.53mm x40um, 60°C to 270/290°C) (Figure 14). The contents of all bottles were tested for biogas composition (methane and carbon dioxide) daily for the first 1.5 weeks, and then once a week for 5.5 weeks until all the bottles showed plateauing cumulative methane production. After completion of the study, the pH was measured with a pH meter (EDT Instruments RE 357 Tx Microprocessor pH meter) and the visual appearance of the content in the bottles was described and recorded.

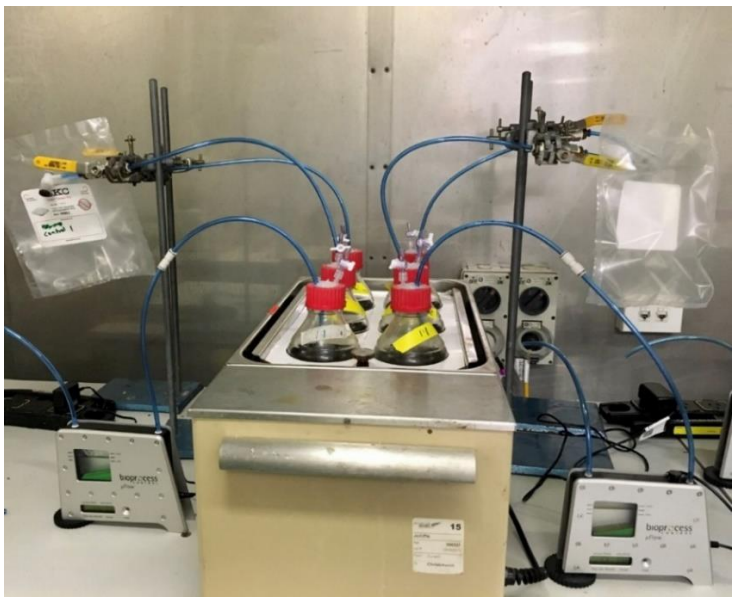

Figure 13: Manure slurry study set-up

Figures 14: Gas GC (left) and gas syringe (right)

4.3.2. Biochemical methane potential of first pond digestate

Biochemical methane potential was assessed to understand the first pond digestate's content of organic matter that is still susceptible to anaerobic degradation. A ratio of 1:1 (g VS) of digestate (original VS concentration 1 444 mg/L) and inoculum (original VS concentration 21 740 mg/L) was used. Due to the relatively low VS concentration in the digestate only one concentration of digestate was used, namely the original without dilutions. The test was run in triplicate. The digestate from the first pond was collected at the farm as previously described in section 4.2.1 and the VS was determined as described in section 4.2.3. To setup the test, the digestate (i.e. the substrate) was mixed with inoculum (i.e. the source of active methanogenic bacteria).

Inoculum (6 ml) and digestate (90 ml) were added to 125-ml serum bottles, which were then flushed with nitrogen gas and sealed with rubber septa and open aluminium crimp caps. The bottles were placed in a temperature-controlled room at 37°C (Figure 15, left) for 8.5 weeks. Positive controls and blanks were prepared and used in the same way as described in subsection 4.3.1.. A pressure-lock syringe with a needle was used to sample gas from the headspace (29.37 ml) of the bottles. Pressure was measured with a water manometer giving produced gas volume (Figure 15, right). The gas was then analysed in a gas chromatograph (Agilent Technologies 7820A GC System) for methane and carbon dioxide concentrations. The contents of all bottles were tested for biogas composition (methane and carbon dioxide) daily for the first 1.5 weeks, then every third day for 1.5 weeks and then once a week for four weeks until all the cumulative methane production in the bottles plateaued. After completion of the study the pH was measured with an EDT Instruments RE 357 Tx Microprocessor pH meter and the visual appearance of the content in the bottles was described and recorded.

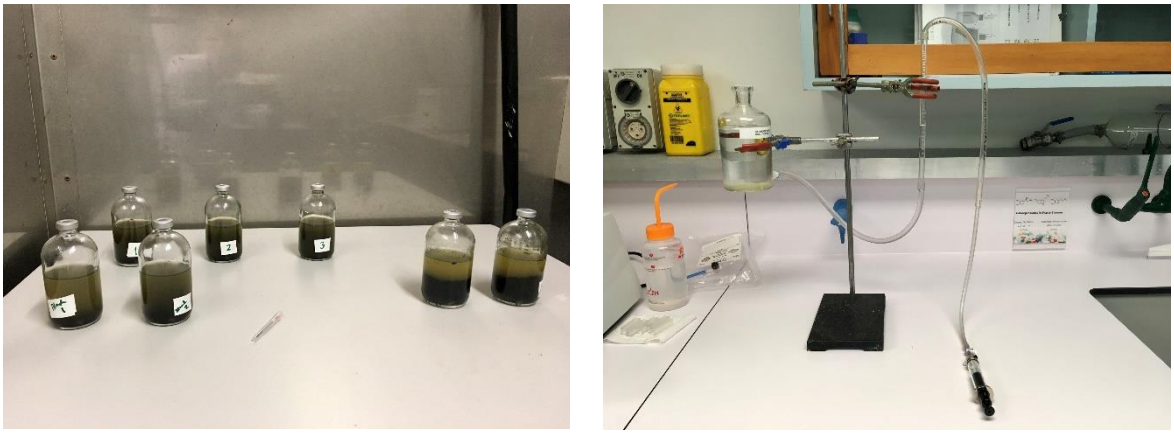

Figure 15: Study set-up for measuring the biochemical methane potential of first pond digestate (left) and pressure measured with water manometer (right)

4.3.3. Biochemical methane potential of manure slurry co-digested with dairy by-product

For this test the manure slurry was diluted with deionised water to produce a 0.5:1 (g VS) substrate to inoculum ratio (same ratio as used in study described in section 4.3.1). The experimental set-up was the same as in section 4.3.1., but this time all six Shott bottles contained the same 0.5:1 g VS concentration of the manure slurry. Concentrations of 5 %, 10 % and 15 % dairy by-product were used in the mix of manure slurry and dairy by-product to mimic possible scenarios in the anaerobic pond when the farmer adds spoilt or leftover dairy by-product to the pond. Each dairy by-product concentration was tested in duplicates. Biogas composition (methane and carbon dioxide) and biogas volume were measured as described in section 4.3.1 (see also Figure 15). Duplicates of positive controls and blanks were used as described in section 4.3.1. After completion of the study, the pH was measured with an EDT Instruments RE357Tx pH meter and the visual appearance of the content in the bottles was described and recorded.

5. Results

The seasonal variation of key physicochemical parameters in the manure slurry and in the digestate of the anaerobic ponds is reported in section 5.1. These results, in combination with weather data, address objective A. Section 5.3.1 and 5.3.2 present the results from the biochemical methane potential studies on manure slurry and first pond digestate. This addresses objective B1. Lastly, in section 5.3.3., the results from the biochemical methane potential test of manure slurry co-digested with different concentrations of dairy by-product are presented, addressing objective B2. A significance level of 0.05 has been used and all statistical tests were two-tailed.

5.1. Seasonal study

As mentioned in Chapter 4, samples from the first and second ponds were collected from the sample points indicated in Figure 6. However, in August 2020, the sample from the first pond was collected from the transfer pipe between the first and the second pond, and the results from this sample are therefore not included in this section. Appendix D lists observations made during all the sampling events, as well as comments made by the farmer in relation to the manure slurry tank, first pond, second pond and flare.

5.1.1. Temperature

The temperature of the manure slurry and the digestate from the first and second pond, as measured at the time of sampling, followed the trend of the air temperature (Figure 16). The temperature was highest in the manure slurry and lowest in the digestate from the second pond. The data in Figure 16 show that the temperature in the manure slurry, as well as the digestate from the first and second pond was higher in November to April (here called "summer months"), than May to October (here called "winter months") during 2020-2021 (sampling period). Two-sample t-tests (also called independent samples t-test), assuming unequal variances, confirmed that the temperatures in the summer and winter months were significantly different in all cases, $p<0.01$. (Table 3). In the following sections, significance tests comparing values for summer and winter months have therefore been performed for the selected key parameters.

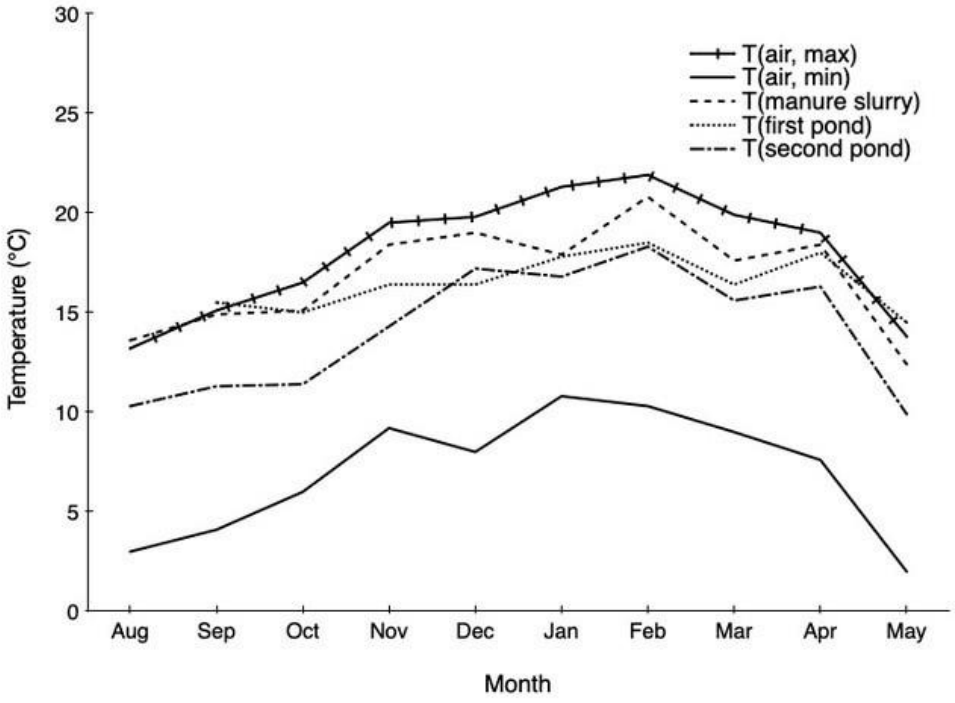

Figure 16. Minimum and maximum air temperature and temperature in manure slurry and digestate from the first and second pond from August 2020 to May 2021

Table 3. Results from the significance test (two-sample t-test assuming unequal variances) of temperature differences between summer and winter months.

Tank/Pond	df	t stat	p
Manure slurry tank	5	-5.98	<0.01
Digestate from 1st Pond	7	-4.62	<0.01
Digestate from 2nd Pond	8	-8.46	<0.01

5.1.2. TKN and ammonia nitrogen

The concentrations of TKN (mg/L), ammonia-nitrogen (mg/L), and the proportion (%) of ammonia-nitrogen to TKN in the manure slurry and the digestate from first and second ponds are shown in Figures 17, 18 and 19 for each of the sampling events. Table 4 summarises the ranges and means of the measured values for each tank/pond, and the proportion of ammonia-nitrogen per TKN.

Table 4. Range of values and means for TKN and ammonia-nitrogen (expressed as nitrogen), as well as the contribution of ammonia-nitrogen to TKN for the different tank/ponds.

Tank/Pond	TKN (mg/L)	Ammonia-Nitrogen (mg/L)	Ammonia-Nitrogen/TKN (%)
Manure slurry tank	~ 1,700 – 5,800 (mean: 3,674)	1,600 - 5,200 (mean: 3,209)	70-103
Digestate from 1st Pond	~ 2,400 – 2,800 (mean: 2,606)	~ 2,400 – 2,800 (mean: 2,590)	95-110
Digestate from 2nd Pond	~ 2,300 – 2,800 (mean: 2,614)	~ 2,400 – 2,800 (mean: 2,576)	94-106

Concentrations of TKN and ammonia-nitrogen in the manure slurry varied considerably between sampling events as shown by the ranges, but the variation in the digestate was smaller (Table 4). For all the months (except September and October), two TKN tests were run per sample. The differences between the two duplicates were mostly very small, less than 2.3% for all samples, except for two samples of manure slurry from the tank in December, where the difference was 4.5 %, and February, where the difference was 14.9 %.

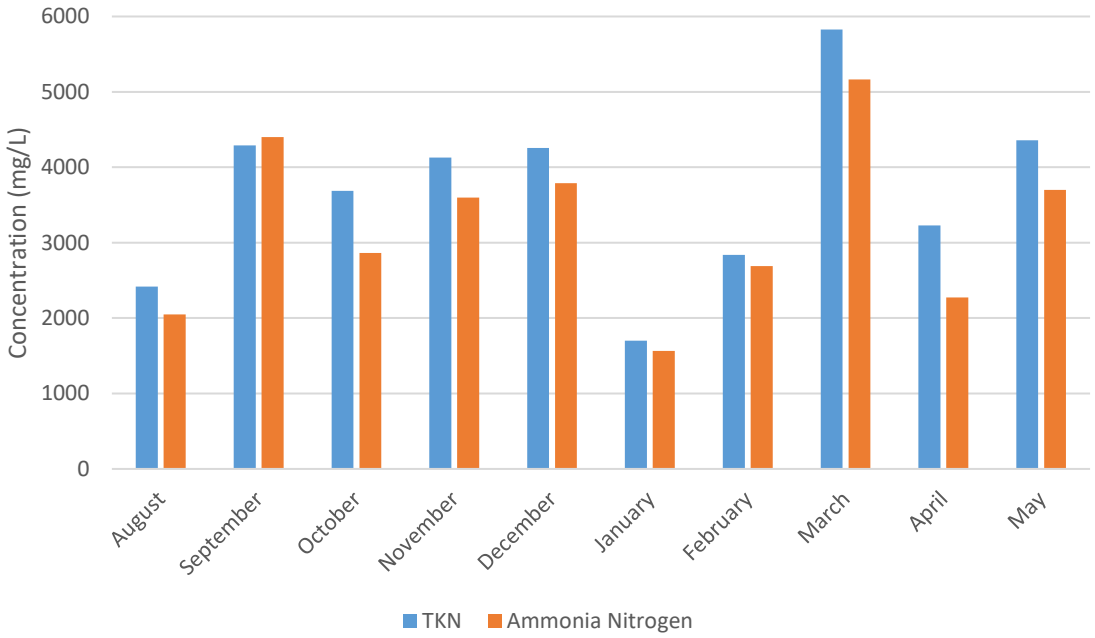

Figure 17. Concentration of TKN and ammonia-nitrogen in manure slurry

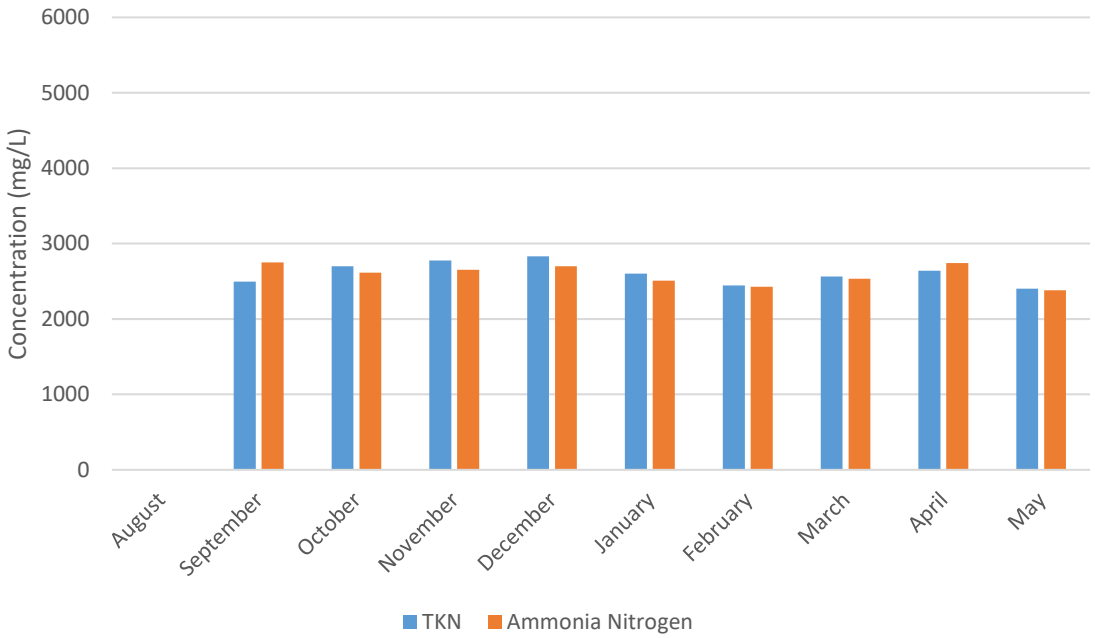

Figure 18. Concentration of TKN and ammonia-nitrogen in the first pond

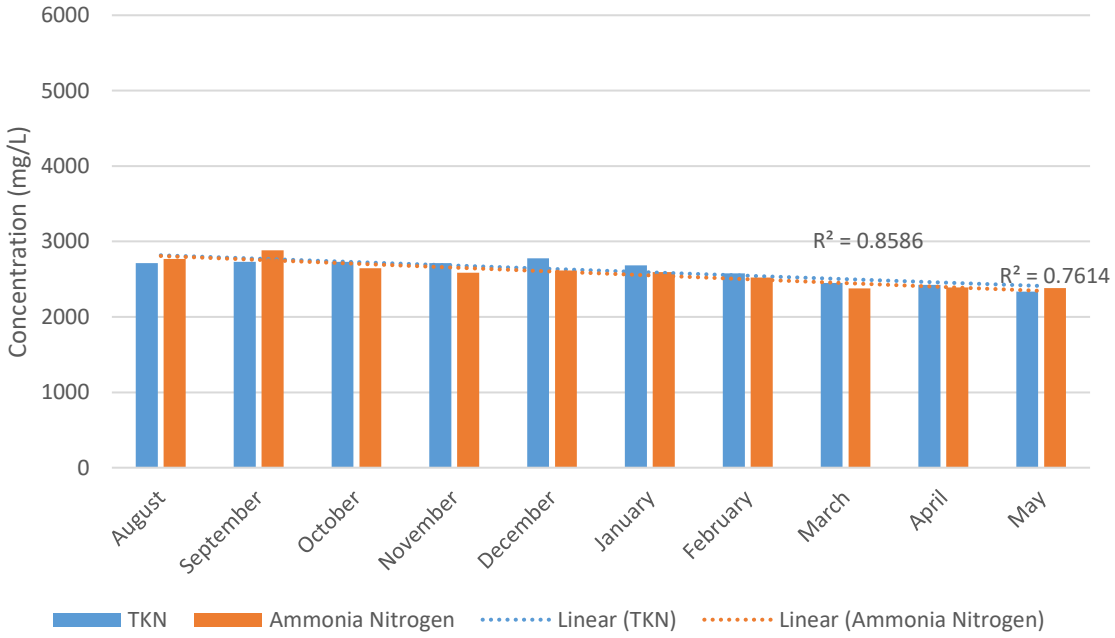

Figure 19. Concentration of TKN and ammonia nitrogen in the second pond

Concentrations of ammonia nitrogen in September in the manure slurry (Figure 17), September and April in the first pond digestate (Figure 18) and in August, September and May in the second pond digestate (Figure 19) are higher than the concentration of TKN. This is not possible, since ammonia nitrogen and organic nitrogen are the two components of TKN. When checking the accuracy of the measurement equipment, a reference liquid (acetanilide and deionised water) was used. The reference liquid contains 10.36 % nitrogen, but the mean value measured by the equipment in this study was 9.98 % (it varied between 9.58 to 10.24 %) for the reference liquid. A one-sample Z-test showed that the measured percentage was significantly different from 10.36% ($Z = -4.32$, $p<0.01$), suggesting a small systematic error in the measurements.

In Figure 19 there appear to be a decreasing trend of both TKN and ammonia nitrogen, from August to May in the second pond. However, two-sample t-tests assuming unequal variances showed no significant differences between summer and winter months for either of these two variables.

5.1.3. TS and VS

The concentrations of TS and VS (mg/L) of the manure slurry and digestate from the first and second pond are shown in Figure 20, 21 and 22, respectively. Table 5 summarises the ranges and mean values for each tank/pond, and the proportion of VS per TS. The levels of TS and VS in the manure slurry varied substantially between sample events. As illustrated in Figure 20, no seasonal variations can be discerned, although the months of February and October showed higher values for both TS and VS than in the other months.

Table 5. Range of values and means, as well as the proportion of VS per TS for the different tank/ponds.

Tank/Pond	TS (mg/L)	VS (mg/L)	VS/TS (%)
Manure slurry tank	~ 12,000 – 51,000 (mean 31,214)	7,800 - 44,000 (mean 22,704)	64-86 (mean 73)
Digestate from 1st Pond	~ 7,400 – 10,200 (mean 8,702)	~ 3,800 – 5,700 (mean 4,630)	51-55 (mean 53)
Digestate from 2nd Pond	~ 6,300 – 8,300 (mean 7,427)	~ 2,300 – 4,300 (mean 3,491)	36-51 (mean 47)

In the digestate from the first pond, the variation in TS and VS between sample events was low and the relationship between TS and VS is very similar for all the sample events. As can be seen by the trend lines in Figure 21, the concentrations for both TS and VS seem to decrease slightly from August to May.

In the digestate from the second pond, the variation between sample events was also low, although slightly higher than for the digestate of the first pond. As shown by the trend lines in Figure 22, the concentrations for both TS and VS seem to decrease slightly from August to May. Two-sample t-tests assuming unequal variances show no significant differences between summer and winter months for either of TS or VS.

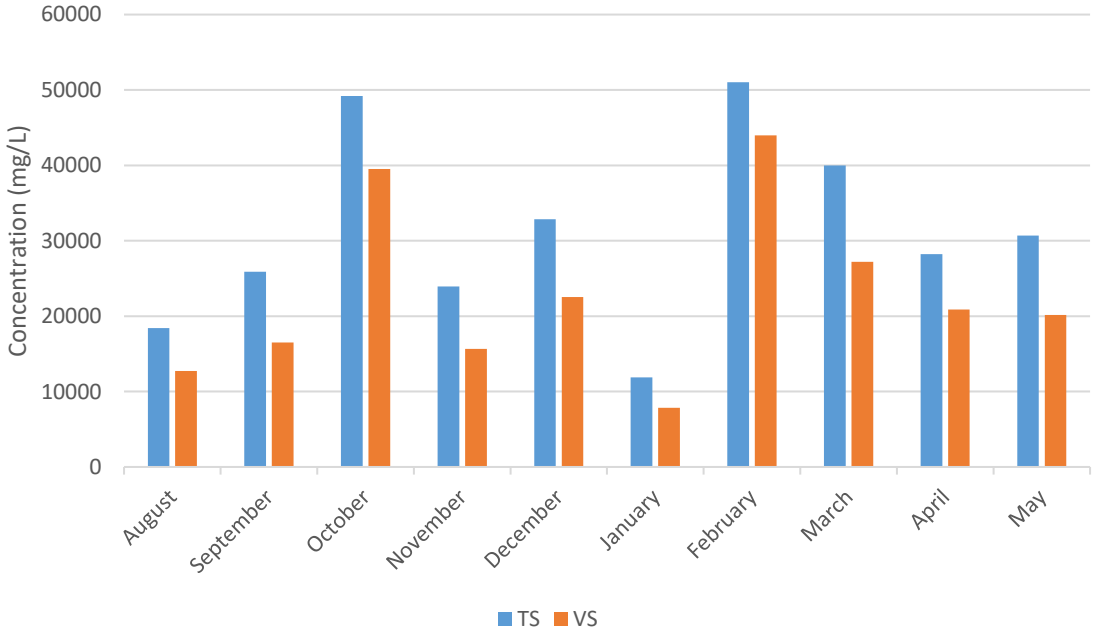

Figure 20. Concentrations of TS and VS in manure slurry

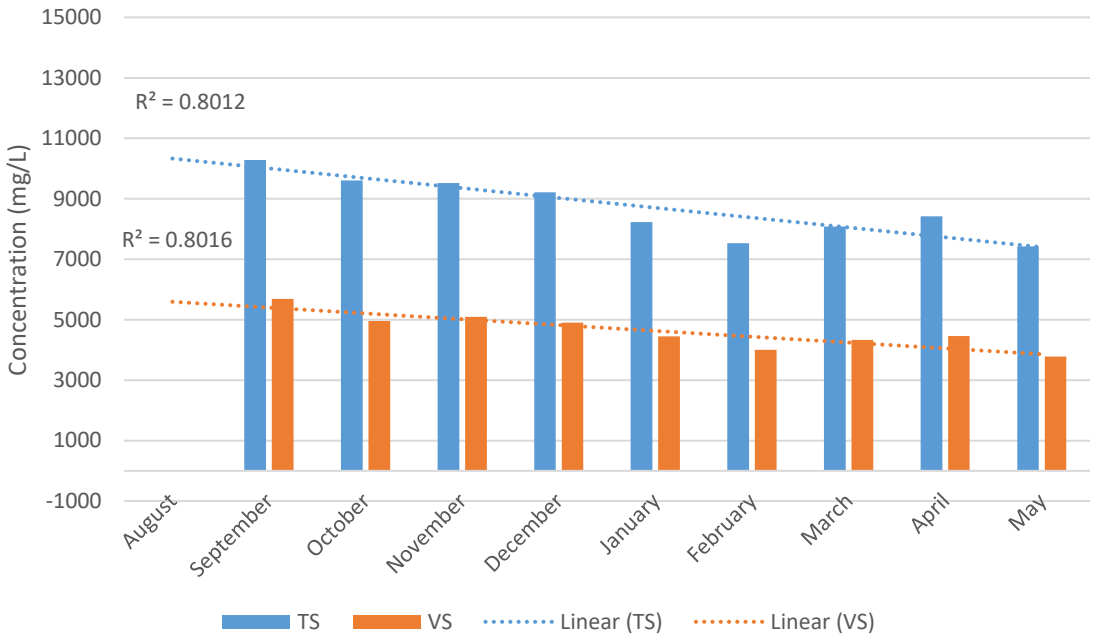

Figure 21. Concentrations of TS and VS in the first pond

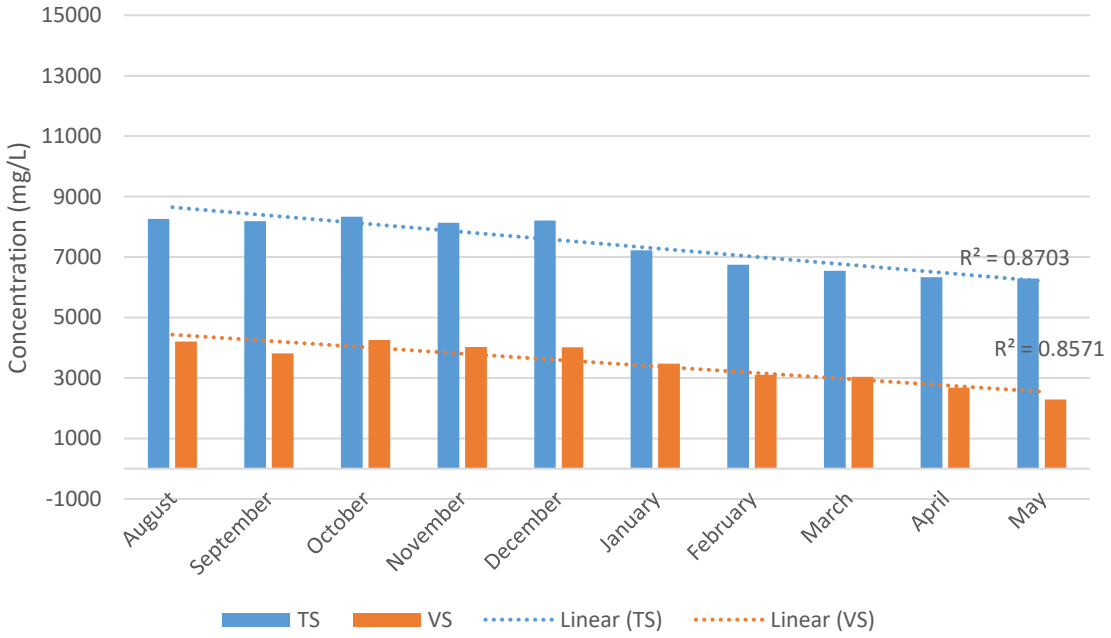

Figure 22. Concentrations of TS and VS in the second pond

5.1.4. Settleable solids

The results for settleable solids from the digestate from the two ponds were similar. For the first pond, digestate settleable solids varied between 0.8 to 5 ml/L, and for the second pond digestate settleable solids varied between 0 and 1.5 ml/L. It was not possible to analyse for settleable solids in the manure slurry due to its dark colour. Two-sample t-tests assuming unequal variances show no significant differences between summer and winter months for settleable solids.

5.1.5. pH and alkalinity

The pH in manure slurry, first and second pond is shown in Figure 23. The mean pH in the manure slurry was 7.0 ± 0.9, however mean pH for the months of August, September, October, November, December, March and May was 7.3 ± 0.3. In January, February and April, pH was between 6.1 and 6.7. The mean pH in the digestate from the first pond was 7.4 ± 0.1 and the mean pH from the digestate from the second pond was 7.6 ± 0.2. From the trend lines it seems that pH decreases from August to May in manure slurry, is stable over all the month for the first pond and might increase very slightly in the second pond.

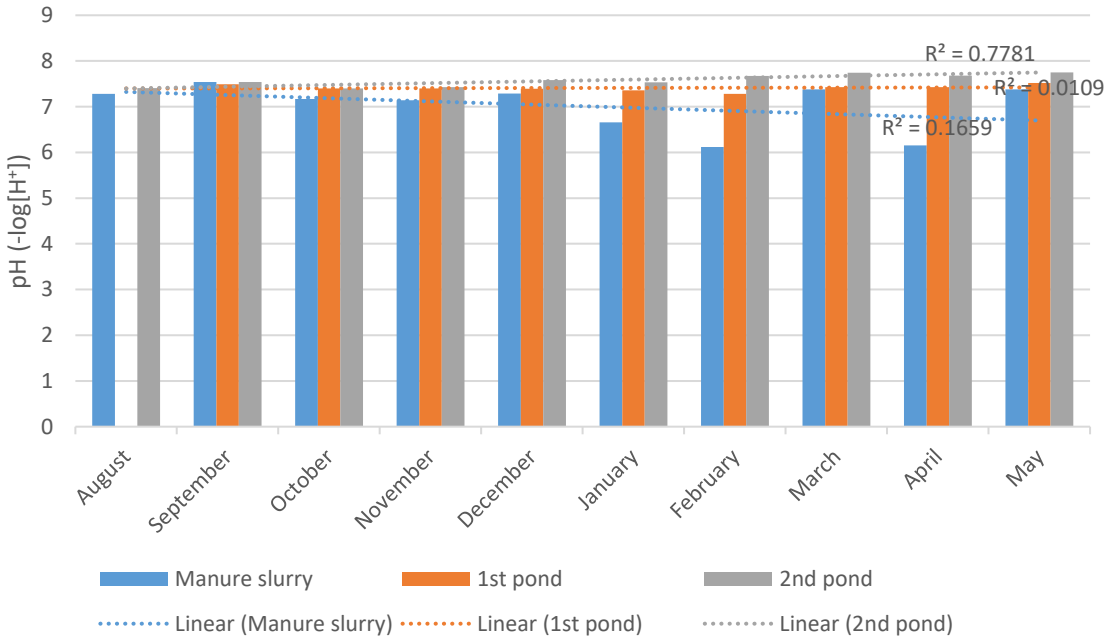

Figure 23. The pH in manure slurry, first and second pond

The variability of alkalinity of manure slurry and digestate from the first and second ponds is shown in Figure 24. The alkalinity of the manure slurry varied widely. The alkalinity of the digestate from the two ponds was more stable. The alkalinity minimum, maximum and mean is shown in Table 6. Two-sample t-tests assuming unequal variances show no significant differences between summer and winter months for pH or alkalinity.

Table 6. The alkalinity minimum, maximum and mean in manure slurry and pond digestate.

Tank/Pond	**Alkalinity (mg/L $CaCO_3$)**
Manure slurry tank	~4,700 - 16,300 (mean 10,415)
Digestate from 1st Pond	~8,700 - 10,700 (mean 9,722)
Digestate from 2nd Pond	~9,700 - 10,700 (mean 10,115)

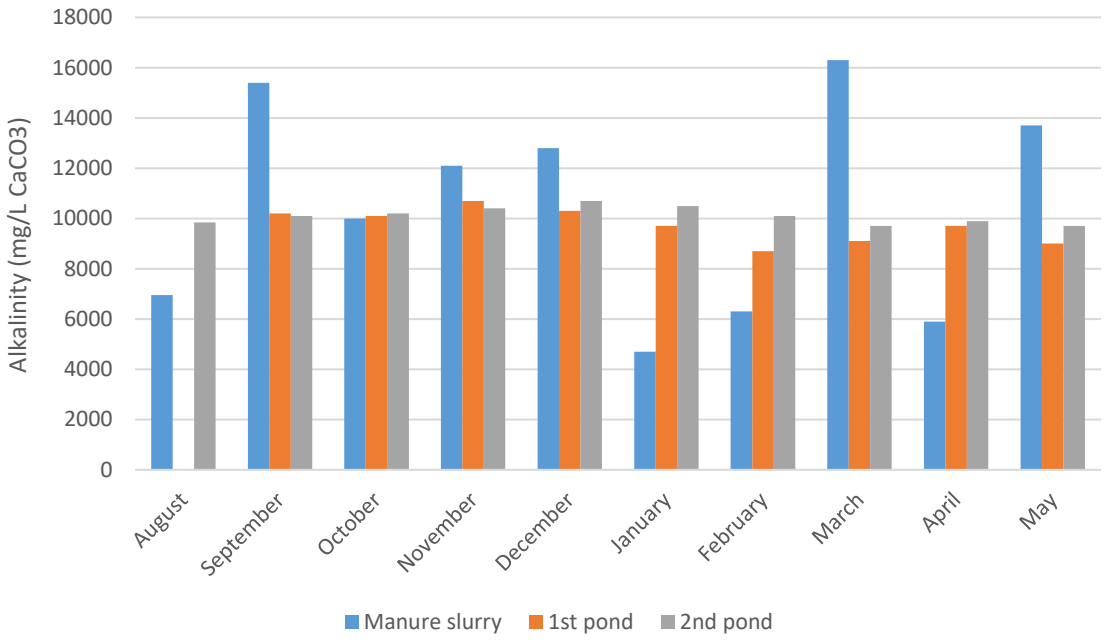

Figure 24. Alkalinity of manure slurry, and digestate from the first and second ponds (mg/L $CaCO_3$)

5.1.6. Phosphate and sulphate

The concentrations of phosphate (PO_4^{3-}) in manure slurry, the first and the second pond are shown in Figure 25. The phosphate concentration in manure slurry varied between 400 and 1,500 mg/L, with a mean of 878 mg/L. In February, March and April, the concentrations were very high. The phosphate concentrations in the digestate from the two ponds were more consistent with the concentrations in the first pond digestate varying between 260 and 470 mg/L, with a mean of 381 mg/L and the phosphate concentration of the digestate of the second pond varying between 290 and 410 mg/L with a mean of 335 mg/L.

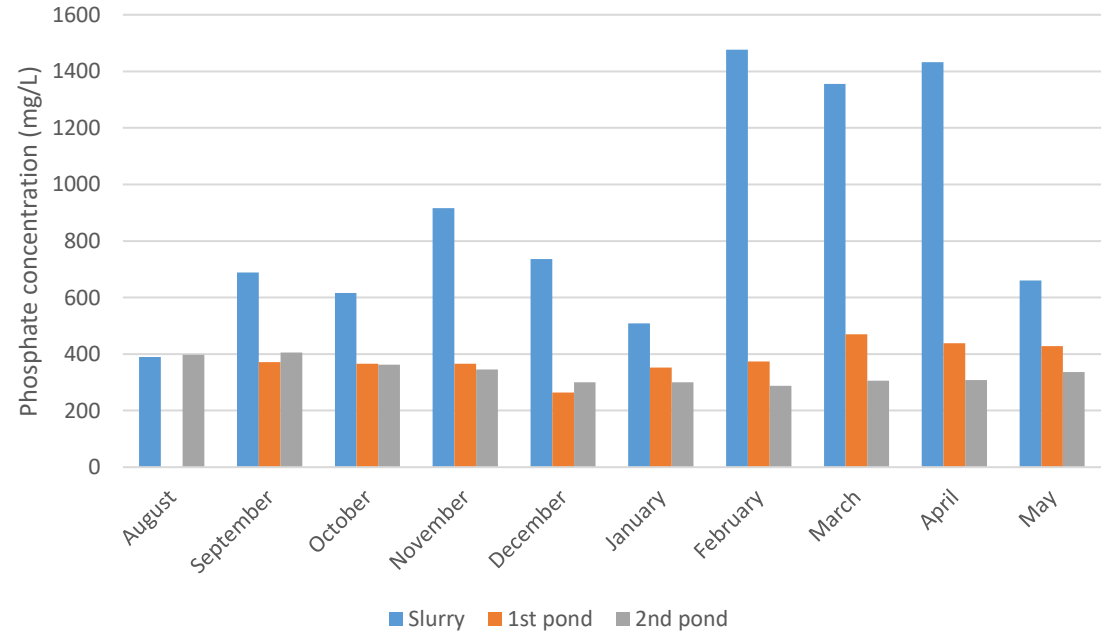

Figure 25. Phosphate concentrations in manure slurry, first and second ponds

A two-sample t-tests assuming unequal variances show no significant differences between the summer and winter months for phosphate in the digestate of the first pond. However, two-sample t-tests assuming unequal variances show significant differences between summer and winter months for phosphate in both the manure slurry ($t(7) = -2.69$, $p = 0.03$) and the digestate from the second pond ($t(5) = 3.71$, $p = 0.01$). As can be seen in Figure 25 the phosphate concentration is higher in the manure slurry in the summer months, while the phosphate concentration is higher in the second pond in the winter months.

Sulphate concentrations were analysed once (due to cost constraints) from the October sampling event in manure slurry, and the digestate from the two ponds and are shown in Table 7. The concentration of sulphate decreased from the manure slurry to the first pond, where it was about one third of the concentration of the manure slurry and further still to the second pond, where it was not detected. Since only one analysis of this parameter was done, no significance test was performed.

Table 7. Sulphate concentrations in manure slurry, and digestate from the first and second pond.

Sample	Sulphate (mg/L)
Manure Slurry	76
1st pond	21
2nd pond	<L.O.D.

5.1.7. VFAs

Acetic, propionic and butyric acids were present in all manure slurry samples. The concentration of acetic acid varied widely over the season between 2,500 and 6,600 mg/L, with a mean of 4,182 mg/L. The concentration of propionic acid was more consistent and varied between 1,700 and 2,700 mg/L, with a mean of 2,086 mg/L and the concentration of butyric acid varied between 170 and 300 mg/L, with a mean of 212 mg/L. The concentrations of the VFAs acetic, propionic and butyric acids in manure slurry are shown in Figure 26. In Table 8 the ratios of propionic and butyric acid to acetic acid in manure slurry, first and second pond over the ten months of sampling are shown.

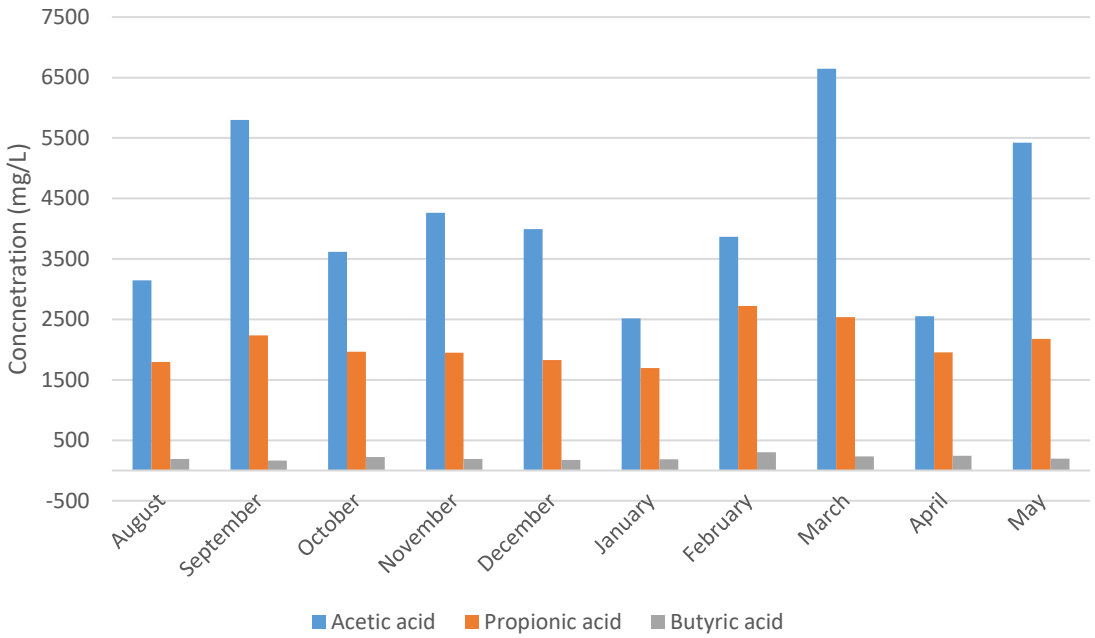

Figure 26. Acetic, propionic and butyric acids in manure slurry

The concentrations of the VFAs acetic, propionic and butyric acids in digestate from the first pond are shown in Figure 27. The concentration of acetic acid varied between 1,000 and 1,900 mg/L, mean 1,482

mg/L. The concentration of propionic acid was more consistent and varied only between 1,200 and 1,400 mg/L, mean 1,251 mg/L. Butyric acid was only found in the samples from October, March, April and May and the concentration varied between 140 and 270 mg/L those months, mean 171 mg/L.

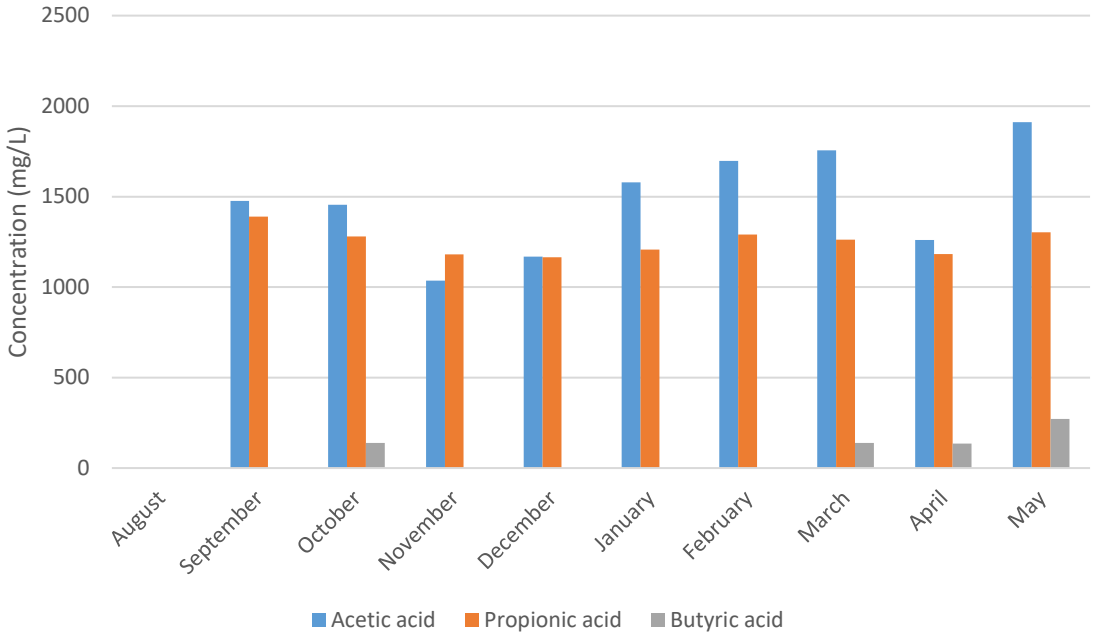

Figure 27. Acetic, propionic and butyric acid in first pond

Figure 28 shows the concentrations of the VFAs acetic, propionic and butyric acids in the digestate from the second pond. The concentration of acetic acid varied between 900 and 2,100 mg/L, with a mean of 1,328 mg/L. Propionic acid was detected only in the samples from August to October, and the concentration was approximately 1,200 mg/L. Butyric acid was only found in the months of August, March, April and May and the concentration was approximately 136 mg/L. Two-sample t-tests assuming unequal variances show no significant differences between summer and winter months for any of the VFAs analysed.

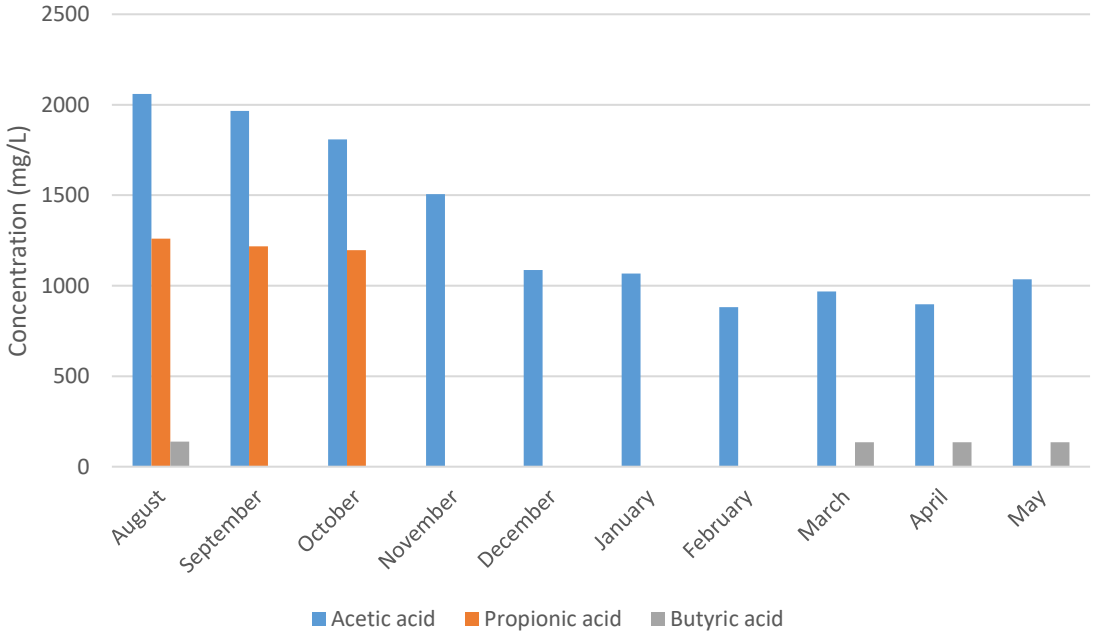

Figure 28. Acetic, propionic and butyric acid in second pond

Table 8. Propionic and butyric acid in ratios to acetic acid in manure slurry, 1st and 2nd pond over the ten months of sampling.

Month	Propionic acid (ratio to acetic acid)			Butyric acid (ratio to acetic acid)		
	Manure slurry	1st pond	2nd pond	Manure slurry	1st pond	2nd pond
August	0.57	-*	0.61	0.06	-*	0.07
September	0.39	0.94	0.62	0.03	0	0
October	0.54	0.88	0.66	0.06	0.10	0
November	0.46	1.14	0	0.05	0	0
December	0.46	1.00	0	0.04	0	0
January	0.67	0.76	0	0.07	0	0
February	0.70	0.76	0	0.08	0	0
March	0.38	0.72	0	0.04	0.08	0.14
April	0.77	0.94	0	0.10	0.11	0.15
May	0.40	0.68	0	0.04	0.14	0.13

* No sampling done in 1st pond.

As mentioned in Section 4.2.3, samples for VFA analysis were stored frozen before analysis due to technical difficulties (broken machine) from the month of March. However, the manure slurry March sample was tested both directly after sampling, treatment and preservation, as well as after being frozen for two months. As can be seen in Figure 29 the difference in concentrations between samples analysed from the fresh material and the frozen is minimal and, although the data are too limited to draw any in-depth conclusions, they indicate that after two months in the freezer the VFAs are still mostly intact.

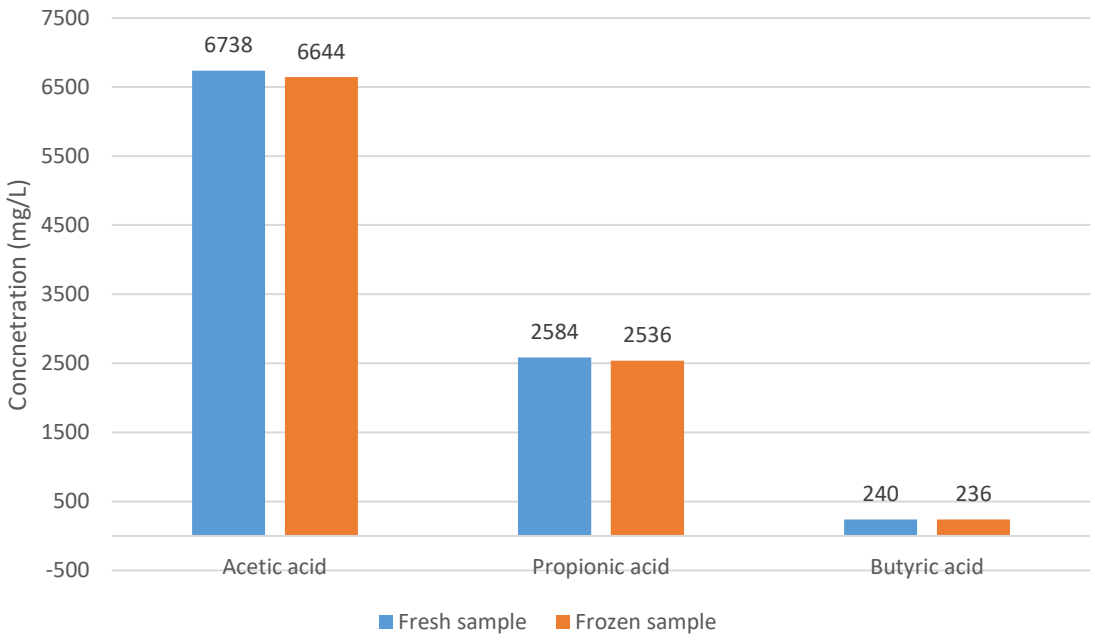

Figure 29. VFAs concentrations in fresh and frozen manure slurry from the March sample

5.1.8. Electric conductivity and oxidation-reduction potential

Electric conductivity in manure slurry, first and second pond digestate had a mean of 23.2 ± 11 mS/cm, 20.9 ± 1.4 mS/cm, and 21.6 ± 1.4 mS/cm respectively. The mean oxidation-reduction potentials in the manure slurry, first and second pond digestate were -328 ± 108 mV, -328 ± 28 mV, and -343 ± 23 mV respectively. Two-sample t-tests assuming unequal variances show no significant differences between summer and winter months for electric conductivity or oxidation-reduction potential.

5.1.9. Total oil and grease content

Total oil and grease content in manure slurry, and the digestate from the two ponds is shown in Table 9. The concentration was highest in the manure slurry and decreased in stages in the first and second pond. The concentration only decreases slightly (5%) from the manure slurry sample to the sample from the digestate of the first pond. The decrease in concentration is higher (17%) between the digestate from the first to the second pond and the decrease in concentration between the manure slurry and the digestate from the second pond is 21%. Since only one analysis of this parameter was done, no significance test was performed.

Table 9. Total oil and grease content in manure slurry, and digestate from the first and second pond

Sample	Total Oil & Grease (ppm w/w)
Manure slurry	630
1st pond	600
2nd pond	500

5.1.10. Methane, carbon dioxide and hydrogen sulphide concentrations

Figures 30 and 31 show methane and carbon dioxide (%) and hydrogen sulphide (ppm) concentrations of the biogas produced by the first and the second ponds from the sampling carried out each month. Oxygen content varied between 0 and 6 % in the biogas produced from both ponds. The remaining gas is probably mostly nitrogen and varied between 0 and 30 % in the biogas from the first pond and between 0 and 58 % in the biogas from the second pond. As can be seen in the figures, the methane concentration in both ponds varied over the season, although no clear trend can be seen. As noted in Appendix D, the flare was burning 24 hours per day in November and December. The range of the methane concentrations from the two ponds were similar, with the first pond varying between concentrations of 40 and 70%, with a mean of 56 %, and the second pond varying between 20 and 70%, with a mean of 50 %. At the March sampling, the gas meter malfunctioned and was sent for calibration to the manufacturer, so no data were collected. As can also be seen in the figures, the concentration of hydrogen sulphide from the two ponds varied greatly, with the range for the first pond between close to 0 and up to 5,000 ppm, which is the maximal concentration the meter can measure, and a mean of 2,940 ppm. The range for the second pond varied between 850 up to the detection limit of the meter at 5,000 ppm, with a mean of 2,970 ppm. For the March sampling the meter malfunctioned and no data were recorded and for the April sampling a different type of gas meter was used while waiting for the calibrated one to return and this meter was not able to measure hydrogen sulphide, so no data were recorded for these two months. As can be seen in the figures, the two ponds produced similar concentrations of carbon dioxide. The first pond produced carbon dioxide of a concentration varying between 24 to 35%, with a mean of 30%. The second pond produced carbon dioxide of a concentration varying between 19 to 32%, with a mean of 27%. The ratios of the mean concentrations of methane to the mean concentration of carbon dioxide were very similar, with 1.8 ± 0.6 for the first pond and 1.8 ± 0.7 for the second pond. For the March sampling the meter malfunctioned and no data were recorded. Two-sample t-tests assuming unequal variances show no significant differences between summer and winter months for either of methane, carbon dioxide or hydrogen sulphide.

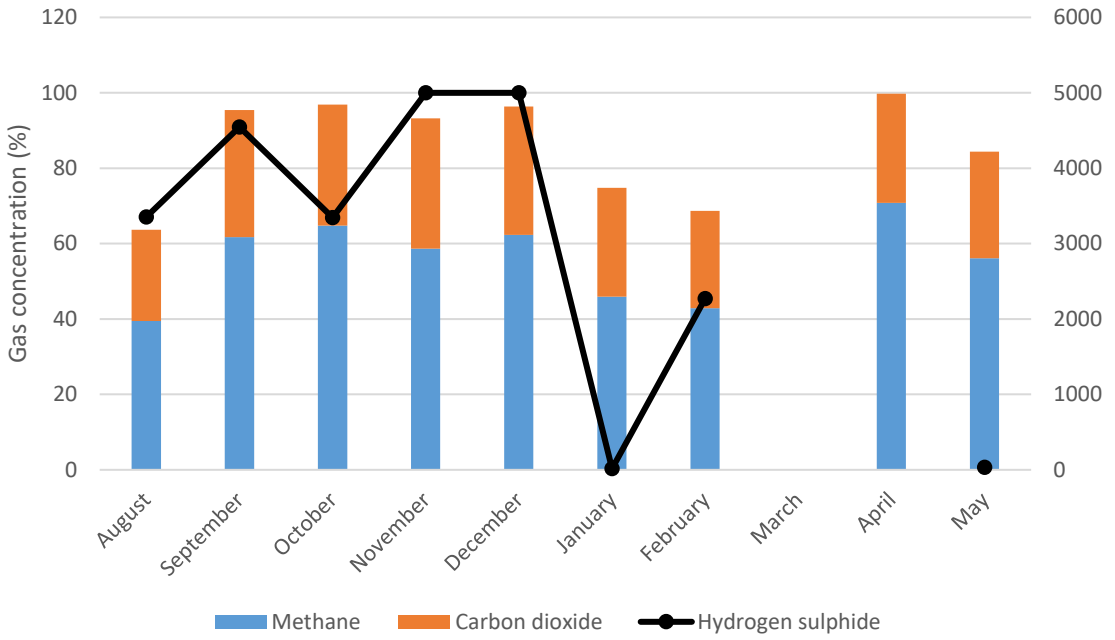

Figure 30. Methane, carbon dioxide (%) and hydrogen sulphide (ppm) concentrations at each sampling from the first pond

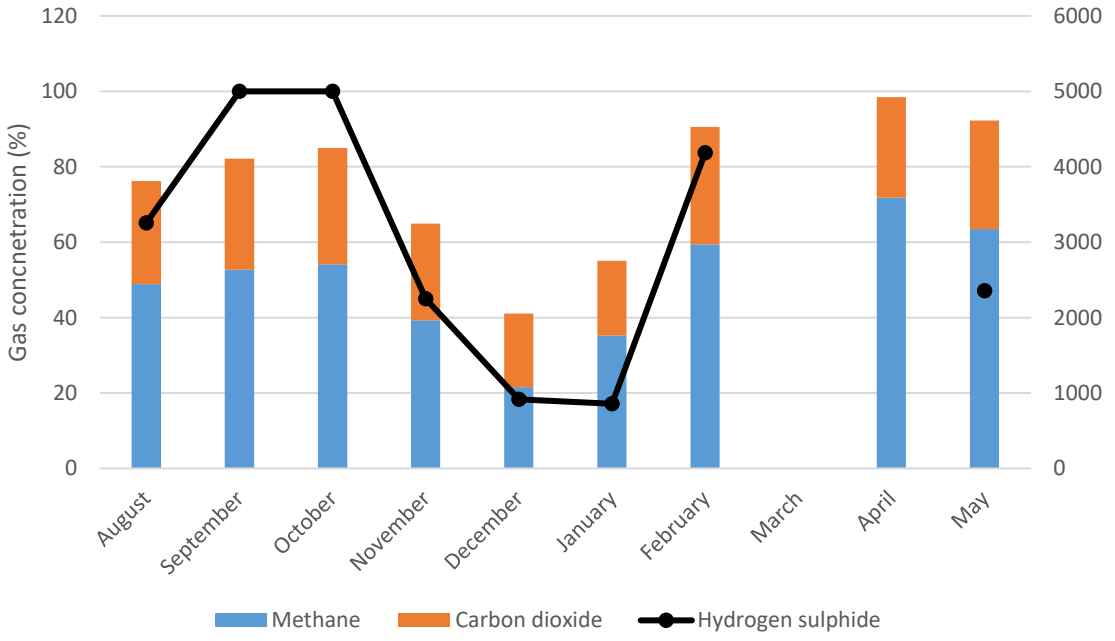

Figure 31. Methane, carbon dioxide (%) and hydrogen sulphide (ppm) concentrations each month from the second pond

5.2. Methane potential studies

From August to December 2021, experiments were performed in the laboratory to assess the methane potential of manure slurry, first pond digestate, as well as the impact of different concentrations of dairy by-product on methane production. As mentioned in Section 4.3.1., two different substrate to inoculum

ratios were used in the study of the methane potential of manure slurry: 1:1 and 0.5:1 (g VS). In the study of methane potential of the first pond digestate, a 1:1 substrate to inoculum ratio was used.

In the study of the impact of dairy by-product on methane potential the ratio of 0.5:1 (g VS) substrate to inoculum ratio was used and mixed with 5, 10 or 15 % dairy by-product.

All gas samples were collected in the temperature-controlled room at 37°C at 1 atm. The use of blanks enabled subtraction of the small amounts of methane still produced by the inoculum. The use of controls confirmed that the inoculum had an adequate microbial activity, which could be concluded from the analysed methane concentrations and that the Tedlar® bags filled up and had to be emptied once during the duration of the study period for both studies.

The methane and carbon dioxide concentrations in blanks and controls are shown in Appendix E.

5.2.1. Methane potential of manure slurry

As can be seen in Figure 32, the cumulative methane produced per waste VS added was comparable for all three samples for the 1:1 solution up to day 29 of the test Thereafter the methane production for sample $1{:}1_1$ increased fast and above the other samples. For sample $1{:}1_2$ and sample $1{:}1_3$ the methane production increased to day 41 and then stopped.

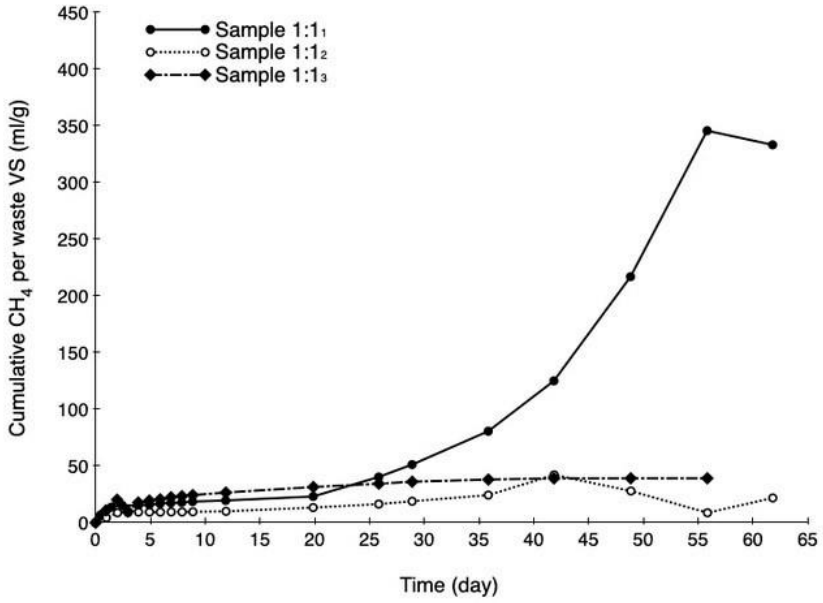

Figure 32. Cumulative methane produced (ml) per waste VS added (g) for manure slurry solution 1:1 without correction for the mean cumulative methane produced by the inoculum (blanks).

As can be seen in Figure 33, the cumulative methane produced per waste VS added was comparable for all three samples for the 0.5:1 ratio up until day 22. The analysis for sample $0.5{:}1_1$ on day 29 deviates considerably from the general trend. This sample was analysed during lockdown and was therefore performed by someone else than the author of this thesis who did it for the first time and it is therefore difficult to conclude if there were any anomalies in the sampling and analysing. Because of this it is unclear whether the methane production continued like in sample $0.5{:}1_2$, or if it had ceased. On day 36 the methane production for sample $0.5{:}1_1$ ceased. The methane production for sample $0.5{:}1_2$ increased to day 29. The analysis for sample $0.5{:}1_3$ on day 29 also deviates much from the general trend, and was also taken during lockdown by the same person who did sample $0.5{:}1_1$. The methane production continued to increase to day 62, when the study had to be completed.

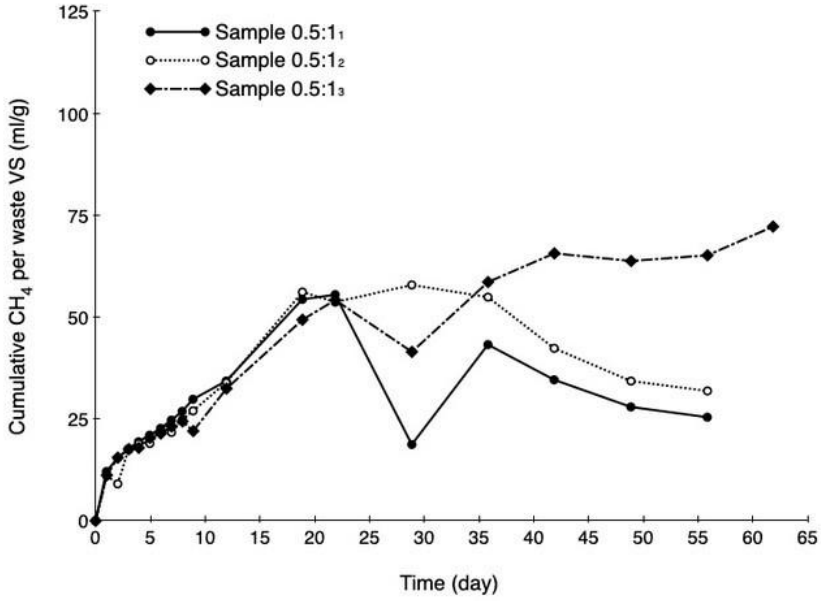

Figure 33. Cumulative methane produced (ml) per waste VS added (g) for manure slurry solution 0.5:1 without correction for the mean cumulative methane produced by the inoculum (blanks).

Descriptive statistics regarding cumulative methane production, highest methane concentrations analysed, and the cumulative methane produced per waste VS added for the manure slurry solutions 1:1 and 0.5:1, are provided in Table 10.

Table 10. Descriptive statistics regarding the manure slurry solutions 1:1 and 0.5:1

Ratio of manure slurry to inoculum (g VS)	**Day on which Cumulative methane produced peaked (day)**	**Peak Cumulative methane produced (ml/day)***	**Highest methane concentration (%)**	**Peak Cumulative methane produced/waste VS (ml/g)***
$1{:}1_1$	56	2,145	78	335
$1{:}1_2$	42	200	123**	31
$1{:}1_3$	56	181	84	28
Mean 1:1	**51**	**842**	**95**	**131**
$0.5{:}1_1$	22	108	79	34
$0.5{:}1_2$	29	115	82	36
$0.5{:}1_3$	62	161	82	50
Mean 0.5:1	**38**	**128**	**81**	**40**

* After correcting for the mean cumulative methane produced by the inoculum (blanks)
** The figure of 123% is probably due to an error during analysis. The second highest methane concentration was found one week later, at next analysis event, and was a more plausible 76%.

After the tests were terminated, the pH of the liquid in the bottles was measured and visible characteristics were noted, see Table 11. The pH was similar between samples for both the 1:1 and the 0.5:1 solutions. The pH is slightly lower in the 0.5:1 solutions.

The mean methane concentration in the blanks was 29 ± 11% and the cumulated methane production was 70 ± 25 ml. The monitoring of the methane concentrations in the blanks ceased on day 29 due to lockdown. Since access to the lab was limited, focus had to be on the actual samples. The methane concentration in the controls increased to 74 % and 79 %, in day 20 and 26 respectively. The analysis of the methane concentrations in the control samples also ceased on day 26 due to lockdown. The gas volume from the controls were 1,200 ml and 1,320 ml, with a mean of 1,260 ml.

Table 11: pH and descriptions of content in bottles of manure slurry 1:1 and 0.5:1 solutions when study was finished

Bottle	pH	Description
$1:1_1$	7.76	Dark green colour. A lot of white lumps floating
$1:1_2$	7.76	Semi-dark brown. Small amount of white foam floating on surface
$1:1_3$	7.77	Semi-dark brown. No visible white
Mean 1:1	**7.8**	
$0.5:1_1$	7.60	Dark brown. Small amount of white foam floating
$0.5:1_1$	7.55	Light brown. Small amount of white foam floating
$0.5:1_1$	7.56	Light brown. Small amount of white foam floating
Mean 0.5:1	**7.6**	
$blank_1$	7.38	Light brown
$blank_2$	7.79	Light brown
Mean blanks	**7.6**	
$control_1$	7.60	Dark brown
$control_2$	7.62	Dark brown
Mean controls	**7.6**	

5.2.2. Methane potential of first pond digestate

The mean methane concentration in the blanks was 14 ± 0 % and the cumulative methane production was 8 ± 0 ml. Due to lockdown sampling was interrupted, and when arrangements had been made to continue on day 18 the methane concentration had dropped to 0. The methane concentration in the controls increased to a maximum of 61 % and 65 %, on day 6 and 10 respectively.

Descriptive statistics regarding cumulative methane production, highest methane concentrations analysed, and the cumulative methane produced per waste VS added for the first pond digestate, see Table 12.

Table 12. Descriptive statistics regarding the first pond digestate.

Sample number	Cumulative methane produced peaked (day)	Cumulative methane produced peak (ml)*	Highest methane concentration (%)	Cumulative methane produced/waste VS peak (ml/g)*
Sample 1	27	9	32	72
Sample 2	34	21	60	162
Sample 3	40	49	71	377
Mean	**34**	**26**	**54**	**204**

* After correcting for the mean cumulative methane produced by the inoculum (blanks)

As can be seen in Figure 34, the cumulative methane produced per waste VS added was uniform for all three samples up to day 10, thereafter the methane production increased in sample 1 up to day 27, in sample 2 to day 34 and in sample 3 to day 40.

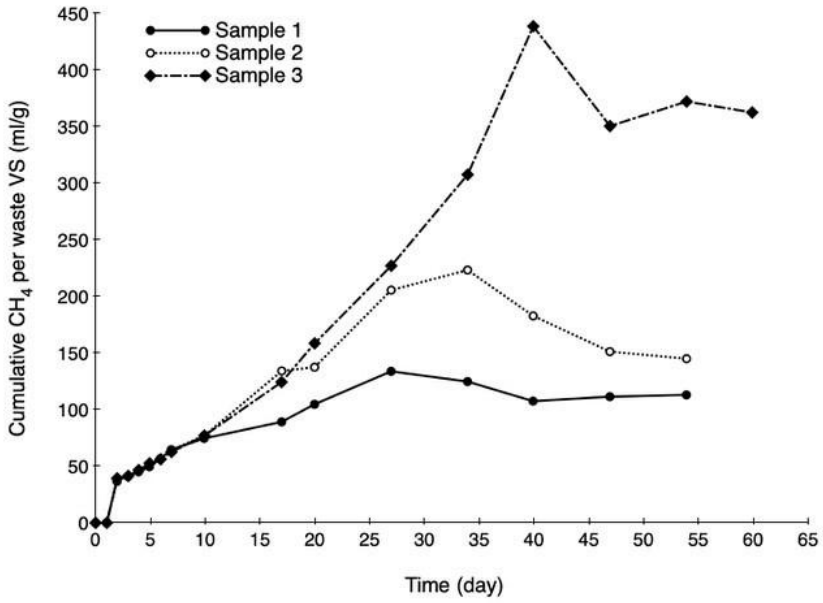

Figure 34. Cumulative methane produced (ml) per waste VS added (g) for first pond digestate without correction for the mean cumulative methane produced by the inoculum (blanks).

After the study was finished the pH in the bottles was measured and visible characteristics were noted, see Table 13.

Table 13. pH and descriptions of content in bottles of first pond digestate at completion of the study.

Bottle	pH	Description
Sample 1	7.83	Light brown/yellow. Some white brown lumps floating. 0.5 cm brown/black sludge at bottom
Sample 2	8.20	Light brown/yellow. No white lumps. 0.5 cm brown/black sludge at bottom
Sample 3	7.75	Light brown/yellow. No white lumps. 0.5 cm brown/black sludge at bottom
Mean	**7.9**	
Blank 1	6.65	Clear liquid without colour. 0.5-1 cm brown/black sludge at bottom
Blank 2	6.26	Clear liquid without colour. 0.5-1 cm brown/black sludge at bottom
Mean blanks	6.5	
Control 1	8.37	Brown. 2 cm brown/black sludge at bottom
Control 2	7.56	Lighter brown than control 1. 2 cm brown/black sludge at bottom
Mean controls	8.0	

5.2.3. Methane potential of slurry co-digested with dairy by-product

The mean methane concentration in the blanks was 14.5 ± 1.8 % and the cumulative methane production was 41 ± 1 ml. The attached Tedlar® bags reminded flat for the whole study period, indicating the volume gas produced was not high enough to fill up the Tedlar bags. The methane concentration in the controls increased to a maximum of 70 % and 76 % on day 16 and 41 respectively. The use of controls confirmed that the inoculum had an adequate microbial activity, which could be concluded from the analysed methane concentrations and that the Tedlar® bags filled up and had to be emptied once during the duration of the study period. The gas volume from the controls were 2,200 ml and 2,300 ml, with a mean of 2,500 ml. The study had to be concluded due to time constraints on day 41.

For descriptive statistics regarding the dairy by-product manure slurry mixes' cumulative methane production, highest methane concentrations analysed, and the cumulative methane produced per waste VS added, see Table 14.

Table 14. Descriptive statistics regarding the dairy by-product manure slurry mixes.

Percent dairy by-product in the 0.5:1 ratio of manure slurry to inoculum (g VS)	Cumulative methane produced peaked (day)	Cumulative methane produced peak (ml)*	Highest methane concentration (%)	Cumulative methane produced/waste VS peak (ml/g)*
5 $\%_A$	12	106	75	35
5 $\%_B$	41	266	82	87
Mean 5%	**27**	**186**	**79.5**	**61**
10 $\%_A$	41	117	79	39
10 $\%_B$	41	131	80	43
Mean 10%	**41**	**124**	**79.5**	**41**
15 $\%_A$	41	58	53	19
15 $\%_B$	41	53	49	17
Mean 15%	**41**	**55.5**	**51**	**18**

* After correcting for the mean cumulative methane produced by the inoculum (blanks)

As can be seen in Figure 35, the cumulative methane produced per waste VS added for the two 5 % dairy by-product manure slurry mixes was uniform for the two samples until day 13, thereafter the methane production for sample 5$\%_A$ started to decrease, whereas for 5$\%_B$ the methane production increased to day 16, before plateauing until day 22, after which an increase in volume made the curve jump up and then plateaued again in methane concentration only to increase in volume again on day 41. The sudden jumps in methane production occurred irrespectively of the change in sampling interval.

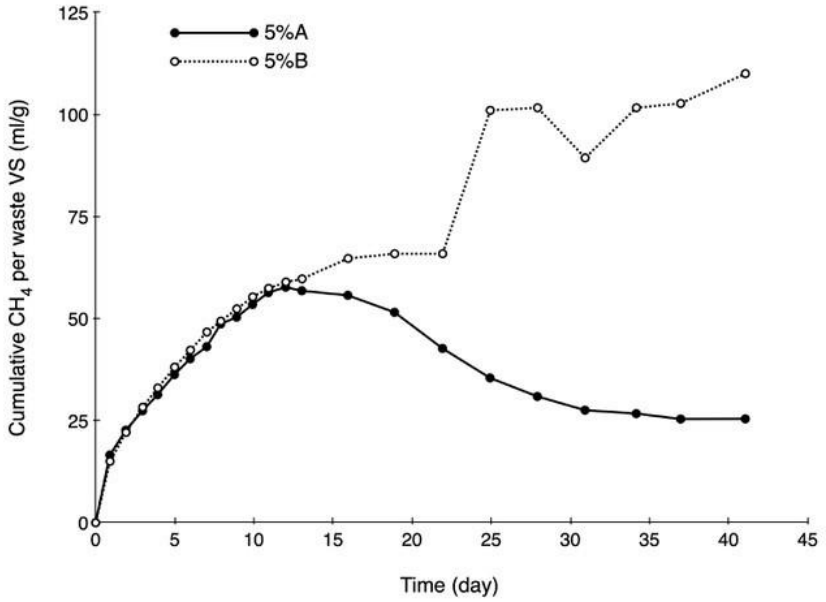

Figure 35. Cumulative methane produced (ml) per waste VS added (g) for manure slurry containing 5 % dairy by-product (without correction for the mean cumulative methane produced by the inoculum, i.e. blanks).

As can be seen in Figure 36, the final cumulative methane produced per waste VS added for the two 10 % dairy by-product manure slurry mixes were similar although the rates at which methane was produced were quite different. The cumulative methane produced for 10 $\%_A$ increased slowly in the beginning. After the initial lag phase, the production rate increased between day 16 and 22 up to day 31, before starting to level out. On the contrary for sample 10 $\%_B$ the cumulative methane produced increased steadily, up to day 31, without an initial lag phase, before starting to level out.

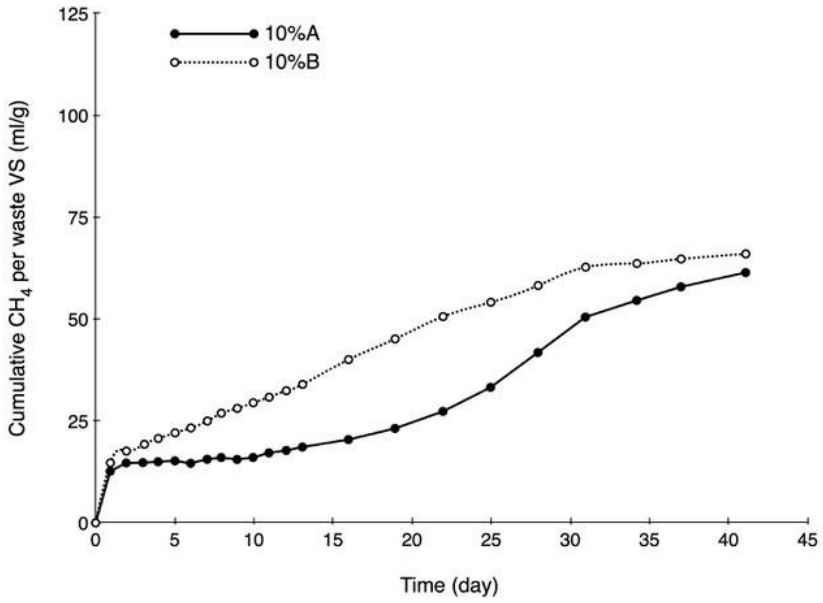

Figure 36. Cumulative methane produced (ml) per waste VS added (g) for manure slurry containing 10 % dairy by-product (without correction for the mean cumulative methane produced by the inoculum, i.e. blanks).

As can be seen in Figure 37, the cumulative methane production tor the two 15 % dairy by-product manure slurry mixes were very similar to each other and followed the same development as the 10 %B until day 22. After the initial lag phase, the cumulative methane produced increased from day 25 and continued to increase steadily to day 41, when the study was concluded.

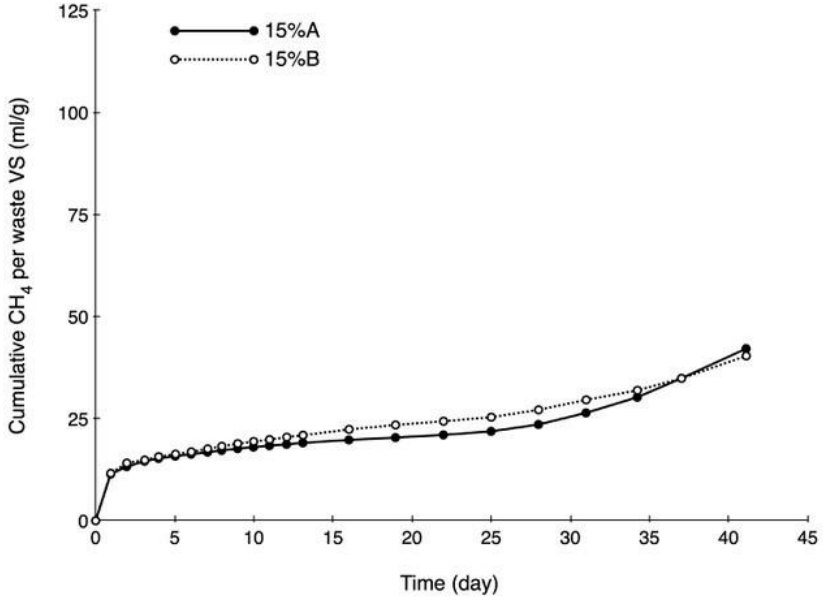

Figure 37. Cumulative methane produced (ml) per waste VS added (g) for manure slurry containing 15 % dairy by-product (without correction for the mean cumulative methane produced by the inoculum, i.e. blanks).

After the study was finished the pH in the bottles was measured and visible characteristics were noted, see Table 15 and Figures 38 and 39.

Table 15. pH and descriptions of content in bottles of manure slurry 0.5:1 solution with different concentrations of dairy by-product at completion of the study.

Bottle	pH	Description
5 %$_A$	7.73	Very dark brown, clear liquid. 3.5 cm of black, fine sludge at bottom. No visible dairy by-product
5 %$_B$	7.58	Light brown/yellow, clear liquid. 2.5 cm of black, fine sludge at bottom. No visible dairy by-product
Mean 5%	**7.7**	
10 %$_A$	7.46	Middle brown, cloudy liquid. 1 cm of black, a bit fibrous sludge at bottom. White dairy by-product and some black fibrous material floating.
10 %$_B$	7.54	Light brown/yellow, clearer liquid than 10A%. 2 cm of black, a bit fibrous sludge at bottom. Less white dairy by-product and more black fibrous material floating than 10A%.
Mean 10%	**7.5**	
15 %$_A$	6.94	Dark green/brown, cloudy liquid. 1 cm of black and white, course and fibrous sludge at bottom. A white, green and black fibrous crust was building up in spreading bubbles. Some bubbles thicker than 0.5 cm. White dairy by-product lumps floating
15 %$_B$	6.83	Dark green/brown, cloudy liquid. 1.5 cm of black and white, course and fibrous sludge at bottom. A white, green and black fibrous soft crust was building up in spreading bubbles. More than in 15A%. Some bubbles about 2cm thick. The rest varies from a few mm. White dairy by-product lumps and some black, fibrous material floating
Mean 15%	**6.9**	
Blank$_A$	7.88	Light brown/yellow, clear liquid. 0.5-1 cm black, fine sludge at bottom
Blank$_B$	7.94	Light brown/yellow, clear liquid. 0.5 cm black, fine sludge at bottom
Mean blanks	**7.9**	
Control$_A$		Dark brown, clear liquid. 0.5 cm black, fine sludge at bottom
Control$_B$		Light brown/yellow, clear liquid. 0.5 cm black, fine sludge at bottom

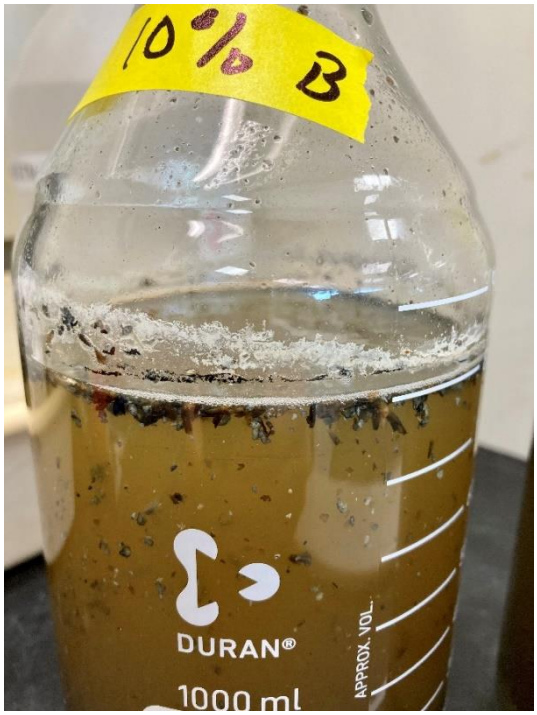

Figure 38. White dairy by-product and black fibrous material/grains floating in the 10 % dairy by-product concentration solution at completion of study.

Figure 39. White, green and black fibrous soft crust was building up in spreading bubbles and white dairy by-product lumps and black, fibrous material/grains floating in the 15 % dairy by-product concentration solution at completion of study.

6. Discussion

This research had two distinct parts, i.e., the study in the field to investigate how the conditions of the anaerobic digestion and treatment system on the farm varied over the seasons and the laboratory-based study of methane potential. This section is therefore divided into two separate subsections, which explain the two parts of the study. Firstly, the results of the seasonal study are discussed in subsection 6.1 Seasonal study. Secondly, the results of the laboratory-based study are discussed in the subsection 6.2 Methane potential studies. Finally, the implications for the treatment system on the farm of the findings in the two parts of this study, are discussed in subsection 6.3.

6.1. Seasonal study

During the sampling period, which spanned from August 2020 to May 2021, variation could be observed for all measured parameters in the manure slurry tank, as well as in the first and second pond. The largest variations were observed in the manure slurry, which is believed to be largely due to the limited size of the tank to buffer changes in the composition of the slurry over time. The retention time in the manure slurry tank was a fraction of the retention time in the first and second pond (one week compared to 5-6 months), which means that the parameters measured in the manure slurry are expected to be influenced to a larger extent by variations in the origin of the manure slurry, that is, depending on from what stages in the pig production cycle the manure slurry comes from.

It is not known from what stages of the pig production the manure slurry in the tank was from at each of the different sampling events. However, it is known that the feed and amount of ingested water varies in the different stages of the production cycle. In addition, the metabolism and digestion of the animals also depends on what stages the pigs are in. Because the contents from different sheds, which are at different stages of the production cycle, are emptied into the manure slurry tank at specific times, the variations of measured parameters in the manure slurry are expected to be large. In addition to the factors explained above, the researcher learned in discussions with the farmer that dairy by-product was emptied into the manure slurry tank a number of times, as mentioned in section 4.1.1., which can help to explain the large variations in pH and alkalinity (see subsection 6.1.5. pH and alkalinity). In the two covered ponds, that are far larger than the manure slurry tank and where the material is stored for a considerably longer time than in the tank, the material is more homogeneous. The results reflect the variability of the characteristics of the samples at each stage of the treatment process and show clearly that the variability is much higher in the manure slurry in the tank, than in the two covered ponds.

As such, the measurements in the first and second pond are believed to be more representative than the measurements of parameter in the manure slurry.

In the sections below, the variation in temperature during the season is first discussed, which is followed by a discussion of the other measured parameters in separate section.

6.1.1. Temperature variations

Being a seasonal study, it is relevant to explore how parameters vary during the year because temperature is known to strongly influence the anaerobic digestion process (Kinnunen et al., 2014). Because the study spanned only 10 months, with samples taken every month from August 2020 to May 2021, a simplified comparison between seasons was deemed the most representative and reliable option.

The temperatures in the tank and the ponds showed the same trends as the air temperature measured at the closest NIWA weather station, with the temperatures in November to April being higher than May to October. Because significance tests showed differences between the average temperatures in the tank and ponds for these months, it was decided to consider November to April as the "summer months" and May to October as the "winter months". Subsequent analyses of significant variations between seasons used the grouping of summer vs. winter months. Significant seasonal differences were only observed for phosphate in manure slurry and in digestate from the second pond, which are discussed in Section 6.1 5.

The division into seasons, e.g., summer and winter, could potentially have been done in other ways. However, temperature was considered the most suitable parameter to consider when splitting the data into seasons, because temperature is known to strongly influence the anaerobic digestion process (Kinnunen et al., 2014). Also, pond and tank temperature were used instead of air temperatures when deciding the seasons due to the liquid temperatures are more relevant to the processes in this study examining anaerobic digestions. The "winter" and "summer" months for air and liquid temperatures might not always coincide, due to the time it takes to heat and cool the liquid contents of the ponds.

As mentioned in Section 2.1 anaerobic digestion can take place to various extents under different temperatures. Depending on the temperature in the pond, different organic loading rates can be applied. The higher temperature provided in a heated digester (mesophilic or thermophilic conditions) enables a higher organic loading rate. The temperatures recorded in this study ranged between 14.5 to 18.5°C (mean: 14.7°C) in the first pond and 10 to 18.5 °C (mean: 14.1°C) in the second pond and operate hence under psychrophilic conditions. Under psychrophilic conditions anaerobic digestion occurs, but slow and this require a lower VS loading rate (0.02–0.46 kg VS/m3/d for psychrophilic digester as compared to 2.7 to 17.7 kg VS/m3/d for a mesophilic digester) and at least double the solids retention time of mesophilic digesters to achieve the same volatile solids reduction (Park and Craggs, 2007). For more discussions about organic loading rates and hydraulic retention times in this study, see subsection 6.3..

6.1.2. TKN and ammonia nitrogen

TKN consists of ammonia nitrogen and organic nitrogen, but the relative proportion of nitrogen form varied between the tank and the ponds. The results showed that the fraction of ammonia nitrogen is larger than the fraction of organic nitrogen for manure slurry, which is in line with results presented by Chastain and Smith (2019). Furthermore, Chastain and Smith (2019) showed that the ammonia fraction is even larger in the digestate of anaerobic ponds, because some of the organic nitrogen has oxidised to mostly ammonia nitrogen. This is consistent with results of this study, where it can be seen in Figures 17, 18 and 19 in Section 5.1.2, that the ammonia concentration typically is higher relatively to the TKN concentration for the two ponds than for the manure slurry.

The concentrations of both TKN and ammonia nitrogen are on average higher in the manure slurry in the tank than in the digestate in the ponds. This is likely due to emission of ammonia from manure slurry being the highest the first ten days of storage, followed by a decrease in ammonia emission with storage time (Qu and Zhang, 2021). The manure slurry is stored in the tank for up to seven days before transfer to the first pond, and most ammonia loss is expected to take place in the tank. It is therefore expected that the ammonia concentration in the tank should, on average, be higher than the ammonia concentration in the ponds. Emission of ammonia occurs from pH 7 in manure slurry, although ammonia emission increases with increased pH (Qu and Zhang, 2021). The average annual temperature for the area in which the farm is located is about 11°C (as mentioned in section 4.1 and can be discerned from figure 16 in subsection 5.1.1.). As shown by Misselbrook et al. (2016) ammonia emission from pig manure slurry occurs at temperatures of approximately 9 to 17°C, although emission increases with temperature. The average temperature of 11°C and the measured pH is therefore sufficient for sustained ammonia emissions.

In manure slurry the concentrations of TKN and ammonia nitrogen were correlated within a sampling event, but varied widely between events. This is most likely explained by the variation of manure slurry origin, as discussed in Section 6.1.

The variation of TKN and ammonia nitrogen concentrations between samples in the two ponds is small. This is probably because the homogeneity in the digestate increases in the larger ponds with much longer retention times. As can be seen from the trend lines in Figure 19 in Section 5.1.2 it appears both the TKN and ammonia nitrogen concentrations decrease slightly in the second pond from August to May. However, the biggest difference between the highest and lowest concentrations are only about 400 mg/L for TKN and about 500 mg/L for ammonia nitrogen and as was mentioned in Section 5.1.2, there was no significant difference between summer and winter months in TKN and ammonia nitrogen concentrations in manure slurry or the digestate from the two ponds.

As mentioned in Section 5.1.2., there were two TKN tests performed on each sample and they were mostly very similar. The exception was for the manure slurry from the tank in December and February, when the difference was 4.5 % and 14.9 % respectively. The reason for the differences in the concentrations in the duplicate samples for these two cases are unknown, but could be due to the heterogeneity of the manure slurry.

In a few of the samples the concentration of ammonia is higher than TKN, which is, by definition, impossible. One possible explanation could be that in those samples most of the TKN is ammonia nitrogen and the difference is within the analytical error, as described in Section 5.1.2. However, it is unknown if the error is the same regardless of nitrogen concentration and if this alone can explain why the concentration of ammonia nitrogen was higher in some samples.

The concentrations of TKN and ammonia nitrogen in this study were high (TKN mean: 3,700 mg/L and ammonia nitrogen mean: 3,200 mg/L in manure slurry and TKN mean: 2,600 mg/L and ammonia nitrogen mean: 2,600 mg/L first pond digestate) for both manure slurry and digestate in the ponds compared to other studies by Heubeck and Craggs (2010) (TKN: 1,544 mg/L, ammonia nitrogen: 838 mg/L in manure slurry and TKN: 1,311 mg/L and ammonia nitrogen: 1,076 mg/L in pond digestate) and Kafle and Chen (2016) (TKN: 1,092 mg/L, ammonia nitrogen: 510 mg/L in manure slurry and TKN: 978 mg/L, ammonia nitrogen: 620 mg/L in first pond digestate). Also, the ammonia nitrogen concentrations reported by Moset et al. (2012) (ammonia nitrogen: 2,400 mg/L for manure slurry and 2,000 mg/L for pond digestate), was lower than in this study. However, the ammonia nitrogen concentration in manure slurry in this study was the same as reported by Lee and Han (2016) (ammonia nitrogen: 3,200 mg/L). To conclude, the concentrations of TKN and ammonia nitrogen in this study were high, although similar concentrations could be found in other studies.

Yenigün and Demirel (2013) stated that anaerobic digesters can function at high concentrations of ammonia if the microbial community is acclimated to increasing levels of ammonia over time. For pig manure with acclimatised microorganism populations a concentration of up to around 3,000 mg/L could be endured (Yenigün and Demirel, 2013). The concentrations in the anaerobic ponds in this study are below inhibitory thresholds and the microorganism are considered acclimatised. However, the concentrations of ammonia nitrogen are rather high in this study and in the upper range of reported ammonia nitrogen concentrations of functional pig manure slurry anaerobic ponds.

Ammonia is one of several odorous compounds that emanate from pig farms (Trabue et al., 2011; Trabue et al., 2019). Depending on properties, such as odour thresholds and chemical stability, some odorous compounds are an issue only at a short distance from the farm and manure slurry storage, whereas others are a problem even at long distances. Ammonia is mostly perceived as an odorous compound very close to the manure slurry storage and is very sensitive to dilution, and hence not an odour issue for neighbours and the general community. (Trabue et al., 2019). No study was found identifying a connection between concentrations of ammonia nitrogen in pond digestate and concentrations of ammonia in air causing an odour issue.

6.1.3. TS/VS

The TS and VS concentrations in the manure slurry is highly variable, whereas the variation between sampling events is much smaller in the ponds. The reasons for the higher variation in the concentrations of TS and VS between sampling events in manure slurry compared to the ponds, are most likely the same as for the variation in TKN and ammonia nitrogen, i.e., it depends on the variation of manure slurry origin and that the homogeneity increases in the larger ponds with longer retention times, as discussed previously.

The total mean VS removal for both ponds together was about 85 %, which is a high proportion compared to findings in other Aotearoa New Zealand farm pond systems for treating pig slurry. For example, Craggs et al. (2008) reported a removal of 68 % in the pond system of a piggery. The observed VS removal in this study suggests that the treatment works well, since VS removal is the main purpose of the pond (Heubeck and Craggs, 2010; Park and Craggs, 2007) and hence an indicator of the function of the pond. However, as

much material is caught in the crust of the first pond, and hence was not possible to include in the samples, it is possible that the results overestimate the total VS removed.

In the manure slurry, the VS is rather high compared to the TS (mean variation between TS and VS manure slurry: 73% ± 13%), compared to the first (mean variation between TS and VS first pond: 53% ± 2%) and second pond (mean variation between TS and VS second pond: 47% ± 11%). This is likely due to the microbial activity in mainly the first pond, where the organic material breaks down, the inorganic material deposits in the sediment and some organic material is captured in the floating crust, partly escaping break down.

As can be seen from the trend lines in Figures 21 and 22 in Section 5.1.3, it appears both the TS and VS concentrations in the first and second pond decreases from August to May. However, as was mentioned in Section 5.1.3, there was no significant difference between summer and winter months in TS and VS concentrations in manure slurry or the digestate from the two ponds. In this study, focus was on seasonal changes and not changes from start to end of this study, and therefor data to support or reject any hypothesis regarding change over time was not collected.

6.1.4. Settleable solids

The dark colour of the manure slurry made it too difficult to determine settleable solids, but from the first and second pond it appears that the concentration of settleable solids in the ponds are low (0.8 to 5 ml/L in the first pond and 0 and 1.5 ml/L for the second pond digestate) and the settable solids consisted mostly of sand. However, the samples were collected at a depth of about 1.2 metres in the two ponds. The first pond has a depth of five meters and the second pond usually has a depth of about two meters. This means that the sample for settleable solids in the first pond is taken rather close to the surface and hence might have missed settleable solids that have already settled closer to the bottom. In the second pond however, the sample was taken much closer to the bottom, indicating there is not much settleable solids at all in this pond.

6.1.5. pH and alkalinity

The pH value in the manure slurry was usually between 7.0-7.5, but for three sampling events the pH value dropped to almost 6. One of these sampling events was in February and dairy by-product had been discharged into the manure slurry tank five days prior to sampling. The pH of the dairy by-product is 4.7. It is unknown if something similar had happened the other times the pH was very low.

For the two ponds, the pH value was consistently around 7.5 during the entire season. The usual neutral/slightly alkaline environment of pig manure slurry creates a stable and favourable environment for the methanogens. According to Anderson et al. (2003) the optimal pH range for methanogenesis is relatively narrow at 6.5-8.0. The fact that the pH in the two ponds remains stable around 7.2 to 7.8 indicates balance in the microorganisms and no accumulation of VFAs. If acid utilization is inhibited or too slow due to for example organic overload, this can cause an accumulation of VFAs and a drop in pH (Chen and Neibling, 2014). If VFAs where to accumulate and cause the pH to drop this could create an unfavourable environment for the methanogens and even stop methanogenesis completely.

Alkalinity is a measure of the waste's buffer capacity. Buffer capacity is the ability of the waste to neutralize acids. A high alkalinity is an indication that the system has a good buffer capacity and hence is more stable. Alkalinity in a functional anaerobic digester can range between 1,500 and 5,000 mg/L as $CaCO_3$ (K. Schnaars, 2012). The alkalinity was high in both the manure slurry and the digestate from the ponds. The alkalinity in the manure slurry in this study varies between 4,700 and 16,300 mg/L as $CaCO_3$ with a mean of 10,400 mg/L as $CaCO_3$. It was consistently high as compared to studies by Kafle and Chen (2016), Marchetti et al. (2019) and Rico et al. (2017), who found alkalinity in pig slurry in the ranges of 3,500, 2,300, 9,000 mg/L as $CaCO_3$, respectively. The alkalinity was at its lowest (although still comparably rather high) for the months of January, February and April and thus coincided with the months of the lowest pH. This is consistent with the relationship between pH and alkalinity (American Water Chemicals, Inc., 2022) and

suggests that the lower pH measured in the manure slurry those months, put a higher strain on the generally high alkalinity of manure slurry and thus lowering it. The alkalinity in the two ponds in this study is also high and stable in all samples, with means of 9,700 and 10,100 mg/L as $CaCO_3$, respectively, which is consistent with the equalising effect of the bigger ponds (compared to the small manure slurry tank) when receiving small amounts of manure slurry of low pH. The mean alkalinity in the first pond in this study is comparable to concentrations of 4,460 and 13,800 mg/L as $CaCO_3$ in anaerobic ponds treating pig slurry in studies by Kafle and Chen (2016) and Cerrillo et al. (2016), respectively. The ammonia concentrations are as mentioned above generally high in the samples of this study and as is reported by Dickson (1981), ammonia can contribute to alkalinity.

6.1.6. Phosphate and sulphate

The results show that the concentration of phosphate in the manure slurry was much higher than the phosphate concentration in the digestate of both ponds. As mentioned in Section 5.1.5, the mean concentration of phosphate was 880 mg/L in the manure slurry, 380 mg/L in the first pond and 335 mg/L in the second pond. This can be compared to the 463 mg/L that Kafle and Chen (2016) found in swine manure and the 602 mg/L from anaerobic digestion in batch tests of swine manure incubated at 36.5 °C. Phosphate concentrations in manure slurry in this study varied widely, which is likely dependent on the production stage the manure slurry originated from. The average concentration in the ponds was much lower than that in the manure slurry, which indicates that phosphorous is most likely precipitating into sediment in the first pond. Unfortunately, analysis of the sediment was not possible in this study, because the depth sampler device available was too big to fit through the sampling port.

One possible explanation for the much lower mean concentration of phosphate in the ponds compared to the manure slurry is the formation of struvite. In order for struvite to form, three key factors are required; the presence of magnesium, phosphate and ammonia in a 1:1:1 molar ratio (Hao et al., 2008), as well as a pH value between 7.5 and 10.5 (Kim et al., 2017). The presence of magnesium and whether these components exist in a stoichiometric molar ratio is unknown in this study, but conditions of pH is fulfilled in the second pond for the months of December to May and also in September. Struvite formation can occur when pH is above 7.5 and those struvite crystals might then end up in the pipes or on the pond walls, as described by Shi et al. (2021), which may be the reason for the significantly lower phosphate concentration in the second pond during the summer months. However, it should be added that there was no significant difference in the pH values during the summer and winter months. As mentioned, the ratio of magnesium to phosphate is unknown, and no quantification of struvite in the pipes or on the walls was done. Therefore further investigation would be needed in order to test this hypothesis.

As mentioned earlier, a condition for struvite formation is the presence of magnesium and phosphorous, which may be contained in the dairy by-product used as pig feed. According to Shi et al. (2021) dairy waste usually has a high content of phosphorous and magnesium and has a high potential to form struvite under the right conditions. Most of the waste in the ponds in this study is pig manure slurry, but the addition of dairy by-product to the pig feed, and to some extent directly to the pond, might contribute to an increased risk of struvite formation. However, laboratory studies investigating if and how this dairy by-product effect struvite formation in pig slurry would be needed before any conclusions can be drawn.

As can be seen in Figure 25 in Section 5.1.5, the phosphate concentration is significantly higher in the manure slurry during the summer months than during the winter months. The explanation for the significantly higher phosphate concentration during the summer months, might be because dairy by-products usually contain high concentrations of phosphorus, and is fed to the pigs during October to May, and hence possibly resulting in the increase in the phosphate concentration found in the manure slurry.

As can be seen in Figure 18 in Section 5.1.2 the trend line for ammonia in the second pond indicates a decrease in the ammonia concentration with time, i.e., from the start to the finish of the field study. The lower concentrations of ammonia during the summer months could be an indication on struvite formation in this pond. However, no significant difference could be shown between summer and winter months for the concentration of ammonia for any of the ponds.

The concentration of sulphate was only determined once, at which time the concentration in the manure slurry (approximately 76 mg/L) was three times as high as that in the first pond (approximately 21 mg/L). The sulphate concentration in the second pond was below detection level. This reduction in concentration was most likely due to sulphate-reducing microorganisms and resulted in the production of hydrogen sulphide (Muyzer and Stams, 2008). The concentration of sulphate in the first pond in this study can be compared to a study made by Lin et al., (2017), where concentrations of 28.8 mg/L sulphate in anaerobic digesters using pig manure slurry was reported. In the same study, the concentration of hydrogen sulphide in the biogas from those digesters varied between approximately 350 to 600 ppm. As mentioned in Section 5.1.9, the concentration of hydrogen sulphide from the first pond in this study varied between 0 and 5,000 ppm, (5,000 ppm was the meter's maximum detection limit), showing considerably higher variation and most of the time considerably higher concentrations of hydrogen sulphide, than in the study by Lin et al., (2017). As reported by Liamleam and Annachhatre (2007) some sulphate-reducing microorganisms oxidise organic compounds like lactate acid (present in sour milk or possibly sour dairy by-product) and others compete with methanogens and acetogens for hydrogen (H_2) in anaerobic conditions. If theses strains of sulphate-reducing microorganisms exist in the ponds in this study, which could be a possible explanation for the varying and at most sample events higher concentrations of hydrogen sulphide, than in the study by Lin et al., (2017). However, what strains of sulphate-reducing microorganisms were present in the ponds in this study are unknown and so is the possible presence of lactate discharged into the ponds and those issues would need to be investigated in a separate study.

The concentrations of sulphate in manure slurry and digestate from the ponds in this study were much lower than concentrations reported by Moset et al. (2012) (320 mg/L in manure slurry and 390 during anaerobic digestion). This can likely, to some extent, be explained by the manure slurry being more diluted in Aotearoa New Zealand as compared to that in Denmark where Moset et al. (2012) performed their study.

6.1.7. VFAs

Results show that the mean concentration of acetic acid in the manure slurry in this study was lower compared to past studies, whereas the concentration of propionic acid was similar (Moset et al., 2012). Moset et al. (2012) reported concentrations of 6,150 mg/L for acetic acid and 2,440 mg/L for propionic acid in pig manure slurry, which can be compared to 4,180 and 2,090 mg/L measured in this study. However, the pig slurry collected by Moset et al. (2012) was from commercial pig farms in Denmark, and therefore likely more concentrated than the manure slurry used in this study. The pig manure slurry used in the study by Moset et al. (2012) was anaerobically digested in a continuously stirred reactor operating under thermophilic (52°C) condition, which is quite different from the conditions of this study. No studies of anaerobic farm pond systems reporting concentrations of VFAs separately (as acetic acid, propionic acid, etc.) were found. Figure 26 in Section 5.1.6 show no obvious trend and the concentrations of acetic, propionic and butyric acids are likely mostly dependent on the manure slurry origin, as discussed previously.

According to Gourdon and Vermande (1987), an increase in propionic acid can be a sign of disturbance in the anaerobic digestion process. As described by Marchaim and Krause (1993), an increase of the ratio of propionic to acetic acid can also be a sign of overloading of the system. According to Hill et al. (1987) a propionic to acetic acid ratio of more than 1.4 is an indicator of anaerobic digestion nearing digester failure.

In the first pond, the ratio of propionic to acetic acid was lower than the previously mentioned limit of 1.4. As can be seen in Figure 27 in Section 5.1.6, the ratio of propionic to acetic acid was highest in the months of September, October, November, December and April in the first pond. However, as mentioned in Section 5.1.6, two-sample t-tests assuming unequal variances show no significant differences between summer and winter months for any of the VFAs analysed. The highest propionic to acetic acid ratio in the first pond was 1.1 in November and 1.0 in December, which is far from the ratio indicating digester failure. For the first pond there is no obvious trend of change in VFAs ratio with season or time. The relatively high propionic to acetic acid ratio most months, might be a sign of a slight pond imbalance.

In the second pond, the ratio of propionic to acetic acid was much lower than the previously mentioned limit of 1.4, and there seemed to be an increase of acetic and propionic acid concentrations during the

colder winter months. As can be seen in Figure 28 in Section 5.1.6, it appears that the ratio of propionic to acetic acid is highest in the months of August, September and October. Those months are all in winter, when the temperature is lower and consequently the anaerobic digestion is slower. Furthermore, the trend in the second pond suggests acetic acid accumulation during the winter months and also an increase in propionic to acetic acid ratio, indication a slower process, during the winter months. However, as mentioned in Section 5.1.6, two-sample t-tests assuming unequal variances show no significant differences between summer and winter months for any of the VFAs analysed. For the second pond, the propionic to acetic acid ratio never approached 1.4.

According to Gourdon and Vermande (1987), concentrations of up to 6,000 mg/L of propionic acid were insufficient to inhibit methanogenesis or acetogenesis, and only had a small effect on the acidogenesis. The concentration of propionic acid was always less than 1,400 mg/L in all ponds. The pH of the ponds was stable and neutral/slightly basic during the entire sampling period. No clear trend can be seen of accompanied increased ratio of carbon dioxide to methane, which according to Marchaim and Krause (1993) also is an indicator of nearing overload of the anaerobic digestion process. The neutral/slight alkaline pH and no trend in increased ratio of carbon dioxide to methane suggest the ponds might manage to stay within an acceptable range even during the winter months.

A comparison between fresh and a frozen manure slurry sampled in March shows that the difference between concentrations of VFA is minimal. Although the data are too limited to draw any definitive conclusions, the results indicate that freezing did not alter the concentration of VFAs. This conclusion is in line with the findings in a study by Wagner et al. (2017), who found that concentration of VFAs essentially unchanged after being frozen for 32 days. The fact that the manure slurry and the digestate was frozen before analysis for the months of March and April has therefore likely not influenced the results.

6.1.8. Electric conductivity and oxidation-reduction potential

Electric conductivity in manure slurry (23.2 mS ± 11), first (20.9 mS ± 1.4) and second pond (21.6 mS ± 1.4) digestate clearly suggests a relatively high salinity (compare to deionized water: 0.00005 mS/cm, fresh groundwater typically less than 0.100 mS/cm and seawater 50 mS/cm (LAWA, 2021) and 15 mS/cm found in pig slurry by Provolo and Martínez-Suller (2007). The electric conductivity measured in this study is comparable to other studies such as Petersen et al. (2013) who found electric conductivity varying between 15 and 30 mS/cm in pig slurry, suggesting the measured electric conductivity in this study is within the normal range for pig manure slurry. The electric conductivity is similar in all three fluids collected, although the variability is higher in the manure slurry, probably indicating the heterogeneity of that material, as noted previously.

The oxidation-reduction potential in the manure slurry, first and second pond digestate clearly indicates that the manure slurry and the contents in the ponds are anaerobic. The oxidation-reduction potential is similar in all three fluids, but as can be seen on the range, the variability is greater in the manure slurry, indicating the heterogeneity of that material.

6.1.9. Total oil and grease

The concentration of oil and grease in manure slurry and digestate is similar to that found in wastewater from oil and grease rich food processing plants. The dairy by-product fed to the pigs September to May and sometimes directly to the first pond during these months contains approximately 76 g/L (76,000 mg/L) of fat. The concentrations of oil and grease in the manure slurry, and digestate from the first and second pond were approximately 630, 600 and 500 mg/L respectively. For comparison, oil and grease concentrations in wastewater from food process industries can be 1,400 mg/L from the homogenization tank in a vegetable oil refinery or 480 mg/L in wastewater samples from the removal of waxes line (Pintor et al., 2015). No data from other studies on analysed oil and grease concentrations in pig slurry or pond digestate have been found to use for comparison. Ideally data from similar Aotearoa New Zealand pig farms, not using dairy by-product in their pig feed, but also using anaerobic ponds for their waste treatment, should be used for a comparison of the concentrations of oil and grease in manure slurries and pond

digestate and by extension an evaluation of the impact of the use of dairy by-product in pig feed on the performance of the anaerobic digestion pond systems.

Wastewater high in oil and grease usually requires treatment techniques such as coagulation/flocculation, dissolved air flotation, and membrane separation (Pintor et al., 2016, Collin et al., 2020) due to its complexity and often associated issues such as inhibition by long chain fatty acids, sludge floatation, washout, and scum formation (Salama et al., 2019). Higher methane production and higher biodegradation efficiency in wastewater containing high concentrations of oil and grease are achieved at thermophilic temperatures (Li et al., 2013, Kabouris et al., 2009). The treatment techniques mentioned above increase the cost of the treatment and can in many cases even be unmanageable at farm level. The issues of sludge floatation and scum formation observed with the treatment system on the farm in this study are similar to issues arising when using anaerobic digestion for the treatment of oily and greasy wastewater, as mentioned above. However, in this study the concentrations of oil and grease were only analysed once (in August). In order to investigate a possible correlation to temperature (season) for this parameter, the oil and grease analysis would have been needed to have been carried out each, or most, of the months in the study.

6.1.10. Methane, carbon dioxide and hydrogen sulphide concentrations

The mean methane concentration found in this study was rather low, whereas the mean hydrogen sulphide concentration was high compared to other studies. The mean methane concentration for the anaerobic ponds in this study (first pond average: 56 % ± 16, second pond average: 50 % ± 29), is rather low compared to 72 %, standard deviation 2.3, found by Park and Craggs (2007). This indicates the process is not optimal, since other circumstances (such as pig slurry in Aotearoa New Zealand conditions) are similar. However, in the study by Park and Craggs (2007), the manure slurry was passed through a solids separator before being pumped to the anaerobic pond. Also, there is no mention of the use of dairy by-product in the feed or directly into the pond. Excess solids increases the risk of overloading the pond system and the additional fats from the dairy by-product increases the risk of biomass flotation and wash out, which decreases the performance of the pond.

The mean hydrogen sulphide concentrations for both ponds are very similar. The variability is high both between events and between ponds (mean first pond: 2,950 ppm ± 2,950, mean second pond: 2,970 ppm ± 2,120). According to United States Department of Labour (2022), the odour threshold for when people are able to smell hydrogen sulphide is when concentrations reach between 0.01-1.5 ppm. However, it should be noted that the concentrations exceeded the detection range at several of the sampling events, so the concentrations for those months and hence also the total mean might actually be higher than stated. The concentration of hydrogen sulphide in the biogas measured at the farm was as an average of what is considered high concentrations, according to St-Pierre and Wright (2017), who considered between 2,000 to 3,000 ppm to be high. The trend discerned is of high variability in concentrations of hydrogen sulphide in both ponds, and there were no clear correlations between the ponds or to temperature.

For the carbon dioxide concentrations the trend is similar to the methane concentrations, as can be seen by the mean ratio of methane to carbon dioxide (first pond: 1.8 ± 0.6, second pond: 1.8 ± 0.7). However, since the biogas composition was only measured for a few seconds once a month and therefor is rather uncertain, so are the ratios.

To measure the methane, carbon dioxide and hydrogen sulphide concentrations for a few seconds once a month was not sufficient to draw any proper conclusions, since the composition of the biogas at all other times is unknown as is the amount produced. The methane production and rate would have needed to be measure with, for example, a flow meter. However, it was not possible to install one in this study. The methane concentrations were highly variable from time to time, and so was the use of the flare, both indicating that the methane production was irregular.

Since the use for heat or electricity requires a more reliable supply the most economical "use" might be flaring to avoid the release of methane to the atmosphere, though a continuous measuring of the methane production would be needed to confirm this. In the study the two ponds had similar methane

concentrations, but in a different pattern and within a wider range. This indicates much of the degradation is also taking place in the second pond and this could be due to wash-out of un-degraded organic material floating on the top of the first pond.

6.2. Methane potential studies

The results suggest that methane potential can vary substantially between samples, as well as the time required to reach the maximum cumulated methane produced. This is most likely the result of the heterogeneity of the material. Co-digestion of manure slurry and different concentrations of dairy by-product suggests a higher concentration of dairy by-product increases the lag phase for methane production. A higher concentration of dairy by-product also seems to increase the risk of creation of a crust in the digester and decrease the degradability of the organic material.

In the two sections below, the variation of methane potential is first discussed in subsection 6.2.1., which is followed by a discussion of the effect of different concentrations of dairy by-product on methane potential in subsection 6.2.2.

6.2.1. Methane potential studies of manure slurry and first pond digestate

Although the manure slurry used in those bench-scale experiments were from the same grab sample and shaken before use, large differences in methane production were observed for the manure slurry with the 1:1 (g VS) substrate to inoculum ratio. Samples $1:1_2$ and $1:1_3$ showed very similar methane production (29.5 $\pm$ 1.5 ml/g). Conversely, sample $1:1_1$ showed an increase in methane production from day 20, with a sharper increase from day 36, finishing at a cumulative methane produced ten times that of samples $1:1_2$ and $1:1_3$ (335ml/g). At the completion of the study (41 days), the pH was very similar for the three samples at 7.8. However, sample $1:1_1$ was slightly different in colour (dark green as opposed to semi-dark brown as samples $1:1_2$ and $1:1_3$) and also contained a plethora of white floating lumps of dairy by-product (as opposed to a little to no white lumps in sample $1:1_2$ and $1:1_3$). Those differences might be due to a different composition of material in sample $1:1_1$ that might explain the much higher methane production. Notable is that the methane development in sample $1:1_1$ started to increase sharply after 20 days and this was also the sample with most visible dairy by-product.

Diluting the manure slurry seems to have created a more homogenous mix, which provided more consistent methane production. The results for the study of the manure slurry samples of the 0.5:1 (g VS) substrate to inoculum ratio showed similar cumulative methane production (40 $\pm$ 10 ml/g). Sample $0.5:1_1$ and $0.5:1_2$ reached their maximum cumulative methane produced at day 22 and 29, whereas sample $0.5:1_3$ reached its maximum on day 62, when the study had to be concluded, and it is therefore unknown whether this was its maximum or it the methane production would have continued had the study not been concluded. The final pH was very similar for all three samples at 7.6. The colour (dark to light brown) and amount of visible white foam floating on the surface were similar in all samples. Because of the more stable results from the study with the 0.5:1 (g VS) substrate to inoculum ratio, this was chosen in the subsequent parts of the study when different concentrations of dairy by-product were added.

From the study of the first pond digestate samples of the 1:1 (g VS) substrate to inoculum ratio, it is clear that the cumulative methane produced per waste VS added varies. The higher the maximum methane yield, the longer it took to reach it. The difference in the methane output could be due to the heterogeneity of the material, in combination with the small size of bottles (hence a small sample where possible heterogeneity would be more pronounced), although the first pond digestate showed more homogeneity than the manure slurry.

Similar to the manure slurry samples of the 1:1 (g VS) substrate to inoculum ratio, the variability between samples is large for the first pond digestate samples of the 1:1 (g VS) substrate to inoculum ratio. The mean methane potential is higher for the first pond digestate than for both the manure slurry ratios. However, the highest cumulative methane produced in the first pond digestate (377 ml/g) is similar to the highest cumulative methane produced in the manure slurry of the 0.5:1 (g VS) substrate to inoculum ratio (335 ml/g), although the time to achieve this is shorter, namely 40 and 56 days respectively. This increased rate

could be because the digestate in the first pond was more degraded, with finer particles and more surface area, and hence more accessible to the microorganisms, which is in line with results presented by Vigueras-Carmona et al. (2011).

6.2.2. Methane potential of slurry co-digested with dairy by-product

The studies of methane production were conducted in a temperature-controlled room with a constant temperature of 37°C, whereas the pond at the farm operates in ambient temperature where water temperature fluctuated between 14.5 to 18.5 °C over the study period. During the study period, the maximum air temperature fluctuated between 13 to 22°C and the minimum air temperature varied between 2 and 10°C, thus that the farm ponds operate under psychrophilic conditions. Li et al. (2013), Jianga et al. (2018) and Zhang et al. (2014) demonstrated that the anaerobic digestion of fats, oil and grease at higher temperatures have a higher methane production, than it has at lower temperatures and more complete degradation of organic material. Although this study was performed at a temperature of 37°C, there was still some floating of dairy by-product and organic matter in the samples containing 10% dairy by-product (Figure 38). In the samples containing 15% dairy by-product there was a build-up of a crust (Figure 39). The bottom sludge was quite different in the different samples, where the lower concentration of dairy by-product seemed to generate a finer black sludge and the higher doses of dairy by-product seemed to generate a courser material and also residues of the dairy by-product (Table 15). The formation of a crust and the coarseness of the material supports the hypothesis that a high concentration of dairy by-product can slow down or even stop a full degradation of the organic material.

The laboratory results suggest that the crust observed in the first pond at the farm is at least partly a result of the addition of dairy by-product. In the co-digestion of manure slurry with 15 % dairy by-product, a build-up of a crust was seen, i.e., much like the crust of the first pond on the farm. The crust in the study was soft, but this could be because of the higher temperature (much warmer than in the first pond) or the short time the crust had had to build up. This is consistent with the findings of Palatsi et al. (2011) who reported that the presence of oil and grease in anaerobic digesters can lead to biomass flotation and subsequent wash-out. Also, the final pH of the manure slurry co-digested with 15 % dairy by-product was slightly lower than that in the other samples containing lower concentrations of dairy by-product (Table 15). This may indicate the accumulation of fatty acids, produced as an intermediate product during lipid hydrolysis, which inhibit methanogenesis. However, as can be seen in studies by Usman et al. (2020) and Amha et al. (2017), this inhibition is many times temporary and after a lag phase in methane production (which was observed in this study) methane production resumes.

Methane production from the two samples with 15% dairy by-product, were very similar (Figure 37). There was a clear lag phase in both samples before methane production picked up around day 25. The methane concentrations reached ~50 %, and appeared to be continuing to increase, when the study was concluded at day 41 (Table 14). In the two samples with 15% dairy by-product the bottom sediment was black and white, coarse and fibrous (Table 15), indicating that the material and dairy by-product not fully degraded. The manure slurry co-digested with 15% dairy by-product reached a maximum of approximately 18 ml/g of cumulative methane produced per waste VS added, although the study was concluded too early to know the final value for cumulative methane production (Table 14).

In the manure slurry co-digested with 10% dairy by-product there a crust appeared to form, although it was less pronounced than for manure slurry co-digested with 15 % dairy by-product. Black fibrous material/grains were observed floating on the surface. In one of the samples ($10\%_A$), there was also a clear lag phase, and the methane production started to pick up after 16 days. In the other sample ($10\%_B$), there was no lag phase, but the methane production increased steadily from the start (Figure 36). For the manure slurry co-digested with 10% dairy by-product, the methane concentrations plateaued at almost 80% at day 31 and 41, when study was concluded. Notably, the sample with the lag phase in methane production ($10\%_A$), reached a final 80% methane concentration. The bottom sludge was a bit fibrous, but less so than for the manure slurry was co-digested with a concentration of 15 % dairy by-product and no white dairy by-product was visible, indicating a higher degree of degradation (Table 15). The manure slurry co-digested

with 10% dairy by-product reached a maximum of approximately 40 ml/g of cumulative methane produced per waste VS added (Table 4).

The two samples of manure slurry co-digested with 5% dairy by-product were very similar at the start, with the methane production starting immediately for both samples. The methane production stopped faster than for the samples with concentrations of 10 or 15% dairy by-product. The samples reached methane concentrations of 75 and 82 % for sample $5\%_A$ and $5\%_B$ respectively, at day 12 and 22 respectively. For sample $5\%_A$ the methane production stopped by day 12. At day 22 the methane production in sample $5\%_B$ increased sharply. At day 41 there is another sharp increase, although not as much as at day 22. The methane concentration started to decrease at day 22, but the cumulative volume increased to day 41, when the study was concluded. It is therefore hard to tell the increase in volume would have continued. Even if the methane concentration was declining, it was still high on 76%.

The bottom sludge was black and looked like soil with no white or bigger particles visible, i.e., it appeared more degraded compared to the bottom sludge in the bottles containing manure slurry co-digested with 10 or 15% dairy by-product (Table 15). For the samples of manure slurry co-digested with 5% dairy by-product, the mean cumulative methane produced per waste VS added (61 ± 26 mg/L, Table 14) was higher than for the samples of the 0.5:1 (g VS) substrate to inoculum ratio (the same concentration of manure slurry) without added dairy by-product, (40 ± 10 ml/g, Table 10). The manure slurry samples co-digested with a concentration of 5% dairy by-product reached maximum cumulative methane production faster (27 ± 15 days, Table 14) than the manure slurry samples (of the 0.5:1 (g VS) substrate to inoculum ratio) without any added dairy by-product (38 ± 24 days, Table 10). Interestingly, the manure slurry samples with added 5% of dairy by-product produced more cumulative methane per waste VS (ml/g) and at a faster rate, than the samples of the same manure slurry concentration without any added dairy by-product.

When comparing the manure slurry samples without added dairy by-product to the manure slurry co-digested with 10% dairy by-product (mean cumulative methane produced per waste VS added 41 ± 2 mg/L and mean day of reaching maximum cumulative methane production of 41, Table 14), they are very similar, especially for the sample $10\%_A$ (without lag phase). For sample $10\%_B$ the maximum cumulative methane produced and the day the maximum concentration was reached is similar to the manure slurry co-digested with a concentration of 5% dairy by-product, but because of the lag phase of the manure slurry containing added dairy by-product, the rate of methane production is faster when it actually starts. Also, since the study was concluded on day 41 it is unclear if the maximum cumulative methane produced would have increased more, however the production seemed to have started to stagnate. When comparing the rates of methane production from the samples with the manure slurry co-digested with 15% dairy by-product, with their mean cumulative methane produced per waste VS added (18 ± 1 mg/L, Table 14) and mean day of reaching maximum cumulative methane production (41 days, Table 14), the delayed onset of methane production becomes very obvious, and the time needed to produce similar methane volumes would require longer time, if it at all would reach the same amounts. Because the study was concluded on day 41 it is not known what the maximum cumulative methane production would be, but the methane production appears to continue to be still increasing.

6.3. Implications of findings for treatment system on farm

The Organic Loading Rate (OLR) of the first pond is 0.130-0.144 kg VS/m3/d, which is within the range of 0.02–0.46 kg VS/m3/d suggested by Park and Craggs (2007) and Craggs et al. (2008) for unheated anaerobic ponds in a temperate climate like Aotearoa New Zealand, i.e., where the temperature conditions in the ponds vary between psychrophilic and mesophilic. The Hydraulic Retention Time (HRT) for the first pond (maximum pond volume 4 500 m3) is 158 - 175 days as compared to 343 days in a study by Heubeck and Craggs (2010). This indicates a rather short retention time in this study compared to a similar farm in Aotearoa New Zealand, especially considering the issues with oil and grease. In the study by Heubeck and Craggs (2010) there was no issues with oil and grease, which due to is lag phase might call for extra retention time. Also, the first pond is fed once a week, which averages a flow of 25.7 - 28.5 m3/day, as compared to an average flow of 21 m3/d reported by Heubeck and Craggs (2010). What has been mentioned above

suggests that a higher HRT is recommended for the pond receiving the manure slurry from the collection tank. One way to achieve this could be to reverse the order to where the manure slurry enters the ponds by pumping the manure slurry from the collection tank to the second and bigger of the ponds (maximum pond volume 10 244 m3). The OLR of this pond would be 0.06 kg VS/m3/d and the HRT would be 359 – 399 days. Lowering the organic loading rate and increasing the hydraulic retention time could mitigate the issue with the oil and grease induced build-up of a crust and following wash-out (Li C. et al., 2013.), although since the pond would still operate under psychrophilic conditions it is unclear with how much. From this study it was clear that methane was being produced in both ponds, suggesting a lot of organic material leaving the first pond undigested or only partly digested, which also supports the need of an increased retention time (compared to the existing retention time). Another reason for the volume of first pond to be insufficient might be that not all the theoretical volume in the pond is actually available because there might be considerable amounts of scum.

As observed in the bench-scale study of the co-digestion of 5% dairy by-product, the anaerobic digestion of the manure slurry with some dairy by-product ran smoothly under mesophilic conditions and even increase methane production and rate. As shown by the study of manure slurry co-digested with 15% dairy by-product, methane production occurred even with rather high concentrations of dairy by-product, although a long lag time was observed. However, the study was conducted as batch tests, where no new dairy by-product was added and under mesophilic conditions that most likely increase the rate of degradation of oil and grease; whereas the farm pond operates as a continuous system under psychrophilic conditions. It is therefore likely that the farm pond system could tolerate a lower concentration of dairy by-product than that observed in the laboratory study.

The concentration of oil and grease does not decrease much from the manure slurry to the digestate in the second pond, which suggests that much of the organic material is not degraded as it is trapped in the floating crust or washed out of the system. This indicates that the amount of oil and grease is too high for this type of treatment system and suggests that the additional dairy by-product presently disposed of directly to the pond should be disposed of in a different way.

The concentration and volume of methane produced at the farm is inconsistent, and hence to flare it is most likely the best option as compared to producing electricity and heat generation, which require a steady production to be economically viable (Costa et al., 2015, Jarvie, 2019).

7. Conclusions

From the seasonal study it could be seen that the concentrations of most parameters analysed in the manure slurry varied widely between sampling occasions, whereas the concentrations were more consistent in the two ponds. The only parameter that showed significant difference between summer and winter months was phosphate, which showed higher concentrations in manure slurry and lower concentration in digestate from the second pond during the summer than the winter months. A possible explanation for higher phosphate concentrations in manure slurry in summer is the use of phosphate rich dairy by-product in the pigs' feed during the summer months and also discarding of old dairy by-product directly into the tank at times during the same time period. For the digestate from the second pond, a possible explanation for the lower concentration of phosphate in summer could be struvite formation during the warmer months. The mean methane concentration from the ponds found in this study was rather low, whereas the mean hydrogen sulphide concentration was high, compared to other studies. In this study the two ponds had similar methane concentrations, but in a different pattern and within a wide range. This indicates much of the degradation is taking place in the second pond and this could be due to wash-out of un-degraded organic material floating on the top of the first pond.

The laboratory experiments investigating two different ratios of manure slurry showed that the methane concentration and cumulative methane produced varied more between samples for manure slurry of the inoculum ratio 1:1 (g VS) solution than for the 0.5:1 solution, probably due to higher heterogeneity of the material. The mean methane potential was higher for the first pond digestate than for both the manure slurry ratios. Also, the time to reach the maximum cumulative methane produced was shorter for the first pond digestate than for both the manure slurry ratios. This increased rate could be because the digestate in the first pond was more degraded, with finer particles and more surface area, and hence more accessible to the microorganisms. In general, the methane concentration and cumulative methane produced varied largely between tests, which may be due to the heterogeneity in the material.

The laboratory experiments of co-digestion of manure slurry and three different concentrations of dairy by-product showed a longer lag phase for methane production, more build-up of crust and less degradation of organic material for higher concentrations of dairy by-product. The overarching conclusion of the study is that there are indications of overload issues in the waste system. One way to address this could be to increase hydraulic retention time. This can be achieved by reversing the flow order of the ponds, i.e., to make the larger second pond as the first pond and the smaller first pond as the second pond. Furthermore, leftover dairy by-product should be discarded elsewhere in order to lower the risk of wash-out of un-degraded organic material and irregular methane production.

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Appendix A – Ethics approval

UNIVERSITY OF CANTERBURY
Te Whare Wānanga o Waitaha
CHRISTCHURCH NEW ZEALAND

HUMAN ETHICS COMMITTEE
Secretary, Rebecca Robinson
Telephone: +64 03 369 4588, Extn 94588
Email: human-ethics@canterbury.ac.nz

Ref: HEC 2019/13/LR-PS

6 June 2019

Anna Nilsson
Civil and Natural Resources Engineering
UNIVERSITY OF CANTERBURY

Dear Anna

Thank you for submitting your low risk application to the Human Ethics Committee for the research proposal titled "Biogas and Phosphorous Recovery".

I am pleased to advise that this application has been reviewed and approved.

Please note that this approval is subject to the incorporation of the amendments you have provided in your email of 29th May 2019.

With best wishes for your project.

Yours sincerely

Dr Dean Sutherland
Chair, Human Ethics Committee

Appendix B – Safety measures taken during field work/laboratory work

Table B1 lists possible safety hazards and strategies to mitigate them.

Table B1. Safety hazards and mitigation strategies.

Hazard	**Mitigation strategy**
Pathogenic infection from handling animal waste.	Use proper personal protective equipment (PPE): wear gloves, dust mask. Always wash gear, tools and hands after use/handling. Clean surfaces with a bleach solution.
Infection of hepatitis from handling animal waste.	Student is vaccinated for hepatitis.
Collecting samples at site.	A safety harness is used if there is a risk to slip and fall into a tank/pond. Gumboots and overalls are used to avoid contamination. When collecting samples there is always two people present, so one could call for help if needed.
Driving to collection site.	Caution is taken when driving to and from site and traffic regulations, such as speed limits, are followed.
Hazardous chemicals and other substances.	The student has attained the lab work safety introduction by lab staff. Read the Material Safety Data Sheet (MSDS) and handle the substance with the appropriate care and be aware of the location of safety and treatment equipment such as eye wash station. Wear appropriate personal protective equipment (PPE) depending on substance, such as lab coat, gloves and dust mask. Use of fume hood when appropriate.
Flammable and explosive gases.	The student has attained the lab work safety introduction by lab staff. Read the Material Safety Data Sheet (MSDS) and handle the substance with the appropriate care and be aware of the location of safety and treatment equipment such as fire extinguishers and fire blankets. Wear appropriate personal protective equipment (PPE) depending on substance, such as lab coat, gloves and dust mask. Use of fume hood when appropriate.
Slipping and falling in the lab or on site.	Maintain situational awareness of your environment at all times.

Appendix C – Summary of information about the farm

In Table C1 is a summary of the most important information about the farm included in this study and its ponds.

Table C1. Summary table on farm characteristics.

Descriptor	Farm
Location	50 km North West of Christchurch, Canterbury region, South Island.
Production	479 sows, boars and gilts, 1,140 weaners and about 570 each of porkers, growers and finishers. 3,500 Standard Pig Units (SPU) in all.
Housing	Indoor.
Manure type and management up till anaerobic pond	Slurry, effluent from each shed stored for different amount of weeks, then sluiced to central tank and thereafter pumped to covered pond.
Frequency of feeding the anaerobic pond	Once a week.
Feedstock	Pig effluent, periodically small amounts dairy by-product from cleaning out storage tanks/spoiled product.
Volume of effluent	180 - 200 m^3/week.
Drinking water	Treated and from the county domestic supply.
Wash down water	Untreated river water.
Covered first pond surface area	1,500 m^2
Covered first pond bottom area	300 m^2
Covered first pond – depth, surface length and width	D = 5 m, L = 50 m, W = 30 m
Covered first pond – bottom length and width	L = 30 m, W = 10 m
Maximum covered first pond volume	4,500 m^3
Lining and cover material	Bottom lining: high density polyethylene (HDPE). Cover material: low density polyethylene (LLDPE).
Covered second pond – depth, surface length and width	D = 5.5 m, L = 50 m, W = 50 m Digestate level varies between 0.5 – 2 m
Covered second pond – bottom length and width	L = 35 m, W = 35 m
Lining material	Bottom: high density polyethylene (HDPE)
Covered second pond surface area	2,500 m^2
Covered second pond bottom area	1,225 m^2
Maximum covered second pond volume	10,244 m^3
Covered second pond used volume	931 – 3,725 m^3
Biogas collection	Ring pipeline under cover
Placement of inlet and outlet pipes	Inlet: Through the sludge port at the very bottom of the pond diagonally from the outlet, pipe diameter 150 mm Outlet: 1 m below surface, in-line double T, pipe diameter 150 mm
Biogas disposal	Flared

Appendix D – Characteristics and events when sampling

In Table D1 is a summary of characteristics and events noted on or in close proximity to sampling.

Table D1. Summary table of characteristics and events when sampling

Month	Manure slurry tank	1st pond	2nd pond	Flare
Aug	Manure slurry added from tanker at sampling = much movement and manure slurry in tank	Hard crust about 30-50 cm		Gas collecting pipes open 45 min while valves installed in end caps. Flared turned off, gas readings taken two hours later
Sep	No transfer of slurry			
Oct	Manure slurry added from tanker at sampling, i.e., much movement and manure slurry in tank			
Nov	No transfer of slurry			On 24 hours a day, off two hours before reading
Dec	No transfer of slurry	Farmer tried to stir pond with pump just before sampling without success. Crust felt softer but thicker, about one meter	Digestate thicker, maybe disturbances from tanker pumping up digestate disturbing the settled particles on pond bottom	On 24 hours a day, but turned off previous afternoon
Jan	No transfer of slurry, very low level in tank	Hard crust on top		Turned off previous afternoon, blows out every five days. If left off one day works again
Feb	Level relatively low. DAF poured into tank five days prior to sampling. Strong odour of rancid fat. DAF floating on top, a lot of particles/chunks/foam of white. Colour of slurry white/greyish. Greasy feeling to everything it touched			Turned off previous afternoon
Mar	Tank almost empty, manure slurry thick and lumpy. DAF still visible			Turned off previous afternoon
Apr	Full tank. Weaner shed emptied into tank three days before sampling			Turned off previous afternoon
May	No transfer of slurry. Full tank. No DAF in feed for two weeks. Two weeks previously water to flush pipes after emptying tank into 1st pond left on overnight instead of the usual couple of hours	Thick, but soft crust, about 85 cm thick		Turned off previous afternoon

Appendix E – Measured methane and carbon dioxide concentrations in blanks and controls

In the tables below, the methane and carbon dioxide concentrations in blanks and controls for the methane potential studies of manure slurry, first pond digestate and manure slurry co-digested with dairy by-product are shown, see Tables E1, E2 and E3.

Table E1. Methane and carbon dioxide concentrations in blanks and controls for the methane potential studies of manure slurry

Date	$Blank_1$		$Blank_2$		$Control_1$		$Control_2$	
	CH_4 (%)	CO_2 (%)	CH_4 (%)	CO_2 (%)	CH_4 (%)	CO_2 (%)	CH_4 (%)	CO_2 (%)
8/4/21	0	0	0	0	0	0	0	0
8/5/21	13.8	6.9	14.5	14	15.1	17.8	13.7	8
8/6/21	18.4	11.2	14.1	9.5	20.1	28.7	26.7	44.7
8/7/21	20.8	11.5	14.4	9.7	29	69.1	29.3	69.2
8/8/21	23.2	11.9	14.8	9.8	31.2	74.5	31.3	74.3
8/9/21	27.3	12.4	14.9	10	33.8	72.9	34.1	72.3
8/10/21	29.6	12.9	15.3	10.1	37.1	70.2	37.7	69.3
8/11/21	31.3	13	15.6	10.1	40.4	66.2	41.3	65.3
8/12/21	30.7	12.6	15.7	10.2	43.8	61.9	44.5	61.1
8/13/21	33.8	13.8	15.9	10.2	47.9	57.5	47.7	57.5
8/16/21	36.4	14.6	16.2	10.2	63.6	44	63.4	45.6
8/24/21	39.4	15.7	15.9	10.3	74	29.5	77.4	30
8/30/21	40	16.1	14.4	10.3	70.1	27	78.5	27.7
9/2/21	38.6	16.4	18.4	7.8	n/a	n/a	n/a	n/a

Table E2. Methane and carbon dioxide concentrations in blanks and controls for the methane potential studies of first pond digestate

Date	Blank 1		Blank 2		Control 1		Control 2	
	CH_4 (%)	CO_2 (%)	CH_4 (%)	CO_2 (%)	CH_4 (%)	CO_2 (%)	CH_4 (%)	CO_2 (%)
6/08/21	0	0	0	0	0	0	0	0
7/08/21	0	6.5	0	6.2	18.5	11.5	19.1	15.4
8/08/21	14.2	7.1	0	6.7	0	6.7	30.5	33.3
9/08/21	14.9	7.3	14.2	6.8	44.3	43.2	41.8	44.7
10/08/21	14.6	7.3	13.8	6.9	50	45.4	48.2	47.1
11/08/21	14.4	7.3	14.2	6.9	56	42.8	46.5	6.9
12/08/21	14.7	7.4	14.3	7	61.2	40.6	54.5	44
13/08/21	14.8	7.5	14.2	7	56	41.2	59.2	42.2
16/08/21	14.1	7.1	14.4	7.1	49.9	37.7	64.7	36.9
24/08/21	0	7.3	0	7.7	33.9	27.7	52.3	37.1
30/08/21	0	7.1	0	8.5	17.5	18.2	51.5	41.8
2/09/21	13.8	7.9	0	9.4	15.3	13.5	35.3	31.6

Table E3. Methane and carbon dioxide concentrations in blanks and controls for the methane potential studies of manure slurry co-digested with dairy by-product

Date	$Blank_A$		$Blank_B$		$Control_A$		$Control_B$	
	CH_4 (%)	CO_2 (%)	CH_4 (%)	CO_2 (%)	CH_4 (%)	CO_2 (%)	CH_4 (%)	CO_2 (%)
18/10/21	0	0	0	0	0	0	0	0
19/10/21	14.1	8.7	14.2	8.8	14.6	12	14.6	11.9
20/10/21	14.2	9.1	14.3	9.1	27.8	47.7	16.6	17.1
21/10/21	14.3	9.3	14.2	9.2	31	69	30.7	68.2
22/10/21	14.1	9.3	14.4	9.3	33.1	71.5	33.1	70.2
23/10/21	14.4	9.5	14.5	9.4	36.4	68.3	35.7	67.8
24/10/21	14.4	9.5	15.4	12.4	39.1	64.3	38.2	63.8
25/10/21	14.6	9.6	14.3	9.4	42.9	60.4	41.7	60.1
26/10/21	14.6	9.5	14.6	9.4	47.1	56.9	45.3	57
27/10/21	14.8	9.5	14.4	9.4	52.3	52.5	48.7	52.9
28/10/21	14.8	9.5	14.4	9.4	58	48.7	52.9	49.4
29/10/21	14.8	9.5	14.4	9.4	62.3	44.6	57.7	45.6
30/10/21	16.3	9.7	14.4	9.4	66.5	40.3	62.8	42.6
31/10/21	15	9.4	14.4	9.3	66.9	36.8	65.3	38.9
3/11/21	14.9	9.4	14.3	9.3	70	32.3	73.7	34.6
6/11/21	15.2	9.3	14.3	9	69.5	29.9	73.9	32
9/11/21	15.1	9.3	14.3	9.2	56.7	27.1	74.3	30.2
12/11/21	15.2	9.2	14.3	9.3	48.4	28	74.2	28.2
15/11/21	15	9.2	14.2	9.2	39.6	26.7	74.7	27.3
18/11/21	15.2	9.2	14.2	9.2	32.9	24.8	75.8	26.5
21/11/21	15	9.2	14	9.1	27.9	23.1	74.4	25.3
24/11/21	14.6	8.9	13.7	8.8	22.4	21.3	75	24.4
28/11/21	14.5	9.4	13.6	9	20.6	20.6	76.1	23.9