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Since a number of decades the Netherlands faces manure surpluses, because the amount of phosphate produced in animal manure is larger than the amount that can be applied on agricultural land according to the application limits. This surplus needs to be exported from the Dutch agricultural sector. The costs of manure export are however high, and therefore new, simple and cheap innovative techniques are needed to recover phosphate from fresh or digested manure (digestate). The relative small amount of concentrated recovered P can be transported more economically for use outside the Netherlands or can be utilized as secondary P resource for industries, e.g. for the production of fertiliser. We report laboratory and pilot experiments that were carried out in search for cheap and innovative techniques of phosphorus recovery. The main goal of the experiments was to reduce the P-content in pig slurry or digested pig slurry by 25% to 75%. If this goal can be reached with -recovery, in principle all manure including its valuable components (organic matter and other nutrients) can be applied sustainably on agricultural land in The Netherlands. The results show that both on laboratory scale and pilot scale 25-75% of P can be technically recovered with the so called 'acid-base approach'. From a sustainability point of view the impact is positives in terms of energy savings, CO_2-savings, phosphorus savings and also nitrogen savings. The economical perspective is also positive but will strongly depend on the disposal prices of treated pig slurry with a reduced P content and its value as substitute for mineral N fertiliser and value in terms of organic soil improver on the manure market.

Keywords: phosphate, manure, digestate, intensive livestock production, phosphate recovery, pig slurry, manure treatment, manure separation.

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Preface

This project was funded by the Dutch Farmers organisation ‘Land- en Tuinbouw Organisatie Nederland’ (LTO) and the Dutch Ministry of Economic Affairs. It is one of the projects within the ‘Topsector agreement’ between the government and the private sector called ‘Meerwaarde Mest en Mineralen (Added value Manure and Minerals)’ (project numbers AF12178 and 16137b).

New innovative approaches are needed to close the phosphorus (P) cycle in The Netherlands because the agricultural sector currently produces about 25% more P, in the form of manure, than can be applied on land. One promising solution to deal with the surplus amount of P in manure is to recover the surplus of P in the form of a mineral P product for use as a P fertiliser (for export) or as a raw P feedstock for the P fertiliser industries. This idea for ‘closing the manure P cycle in The Netherlands’ has been circulating for a while, but was never thought well over until in 2013 a Public Private Partnership (PPP) was set up with the Dutch Farmers Organisation LTO and the Ministry of Economic Affairs to investigate this option seriously. The first step of the Public Private Partnership study was to set up simple laboratory experiments to explore the technical opportunities of P recovery and was published by Schoumans et al. (2014). This study gave the ‘proof of principle’, that P can be recovered from both the liquid fraction and the solid fraction of animal manure. Therefore, as a next step, a second study was proposed including both laboratory experiments with manure samples of varying origin, and pilot plant experiments. The results of this second study are presented in this report.

Besides funding from the public-private sector collaboration, additional funding from the province of Gelderland was used to construct the pilot installation at Groot-Zevert Vergisting in Beltrum. Groot-Zevert Vergisting has put a lot of effort in the project and was responsible for the realisation and operational functioning of the pilot installation. The pilot installation, which was built by Wilba Techniek, was used to test the practical applicability of the developed technologies.

The research was carried out between 2014 and 2017 by Wageningen Environmental Research (Alterra) with support of the Soil Quality Laboratory (CBLB).

The focus of this report is to document the laboratory and pilot experiments and, to evaluate their perspectives in terms of cost and environmental benefits.

The authors

Summary

In the Netherlands, the intensive husbandry produces large amount of manure, which can only be partly applied on agricultural land due to restrictions on phosphate and nitrogen applications standards. Farmers with a phosphate surplus have to export a part of that surplus to regions outside the Netherlands. The costs of manure export are however high, and therefore new, simple and cheap but innovative techniques are needed to recover phosphate from fresh or digested manure (digestate).

The main focus of this research report is to evaluate technical opportunities for a cost-efficient approach to reduce the P content of manure or digested manure, and to recover P in the form of a mineral product which can be exported or used as secondary resource for P requiring industries. In this study both laboratory and pilot experiments were carried out. In the laboratory, a set of samples of manure and digestate were analysed to determine the range in P-release and P-recovery. Pilots studies were set up to explore the practical applicability of the technique. Based on this information the business options and agronomical and environmental aspects were evaluated.

Two approaches of P recovery techniques were studied. One approach concerned the liquid fraction of slurries obtained after low tech separation (the 'Mg-approach'). Herewith, the liquid fraction was treated by addition of magnesium chloride in order to form magnesium phosphate minerals like struvite. In the other approach, the solid fraction obtained after high tech separation of manure/digestate was treated with sulphuric acid after which the acidified digestate was separated into a P-poor solid and P-rich liquid fraction. Next, P was precipitated from the liquid fraction through addition of calcium hydroxide (acid-base approach).

The Mg-approach turned out to be unsuccessful because the produced struvite crystals in the low-tech separated solution were too small to separate them from the other particles in the suspension. Different approaches to increase the crystal size were not effective.

With the acid-base approach it was possible to recover high amounts of P from the solid fraction of manure or digestate. The solid fraction was obtained after high tech separation (e.g. centrifugation) and contained 83 (± 6)% and 78 (±14)% of the P in the ingoing P of pig slurry or digestate, respectively. For pig slurry about 99 (± 5)% of the P in the solid fraction was released upon acidification until pH 5. For digestate this number was slightly lower (74 (± 20)%). For pig slurry about 76 (± 42)% of the released P was recovered as calcium phosphate upon addition of calcium hydroxide while for digestate this percentage was lower (36 (± 29)%). The residual amount of P remains within the supernatant and is therefore not to be lost because it is planned to recirculate the supernatant flow in the future P recovery installation.

The acid-base approach was further tested in a pilot-scale installation at Groot Zevert Vergisting (Beltrum, The Netherlands). The pilot tests were conducted with solid fraction of digestate obtained after low-tech separation technique (*i.e.* screw press). Using a two-step acidification approach, about 75% of the ingoing P of the solid fraction was released. About 90% of the released P was subsequently recovered as Ca~P product after addition of lime. The Ca~P product was dried at low temperatures and grinded. Thereafter, the composition and agronomical value of the product was determined. The dry matter and P_2O_5 content were resp. 82% and 14% and different P extractions indicated that the availability of P is comparable to that of chemical P fertilisers. The S content was still rather low because the extractions were performed with groundwater meaning that there was no accumulation of salts. To reduce the water consumption, it is planned to recirculate the water within the P stripper which may lead to accumulation of salts. The P-stripper is called Re-P-eat ('**Re**covery of **P** to **eat**' ensuring food production by recycling P because of the finite natural P resources).

Besides the technical performance also the economic aspects were evaluated. The costs of chemicals for maximal P recovery are about € 4.50 per ton solid fraction of digested pig slurry, which equals to about € 1.40 per ton digested pig slurry. Taking into account the investments, depreciation, maintenance, chemicals and management, the annual cost are estimated at about 270 k€ for the treatment of 100 000 ton digested pig slurry. The main uncertainty is the price of disposal of treated (digested) pig slurry with the reduced P content in the nearby region; in particularly, the price to be paid to arable farmers. The use of P-reduced digestate has advantages for the arable farms since less mineral N-fertilisers have to be bought and more organic matter can be applied. This can help to maintain the organic matter content of arable land and can reduce the costs of mineral fertilizers with hundreds of euros per hectare. This should have impact on the acceptance of this type of P poor slurry or on P poor solid fraction, and consequently on the prices on the manure market. However in which way and how much is difficult to predict.

Finally the sustainability and environmental aspects were evaluated. The overall energy requirement of the P-recovery scenario are 10% lower compared to the reference scenario in which unprocessed digestate is exported. For each large scale digester (100 000 ton of pig slurry), 1.2 TJ of energy can be saved each year by implementation of the P-recovery method compared to the current practice of manure export. If the Dutch P-surplus is to be lowered with 50%, about 5 Mton pig slurry has to be treated (in 50 plants like Groot Zevert Vergisting). In that situation about 10 Mton P_2O_5 will be recovered per year as Ca~P that can be used as substitute for rock phosphate and the energy savings will be 60 TJ per year (50 plants of 1.2 TJ per plant per year). The CO_2-savings due to extra organic matter accumulation in Dutch soils will be approx. 360 kton CO_2 per year. Furthermore, each year 1.2 kton N (Neff 80% and N content of 7.1 kg N/ton) can be utilised as replacement for mineral fertiliser. This will give an additional energy saving of 58 TJ each year.

This study shows that the technical performance to recover P as calcium phosphate from manure or digestate, compared to recover P as struvite, is good. The treated organic material with a lower P-content can be applied to arable land as soil conditioner in relative high amount compared to the solid fraction of non-treated manure or digestate. In addition, it will reduce the use (costs) of mineral N-fertiliser remarkably. However, it is unclear how this will influence the prices on the manure market. From an sustainability and environmental point of view, P recovery has benefits because it reduces the number of transport movements compared to the situation in which the excess amount of P is exported in the form of manure.

1 Introduction

The intensification of the husbandry in the Netherlands has contributed to the increase of food production. After WW II, the livestock numbers have increased substantially in the Netherlands up to 10 million cows, 14 million pigs and 95 million poultry in 1990. Although livestock numbers (cows, pigs) have somewhat declined (about 10-20%) during the last decade due to restrictions on production of milk and number of animals (production rights), the agricultural P balance of the Netherlands over the last decade is still positive (Table 1.1; Smit et al. (2015)). In 2005, about 70% of the total amount of imported P was used by agriculture as feed and fertiliser. Since then, the use of mineral P fertiliser has strongly decreased (Table 1.1). In more recent years (2012-2014), the P input to agriculture was dominantly caused by the use of P in feed (90%) with only a minor contribution of P-fertilisers (6%) and other products (4%)[1]. On average (years 2005, 2008 and 2011), 46% of the total P import is exported as products, and consequently, 54% of the imported P remains in the Netherlands mainly as manure and waste from municipals and industries.

Table 1.1 *National P balance of the Netherlands in 2005, 2008 and 2011 (data Smit et al., 2015).*

		2005	2008	2011
		(million kg P y^{-1})		
Import				
	Feed & additives	57.6	68.2	67.1
	Fertiliser	21.0	12.0	7.0
	Food	28.0	31.1	32.9
	other	1.6	3.5	3.6
	Total	108.2	114.8	110.6
Export				
	Food	37.5	47.6	49.2
	Non-Food	1.3	1.2	1.3
	Manure	7.0	12.8	16.0
	Waste	2.7	2.0	2.4
	Total	48.5	63.6	68.9
Balance		59.7	51.2	41.7

Table 1.2 shows the Dutch agricultural P balance in the period 1970-2013. Since 1995, the P surplus has fallen sharply (Table 1.2) for three reasons: (1) less use of mineral fertilisers, (2) a reduction of the P content in animal feed, mainly achieved by adding phytase to feed to increase the digestibility of the P in the feed, and (3) an increase in the export of manure. Before the mid-1980s, most of the produced manure was applied on agricultural land. Since 1987, the Manure Act has restricted the maximum amount of P that can be applied to agricultural land in order to reduce the P accumulation in soils and subsequent P losses to surface waters.

The Dutch agricultural sector produces about 75 million kg P per year in de form of animal manure of which 25% cannot be applied in the Netherlands because of P application limits for agricultural land (Koeijer et al. 2012). This percentage can increase if the P application limits for agricultural land would become more strict in an attempt to meet the objectives of the Water Framework Directive (EEC 2000). An increase in the production of manure-P is not expected because the number of pigs and poultry are already controlled by animal rights and from 2017 onwards, the P-production of the dairy sector will also be controlled based on the maximum allowable P production and animal numbers.

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[1] http://www.clo.nl/indicatoren/nl0095-balans-van-fosfor

Table 1.2 *The agricultural soil P balance (million kg P) of the Netherlands (Source CBS-statline, 2014).*

Million kg P	1970	1986	1990	1995	2000	2005	2010	2013
IN								
Manure	60	113	99	89	76	67	62	55
Fertiliser	47	36	33	27	27	21	13	5
Other	4	8	8	5	5	5	3	4
Total	111	157	140	121	108	93	78	64
OUT								
Harvest	26	65	65	57	60	55	54	54
Accumulation	85	92	75	64	48	38	24	10

A market oriented approach and co-operation with stakeholder industries is needed to develop cost-effective approaches for the treatment and disposal of the excess amount of manure in The Netherlands. Such an approach should guarantee that manure is processed into mineral P products and P-reduced organic products against a compatible price (SCOPE 2014; Schoumans et al. 2010; Schoumans et al. 2015). Since 25% of the total-P production in terms of manure cannot be applied on land due to restrictions in P application standards, a possible approach would be to lower the P-content of all manure by at least 25% or achieve higher recovery in a part of the manure. After lowering the P-content of the manure, more manure can be applied on agricultural land within the application limits in The Netherlands. An advantage of this approach is that farmers can apply more organic matter on arable land which has a beneficial effect on soil quality and soil carbon stocks. The recovered mineral P can be exported as a fertiliser or can be used a raw material for the production of high-grade mineral P fertilisers by the P fertiliser industry. Therefore, this project was initiated in order to evaluate the practical, technical and economic feasibility of P-recovery from manure.

This report focusses on recovery of P from (digested) pig slurry, because pig slurry has a relatively high P content and a low N/P ratio meaning that its composition is unfavourable compared to e.g. dairy slurry which has a lower P content and higher N/P ratio. As a consequence, most of the produced dairy slurry can be applied within the Netherlands whereas most of the pig slurry has to be exported (with our without treatment). Moreover, the composition of pig slurry is favourable for P-recovery because of the rather high P content of pig slurry (3-4 kg P_2O_5 per ton) and because this P is mostly present in inorganic form (Gerritse and Vriesema 1984; Brod et al. 2015; Ajiboye et al. 2007).

Manure separation is an upcoming technique in manure treatment facilities and is used to separate manure into a solid and a liquid fraction. Mostly, the solid fraction is rich in organic matter and has a high P content whereas the liquid fraction contains most of the N and K (Schoumans et al. 2010; Velthof 2015). However, the distribution of nutrients over the solid and liquid fraction strongly depends on the type of separator used (Schröder et al. 2009). Using a low-tech separator (e.g. sieve press), a relatively large fraction of P and organic matter are present in the liquid fraction. In contrast, using a high-tech separator (e.g. decanter), most of the P and organic matter are present in the solid fraction leaving a liquid with a rather low P content. The liquid fraction still contains too much nutrients for disposal to a waste water treatment plant or direct discharge to surface waters. Therefore, reversed osmoses is often used to process the liquid fraction into a concentrated NK-solution (mineral concentrate) and a cleaned water fraction (permeate) which can be discharged to surface water (Velthof 2015). The currently applied ‘best practice’ of manure treatment is to use a high-tech separator and to export the solid fraction, which is rich in organic matter and P, meaning that P is exported in a more concentrated product compared to the untreated manure. However, this practice has two major disadvantages: Firstly, despite the high concentration of P in the solid fraction, large volumes of manure need to be transported over long distances (500 km or longer) which is associated with high costs and a high CO_2 impact. Secondly, due to the export of the solid fraction, large amounts of organic matter are exported whereas organic matter is a valuable component and Dutch farmers want to keep and apply this organic matter on their own (arable) soils.

The main focus of this research is to evaluate options for a cost-efficient approach to reduce the P content of manure with at least 25% and to recover P in the form of a mineral product which can be exported or used as secondary resource for P requiring industries. Although experimental results exist on P-recovery from wastes like sewage sludge, information on P-removal from animal manure is limited. The first step of the Public Private Partnership study was to set up simple laboratory experiments to explore the technical opportunities of P recovery and was published by Schoumans et al. (2014). This study gave the ‘proof of principle’, that P can be recovered from both the liquid fraction and the solid fraction. Therefore, as a next step, a second study was proposed including both laboratory experiments with manure samples of varying origin, and pilot plant experiments. The focus is on technical opportunities for P-removal from animal manure, and mainly on pig slurry and co-digested pig slurry. In this report often the term manure or pig slurry is used and refers to both forms.

The specific objectives of this study were:

- To determine the practical feasibility of P recovery from the liquid fraction of pig slurry or digestate obtained after low-tech mechanical separation. P will be recovered by adding magnesium hydroxide followed by removal of precipitated P as magnesium phosphate (e.g. struvite).
- To determine the practical feasibility of P recovery from the solid fraction of pig manure or digestate obtained after high-tech mechanical separation. The process includes an acidification step for P extraction followed by mechanical separation and recovery of P from the P rich solution by addition of calcium hydroxide.
- To retrieve practical information from the implementation of both techniques.
- To evaluate the economical- and environmental aspects of the proposed techniques.

2 Design, materials and methods

In this chapter the principles and experimental design of both the laboratory and pilot study regarding the P recovery from the liquid fraction and the solid fraction are described in detail.

2.1 Principles and experimental design

2.1.1 P-recovery from the liquid fraction of manure using the 'Mg-approach'

The first part of this project focusses on the possibilities to recover P from the liquid fraction of manure (including digestate[2]) through the addition of magnesium hydroxide and subsequent recovery of P in the form of Mg~P minerals (*e.g.* struvite). In this study this is defined as the 'Mg-approach' and is in line with the proof of principle described by Schoumans et al. (2014). For this approach (Figure 2.1), manure needs to be separated into a solid and a liquid fraction using low-tech separation techniques (*e.g.* filtration). Low-tech separation techniques generate a liquid fraction with a relative high P content due to the presence of dissolved orthophosphate[3] ($H_xPO_4^{(3-x)}$) and suspended particles. For pig slurry, these suspended particles are thought to consist mainly of inorganic P forms, since the majority (>80%) of P in pig slurry is present as inorganic P (Gerritse and Vriesema 1984). The dissolved P might be recovered from the liquid fraction after addition of $Mg(OH)_2$ due to precipitation of struvite. In addition, colloidal / suspended particles (containing P) might also flocculate. Next, the precipitated P and flocculated P can be recovered from the liquid fraction by mechanical separation (Schoumans et al. 2014). The advantage of the Mg-approach (See Figure 2.1) compared to the Acid-Base approach (see also section 2.1.3) studied and described by Schoumans et al. (2014), is that low-tech separation techniques can be used and no acid needs to be added to the manure (less costs). A possible disadvantage could be that P-recovery is lower, and/or that the product is of lower quality due to the presence of organic matter, which makes the precipitate less attractive for use as secondary P resource for P-fertiliser industries. Figure 2.1 gives a schematic presentation of this method.

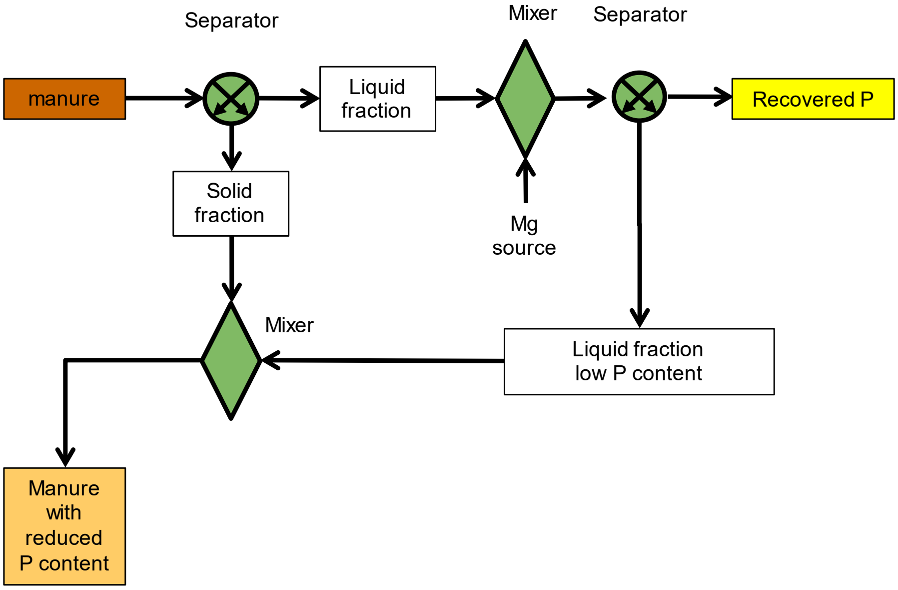

Figure 2.1 *Schematic representation of the concept of P-recovery from the liquid fraction of low-tech separated pig slurry.*

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[2] Digestate in the Netherlands results dominantly from co-digestion of manure with co-digestion feedstock. The Fertiliser Act requires that at least 50% manure is used.

[3] Orthophosphate: PO_4^{3-} and/or its dissociation products.

The amount of P recovered using the Mg-approach strongly depends on the extent to which the Mg dosage leads to the formation of large crystals which can be separated from the liquid manure. As such, it is important to understand the underlying chemical precipitation processes. Mineral P particles can be formed and recovered from the liquid fraction via three pathways:

I. Precipitation of the dissolved orthophosphate in the form of struvite induced by an increase in pH and addition of Mg^{2+}.
II. Dissolution of mineral P particles (calcium phosphates) followed by the precipitation of P in the form of struvite.
III. Coagulation and flocculation of colloidal P particles due to the increased Mg activity.

The extent to which P is recovered in the form of struvite depends on the concentration of dissolved P (pathway I) and/or the tendency of mineral P particles to dissolve and re-precipitate (pathway II). Pathway I and II are also strongly dependent on the pH and the Mg^{2+} activity of the liquid fraction, because often sufficient NH_4^+ and K^+ is available in the liquid fraction. Increasing the pH (>8) and adding Mg^{2+} stimulates precipitation of soluble phosphate as magnesium ammonium phosphate (MAP, NH_4-struvite or just called struvite), magnesium potassium phosphate (K-struvite), and/or magnesium hydrogen phosphate. The latter product is easily soluble as soon as the conditions change. In pathway III, only the flocculation and separation of colloidal P is improved whereas the chemical identity of the P particles remains unchanged.

Since struvite is able to form rather large crystals, formation of struvite is preferred over other minerals such as magnesium- or calcium phosphates which have a much lower tendency to form large crystals. For this reason, magnesium hydroxide is used rather than calcium hydroxide. The pH is an important factor determining which products will be formed (Lindsay et al. 1989; Greaves et al. 1999; Le Corre et al. 2009). The following reactions may occur:

1. Magnesium ammonium phosphate (MAP): NH_4-struvite ($8.5 < pH < 9.5$[4]):

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O + H^+$$

2. Magnesium potassium phosphate: K-struvite ($9 < pH < 10.5$):

$$Mg^{2+} + K^+ + HPO_4^{2-} + 6H_2O \rightarrow MgKPO_4.6H_2O + H^+$$

3. Magnesium hydrogen phosphate ($pH < 8.5$):

$$Mg^{2+} + HPO_4^{2-} + 6H_2O \rightarrow MgHPO_4.6H_2O$$

The struvite crystallisation process can be divided into nucleation (the formation of the first precipitates in small nuclei), and then crystal growth. The nucleation takes place almost instantaneously, provided that the conditions of pH and molar ratio of constituent ions, NH_4, Mg, $H_x(PO_4)^{(3-x)}$ in solution are met (N:P:Mg=1:1:1). According to thermodynamics, smaller struvite crystals are supposed to dissolve in favour of the growth of larger crystals with time (i.e. Ostwald ripening mechanism (Delgado-López et al. 2014; Fang et al. 2016)). Formation of struvite has been studied intensively in communal and industrial waste water. Not only struvite but other minerals co-precipitate as well (Lind et al. 2000; Van Rensburg et al. 2003; Ekama et al. 2006; Ganrot et al. 2007; De Graaff 2010; Wu and Zhou 2012). Examples from literature on animal slurries refer often to laboratory experiments (Szogi and Vanotti 2009; Shen et al. 2012; Wahal et al. 2011; Wendler Fernandes et al. 2012; Shepherd, Burns, et al. 2009b). Westerman et al. (2010) present encouraging results on struvite formation in digestate from swine slurry with a continuous flow bed crystallizer (65% P recovery at a cost of $0.0146/kg of live weight pig slaughter). Also Jordaan et al. (2010) show good results with liquid fractions of animal slurries after filtration or centrifuging.

Schoumans et al. (2014) studied the impact of pH (pH 8 and 9.5) and Mg-source ($Mg(OH)_2$, $MgCl_2$ or MgO) on the P-recovery from the liquid fraction of pig slurry or digestate. They concluded that the effects of different pH-values and Mg-sources on phosphorus recovery were small and suggested to study Mg~P formation and recovery without further adjusting the pH (pH approximately 8).

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[4] Indicative. Ranges of pH follow Colsen (2002). Optimal pH range depends on the composition of the matrix from which struvite is precipitated.

Furthermore, they found that Mg addition stimulates flocculation and facilitates the separation of solids from liquid fraction, but that the produced P deposit still contained large amounts of organic matter. From these first experiments, as a proof of principle, it was concluded that substantial amounts of P as Mg~P precipitate could be recovered, but that the precipitated P could not be separated from the organic rich colloids. In order to recover at least 25% of the P from the manure this approach seems to be successful.

In order to evaluate the options of the Mg-approach to recover P, two main experiments have been carried out:

- Laboratory experiments with several types of (digested) pig slurry (see section 2.2.3).
- Chemical analysis of samples from a pilot installation for P recovery at a manure digestion plant (see section 2.3).

2.1.2 P-recovery from the solid fraction of manure ('acid-base approach')

The pH of pig slurries and digestates usually varies between 7 and 8. The phosphates are largely associated with precipitates of calcium as dicalcium phosphate, or with ammonium and magnesium as struvite (Bril and Salomons 1990). Therefore, a large part of the available phosphate minerals in manure or manure fractions can be released by lowering the pH (Forbes et al. 2008; Masse et al. 2008; Makara and Z. 2015; Schoumans et al. 2014). Also phosphorus bound in organic matter may be released by hydrolysis by reducing the pH (Chen et al. 2007; Pagliari and Laboski 2012). Phosphorus that has been released (as $H_2PO_4^-$, HPO_4^{2-} and/or PO_4^{3-}) can be recovered by separation of this acid liquid phase and addition of an alkaline source, for example $Ca(OH)_2$, forcing precipitation of a Ca~P which finally can be removed from solution by filtering the suspension (Schoumans et al. 2014). This leads to a relatively small volume of highly concentrated P-rich precipitates that can be easily exported or used as secondary resource for fertiliser P industries (Ehman et al. 2017; VCM 2015). After the recovery of P from manure or digested manure, the remaining organic fraction with a low P content can be better applied as nutrient source taking into account the maximum application standards of P. Export of manure to neighbouring countries can be avoided, so costs for export can be minimized by removing part of the phosphate from animal manure. Of course the costs of P-removal has to be lower than the economic gain of animal manure with low P content and the lower cost of export.

Figure 2.2 gives a schematic visualisation of the concept/design of P-recovery from pig slurry by means of an acid-base approach as developed and suggested by Schoumans et al. (2014).

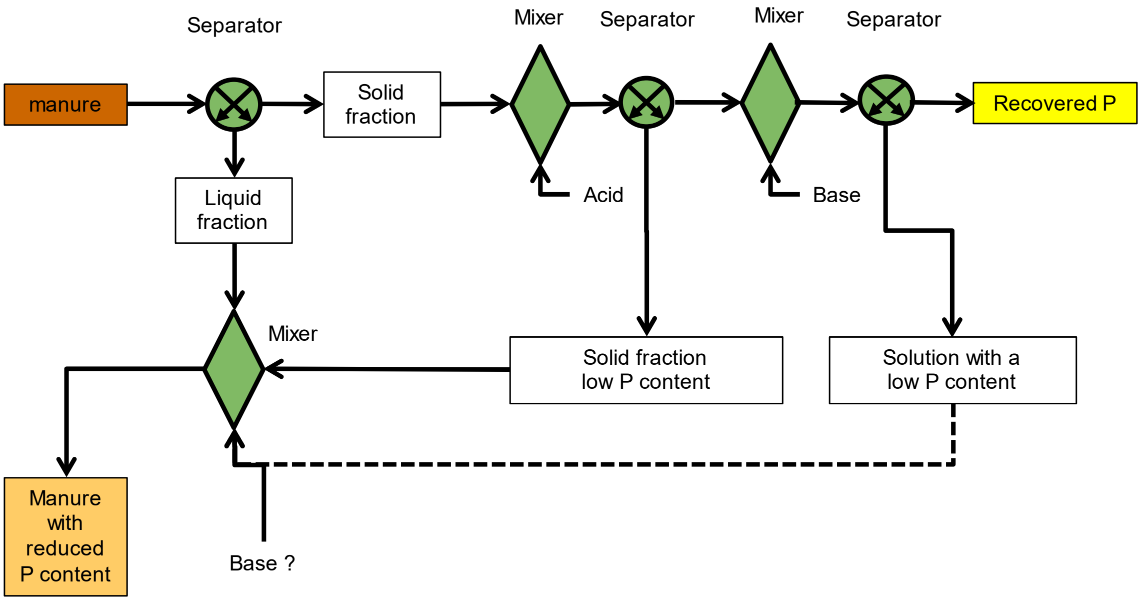

Figure 2.2 *Schematic representation of proposed steps to reduce the P-content in pig slurry by treatment of the high-tech separated solid fraction of the pig slurry.*

The slurry is separated into a solid and liquid fraction. The solid fraction is acidified and homogenized, which will lead to a release of P into solution. The solution with the high P concentration is separated from the manure suspense and thereafter the soluble P is precipitated by adding calcium hydroxides. Calcium phosphates will be formed which can be separated from the solution as P deposit. Both the solid fraction and the solution with the low P content (after separating the P deposit) can be combined into manure with a reduced P content. The pH of the solid fraction can also be increased by just adding some lime if needed. It is well known that animal type, feed type and duration of manure storage influence the composition of manure and, as a result, the buffer capacity of the manure. In the current research reported here, a broad selection of manures have been studied.

In order to evaluate the options of the Acid-Base approach to recover P, two main experiments have been carried out:

- Laboratory experiments with several types of pig slurry (see section 2.2.4).
- Chemical analysis of samples from a pilot installation for P recovery at a manure digestion plant (see section 2.3).

2.2 Materials and Methods

2.2.1 Manure and digestate samples and separation

First observational research was conducted with manure from three farms in the Netherlands. Experiences with these samples led to a larger survey. For this survey manure and digestates were sampled from seven biogas plants located in the Netherlands treating either mainly[5] pig slurry (plant 1-6) or dairy slurry (plant 7) next to co-digestion feedstocks. At each plant, the ingoing manure as well as the outgoing digestate was sampled. In total, seven samples of manure and seven samples of digested manure were taken (Table 2.1). At all plants, co-substrates, often silage maize, were added to the digester. However, the actual feedstocks and the ratio between co-substrates and manure was unknown[6]. Samples of manure and digested manure were stored at 2-4 °C. Laboratory samples were taken after homogenising the samples.

Separation of manures and digestates
To mimic a low-tech separation, slurry and digestates were separated via a 710 μm sieve into a liquid and solid fraction. To mimic a high-tech separation technique, manures and digestates were separated by centrifugation at 3500 rpm for 10 minutes. The applied force during centrifugation amounts to 1880 x *g*. The mass of manure/digestate in the solid and liquid fractions was measured. The solid and liquid fractions were stored at 2-4 °C until they were used in further experiments.

The liquid fractions of the manure/digestate samples, obtained after sieving (710 μm), were used in the laboratory experiments to test the Mg-approach (Table 2.1). The solid fractions of the manure/digestate samples, obtained after centrifugation (rpm 3500[7] equal to 1880 x *g*), were used for laboratory experiments testing the acid-base approach (par. 2.2). Within the text, manures are denoted as M1-M7 whereas digestates are denoted as D1-D7.

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[5] The term dominantly is used, because at digestion plants often also manure of other animals is digested.

[6] In the Netherlands currently co-digestion is the main form of biogas production. The ration of a digestion is 50% animal manure and 50% substrates such as silage maize, silage grass and spent products of biodiesel and ethanol products. These substrates are called co-substrates as animal manure is part of the ration.

[7]

rpm	times *g*
300	10
3500	1880
10000	15300

Table 2.1 *Overview of the use of manure and digestate samples and fractions in laboratory experiments.*

No	Type of manure	Characteristics
1,8	Pig slurry	>50% pig slurry
2	Pig slurry	>45% pig slurry and > 4% cattle slurry
3	Pig slurry	>40% pig slurry and > 10% cattle slurry
4	Pig slurry	>50% pig slurry
5	Pig slurry	>50% manure (pig, cattle, rabbit)
6	Pig slurry	>50% pig slurry
7	Dairy slurry	>50% cattle slurry, hydrolysis pretreatment

Manure and digestate of farm number 1 was sampled twice. Results of the second sampling are shown in the figures for manure and digestate respectively as number 8.

2.2.2 Chemical analysis on manure and digestate samples

Chemical analyses were conducted by the laboratory of Wageningen University and Research (Environmental Sciences Group CBLB (Chemical Biological Soil Laboratory[8])). The manure and digestate samples as well as the liquid and solid fractions obtained from these samples, were analysed for the following parameters:

- pH and EC (In solid fractions 5:25 (w/v), in liquid fraction directly (in-house method CBLB);
- Dry matter (DM) content (gravimetric method, drying at 105 C°; ISO-11465);
- Organic matter (OM) content (loss-on-ignition, at 550 C°);
- Total P and N (after H_2SO_4-H_2O-Se destruction on fresh samples);
- Total Ca, Mg, K, Fe, and Al (after aqua-regia destruction on dried samples);
- Orthophosphate and ammonium after extraction with water (manure : liquid ratio of 1:40).

Methods of CBLB are given by Houba et al, (1997) and Temminghoff et al (2000, 2004).

For the liquid and solid fractions, the Separation Efficiencies (SE) for water, DM, OM, P, N and K were determined according to equation 1. In general, the SE of the components is related to the solid fraction, if not it will be explicitly mentioned.

$$\text{Separation Efficiency component (SE)} = \frac{[\text{quantity of this component in solid of liquid fraction}]}{[\text{total quantity in the manure}]} \times 100\ (\%) \qquad (1)$$

2.2.3 Laboratory experiments Mg-approach on liquid fraction

The Mg-approach laboratory experiments were carried out by three tests:

- Test 1: Testing the effect of incubation time and Mg-P ratio on P-recovery
- Test 2: Testing the approach on the liquid fraction of 14 digestate/manure samples
- Test 3: Testing the conditions to enhance struvite crystal growth rate by means of a sequencing batch experiment

Test 1: Testing the effect of incubation time and Mg-P ratio on P-recovery
The objective of this first test is to determine the optimal Mg to P ratio and incubation time for P recovery from the liquid manure fraction. These parameters are considered to be important to form Mg phosphate precipitates like struvite and magnesium phosphates and to facilitate the flocculation of the particles in the liquid phase. Though it is know that pH plays an important role in struvite formation, the pH was kept constant because previous work showed that pH has little effect on the total P recovery from the liquid fraction as reported in Schoumans et al. (2014).

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[8] http://www.wur.nl/en/Expertise-Services/Research-Institutes/Environmental-Research/Facilities-Products/Laboratories-Environmental-Sciences-Group/Chemical-Biological-Laboratory-Bodem-soil/Services.htm

The experiment was performed with liquid fractions from manure and digestate, obtained after 710 µm filtration, from two biogas plants (no. 1 and 3). A beaker glass was filled with 100 mL of liquid fraction. Next, an amount of Mg was added as $MgCl_2$ to reach a molar Mg/total-P ratio of 1.3, 1.6 and 1.9 in the liquid fraction, taking into account the total amount of Mg already present in the liquid. The increase of the volume due to Mg-addition (8 mL) was small compared to the volume of the sample (100 mL) fraction. The slurries were slowly mixed (60-80 rpm magnetic stirrer) during Mg addition and incubation.

After addition of the Mg, registration of the reaction time started and samples were taken after 1 hour, 1 day and for one manure sample also after 14 days. The samples were centrifuged at 3500 rpm. Masses of the pellet and supernatant were weighed as well as the volume of the supernatant. The pellets were analysed for dry matter content, and organic matter content, total-P, total-N, total-K, Ca and Mg using the methods as described in par. 2.2.2. The size of the crystals in the pellets were measured by means of a microscope. For this purpose, about five crystals with a size of at least 5 mm were randomly selected and measured. Figure 2.3 shows the sequential steps of this experiment.

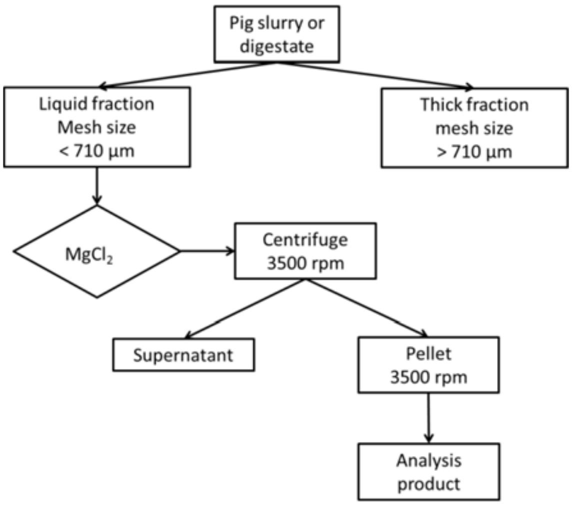

Figure 2.3 *Laboratory approach to separate P rich material from the liquid fraction of slurry of digestate after* $MgCl_2$ *addition.*

Test 2: Testing the Mg-approach on 14 digestate/manure samples

In the second test, the Mg-approach was tested on a large number of liquid fractions in order to study the effect of digestion and composition of the liquid fraction on the P-recovery. The experiments were performed with the liquid fractions (710 µm filtration) from the seven manure and digestate samples. Based on the outcomes of test 1, it was decided to use a molar Mg/P ratio of 1-1.3 (liquid fraction) and an incubation time of 1 day. The further execution of the experiment was similar to test 1. After addition of Mg (as $MgCl_2$) and leaving the samples for 1 day, the suspension was separated into a pellet and supernatant by centrifugation (3500 rpm). Next, the composition of the pellet as Mg~P product was measured using the analyses described above. The size of the crystals in the pellets was determined using a microscope (five measurements per sample).

Test 3: Testing the possibilities to enhance struvite crystal growth rate in a sequencing batch experiment

The goal was to determine whether struvite crystals can grow in animal slurries to such extent that the crystals can be separated more easily from organic substances by washing. There are indications that struvite crystal growth requires a continuous supply of the constituting ions (Doyle and Parsons 2002). Overdosing would stimulate further nucleation and thus production of smaller crystals. Therefore we chose a sequencing batch experiment, whereby new liquid fraction (with P, Mg and NH_4) and chemicals are frequently added to the reactor.

An important question is whether mineral P precipitates that are present in manure (mostly Ca-P solids) dissolve in favour of struvite crystal growth. In this context, there are two competing hypotheses:

1. Due to struvite crystal growth the ortho-P concentration in solution decreases, Ca-P solids will dissolve and together with the availability of NH_4 and Mg, ortho-P will be converted to struvite, as long as the conditions for struvite formation are kept favourable. According to this hypothesis, the Mg/P molar ratio should be based on total Mg and P (instead of dissolved). Residence time is an important variable because it takes time for the described process to take place.
2. Struvite crystal growth is (only) determined by the amount of P (and Mg and NH_4) in solution. According to this hypothesis, the Mg / P molar ratio must be based on the amount of Mg and P in solution. However, the Mg/P molar ratio in solution in our starting material appeared to be in the range of 2, i.e. no extra Mg would be required, according to this hypothesis.

The experiment was performed with about 1 L of liquid fraction. After Mg dosage the slurries were left for 2-3 days during which the larger particles would settle at the bottom of the beaker. After a day, the upper part was decanted and new fresh liquid manure was added to the beaker. As such, the crystals remain in the beaker and crystal growth might be stimulated through the continuous supply of Mg and P (Figure 2.4). The sequencing batch laboratory experiment was carried out with the liquid fraction (separated over 500 µm) of pig slurry which was sampled at the pilot installation at Groot Zevert, except for the first round of the experiment when the separation of digestate was performed at the laboratory using a 710 µm sieve.

The experiment was performed with three treatments with different amounts of Mg supplemented in order to reach molar Mg/P ratios of 1.6, 0.7 and 0.8 with two replicates (6 reactors). The Mg dosages were calculated after taking into account the Mg and P content of the original digestate. The molar ratio 0.7 treatment can be considered as a reference, without any Mg addition. Magnesium was added as MgO. Furthermore, the pH was adjusted to 9 by titration with 6 M NaOH, because struvite as main Mg~P precipitate will be formed at this pH (see 2.1.1). The slurries were gently mixed during addition of chemicals but no mixing was applied during the settlement of the particles.

After 7 rounds, settled solids were sampled and analysed for total Mg and P with ICP after extraction with 0.01 M HCl (1:80 (w/v), one hour shaking, centrifuging with 10.000 rpm during 10 minutes, supernatant filtered over 0.45 µm)[9]. After 3 rounds, the supernatant solution was sampled and analysed for elemental composition before and after centrifugation (3500 rpm). After centrifuging, also ortho-P was analysed with SFA. Furthermore, subsamples from the settled solids were used for microscopic observation. Five larger crystals were randomly chosen as an indication of the size of the crystals. Furthermore, the remaining crystals were counted, distinguishing between the size classes smaller and larger than 0.05 mm. Results of microscope counts were not converted to original reactor volumes, but presented as such.

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[9] Used as an indicative fast method to determine the increase of the amount of precipitated P.

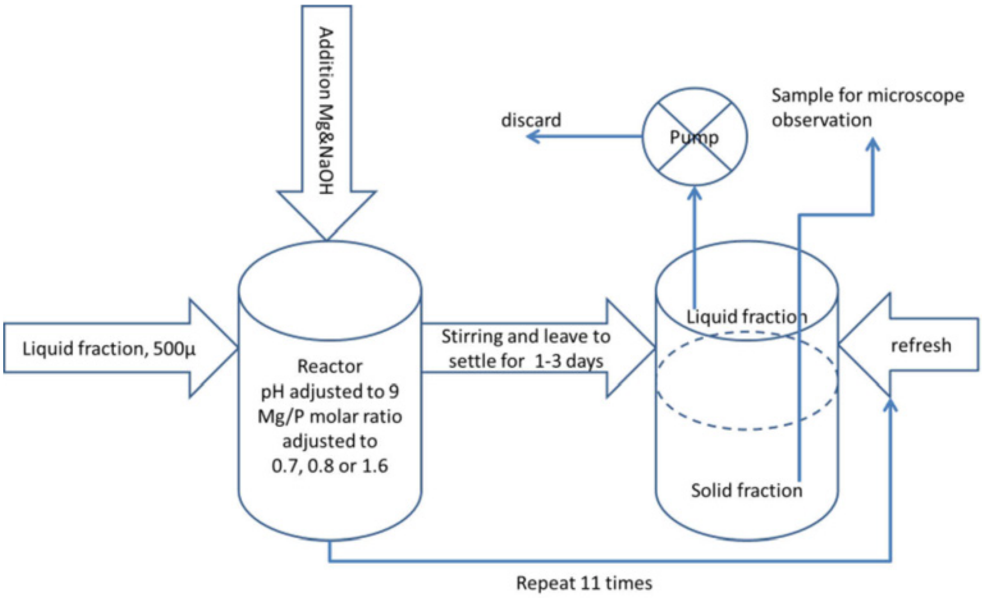


Figure 2.4 *Design of the sequential batch experiment in which the effect of manure replenishments on struvite crystal growth was tested.*

2.2.4 Laboratory experiments ‘Acid-Base approach’ on solid fraction

This part of the laboratory study consists of four experimental tests:

- Test 1: Analysing the composition of the recovered calcium phosphate product
- Test 2: Determining the acid consumption by the solid manure fractions
- Test 3: Release of P from the solid manure fraction after acidification
- Test 4: Testing the recovery of P from the acid extraction solution

The experiments were performed with the solid fraction of manure/digestate obtained after centrifugation at 3500 rpm (par. 2.2.1).

Test 1: Analysing the composition of the recovered calcium phosphate product
The P-rich pellets obtained in test 3 were analysed for the following parameters:

- Dry matter content and organic matter content
- Total P
- Total Ca, Mg, K, Al, Fe, Cd, Cr, Cu, Ni, P, Pb and Zn
- $CaCO_3$

Test 2: Determining the acid consumption by the solid manure fractions
The amount of acid needed to reduce the pH of liquid manure was determined by titrating 14 solid fractions of manure and digestate. A sample of about 100 ml solid material was added to a 400 ml beaker and 100 mL of demineralised water was added as dilution agent. During the titration, the slurry was stirred with a magnetic stirrer. The pH was measured with a pH electrode. A concentrated H_2SO_4 solution (2 M) was added stepwise and the pH was registered after stabilisation. In general, stabilisation was reached within minutes. This information was used to determine how much H^+ is needed to reduce the pH of the solid fraction to a certain pH-value.

Test 3: Release of P from the solid manure fraction after acidification
The amount of P released from the solid fractions was determined at predefined pH-values. The pH of the solid manure/digestate fractions were lowered with a concentrated H_2SO_4 solution (2 M). The required acid dosages were derived from test 1. The solid fractions were mixed with water in a 1:2 (solid/water) ratio in order to obtain a slurry. After adjustment of the pH, the slurries were centrifuged at 3500 rpm for ten minutes and the supernatant was filtered (0.45 µm) and analysed for ortho-P. Besides, the total-P concentration in the non-filtered supernatant was measured after destruction (wet oxidation). This information was used to determine the P recovery at certain pH values.

Test 4: Testing the recovery of P from the acid extraction solution
First, 100 gram of solid fraction of manure/digestate was mixed with 100 mL of water and subsequently acidified to a predefined pH (6.5, 6.0, 5.5 and 5.0) using a concentrated H_2SO_4 solution of 2 M. Next, the slurries were centrifuged (3500 rpm, 10 min) and the P-rich supernatant was decanted. The supernatant after filtration over 0.45 µm was analysed for ortho-P (after filtration) and total-P after destruction (H_2SO_4-H_2O_2). Phosphate was precipitated from the supernatant by the addition of $CaOH_2$ salt under stirring with a magnetic stirrer. Calcium hydroxide was dosed until a pH of 8 was reached again and this pH remained stable during 15 minutes, which should lead to precipitation of calcium phosphate. After an equilibration time of 15 minutes, the solutions with the freshly formed Ca~P particles were centrifuged at 3500 rpm and the supernatant was analysed for ortho-P and total-P. The amount of P recovered in the pellet was calculated from the difference in P concentration in the supernatant before and after $CaOH_2$ dosing.

Analyses on PO_4-P on the SFA followed within 48 hours after sampling. Analyses on total-P were conducted in stored acidified samples (before storage samples were acidified with minute quantity of 0.14 M HNO_3).

2.3 Pilot experiments

2.3.1 P recovery from the liquid fraction of manure (‘Mg-approach’)

In order to evaluate the option of phosphate recovery from the liquid fraction a pilot experiment was carried out at Groot-Zevert Digestion (Beltrum, The Netherlands) in the period October 2014 – March 2015. In Figure 2.5 a scheme of the setup is shown, which is in line with Figure 2.2, and in Figure 2.6 a picture of the installation is shown. Digested pig slurry was separated by a screw press (approx. 700 µm) in order to separate coarse material. In addition the liquid fraction was further separated over a 300 – 400 µm filter. The received liquid fraction was collected in a first silo (10 m^3) where magnesium chloride solution (32% $MgCl_2$)was added to the liquid fraction and slowly stirred with a rotor. During the monitoring 0, 11 or 17 litre $MgCl_2$ solution was tested in different experiments. The amount of $MgCl_2$ varied over time for these experiments resulting in a ratio Mg : P_{tot} from 0.83 (± 0.37) to 2.11 (± 0.83). A second silo was available as buffer tank (Figure 2.7) but was not used in practice. The phosphate rich product was directly collected by filtrating the material from the first silo over a rotating sieve (80 – 150 µm). Samples were taken from all stages of the treatment (as mentioned in Figure 2.5) and the following codes were used:

Code	Description code
M	ingoing manure and co-digestion feedstock
D	resulting digestate D used as ingoing material for P recovery
Fsolid	solid fraction of the screw press separator with sieves 700 µm (3/11/2014-11/12/2014) or 500 µm (12/12/2014-24/01/2015)
Fliquid	liquid fraction of the of the screw press separator with 700 µm (3/11/2014-11/12/2014) or 500 µm (12/12/2014-24/01/2015))
RDsolid	solid fraction of the of the Rotary drum separator (350 µm (300-400 µm))
RDliquid	liquid fraction of the of the Rotaru drum separator (350 µm (300-400 µm))
R1	liquid fraction after addition of magnesium in mixing tank
R2	liquid fraction after storage in the buffer tank before separation
RFSsolid	solid Mg~P product after separation over a rotating fabric belt separator (three parts: 80, 120 and repeated 120 µm) alternative name Wet Mg~P cake
RFSliquid	liquid fraction with reduced P content after separation over a rotating fabric filter sieve (three parts: 80, 120 and repeated 120 µm)

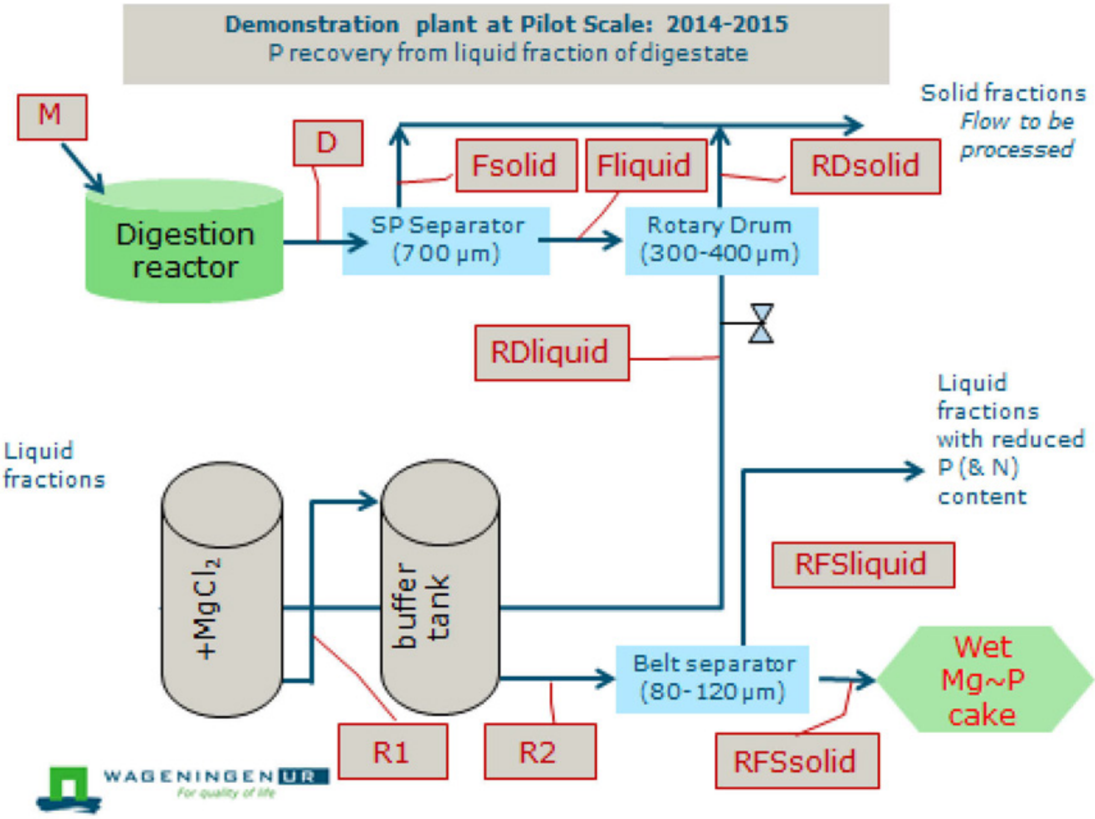


Figure 2.5 *Scheme of the 'Mg approach' pilot installation at Groot-Zevert Digestion (Beltrum, the Netherlands).*

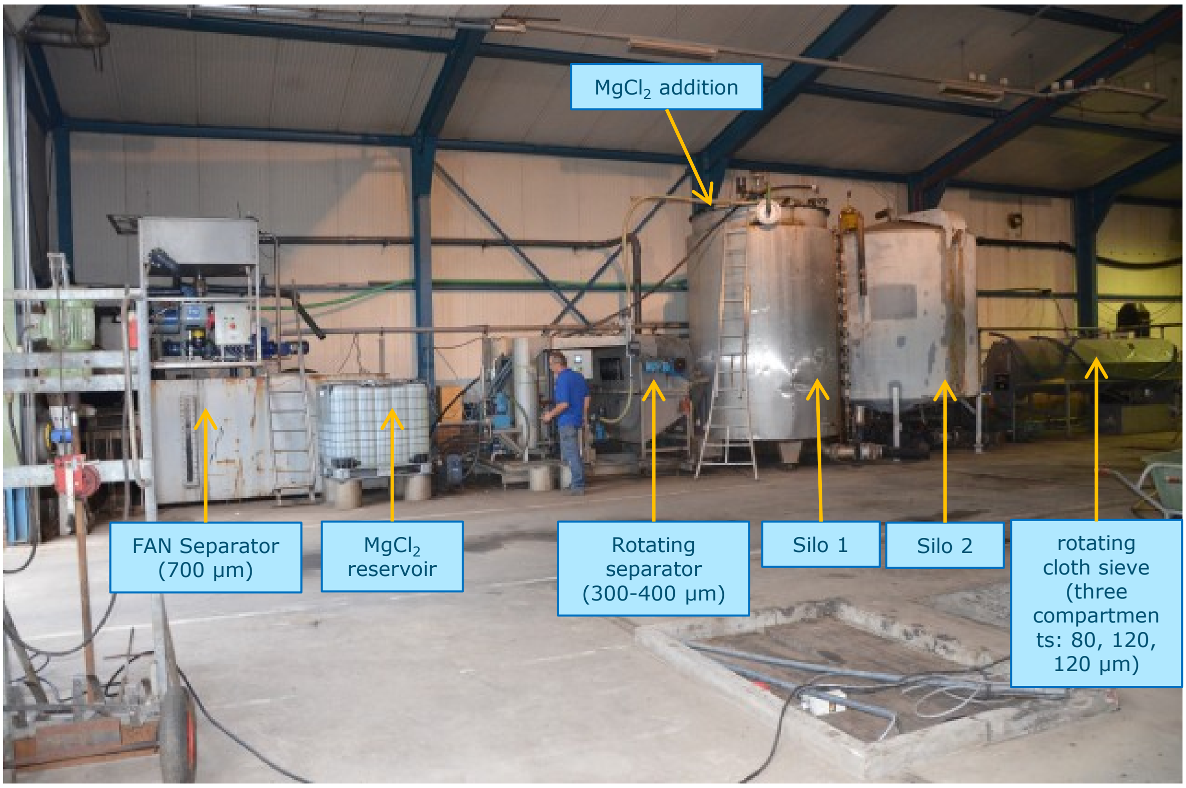


Figure 2.6 *Pilot installation of the 'Mg approach' at Groot-Zevert Digestion (Beltrum, the Netherlands).*

2.3.1.1 Maximum struvite crystal growth rate in a sequencing batch experiment

This laboratory experiment (Figure 2.7) started on 28-01-2015 with 1 L of liquid fraction for each treatment, obtained by sieving stored (5 °C) fattening pig digestate from Groot Zevert Vergisting (code D of 18-12-2014) over 710 µm in the laboratory. After two rounds of refreshment, the liquid fraction of low-tech separation (code Fliquid) of Groot-Zevert was used as obtained from Groot Zevert Vergisting without a form of pre-treatment other than homogenizing.

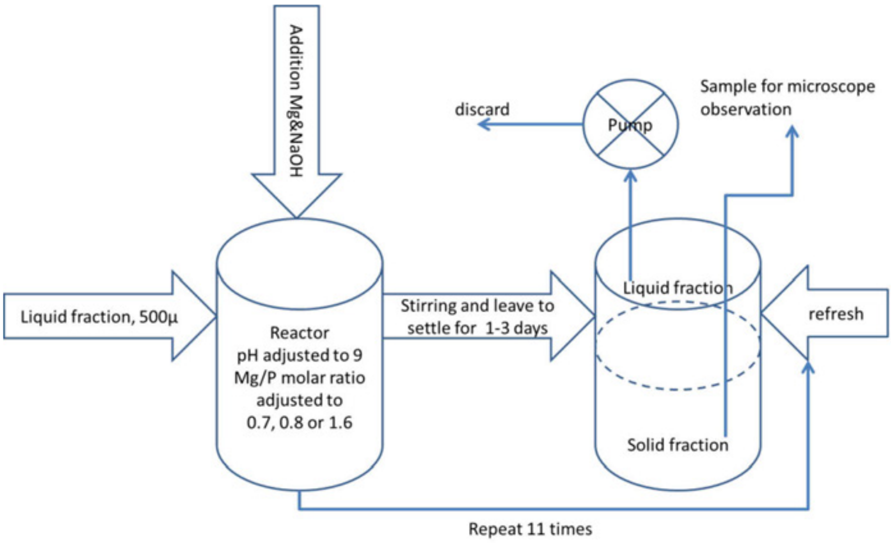


Figure 2.7 *Design of the sequencing batch experiment. For the first 3 batches the reactor was a 1 L cylinder glass, later batches were added to 3 L beakers. A total of 6 reactors was used for three treatments (Mg/P) in duplicate.*

We applied three treatments with different amounts of Mg supplemented in order to reach molar Mg/P ratios of 1.6, 0.7 and 0.8) with two replicates (6 reactors). The molar ratio 0.7 treatment can be considered as reference, without any Mg addition. The molar ratio 1.6 is the highest recommended ratio to enhance struvite crystal growth. The 0.8 molar ratio (based on total Mg/P) is derived from the assumption that about 10% of total P is present as ortho-P, and that an equivalent amount of soluble Mg should be applied to form struvite (molar ratio 1 based on soluble Mg and P).

For the first 3 refresh rounds 1 L glass cylinders were used. For later rounds 3 L glass beakers were used, because of the accumulation of settled solid fraction. Weight was recorded throughout the experiment before and after refreshing. A MgO suspension (25/100 m/m) was prepared with MgO from Nedmag Industries, the Netherlands (985 g MgO/kg; 325 mesh). Before refreshing, Mg was added to the digestate liquid fraction to adjust the Mg/P ratio for each treatment (taking into account the Mg and P content of the original digestate), and the pH was adjusted to 9 by titration with 6 M NaOH. The same was done with the first amount of digestate added to the reactor. Digestate was mixed with a magnetic stirrer during Mg addition and titration. The mixture of digestate with chemicals was poured into the cylinders (later beakers) and left to settle. Cylinders and beakers were kept at room temperature throughout the experiment. After a couple of days (2-3 refresh rounds per week), the supernatant solution was removed with a pump and discarded. After mixing the settled solids, a sample (circa 20 grams) was taken and kept in a refrigerator (5 °C) for a few days until crystal size analysis. The reactor volume was subsequently supplemented with newly prepared digestate liquid fraction (Mg/P ratio and pH 9). After gently mixing (cylinders end-over-end; beakers with a spoon) the reactors were left to settle for the next round. A subsample (0.5-1.0 gram) was taken to prepare a slide (10x10cm) for microscope observation. 5 Larger crystals were randomly chosen for size measurement, the remainder was counted, distinguishing between the size classes smaller and larger than 0.05 mm. Results of microscope counts were not converted to original reactor volumes, but presented as such.

After 3 rounds supernatant solution was sampled, and after 7 rounds settled solids were sampled for total Mg and P with ICP after extraction with 0.01 M HCl. The supernatant solution was analysed twice, once with, and once without centrifuging. After centrifuging, also ortho-P was analysed with SFA.

2.3.2 P recovery from the solid fraction of manure ('acid-base approach')

This part of the laboratory study consist of four experiments:
1. Experiments to derive the overall titration curve
2. Experiments to determine the P release into solution at fixed pH's
3. Experiments to determine the P recovery from the solution at fixed pH's
4. To determine the composition of the end product

Titration curves (experiment 1) were determined by adding H_2SO_4 to samples of the solid fraction of the manure or digestate to a pH of 4. A high-tech separation technique (centrifuge 3500 rpm) was used to collect most of the solid material of manure or digestate. A sample of 100 ml solid fraction was added to a 400 ml beaker of known weight and 100 mL of demi-water was added. The weight of the sample was registered. The sample was mixed with a magnetic stirrer. The pH was measured with a pH electrode (Thermo Scientific. Orion. 8115BNUWP Ross Ultra Semi-Micro pH). Next 1 ml 2 M H_2SO_4 was added and the pH was registered after stabilisation. Then the next additions of each time one ml 2 M H_2SO_4 followed. In general, stabilisation was reached within minutes. This information was used to determine how much H^+ is needed to reduce the pH of the solid fraction to a certain pH.

P-release (P-solubilisation; experiment 2) from the solid fraction of the slurries into solution was measured at predetermined pH values. For each pH a separate sample of the solid fraction was taken and the required amount of acid was added to reduce the pH to the required value (based on the derived overall titration curves; experiment 1).The ratio solid fraction : solution was standardized to 1:2. At the required pH the whole sample was centrifuged at 3500 rpm during ten minutes and a subsample of the supernatant was filtered (0.45 µm) to measure ortho-P and in a non-filtered part the total-P concentration was measured after destruction (wet oxidation). This information was used to determine the options of P recovery at varying pH.

The P recovery (experiment 3) was determined for each solid fraction at 4 pH values based on the information of experiment 2 (6.5, 6.0, 5.5 and 5.0). The same procedure was used to reduce the pH of the solid fraction and to retrieve the P-rich solution (experiment 2), but in this case the manure – solution ratio was not the same for all samples. A known weight of solid fraction of circa 100 gram solid fraction was used and 100 ml demineralized water before adjusting the pH. After setting the pH at the required value the sample was separated by centrifuging at 3500 rpm during ten minutes into a supernatant and a solid fraction. From the P-rich supernatant a sample was taken for the determination of ortho-P and total-P. $CaOH_2$ was added to the rest of this P-rich solution of the supernatant until a pH of 8 was reached, which will lead to precipitation of calcium phosphate. After centrifugation at 10.000 rpm the supernatant was sampled to determine again the ortho-P and total-P concentration. The P recovery in the pellet was calculated as the difference between the quantity of P in the solid fraction and the quantity of P in the supernatant after acid treatment.

The composition of the end product (experiment 4) was determined for the pellet material from the acid – base approach (acidify to pH 5 and add base to pH 8). The amount of dry matter, organic matter, total P, Ca, Mg, K, $CaCO_3$, Al, Fe, Cd, Cr, Cu, Ni, P, Pb en Zn were measured.

Figure 2.8 shows the Pilot installation of the 'Acid-base approach' at Groot-Zevert Digestion (Beltrum, the Netherlands), which exits of:
- A two-step simple mechanical separation (FAN 700 µm) and rotating separation (300-400 µm) of the solid fraction of digested pig slurry.
- Acidification tank for the acidification of the solid fraction (for acidification groundwater, recycled water (or recirculation water or effluent of the ammonia stripper was used in different batches).
- Separator (about 70 µm) to collect the P-rich solution and P-poor organic matter.
- Precipitation tank of Ca~P with at the bottom the outlet of Ca~P product.

Figure 2.8 *Pilot installation of the 'Acid-base approach' at Groot-Zevert Vergisting (Beltrum, the Netherlands).*

3 Composition of manure and digestate and effect of separation technique

3.1 Composition

The average composition of the manure and digestate is given in Table 3.1. In Annex 1 data for each location, manure and digestate are given.

In general, the average dry matter content of digestate was higher than for manure but the percentage organic matter in this dry matter was lower. The pH of the digestates is on average 1.3 pH-unit higher than the pH of the manures. The mineral content (N, P, K, Ca) based on fresh material of the digestate is higher than for the manure. Higher values for dry matter content, pH and minerals are due to the decomposition of part of the organic matter during the digestion processes of the co-digestion feedstock used to increase biogas production. A consequence of these digestion processes is the higher value for the EC.

The ortho-P concentration is rather difficult to determine. Ortho-P measurement requires a dilution with demi-water because the sample material is often too heavily loaded with particles which hinders filtration. However, dilution might introduce a solubilisation of phosphate minerals present in the samples and can lead to overestimating the actual ortho-P concentration in solution if the dilution factor is taken into account. However, if it is assumed that the ortho-P concentration in solution is in equilibrium with these minerals after dilution, the dilution factor does not have to be taken into account. In this study a dilution factor of 40 (V/V) was used. The measured ortho-P concentrations in digestates have a similar order of magnitude as in manure. Since it is assumed that after dilution the amount of solubilized phosphorus is in equilibrium with the phosphate minerals, the total amount of P in solution is about 1% (1.05% for manure and 0.86% for digestate) of the total amount of phosphorus present.

3.2 Effect of separation technique

The separation technique determines the phosphorus content and distribution over liquid and solid fractions. We tested the effects of low-tech and high-tech separation. A low-tech separation is a simple straightforward technique that requires low energy input and can be used on e.g. farm scale. Simple techniques are the use of a settling tank or rotary sieve. Investment costs are relatively low. High-tech separation techniques are generally used on semi-industrial and/or industrial scale. A higher energy input is required and the investment costs are also higher. Annex 1 gives an overview of different separation techniques used for treatment of pig slurry and manure of dairy cows including results of separation efficiency (product, dry matter, nitrogen & phosphorus), capacity (m^3/hour) and references.

The samples of manure (pigs, dairy cattle) and digestates were separated in the laboratory by means of a sieve (710 µm; low-tech separation) and by centrifuging (3500 rpm; high-tech separation). The separation by a sieve was used as low-tech separation technique to get a P-rich *liquid* fraction (to be used for the 'liquid fraction approach'). The separation by centrifuging was used to simulate a high-tech separation technique to get a P-rich *solid* fraction (to be used for the 'solid fraction approach').

For this study large volumes (3 x 20 L) of manure and digestate were collected at seven locations where the manure was co-digested with 50% manure and 50% co-digestion feedstock. At six of the seven locations pig slurry and digestate were sampled and on one of the location dairy slurry and digestate. The exact ratio manure – other substrates (co-material) are not known but due to regulatory requirements of the Dutch Fertiliser Act at least 50% manure has to be used. Often maize silage is used as co-substrate.

Subsamples of the manure and digestate were separated by sieving or centrifuging. Ingoing manure or digestate and the separated liquid fractions (710 µm) and solid fractions (3500 rpm) were analysed on chemical and physical characteristics.

In Table 3.1 the average composition of the materials are shown. The content is expressed per kg fresh material (manure/digestate, and the liquid fraction and solid fraction). Annex 1 gives the full chemical and physical characteristics of the sampled slurries and digestates of the seven farms/companies.

Digested manure 2 has a high total P content compared to the original manure (4.5 g/kg compared to 1.0 g/kg) and also the P-PO_4 content is much higher (2.7 g/kg compared to 0.7 g/kg). The reason for this is unclear, but is probably caused by the used added material (cosubstrates). The average ortho-P (P-PO_4) content of all pig slurry is 0.7 g/kg fresh material and the average total P content is 1.7 g/kg. The P-PO_4 and total-P values of the sieved liquid fraction (710 µm) are on average quite similar with those of the non-sieved material.

The digestate was sometime difficult to separate, especially digestate 3 and 5 (see Annex 2).

The solid (mass) fraction for sieved pig slurry and digestate varies from 31.4% to 68.4% and 44.3% to 55.4% respectively. Centrifuging yielded higher values for the solid fraction, i.e. 36.3% – 63.4% for manures and 47.8% - 52.2% for the digestates. By high-tech separation, as conditioned by our experiment, one can gain a somewhat higher dry matter content.

The dry matter content and organic matter content in the liquid fraction are about 4% lower than in the non-sieved materials.

The separation efficiency of P (SE-P) of the liquid fraction (710 µm) is on average for pig slurry 69% and 53% for the digested manure. However in both cases more than 50% of the P is accumulated in the liquid fraction when using the low-tech separation technique. When using the high-tech separation technique of centrifuging, the average separation efficiency of P (SE-P) of the solid fraction (3500 rpm) is for pig slurry 86%, and for digestate 77%. Thus the separation technique contributes strongly to the potential for phosphorus recovery. The same applies to Ca en Mg. In contrast, recovery of N and K are lower for the solid fraction from high-tech separation compared with the liquid fraction of the low-tech separation technique.

In the liquid fraction of sieved (710 µm) digested manure the SE of the measured elements (P, N, Ca, K, Mg) is also about 50%.

Table 3.1 *Average[1] chemical composition of the non-separated manures and digestates, their liquid fractions (low-tech separation) and their solid fraction (high-tech separation), expressed per kg of fresh product.*

Parameter	Unit	Manure			Digestate		
		Not separated	Sieved < 710 µm	Centrifuged 3500 rpm	Not separated	Sieved < 710 µm	Centrifuged 3500 rpm
Dry matter (DM) 105°C	%	10.2	5.7	15.7	12.8	8.3	16.5
Dry matter, 70°C	%	8.2	*	*	11.0	*	*
Organic matter	%	7.4	3.6	11.6	8.7	4.9	11.6
Organic matter (105-550°C)	%DM	72.5	63.3	74.3	67.7	58.9	70.4
pH	[-]	7.4	7.7	7.8	8.1	8.1	8.2
EC	mS	21.8	27.4	31.8	27.8	34.6	42.1
Total-N	g/kg	5.76	5.32	7.64	7.47	7.13	8.44
NH_4-N	g/kg	3.32	3.34	3.09	4.04	4.07	4.04
Total-P	g/kg	1.73	1.73	4.11	2.65	2.54	4.19
Ortho-P (PO_4^{3-}- P)	g/kg	0.017	0.018	0.019	0.024	0.026	0.026
Total-K	g/kg	4.25	4.15	4.40	4.46	4.35	4.54
Total-Ca	g/kg	2.49	1.88	4.03	3.06	2.58	4.09
Total-Mg	g/kg	1.18	1.17	2.71	1.22	1.01	2.02
Solid fraction	%	*	31.4	36.3	*	44.3	47.8
Liquid fraction	%	*	68.4	63.4	*	55.4	52.2
Separation efficiency, P	%	*	68.8	85.6	*	52.6	77.3
Separation efficiency, N	%	*	63.4	47.8	*	52.8	53.8
Separation efficiency, K	%	*	66.7	37.9	*	54.5	49.2
Separation efficiency, Ca	%	*	54.4	59.1	*	46.8	64.5
Separation efficiency, Mg	%	*	68.0	83.9	*	46.4	77.9
Ortho-P after dilution/Total-P	%	1.05	1.10	0.46	0.86	0.92	0.58
Ortho-P/Total-P corrected for dilution factor	%	41.9	44.1	18.5	32.9	36.6	23.2

[1] Pig: Average of six manure/digestate samples from different locations. Dairy cows: Manure and digestate from one location.

4 P recovery from the liquid fraction of manure

In this chapter we report the results of the laboratory and pilot scale studies on phosphorus recovery from the liquid fraction. The following topics are reported.

- Laboratory studies on the phosphorus recovery from the liquid fraction of separated manure or digestate through struvite production as affected by the molar ratio of magnesium to phosphorus and incubation time;
- Observational research of struvite production on pilot scale.

4.1 Effect of the incubation time on the P recovery and crystal growth

4.1.1 P recovery

Manure 1 and 3 and digestate 1 and 3 were used to analyse the effect of the molar ratio Mg/P and incubation time on the P recovery from the liquid fraction and on the growth of crystals. Annex 3 reports on the data of the measurements. Figure 4.1 summarizes these data. Recovery of phosphorus was larger for the manure compared with the digestates (co-digested pig slurry). Manure 1 and digestate 1 yielded higher P recoveries than manure 3 and digestate 3. Digestate 1 had a higher recovery than manure 1, however digestate 3 had a lower recovery than manure 1.

An ANOVA t-test was performed on data of the P recovery. There was no significant effect of the molar ratio Mg and P on the P recovery (data not given). Incubation time did not affect the recovery either; only for manure 3 a higher recovery with an increase of the incubation time was found. For manure 3 with an molar ratio of 1.3 and incubated during 1 hour, 1 day and 14 days P recoveries were respectively 82.3%, 86.4% and 98.5%.

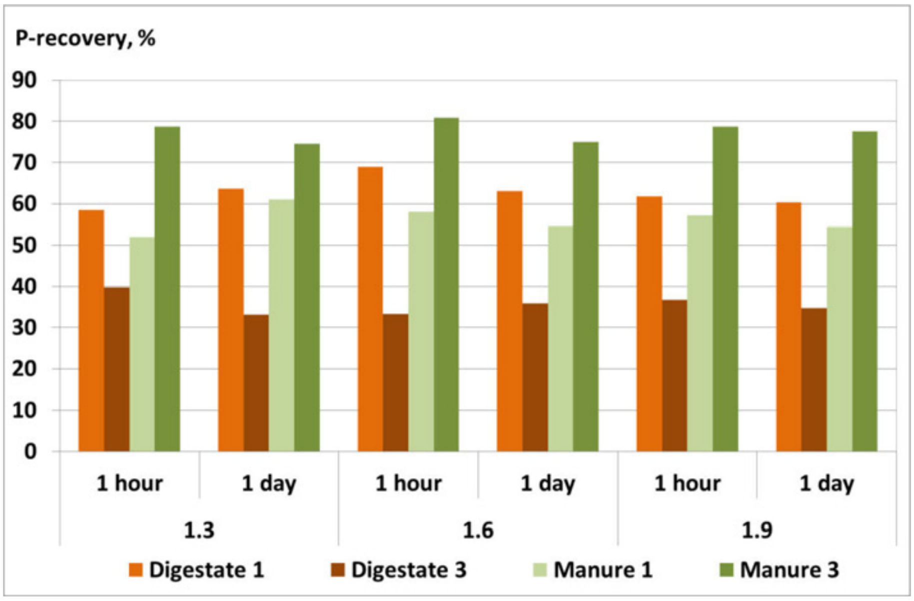


Figure 4.1 *The influence of molar ratio Mg and P (1.3, 1.6 and 1.9) and incubation time (1h and 1 day) on the average P recovery of digestate (digestate 1 and 3) and pig slurries (manures 1 and 3) as percentage of total P content.*

4.1.2 Crystal growth

Crystal growth was measured via microscopy by measuring length and width of 5 larger crystals. First we made observations which size of crystals (length, width) were found in the manures and digestates under a standardised molar ratio Mg/P. Next effects of molar ratio Mg/P and incubation period were factors studied. Data are given in Tables 4.1 and 4.2.

4.1.2.1 Observations at molar ratio Mg/P of 1.3 after one day of incubation

Observations of the crystals length and width found after standardising the molar ratio of Mg/P to 1.3 and one day of incubation are shown in Table 4.1. Photos are presented in Annex 4 as illustration.

In digestates the length of the crystals varied from 0.20 to 0.57 mm while the width varied from 0.13 mm to 0.20 mm. For the manures the length of the crystals varied from 0.16 to 0.50 mm and the width from 0.07 mm to 0.36 mm. Taking the standard deviation into account, these changes in length and width mere random variation.

Table 4.1 *Mean length and width of struvite crystals found in the manures and digestates after standardizing the molar ratio Mg/P to 1.3 after one day of incubation.*

Product	Length (mm)	SD[1] (mm)	n[2]	Width (mm)	SD (mm)	n
Digestate 1	0.49	0.29	9	0.20	0.11	9
Digestate 2	0.20	0.09	10	0.10	0.05	10
Digestate 3	0.57	0.43	5	0.20	0.17	5
Digestate 4	0.20	0.04	10	0.13	0.03	10
Digestate 5	0.25	0.05	10	0.19	0.07	10
Digestate 6	0.21	0.06	10	0.14	0.04	10
Digestate 7	0.21	0.08	10	0.14	0.07	10
Average for digestates	***0.28***	***0.21***	***64***	***0.15***	***0.08***	***64***
Manure 1	0.34	0.27	5	0.17	0.19	5
Manure 2	0.27	0.06	10	0.14	0.07	10
Manure 3	0.50	0.14	5	0.36	0.17	5
Manure 4	0.30	0.07	10	0.13	0.03	10
Manure 5	0.22	0.09	10	0.13	0.07	10
Manure 6	0.16	0.04	10	0.07	0.02	10
Manure 7	0.20	0.07	10	0.15	0.04	10
Average for manures	***0.26***	***0.14***	***60***	***0.15***	***0.11***	***60***
Overall average	***0.27***	***0.18***	***124***	***0.15***	***0.10***	***124***

[1] SD: Standard Deviation

[2] n: number of observations

4.1.2.2 Factorial experiments

The average lengths of the crystals used in the experiment varied between 0.29 and 0.86 and the width between 0.14 and 0.38 mm (Table 4.2). The width for manure 1 is slightly larger compared to manure 3 and digestate 1 and 3. There are no significant differences between the last 3 samples (ANOVA t-test). Overall significant differences were not found. After an incubation time of 1 day the width is slightly larger than after an 1 hour. There is no significant proof that the molar ratio or the incubation time influences the crystal growth, only a slight positive effect of the incubation time on the width of the crystals. The effect of the ingoing material (manure of digestate) has a larger effect on these growth characteristics (this was also found for the P-recovery; Figure 4.2).

The effect of incubation time was not significant. Although in one sample (manure 3) the P recovery increased from 74.6% to 90.4% at a molar ratio of 1.3 and longer incubation time (more than two weeks) there was also in this case no effect on the crystal growth in length and width. Based on this orientation tests, it was decided to use the lowest Mg-P molar ratio (1.3) and an incubation time of 1 day to determine the P recovery of all manure and digestate samples.

4.1.3 Determination of the composition of the end product, P recovery and crystal growth at fixed Mg-P molar ratio and reaction time

The recovery of P from the separated liquid fraction (710 µm) of all manure and digestate samples were determined at a molar ratio of 1.3 Mg to 1 total-P (liquid fraction) and an incubation time of 1 day. As Mg source $MgCl_2$ was used. After the incubation the suspension was separated into a pellet and supernatant by centrifuging (3500 rpm). The composition of the pellet as Mg~P product was measured. The P recovery was calculated as percentage of the total amount of P present in the manure or digestate. Figure 4.2 gives the results of the P recovery of all manure and digestate samples.

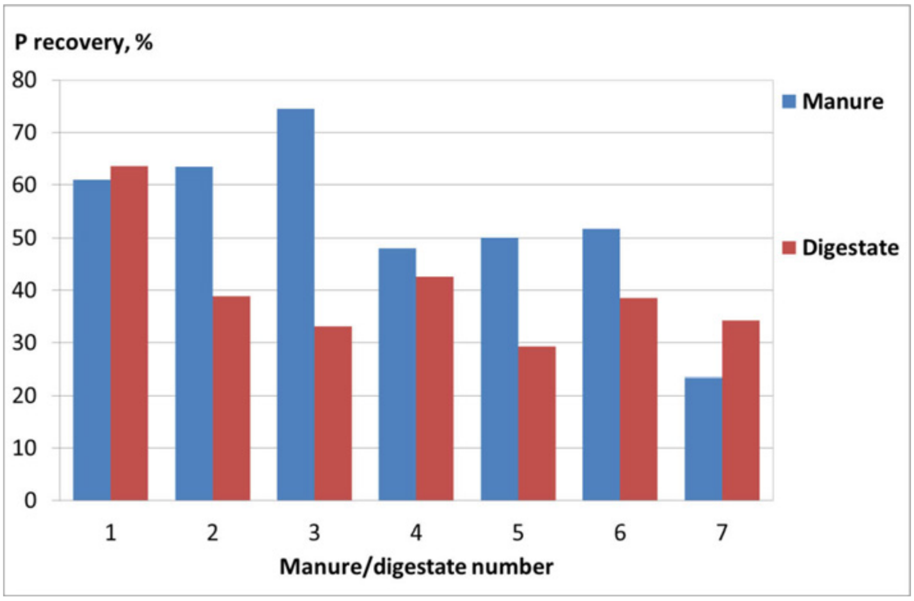


Figure 4.2 *P recovery from manure and digestate after addition of $MgCl_2$ at a Mg-P molar ration of 1.3 and an incubation time of 1 day of the sieved (710 µm) liquid fraction of the manure or digestate (1-6 pig; 7 dairy).*

The P recovery of pig slurry (numbers 1-6 in Figure 4.2) is often higher than to the P recovery of the digestates (numbers 1-6 Figure 4.2). For the one dairy slurry (number 7) the results are opposite. The average P recovery from the pig slurries is 58.1% (±12%) and from the pig digestate 41.0% (±10.1%). The lower fraction for the digestates is caused by the fact that digested manure was difficult to separate at 3500 rpm (experience at the laboratory).

Table 4.2 *Mean length and width of struvite crystals in mm in the recovered product at different P_{tot} - Mg ratios and incubation time.*

Product	Incubation time	Molar ratio of Mg to P_{total}																	
		1.3						1.6						1.9					
		Length (mm)			Width (mm)			Length (mm)			Width (mm)			Length (mm)			Width (mm)		
		Mean	SD[1]	n[2]	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n
digestate 1	1 hour	0.57	0.16	5	0.35	0.10	5	0.60	0.12	4	0.38	0.05	4	0.53	0.21	5	0.29	0.16	5
	1 day	0.50	0.29	7	0.19	0.09	7	0.86	0.27	5	0.36	0.08	5	0.46	0.16	5	0.23	0.13	5
digestate 3	1 hour	0.53	0.27	6	0.29	0.15	6	0.35	0.06	5	0.27	0.09	5	0.47	0.13	6	0.25	0.14	6
	1 day	0.57	0.43	5	0.20	0.17	5	0.51	0.36	4	0.18	0.06	4	0.60	0.15	6	0.21	0.09	6
manure 1	1 hour	0.38	0.08	5	0.36	0.27	5	0.29	0.06	2	0.15	0.07	2	0.37	0.07	5	0.18	0.05	5
	1 day	0.34	0.27	5	0.17	0.19	5	0.57	0.28	3	0.20	0.09	3	0.30	0.25	5	0.14	0.07	5
manure 3	1 hour	0.49	0.27	6	0.35	0.29	6	0.40	0.15	5	0.28	0.29	5	0.53	0.33	6	0.19	0.06	6
	1 day	0.50	0.14	5	0.36	0.17	5	0.62	0.29	5	0.31	0.16	5	0.63	0.31	6	0.24	0.11	6

[1] SD: Standard deviation

[2] n: number of observations

In Figure 4.3 an overview is given of the average P mass balance of the laboratory tests to recover P from the liquid fraction. After low-tech separation on average about 75 (±15.1)% of the manure mass and 57 (±10.5)% of the digestate mass is available as liquid fraction. After addition of $MgCl_2$ and separation of the product about 64% (range: 47% - 90%) of the total amount of the P in pig slurry can be recovered in the pellets. For digestate the average value is 44% (range : 29% - 69%). P recovery from dairy slurry (23%) or digested slurry (34%) (both only one sample) is relative low compared to pig slurry. This is probably caused by the relative high Mg content in dairy slurry which causes that most P is present in the solid fraction (> 710 μm).

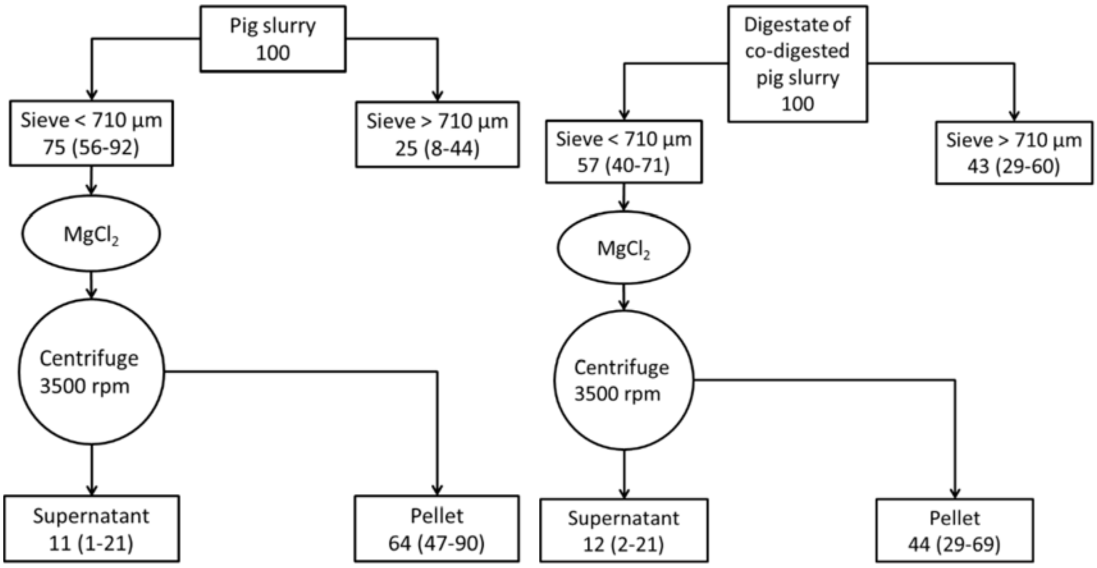


Figure 4.3A *Average recovery of phosphorus after sieving in liquid and solid fractions and after treatment with $MgCl_2$ in supernatant and pellet as a percentage of phosphorus in pig slurry (left) and digested pig slurry (right). The range (minimum and maximum) is given between brackets. Number of observations of pig slurry is six.*

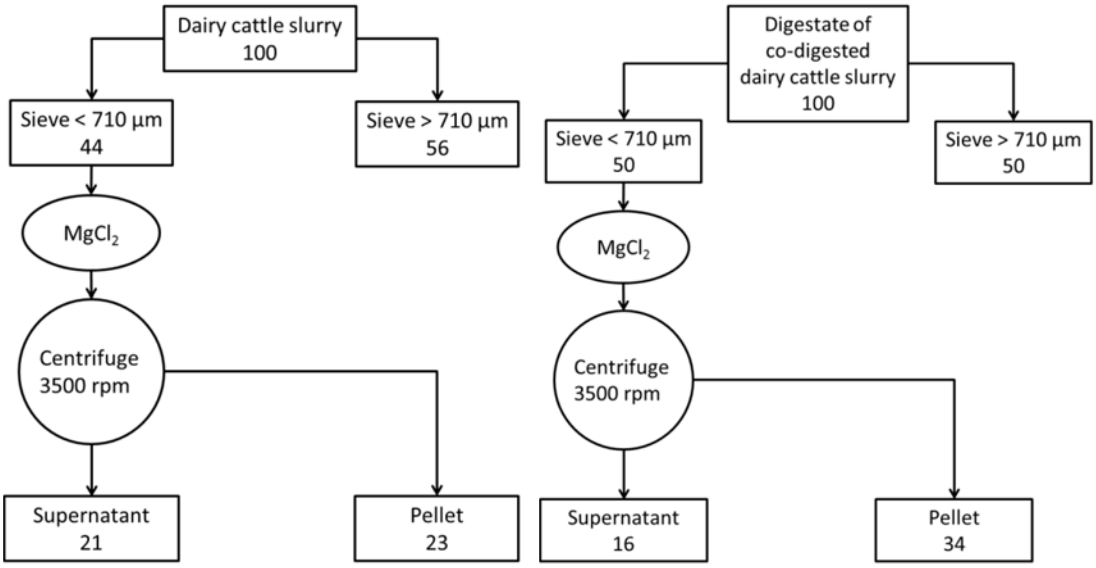


Figure 4.3B *Recovery of phosphorus after sieving in liquid and solid fraction and after treatment with $MgCl_2$ in supernatant and pellet as a percentage of phosphorus in dairy cattle slurry (left) and digested dairy cattle slurry (right). Number of observations of dairy slurry is one.*

The composition of the recovered material (called pellet) is shown in Table 4.3. About 21.9% (mass) of the source material (pig slurry) is collected as product with a dry matter content of 15% (for pig slurry) and 26.9% (for digested pig slurry) with a dry matter content of 16%. For dairy slurry the dry matter contents are lower (10.9% and 10.4%). About 67% of the dry matter content of the product (pellet) is organic matter and for digested pig slurry about 64% (range 59-75%). The organic matter content of the pellet is 10% of fresh product. The pellet contains water (~85%) and organic matter. To prevent the need for transporting this water, a volume reduction can be accomplished by increasing the dry matter content, e.g. by drying. The organic matter content of the recovered material is relative high. As raw material for P fertiliser production initially an organic matter content of less than 5% was mentioned, but it seems that higher contents are also acceptable.

There are small differences in the N, P and Mg content (expressed per kg dry matter of the pellet) between pig slurry and digested pig slurry. But the average values of digestate are lower. The average P recovery as pellet (compared to the total amount in the source material (liquid fraction)) is 52.6% for manure and 38.6% for digestate. So, 50% more P can be recovered from manure than from digestate. Although P is strongly accumulated in the recovered pellet material, the volume of the pellet material and the amount of organic matter in the pellet material are substantial.

Table 4.3 *P-recovery of 7 manures and 7 digestates at a molar ratio Mg and P of 1.3 and incubation time (1 day).*

Source	Animal	Number	Recovered material as pellet	DM	OM	OM	C	N-NH4	P-PO4	Mg	Recovery from liquid fraction		
			%	% pellet	% DM	% pellet	% DM	g/kg DM	g/kg DM	g/kg DM	N	P	Mg
Manure	pig	1	35.2	14.9	65.9	9.8	38.2	54.1	39.8	34.4	32.8	61.0	77.1
Manure	pig	2	15.3	15.3	72.4	11.1	42.0	57.5	35.9	31.5	21.0	63.4	83.6
Manure	pig	3	20.4	14.7	60.9	9.0	35.3	63.4	36.1	31.2	35.1	74.6	96.5
Manure	pig	4	27.5	17.9	60.4	10.8	35.0	56.0	38.9	36.3	23.1	48.0	56.0
Manure	pig	5	26.7	15.1	67.4	10.2	39.1	67.3	44.1	39.4	22.6	50.0	61.0
Manure	pig	6	19.3	14.3	65.3	9.4	37.9	68.2	45.6	36.4	22.4	51.7	81.7
Manure	cattle	7	15.5	10.9	75.1	8.2	43.6	46.2	12.6	14.1	10.3	23.4	3.1
Digestate	pig	1	29.9	16.0	60.2	9.6	34.9	60.5	49.7	40.5	32.7	63.6	110.7
Digestate	pig	2	22.0	19.6	50.0	9.8	29.0	59.0	78.3	50.6	21.5	38.8	148.8
Digestate	pig	3	26.1	14.8	63.9	9.4	37.0	69.2	28.7	28.2	17.1	33.1	56.3
Digestate	pig	4	32.9	17.5	58.9	10.3	34.2	60.8	35.8	33.3	19.8	42.6	59.5
Digestate	pig	5	30.7	18.0	57.5	10.4	33.4	44.8	28.8	25.6	15.5	29.3	46.2
Digestate	pig	6	33.6	15.4	61.6	9.5	35.7	58.0	24.7	22.4	23.6	38.5	55.9
Digestate	cattle	7	14.6	10.4	73.8	7.7	42.8	55.1	15.1	16.2	16.4	34.4	26.5
Manure	pig	Mean	21.9	14.7	66.8	9.8	38.8	59.3	35.9	31.7	23.2	52.6	64.7
Digestate	pig	Mean	26.9	16.1	60.6	9.5	35.2	57.1	37.0	30.4	20.3	38.6	70.1

4.1.4 Results sequencing batch experiment

Because of the limited crystal growth both in the laboratory experiments (section 4.1.1 – 4.1.3) and the pilot experiments (section 4.2) sequencing batch experiments were carried out to investigate if crystal growth can be stimulated. For the sequencing batch experiment both samples of digestate (D) and liquid fraction were collected from Groot-Zevert (Table 4.4). For the first three rounds of the experiment digestate D of sampling date 18-12-2014 of Groot Zevert was sieved over 710 µm in the laboratory, and the resulting liquid fraction was used, while for the later rounds the liquid fraction of the first separation (LF 2-2-2015) of Groot Zevert was used.

Table 4.4 *Composition of the liquid fractions of pig digestate, used for the sequencing batch experiment. For the first three rounds D 18-12-2014 was used after sieving over 710 µm, for later rounds Fliquid 2-2-2015 was used directly. Other rows for comparison. prod=per kg product, DM=per kg dry matter. Averages refer to the indicated period.*

Date	Source	Rounds	EC	pH	DM	Ca	K	Mg	P	Ca	K	Mg	P	Molar ratio Mg/P
			mS/cm	[-]	%	mg/kg prod	mg/kg prod	mg/kg prod	mg/kg prod	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM	[-]
18-12-2014	D[1]	1,2,3	31	7.6	5.7		4389	861	1727		76965	15102	30284	0.64
18-12-2014	LF[2]				5.4		4578	1022	1991		85154	19016	37034	0.66
2-2-2015	D				6.6	2341	4273	1030	2129	35466	64735	15610	32253	0.62
2-2-2015	LF	4-11			5.3	2122	4331	927	1941	40163	81972	17546	36736	0.61
29-10-2015 29-1-2015	Average D		29.5	7.4	6.8	2212	4265	1026	2047	33865	65412	14915	30085	0.63
29-10-2014 2-1-2015	Average LF		32.0	7.5	5.1	1919	4045	897	1776	38105	79570	17472	34458	0.66

[1] D: digestate

LF: liquid fraction 1st separation (Fliquid)

The overall results of the sequencing batch experiment (Figure 4.4) show there is only a slow growth of crystals, both in length (4.4a) and number(4.4c). Growth of width (4.4b) and volume (number*length*width^2; 4.4d) is less clear. According to ANOVA analyses, crystal length increases significantly with the number of refreshments ($p<0.05$). Based on LSD analysis the difference becomes significant after the 8th refreshment. Only the 1.6 Mg/P treatment differs significantly in length ($p>0.05$) from both other treatments. There is also a significant interaction of Mg/P and number of refreshments, i.e. the difference between Mg/P is larger for later refreshments.

So, best results were obtained for the 1.6 Mg/P molar ratio treatment, but even for this treatment, growth in length is limited to about 0.2 mm for the entire period of 32 days (see trend line in Figure 4.4a). This implies that a residence time of at least 2 months would be necessary for reaching the 0.5 mm length, considered to be the minimum size for effective separation from the organic matrix.

While the 1.6 molar ratio treatment produced the longest crystals, it did not yield the largest number or volume of crystals > 0.05 mm (Figure 4.4c and 4.4d; results for crystals <0.05 mm not shown). No statistically significant effect of Mg/P ratio was found on total crystal numbers, but there was a significant effect of the number of refreshments and of the interaction of Mg/P and number of refreshments on the number of smaller crystals (<0.05 mm), indicating an increasing number of smaller crystals with higher Mg/P and number of refreshments. For the larger crystals (>0.05 mm) a significantly higher number was found for the 0.8 Mg/P treatment compared to other treatments and the effect of the (Mg/P) x refreshments interaction proved to be significant as well.

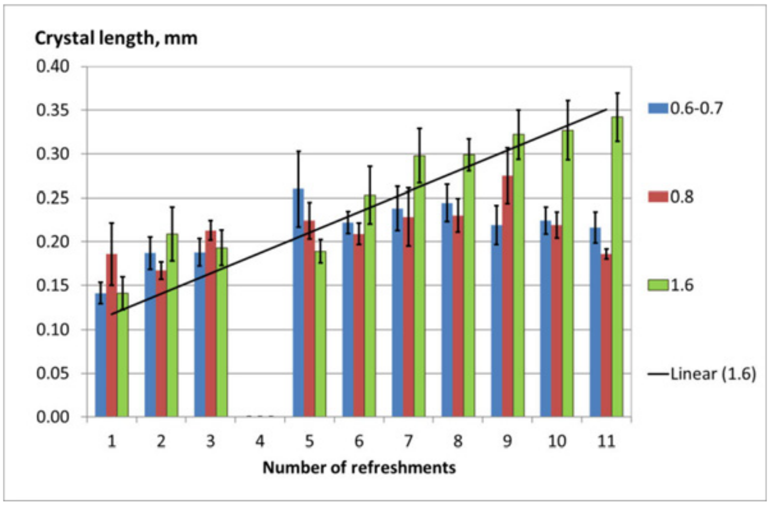


Figure 4.4a *Crystal growth in the settled solid fraction for molar Mg/P ratios of 0.7, 0.8 and 1.6. Average length of crystals > 0.05 mm (bars) with standard error of means (whiskers). The linear trend line is for the Mg/P 1.6 treatment only.*

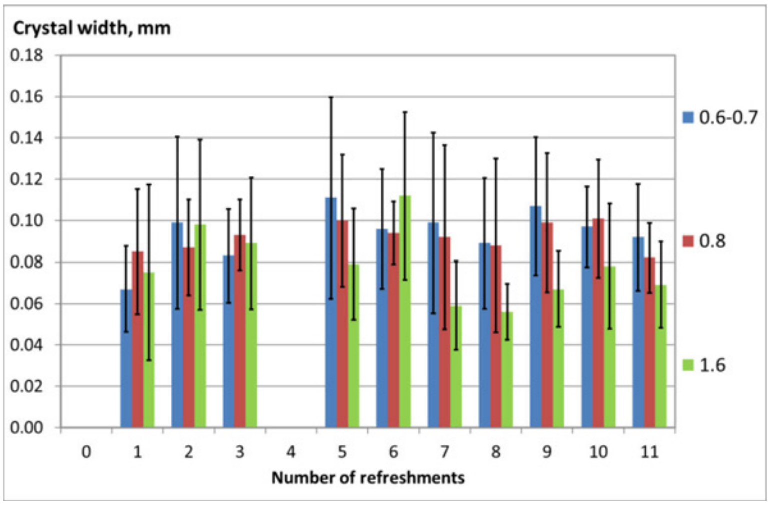


Figure 4.4b *Crystal growth in the settled solid fraction. Average width of crystals > 0.05 mm.*

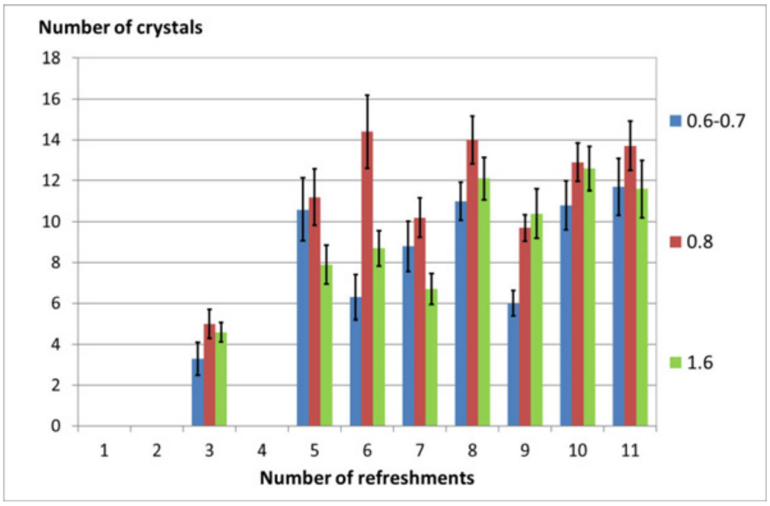


Figure 4.4c *Crystal growth in the settled solid fraction. Average number of crystals > 0.05 mm (bars) with standard error of means (whiskers). The log trend line is for the Mg/P 0.8 treatment only.*

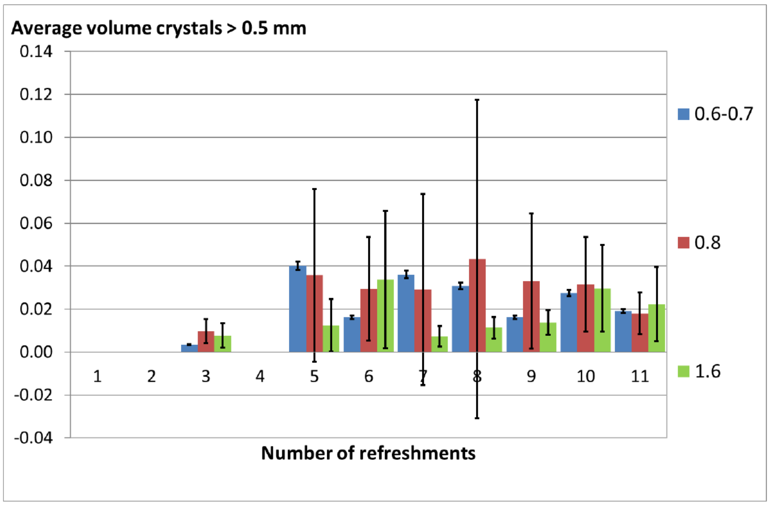


Figure 4.4d *Crystal growth in the settled solid fraction. Average volume of crystals > 0.05.*

The difference in crystal length between the molar ratio treatments can be distinguished after 5 rounds of refreshment. In order to test whether this is due to progressive depletion of Mg or P in the reactors we took samples from the supernatant solution. First we did an acid extraction to analyse all Mg and P present in the supernatant, including solids (Table 4.5). The amounts of Mg and P appeared to be highly variable (compare duplicates). The total amount of Mg present in the supernatant cannot be ranked according to the treatment Mg additions, nor does the amount of P present show any relation with treatments. Therefore we decided to reanalyse the supernatants after centrifuging in order to distinguish between reactants in solution and in solids (Table 4.6).

Table 4.5 *Composition of the supernatant solution after three rounds of refreshment, determined with ICP, after acid extraction with 0.01 M HCl. Untreated liquid fraction for comparison. Individual results of the treatment duplicates are presented.*

Mg/P ratio	pH	K	Mg	P	Mg/P
		mg/kg	mg/kg	mg/kg	-
untreated	n.a.	4331	927	1941	0.61
1.6	9.2	4780	1853	1749	1.35
0.6 - 0.7	8.9	4083	1330	2557	0.66
0.8	8.92	4278	224	411	0.70
1.6	9.26	3963	494	103	6.12
0.6 - 0.7	8.88	4034	1004	2017	0.64
0.8	8.92	4091	1366	2304	0.76

Table 4.6 *Composition of the supernatant solution after three rounds of refreshment, after centrifuging (10.000 rpm), determined with ICP, except for PO_4-P (with SFA). Untreated liquid fraction for comparison (Table 4.5). Individual results of the treatment duplicates are presented.*

Mg/P initial	pH	K	Mg	P	PO4-P	Mg/P end
		mg/kg	mg/kg	mg/kg	mg/kg	
untreated	n.a.	4331	927	1941	0.61	
1.6	8.9	4640	544	10	1.48	69.4
0.6 - 0.7	8.9	4400	2.4	274	249.2	0.01
0.8	8.9	2112	1.6	131.2	127.6	0.02
1.6	9.2	4360	480	11.6	1.32	52.79
0.6 - 0.7	8.9	4280	3.2	284.4	256.4	0.01
0.8	9.1	4360	4.8	159.6	147.6	0.04

The results clearly show that the amount of Mg in solution is almost completely depleted in the treatments with low Mg addition (Mg/P <1.0). Further growth of struvite crystals is probably not possible here due to lack of Mg in solution. In the treatment with highest Mg addition it is the other way around, i.e. the amount of P in solution is depleted. This is even more distinct for the amount of PO_4-P, which is considered to be the driving force for struvite formation and growth. Further growth of struvite crystals is not possible here due to lack of P. Both situations are clearly reflected in the resulting molar Mg/P ratio in solution. While the Mg/P ratio in the supernatant is still 50-70 in the 1.6 molar ratio treatment, it is close to zero in both other treatments. After 7 rounds of refreshment, we also determined the composition in the settled solid fraction (Table 4.7).

The amount of Mg and P in the solid fraction of the no extra Mg treatment (0.6-0.7) shows an increase with a factor 2.5 which can only be attributed to settlement of solids from the added liquid fraction. The ranking of the amount of Mg in the settled solids reflects the Mg addition treatments, but this is not the case for P. There is no clear increase in solid P with more Mg addition. Apparently we did not succeed to effectively stimulate selective struvite formation. We also calculated the molar ratio of Mg and P content of the solid fraction (Table 4.7). This deviates from a molar ratio of 1. Solid fractions appear to be undersaturated or oversaturated thus not pointing on the formation of struvite solely.

Table 4.7 *Composition of the settled solid fraction after 7 rounds. Untreated liquid fraction for comparison (Table 4.5). ΔMg/ΔP is the molar ratio of the difference between settled solids and original liquid fraction ΔMg/ΔP.*

Mg/P initial	pH	K	Mg	P	Mg/P end
		mg/kg	mg/kg	mg/kg	
untreated	n.a.	4331	927	1941	0.61
1.6	n.a.	5247	4492	4676	1.23
0.6 - 0.7	n.a.	5292	2436	4684	0.66
0.8	n.a.	5272	2795	4756	0.75
1.6	n.a.	4998	4342	4740	1.17
0.6 - 0.7	n.a.	5061	2469	4744	0.66
0.8	n.a.	5060	3083	5157	0.76

Although we applied ideal circumstances for struvite growth in animal slurry according to the literature, i.e. continuous refreshment, sufficient Mg (Mg/P=1.6 treatment), pH = 9, we did not produce sufficient larger crystals for feasible harvesting. However, we did not apply high-tech separation of the liquid fraction to prevent interference by organic matter, nor did we continuously mix the reactor, as a consequence of the strategy to recover the solid fraction by settlement. This leaves room for improvement by either applying better separation techniques before struvite production for less interference by organic matter, or by more efficient continuous flow crystallization and separation techniques (Westerman et al. 2010; Shepherd, Burns, et al. 2009a, 2009b; Shepherd, Burns, Raman, et al. 2009). More effective mechanical separation of the liquid fraction, however, has the disadvantage of separation of solid P before struvite formation, unless the original material is acidified to dissolve solid P and increase P content of the liquid fraction. Acidifying the slurry, however, requires acid and after mechanical separation addition of more basic solution, in order to reach the optimal pH of 9 for struvite formation. These extra costs would have to be weighed against the extra struvite yield.

Continuous flow crystallization and separation also tends to be costly, despite the positive results of Westerman et al. (2010). These authors used pig slurry from sows, which tends to have a much lower dry and organic matter content, which possibly explains why the separation of struvite from manure was more successful in their experiments.

In order to test whether crystal growth could continue with time, we incubated the beakers from the sequencing batch experiment after the last round, for 92 days in a 20^{o} C climate room at the laboratory, and repeated the crystal growth measurements (Table 4.8). During incubation a crust was formed on top of the liquid fraction in the beakers. At sampling after 92 days for crystal growth measurements, the crust had completely disappeared. Both crust formation and disappearance shows microbiological activity and thus unstable conditions during the incubation.

The results show no further crystal growth during incubation, crystal length was even reduced from 0.34 mm after the 11th round to 0.19 mm after incubation in the Mg/P 1.6 treatment (Table 4.8, length).

The positive effect of Mg addition (Mg/P 1.6) during the sequencing batch experiment on crystal length was nullified during incubation. The same holds for total crystal number. Both the total number, and the number of crystals <0.05 mm, was significantly reduced during incubation. After incubation the largest number of crystals is found in the 0.8 Mg/P treatment for both size classes.

Table 4.8 *The effect of 92 days of incubation (20^{o}C) on crystal size and number in the sequencing batch experiment beakers. Results immediately after round 11 and after 3 months of incubation. Different letters indicate significant difference (LSD 5%) according to ANOVA analysis per separate variate.*

	Date	Mg/P molar ratio		
		0,.6 - 0.7	0.8	1.6
Length (mm)				
Round 11	2-3-2015	0.22a	0.19a	0.34b
Incubation	2-6-2015	0.22a	0.19a	0.19a
Total number				
Round 11	2-3-2015	328a	329a	371b
Incubation	2-6-2015	165c	196d	149c
Number >0.05mm				
Round 11	2-3-2015	11.7a	13.7a	11.6a
Incubation	2-6-2015	4.4b	8.6c	4.0b

From the sequencing batch experiment we conclude that it is not possible or feasible to produce recoverable Mg-phosphates by stimulating struvite crystal growth in animal slurries without (more costly) high-tech separation techniques. The subsequent incubation experiment shows that crystals do not grow with time, but even shrink under unstable conditions without constant or frequent addition of the constituting elements.

4.2 Results on pilot scale

Laboratory studies were further evaluated through testing on pilot scale (Pilot). The design of the Pilot is given in section 2.3. The results of the Pilot are visualised in figures 4.5a, b and c. The tests on P recovery from the liquid fraction (the Mg approach) were carried out in the period August 2014 – February 2015. In the period August – October 2014 individual elements of the pilot were tested, adjusted and/or improved. From the end of October samples of different flows were taken to monitor the performances of individual processes. From the very first results it was observed that a too limited growth of crystals hindered the P recovery. Several factors were thought to be involved: the presence of organic matter, the molar ratio of Mg to P and the activity of P, Mg and NH_4-N in the liquid fraction. Of these, the molar ratio of Mg to P was thought to be the most simple adjustable parameter.

The effect of addition of $MgCl_2$ on P recovery was therefore tested. For this, three levels of $MgCl_2$ (32% solution, technical grade) were added: no addition, 17 litre and during the test phase lowered to 11 litre $MgCl_2$ per m^3 liquid fraction from low-tech separation of co-digested pig slurry. Low-tech separation was performed by sieving the digestate over 350 µm.

In Figure 4.5 the P content of the separated digested liquid fraction (inflow Fliquid) and the P content in the final product (RFSsolid) and separated liquid suspension (RFSliquid) are shown for each level of Mg addition (17, 11 and zero $MgCl_2$ respectively). In Annex 5 the average of measured parameters are given for each Mg level.

The average P content of the product after addition of Mg did not differ much from the average P content without addition (Figure 4.5 and Table 4.9). The P content of the product (RFSsolid), after addition of 11 litre $MgCl_2$ per m^3, was slightly higher than from the reference without Mg addition, however the size of the struvite crystals were smaller. There is an indication that crystals were lost by using the belt sieve. Crystal sizes of ingoing liquid fraction after storage in the buffer tank before separation had lower values for length and width than outgoing wet cake (RFSsolid). During the Pilot the flow was not measured, and therefore no clear mass balances and separation efficiency could be calculated. From visual observations at the Groot-Zevert site it was concluded that with Mg addition the amount of separated product (RFSsolid) was slightly larger than without Mg addition, but the dry matter content did not change much due to Mg addition (Table 4.9). The main problem is that no clear crystal growth was observed. Without crystal growth it is not possible to increase the P content of the final product substantially. But laboratory studies (4.1.4) to increase crystal size did not yield substantial progress. The liquid fraction approach was therefore amended by the solid fraction approach.

Table 4.9 *Molar ratio of Mg and total-P, dry matter content, length and width of struvite crystals and P content of the inflow of the struvite reactor (Fliquid), intermediate liquid fraction after storage in the buffer tank before separation (R2) and the outflow (RFSsolid and RFSliquid).*

$MgCl_2$-addition,	**Source**	**Molar Mg/P**			**Dry matter, %**			**Length, mm**			**Width, mm**			**Total P, mg P/kg**		
L 32% solution		**Mean**	**SD**	**N**	**Mean**	**SD**	**N**	**Mean**	**SD**	**N**	**Mean**	**SD**	**N**	**Mean**	**SD**	**N**
0	Fliquid	0.66	0.09	13	5.04	0.41	5	*	*	*	*	*	*	1776	457	13
	R2	0.73	0.28	12	5.29	0.18	6	0.19	0.07	7	0.09	0.02	7	1947	284	12
	RFSsolid	0.76	0.17	12	11.6	0.81	6	0.25	0.06	10	0.13	0.06	10	2384	252	12
	RFSliquid	0.75	0.25	12	2.05	0.64	6	*	*	*	*	*	*	904	384	12
17	Fliquid	0.66	0.16	6	4.67	1.59	3	*	*	*	*	*	*	1310	415	8
	R2	1.70	0.32	8	6.01	0.13	5	*	*	*	*	*	*	1700	164	8
	RFSsolid	1.54	0.27	8	12.38	0.33	5	0.31	0.11	8	0.18	0.08	816	2201	144	8
	RFSliquid	2.01	0.41	8	3.29	0021	5	*	*	*	*	*	*	914	124	8
11	Fliquid	0.65	0.06	17	*	*	0	*	*	*	*	*	*	1748	361	17
	R2	1.23	0.31	17	*	*	0	0.13	0.05	13	0.08	0.03	13	1849	209	17
	RFSsolid	1.14	0.21	17	*	*	0	0.21	0.09	16	0.12	0.06	16	2568	470	17
	RFSliquid	1.32	0.39	17	*	*	0	*	*	*	*	*	*	956	250	17

With:

Fliquid = liquid fraction of the outflow of the screw press separator with 700 µm (3/11/2014-11/12/2014) or 500 µm sieve (12/12/2014-24/01/2015));

R2 = liquid fraction after storage in the buffer tank before separation;

RFSsolid = solid Mg~P product after separation over a rotating fabric belt separator (three parts: 80, 120 and repeated 120 µm), alternative name Wet Mg~P cake;

RFSliquid = liquid fraction with reduced P content after separation over a rotating fabric filter sieve (three parts: 80, 120 and repeated 120 µm).

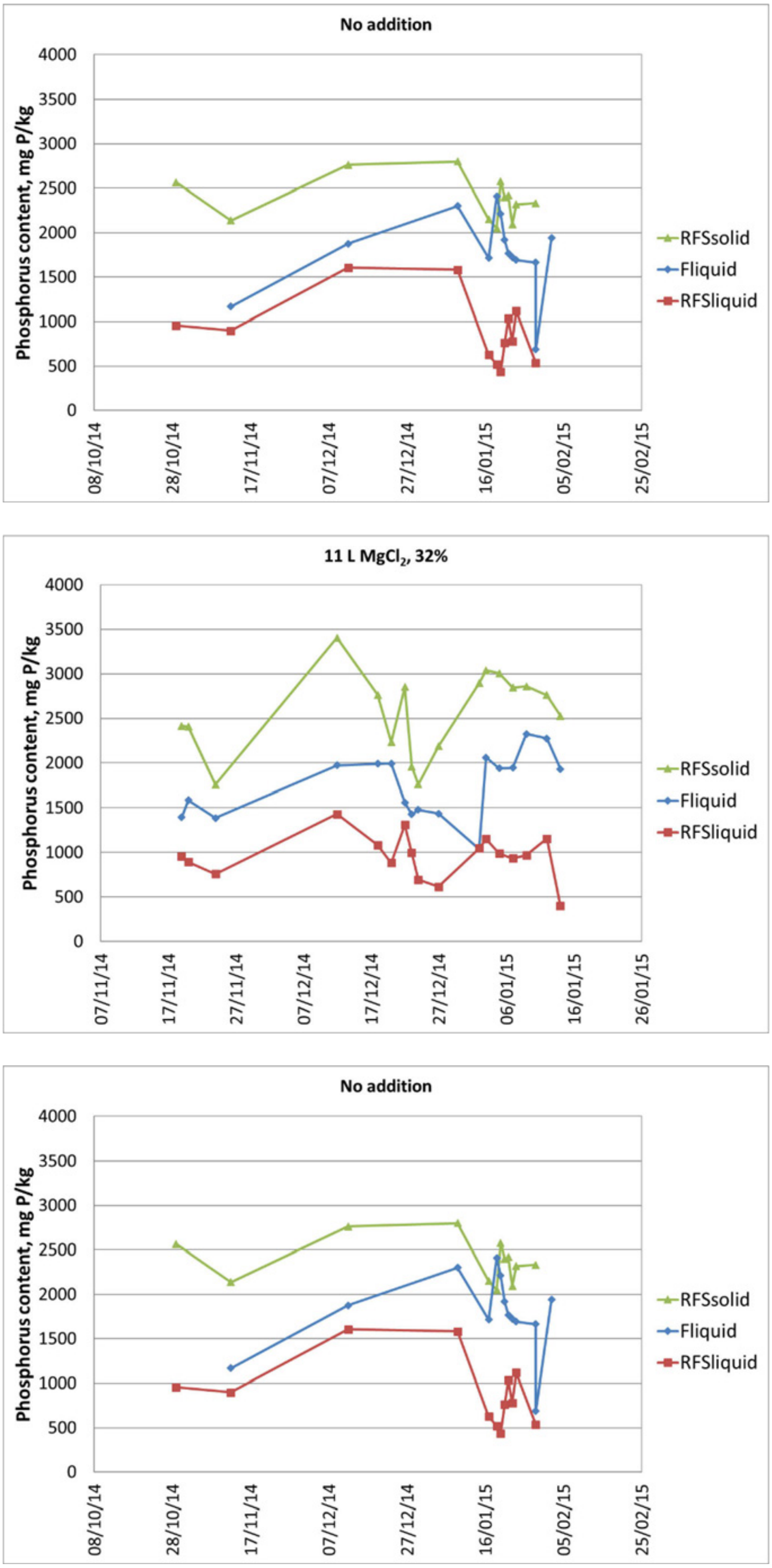


Figure 4.5 *Measured P content over time of the liquid fraction of digested manure as input (Fliquid) and final products the solid P product (RFSsolid) and the remaining of liquid fraction separated from the solid product (RFSliquid) for three levels of $MgCl_2$ addition (17, 11 and zero litre of a 32% $MgCl_2$-solution per m^3 liquid fraction of digestate).*

5 P recovery from solid fraction, laboratory studies

In order to determine the phosphate recovery from the solid fraction of manure and digested manure, several experiments have been carried out. At first, the acid requirement was determined to reduce the pH to a required level. Based on this information the P release from the solid fraction was determined at different pH and at a fixed solid fraction – solution ratio. The release of P is an indicator of the potential recovery of phosphate. Since manure exists of different fractions also for four fractions separately the acid requirements and P release was determined. Finally, for all manure and digested manure samples, the actual P recovery was determined including the composition of the produced calcium phosphate.

In this chapter the results of the following laboratory experiments are described:
1. acid requirement by means of a titration curve
2. the P release into solution at fixed pH's
3. acid requirement and P release of fractions of manure
4. the P recovery from the solution at fixed pH's
5. the composition of the end product

5.1 Acid requirement of the solid fraction by means of a titration curve

The titration curves (par. 2.2.4) were determined to assess the acid requirement needed to lower the pH to designated values. This information serves experiments to determine the P release as a function of pH under condition of equal solid-liquid ratios for all samples of manure and digestate for a specific chosen pH (pH=6). Figure 5.1 shows the titration curves of manure (M) and digestate (D) samples of fresh solid fraction obtained after centrifugation at 3500 rpm. Manure (M1) and digestate (D1) of farm number 1 was sampled twice. Results of the second sampling are shown in the figures for manure and digestate respectively as M8 and D8.

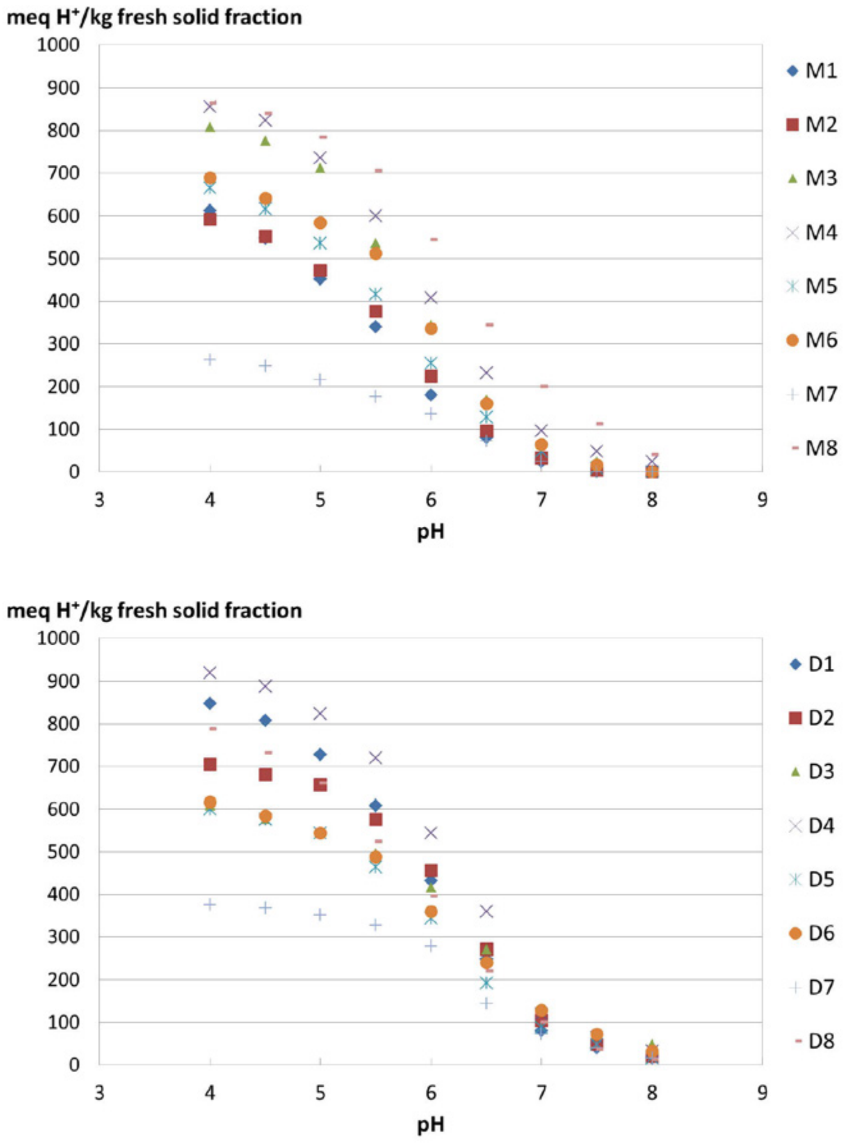


Figure 5.1 *Amount of acid (meq H$^+$/kg fresh solid fraction) needed to lower the pH of solid fraction of manure or digestate to a designated pH.*

The buffer capacity of the solid fraction of manure and digestate is relative low between pH 8 and 7 and below pH 5: i.e. small quantities of acid cause relatively large changes in pH. The buffer capacity of dairy slurry (D7; **+** markers in Figure 5.1 and following figures) is below pH 6 much smaller than the buffer capacity of pig slurry.

To lower the pH to 4 about 600-900 meq H$^+$ per kg fresh solid fraction is needed. The acid requirements in digestate are often higher compared to manure, due to the fact that the initial pH of digested manure is higher compared to manure. On average, the acid requirement of digestate is 27% (-26% to +86%) higher compared to manure to reach pH 5.5 and 7% (-25% to +42%) higher to reach pH 4 for both pig and cattle manures and digestates. For manure and digestates from pigs these values for pH 5.5 and pH 4 are respectively 40% (-7 to + 86%) and 12% (-25 to 42%) and for cattle (one location) -5% and -10%. The acid requirement will depend on the required P recovery. The manure of dairy cattle was pre-treated (hydrolysed) which explains the somewhat lower acid requirement.

5.2 Release of phosphate from the solid fraction of manure or digestate

The degree of P recovery strongly depends on the degree of solubilisation of P from the solid fraction. For each solid fraction of manure or digestate, depending on the results of the titration experiments (section 5.1) 7 - 9 subsamples were taken and each subsample was brought to a range of pH values. A solid fraction – demi water (included acid) ratio of 2 (w/v) was used. After lowering and stabilisation of the pH, samples were centrifuged at 3500 rpm during 10 minutes and thereafter the ortho-P concentration was measured in the supernatant. Results are shown in Figure 5.2. The P concentration of pig slurry increased to values between 1500 and 2000 mg P L^{-1}. At pH below 5 the P concentration did not increase further and was considered as stable. The P release concentrations of the solid fractions of pig slurry were quite similar above pH 5.5.

The P release from the solid fraction of dairy cattle slurry at different pH (M7 in Figure 5.2) is low compared to the solid fraction of pig slurry, due to the lower P content of cattle slurry (Table 3.1).

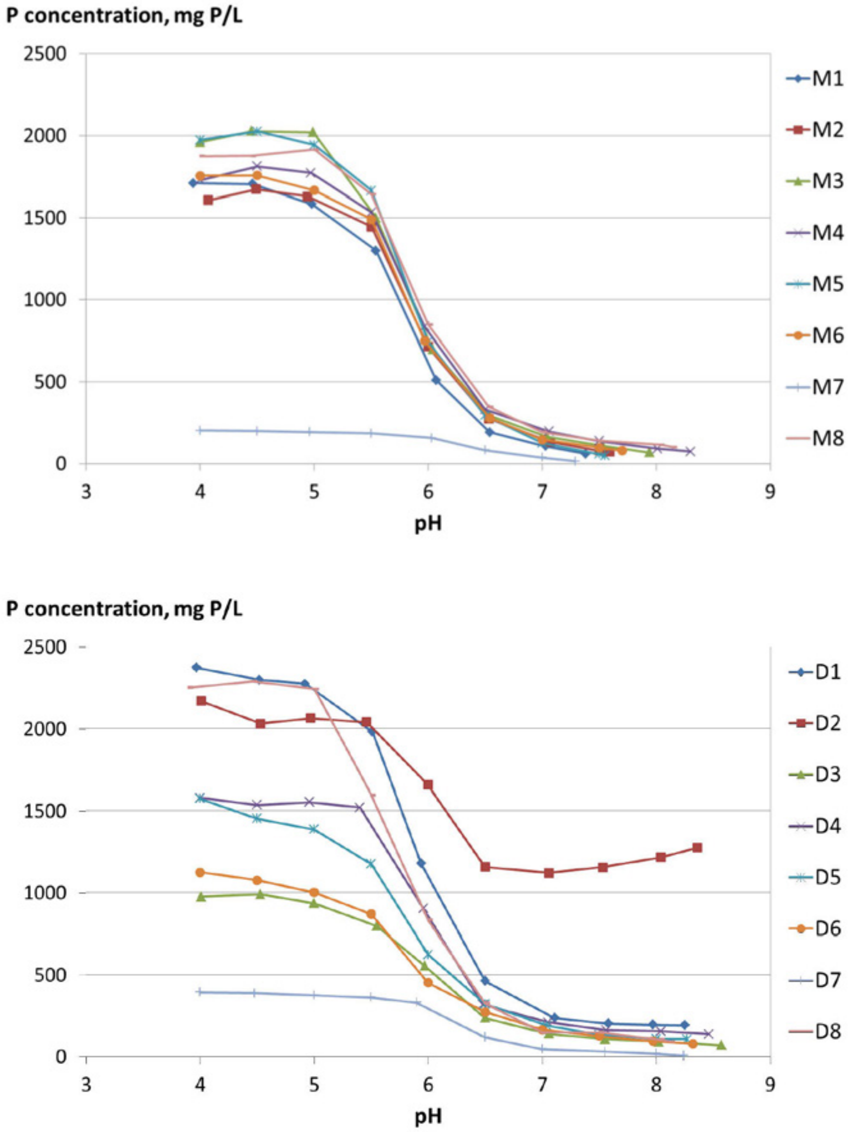


Figure 5.2 *Measured P concentration in solution for different pH values after the acidification of the solid fraction (top manure samples, bottom digestate samples).*

The variation of the P concentration of solid fractions of digestate at lower pH's is much larger than the concentrations measured for solid fraction of non – digested manure (Figure 5.2). This is mainly caused by the co-digestion material (feedstock) used. In the Netherlands it is obligatory to digest at least 50% manure besides co-digesting feedstocks. One of the digested manure samples (D2) has already a very high P release at pH 7-8.5, which is probably caused by the different co-digestion feedstock used. Use of co-digestion feedstock has also increased the P concentration of co-digested cattle slurry (D7) compared to none digested cattle slurry (M7).

In Figure 5.3 the P release is expressed in mg P per kg separated fresh solid fraction of manure or digestate and in Figure 5.4 as kg P_2O_5 per 1000 kg manure or digestate.

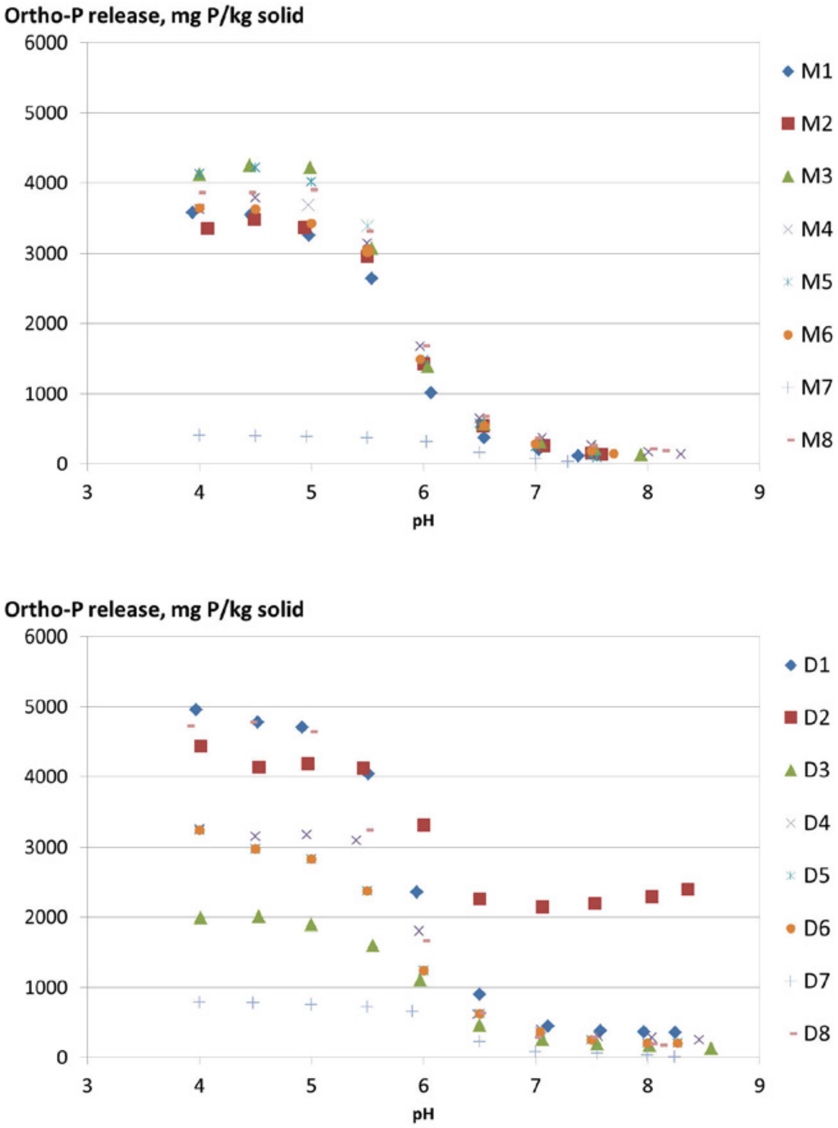
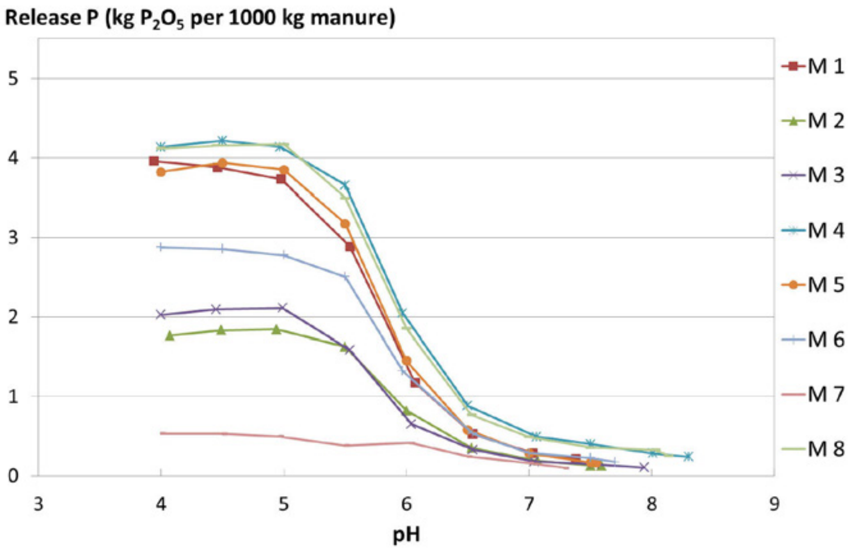


Figure 5.3 *P release of the solid fraction into solution expressed in mg P per kg solid material (centrifuged at 3500 rpm) as function of the final pH in solution (top manure samples, bottom digestate samples).*



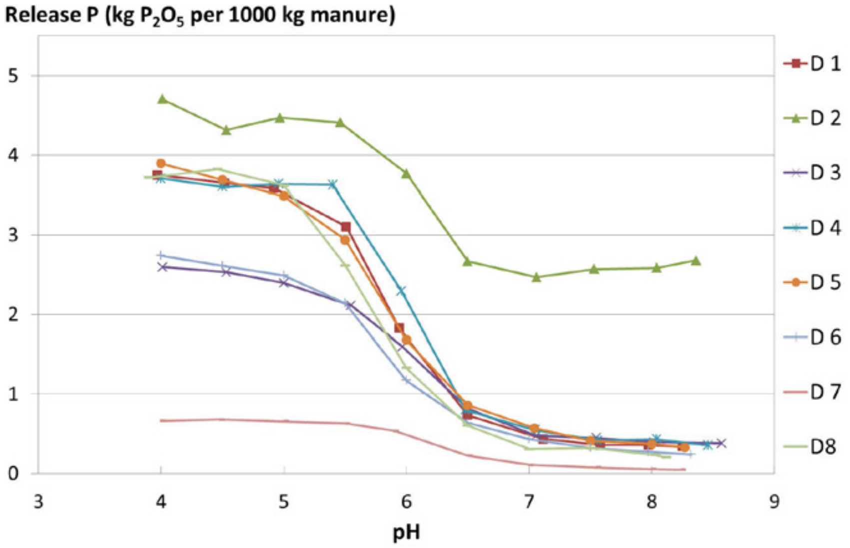


Figure 5.4 *P release into solution expressed in kg P_2O_5 per 1000 kg manure (top) or digestate (bottom) as function of the pH.*

The differences in P release of pig slurries (Figure 5.3 and 5.4 top; samples M1 to M7) are relative small compared to their digestates (Figure 5.3 and 5.4 bottom; samples D1 to D7). Below pH 6.5-7 the P release increases remarkably with increasing acidity. The release of P per kg solid fraction of digestate differs remarkably from pig slurry. The P release (mg/kg solid) of co-digested material can be higher (e.g. D1, D2) or lower (e.g. D3, D6) than the corresponding manure (M1, M2, M3 and M6, respectively), indicating that some of the co-digestion feedstock has a lower amount of soluble P per kg solid material. One of the digestates (D2) had already a high P release at alkaline pH (7-8.5). In this situation a co-digestion feedstock was used with highly soluble P components in the whole pH range (pH 4 – pH 8.5), but the feedstock is unknown. The release of P in dairy slurry (M8) or its digestate (D8) is low compared to co-digested pig slurry as already said due to the lower P content of dairy slurry (Table 3.1). However the relative fraction which is released from dairy slurry is comparable with releases of pig slurries. This absolute amount of P that is released from the solid fraction is the amount of P that can be potentially recovered from manure or digestate.

The fraction of released P from manure and digestate at different pH is shown in Figure 5.5. For pig manure about 75-83% was released at pH below 5 and even at pH 5.5 about 60-70% of the P was released. At pH 6 the P release varies between 23 and 40%. In dairy cattle slurry (one sample ; M7) the potential P recovery is much lower (max 50%) and the curve is rather flat compared to pig slurry. Although the absolute P release varies between the different pig slurry digestates (see figures 5.2, 5.3

and 5.4), the potential P recovery as a percentage of total P varies much less. Digestate D8 has the highest potential recovery. This digestate came from the same farm as digestate sample D1. Samples D8 and D1 differ in age, D8 was taken directly from the biogas reactor, D1 was a digestate that had been stored during ~4 months. There is a difference for this location in the ratio released P/total P in manure and the ratio released P/total P in digestate. At low pH (pH < 5) about 20% more P was recovered from manure than from digestate. Probably, the type of co-digestion feedstock is responsible for the difference, because the potential P recovery of fresh pig slurry (M8) did not differ much from the earlier sampled pig slurry (M1).

To prevent emission of H_2S often iron compounds are added during the digestion process. For three locations the Fe content was measured both for manure and its digestate. No differences in Fe content were found between samples M1 and D1 and between M8 and D8. Sample D2 had 4158 mg Fe/kg compared to 3989 mg Fe/kg in M2, clearly indicating an addition of iron compounds. The formation of iron phosphates may have caused the lower P release from solid fractions of digestate D2 (40% at pH 4, Figure 5.5) than from manure M2 (70%).

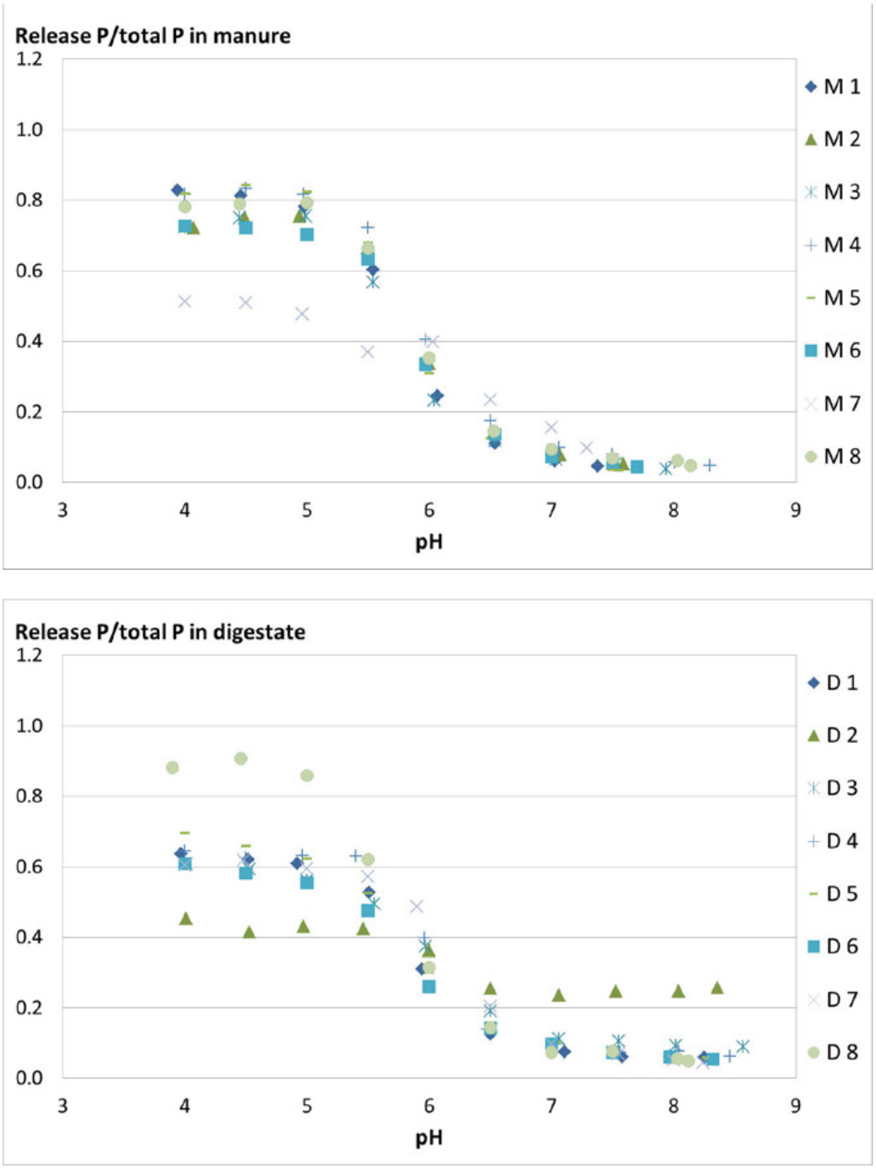


Figure 5.5 *P release into solution as a fraction of total P in the ingoing manure (top) or digestate (bottom) as function of the pH.*

If the release of P is related to the amount of P in the fresh solid fraction of manure, sometimes a higher than 100% P release was calculated at pH < 5 (Figure 5.5) due to variation caused by sampling for experiments and analyses, and analytical deviations caused by laboratory procedures. The fresh solid fraction was produced by centrifuging at 3500 rpm. This method is compared with results from a decanter centrifuge. The potential P recovery is much higher than obtained by the sieve method. The results clearly show that removing finer particles (< 106 μm) from the liquid fraction into the solid fraction, will increase the potential recover P.

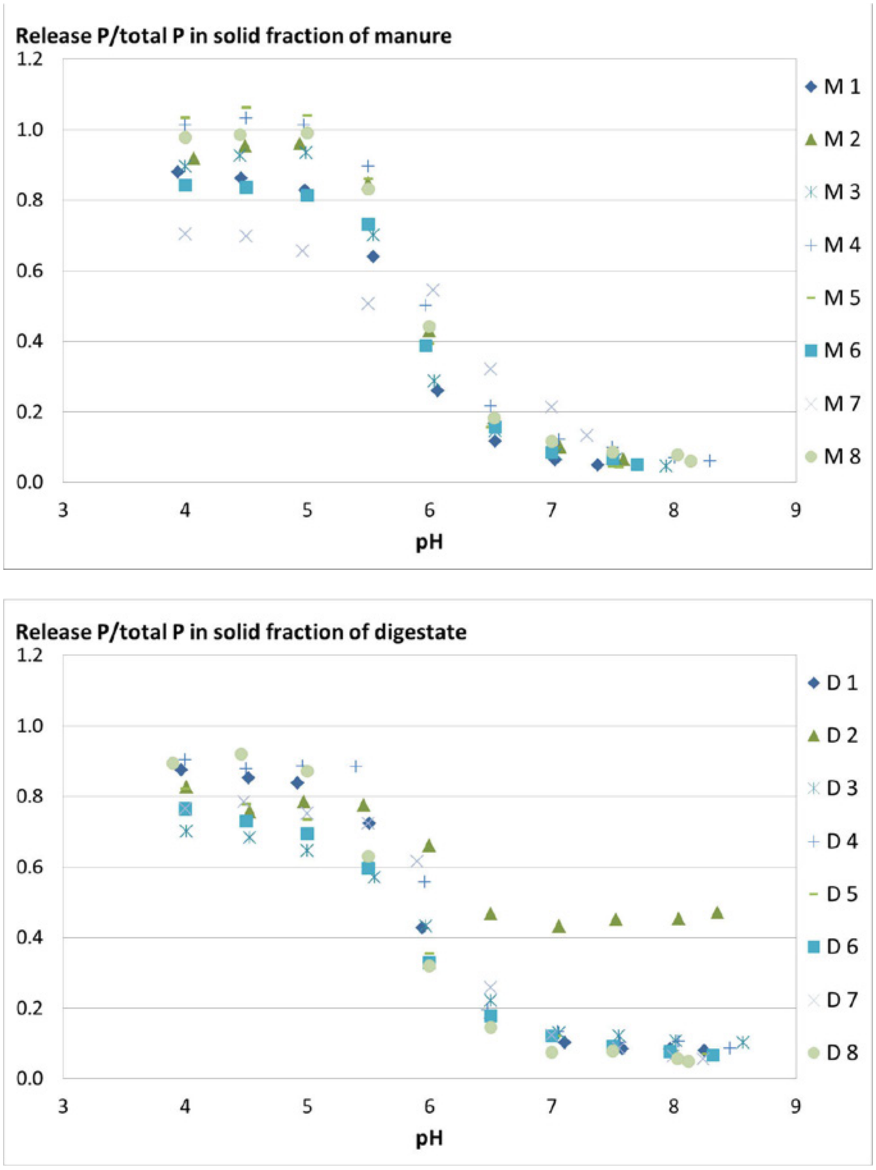


Figure 5.6 *P release into solution compared to the total amount of available P in the solid fractions of manure (top) or digestate (bottom) as function of the pH.*

5.3 Acid requirement and release of phosphate of fractions of manure

This paragraph gives results of fractionation of one sample of pig slurry into four sieve fractions of ≤ 106 μm, 106 – 250 μm, 250 – 500 μm and > 500 μm. These fractions were obtained by sieving pig slurry over different mesh sizes[10]. The mass balance of this sieve procedure was determined. In percentage the sieve fractions ≤ 106 μm, 106 – 250 μm, 250 – 500 μm and > 500 μm accounted for 51%, 5%, 7% and 37% of total mass. So half of the pig slurry passed the 106 μm sieve and about a third did not pass the 500 μm sieve. The acid requirement was determined by titration after re-suspending each sieve fraction with demi-water to a total volume of 1 L.

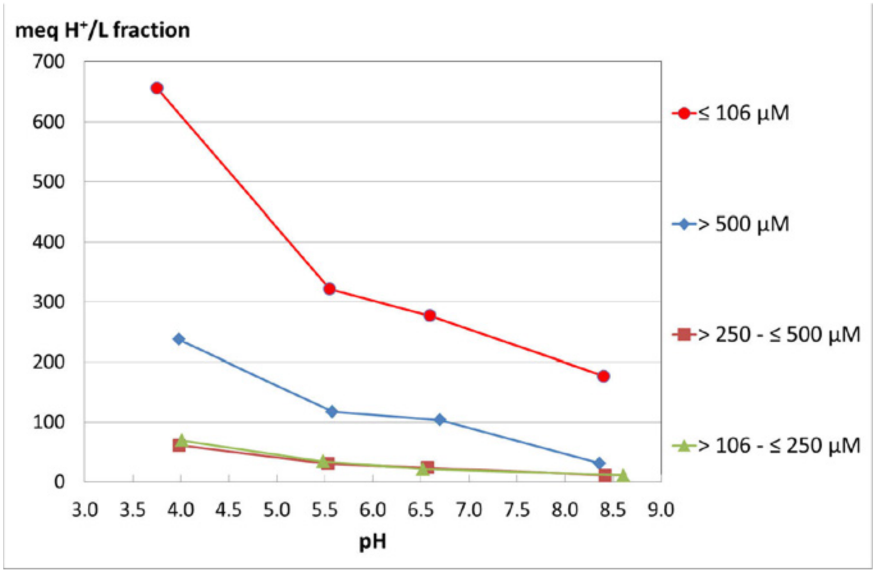


Figure 5.7 *Amount of acid (meq H^+/L) needed to lower the pH of four sieve fractions of pig slurry diluted to 1 L.*

The finest sieve fraction of ≤ 106 μm needed more sulphuric acid than the largest sieve fraction of > 500 μm. Both sieve fractions needed more acid than the sieve fraction > 250 - ≤ 500 μm and > 106 μ - ≤ 250 μm. This is directly linked with the much larger volumes of the largest and smallest sieve fractions which were diluted up to 1 L. If the acid requirement is expressed per litre of undiluted sieve fraction then the smallest sieve fractions require the largest quantities of acid (Figure 5.6).

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[10] One litre of homogenised pig slurry was sieved over 500 μm, the solid fraction (> 500 μm) was the first fraction. Remaining liquid fraction was sieved over 250 μm leading to a second fraction of 250 – 500 μm and a second liquid fraction. This second liquid fraction was then sieved over 106 μm. This last sieving resulted in two fractions: 106 – 250 μm and ≤ 106 μm.

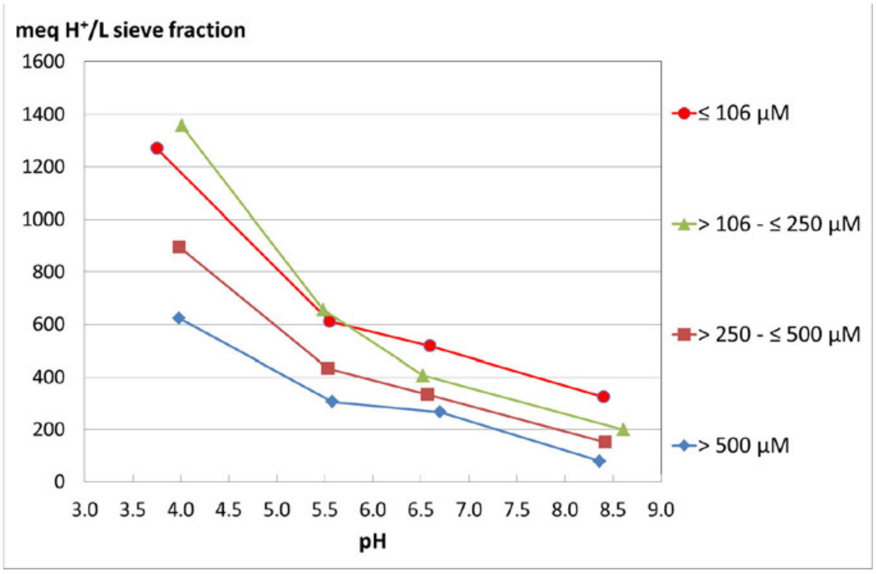

Figure 5.8 *Amount of acid (in meq H^+/L undiluted pig slurry fraction) needed to lower the pH for four sieve fractions of pig slurry.*

By acidification the quantity of potentially available phosphorus increased from in total 426 to 2709 mg P (Figure 5.9). All fractions released more P with a decrease of the pH. The finest sieve fraction showed however no further increase in P release by acidification from pH 5.5 to pH 3.9 (Figure 5.9). The coarser fractions still released more P at pH 3.9 than at pH 5.5 (Figure 5.9). We assume that in the finest sieve fraction a complete dissolution of mineral P was reached at pH 5.5 while in coarse fractions the inorganic P was more embedded.

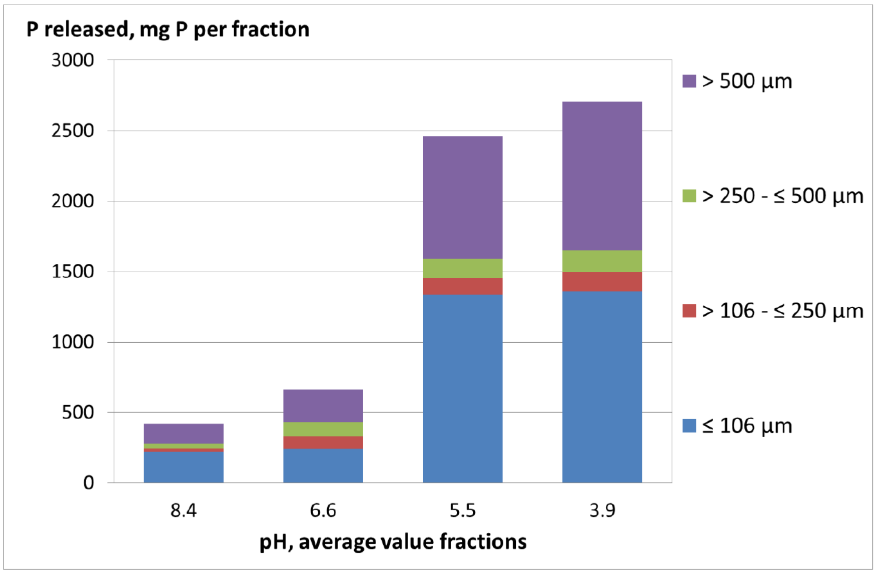

Figure 5.9 *Averaged phosphorus recovery (mg P per fraction) for four sieve fractions at four pH values of pig slurry.*

The quantity of acid required to recover phosphorus is given in Figure 5.10. This quantity is expressed as the molar ratio of H^+ to P. The finest fraction (≤ 106 µm) required twice as much acid as the coarsest fraction (> 500 µm) to release the same amount of P. Fractions between 106 and 500 µm required the least acid.

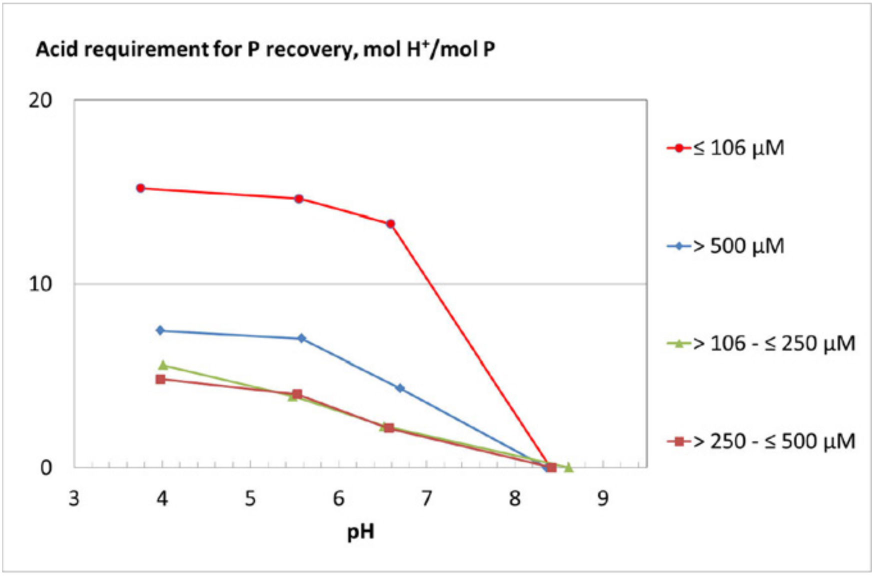

Figure 5.10 *Acid requirement for P recovery (in mole H/mole P) for four sieve fractions and four averaged pH values of pig slurry.*

In Figure 5.11 the percentage phosphorus released from each fraction is given as percentage of total P in pig slurry. Up to 50% of the phosphorus recovered was released by the finest fraction, about 40% by the coarsest fraction while the fractions between 106 – 500 µm only contributed to 10% of the released P. This results shows that at low recovery requirements (<40%) low-tech separation technique (relative low costs) can be used to collect the coarse fraction for P recovery.

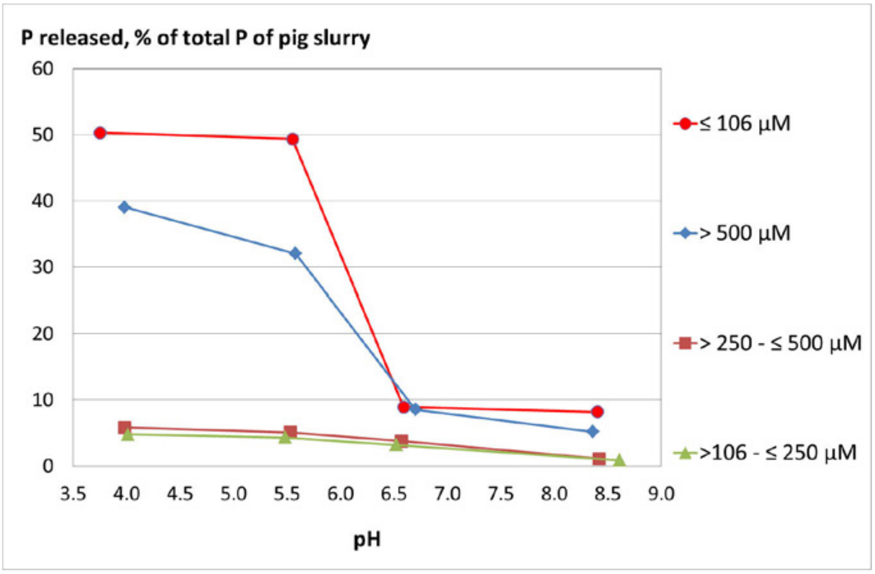

Figure 5.11 *Phosphorus recovery (mg P per fraction) for four sieve fractions and four averaged pH values of pig slurry*

5.4 Amount of P recovered from the solid fraction

The actual amount of P recovered from the solid fraction was analysed by destruction of fresh material of precipitated calcium phosphate (2.1.2 and 2.3.2). As a result of a fierce reaction of some samples with mineral acid (used for the destruction) these required a second analysis. For this second analyses only dried material of the calcium phosphate was available and used for the analysis. The quantity of dried material available was limited, however. The data presented are based on both analyses excluding data affected by analytical errors.

The P recovery of the collected calcium phosphate was determined for each solid fraction of the resource materials manure and digestate at 4 pH values. The recovery is expressed as a percentage of the ingoing total P in the solid fraction. Due to limited material for analysis, recoveries were semi-quantitative, shown in recoveries that were sometimes higher than 100% (Figure 5.12). Figure 5.13 shows the average P recoveries and standard deviation for pig slurry and digested pig slurry.

Virtually all ortho-P released by acidification to pH 5 was recovered. With an increase of the pH the P recovery declined. For the solid fraction of manure the recovery declined from roughly 100% at pH 5 to 30% at pH 6.5, mainly because less P was released at higher pH values. The recovery from the solid fraction of digestates was lower compared to the non-digested slurries. At pH 5 roughly 80% was recovered to roughly 25% at pH 6.5. Again, the lower recovery can possibly be attributed to the co-digestion feedstock and the use of iron compounds during biogas production. Overall the variation between recoveries from solid fraction of digestate is larger than from solid fraction of manures (Figure 5.12), which is comparable with the result of the P releases (Figure 5.6).

Figure 5.14 gives a summary of the fate of phosphorus of the each step of the ‘acid-base approach’ (in percentages) starting from 100% in the original slurry or digested slurries. Due to the high tech separation technique most of the P accumulates in the acid fraction.

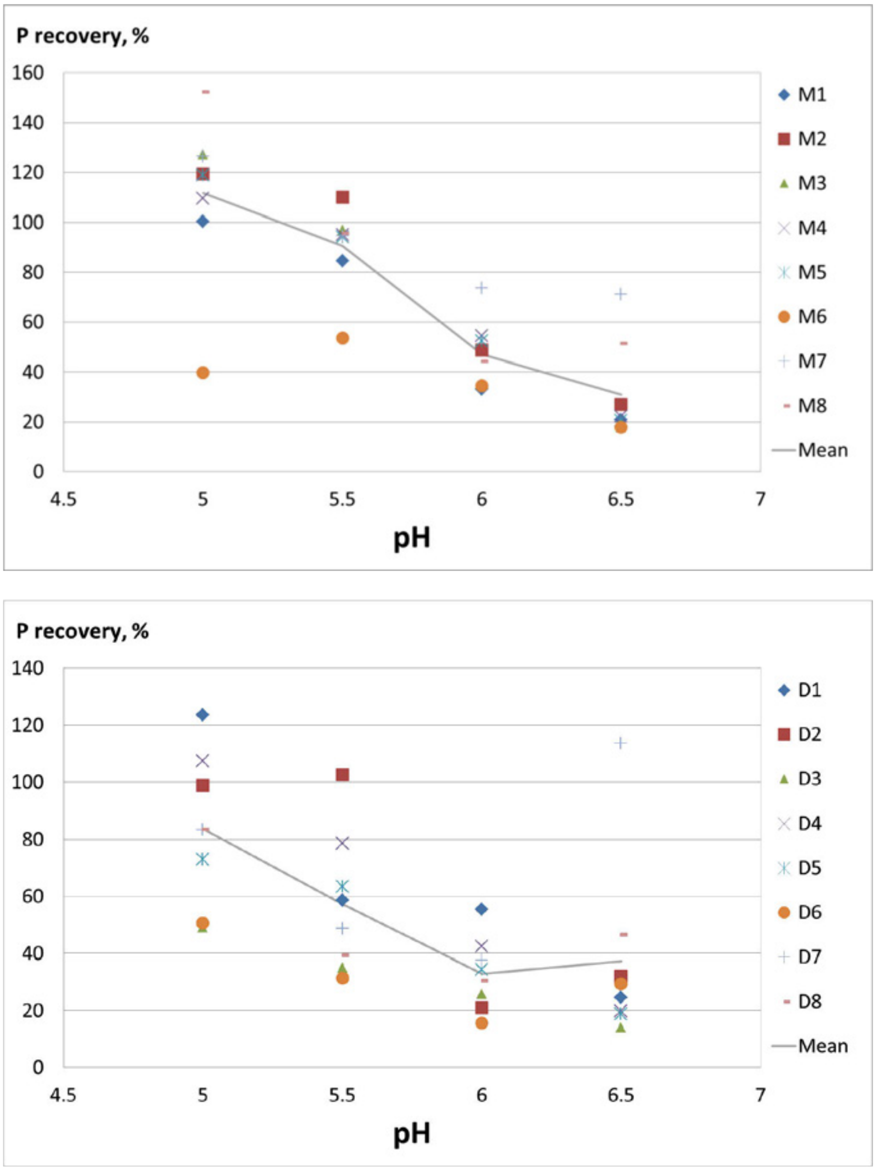

Figure 5.12 *The recovery of P in the collected product (at 4 pH values) as percentage of the quantity of P present in the solid fractions of manure or digestate.*

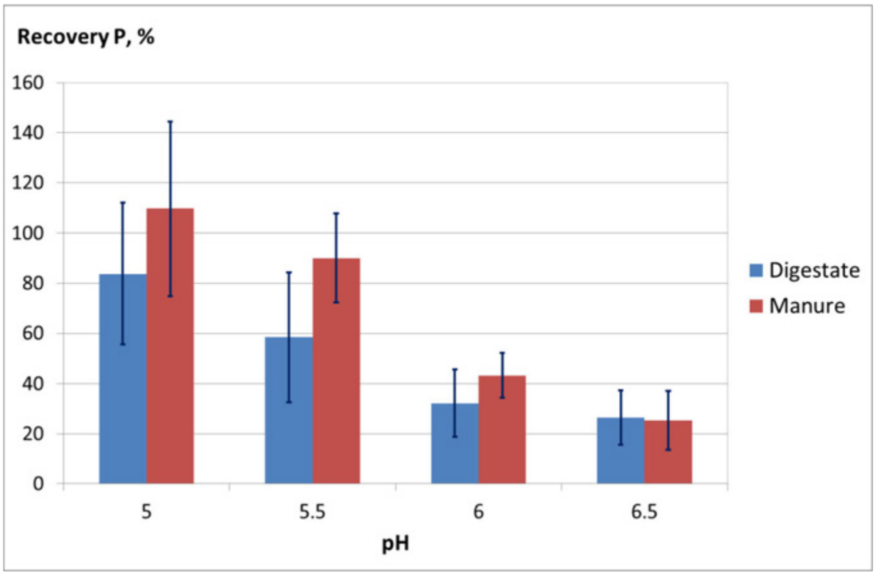

Figure 5.13 *Average P recovery in the collected product at 4 pH values compared to the P content of solid fraction of manure or digestate of dairy cattle (top, one sample) and pig (bottom, seven samples).*

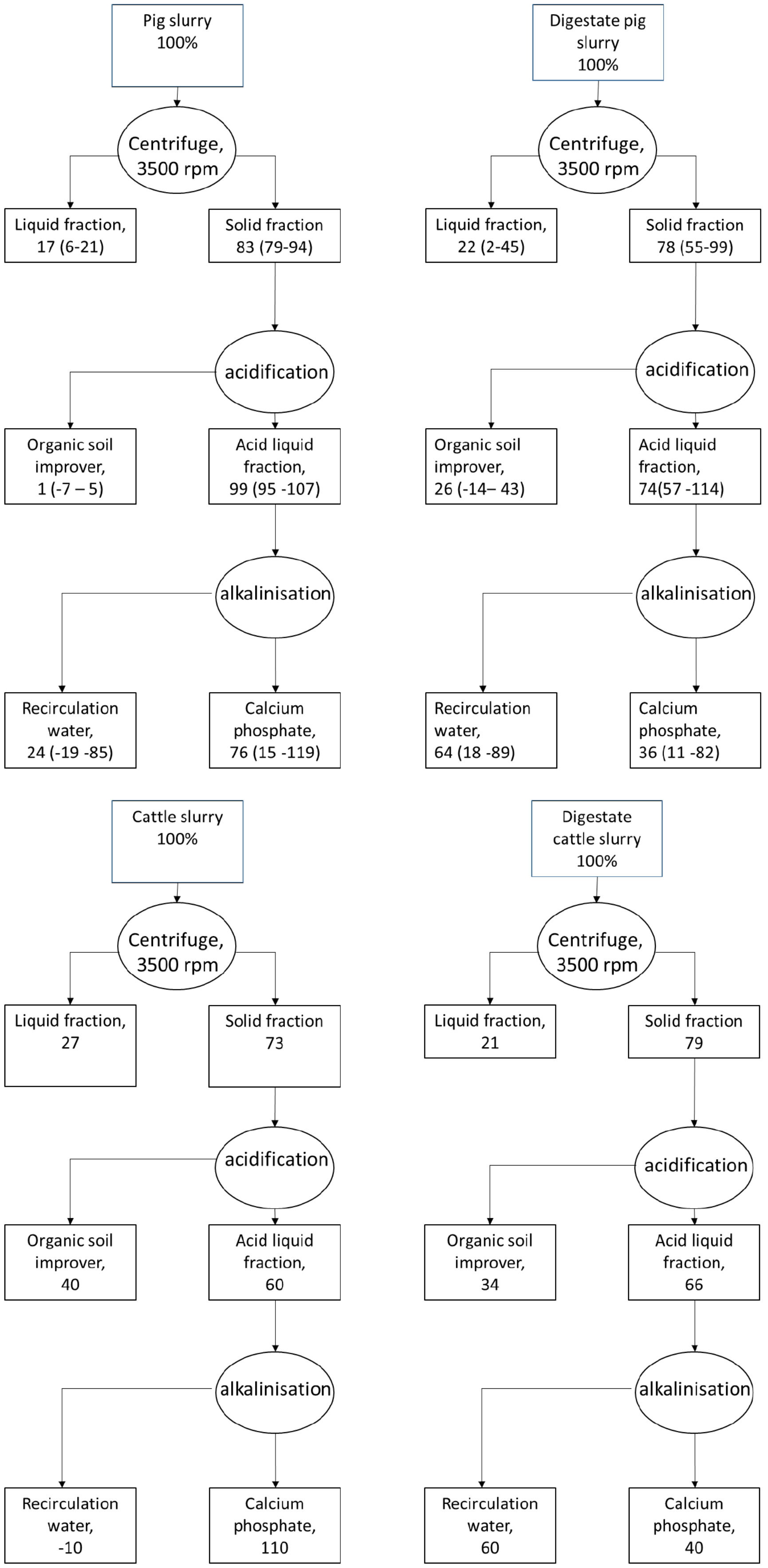

Figure 5.14 *Average recovery of phosphorus after centrifugation and acid-base treatment in supernatant and pellet as a percentage of phosphorus in pig slurry (top left), digested pig slurry (top right), dairy slurry (bottom left) and digested (bottom right). The range (minimum and maximum) is given between brackets. Number of observations of pig slurry is six and dairy slurry one.*

5.5 Required amounts of acid and base

Based on the experiment to determine the actual P recovery (Section 5.4), the average amount of acid required to lower the pH to target values of 5, 5.5, 6 and 6.5 was calculated and is presented in Table 5.1. The table also shows the average amount of base needed to increase these four pH's to the target value pH 8 needed for recovery of calcium phosphate. Results are differentiated to type of fertilising products digestate and manure and to animal species: dairy cattle and pig.

A lower pH requires a larger amount of acid. On average the solid fraction of digestate requires more acid than the solid fraction of manure. Solid fractions of digestate or slurry from pigs require more acid than solid fractions of digestate or manure from dairy cattle.

The amount of base needed to increase the pH after acidification to the target pH for recovery of calcium phosphate depends on the previous targeted values for acidification. The lower the pH after acidification is, the higher the required amount of base becomes. Again solid fractions of digestate and slurry of pigs require more alkalinity than those for dairy cattle. Once again, the dairy cattle manure has been processed through a hydrolysis step. If this hydrolysis step exerts an effect on both requirements for acid or base, is not known.

Table 5.1 *Average requirement with standard deviation for acid (H_2SO_4) of the fresh solid fraction to lower the pH to four given target values of the pH and the average requirement of base ($Ca(OH)_2$) with standard deviation to increase the target value for calcium phosphate recovery of 8.*

Fertiliser	Animal	pH	Acid requirement		Base requirement	
			Average	Standard deviation	Average	Standard deviation
			meq H+/kg fresh solid fraction		meq OH-/kg fresh solid fraction	
Digestate	Dairy cattle	5	349.7	*[1]	150.5	*[1]
		5.5	327.7	*	150.8	*
		6	279.8	*	137.2	*
		6.5	142.9	*	123.8	*
	Pig	5	662.2	113.4	238.0	64.2
		5.5	568.7	91.2	189.8	49.4
		6	431.7	71.8	150.5	34.9
		6.5	265.7	62.1	120.3	31.6
Manure	Dairy cattle	5	215.1	*	241.8	*
		5.5	183.4	*	233.4	*
		6	135.2	*	213.7	*
		6.5	72.0	*	131.6	*
	Pig	5	620.6	140.4	304.7	72.6
		5.5	512.4	143.3	244.0	93.5
		6	336.2	133.3	191.8	90.2
		6.5	173.7	90.0	170.6	90.5

[1] * one sample, standard deviation cannot be derived.

5.6 Composition of the calcium phosphate product, laboratory experiment

The results of research described in the previous paragraphs served to test the proof of principle of the production of calcium phosphate from solid fractions of manure and digestate. In this paragraph we present results on the composition of this calcium phosphate product. To determine this composition, we processed in the laboratory a larger volume of solid fraction to produce for enough material for chemical identification purposes. For this purposed we used solid fractions of M1, D1, M2, D2, M8 and D8. Again, sample material M1, D1, M8 and D8 origins from the same location: Groot Zevert. The differences are that M8 and D8 are samples of fresh manure and fresh digestate while M1 and D1 origins from stored and aged materials.

The procedure of the acid – base approach (acid to pH 5 and then return with base to pH 8) was followed. After addition of the base to obtain pH 8, calcium phosphate was formed and this product was collected by centrifuging at 3500 rpm during 10 minutes. The calcium phosphate was analysed on contents of dry matter, organic matter, total P, Ca, Mg, K, $CaCO_3$, Al, Fe, Cd, Cr, Cu, Ni, P, Pb and Zn following the analytical procedures given in chapter 2. Table 5.2 summarizes the results per unit the product and per unit dry matter. For comparison with regulatory standards for fertilisers in the Netherlands, phosphorus, potassium, calcium and magnesium are expressed in respectively P_2O_5, K_2O, CaO and MgO.

Table 5.2a *Composition of the calcium phosphate product per unit fresh matter and per unit dry matter (n=6), major elements.*

Parameter	Mean, % product	Standard deviation, % product	Mean, % dry matter	Standard deviation, % dry matter
Dry matter	14.6	1.9	100	*
Organic matter	4.2	0.3	29.1	4.9
Organic carbon	1.8	0.2	12.3	2.7
$CaCO_3$	0.3	0.1	1.9	0.7
N	0.5	0.2	3.8	1.5
P_2O_5	3.7	0.6	25.5	1.8
K_2O	0.3	0.03	1.7	0.2
CaO	3.8	0.9	25.5	3.9
MgO	0.9	0.2	6.3	2.2

[1] Excluding D2 which had an elevated iron content of 4158 mg Fe/kg product or 23502 mg Fe/kg dry matter

Table 5.2b *Composition of the calcium phosphate product per unit fresh matter and per unit dry matter (n=6), minor elements.*

Parameter	Mean, mg/kg product	Standard deviation, mg/kg product	Mean, mg/kg dry matter	Standard deviation, mg/kg dry matter
Cu	30.7	17.0	220	133
Zn	87.7	25.9	621	209
Al	69.8	29.5	502	268
Fe[1]	351	90.4	2486	560
Cd	0.057	0.009	0.4	0.1
Cr	0.608	0.131	4.1	0.4
Ni	0.649	0.193	4.4	1.1
Pb	0.141	0.011	1.0	0.1

[1] Excluding D2 which had an elevated iron content of 4158 mg Fe/kg product or 23502 mg Fe/kg dry matter

The calcium phosphate (produced in the laboratory) consist of (on average) 3.7% P_2O_5, 3.8% CaO, 0,9% MgO, 14.6% dry matter and 4.2% organic matter. The percentage organic matter is overestimated due to the loss of NH_3 during the ignition of the pellet. The ratio of organic carbon to organic matter is 0.43. We found no differences in the organic carbon to organic matter ratio between manures and digestate.

In the dry matter the calcium phosphate product has 25.5% P_2O_5, 25.5% CaO and 6.3% MgO. Compared to soft rock phosphate (Gafsa phosphate[11], 97% dry matter) which has 28-29% P_2O_5, 48-50% CaO and 0.6-0.7% MgO and 13.6-15.9% $CaCO_3$, the calcium phosphate produced in the laboratory had a similar phosphate content and a lower CaO-content. This combination of P_2O_5/CaO shows a perspective for use of the calcium phosphate product as secondary raw material for fertiliser production.

However, the calcium phosphate product cannot meet requirements for EU fertilisers regulated by EU regulation 2003/2003. Because the product is made from manure, the product is designated as manure and therefore it has to comply with regulations for manure. This follows from the definition of animal manure of the Nitrate directive 91/676/EEC. If this definition of manure from the Nitrate directive is not in force, then the calcium phosphate can meet requirements of national fertiliser regulations of the Netherlands. However it still contains an amount of nitrogen and therefore, also the definition of the ND applies. The contents of heavy metals Cd, Cu, Cr, Ni, Pb and Zn are low and generally meet current regulatory requirements for fertilisers in the Netherlands. One product made from M2 has a too high Cu/P_2O_5 content (i.e. 2233 mg Cu/kg P_2O_5 while the maximum is 1875 mg Cu/kg P_2O_5). On 17 March 2016 the European Commission presented a first draft of a Circular Economy Package with new rules on organic and waste-based fertilisers in the EU. At the time of writing this report proposed criteria for product function categories and component material categories are subjected in an assessment process. It is important that the calcium phosphate product is defined as a product in the component material category (European Commission, 2016)[12].

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[11] http://www.gct.com.tn/english/fertil.htm

[12] Proposal for a REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL laying down rules on the making available on the market of CE marked fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009, COM/2016/0157 final - 2016/084 (COD), http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52016PC0157

6 P recovery solid fraction, pilot scale

The results of the laboratory experiments were applied to practical experiments on pilot scale. During the testing period several experiments were carried out. In this chapter the monitoring design of the pilot installation (section 6.1), the practical implementation of the batches carried out (section 6.2) and the results of the pilot batches (section 6.3) are reported.

6.1 Design of the pilot

During the reporting period the technical design of the pilot was converted from a system for recovering secondary phosphate minerals (mainly struvite) to a system for recovering phosphorus as calcium phosphate. The pilot plant is built at Groot Zevert Vergisting B.V. in Beltrum, the Netherlands. The main activity of Groot Zevert Vergisting is production of biogas using a wet co-digestion process. Co-digestion feedstocks are digestive track content, glucose waste of a dairy industry and permeate from whey processing). The main feedstock is pig slurry from fattening and breeding livestock farms. Pig slurry amounts at least 55% of the total feedstock. Due to the biogas production only digestate is tested as feedstock for secondary phosphorus recovery.

The pilot system operates as a batch system.

The processes of the recovery of phosphorus and resulting flows are numbered. In short:

The process starts with a two-step separation of digestate (or pig slurry) by a mechanical separator (Mechanic separator 1). First digestate (or pig slurry) was separated with a sieve of 500 µm. The resulting liquid fractions were sieved over 150 µm.
The liquid fraction (LF1) produced by the 150 µm sieve is stored in a tank and is used as fertiliser. This liquid fraction has also been used for other research purposes which do not belong to this study. These other research purposes are stripping of ammonia from this liquid fraction which results in an liquid ammonium sulphate fertiliser and an effluent. The effluent of the ammonium stripper was tested in the pilot as an alternative dilution agent (see step 5).

The solid (thick) fraction of the sieves of 500 µm and 150 µm is transferred to the mix tank (SF1), diluted and mixed to a homogeneous suspension. During the reporting period of the research with the pilot plant different dilution agents (groundwater, recycle water (see step 11) or the effluent of an ammonium stripper) were tested as well as different ratios of solid fraction to dilution liquid (1:3 – 1:9 (w/v)).

After transfer of the solid fraction in tank SF1 two processes start simultaneously, both conditioned by continuous mixing of solids and added liquids.

Addition of the acid. During this test phase sulfuric acid was used (50% solution, in some cases 70%). Furthermore, separately a dilution agent (groundwater, or recycle water (see step 11) of effluent ammonium stripper (see step 2)) was added.
The addition of acid stopped when the pH value was reached which is needed for the research and remained stable over a period of approximately 15-30 minutes.
When the target value of the pH remained stable for approx. 15 minutes, the diluted and acidified mixture was transferred to a second mechanical separator (Mechanic separator 2).

From the diluted and acidified mixture this second separator produced an acid liquid (LF2) which was transferred to a sedimentation tank. The sieve size was initially 100 µm until this sieve broke, from batch number 16 onwards a sieve with size 80 µm was used.

The second separation also produced a P depleted solid organic fraction (SF 2) which can serve as an alternative organic soil amendment. This solid fraction can undergo a second dilution and acidification step followed by a third separation step (Mechanic separator 3). For the description see steps 13, 14 and 15.

To the acid liquid (LF2) a 20% suspension of $Ca(OH)_2$ is added until a target value of pH 8 is reached which remains stable for another 15-30 minutes. During this process the acid liquid and the $Ca(OH)_2$ suspension are mixed. When the pH reached the target value and remained stable, the mixing process stopped. Due to gravity a sediment was formed on the bottom of the sedimentation tank leading to a clear supernatant and an opaque sediment.

After reaching a separation in an almost clear liquid supernatant and an opaque sediment the fourth separation step was carried out. In the original design a mechanical separator (Mechanical separator 4) was foreseen. However, during the test period of the study this fourth separation step was replaced by a gravity step in a sediment tank.

The clear supernatant was separated by draining via a tap just above the sediment. This supernatant can be reused in the recovery process. Therefore we define this supernatant as recycling water. Recycling water prevents a growth in volumes of manure, and is therefore a necessity. During the report period occasionally groundwater or effluent of an ammonia stripper was used as "recycled water".

The sediment containing the precipitated phosphate product was drained via a tap in the bottom of the sedimentation tank.

In some batches the acid solid fraction was washed again with acid to check the additional P recovery, because in solid fraction contains still 70% of water with a high P concentration. By washing this amount of soluble P the amount of recovered P will increase. For this washing procedure, the acid solid of step 8 fraction was transferred to tank SF2 and steps 4 and 5 were carried out for a second time. In the current pilot SF2 is identical to SF1. After reaching the target value for the pH the third mechanical separation step (Mechanic separator 3) was carried out.
Step 13 results in a liquid fraction that was used as recycled water in next batches.
Step 13 also results in a acidified and P depleted solid fraction (SF3) which can serve as an alternative organic soil amendment.

The schematic overview of the pilot design including monitoring aspects (see numbers) is shown in Figure 6.1. The design of the pilot plant was adjusted based on new insights obtained during the test phase. The first batches started with complete manual operation but gradually processes as pH measurement, acid addition, $Ca(OH)_2$ addition and measurement of flows were automated. At the end of the experimental phase (March 1th, 2017) steps 3, 4, 5, 6 and 7 were automated processes, other processes are currently in a mitigation process from manual to automatic processes. Mass balances based on measurement of fluxes and masses are therefore not yet available for the complete recovery process. Mass balances were estimated by calculation of masses in ingoing digestate (1) and liquid fraction 2 based on measured weight of solid fraction 3 and composition of digestate (1), liquid fraction (2) and solid fraction (3). The method of calculation is given in Annex 5. For processes 10, 11 and 12 mass balances were based on expert judgement, i.e. ratio between produced volumes of recycled water and sediment was 3 : 1. Adjustments of the sedimentation tank standardised the volume of the sediment to 1350 L due to the installation of a tap for recovering recycled water. From batch nr. 14 onwards the volume of the sediment 12 was kept constant at 1350 L. The volume of recycled water was estimated from measured flows in steps 7 and 9 and the volume of sediment.

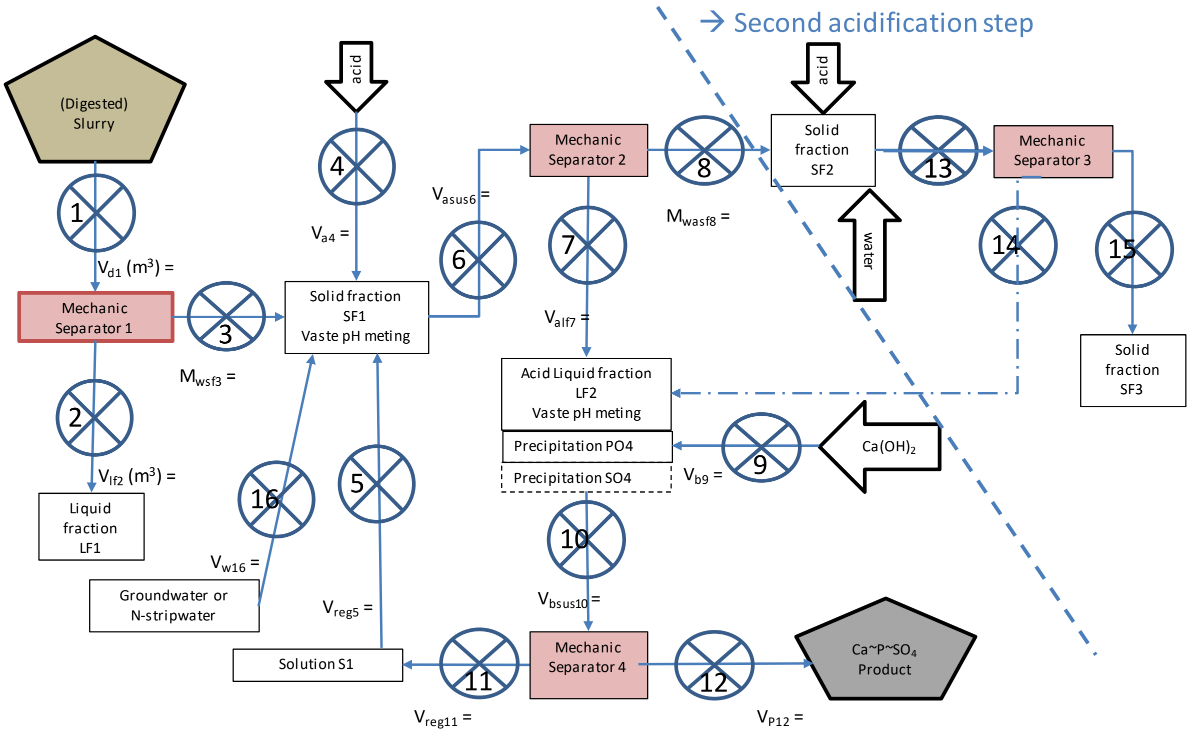

Figure 6.1 *Schematic overview of the pilot scale phosphorus recovery plant at Groot Zevert Vergisting, Beltrum, the Netherlands. Numbers are options to take samples.*

6.2 Practical processing of the batches

During the report period 29 batches were processed under the auspices of Wageningen Environmental Research. Per batch a measured quantity (kg) of solid fraction was placed in mix tank SF1 and mixed with a measured quantity of dilution agent (groundwater, recirculation water of the plant or effluent of ammonium stripper or (S1; n° 11 in Figure 6.1)) until (visual) a homogeneous suspension was obtained.

Next sulphuric acid (50%) was added (step 4 in Figure 6.1) to reach the target value of pH 5. Initially pH was measured manually, from batch 14 onwards pH was registered automatically.

After stabilisation at pH 5 (in practice $4.7 \leq \text{pH} < 5$ for at least 15 minutes) the second separation started. The weight of separated solid fraction 8 and the volume of the acidified liquid fraction 7 were measured. The latter was pumped into the sedimentation tank. Next a 20% calcium hydroxide suspension was added to the acid liquid fraction 7 until (visually) a homogeneous suspension was obtained with the target value pH 8. The measurement of the pH was conducted manually. When the target value was reached and remained stable (in practice ($8 \leq \text{pH} < 8.4$ for at least 15 minutes) the mixer was turned off. Due to gravity the suspension separated into an almost clear supernatant (recycling water) and a calcium phosphate sediment. The length of the sedimentation process varied per batch between 4 hours and 72 hours (weekend).

Some of the batches were used for testing the technical equipment or the production of recycling water. Two of these 29 batches followed also steps 13 – 15. A restricted monitoring program was conducted. Samples were taken by the technicians from steps 1, 2, 3, 7, 8, 10, 11 and 12. Chemical analyses follow methods given in chapter 2.

6.3 Results

The sequence of the batches followed an interactive innovative process: when results were obtained with a batch, the design and the technical management of the pilot plant was adjusted for the next batch. The first aim of the report period was to test the pilot facility. The second aim was to test the effects on recovery of phosphorus of:

- the dilution agent in combination with the requirement of acid and calcium hydroxide;
- composition of intermediate products and end product;
- the ratio of the solid fraction to dilution agent;
- repeated extraction of the organic fraction remaining after the 1st treatment with acid;
- the estimation of the mass balances.

6.3.1 Effect of dilution agent on acid and calcium hydroxide requirement

6.3.1.1 Acid requirement

The dilution agent is needed to obtain a mixture of the solid fraction and a liquid that can be pumped. We have tested the effect of the dilution agent. On the location of the pilot three dilution agents are available: groundwater, recycled water (step 11) and the effluent of an ammonia stripper which was tested during the reporting period of the pilot. The ammonia stripper was tested with the liquid fraction of the first separation (step 2). Obviously, using recycled water or the effluent of the ammonia stripper is preferred as re-use does not lead to an increase of the volume of manure.

Thus three dilution agents were tested during the reporting period: groundwater, recycled water (step number 11) and effluent of the ammonium stripper. The quantity of acid required to lower the pH to 5 depends on the solid fraction but not on the ratio of dilution agent to the solid fraction (Figure 6.2). Exemption is effluent of the ammonia stripper which showed an increase in acid requirement with increasing ratio (Figure 6.2). This is attributed to calcium carbonate formed by sodium hydroxide addition during the ammonia strip process.

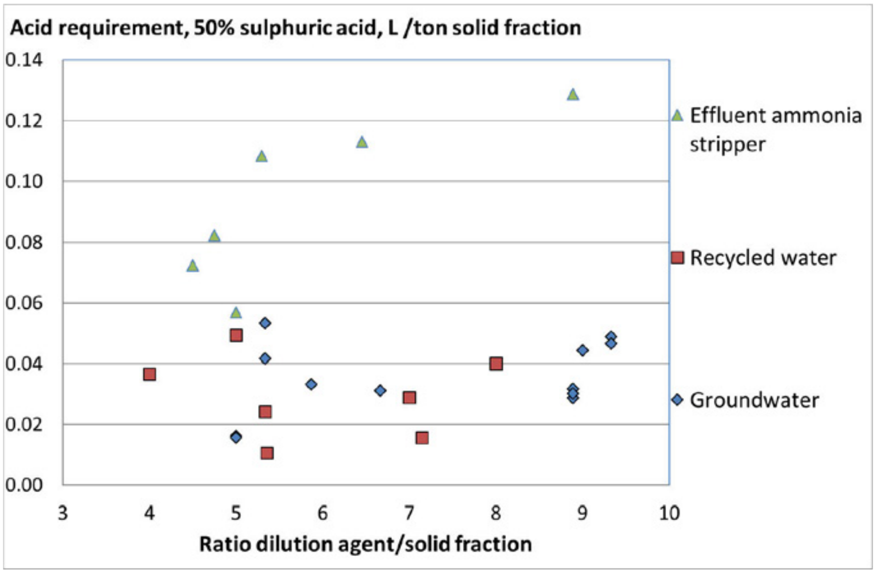

Figure 6.2 *Acid requirement (L 50% sulphuric acid per ton of mixture of solid fraction and dilution agent) for three different dilution agents as a function of the ratio of dilution agent to solid fraction.*

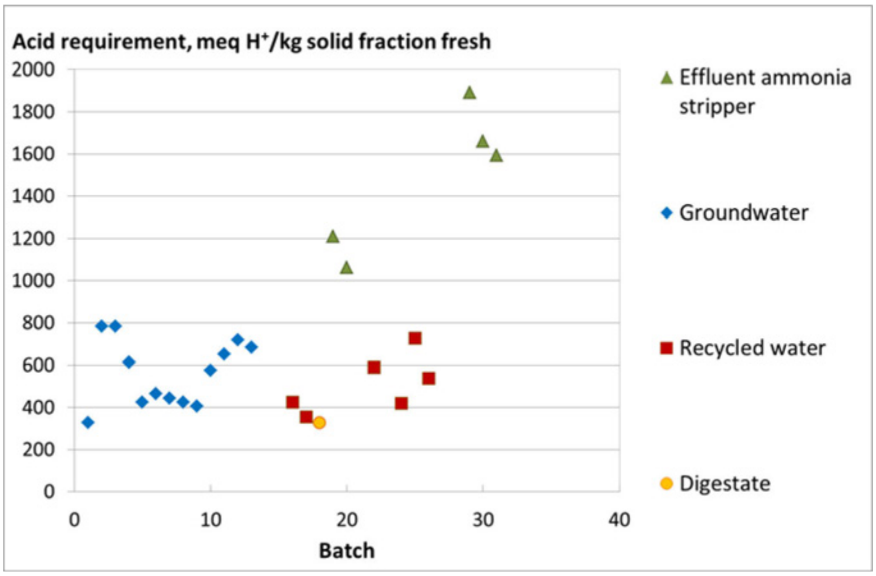

Figure 6.3 *Acid requirement in meq H^+ for three different dilution agents per kg solid fraction and acid requirement of digestate per kg.*

Effluent of the ammonia stripper requires more acid to lower the pH to the target value of 5 than recycled water or groundwater. During the test the ammonia stripper was not yet functioning well, because only the CO_2 stripper was working well and the ammonia recovery was not functioning well; this yielded an effluent with still a high buffer capacity. Recycled water and groundwater do not differ in the quantity of sulphuric acid needed to lower the pH to 5.

Testing the effluent of the ammonia stripper showed that care should be taken to avoid forming of $CaCO_3$ sediments. Hoses from the ammonia stripper transport the effluent by means of pressure to the acidification tank (SF1). After reducing the pressure the effluent separated which caused a sediment forming in the connecting hoses. These sediments consist of carbonates (as shown by the foam formed after acid addition). But avoiding these carbonate-rich sediments by vigorous cleaning was still not enough for reducing the acid requirement. Recycled water, although alkaline with pH 8, has apparently no particular carbonates in suspension as it’s acid requirement equals groundwater.

Figure 6.3 relates acid requirement expressed as H^+/kg solid fraction fresh to batch numbers. Please note that the acid requirement is confounded with the ratio of the dilution agent to solid fraction in case the dilution agent is alkaline. For example, this confounding is present for batches 29, 30 and 31 which had effluent of ammonia stripping as dilution agent. The ratio of dilution agent to solid fraction declined from 8.9, via 6.5 to 5.3. This decline logically reduces acid requirements which is shown as a declining trend. Recycled water or groundwater are not alkaline.

Tests were conducted with different ratios of dilution agent and solid fraction (mixture). If results of these different solid fractions are averaged over batches for groundwater, recycled water and effluent of the ammonia stripper their weights are respectively 534 kg, 714 kg and 670 kg and the average dilution agent and solid fraction were resp. 8.0, 5.9 and 6.0. The average acid requirement (50% H_2SO_4) are respectively 40.7, 34.5 and 101.1 L 50% H_2SO_4.

The overall acid requirement per dilution agent in meq H^+/kg solid fraction fresh is given in Table 6.1. For groundwater and recycled water no clear trend was found between acid requirement and the ratio of dilution agent to solid fraction. Groundwater had an average acid requirement of 574 meq/kg solid fraction fresh, recycled water had an overall requirement of 509 meq/kg solid fraction fresh and effluent of the ammonia stripper required 1484 meq/kg solid fraction fresh.

6.3.1.2 Calcium hydroxide requirement

The quantity of calcium hydroxide suspension (20%) needed per volume of acid liquid fraction after acidification and separation per batch (step 7) is given in Figure 6.4.

One expects that more calcium hydroxide is needed at a higher volume of acid liquid fraction. However, there is no clear relation between the acid-liquid volume of the batches and the required quantity of calcium hydroxide suspension needed to raise the pH to the target value of 8. Since the pH was corrected manually, experience in adjusting the pH increased over time. Contrary to the addition of acid where the stability of the pH required some time to establish, addition of calcium hydroxide suspension immediately caused a stable pH.

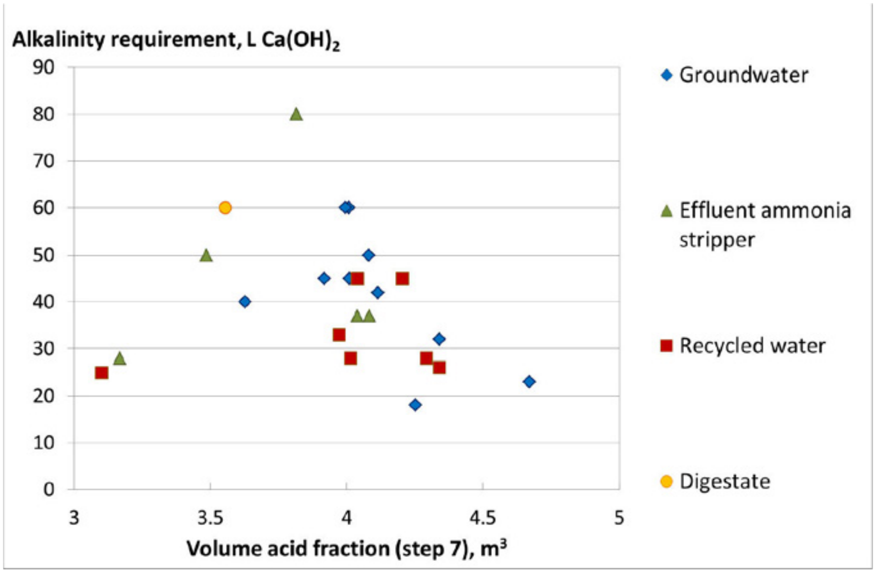

Figure 6.4 Calcium hydroxide requirement in litre 20% $Ca(OH)_2$ suspension in relation to the volume of acid liquid fraction (step 7) for three different dilution agents and for digestate.

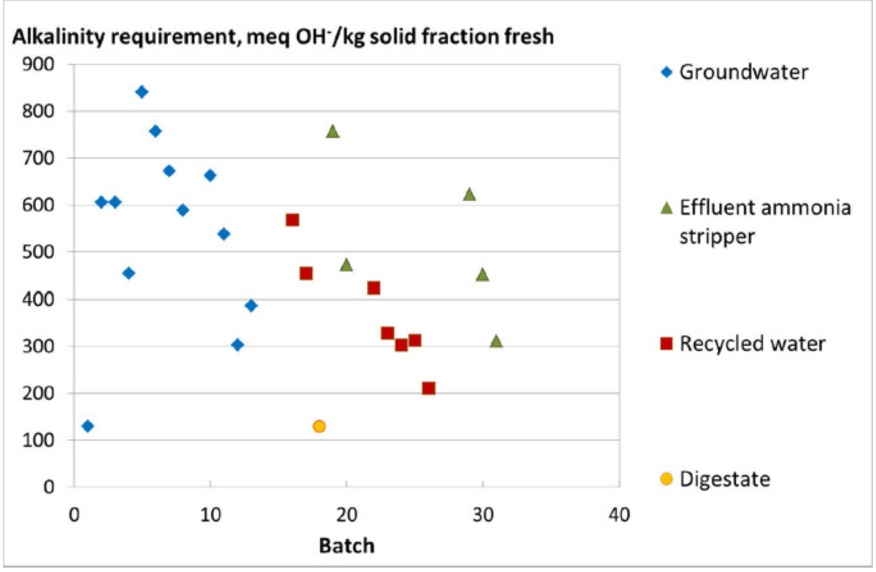

Figure 6.5 Calcium hydroxide requirement in meq OH^-/kg solid fraction fresh for three different dilution agents and digestate for individual batches.

The ortho-P concentration before addition of the calcium hydroxide suspension is given for all batches in Figure 6.6 for sample material of step 7. The total-P concentration of the liquid on top of the sediment that was formed after addition of the calcium hydroxide suspension and after sedimentation of step 11 is given in Figure 6.7. Ortho-P was measured twice (batches 1 and 2 with respectively 0.0092 and 0.0017 mg P/L, total-P was not measured). During the pilot the concentration tended to increase with consecutive batches. Low values (outliers) are for batch number 28 are caused by repeated extraction of phosphorus depleted organic fraction (step 8).

Table 6.1 *Acid requirement (H_2SO_4) of solid fraction fresh for three dilution agents with standard deviation fraction to lower the pH to the target value of pH 5 for different ratios of dilution agent/ solid fraction and the average requirement of alkalinity ($Ca(OH)_2$) with standard deviation to increase the pH target value of 8 for calcium phosphate recovery. With counts the number of batches is given.*

Fertiliser	Ratio dilution agent / solid fraction	Acid requirement			Alkalinity requirement		
		Average	Standard deviation	Number of batches	Average	Standard deviation	Number of batches
		meq H+/kg solid fraction fresh			meq OH-/kg fresh solid fraction		
Digestate[1]	*	327	*	1	130	*	1
Groundwater	5.3	726	98	3	555	87	3
	5.9	489	*	1	262	*	1
	8.3	575	*	1	662	*	1
	8.9	433	23	5	715	109	4
	9	652	*	1	538	*	1
	9.3	701	23	2	345	59	2
	overall	***574***	***140***	***13***	***556***	***176***	***12***
Recycled water	4	538	*	1	210	*	1
	5	726	*	1	312	*	1
	5.3	356	*	1	454	*	1
	6	419	*	1	303	*	1
	7	426	*	1	448	*	1
	8	590	*	1	424	169	2
	overall	***509***	***136***	***6***	***371***	***118***	***7***
Effluent ammonia stripper	4.5	1064	*	1	473	*	1
	4.8	1211	*	1	757	*	1
	5.3	1593	*	1	312	*	1
	6.5	1662	*	1	452	*	1
	8.9	1892	*	1	622	*	1
	overall	***1484***	***438***	***5***	***523***	***171***	***5***

[1] no separation of pig slurry.

In general, the liquid fraction obtained from the sedimentation tank (step 11, used as dilution agent as recycled water) had low P concentrations. Some outliers were found. All values higher than 0.04 mg total-P/L were found for the effluent of the ammonia stripper; this might be caused by the use of anti-foam agent in combination with the use of sodium hydroxide for the peptisation of particles during the ammonia stripping process. An outlier is also found for batch 18 where pig slurry was tested; this batch, however, did not lead to sedimentation after calcium hydroxide addition. Ignoring these outliers, addition of the calcium hydroxide suspension caused a major reduction of P in the liquid phase (~ > 96%).

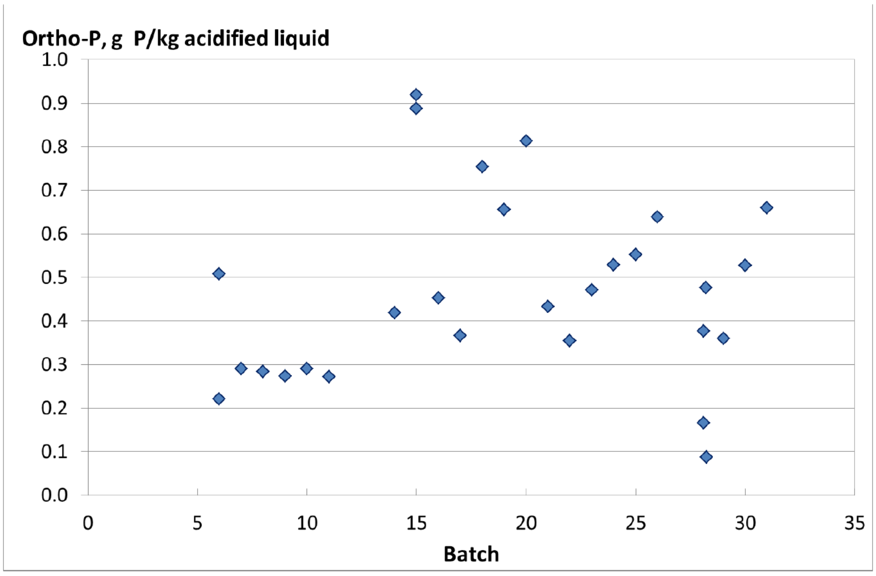

Figure 6.6 *Ortho-P (PO_4^{3-}-P, mg P/kg) of the acid liquid fraction (step 7) per batch.*

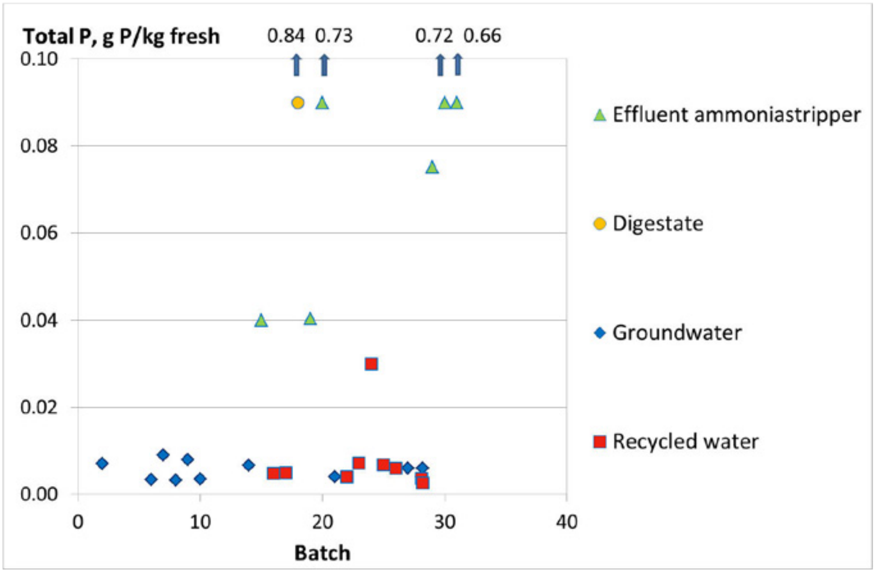

Figure 6.7 *Ortho-P (P, mg P/kg) of calcium hydroxide treated acid liquid (step 7) obtained draining from the sediment of the calcium phosphate (step 11) for three different dilution agents for different for different batches.*

6.3.2 Composition of the intermediate products and end-products, pilot plant

6.3.2.1 Analyses for the mass balance

During the reporting period samples were taken from location1, 2, 3, 5, 7, 8, 10, 11 and 12. For the ingoing digestate, liquid and solid fractions of the first separation step and the intermediate products the results are given in Annex 6. For the P depleted organic fraction which serves as an organic soil amendment (step 8) and the calcium phosphate product (step 12) are given the results in Tables 6.2 and 6.3a.

Since no significant effects were found of the dilution agent on the composition for total-P, the composition is averaged over dilution agents and dilution ratios.

The dilution agent had no effect on the total P content, nor on the contents of dry matter, organic matter, pH, total N. Recycled water and effluent of the ammonia stripper had higher S- and Na-contents[13] and tended to have higher K-total contents but lower Mg- and Ca-contents compared to groundwater (data not given). The ingoing solid fraction (step 3, Annex 6) had a median value 4.29 g P/kg fresh. The acid treatment resulted in an organic fraction with a median value of 0.91 g P/kg fresh. In most case the acidification was a single treatment (see section 5.3.4). The ratio of organic matter to phosphorus (OM/P, w/w) of the ingoing solid fraction is 7.3 while this ratio for the organic fraction of step 8 is 31.6. Acidification clearly resulted in a P depleted organic fraction. Overall a reduction of the P content of a factor 4.3 was obtained.

The pH of this P depleted organic fraction is mild acidic to neutral. On average the pH was 6.37 (range 5.47 – 6.98). This mild acidic to neutral pH serves agronomic use (Annex 7).

Table 6.2 *Composition in fresh matter of the phosphorus depleted organic fraction of the second separation (step 8), averaged over dilution agents with minimum, maximum, standard deviation and counts.*

Parameter	Unit	Average	Median	Minimum	Maximum	Standard deviation	Count
Dry matter (DM)	%	30.4	31.0	24.5	35.4	3.1	28
Organic matter	% in DM	92.4	92.7	89.5	95.1	1.6	28
Volumetric mass	g/L	753	735	539	989	142.7	26
pH	[-]	6.37	6.43	5.47	6.98	0.37	28
N-total	g N/kg	4.01	4.05	3.10	5.20	0.61	28
P-total	g P/kg	1.13	0.91	0.40	4.72	0.94	28
K-total	g K/kg	2.16	2.06	0.13	5.08	1.27	27
Mg-total	g Mg/kg	0.90	0.77	0.08	2.41	0.54	27
Ca-total	g Ca/kg	4.05	3.55	0.89	11.56	2.12	27

The sedimentation tank of the Ca~P product produces a liquid sediment with on average 3.4% dry matter. Due to this low dry matter content (and thus high moisture content) the contents of minerals in the wet solution product are low (Table 6.3).

The dilution agent had an effect (trend) on the percentage dry matter and the contents of N-total, NH_4-N, K-total and Ca-total (derived from median). In general percentage and contents followed groundwater > recycled water > effluent of the ammonia stripper. The dilution agent had no effect on the contents of total-P and Mg-total nor on contents of organic matter or pH.

Higher contents of N-total, NH_4-N, K-total and Mg-total are to be expected due to the higher values found for the effluent initially (Annex 7).

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[13] Analyses on S and Na required the destruction with $HNO_3/HF/H_2O_2$ (magnetron). This destruction leads to somewhat higher P contents (Table 6.2) also.

Table 6.3a *Composition in fresh matter of calcium phosphate (step 12) per dilution agent and with their average with minimum, maximum, standard deviation and counts.*

Parameter	Dilution agent	Unit	Average	Median	Minimum	Maximum	Standard deviation	Count
Dry matter (DM)	Groundwater	%	2.68	2.97	0.38	5.15	1.27	14
	Recycled water		3.72	3.64	1.32	6.53	1.52	9
	Effluent ammonia stripper		4.72	4.75	4.39	5.32	0.32	6
	Average		***3.44***	***3.50***	***0.38***	***6.53***	***1.46***	***29***
Organic matter	Groundwater	% in DM	46.83	48.80	24.44	53.41	7.58	14
	Recycled water		41.99	42.12	34.21	53.28	6.40	9
	Effluent ammonia stripper		47.09	46.84	43.37	51.56	3.49	6
	Average		***45.38***	***46.11***	***24.44***	***53.41***	***6.78***	***29***
Volumetric mass	Groundwater	g/L	1003	1000	981	1019	11.6	11
	Recycled water		1015	1009	1002	1039	14.7	9
	Effluent ammonia stripper		1013	1016	994	1020	10.2	6
	Average		***1010***	***1010***	***981***	***1039***	***13.3***	***26***
pH	Groundwater	[-]	8.55	8.44	7.76	9.78	0.59	14
	Recycled water		8.62	8.70	8.18	9.24	0.33	9
	Effluent ammonia stripper		8.55	8.61	8.00	9.07	0.43	6
	Average		***8.57***	***8.55***	***7.76***	***9.78***	***0.48***	***31***
N-total	Groundwater	g N/kg	0.94	0.86	0.42	2.16	0.45	14
	Recycled water		1.61	1.46	0.84	3.09	0.72	9
	Effluent ammonia stripper		2.56	2.53	2.22	3.00	0.27	6
	Average		***1.49***	***1.26***	***0.42***	***3.09***	***0.81***	***29***
NH_4-N	Groundwater	g N/kg	0.47	0.47	0.37	0.59	0.09	5
	Recycled water		1.00	0.82	0.60	1.80	0.39	9
	Effluent ammonia stripper		1.42	1.45	1.24	1.72	0.16	6
	Average		***1.02***	***0.91***	***0.37***	***1.80***	***0.47***	***20***
P-total[1]	Groundwater	g P/kg	1.19	1.08	0.15	3.26	0.84	14
	Recycled water		1.40	1.40	0.06	3.00	0.87	9
	Effluent ammonia stripper		1.19	1.08	0.99	1.80	0.31	6
	Average		***1.25***	***1.16***	***0.06***	***3.26***	***0.76***	***29***
P-total[2]	Groundwater	g P/kg	1.46	1.62	0.18	2.28	0.72	7
	Recycled water		1.95	1.72	1.19	2.93	0.89	3
	Effluent ammonia stripper		1.16	1.15	1.14	1.18	0.02	3
	Average		1.50	1.28	0.18	2.93	0.69	13
K-total	Groundwater	g K/kg	0.70	0.48	0.13	3.97	0.96	14
	Recycled water		1.59	1.45	0.83	4.12	1.00	9
	Effluent ammonia stripper		3.02	3.27	2.05	3.42	0.52	6
	Average		***1.46***	***0.88***	***0.13***	***4.12***	***1.26***	***29***

Parameter	Dilution agent	Unit	Average	Median	Minimum	Maximum	Standard deviation	Count
Mg-total	Groundwater	g Mg/kg	0.53	0.45	0.11	1.16	0.32	14
	Recycled water		0.96	0.85	0.43	2.17	0.54	9
	Effluent ammonia stripper		0.59	0.56	0.47	0.86	0.14	6
	Average		***0.68***	***0.60***	***0.11***	***2.17***	***0.41***	***29***
Ca-total	Groundwater	g Ca/kg	5.01	2.33	0.22	35.48	8.99	14
	Recycled water		2.97	3.16	0.41	5.46	1.61	9
	Effluent ammonia stripper		3.80	3.76	3.25	4.46	0.41	6
	Average		***4.13***	***3.58***	***0.22***	***35.48***	***6.25***	***29***
S-total[2]	Groundwater	g S/kg	1.84	1.84	0.95	2.94	0.79	7
	Recycled water		4.54	4.19	2.70	6.73	2.04	3
	Effluent ammonia stripper		3.92	3.92	3.50	4.35	0.43	3
	Average		2.92	2.78	0.95	6.73	1.62	13
Na-total[2]	Groundwater	mg Na/kg	0.22	0.15	0.11	0.51	0.14	7
	Recycled water		0.41	0.43	0.35	0.46	0.06	3
	Effluent ammonia stripper		1.13	1.17	0.95	1.27	0.16	3
	Average		0.48	0.35	0.11	1.27	0.40	13

[1] destruction H_2SO_4 – H_2O_2 – Se

[2] total destruction $HNO_3/HF/H_2O_2$ (magnetron)

6.3.2.2 Analyses for the assessment of the agronomical value

Sample material of one experiment collected during a full run of the pilot was drained by means of a IBC sieve bag. For this batch groundwater was used. Next the resulting filter cake was spread in a warehouse and dried by forced air at prevailing temperature (~10˚C). Sample material was grinded in two phases. First lumps of dried filter cake were crushed to approximately 2 mm size. Next crushed material was grinded over 0.25 mm. Grinded sample material was analysed with analytical standards for conformity assessment for mineral phosphate fertilisers, sulphur, nitrogen and particle sizes.

Table 6.3b *Analytical results[1] of air dried and grinded calcium phosphate according to standards for mineral fertilisers focussed on phosphorus and particle sizes.*

Parameter	Method	Unit	Value
Dry matter[2]	NEN-EN 12880:2001 en	%	81.7
P_2O_5	Mineral acid soluble, ISO 11885, E 22	%	14.06
P_2O_5	Neutral ammonium citrate soluble, ISO 11885, E 22	%	13.64
P_2O_5	Water soluble, ISO 11885, E 22	%	0.16
P_2O_5	Formic acid soluble, ISO 11885, E 22	%	14.05
P_2O_5	Alkaline ammonium citrate soluble, ISO 11885, E 22	%	11.28
S	ISO 11885, E 22	%	1.93
S	Water soluble, ISO 11885, E 22	%	1.30
N	Total nitrogen, VDLIFA II, 3.5.2.7	%	2.06
NH_4-N	Ammoniacal nitrogen, EN ISO 11732, E 23	%	0.22
NO_3-N	Nitrate nitrogen, ISO 13395; #6	%	<0.01
K_2O	Mineral acid soluble, ISO 11885, E 22	%	0.52
MgO	Mineral acid soluble, ISO 11885, E 22	%	2.69
Chloride	DIN EN ISO 10304-1; #6	%	0.22
Passing < 0.063 mm	Dry sieving VDLUFA II, 6.5.1	%	33.56
Passing < 0.200 mm	Dry sieving VDLUFA II, 6.5.1	%	89.03
Passing < 0.125 mm	Dry sieving VDLUFA II, 6.5.1	%	81.67
Passing < 0.630 mm	Dry sieving VDLUFA II, 6.5.1	%	99.97

[1] Analyses conducted by LUFA Nord-West, Hameln, Germany

[2] Wageningen University and Research, Wageningen Environmental Research, Chemical Biological Soil Laboratory (CBLB)

The phosphate soluble in neutral ammonium citrate (NAC) is 97% of the quantity soluble in mineral acid. The solubility in formic acid equals mineral acid soluble phosphorus. Alkaline ammonium citrate soluble phosphorus is 80% of mineral acid soluble phosphorus. These chemical analyses indicate that phosphorus is available for crops.

Analyses also show that the ratio of ammonical nitrogen to total nitrogen has been changed by forced air drying. In the wet calcium phosphate sludge the ratio is 0.55 (Table 6.3a). After drying the ratio is 0.11 what points out that ammonia volatilisation occurred during the process of drying.

Interesting are the relative low values for total S and water soluble S in the dried calcium phosphate product (Table 6.3b). In the air dried material 1.93% S is found (i.e. 2.36% S in the dried matter (23.6 g/kg dry matter)). The S content in the calcium phosphate sludge (number 12) with 2.97% dry matter before draining is 1.84 g/kg fresh, which leads to 60.94 g S/kg dry matter. Apparently, draining removed 37,34 g/kg dry matter pointing to relatively high sulphate concentrations in solution (number 11). The fate of sulphate during processing is currently studied.

6.3.3 Ratio dilution agent to solid fraction

The effect of the ratio of dilution agent to solid fraction on the phosphorus recovery was tested in two series of experiments using recycled water (and groundwater) and effluent of the ammonia stripper. The phosphorus recovery was assessed as the separation efficiency i.e. the quantity of phosphorus recovered as calcium phosphate (step 12) as percentage of the ingoing phosphorus in the solid fraction of the first separation step (step 3).
The separation efficiency was calculated following two approaches:

1. The quantity which was actually recovered as calcium phosphate (step 12).
2. The quantity which is potentially available for recovery i.e. this is the quantity present after dilution (step 5) and acidification (step 4) and separation into an acid liquid fraction (step 7) deducted with the quantity present in the liquid fraction drained of from the sedimentation tank (used as recycled water, step 11).

Figure 6.8 reports the results for recycled water and groundwater for different ratio’s based on the quantity which was actually recovered. For the highest ratio, insufficient recycled water was available, so groundwater was used.

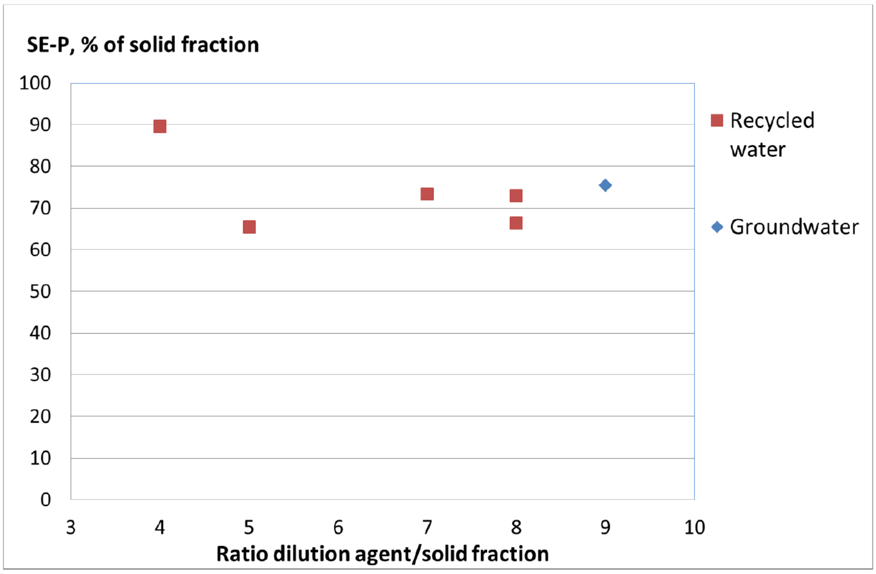

Figure 6.8 *Separation efficiency for phosphorus (SE-P, percent of total phosphorus in the solid fraction) for different ratios dilution agent to solid fraction, based on measurement of calcium phosphate product of step 12. Groundwater or recycled water were used as dilution agent.*

In general, the separation efficiency increased with higher ratio (Figure 6.9). However, not all phosphorus was recovered, which follows from a calculation using the total amount which is potentially available (Figure 6.9). Potentially more phosphorus can be recovered when increasing the ratio.

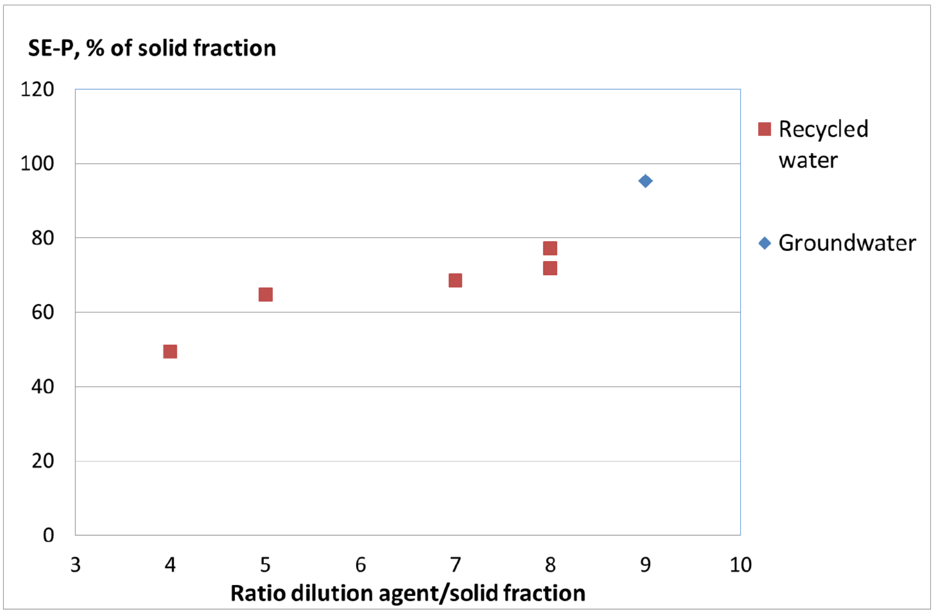

Figure 6.9 *Separation efficiency for phosphorus (SE-P, percent of total phosphorus in solid fraction) for different ratios dilution agent to solid fraction using groundwater or recycled water as dilution agent. Results are based on measurement of products of step 7 and 11 and calculating the difference in mass balance.*

The use of the effluent of the ammonia stripper resulted in more variable results (Figure 6.10). Recovery tended to increase based on actual measured phosphorus recovered as calcium phosphate. This trend is not found when the recovery was related to the quantity that can be potentially recovered (Figure 6.11). Overall, the use of effluent of the ammonia stripper resulted in lower recoveries than groundwater or recycled water.

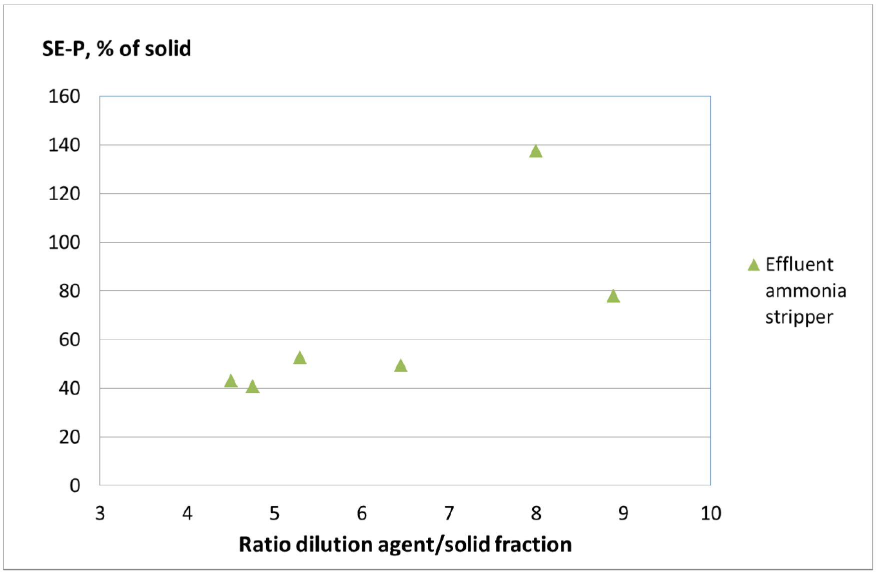

Figure 6.10 *Separation efficiency for phosphorus (SE-P, percent of total phosphorus in solid fraction) for different ratios dilution agent to solid fraction, based on measurement of the calcium phosphate product of step 12. Effluent of the ammonia stripper was used as dilution agent.*

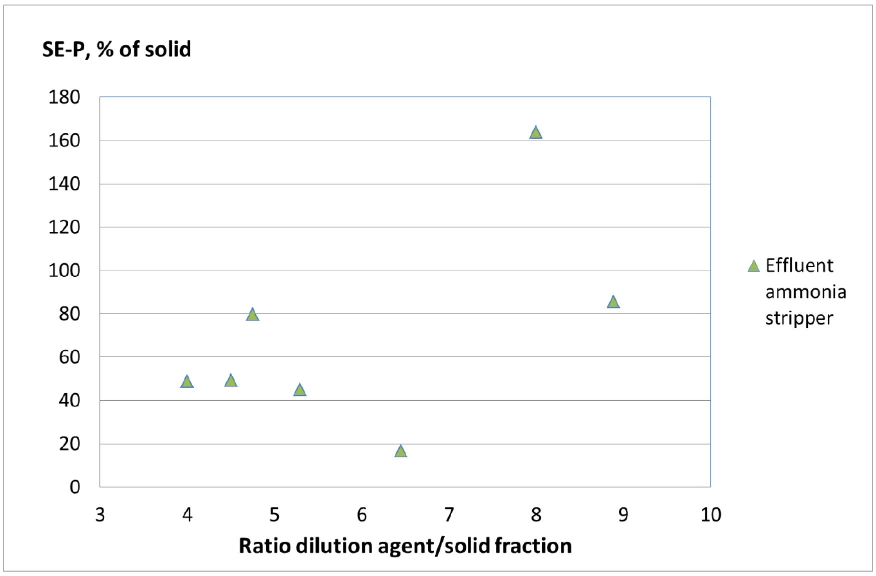

Figure 6.11 *Separation efficiency for phosphorus (SE-P, percent of total phosphorus in solid fraction) for different ratio's dilution agent to solid fraction using effluent of the ammonia stripper as dilution agent. Results are based on measurement of products of step 7 and 11 and calculating the difference in mass balance.*

6.3.4 Repeated extraction

6.3.4.1 Experiences with screw press

The quantity of phosphorus in the solid fraction after one acidification step (step 8) is smaller than in the solid fraction (step 3) of the ingoing digestate (step 1). The ingoing solid fraction has a median content of 3.04 g/kg fresh while the median content in the organic fraction (step 8) is 0.91 g/kg. Although the P content is reduced, a lower phosphorus content will even better serve reuse on agricultural land (better fit to the requirements). We therefore tested if a second treatment with acid lowers the phosphorus content further (repetition of the steps 4, 5, 6 leading to 13, 14 and 15; see Figure 6.1) resulting in a twice acidified and phosphorus depleted solid organic fraction (step 15).

The repeated extraction was tested twice: first time with an initial quantity of 450 kg solid fraction, the second time with an initial quantity of 750 kg. Table 6.4 reports the average composition of the organic fraction of the first extraction (step 8) and of the organic fraction after two extractions (step 15) with standard deviations.

Table 6.4 *Composition in fresh matter of the organic solid fraction after the first acidification step and a second acidification step (step 12), averaged over dilution agents (with standard deviation, n=2).*

Parameter	Organic fraction, 1st extraction, step 8		Organic fraction, 2nd extraction, step 15	
	Average	Standard deviation	Average	Standard deviation
Dry matter (DM), %	33.15	1.65	32.40	0.60
Organic matter, % DM	91.90	1.10	93.40	1.65
Volumetric mass, g/L	776	67	680	1.50
N-total, g/kg	3.58	0.38	3.22	0.17
P-total, g/kg	0.93	0.03	0.40	0.08
K-total, g/kg	1.70	0.36	2.15	0.64
Ca-total, g/kg	4.27	0.02	3.18	0.31
Mg-total, g/kg	0.90	0.00	0.64	0.05

A repeated extraction decreases the phosphorus content from 0.93 g/kg fresh solid fraction to 0.40 g/kg fresh. Also calcium and magnesium contents are lower. Repeated extraction does not affect the contents of dry matter, organic matter or potassium (given the large standard deviation).

Separation efficiency were respectively 130% for the batch using 450 kg solid fraction and 53% for the batch using 750 kg solid fraction. This averaged to 90% (standard deviation is 39%).

The quantity of extra phosphorus recovered as calcium phosphate in the second step is small compared to the quantity of calcium phosphate recovered after the first acidification step (Table 6.5). The actual recovery of the first extraction step was on average 1.11 kg from the ingoing 3.40 kg with the solid fraction of the 1st separation. The second acidification yielded an additional 0.25 kg P (Table 6.5). When compared to the potential for recovery of calcium phosphate of 2.07 kg the potential for recovery of the second acidification step of 0.45 kg is lower (although in absolute terms higher when compared to actual). As a result the repeated extraction does not lead to a much higher separation efficiency.

Table 6.5 *Mass balances of two times repeated acid extraction with means and standard deviation (n=2).*

Extraction	Product	Step	Mass, kg P per product per extraction			
			1st (Batch 28.1)	2nd (Batch 28.2)	Average	Standard deviation
1	Solid fraction, 1st separation	3	1.84	4.95	3.40	1.56
1	Dilution agent groundwater	5	0	0	0	0
1	Acid liquid fraction, 2nd separation	7	1.81	2.35	2.08	0.27
1	Solid fraction, 2nd separation	8	0.38	0.53	0.46	0.07
1	Calcium phosphate, actual	12	1.99	0.22	1.11	0.89
1	Calcium phosphate, potential	12 (step 7 – 11)	1.80	2.33	2.07	0.27
2	Dilution agent recycled water	5	0.01	0.01	0.01	0.00
2	Acid liquid fraction, 2nd separation	7	0.60	0.31	0.46	0.15
2	Solid fraction, 2nd separation	8	0.18	0.16	0.17	0.01
2	Calcium phosphate, actual	12	0.08	0.42	0.25	0.17
2	Calcium phosphate, potential	12 (step 7 – 11)	0.59	0.30	0.45	0.14

6.3.4.2 Experience with decanter centrifuge

At Groot Zevert a decanter centrifuge was available for research purposes. The decanter yielded a solid fraction which was used for a repeated extraction. No sample material was available from the separated liquid material and also not from the original material before separation. The ingoing solid fraction has as a median content of 8.78 g P/kg fresh while the content in the organic fraction (step 8) is 2.59 g P/kg (Table 6.6). The decanter centrifuge produced a solid fraction with a higher P content compared to the screw press (Table 6.5).

Repeated extraction reduced the P content with a factor two from 2.59 g P/kg to 1.35 g P/kg. Due to the higher P content of the solid fraction of the decanter centrifuge, more extractions are needed to reach an agronomical preferred P content.

The solid fraction of the decanter centrifuge had higher contents of N, Ca and Mg, but the content of K was lower. Repeated extraction lowered the contents of these nutrients of the organic fraction. Repeated extraction does not affect the contents of dry matter content, organic matter or potassium (given the large standard deviation).

Table 6.6 *Composition in fresh matter of the organic solid fraction after the first acidification step and a second repeated acidification step (step 12), averaged over dilution agents with standard deviation (n=2).*

Parameter	Organic fraction, 1st extraction, step 8		Organic fraction, 2nd extraction, step 15	
	Average	Standard deviation	Average	Standard deviation
Dry matter (DM), %	30.4	1.27	30.9	1.10
Organic matter, % DM	86.5	0.73	89.3	0.72
Volumetric mass, g/L	721	78	662	49
N-total, g/kg	5.92	0.49	5.03	0.23
P-total, g/kg	2.59	0.60	1.35	0.40
K-total, g/kg	0.58	0.41	0.22	0.17
Ca-total, g/kg	7.63	2.24	3.99	1.68
Mg-total, g/kg	1.88	0.64	0.99	0.15

Separation efficiency were on average 97% (standard deviation 5%). Again, a repeated extraction does not serve a higher separation efficiency. The quantity of extra phosphorus recovered as calcium phosphate is small compared to the quantity of calcium phosphate recovered after the first acidification step (Table 6.7). The average actual recovery of the first acidification step 3.15 kg from the ingoing 6.84 kg with the solid fraction of the 1st separation. The second acidification yielded an additional 0.48 kg P (step 8 Table 6.7). If compared to the potential for recovery of calcium phosphate of 5.08 kg the potential for recovery of the second acidification step of 1.71 kg is relatively lower (although in absolute terms higher compared to actual).

Table 6.7 *Mass balances of two times repeated acid extraction with means and standard deviation (n=2).*

Extraction	Product	Step	Mass, kg P per product per extraction			
			1st (Batch 32+33)	2nd (Batch 34+35)	Average	Standard deviation
1	Solid fraction, 1st separation	3	7.12	6.55	6.84	0.29
1	Dilution agent groundwater	5	0	0	0	0
1	Acid liquid fraction, 2nd separation	7	5.69	4.64	5.17	0.52
1	Solid fraction, 2nd separation	8	1.44	0.91	1.18	0.27
1	Calcium phosphate, actual	12	3.34	2.96	3.15	0.19
1	Calcium phosphate, potential	12 (step 7 – 11)	5.68	4.47	5.08	0.61
2	Dilution agent recycled water	5	0.005	0.017	0.011	0.01
2	Acid liquid fraction, 2nd separation	7	1.81	1.62	1.72	0.10
2	Solid fraction, 2nd separation	8	0.55	0.41	0.48	0.07
2	Calcium phosphate, actual	12	2.68	2.32	2.50	0.18
2	Calcium phosphate, potential	12 (step 7 – 11)	1.8	1.61	1.71	0.10

6.3.5 Potential and actual recoveries of dry matter, nitrogen and phosphorus

Data of the monitoring of the processes of the pilot of fluxes and masses is complete for steps 3, 4, 5, 7 and 8. Mass of ingoing digestate (step 1) and outgoing liquid fraction of the first separation (step 2) were calculated (Annex 5). Masses of outgoing liquid fraction after sedimentation (step 11) and the calcium phosphate product (step 12) were standardised after batch 16 through a fixed volume of sediment (1350 L). Volume of the liquid fraction (recycled water) was calculated from measured volume of acid liquid fraction (step 7), calcium hydroxide suspension (step 9) and the fixed volume of sediment. Mass balances were used to calculate separation efficiencies of phosphorus recovery from the solid fraction of the first separation (step 3). Two recoveries were calculated: the potential recovery and the actual recovery. The potential recovery is the quantity of dry matter, nitrogen or phosphorus present in the acid liquid fraction after the second separation step (step 7) compared to the quantity present in the ingoing solid fraction (step 3) and dilution agent (step 5). The actual recovery is the quantity of dry matter, nitrogen or phosphorus present in the calcium phosphate product (step 12) compared the quantity present in the acid liquid fraction (step 7). Recoveries are expressed as a percentage[14]. Potential recoveries are expected to be higher than actual recoveries.

6.3.5.1 Product

The calculated the separation efficiency of the separated solid fraction as percentage of the ingoing digestate based on measured contents of dry matter, nitrogen and phosphorus (see Annex 5) is given in Table 6.8. Although there are differences between separation efficiencies for these three parameters the order of magnitude is similar when taking into account their standard deviations. Roughly 10% of the mass of the digestate entered the pilot (Table 6.8). Dilution agent did not influence this separation efficiencies. Batches with recycled water appear to have consistently lower separation efficiencies. A cause for this finding remains unclear.

Table 6.8 *Separation efficiencies of total fresh mass (product) of the solid fraction of the first separation of the ingoing digestate, average, minimum, maximum, standard deviation and count in percentage for dry matter, nitrogen and phosphorus.*

Parameter	Dilution agent	Average	Minimum	Maximum	Standard deviation	Count
Dry matter	Groundwater	6.0	3.3	7.8	1.85	7
	Recycled water	4.0	3.2	5.1	0.96	3
	Effluent ammonia stripper	5.1	3.6	8.2	1.84	5
	Overall	***5.3***	***3.2***	***8.2***	***1.78***	***15***
Nitrogen	Groundwater	22.9	3.3	47.5	15.9	7
	Recycled water	4.3	2.3	6.0	1.98	4
	Effluent ammonia stripper	11.0	1.5	22.1	8.7	5
	Overall	***14.6***	***1.5***	***47.5***	***13.7***	***16***
Phosphorus	Groundwater	9.6	2.0	17.4	5.95	7
	Recycled water	3.6	2.7	4.1	0.81	3
	Effluent ammonia stripper	9.0	0.9	15.5	5.50	5
	Overall	***8.2***	***0.9***	***17.4***	***5.43***	***15***

6.3.5.2 Dry matter

Potential and actual recoveries derived from dry matter contents are given in Table 6.9.
Potential recoveries are lower than actual recoveries. This finding is ascribed to the low contents of dry matter of the acid liquid fraction (step 7, median 1.3%) in combination with the presence of bicarbonate and ammonium nitrogen. Bicarbonate has not been measured but is assumed to be present. Ammonium nitrogen has been measured in two samples only, showing that 70% of the nitrogen (0.80 g N-total/kg) is present as ammonium (0.57 g NH_4-N/kg).

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[14] Results for batches 8, 19, 22, 24, 25 and 28.2 showed negative recoveries which are contributed to sampling errors. These batches were excluded when summarizing the results.

Table 6.9 *Potential and actual recoveries for dry matter of the solid fraction of the first separation as percentage of ingoing dry matter of digestate, average, minimum, maximum, standard deviation and count.*

Parameter	Dilution agent	Average	Minimum	Maximum	Standard deviation	Count
Potential	Groundwater	26.1	15.4	38.7	8.65	7
	Recycled water	35.7	26.7	38.7	5.09	6
	Effluent ammonia stripper	48.8	34.7	56.3	9.69	4
	Overall	***34.1***	***15.4***	***56.3***	***11.68***	***17***
Actual	Groundwater	43.5	9.8	83.8	27.03	6
	Recycled water	60.0	32.7	77.5	13.74	8
	Effluent ammonia stripper	45.3	25.6	63.3	12.56	6
	Overall	***50.7***	***9.8***	***83.8***	***19.11***	***20***

6.3.5.3 Nitrogen, solid fraction

The calcium phosphate product of step 12 also contains nitrogen (§ 6.3.2, Table 6.3). Therefore the potential and actual recoveries were derived for nitrogen, and are given in Table 6.10. Potential recoveries are higher than actual recoveries. Batches 15 (recycled water) and 20 (groundwater) had higher quantities of nitrogen compared to the ingoing solid fraction or outgoing calcium phosphate product, leading to too high potential recoveries. If these outliers are ignored the overall recovery is 73% from which 40% was actually recovered (Table 6.10). Acidification thus releases a larger part of the nitrogen from the solid fraction (step 3) into solution and about half of this nitrogen is found in the calcium phosphate product.

Table 6.10 *Potential and actual recoveries for nitrogen of the solid fraction of the first separation as percentage of ingoing nitrogen of digestate, average, minimum, maximum, standard deviation and count.*

Parameter	Dilution agent	Average	Minimum	Maximum	Standard deviation	Count
Potential	Groundwater	64.5	40.1	95.9	20.57	7
	Recycled water	83.5	65.8	104.0	13.82	6
	Effluent ammonia stripper	71.8	66.4	80.2	5.99	4
	Overall	***72.9***	***40.1***	***104.0***	***17.26***	***17***
Actual	Groundwater	34.7	20.6	51.7	11.30	6
	Recycled water	46.5	36.0	58.3	8.24	8
	Effluent ammonia stripper	38.3	32.0	45.0	4.61	6
	Overall	***40.5***	***20.6***	***58.3***	***9.56***	***20***

6.3.5.4 Phosphorus, solid fraction

Potential and actual recoveries derived from phosphorus contents are given in Table 6.11. Potential recoveries are higher than actual recoveries. When compared to the ingoing solid fraction or outgoing calcium phosphate product batches 15 (recycled water) and 20 (groundwater) contained larger quantities of phosphorus, leading to too high potential recoveries. If these outliers are ignored the overall recovery is 76% from which 72% was actually recovered (Table 6.11). Overall, acidification of the solid fraction from the first separation results in a release of phosphorus that is found for three quarters in the acid liquid fraction (step 7) and one quarter remains in the solid organic fraction (step 8). About 90% of this phosphorus that can potentially be released is recovered in the calcium phosphate product. Based on the results presented in Table 6.7 it is concluded that at least a two-step approach is needed to recover 90% of the available inorganic P from the solid digestate resulting in a (treated) organic matter product / organic soil improver with a P content of 0.41 kg P per kg (Table 6.7).

Table 6.11 *Potential and actual recoveries for phosphorus of the solid fraction of the first separation as percentage of ingoing phosphorus of digestate, average, minimum, maximum, standard deviation and count.*

Parameter	Dilution agent	Average	Minimum	Maximum	Standard deviation	Count
Potential	Groundwater	88.7	47.4	144.0	31.5	7
	Recycled water	63.8	45.0	85.3	13.0	6
	Effluent ammonia stripper	72.2	57.8	92.5	14.60	4
	Overall	***76.1***	***45.0***	***144.0***	***24.4***	***17***
Actual	Groundwater	58.1	9.5	109.9	33.08	6
	Recycled water	92.7	13.3	137.7	38.21	8
	Effluent ammonia stripper	57.5	37.6	77.9	16.56	6
	Overall	***71.8***	***9.5***	***137.7***	***34.72***	***20***

7 Business model serving circular economy

7.1 Business case definition

In this study, two sustainable options for processing manure have been developed and tested. Processing manure should make it unnecessary to transport large volumes over long distances. The studied options were an Mg-approach and an acid-base approach. Recovery of P with the Mg-approach was possible, but struvite crystals remained too small to be separated from organic residues (see chapter 4). Thus, the Mg-approach required more steps in manure processing techniques which are out of the scope of this study. With the acid-base approach P could be recovered as calcium phosphate (Ca~P); this was shown both in the laboratory and at pilot scale, and is a promising technical concept to recover P. In this new concept, digestate of pig slurry co-digested with other substrates is processed to a Ca~P product and a solid manure fraction with a low P content. The recovered Ca~P can be exported or used as a raw material for the production of high-grade mineral phosphate fertilisers. The P-reduced solid fraction of digestate can be applied in the nearby region as an organic soil improver within the P application limits for agricultural land.

The P-recovery technology can be implemented on existing biogas plants or manure treatment plants without a digester. After solid-liquid separation of the manure or digestate, the solid fraction will be processed in the P recovery unit. A main feature is that after initialisation the process uses process water that is recirculated which is derived from the liquid fraction from digestate or manure. The P recovery approach can be integrated with an approach for treatment of the liquid fractions of manure or digestate (for recovery of N and K and to obtain purified water). This will have benefits because part of the N-stripped water can be used for the acidification step of the solid fraction (mixture of solid fraction and N-stripped water from the liquid fraction; see Figure 6.1).

At the pilot location Groot Zevert Vergisting B.V. in Beltrum the P-stripper is called Re-P-eat; ‘Recovery of P to eat’). A combination with the treatment of the liquid fraction (called GENIAAL) is foreseen, and will be tested as next steps. The GENIAAL concept was developed by Nijhuis Industries and Groot Zevert Vergisting B.V. The combination of both Re-P-eat and GENIAAL is called ‘Groene Mineralen Centrale[15]‘, abbreviated as GMC, and serves a total treatment of digestate into marketable products (N-, P-, K-mineral concentrates, an organic soil improver with a low P content and clean water). At GMC manure will be processed following the steps:

(i) Digestion of manure and co-substrates to facilitate biogas production.
(ii) Separation of digestate into a solid and liquid fraction by use of a decanter.
(iii) Treatment of liquid fraction by means of ammonia N-stripping or membrane technologies to produce a concentrated mineral N-fertiliser, and/or a K-concentrates and clean water (GENIAAL).
(iv) Treatment of the solid fraction to produce a P-reduced organic soil amendment and calcium phosphate using the acid-base approach (Re-P-Eat).

Figure 7.1 shows a simplified scheme of the GMC approach. With this concept of manure treatment many products can be made, adjusted or combined in such a way that they serve the nutrient requirements of crops (N-P-K ratio).
In this chapter we focus on the business model for the installation to recover only as this is the topic of our study.
For the business model data are needed on the fertilising products that can be marketed in the nearby region. The fertilising products are digestate, solid and liquid fractions of digestate and organic soil improver with a low P-content. Ca~P is assumed to be exported or used by the fertiliser industry as secondary resource.

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[15] Mineral Nutrient Recovery Plant

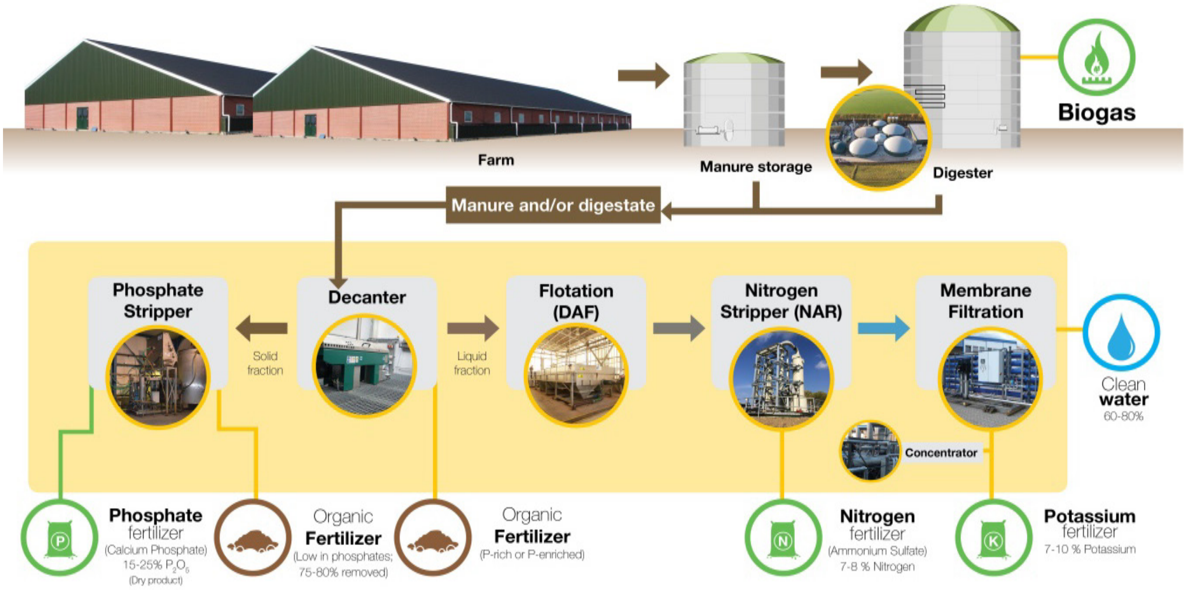

Figure 7.1 *Scheme of the 'Groene Mineralen Centrale' at Groot Zevert Vergisting B.V. for the treatment of manure for obtaining fertilising products.*

7.2 Costs and benefits

7.2.1 Requirement and costs of chemicals

For the conversion of the P-rich solid fraction of digestate or manure into Ca~P and an organic soil improver with a low P content, sulphuric acid is used for the acidification step and calcium hydroxide for the precipitation reaction (see chapter 5 and 6). The required amount of acid depends on the planned P recovery and thus on the required lowering of the pH during the acidification step (see figures 5.2 to 5.6). In the laboratory different pH's have been studied for 7 pig slurries and 7 co-digested pig slurries, and the results are described in par. 5.5 and summarised in Table 5.1. In the pilot study only pH 5 has been studied for one type of co-digested pig slurry in order to quantify maximum P recovery in a pilot plant. The acid and the calcium hydroxide requirements of the pilot study are described in par. 6.3.1 and summarised in Table 6.1.

In the laboratory study a highly efficient centrifuging technique was used to separate the solid fraction (that contains most of the P), while in the pilot study most of the batch experiments have been carried out with a solid fraction which was produced by means of a less efficient separation technique by using a screw press, which result into a lower P content of the solid fraction. In order to acidify co-digested pig slurry to pH 5, 621 (± 140) meq H^+ per kg fresh solid fraction is required and 305 (± 73) meq OH^- per kg fresh solid fraction is needed to increase the pH to 8. In the pilot study this was 553 (± 139) meq H^+ per kg fresh solid fraction and 488 (± 155) meq OH^- per kg fresh solid fraction. In many batches the calcium additions were done by hand and by measuring pH manually. It was observed from the pH that often more hydroxide was added than needed for reaching pH 8, but over time the addition was optimised. The additions of sulphuric acid and calcium hydroxide in the pilot study are in line with the results of the laboratory study when taking into account the standard deviations. Since the laboratory results were based on much more samples from different treatment plants and on different pH values, the laboratory data (Table 5.1) were used for estimating the costs of the chemicals needed.

The prices of sulphuric acid and calcium hydroxides (Table 7.1) highly depend on the concentration and purity of the products. For manure processing technical grades suffice. As an alternative, lower grade by-products of industrial processes can be used, which can be financially attractive. For calcium hydroxide also powder calcium oxide is presented, because it can be easily suspended in water to produce the required calcium hydroxide concentration or direct used as powder added to the acidification tank which requires a different dosage approach (not yet tested in the pilot). The estimated costs for processing a ton solid fraction are shown in Table. 7.2 based on average and high prices of the required chemicals.

Table 7.1 *Price range of sulphuric acid, calcium hydroxide and calcium oxide.*

Chemical commodity	Quality	Price Range (US$/tonnes)		Values chosen (€/tonnes)
Sulphuric acid	Industrial, bulk, 98%	100	300	130
Calcium hydroxide	Fertiliser grade (liming material; 85-95%)	60	130	75
Calcium oxide	Fertiliser grade (liming material; 85-98%)	80	150	

Source: wholesaler.alibaba.com

Table 7.2 *Required amounts and costs of chemicals per ton separated solid fraction of co-digested pig slurry to recover 25, 35, 75 and 80% of P from the solid fraction (resp. at pH 7, 6.5, 6 and 5).*

parameter	unit				
		25%	35%	75%	80%
required amounts of acid	meq H+/kg solid	266	432	569	662
	kg H_2SO_4/ton solid	13	21	28	32
required final pH after acidification	(-)	6.5	6	5.5	5
required amounts of base	meq OH/kg solid	120	151	190	238
	kg $Ca(OH)_2$/ton solid	4	6	7	9
final pH to form Ca~P	(-)	8	8	8	8
estimated costs H_2SO_4: 130 €/ton	€/ton solid pig slurry	€ 1.69	€ 2.73	€ 3.64	€ 4.16
average costs $Ca(OH)_2$: 50 €/ton	€/ton solid pig slurry	€ 0.30	€ 0.45	€ 0.53	€ 0.68
Total acid + base (average)	**€/ton solid pig slurry**	**€ 1.92**	**€ 3.03**	**€ 3.97**	**€ 4.66**

The average costs of chemicals needed to recover 80% of the P from the *solid fraction* of digested manure is estimated at € 4.66. The separated solid fraction is about 30% (or even less) of the mass of the pig slurry as a whole, which means that *per ton co-digested pig slurry* the costs of chemicals are lower: € 1.40.

7.2.2 Investment costs

An estimate was made for the investment costs of constructing a full-scale P-recovery unit for the treatment of 100 000 ton digestate (Table 7.3). In Table 7.4 the annual costs of the installation are shown by taking into account the depreciation, maintenance and management. In Table 7.5 the nett costs of the chemicals and products are presented. For calcium phosphate minimum and maximum prices were assessed based on bulk prices on the market.

Table 7.3 *Estimated investment costs for the construction of a full-scale P-recovery unit for the treatment of 100 000 ton digestate per year and estimated consumption of energy.*

Investment cost for the treatment of 100.000 ton digestate	Investments	Energy kWh
Storage silos 1000 tons of digestate	€ 100,000	
Tray thick fraction + mortar	€ 50,000	10
8 polyester silos of 40m^3 with stainless steel agitator	€ 120,000	40
13 pumps	€ 90,000	55
1 storage tank for acid	€ 35,000	
1 storage tank base	€ 35,000	
4 mixing tanks with agitators + load cells	€ 80,000	16
4 acid phase separators	€ 204,000	6
2 bases phase separator	€ 250,000	10
Centrifuge for P-product	€ 100,000	15
Control, pipes etc.	€ 394,200	5
Total	€ 1,458,200	157

Table 7.4 *Costs of depreciation, maintenance, management and electricity of the P-recovery installation.*

Annual costs installation	Value	(€/j)
Repayment in 10 years = (Depreciation + 5% interest)		€ 188,844
Maintenance (4% of installation costs)		€ 58,328
management and cost location (2% of installation costs)		€ 29,164
power supply (8h per day; 5 days/week)	0.050 per kWh	€ 16,328
Annual costs installation		**€ 292,664**

Table 7.5 *Estimated profit of chemicals and revenues of calcium phosphate product.*

Nett costs chemicals and products	ton / year	€ / kg	(€ / j)
chemicals (per ton solid fraction)	8000	€ 4.66	€ 37,280
Produced tonnes of phosphate	201	ton P_2O_5	
Minimum price P rock (32% P_2O_5)	*0.176*	*€/kg P_2O_5*	*-€ 56,797*
Maximum price P rock (32% P_2O_5)	*0.327*	*€/kg P_2O_5*	
Nett profit chemicals and revenues P product			**€ 19,517**

Pig farms have to pay about 23 € (19-24 €/m^3 2017)[16] for each m^3 pig slurry picked up by intermediaries for the transport to agricultural land in other regions. If the pig slurry has to be transported over long distances farmers have to pay 3 - 4 € extra for each 100 km[17]. Often, only the P rich solid fraction from separation is transported over long distances. The price up to 200 km will be about 30 € per m^3 solid pig fraction. It is assumed that the prices for the liquid fraction are about 15 € per m^3 for the transport and sale in the nearby agricultural regions (mainly arable land). The overall costs for the disposal of pig slurry without treatment (variant 2) and with P treatment (variant 1) are comparable (Table 7.6), because the costs of the installation are more or less the same as for transport over long distances. However, the intermediaries are not dependent anymore of the political restrictions and legislation in foreign countries. Furthermore, in this current calculation it is assumed that the prices for the disposal of pig slurry with a reduced P content and are the same as the price of the disposal of the liquid fraction of pig slurry, and this is questionable as explained hereafter.

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[16] http://www.mestportaal.nl/mestmarkt/

[17] http://www.boerderij.nl/Home/Achtergrond/2017/6/Meer-druk-op-Duitse-mestmarkt-148903E/

Table 7.6 *Comparison for the treatment of 100 000 ton digestate per year: without (variant 1) and with P-recovery treatment (variant 2).*

	ton		(€/j)
Variant 1: without P treatment	ton		(€/j)
Transport costs long distances solid fraction P rich digestate	8000	€ 30	€ 240,000
Regional transport disposal liquid fraction digestate (€/m3)	92000	€ 15	€ 1,380,000
Total costs without P-treatment			**€ 1,620,000**
Variant 2: with P treatment	ton		(€/j)
Annual costs installation			€ 292,664
Nett costs chemicals and revenues P product			-€ 19,517
Regional transport digestate with a reduced P content (=combined liquid fraction together with low P organic fraction)	100000	€ 15	€ 1,500,000
Total costs with P-treatment			**€ 1,773,146**

A P recovery unit has additional agronomical advantages for the region. First, a major advantage is that more organic biomass can be applied on land as organic soil improver due to the low P content of the processed pig slurry (digestate) compared to the untreated pig slurry or liquid fraction of pig slurry, and secondly more mineral N-fertiliser can be replaced by liquid fractions because of the low P content of the organic soil improver compared to untreated pig slurry.

The most common crop rotation on arable land in the North-Eastern part of The Netherlands on sandy soils and sand – peat mixtures is starch potato, sugar beet and spring barley. For this crop rotation the financial benefits are shown by using different types of slurry (diary slurry, pig slurry and pig slurry with a reduced P) content and by taking into account the application limits for manure (170 kg N/ha) and total application limits for N and P (Table 7.7). The total amount of N that can be applied in terms of manure is 170 kg N/ha. The total amount of P_2O_5 that may be applied to arable crops is 60 kg P_2O_5/ha (when soil P status is sufficient). There is no legislation on application of potassium (K_2O). The crop fertiliser requirements follow the current fertiliser recommendations for mineral N, P_2O_5 and K_2O based on the crop rotation (starch potatoes, sugar beets, spring barley) on sandy soils. The N fertiliser replacement values of the liquid fraction of slurries is 0.8 which means that 80% of the total amount of N is effectively available for crop uptake in the first year compared with mineral nitrogen fertiliser. Consequently, the additional mineral fertiliser demands (total N, P_2O_5 and K_2O) can be calculated to meet the crop requirements. Prices for the mineral fertilisers are of May 2017.
Table 7.7 clearly shows the advantages of using dairy slurry on arable land: there is no need for buying P_2O_5 and K_2O fertiliser (even too much K_2O is applied: 96 kg K_2O/ha), a limited additional amount of nitrogen (50 kg N/ha) is needed and a substantial amount of organic matter (2560 kg/ha) is applied. The costs for additional mineral fertiliser needed is about € 38 per ha.

Without application of slurry the estimated costs for chemical fertiliser is roughly € 600 in order to meet the crop requirements. The costs for chemical fertilisers can be reduced by applying compost in order to meet the requirement of organic matter (2000 – 3000 kg per ha) as well. But using dairy slurry has many advantages for arable farms (both organic matter as well as nutrients application). Moreover, arable farms get paid to accept dairy slurry because of the manure surplus in the Netherlands.

However, there is not enough dairy slurry available on the manure market for all arable land, but for pig slurry there is. The composition of pig slurry does not meet the crop requirements as Table 7.7 shows. Because of the high P_2O_5 content in pig slurry (4.6 kg P_2O_5/m^3) only a limited amount of slurry can be applied (13 ton/ha) taking into account the P_2O_5 application limit (60 kg P_2O_5 per ha). In that case, the amount of applied organic matter is low (560 kg per ha). Consequently, substantial amounts of chemical N and K_2O have to be bought (total costs € 110 per ha).

Since P recovery from pig slurry is technically possible, the P content of pig slurry can be reduced. After reducing the P content in pig slurry from 4.6 kg P_2O_5 to 2.5 kg P_2O_5/m^3, there is no need to buy chemical K_2O fertiliser, and the costs of additional chemical N fertiliser is even somewhat lower

(€ 3,50 per ha) compared to dairy slurry. Furthermore, on average there is almost no excess of K_2O applied (5 K_2O/ha) as with dairy slurry (96 kg K_2O/ha); so less environmental losses of K are expected. The main disadvantage is that sufficient amounts of organic matter are not yet upplied (about 2000 - 3000 kg/ha is required while about 1000 kg/ha is applied). This can be solved by reducing also the N-content of the P-reduced pig slurry by implementing also a N-stripper with in the treatment plant; stripping the N from the slurry also opens other perspectives. For example, the amount of organic matter applied can be increased up to more than 10 000 kg per ha per year if only the solid fraction of pig manure with a reduced P-content (<1.4 kg P_2O_5/m^3) is applied on arable land (with an organic matter content and N and K_2O content of resp. 300 kg/m^3, 4 kg N/m^3 and 2.5 kg K_2O/m^3). Consequently, all slurry liquid has to be treated on the treatment plant into process water that may be discharged to surface water (e.g. with the GENIAAL concept; see par. 7.1). On the other hand also combinations of P reduced solid fraction and partly N-treated liquid fractions can be applied, but this analysis goes beyond this study. Nevertheless, the current analysis already shows the benefits for arable farms to reduce their fertiliser costs by using P reduced pig slurry, which is a source of organic matter that is sufficiently available on the manure market.

Table 7.7 *Comparison of cost efficiency of three different animal manures for reduction of mineral fertiliser use.*

Assumptions			N	P_2O_5	K_2O	
			kg N/ha/y	kg P_2O_5/ha/y	kg K_2O/ha/y	
Application limits			170	60	-	
Requirements (average)	Arable		182.5	60	134.2	
Composition		N-coeff.	N	P_2O_5	K_2O	OM
		(-)	kg N/m^3	kg P_2O_5/m^3	kg K_2O/m^3	kg/m^3
Dairy slurry		0.8	4.1	1.5	5.8	64
Pig slurry		0.8	7.1	4.6	5.8	43
P-treated pig slurry		0.8	7.1	2.51	5.8	43
Application	Applied	Neff	Additional chemical fertilizer requirements			
	manure	manure	N	P_2O_5	K_2O	OM
Manure application	m^3		kg N/ha	kg P_2O_5/ha	kg K_2O/ha	kg/ha
Dairy slurry	40.0	131.2	51	0	-98	2560
Pig slurry	13.0	74.1	108	0	59	561
P-treated pig slurry	23.9	136.0	47	0	-5	1030
Chemical fertilizer costs (estimates)			KAS[*]	TSP[**]	K60[***]	
			€/kg N	€/kg P_2O_5	€/kg K_2O	
Fertilizer prices			0.75	0.75	0.51	
		Total				
Fertilizer costs		€/ha	*€/ha*	*€/ha*	*€/ha*	
NPK Blend fertilizers		590	*245*	*80*	*265*	
Additionale costs fertilizer (after manure application)		€/ha	€/ha	€/ha	€/ha	
Dairy slurry		38.29	38.29	0.00	0.00	
Pig slurry		110.51	80.91	0.00	29.60	
P-treated pig slurry		34.71	34.71	0.00	0.00	

[*] KAS is calcium ammonium nitrate

[**] TSP is triple superphosphate

[***] K60 is muriate of potash

Manure composition: http://www.kennisakker.nl/kenniscentrum/handleidingen/adviesbasis-voor-de-bemesting-van-akkerbouwgewassen-samenstelling-en-wer

Chemical fertiliser prices (May 2017): http://www3.lei.wur.nl/prijzenpopup/Default.aspx?lang=0&ID=15128

7.3 Sustainability assessment

The performance of processing pig slurry or digested pig slurry to a calcium phosphate and an organic soil improver in terms of sustainability is studied by conducting an impact assessment. The sustainability of treatment of the solid digestate fraction will be compared with a reference scenario where P is exported in the form of the solid fraction of digestate. The assessment is based on 100 000 ton digestate per year with an average composition of digestate and the average chemical dosages and recovery efficiencies as determined in the laboratory and pilot study (Chapter 3,5,6).

The environmental impacts of this approach are compared to current practices and the results are given in terms of:

a. the amount of energy saved by not transporting the treated solid fraction compared to the amount of energy needed to remove and recover P from the solid fraction,
b. the amount of Ca~P produced to be used as substitute for phosphate rock,
c. the additional amount of organic matter which can be applied for increasing the soil organic matter content of arable land, in order to contribute to agricultural benefits and the 4‰ Initiative (climate goal),
d. the amount of energy saved because of the reduction of the amount of mineral N-fertilisers consumed.

Ad a) Transport of solid fraction versus P recovery

Reference scenario – export of the solid fraction of digestate

The amount of digestate produced at a biogas plant is assumed to be 100 kton per year with a DM content of 6% and 4 kg P_2O_5 per m^3 ton (1.75 kg P/ton). Separation of the digestate with a decanter (centrifuge; separation efficiency of dry matter of 80%) yields approximately 8 kton of solid fraction with a water content of 40% and a P content of 15.4 kg/ton (Table 7.8; SE-P 71%). The solid fraction is transported over a distance of 500 km (250 km v.v.). The energy used for transport amounts to 2.78 MJ/ton.km[18] meaning that the yearly energy consumption associated with transportation amounts to 11 TJ (8000 * 500 * 2.78; Table 7.8).

Table 7.8 *Energy requirement of the reference scenario: Transport of 123 ton of P per year in the form of solid fraction of digestate.*

Parameter	Unit	value
Digestate	(kton/year)	100
Solid fraction of digestate	(kton/year)	8
P-content of solid fraction	(g/kg)	15.4
Amount of P transported	(ton P/year)	123
Transport distance	(km)	500
Number of truck rides (30 ton/truck)	(-)	267
Energy use transport	(MJ/ton.km)	2.78
Overall Energy consumption – reference scenario	**(TJ/year)**	**11.1**

Acid-Base approach to recover P from the solid digestate

Table 7.9 gives an overview of the energy requirements and products in case 100 kton digestate is treated into an secondary P-resource and a soil conditioner which can be applied in the nearby region.

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[18] http://www.rvo.nl/onderwerpen/duurzaam-ondernemen/energie-besparen/meerjarenafspraken-energie-effici%C3%ABntie/verplichtingen-mja3/mee/monitoring

Table 7.9 *Process parameters and energy requirements of the P-recovery scenario.*

Parameter	Unit	Value
Digestate	(kton/year)	100
Solid fraction of digestate	(kton/year)	8
P-content of solid fraction	(g/kg)	15.4
P-recovery (% of P in solid fraction)	(%)	71
P-recovered as calcium phosphate	(ton P/year)	87.6
Extraction and recovery of P		
Acid consumption	(meq H^+/kg solid fraction)	662
Sulphuric acid (96%) consumption	(kg H_2SO_4/ton solid fraction)	31.1
Sulphuric acid (96%) consumption	(ton H_2SO_4/year)	249
GER-value sulphuric acid (96%)[a]	(MJ/kg H_2SO_4)	2.1
Base consumption	(meq OH^-/kg solid fraction)	238
Calcium hydroxide consumption	(kg $Ca(OH)_2$/ton solid fraction)	8.81
GER-value calciumhydroxide[b]	(MJ/kg $Ca(OH)_2$)	4.3
Replaced rock phosphate	(ton P_2O_5/year)	200.7
GER-value replaced rock phosphate[c]	(GJ/ton P_2O_5)	13.1
Electricity		
Electricity for mixers, pumps and decanter	(MWh)	326.6
Transport of products		
P-reduced solid fraction	(kton/year)	8
Transport distance	(km)	30
Calcium phosphate product (12% dry matter, 15% P_2O_5)	(kton/year)	11.15
Transport distance to fertilizer production plant (100 km v.v.)	(km)	*200*
Gross Energy requirements		
Sulphuric acid (97%)		4.19
Calcium hydroxide (20%)		0.30
Electricity for mixers, pumps and decanter		1.18
Transport of P-reduced digestate		0.67
Transport of calcium phosphate to fertiliser production plant		6.20
Replaced rock phosphate		-2.63
Overall energy consumption – P extraction scenario	**(TJ/year)**	9.90

[a] http://www.rvo.nl/onderwerpen/duurzaam-ondernemen/energie-besparen/meerjarenafspraken-energie-effici%C3%ABntie/verplichtingen-mja3/mee/monitoring

[b] Data taken from Afman et al., 2012; original data source: Ecoinvent database

[c] See Table 4.7 in Gloria I. Guzman Casado, Manuel Gonzalez de Molina, 2017. Energy in Agroecosystems: A Tool for Assessing Sustainability. ISBN 97815317465, htpps://lcnn.loc.gov/2016027442

The solid fraction of the digestate is treated with sulphuric acid to lower the pH to 5 in order to extract P. The average acid dosage as determined in the laboratory tests amounts to 662 meq H^+/kg which corresponds to 249 ton concentrated sulphuric acid (96%) per 100 kton of manure (Table 7.2). This amount is comparable with the average acid dosage needed in the pilot tests. After application of the acid, the manure is separated again and P is recovered from the P-rich liquid fraction through the addition of calcium hydroxide. The average dosage of base amounts to 238 meq OH^-/kg which corresponds to 9 ton of 20%-$Ca(OH)_2$-suspension per 100 kton manure (Table 7.2).

The GER-value (gross energy requirement) of sulphuric acid and calcium hydroxide were used to calculate the energy requirements of the chemicals. The energy requirements for the use of chemicals amounts to 4.5 TJ/year (4.19 and 0.3 TJ/year for acid and base, respectively). The electricity demand for mixing, pumping and dewatering has been estimated based on expert judgement on 1.2 TJ/year.

The process yields 8 kton of P-reduced organic soil improver, to be used by farmers in the nearby region (30 km). Transport of the P-reduced manure requires about 0.67 TJ/year. Furthermore, the process yields about 11.15 kton of calcium phosphate suspension (12% DM and 15% P_2O_5). In the pilot experiments, calcium phosphate was recovered as a suspension with a very low dry matter content of 4%. With the use of simple dewatering techniques (filter bags), it is expected that the dry matter content can be increased to 15%. Transport of calcium phosphate as a suspension to fertiliser production plant would require 6.2 TJ of energy. Since the final product will replace rock phosphate, the amount of energy saved by not using mineral P, produced from rock P imported from Morocco should be included in the analysis as well (-2.63 TJ/year).

The overall energy requirements of the P-recovery scenario are 1.2 TJ/year (about 10%) lower compared to the reference scenario in which manure is transported. For each large scale digester, 1.2 TJ of energy can be saved each year by implementation of the P-recovery method compared to the current practice of manure export. This does not include the energy related to the substitution of mineral N fertiliser of 58 TJ (see section Ad d below).

Ad b) Amount of recovered calcium phosphate as substitute of rock phosphate
As mentioned in Table 7.2 the P recovery in terms of calcium phosphate of one plant will be 200.7 ton P_2O_5 per year. If 50% of the P-surplus of the Netherlands is treated on an identical way (by means of treatment of pig slurry) about 5 Mio ton pig slurry has to be treated (50 plants like Groot Zevert Vergisting). In total about of 10 Mio kg P_2O_5 per year will be recovered as calcium phosphate that can be used as substitute for rock phosphate.

Ad c) Additional amount of organic matter that will stay in the Netherlands and can be applied
As mentioned in Table 7.1, the amount of organic matter which will stay in the Netherlands based on one treatment plant (100 kton pig slurry; equal to 400 ton P_20_5) will be 8 kton per year. If a total amount of 5 million ton pig slurry will be treated (50% of the Dutch P-surplus) about 400 kton organic solid improver will be available for Dutch agricultural soils. This equals to about 170 kton organic matter (containing 58% C) that results in an extra CO_2-savings regarding CO_2 accumulation in the Dutch soils of approx. 360 kton CO_2 per year.

Ad d) Amount of energy saved because of the reduction of the amount of chemical N-fertilisers
The amount of pig slurry with a reduced P content that can be applied on agricultural land within the nutrient application limits is about 24 m^3 per ha which will substitute approx. 136 kg mineral N fertiliser per hectare (Table 7.7). If 5 million ton of pig slurry is treated in such way (50 plants processing 100 000 ton of pig slurry) about 210 000 ha of arable land (5 million ton / 24 m^3) can utilise this P treated pig slurry and consequently each year 1200 ton N (Neff 80% and N content of 7.1 kg N/ton) can be utilised as replacement for chemical fertiliser. The GER-value of chemical N fertiliser is 49 MJ/kg N[19], which means an total annual energy saving of 58 TJ.

7.4 Impact on the P-balance in the region

The amount of excess manure in the province of Gelderland has been calculated using the MITERRA-NL model which includes data on animal numbers, manure production and P-application rate limits for 2012[20]. In 2012, the total manure production in Gelderland corresponded with 13.2 kton P whereas only 7.9 kton P could be used on agricultural land in the province without exceeding the P application limits. This means that 5.3 kton P, or about 40% of the produced manure, cannot be used on agricultural land within the province and must be incinerated (poultry manure) or disposed of in other regions (poultry, pig, dairy manure). Poultry manure accounts for 19% of the P production (2.3 kton P) in Gelderland. Since most of the poultry manure is disposed after composting and exported or by incineration poultry manure does hardly pose a pressure on the P-market of the Netherlands. The surplus of dairy manure is usually transported to other regions in the Netherlands where it is used on arable land whereas most of the pig manure is, or should be, treated and exported to regions outside The Netherlands. The surplus of dairy and pig manure amounts to 3 kton for the province of Gelderland. In Gelderland, the pig industry is responsible for the production of 2 Mton manure

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[19] http://www.biograce.net/content/ghgcalculationtools/standardvalues
[20] https://www.rvo.nl/sites/default/files/2015/04/Tabel%202%20Fosfaatgebruiksnormen%202010%20-%202013.pdf

containing about 2 kton P. This means that the province of Gelderland would need about 20 treatment plants with a capacity of 100 kton per year each if all pig manure would be processed. With the above described P-recovery technology, approximately 56% of the ingoing P can be removed and recovered in the form of calcium phosphate which would result in a yearly removal and recovery of about 1.1 kton P. If all pig manure is treated in this way, the surplus amount of P in the form of dairy and pig manure in the province of Gelderland will decrease by 33%.

8 Synthesis

The agricultural sector in The Netherlands produces about 25% more P via manure than can be used on agricultural land given the phosphate application limits. Currently, a substantial part of the P excess is exported outside the Dutch agriculture mainly through (1) transport of composted poultry litter, (2) as hydrated ash of incinerated poultry litter, (3) as pasteurized P rich solid fraction of (digested) pig slurry (untreated or after drying/pelleting) or (4) as dried and pelletized manures. This is associated with relative high transport costs due to transport of large volumes over long distances (up to 500 km), and consequently high CO_2 emissions related to this transport.

Furthermore, these disposal pathways are no long-term solution of the manure P surplus in The Netherlands. Moreover, phosphate application limits for agricultural land in The Netherlands tend to become stricter. Hence, the need to process and export more manure is urgent. Manures and slurries from cattle are largely reused on grassland and on silage maize of the farms where they are produced or, in case of a surplus, on nearby arable land. Poultry manure is already exported as dried pellets or as compost, or incinerated whereafter the P-rich ash is exported. Thus, solutions are mainly needed for pig slurries. To date, about 50% of the P surplus in manure has to be processed, which equals to 20 - 25 kton P_2O_5 in terms of pig slurry. It is expected that by lowering the P content in feed the P-surplus in pig slurry can be reduced with about 10 to 15 kton P_2O_5. This means that approximately 25% of the P in pig slurry has to be processed and recovered as secondary resource for P requiring industries like P fertiliser industries.

In an explorative study reported in 2014 (Schoumans et al. 2014) it was already shown that there are technical options to recover at least 25% of the P from pig slurries in a rather simple way. Through this recovery, the P-content of pig slurry can be reduced and more manure and organic matter can be applied on agricultural land within the nutrient application limits of the Manure Act. The main aim of current study was to further explore techniques that can reduce the P-content of pig slurry with at least 25%. In the laboratory a set of samples of manure and digestate were analysed in order to determine the range in P-release and P-recovery. Pilots studies were set up to explore the options in practice. Based on this information the business options and agronomical and environmental aspects were analysed further.

Main findings

P recovery approaches
As a follow up of the first explorative studies (Schoumans et al. 2014) the two approaches developed earlier were studied in more detail. One approach concerned the liquid fraction of slurries obtained after low tech separation (the 'Mg-approach'); the liquid fraction was treated by direct addition of magnesium chloride in order to form magnesium phosphates like struvite. In the other approach the solid fraction obtained after high tech separation was chemically treated (the 'acid-base approach'), and P was released by an acidification process where after P was precipitated by means of a liming process.

For the laboratory study manure and digestates were sampled from seven biogas plants (co-digestion) located in the Netherlands, treating either mainly pig slurry (plant 1-6) or dairy slurry (plant 7) next to co-digesting (unknown) feed stocks. At each plant, the ingoing manure as well as the outgoing digestate was sampled. The pilot study was carried at Groot Zevert Vergisting (Beltrum; The Netherlands) on co-digested pig slurry.

Mg-approach
Since most of the phosphate in manure is found in the solid fraction that is associated to both small (<106 μm) and large particles (>500 μm) (see fig. 5.11), a low tech separation was used to enrich the liquid fraction with small particles and phosphate associated at those small particles. Both in the

laboratory studies and the pilot studies a sieve of approx. 700 µm was used. The amount of P in the separated liquid was about 75% (±15.1%) of the ingoing pig slurry, and 57% (±10.5%) of the digested pig slurry. After addition of $MgCl_2$, and separation of the product, about 64% (range: 47% - 90%) of the total amount of the P in pig slurry could be recovered in the pellets. For digestate the average value was 44% (range : 29% - 69%). The dry matter content of the pellet varied between 10-20%, and a substantial part of dry matter was still organic material: 67% for manure and 61% for digested manure. In the pilot study similar results were obtained and additional experiments were set up to increase the amount of P in the end product by increasing the crystal size of the Mg~P precipitates. However, this did not give satisfactory results.

Acid-Base approach

A high tech separation technique was used in order to obtain most of the P in the solid fraction. By decreasing the pH of the solid fraction of slurries or digestate, phosphate is released from the solids and is solubilized in the liquid phase, mainly as inorganic P (ortho-P). After filtration or centrifugation of the suspension with reduced pH, a solution with a high P content is obtained which requires further treatment to recover P (by means of a precipitation reaction by addition of $Ca(OH)_2$). The precipitated P can be filtered as wet solid material.

The laboratory study shows that the amount of P which can be recovered highly depends on the pH after applying acid. P release from the solid fraction strongly increases in the pH range 7 to 5. At pH 5 the highest recoveries were obtained. The relative amount of P accumulated in the solid fraction after high tech separation is 83 (± 6)% and 78 (±14)% of the amount of ingoing P of resp. pig slurry or digested pig slurry. After adding about 600-900 meq per kg fresh solid fraction a pH of 5 was obtained and about 3 – 5 g P per kg solid was released. For pig slurry about 99 (± 5)% of the amount of P in the solid fraction was released and for digestate 74 (± 20)%. The amount of released P can be recovered by adding $Ca(OH)_2$ and separation of the precipitated product (calcium phosphate) by centrifugation. For pig slurry about 76 (± 42)% of the amount of released P was recovered as calcium phosphate while for digestate this percentage was lower 36 (± 29)%. The residual amount of P was accumulated as supernatant. This amount P will not be lost, because this supernatant flow will be used again as recirculation water in the P recovery installation. The produced Ca~P has a dry matter content of about 15%. In the dry matter the Ca~P product has 25.5% P_2O_5, 25.5% CaO and 6.3% MgO. When compared to soft rock phosphate (Gafsa phosphate[21], 97% dry matter) which has 28-29% P_2O_5, 48-50% CaO and 0.6-0.7% MgO and 13.6-15.9% $CaCO_3$, the Ca~P produced in the laboratory had a similar P content and a lower CaO-content. This combination of P_2O_5/CaO shows a perspective for use of the Ca~P product as secondary raw material for fertiliser production. However, the produced Ca~P still contains about 30-40% organic material. This is probably too high to define this Ca~P as a mineral product, although the amount or organic material in the product is just a very small percentage of the amount of organic matter in the pig slurry or digested pig slurry.

In the pilot study at Groot Zevert Vergisting a high tech separation technique, such as a decanter, was not available. Therefore, a two-step separation technique was used by applying screw presses with a 700 µm and a 300-400 µm sieve, respectively, resulting in a solid fraction with a lower P-content compared to the laboratory experiment. Since the pilot study at Groot Zevert Vergisting focusses on the treatment of the solid fraction, in principle the approach could be tested in practice, taking into account the lower P content of the solid fraction. Figure 6.1 shows the scheme of the plant including the options for taking samples. The required amounts of acids and lime ($Ca(OH)_2$) were similar to the amounts used in the laboratory study. Different variables were tested: (1) type of water (groundwater, effluent of ammonia stripper, recycled water of the P-stripper itself) used to dilute the solid fraction into a suspension before acidification, (2) the ratio of solid fraction and amount of water and (3) one or two acid treatments of the solid fraction. The best results were achieved with a two-step acid treatment, a dilution agent-solid fraction ratio of 5 to 8, and by using recycled water of the P-stripper itself. All batches were single batches which means that repeated batches after each other under the same conditions were not carried out yet. This will be part of follow up studies. The collection of the Ca~P after liming also needs further attention, because in the pilot a sedimentation

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[21] http://www.gct.com.tn/english/fertil.htm

tank was used to collect the Ca~P, while in the laboratory a centrifuging technique was used which gave a better performance.

The amount of P released after two-step acidifications is about 75% of the ingoing P of the solid fraction (three quarter is released during the first step and one quarter during the second step). About 90% of the released P could be recovered as Ca~P. In the pilot the Ca~P product still had a high water content (96%) because a sedimentation tank that was used. About 45% of the dry matter consisted of organic residues. The P content was 1.3 g P per kg fresh product. After drying at low temperatures and grinding the material, the agronomical value of the product was determined. The dry matter and P_2O_5 content was resp. 82% and 14% and different P extractions indicated that all P is highly available for crops, comparable to chemical P fertilisers. Relative low values for total S were found in the product. Since single batches were used, more attention is needed in case continuous recycling water of the P-stripper is used.

It was concluded that also in practice on pilot scale the 'acid-base' approach works, using this first prototype of a P-stripper. Although there are still many aspects to focus on for improving the installation and to work in a more continuous setting, there is sufficient trust in the principle/approach to continue with the optimisation procedure. The P-stripper was given the name Re-P-eat ('**Re**covery of **P** to **eat**' ensuring food production by recycling P because of the finite natural P resources).

Business opportunities of P-recovery and agronomical benefits
Based on the prices of sulphuric acid and calcium hydroxides (low grades) the chemical costs for processing a ton of solid fraction were calculated. If only 25% of the total P has to be recovered the costs are about € 2 per ton solid fraction, while for maximal recovery of P (80%) the prices are about € 4.50. The separated solid fraction is about 30% (or even less) of the mass of the pig slurry as a whole, which means that *per ton co-digested pig slurry* the costs of chemicals are lower: € 1.40 for 80% P-recovery.

An estimate of 1.5 Mio € is needed as investment costs to construct a full-scale P-recovery unit for the treatment of 100 000 ton digestate per year. By taking into account the costs of depreciation, maintenance, chemicals and management, annual cost are estimated at about 270 k€. The main cost item is the disposal of treated (digested) pig slurry with the reduced P content in the nearby region 1.5 million €). The total annual costs are comparable with the untreated digested pig slurry where the solid P fraction has to be exported over long distances (1.6-1.7 Mio €). The main uncertainty is the price of disposal to be paid to arable farmers. In the scenario analysis it was assumed that the same price has to be paid. However the advantages for the arable farms are much higher in case pig slurry is used with a lowered P content since less mineral N-fertilisers have to be bought and more organic matter can be applied. This can reduce the costs of mineral fertilizers required with hundreds of euros per ha. Even with lowered P contents in the slurry the amount of organic matter applied are still insufficient (about 1000 kg/ha of the required amount of 2000 – 3000 kg/ha). More slurry and thus organic matter can be applied if the N-content of the P-reduced pig slurry is reduced by implementing a N-stripper in the treatment plant. In that case even more options may be feasible that would yield higher organic matter applications, but this analysis goes beyond this study. Nevertheless, the current analysis already shows the benefits for arable farmers to reduce their fertiliser costs by using P reduced pig slurry, which is, as a source of organic matter, amply available on the manure market.

Sustainability and environmental aspects
The sustainability assessment of treatment of the solid digestate fraction was compared with a reference scenario where P is disposed of by export in the form of solid fraction of digestate. The assessment is based on 100 000 ton digestate per year. The gross energy requirement (GER-value) of transport and treatment costs were included. The overall energy requirement of the P-recovery scenario are 10% lower compared to the reference scenario (unprocessed digestate) in which manure is exported. For each large scale digester, 1.2 TJ of energy can be saved each year by implementation of the P-recovery method compared to the current practice of manure export. Furthermore, the P recovery in terms of Ca~P of one plant will be about 200 ton P_2O_5 /year.

If 50% of the Dutch P-surplus is treated in the way described above, about 5 Mton pig slurry has to be treated (in 50 plants like Groot Zevert Vergisting). In total about 10 Mio kg P_2O_5 will be recovered per year as Ca~P that can be used as substitute for rock phosphate. The total energy savings of 50 plants will be 60 TJ per year. The CO_2-savings due to extra organic matter accumulation in Dutch soils will be approx. 360 kton CO_2 per year. Furthermore, each year 1.2 kton N (Neff 80% and N content of 7.1 kg N/ton) can be utilised as replacement for mineral fertiliser. This will give an extra energy saving of 58 TJ each year.

Implications

Technical opportunities

This study shows that both in the laboratory and in practice (pilot studies) there are technical possibilities to recover P from manure as a secondary source and to produce manure with a lower P-content. In the laboratory, the recovery of P from non-digested pig slurries was higher than from digested pig slurries. In the pilot, only digested pig slurry was studied with also a high recovery from the P-rich solid fraction. It is important to use a high-tech separation technique to transfer most of the P of the ingoing slurry into the solid fraction. This should be improved in follow-up studies, because until now mainly a screw press was used to collect the solid fraction which has a lower P separation efficiency than a decanter (centrifuge). Also, the Ca~P produced needs to be improved in terms of a lower water content and, if possible, a lower organic matter content. Furthermore, much attention needs to be paid to the fate of sulphate originating from sulphuric acid used for lowering the pH. Long term continuous processing of pig slurry is needed under the same conditions to measure the equilibrium concentration of sulphate in both the Ca-P product as well as in the organic soil conditioner with a low P content. Also alternative acids, like organic acids, have to be tested as substitutes for sulphuric acid (sulphate applications). Finally, attention should be given to the number of acidification steps needed to produce pig slurry with a reduced P content which meets the crop requirements in the nearby region of the treatment plant. Since at the pilot plant Groot Zevert Vergisting also an N-stripper will be built, a combined installation has to be built and optimized. This GMC-installation (‘Groene Mineralen Centrale’) will give many options to recover mineral N, P and K products and soil conditioners which can largely meet the organic matter supply of arable land. Technical testing and upscaling to a full scale installation will be an important step of next activities. After reporting the results of the explorative study (Schoumans et al. 2014) important steps were made at pilot scale and brought forward opportunities for a real business case.

Perspective

In order to bring the technical experiences to a next level and for creating new business opportunities, the market value of the products for crop production on arable land should be taken into account. Attention is needed for (1) the possibilities of reducing the use of mineral fertilisers and for (2) the way soil organic matter content can be increased by the organic soil improver with a lower P and, if necessary, reduced N content. Some prior calculations in this report show that there are many options for adjusting the mineral content of slurries and/or the organic soil improvers to the crop requirements. Finally, the recovered P, needs to be disposed outside agriculture, but this amount is small compared to the total amount of P in the pig slurry. Nevertheless, the market values in case of reuse as secondary resource for fertiliser plants still needs attention and should be part of the market study. Finally, the products should be applied and tested on arable land by doing real field experiments in order to obtain information on the agronomical value and environmental benefits of increasing the nutrient use efficiencies.

9 Conclusions and recommendations

Laboratory experiments and pilot studies were designed and carried out to test and quantify the options of P-recovery from pig slurry on both solid fractions (‘acid-base approach’) and liquid fraction (‘Mg approach’) as part of a follow up of a reported explorative study (Schoumans et al. 2014). The goal was to recover at least 25% of the phosphate from pig slurry in order to give perspective for a significant reduction of the Dutch agricultural P surplus. In addition to the laboratory and practical tests and performance in the pilot studies, the economic perspective and environmental aspects were evaluated.

The following conclusions are drawn:

- The laboratory study on pig slurries (n=7) and digested pig slurries (n=7) showed that P-recovery from the separated solid or liquid fraction in amounts of at least 25% is technically feasible.
  - With the ‘acid-base approach’ up to 70-80% of the P can be recovered, because with high tech separation techniques most of the P can be collected in the solid fraction and then extracted. Also on pilot scale P could be recovered from the solid fraction.
  - With the ‘Mg-approach’ less P is recovered because with this approach less P will become available in the separated liquid fraction of (digested) pig slurry, even after low tech separation of the slurry. A main obstacle of the ‘Mg-approach’, which could not be solved, was that the crystal size of the Mg-phosphate produced was too small to facilitate recovery of crystals. Although different experiments have been carried out, the size of the crystal could not be increased in order to separate them from the other particles. This approach was not developed further, after the tests in the laboratory and on pilot scale.
- The costs of chemicals needed for the ‘acid-base approach’ are less than €2 per ton pig slurry.
- The ‘acid-base approach’ is a relatively simple technique and works both in practice and at pilot scale.
- The treated pig slurry has a high organic matter content, but a lower P-content and is therefore suited for use within the system of strict P application standards.
- Compared to a situation in which the solid fraction of manure is exported our approach has the advantage that only small amounts of recovered P has to be exported or used as secondary P-resource.
- The business case of P recovery from pig slurry is comparable with the case without P recovery and export. However, the cost benefits of substitution of a substantial part of mineral N fertiliser on arable land (about 135 kg N/ha) was not taken into account yet, because it is unknown in which way the price will develop of the disposal on arable land of treated pig slurry with a reduced P content. In addition, the value of extra organic matter on arable land is unknown.
- The sustainability impact is positive in terms of energy savings (transport vs treatment), CO_2-savings (additional organic matter), P savings (P recovery as substitute for P from rock phosphate) and N savings (additional N from treated pig slurry as substitute for mineral N fertiliser).
- From a technical and environmental point of view there are many advantages for reducing the P content of pig slurry. The economical perspective will highly depend on the disposal prices of treated pig slurry with a reduced P content, its value as substitute for mineral N fertiliser, and its value in terms of organic soil improver. This market information is not available yet.

Recommendations

- Further tests on pilot scale are needed to regulate the amount and quality of recovered P and to regulate the quality of the soil improver with a low P content. The quality of both products have to meet the standards of end-users.
- Since the options for disposal of pig slurry or digested pig slurry can increase remarkably in case both the N and P content are reduced, the integration of such recovery techniques should be studied in practice on pilot scale.
- The market value of treated pig slurry or digested pig slurry has to be studied.
- Field trials are needed to show the agronomical value of the treated products.

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Annex 1 Composition of manure and digestate and the liquid fraction (710 µm) and solid fraction (3500 rpm)

Code	Animal	Type	Separation sieve size	Solid fraction	Liquid fraction	pH	EC	fraction	DM 105°C	OM	P -PO$_4$ (SFA)	N-NH$_4$ (SFA)	Ca	K	Mg	Total-P	Total-N	SE-P	SE-N	SE-Ca	SE-K	SE-Mg	DS 70°C	OS (105-550°C)	P-PO$_4$*100 /total-P
				%	%	(-)	mS		%	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	%	%	%	%	%	%	%
manure 1	pig	manure	non			7.2	13.3	slurry	11.0	8.1	843	2113	3706	4154	1425	2088	5261						10.1	73.7	40.4
manure 1	pig	manure	710µm	39.1	60.8	7.6	18.2	liquid	7.1	4.6	745	2144	2310	4165	1433	2179	4654	63.5	53.8	37.9	61.0	61.2	*	65.1	34.2
manure 1	pig	manure	3500 rpm	49.3	50.6	7.8	28.7	solid	15.7	11.6	720	1892	3957	4482	2546	4118	7045	97.3	66.0	52.7	53.2	88.1	16.7	74.1	17.5
digestate 1	pig	digestate	non			8.1	27.0	slurry	10.4	6.8	844	3537	3193	4651	1200	2568	6076						8.2	65.7	32.9
digestate 1	pig	digestate	710µm	31.0	68.8	8.0	25.9	liquid	6.4	3.7	929	3488	2249	4564	1217	2645	5721	70.9	64.8	48.5	67.5	69.8	*	57.9	35.1
digestate 1	pig	digestate	3500 rpm	34.7	65.3	8.1	35.2	solid	15.9	11.0	945	3626	4628	4661	2748	5478	8217	74.1	46.9	50.3	34.8	79.5	16.9	69.3	17.3
manure 2	pig	manure	non			7.1	13.7	slurry	9.6	7.4	683	3253	1381	3307	707	1065	5140						6.2	76.8	64.1
manure 2	pig	manure	710µm	19.5	80.4	7.3	25.2	liquid	4.7	3.3	687	3248	1110	3250	722	1083	4693	81.7	73.4	64.6	79.0	82.1	*	69.6	63.4
manure 2	pig	manure	3500 rpm	22.6	77.4	7.4	29.6	solid	14.8	11.4	800	2863	2819	3568	2706	3892	7573	82.4	33.2	46.1	24.3	86.4	15.6	76.9	20.6
digestate 2	pig	digestate	non			8.1	36.5	slurry	13.3	8.0	2531	3355	1981	4332	766	4544	6184						11.6	60.4	55.7
digestate 2	pig	digestate	710µm	47.5	52.1	8.1	46.6	liquid	8.9	4.2	2844	3311	1856	4296	646	4647	6085	53.3	51.3	48.8	51.7	44.0	*	47.8	61.2
digestate 2	pig	digestate	3500 rpm	45.5	54.5	8.3	55.9	solid	16.6	11.2	2537	3435	2834	4470	1073	5502	7116	55.1	52.3	65.0	46.9	63.7	17.1	67.7	46.1
manure 3	pig	manure	non			7.6	28.7	slurry	7.5	4.8	596	3228	1716	3802	817	1219	4707						5.2	63.4	48.9
manure 3	pig	manure	710µm	14.1	85.8	7.9	29.5	liquid	4.3	2.3	660	3343	1619	3689	840	1303	4614	91.7	84.1	80.9	83.2	88.1	*	55.1	50.6
manure 3	pig	manure	3500 rpm	21.2	78.8	8.1	31.0	solid	14.4	9.6	764	3200	4824	3852	3034	4463	7417	77.6	33.4	59.5	21.5	78.6	15.3	66.7	17.1
digestate 3	pig	digestate	non			7.6	17.1	slurry	12.9	9.5	526	5082	2871	2465	1076	1862	8703						10.9	73.7	28.2
digestate 3	pig	digestate	710µm	43.8	55.7	8.1	30.3	liquid	8.4	5.9	514	5132	2398	2614	874	1804	9485	54.0	60.7	46.5	59.1	45.2	*	70.1	28.5
digestate 3	pig	digestate	3500 rpm	50.0	50.0	8.3	37.1	solid	14.8	10.7	471	5020	3933	2790	2083	3358	9325	90.2	53.6	68.5	56.6	96.8	15.5	72.7	14.0
manure 4	pig	manure	non			7.4	29.9	slurry	12.5	8.7	589	3930	3886	6181	1768	2210	6623						11.0	70.2	26.7
manure 4	pig	manure	710µm	44.4	55.3	8.0	33.3	liquid	6.9	4.0	687	3898	2860	6024	1703	2233	6159	55.9	51.4	40.7	53.9	53.3	*	58.2	30.8
manure 4	pig	manure	3500 rpm	49.9	50.1	8.2	35.1	solid	17.7	12.9	751	3643	5808	6591	2920	3913	7523	88.3	56.7	74.6	53.2	82.4	18.4	72.8	19.2
digestate 4	pig	digestate				8.4	33.9	slurry	13.6	9.3	685	5344	4208	5200	1667	2510	9189						12.0	68.7	27.3
digestate 4	pig	digestate	710µm	47.6	51.9	8.3	40.6	liquid	8.7	5.0	706	5623	3511	4999	1424	2413	8462	49.9	47.8	43.3	49.9	44.3	*	58.2	29.3
digestate 4	pig	digestate	3500 rpm	51.7	48.3	8.4	41.9	solid	18.2	13.0	786	5069	4961	5396	2572	4150	10086	85.5	56.7	61.0	53.7	79.8	18.6	71.5	18.9
manure 5	pig	manure	non			7.3	20.2	slurry	11.5	9.0	742	3563	1852	4796	1495	2041	6899						9.6	78.3	36.3
manure 5	pig	manure	710µm	42.3	57.5	7.5	27.3	liquid	6.8	4.7	766	3504	1514	4701	1464	2082	6459	58.7	53.9	47.0	56.4	56.3	*	69.7	36.8
manure 5	pig	manure	3500 rpm	41.4	58.6	7.8	33.4	solid	16.2	12.7	812	3271	2915	4854	2949	4214	8749	85.5	52.5	65.2	41.9	81.7	16.9	78.7	19.3
digestate 5	pig	digestate	non			8.3	27.2	slurry	13.9	9.5	652	3480	3258	3651	1376	2439	7162						12.2	68.5	26.7
digestate 5	pig	digestate	710µm	55.1	44.8	7.9	30.4	liquid	9.3	5.5	719	3422	2872	3598	1058	2169	6444	39.9	40.3	39.5	44.2	34.5	*	59.3	33.2
digestate 5	pig	digestate	3500 rpm	53.7	46.4	8.0	41.9	solid	17.7	12.3	756	3533	3749	3639	1833	3500	7368	77.0	55.2	61.8	53.5	71.5	18.0	69.3	21.6
manure 6	pig	manure	non			7.7	24.9	slurry	8.9	6.5	600	3854	2405	3253	871	1727	5946						6.9	72.9	34.7
manure 6	pig	manure	710µm	29.1	70.7	7.8	30.8	liquid	4.5	2.8	738	3886	1877	3060	827	1504	5363	61.6	63.8	55.2	66.5	67.2	*	62.3	49.1
manure 6	pig	manure	3500 rpm	35.3	64.6	7.8	32.8	solid	15.2	11.6	703	3641	3869	3056	2125	4041	7522	82.7	44.7	56.8	33.2	86.2	15.3	76.4	17.4
digestate 6	pig	digestate	non			8.2	25.3	slurry	13.0	9.0	520	3411	2837	6478	1224	1962	7532						11.1	69.2	26.5
digestate 6	pig	digestate	710µm	40.9	59.1	8.2	33.9	liquid	8.1	4.8	514	3447	2596	6004	837	1583	6591	47.7	51.7	54.1	54.8	40.4	*	59.8	32.5
digestate 6	pig	digestate	3500 rpm	51.4	48.6	8.3	40.6	solid	16.0	11.5	666	3533	4431	6259	1820	3131	8521	82.0	58.1	80.2	49.6	76.4	17.0	71.6	21.3
manure 7	dairy	manure	non			7.0	11.7	slurry	10.2	8.5	167	1641	1091	3827	659	456	3801						8.5	83.3	36.7
manure 7	dairy	manure	710µm	49.7	50.1	7.2	15.3	liquid	5.1	3.9	208	1600	1014	3795	618	404	3470	44.3	45.7	46.5	49.6	46.9	*	76.7	51.4
manure 7	dairy	manure	3500 rpm	54.0	46.0	7.6	26.5	solid	11.3	9.8	246	1254	1534	3695	821	658	3864	77.8	54.9	76.0	52.1	67.2	11.4	87.1	37.5
digestate 7	dairy	digestate	non			7.9	19.1	slurry	6.5	5.0	216	2115	1066	4012	669	481	3669						5.6	77.1	44.9
digestate 7	dairy	digestate	710µm	27.9	72.0	7.8	23.9	liquid	3.6	2.3	155	1984	821	3915	552	336	3265	50.4	64.1	55.5	70.3	59.4	*	64.7	46.2
digestate 7	dairy	digestate	3500 rpm	37.3	63.8	8.1	26.2	solid	10.4	8.2	319	1769	2313	3927	1118	1000	4313	77.7	43.9	81.0	36.5	62.3	10.9	79.1	31.9

Annex 2 Low-tech and high-tech separation techniques

Table A2.1 *Investment costs, capacity and separation efficiencies of various techniques, pigs.*

Scale	Type	Investment costs	Capacity	Separation efficiency				Reference
				Product	Dry matter	Nitrogen	Phosphorus	
		x 1000 €	m3/uur	%	%	%	%	
Farm scale	settling tank			18 (*)	57 (51-63)	*	41 (17-65)	Powers and Flatow, 2002; Reimann, 1989
Farm scale	screen separator	10-30	10-20	23 (1-45)	42 (11-87)	24 (3-51)	30 (2-59)	Holmberg et al., 1983, Vadas, 2006, Pieters et al., 1999, Hegg et al., 1981, Møller et al., 2000
Farm scale	Rotary sieve	10-30	10-20		< 25	*	< 30	Holmberg et al., 1983, Vadas, 2006, Pieters et al., 1999, Hegg et al., 1981, Møller et al., 2000
Farm scale	Vibration screen	10-30	10-20		< 25	*	< 30	Holmberg et al., 1983, Vadas, 2006, Pieters et al., 1999, Hegg et al., 1981, Møller et al., 2000
Farm scale	Curved screen	10-30	10-20		44 (11-87)	*	34 (2-62)	Holmberg et al., 1983, Vadas, 2006, Pieters et al., 1999, Hegg et al., 1981, Møller et al., 2000
Semi industrial	Screw press	25-30	5-15	6 (4-7)	35 (21-64)	11 (4-31)	20 (7-46)	Møller et al., 2000, Vadas, 2006, Møller et al., 2002, Pieters et al., 1999, Pos et al., 1984
Industrial	Filter belt	70	4-30	23 (1-45)	42 (11-87)	24 (3-51)	30 (2-59)	Holmberg et al., 1983, Vadas, 2006, Pieters et al., 1999, Hegg et al., 1981, Møller et al., 2000
Industrial	Filter belt press	70	4-30	23 (1-45)	42 (11-87)	24 (3-51)	30 (2-59)	Holmberg et al., 1983, Vadas, 2006, Pieters et al., 1999, Hegg et al., 1981, Møller et al., 2000
Industrial	Decanter centrifuge	100	4-30	12 (3-26)	60 (33-95)	25 (17-36)	73 (52 - 90)	Vadas, 2006, Møller et al., 2007a, Sneath et al., 1988, Møller et al., 2002, Reimann, 1989

Table A2.1 *Investment costs, capacity and separation efficiencies of various techniques, dairy cattle.*

Scale	Type	Investment costs	Capacity	Separation efficiency				Reference
				Product	Dry matter	Nitrogen	Phosphorus	
		x 1000 €	m^3/uur	%	%	%	%	
Farm scale	Settling tank			18 (-)	55 (42-72)	33 (30-35)	57 (42-70)	Sherman et al, 2000; Converse and Karthikeyan, 2004
Farm scale	Screen separator	10-30	10-20		47 (13-84)	33 (22-49)	33 (20-49)	Vadas, 2006, Hegg et al., 1981, Gilbertson and Nienaber, 1978, Møller et al., 2000, Pain et al., 1978
Farm scale	Rotary sieve	10-30	10-20		< 25		< 30	Vadas, 2006, Hegg et al., 1981, Gilbertson and Nienaber, 1978, Møller et al., 2000, Pain et al., 1978
Farm scale	Vibration screen	10-30	10-20		< 25		< 30	Vadas, 2006, Hegg et al., 1981, Gilbertson and Nienaber, 1978, Møller et al., 2000, Pain et al., 1978
Farm scale	Curved screen	10-30	10-20	24 (4-44)	44 (11-87)		34 (2-62)	Vadas, 2006, Hegg et al., 1981, Gilbertson and Nienaber, 1978, Møller et al., 2000, Pain et al., 1978
Semi industrial	Screw press or press auger	25-30	5-15	14 (2-60)	38 (13-77))	19 (4-60)	14 (3-21)	Møller et al., 2000, Vadas, 2006, Møller et al., 2002, Pos et al., 1984, Wu, 2007, Menear and Smith, 1973
Semi industrial	Screw press	25-30	5-15	14 (2-60)	38 (13-77))	19 (4-60)	14 (3-21)	Møller et al., 2000, Vadas, 2006, Møller et al., 2002, Pos et al., 1984, Wu, 2007, Menear and Smith, 1973
Semi industrial	Screw press	25-30	5-15	14 (2-60)	38 (13-77))	19 (4-60)	14 (3-21)	Møller et al., 2000, Vadas, 2006, Møller et al., 2002, Pos et al., 1984, Wu, 2007, Menear and Smith, 1973
Semi industrial	Filter press	25-30	5-15	14 (2-60)	38 (13-77))	19 (4-60)	14 (3-21)	Møller et al., 2000, Vadas, 2006, Møller et al., 2002, Pos et al., 1984, Wu, 2007, Menear and Smith, 1973
Industrial	Filter belt	70	4-30	24 (4-44)	47 (13-84)	33 (22-49)	33 (20-49)	Vadas, 2006, Hegg et al., 1981, Gilbertson and Nienaber, 1978, Møller et al., 2000, Pain et al., 1978
Industrial	Filter belt press	70	4-30	24 (4-44)	47 (13-84)	33 (22-49)	33 (20-49)	Vadas, 2006, Hegg et al., 1981, Gilbertson and Nienaber, 1978, Møller et al., 2000, Pain et al., 1978
Industrial	Decanter centrifuge	100	4-30	17 (12-23)	63 (44-86)	32 (23-49)	69 (48-83)	Vadas, 2006, Møller et al., 2007a, Møller et al., 2002, Reimann, 1989

Annex 3 Effect of molar ratio Mg and P and incubation time on the P recovery of two manures and two digestates expressed as percentage of total P content

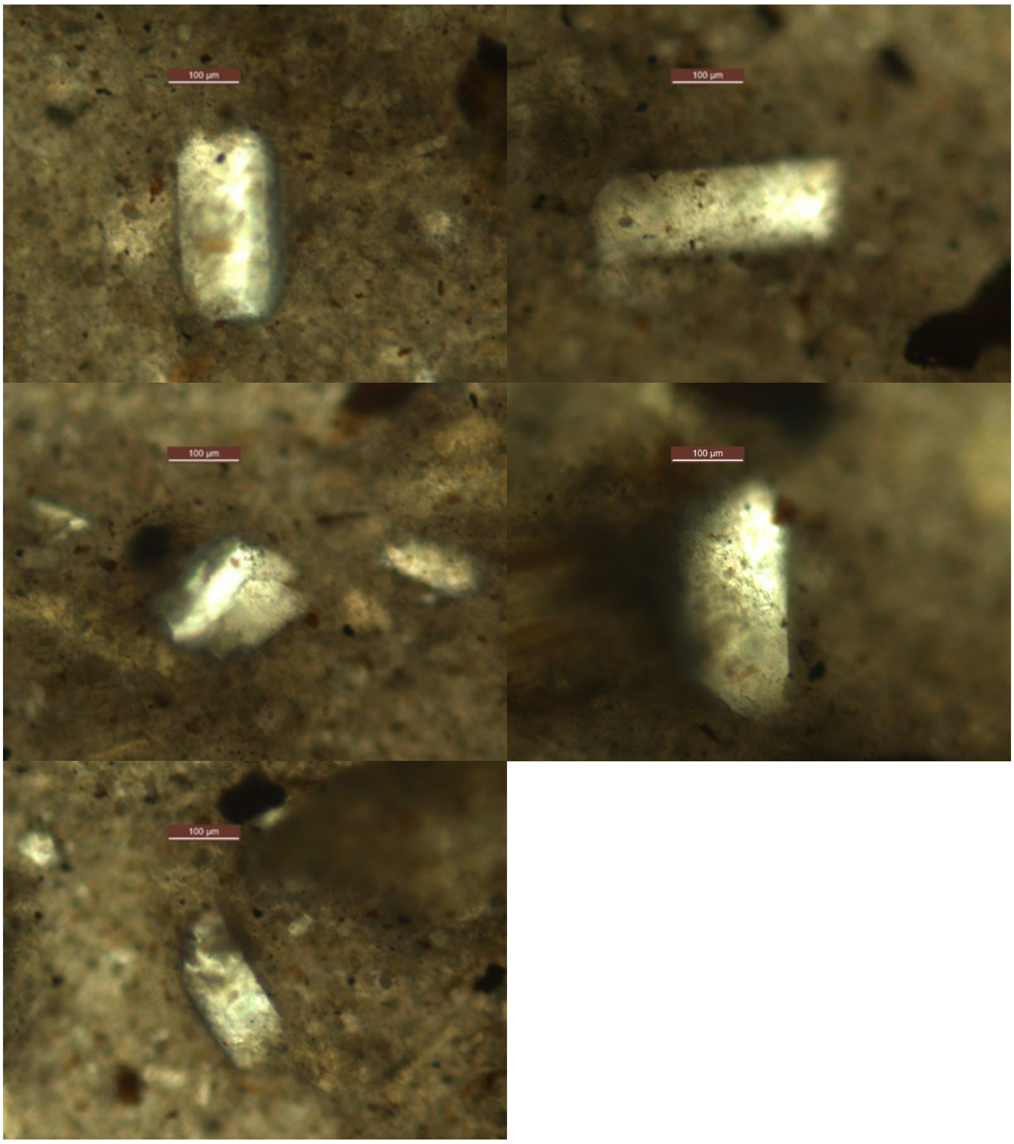
(Batch 2; data-file: Overzicht onderzoek Mg spoor 02072014 OS.xls; Table 2).

P recovery (%)							**Average**			
	1.3		**1.6**		**1.9**		**1.3**	**1.6**	**1.9**	**All**
	1 h	**1 d**	**1 h**	**1 d**	**1 h**	**1 d**				
- Manure 1	52	61	58	55	57	54	56	56	56	56
- Manure 3	79	75	81	75	79	78	77	78	78	79
- Digestate 1	58	64	69	63	62	60	61	66	61	63
- Digestate 3	40	33	33	36	37	35	36	35	36	36
Average										
Manure	70	53	69	65	68	66	61	67	67	61
Digestate	49	39	51	49	49	48	44	50	48	43
Average all	62	46	60	57	59	57	54	59	58	53

Annex 4 Photos struvite crystals

Photos of struvite crystals for manure 4, after one day incubation at a Mg/P molar ratio of 1.3.

The bar in the photos represents 100 µm.



Annex 5 Data chemical analyses monitoring liquid fraction approach

In this annex data on physico-chemical composition of the following flows are given.

Fsolid = solid fraction of the screw press separator with sieves 700 μm (3/11/2014-11/12/2014) or 500 μm (12/12/2014-24/01/2015)
Fliquid = liquid fraction of the of the screw press separator with 700 μm (3/11/2014-11/12/2014) or 500 μm (12/12/2014-24/01/2015))
RDsolid = solid fraction of the of the Rotary drum separator (350 μm)
RDliquid = liquid fraction of the of the Rotaru drum separator (350 μm)
R2 = liquid fraction after storage in the buffer tank before separation
RFSsolid = wet Mg~P product after separation over a rotating fabric belt seperator (three parts: 80, 120 and repeated 120 μm)

Per flow samples were analysed on EC, pH, Dry Matter (DM) and in fresh products (g/kg product) Total P, Total K, Total Ca and Total Mg. Also the contents of these minerals are expressed per kg dry matter (g/kg DM). Molar ratio of Mg to P is included.

During the monitoring also the temperature was measured. Values of temperature are also given.

Data of measurements have been grouped according to the addition of $MgCl_2$ (32%) in Liters (Addition).

Composition of ingoing Digestate (D).

Addition	Parameter	Mean	Median	Minimum	Maximum	SD	N
0	Temperature, degrees C	15.20	15.00	10.20	20.50	3.52	11
11	Temperature, degrees C	15.83	16.00	10.50	18.33	1.89	17
17	Temperature, degrees C	18.11	18.20	16.80	19.70	0.98	8
Overall	Temperature, degrees C	16.15	16.50	10.20	20.50	2.56	36
0	EC, mS	29.54	29.10	26.20	33.10	2.22	11
11	EC, mS	28.92	29.40	22.10	32.70	2.75	16
17	EC, mS	29.07	30.65	21.70	33.80	4.55	8
Overall	EC, mS	29.15	29.60	21.70	33.80	3.02	35
0	pH	7.45	7.90	2.96	8.06	1.49	11
11	pH	7.76	7.69	7.39	8.21	0.23	17
17	pH	8.03	8.05	7.86	8.16	0.09	8
Overall	pH	7.72	7.86	2.96	8.21	0.84	36
0	Dry Matter (DM), %	6.68	6.72	5.11	8.22	1.37	6
11	Dry Matter (DM), %	*	*	*	*	*	0
17	Dry Matter (DM), %	5.53	5.23	4.67	7.21	0.99	5
Overall	Dry Matter (DM), %	6.16	5.57	4.67	8.22	1.30	11
0	Total P, g/kg product	2.05	2.17	1.03	2.66	0.49	12
11	Total P, g/kg product	1.99	1.88	1.37	3.39	0.57	17
17	Total P, g/kg product	1.63	1.62	1.19	1.88	0.23	8
Overall	Total P, g/kg product	1.93	1.87	1.03	3.39	0.51	37
0	Total K, g/kg product	4.27	4.22	4.12	4.79	0.19	12
11	Total K, g/kg product	4.24	4.25	3.92	4.65	0.18	17
17	Total K, g/kg product	4.15	4.12	3.87	4.52	0.18	8
Overall	Total K, g/kg product	4.23	4.22	3.87	4.79	0.18	37
0	Total Ca, g/kg product	2.21	2.16	1.68	2.83	0.47	8
11	Total Ca, g/kg product	2.19	2.19	2.19	2.19	*	1
17	Total Ca, g/kg product	*	*	*	*	*	0
Overall	Total Ca, g/kg product	2.21	2.19	1.68	2.83	0.44	9
0	Total Mg, g/kg product	1.03	1.09	0.49	1.38	0.29	12
11	Total Mg, g/kg product	1.03	0.96	0.70	1.95	0.33	17
17	Total Mg, g/kg product	0.89	0.90	0.61	1.13	0.19	8
Overall	Total Mg, g/kg product	1.00	0.97	0.49	1.95	0.29	37
0	Total P, g/kg DM	30.09	31.52	20.70	33.50	3.61	12
11	Total P, g/kg DM	27.53	27.60	21.08	31.11	2.79	17
17	Total P, g/kg DM	25.21	24.99	19.35	33.05	4.65	8
Overall	Total P, g/kg DM	27.86	28.17	19.35	33.50	3.86	37
0	Total K, g/kg DM	65.41	61.52	50.93	88.55	13.66	12
11	Total K, g/kg DM	62.15	63.24	30.26	86.64	14.65	17
17	Total K, g/kg DM	66.07	68.50	44.21	87.85	17.50	8
Overall	Total K, g/kg DM	64.06	63.24	30.26	88.55	14.67	37
0	Total Ca, g/kg DM	33.87	33.81	30.89	35.70	1.63	8
11	Total Ca, g/kg DM	31.78	31.78	31.78	31.78	*	1
17	Total Ca, g/kg DM	*	*	*	*	*	0
Overall	Total Ca, g/kg DM	33.63	33.55	30.89	35.70	1.67	9
0	Total Mg, g/kg DM	14.92	15.40	9.78	16.90	1.92	12
11	Total Mg, g/kg DM	14.18	14.24	11.81	15.53	0.88	17
17	Total Mg, g/kg DM	13.60	13.49	10.61	16.41	1.78	8
Overall	Total Mg, g/kg DM	14.29	14.34	9.78	16.90	1.53	37
0	mol ration Mg/P	0.63	0.62	0.56	0.76	0.05	12
11	mol ration Mg/P	0.66	0.66	0.58	0.74	0.05	17
17	mol ration Mg/P	1.70	0.80	0.65	3.52	1.35	8
Overall	mol ration Mg/P	0.88	0.66	0.56	3.52	0.74	37

Composition of Fliquid : liquid fraction of the of the screw press separator with 700 µm (3/11/2014-11/12/2014) or 500 µm (12/12/2014-24/01/2015)).

Addition	Parameter	Mean	Median	Minimum	Maximum	SD	N
0	Temperature, degrees C	10.75	10.75	10.20	11.30	0.78	2
11	Temperature, degrees C	13.55	13.55	10.10	17.00	4.88	2
17	Temperature, degrees C	*	*	*	*	*	0
Overall	Temperature, degrees C	12.15	10.75	10.10	17.00	3.28	4
0	EC, mS	32.05	32.05	29.70	34.40	3.32	2
11	EC, mS	32.25	32.25	30.80	33.70	2.05	2
17	EC, mS	*	*	*	*	*	0
Overall	EC, mS	32.15	32.25	29.70	34.40	2.26	4
0	pH	7.49	7.49	7.28	7.69	0.29	2
11	pH	7.56	7.56	7.44	7.68	0.17	2
17	pH	*	*	*	*	*	0
Overall	pH	7.52	7.56	7.28	7.69	0.20	4
0	Dry Matter (DM), %	5.04	4.99	4.47	5.61	0.41	5
11	Dry Matter (DM), %	*	*	*	*	*	0
17	Dry Matter (DM), %	4.67	4.99	2.94	6.07	1.59	3
Overall	Dry Matter (DM), %	4.90	4.99	2.94	6.07	0.93	8
0	Total P, g/kg product	1.78	1.77	0.69	2.41	0.46	13
11	Total P, g/kg product	1.75	1.93	1.04	2.33	0.36	17
17	Total P, g/kg product	1.31	1.35	0.56	1.82	0.41	6
Overall	Total P, g/kg product	1.69	1.72	0.56	2.41	0.43	36
0	Total K, g/kg product	4.05	4.22	1.91	4.34	0.65	13
11	Total K, g/kg product	4.24	4.25	3.90	4.63	0.20	17
17	Total K, g/kg product	4.02	4.00	3.77	4.32	0.19	6
Overall	Total K, g/kg product	4.13	4.21	1.91	4.63	0.42	36
0	Total Ca, g/kg product	1.92	1.88	0.90	2.63	0.44	10
11	Total Ca, g/kg product	2.03	2.03	2.03	2.03	*	1
17	Total Ca, g/kg product	*	*	*	*	*	0
Overall	Total Ca, g/kg product	1.93	1.88	0.90	2.63	0.42	11
0	Total Mg, g/kg product	0.90	0.88	0.45	1.27	0.22	13
11	Total Mg, g/kg product	0.89	0.91	0.52	1.13	0.18	17
17	Total Mg, g/kg product	0.71	0.75	0.17	0.94	0.28	6
Overall	Total Mg, g/kg product	0.86	0.89	0.17	1.27	0.21	36
0	Total P, g/kg DM	34.46	36.74	21.53	39.91	5.73	13
11	Total P, g/kg DM	33.78	36.03	20.38	38.99	5.61	17
17	Total P, g/kg DM	25.97	25.77	19.19	30.08	4.02	6
Overall	Total P, g/kg DM	32.72	34.85	19.19	39.91	6.12	36
0	Total K, g/kg DM	79.57	81.97	64.69	93.99	8.45	13
11	Total K, g/kg DM	82.98	81.75	62.06	105.69	10.48	17
17	Total K, g/kg DM	86.08	75.58	71.09	140.39	26.79	6
Overall	Total K, g/kg DM	82.27	81.27	62.06	140.39	13.52	36
0	Total Ca, g/kg DM	38.11	37.82	29.19	43.45	3.91	10
11	Total Ca, g/kg DM	37.81	37.81	37.81	37.81	*	1
17	Total Ca, g/kg DM	*	*	*	*	*	0
Overall	Total Ca, g/kg DM	38.08	37.81	29.19	43.45	3.71	11
0	Total Mg, g/kg DM	17.47	17.17	12.60	20.95	2.25	13
11	Total Mg, g/kg DM	17.22	17.29	10.13	20.73	2.57	17
17	Total Mg, g/kg DM	13.71	14.85	5.77	17.09	4.01	6
Overall	Total Mg, g/kg DM	16.73	17.07	5.77	20.95	2.99	36
0	mol ration Mg/P	0.66	0.63	0.56	0.83	0.09	13
11	mol ration Mg/P	0.65	0.64	0.56	0.78	0.06	17
17	mol ration Mg/P	3.01	1.93	0.73	9.34	3.32	6
Overall	mol ration Mg/P	1.05	0.65	0.56	9.34	1.54	36

Composition of Fsolid: solid fraction of the screw press separator with sieves 700 µm (3/11/2014-11/12/2014) or 500 µm (12/12/2014-24/01/2015).

Addition	Parameter	Mean	Median	Minimum	Maximum	SD	N
0	Temperature, degrees C	10.90	10.90	10.90	10.90	*	1
11	Temperature, degrees C	10.60	10.60	10.60	10.60	*	1
17	Temperature, degrees C	*	*	*	*	*	0
Overall	Temperature, degrees C	10.75	10.75	10.60	10.90	0.21	2
0	EC, mS	52.00	52.00	52.00	52.00	*	1
11	EC, mS	211.00	211.00	211.00	211.00	*	1
17	EC, mS	*	*	*	*	*	0
Overall	EC, mS	131.50	131.50	52.00	211.00	112.43	2
0	pH	7.99	7.99	7.99	7.99	*	1
11	pH	7.78	7.78	7.78	7.78	*	1
17	pH	*	*	*	*	*	0
Overall	pH	7.89	7.89	7.78	7.99	0.15	2
0	Dry Matter (DM), %	*	*	*	*	*	0
11	Dry Matter (DM), %	*	*	*	*	*	0
17	Dry Matter (DM), %	31.02	31.63	29.66	31.78	1.18	3
Overall	Dry Matter (DM), %	31.02	31.63	29.66	31.78	1.18	3
0	Total P, g/kg product	3.85	3.85	3.48	4.21	0.52	2
11	Total P, g/kg product	4.11	4.29	2.96	4.75	0.58	12
17	Total P, g/kg product	3.57	3.47	2.83	4.20	0.51	6
Overall	Total P, g/kg product	3.92	4.05	2.83	4.75	0.58	20
0	Total K, g/kg product	3.78	3.78	3.74	3.82	0.05	2
11	Total K, g/kg product	3.93	3.87	3.67	4.31	0.19	12
17	Total K, g/kg product	3.82	3.79	3.59	4.09	0.23	6
Overall	Total K, g/kg product	3.88	3.86	3.59	4.31	0.20	20
0	Total Ca, g/kg product	*	*	*	*	*	0
11	Total Ca, g/kg product	*	*	*	*	*	0
17	Total Ca, g/kg product	*	*	*	*	*	0
Overall	Total Ca, g/kg product	*	*	*	*	*	0
0	Total Mg, g/kg product	2.32	2.32	2.21	2.43	0.15	2
11	Total Mg, g/kg product	2.31	2.34	1.96	2.56	0.22	12
17	Total Mg, g/kg product	2.19	2.07	1.83	2.85	0.38	6
Overall	Total Mg, g/kg product	2.27	2.26	1.83	2.85	0.26	20
0	Total P, g/kg DM	10.35	10.35	10.22	10.48	0.19	2
11	Total P, g/kg DM	10.89	11.26	7.81	12.70	1.36	12
17	Total P, g/kg DM	11.26	10.77	8.74	13.87	1.83	6
Overall	Total P, g/kg DM	10.95	10.92	7.81	13.87	1.42	20
0	Total K, g/kg DM	10.25	10.25	9.50	11.00	1.06	2
11	Total K, g/kg DM	10.46	10.26	9.25	12.42	0.85	12
17	Total K, g/kg DM	12.03	11.84	11.02	13.58	1.09	6
Overall	Total K, g/kg DM	10.91	10.90	9.25	13.58	1.17	20
0	Total Ca, g/kg DM	*	*	*	*	*	0
11	Total Ca, g/kg DM	*	*	*	*	*	0
17	Total Ca, g/kg DM	*	*	*	*	*	0
Overall	Total Ca, g/kg DM	*	*	*	*	*	0
0	Total Mg, g/kg DM	6.28	6.28	6.05	6.51	0.33	2
11	Total Mg, g/kg DM	6.13	6.08	4.99	7.96	0.75	12
17	Total Mg, g/kg DM	6.87	6.73	5.63	8.70	1.12	6
Overall	Total Mg, g/kg DM	6.37	6.21	4.99	8.70	0.88	20
0	mol ration Mg/P	0.77	0.77	0.74	0.81	0.05	2
11	mol ration Mg/P	0.72	0.71	0.64	0.87	0.07	12
17	mol ration Mg/P	1.14	1.06	0.82	1.53	0.33	6
Overall	mol ration Mg/P	0.85	0.77	0.64	1.53	0.26	20

Composition of RDliquid : liquid fraction of the of the Rotaru drum separator (350 μm).

Addition	Parameter	Mean	Median	Minimum	Maximum	SD	N
0	Temperature, degrees C	15.21	15.30	10.00	20.20	3.31	11
11	Temperature, degrees C	15.26	15.40	9.80	19.30	2.53	17
17	Temperature, degrees C	17.90	17.80	16.50	19.50	0.96	8
Overall	Temperature, degrees C	15.83	16.15	9.80	20.20	2.74	36
0	EC, mS	33.07	33.50	29.80	34.70	1.52	11
11	EC, mS	32.59	33.15	26.60	36.10	2.57	16
17	EC, mS	32.15	31.85	30.60	34.60	1.37	8
Overall	EC, mS	32.64	33.20	26.60	36.10	2.02	35
0	pH	7.96	7.98	7.65	8.18	0.17	11
11	pH	7.83	7.80	7.50	8.24	0.19	17
17	pH	8.07	8.08	7.84	8.18	0.10	8
Overall	pH	7.92	7.93	7.50	8.24	0.19	36
0	Dry Matter (DM), %	5.05	5.05	4.32	5.54	0.46	6
11	Dry Matter (DM), %	*	*	*	*	*	0
17	Dry Matter (DM), %	5.60	5.72	4.94	6.17	0.46	5
Overall	Dry Matter (DM), %	5.30	5.40	4.32	6.17	0.52	11
0	Total P, g/kg product	1.86	1.79	1.25	2.31	0.31	12
11	Total P, g/kg product	1.78	1.79	1.33	2.44	0.31	17
17	Total P, g/kg product	1.75	1.66	1.39	2.18	0.31	8
Overall	Total P, g/kg product	1.80	1.76	1.25	2.44	0.31	37
0	Total K, g/kg product	4.26	4.25	4.07	4.57	0.12	12
11	Total K, g/kg product	4.26	4.30	4.00	4.55	0.18	17
17	Total K, g/kg product	4.10	4.06	4.02	4.28	0.09	8
Overall	Total K, g/kg product	4.22	4.24	4.00	4.57	0.16	37
0	Total Ca, g/kg product	1.99	1.91	1.73	2.48	0.25	8
11	Total Ca, g/kg product	1.78	1.78	1.78	1.78	*	1
17	Total Ca, g/kg product	*	*	*	*	*	0
Overall	Total Ca, g/kg product	1.97	1.90	1.73	2.48	0.25	9
0	Total Mg, g/kg product	0.94	0.91	0.63	1.20	0.18	12
11	Total Mg, g/kg product	0.92	0.91	0.65	1.20	0.16	17
17	Total Mg, g/kg product	0.95	0.93	0.76	1.14	0.13	8
Overall	Total Mg, g/kg product	0.93	0.92	0.63	1.20	0.16	37
0	Total P, g/kg DM	34.99	36.64	22.50	40.64	5.79	12
11	Total P, g/kg DM	35.50	35.32	26.85	43.15	4.53	17
17	Total P, g/kg DM	31.61	30.77	26.72	38.10	3.73	8
Overall	Total P, g/kg DM	34.49	35.32	22.50	43.15	4.95	37
0	Total K, g/kg DM	80.42	80.74	64.98	98.19	9.14	12
11	Total K, g/kg DM	86.07	84.41	70.06	102.88	9.23	17
17	Total K, g/kg DM	74.82	75.45	69.39	83.54	4.78	8
Overall	Total K, g/kg DM	81.81	81.06	64.98	102.88	9.38	37
0	Total Ca, g/kg DM	38.21	38.51	28.74	42.78	4.21	8
11	Total Ca, g/kg DM	38.68	38.68	38.68	38.68	*	1
17	Total Ca, g/kg DM	*	*	*	*	*	0
Overall	Total Ca, g/kg DM	38.26	38.68	28.74	42.78	3.94	9
0	Total Mg, g/kg DM	17.56	17.40	11.37	21.20	2.68	12
11	Total Mg, g/kg DM	18.35	19.26	14.87	21.49	2.20	17
17	Total Mg, g/kg DM	17.30	17.24	15.29	19.57	1.32	8
Overall	Total Mg, g/kg DM	17.87	17.34	11.37	21.49	2.21	37
0	mol ration Mg/P	0.65	0.63	0.57	0.80	0.06	12
11	mol ration Mg/P	0.66	0.65	0.56	0.78	0.06	17
17	mol ration Mg/P	1.40	0.78	0.65	2.67	0.93	8
Overall	mol ration Mg/P	0.82	0.66	0.56	2.67	0.52	37

Composition of RDsolid : olid fraction of the of the Rotary drum separator (350 µm).

Addition	Parameter	Mean	Median	Minimum	Maximum	SD	N
0	Temperature, degrees C	10.75	10.75	10.50	11.00	0.35	2
11	Temperature, degrees C	10.80	10.80	10.80	10.80	*	1
17	Temperature, degrees C	*	*	*	*	*	0
Overall	Temperature, degrees C	10.77	10.80	10.50	11.00	0.25	3
0	EC, mS	34.95	34.95	32.70	37.20	3.18	2
11	EC, mS	32.60	32.60	32.60	32.60	*	1
17	EC, mS	*	*	*	*	*	0
Overall	EC, mS	34.17	32.70	32.60	37.20	2.63	3
0	pH	7.69	7.69	7.40	7.97	0.40	2
11	pH	8.00	8.00	8.00	8.00	*	1
17	pH	*	*	*	*	*	0
Overall	pH	7.79	7.97	7.40	8.00	0.34	3
0	Dry Matter (DM), %	5.74	5.87	3.33	7.29	1.33	6
11	Dry Matter (DM), %	*	*	*	*	*	0
17	Dry Matter (DM), %	8.92	8.78	8.22	10.01	0.66	5
Overall	Dry Matter (DM), %	7.19	7.29	3.33	10.01	1.95	11
0	Total P, g/kg product	1.51	1.61	0.67	2.02	0.36	12
11	Total P, g/kg product	1.31	1.39	0.66	2.26	0.42	17
17	Total P, g/kg product	1.65	1.74	1.38	1.92	0.19	8
Overall	Total P, g/kg product	1.45	1.51	0.66	2.26	0.38	37
0	Total K, g/kg product	4.21	4.24	4.00	4.32	0.11	12
11	Total K, g/kg product	4.27	4.29	3.89	4.74	0.19	17
17	Total K, g/kg product	4.11	4.11	4.00	4.27	0.09	8
Overall	Total K, g/kg product	4.22	4.22	3.89	4.74	0.16	37
0	Total Ca, g/kg product	1.63	1.81	0.83	1.90	0.38	8
11	Total Ca, g/kg product	1.00	1.00	1.00	1.00	*	1
17	Total Ca, g/kg product	*	*	*	*	*	0
Overall	Total Ca, g/kg product	1.56	1.77	0.83	1.90	0.41	9
0	Total Mg, g/kg product	0.74	0.77	0.20	1.07	0.22	12
11	Total Mg, g/kg product	0.64	0.71	0.28	1.21	0.24	17
17	Total Mg, g/kg product	0.89	0.95	0.67	1.00	0.12	8
Overall	Total Mg, g/kg product	0.73	0.76	0.20	1.21	0.23	37
0	Total P, g/kg DM	26.55	28.03	16.52	31.23	4.40	12
11	Total P, g/kg DM	25.39	25.67	15.33	31.80	5.31	17
17	Total P, g/kg DM	18.11	17.57	16.09	21.63	1.85	8
Overall	Total P, g/kg DM	24.20	24.86	15.33	31.80	5.47	37
0	Total K, g/kg DM	77.60	74.31	49.21	128.44	20.98	12
11	Total K, g/kg DM	88.56	90.07	37.97	124.37	23.34	17
17	Total K, g/kg DM	45.22	46.85	37.77	50.28	4.40	8
Overall	Total K, g/kg DM	75.64	76.03	37.77	128.44	25.81	37
0	Total Ca, g/kg DM	29.62	29.50	24.79	33.15	2.78	8
11	Total Ca, g/kg DM	26.85	26.85	26.85	26.85	*	1
17	Total Ca, g/kg DM	*	*	*	*	*	0
Overall	Total Ca, g/kg DM	29.31	28.50	24.79	33.15	2.76	9
0	Total Mg, g/kg DM	12.69	14.13	6.11	15.25	2.79	12
11	Total Mg, g/kg DM	12.15	12.82	7.81	15.83	3.03	17
17	Total Mg, g/kg DM	9.78	9.28	8.18	11.95	1.42	8
Overall	Total Mg, g/kg DM	11.81	11.95	6.11	15.83	2.84	37
0	mol ration Mg/P	0.61	0.61	0.39	0.78	0.10	12
11	mol ration Mg/P	0.61	0.63	0.47	0.69	0.07	17
17	mol ration Mg/P	1.64	0.78	0.65	3.70	1.29	8
Overall	mol ration Mg/P	0.83	0.64	0.39	3.70	0.72	37

Composition of R2 : liquid fraction after storage in the buffer tank before separation.

Addition	Parameter	Mean	Median	Minimum	Maximum	SD	N
0	Temperature, degrees C	14.47	15.05	9.80	18.60	2.70	10
11	Temperature, degrees C	15.46	15.60	10.40	17.50	1.67	17
17	Temperature, degrees C	17.77	17.85	16.70	18.60	0.78	8
Overall	Temperature, degrees C	15.71	16.00	9.80	18.60	2.20	35
0	EC, mS	32.41	33.10	23.70	35.40	3.01	11
11	EC, mS	34.54	36.40	21.90	38.60	4.78	15
17	EC, mS	38.55	39.30	34.40	42.20	2.87	8
Overall	EC, mS	34.79	35.20	21.90	42.20	4.42	34
0	pH	8.03	8.04	7.78	8.23	0.15	11
11	pH	7.75	7.74	7.38	7.99	0.13	17
17	pH	7.85	7.85	7.79	7.92	0.05	8
Overall	pH	7.86	7.84	7.38	8.23	0.17	36
0	Dry Matter (DM), %	5.29	5.33	5.02	5.49	0.18	6
11	Dry Matter (DM), %	*	*	*	*	*	0
17	Dry Matter (DM), %	6.01	5.95	5.88	6.21	0.13	5
Overall	Dry Matter (DM), %	5.62	5.49	5.02	6.21	0.41	11
0	Total P, g/kg product	1.95	1.98	1.21	2.29	0.28	12
11	Total P, g/kg product	1.85	1.85	1.48	2.24	0.21	17
17	Total P, g/kg product	1.70	1.67	1.55	2.09	0.16	8
Overall	Total P, g/kg product	1.85	1.85	1.21	2.29	0.24	37
0	Total K, g/kg product	4.21	4.24	4.02	4.30	0.09	12
11	Total K, g/kg product	4.15	4.19	3.81	4.39	0.19	17
17	Total K, g/kg product	4.09	4.04	4.00	4.34	0.12	8
Overall	Total K, g/kg product	4.16	4.19	3.81	4.39	0.15	37
0	Total Ca, g/kg product	2.12	2.09	1.98	2.41	0.15	8
11	Total Ca, g/kg product	1.96	1.96	1.96	1.96	*	1
17	Total Ca, g/kg product	*	*	*	*	*	0
Overall	Total Ca, g/kg product	2.10	2.09	1.96	2.41	0.15	9
0	Total Mg, g/kg product	1.08	1.05	0.86	1.50	0.19	12
11	Total Mg, g/kg product	1.75	1.72	1.30	2.32	0.27	17
17	Total Mg, g/kg product	2.26	2.44	1.58	2.79	0.45	8
Overall	Total Mg, g/kg product	1.64	1.58	0.86	2.79	0.53	37
0	Total P, g/kg DM	36.42	37.62	24.51	40.68	4.71	12
11	Total P, g/kg DM	32.78	34.24	24.89	37.83	3.85	17
17	Total P, g/kg DM	28.46	28.13	25.45	33.61	2.30	8
Overall	Total P, g/kg DM	33.03	34.24	24.51	40.68	4.78	37
0	Total K, g/kg DM	79.04	79.91	66.60	85.72	5.74	12
11	Total K, g/kg DM	73.64	73.87	64.26	82.25	5.11	17
17	Total K, g/kg DM	68.52	68.61	63.15	73.77	3.19	8
Overall	Total K, g/kg DM	74.28	73.77	63.15	85.72	6.23	37
0	Total Ca, g/kg DM	39.90	39.62	34.64	44.01	2.73	8
11	Total Ca, g/kg DM	37.21	37.21	37.21	37.21	*	1
17	Total Ca, g/kg DM	*	*	*	*	*	0
Overall	Total Ca, g/kg DM	39.60	39.49	34.64	44.01	2.71	9
0	Total Mg, g/kg DM	20.19	18.96	17.20	30.60	3.82	12
11	Total Mg, g/kg DM	30.87	30.86	24.60	39.00	4.24	17
17	Total Mg, g/kg DM	37.75	39.84	27.46	46.82	7.00	8
Overall	Total Mg, g/kg DM	28.89	28.68	17.20	46.82	8.15	37
0	mol ration Mg/P	0.73	0.65	0.59	1.59	0.28	12
11	mol ration Mg/P	1.23	1.14	0.89	1.95	0.31	17
17	mol ration Mg/P	2.11	1.81	1.24	3.11	0.83	8
Overall	mol ration Mg/P	1.26	1.14	0.59	3.11	0.67	37

Composition of RFSliquid : liquid fraction from fabric belt separator.

Addition	Parameter	Mean	Median	Minimum	Maximum	SD	N
0	Temperature, degrees C	14.24	15.00	10.30	18.20	2.43	12
11	Temperature, degrees C	15.41	15.60	10.40	17.00	1.68	17
17	Temperature, degrees C	17.52	17.65	16.70	18.50	0.71	8
Overall	Temperature, degrees C	15.49	15.70	10.30	18.50	2.15	37
0	EC, mS	21.97	23.10	8.90	33.30	7.16	12
11	EC, mS	24.32	24.00	10.80	32.40	5.39	15
17	EC, mS	31.24	30.45	27.40	38.10	3.20	8
Overall	EC, mS	25.09	25.70	8.90	38.10	6.58	35
0	pH	8.12	8.16	7.60	8.33	0.19	12
11	pH	7.94	7.89	7.58	8.90	0.29	17
17	pH	8.04	8.04	7.97	8.09	0.05	8
Overall	pH	8.02	8.04	7.58	8.90	0.24	37
0	Dry Matter (DM), %	2.05	2.16	1.00	2.63	0.64	6
11	Dry Matter (DM), %	*	*	*	*	*	0
17	Dry Matter (DM), %	3.29	3.18	3.09	3.82	0.31	5
Overall	Dry Matter (DM), %	2.61	2.63	1.00	3.82	0.81	11
0	Total P, g/kg product	0.90	0.84	0.44	1.61	0.38	12
11	Total P, g/kg product	0.96	0.97	0.40	1.43	0.25	17
17	Total P, g/kg product	0.91	0.93	0.71	1.05	0.12	8
Overall	Total P, g/kg product	0.93	0.95	0.40	1.61	0.28	37
0	Total K, g/kg product	2.12	2.14	0.89	3.31	0.80	12
11	Total K, g/kg product	2.45	2.46	1.00	3.33	0.57	17
17	Total K, g/kg product	2.92	2.83	2.69	3.46	0.25	8
Overall	Total K, g/kg product	2.45	2.66	0.89	3.46	0.66	37
0	Total Ca, g/kg product	0.88	0.86	0.59	1.27	0.23	8
11	Total Ca, g/kg product	0.55	0.55	0.55	0.55	*	1
17	Total Ca, g/kg product	*	*	*	*	*	0
Overall	Total Ca, g/kg product	0.85	0.80	0.55	1.27	0.25	9
0	Total Mg, g/kg product	0.53	0.44	0.24	1.06	0.27	12
11	Total Mg, g/kg product	0.96	0.94	0.37	1.66	0.29	17
17	Total Mg, g/kg product	1.44	1.54	0.91	1.93	0.35	8
Overall	Total Mg, g/kg product	0.92	0.92	0.24	1.93	0.44	37
0	Total P, g/kg DM	40.61	41.83	28.59	44.17	4.38	12
11	Total P, g/kg DM	35.65	37.22	26.11	42.97	4.75	17
17	Total P, g/kg DM	27.73	27.35	22.31	31.82	3.22	8
Overall	Total P, g/kg DM	35.55	37.22	22.31	44.17	6.33	37
0	Total K, g/kg DM	95.64	97.90	83.46	102.09	5.60	12
11	Total K, g/kg DM	91.29	90.62	81.88	121.00	9.33	17
17	Total K, g/kg DM	88.82	90.22	79.51	94.65	5.35	8
Overall	Total K, g/kg DM	92.17	91.38	79.51	121.00	7.79	37
0	Total Ca, g/kg DM	51.89	52.26	47.89	59.02	3.70	8
11	Total Ca, g/kg DM	51.60	51.60	51.60	51.60	*	1
17	Total Ca, g/kg DM	*	*	*	*	*	0
Overall	Total Ca, g/kg DM	51.85	52.17	47.89	59.02	3.46	9
0	Total Mg, g/kg DM	23.09	22.37	18.47	33.78	4.03	12
11	Total Mg, g/kg DM	35.52	34.90	27.81	46.47	5.60	17
17	Total Mg, g/kg DM	46.45	45.74	30.53	54.91	9.37	8
Overall	Total Mg, g/kg DM	33.21	33.13	18.47	54.91	9.79	37
0	mol ration Mg/P	0.75	0.67	0.61	1.51	0.25	12
11	mol ration Mg/P	1.32	1.18	0.89	2.22	0.39	17
17	mol ration Mg/P	2.58	2.24	1.35	4.25	1.05	8
Overall	mol ration Mg/P	1.40	1.16	0.61	4.25	0.87	37

Composition of RFSsolid : wet Mg~P product after separation over a rotating fabric belt seperator (three parts: 80, 120 and repeated 120 µm).

Addition	Parameter	Mean	Median	Minimum	Maximum	SD	N
0	Temperature, degrees C	11.80	11.80	10.60	13.00	1.70	2
11	Temperature, degrees C	10.40	10.40	10.40	10.40	*	1
17	Temperature, degrees C	*	*	*	*	*	0
Overall	Temperature, degrees C	11.33	10.60	10.40	13.00	1.45	3
0	EC, mS	15.73	15.73	14.40	17.05	1.87	2
11	EC, mS	17.80	17.80	17.80	17.80	*	1
17	EC, mS	*	*	*	*	*	0
Overall	EC, mS	16.42	17.05	14.40	17.80	1.79	3
0	pH	7.86	7.86	7.75	7.96	0.15	2
11	pH	7.92	7.92	7.92	7.92	*	1
17	pH	*	*	*	*	*	0
Overall	pH	7.88	7.92	7.75	7.96	0.11	3
0	Dry Matter (DM), %	11.63	11.28	11.12	13.24	0.81	6
11	Dry Matter (DM), %	*	*	*	*	*	0
17	Dry Matter (DM), %	12.38	12.26	11.97	12.81	0.33	5
Overall	Dry Matter (DM), %	11.97	11.97	11.12	13.24	0.72	11
0	Total P, g/kg product	2.38	2.37	2.05	2.80	0.25	12
11	Total P, g/kg product	2.57	2.76	1.76	3.40	0.47	17
17	Total P, g/kg product	2.20	2.20	2.03	2.42	0.14	8
Overall	Total P, g/kg product	2.43	2.40	1.76	3.40	0.38	37
0	Total K, g/kg product	3.38	3.38	2.74	3.83	0.32	12
11	Total K, g/kg product	3.34	3.28	2.59	4.05	0.41	17
17	Total K, g/kg product	3.42	3.43	3.14	3.65	0.20	7
Overall	Total K, g/kg product	3.37	3.40	2.59	4.05	0.34	36
0	Total Ca, g/kg product	2.59	2.55	2.39	2.92	0.18	8
11	Total Ca, g/kg product	2.56	2.56	2.56	2.56	*	1
17	Total Ca, g/kg product	*	*	*	*	*	0
Overall	Total Ca, g/kg product	2.59	2.55	2.39	2.92	0.17	9
0	Total Mg, g/kg product	1.41	1.35	1.05	2.09	0.30	12
11	Total Mg, g/kg product	2.25	2.31	1.72	2.88	0.33	17
17	Total Mg, g/kg product	2.64	2.69	2.06	3.25	0.40	8
Overall	Total Mg, g/kg product	2.07	2.14	1.05	3.25	0.58	37
0	Total P, g/kg DM	20.27	20.07	17.37	24.98	2.46	12
11	Total P, g/kg DM	20.53	21.51	14.72	27.06	3.36	17
17	Total P, g/kg DM	17.35	17.43	16.67	18.20	0.54	8
Overall	Total P, g/kg DM	19.76	18.82	14.72	27.06	2.93	37
0	Total K, g/kg DM	28.82	29.08	20.36	34.15	3.94	12
11	Total K, g/kg DM	26.81	26.03	22.07	36.12	3.63	17
17	Total K, g/kg DM	23.88	27.11	0.00	28.49	9.70	8
Overall	Total K, g/kg DM	26.83	27.19	0.00	36.12	5.67	37
0	Total Ca, g/kg DM	22.31	22.04	20.53	24.83	1.25	8
11	Total Ca, g/kg DM	20.54	20.54	20.54	20.54	*	1
17	Total Ca, g/kg DM	*	*	*	*	*	0
Overall	Total Ca, g/kg DM	22.11	21.77	20.53	24.83	1.31	9
0	Total Mg, g/kg DM	11.95	11.25	9.33	17.13	2.28	12
11	Total Mg, g/kg DM	18.00	18.21	14.92	21.15	1.86	17
17	Total Mg, g/kg DM	20.88	21.29	16.19	25.38	3.26	8
Overall	Total Mg, g/kg DM	16.66	17.48	9.33	25.38	4.17	37
0	mol ration Mg/P	0.76	0.71	0.64	1.24	0.17	12
11	mol ration Mg/P	1.14	1.07	0.89	1.56	0.21	17
17	mol ration Mg/P	1.67	1.69	1.16	2.12	0.39	8
Overall	mol ration Mg/P	1.13	1.07	0.64	2.12	0.41	37

Annex 6 Calculation mass digestate and liquid fraction first separation

Flows of ingoing digestate (1) and outgoing liquid fraction (2) of the two step separation (Mechanic separator 1) were calculated from measured weight of the solid fraction and measured chemical composition of digestate (1), liquid fraction (2) and solid fraction (3).

Volumes of digestate (1) and liquid fraction (2) were not measured during the report period.

Volumes can be calculated from mass balances for fresh matter and for a value giving component (e.g. phosphorus, nitrogen).

Mass balance fresh matter

$$M_{\text{digestate}} = M_{\text{liquid fraction}} + M_{\text{solid fraction}} \qquad [1]$$

With:

$M_{\text{digestate}}$: Mass of digestate (1) in kg fresh
$M_{\text{liquid fraction}}$: Mass of liquid fraction (2) in kg fresh
$M_{\text{solid fraction}}$: Mass of solid fraction (3) in kg fresh

Mass balance nutrient, example given phosphorus

$$M_{\text{digestate}} \times P_{\text{digestate}} = M_{\text{liquid fraction}} \times P_{\text{liquid fraction}} + M_{\text{solid fraction}} \times P_{\text{solid fraction}} \qquad [2]$$

With:

$P_{\text{digestate}}$: P content of digestate (1) in g P/kg fresh
$P_{\text{liquid fraction}}$: P content of liquid fraction (2) in g P/kg fresh
$P_{\text{solid fraction}}$: P content of solid fraction (3) in g P/kg fresh

Subtitution of [1] and [2] leads to:

$$M_{\text{digestate}} = M_{\text{solid fraction}} \times \frac{(P_{\text{solid fraction}} - P_{\text{liquid fraction}})}{(P_{\text{digetate}} - P_{\text{liquid fraction}})} \qquad [3]$$

Annex 7 Composition of intermediates and products

Product	Step	Parameter	Average	Median	Minimum	Maximum	Standard-deviation	Count
Digestate	1	Dry matter, %	4.87	4.84	2.96	7.17	0.93	25
		Organic matter, % in the dry matter	65.58	65.34	54.55	72.71	4.17	24
		Volumetric mass, g/L	1020	1017	1001	1051	11.8	24
		pH	8.07	8.09	7.72	8.44	0.17	25
		N-total, g/kg	4.65	4.72	3.15	5.99	0.53	25
		NH4-N, g/kg	*	*	*	*	*	0
		P-total, g/kg	1.19	1.20	0.52	1.98	0.27	25
		ortho-P, g/kg	0.178	0.178	0.178	0.178	*	1
		K-total, g/kg	3.10	3.18	1.49	3.76	0.57	25
		Mg-total, g/kg	0.94	0.77	0.24	3.25	0.71	25
		Ca-total, g/kg	2.34	1.53	0.06	14.49	3.33	25

Product	Step	Parameter	Average	Median	Minimum	Maximum	Standard-deviation	Count
Liquid fraction	2	Dry matter, %	3.31	3.40	1.67	5.17	0.70	24
		Volumetric mass, g/L	1016	1017	999.7	1035	9.33	24
		pH	8.18	8.19	7.84	8.46	0.16	24
		N-total, g/kg	4.18	4.30	2.31	4.81	0.62	24
		NH4-N, g/kg	2.55	2.64	1.28	3.36	0.53	24
		P-total, g/kg	1.01	1.06	0.39	2.27	0.37	24
		ortho-P, g/kg	0.17	0.17	0.08	0.30	0.01	24

Product	Step	Parameter	Average	Median	Minimum	Maximum	Standard-deviation	Count
Solid fraction	3	Dry matter, %	35.71	36.15	8.74	46.05	6.53	25
		Organic matter, % in the dry matter	85.51	86.57	57.26	91.68	6.54	25
		Volumetric mass, g/L	687	719	389	1017	152	24
		pH	8.72	8.73	8.45	8.93	0.14	25
		N-total, g/kg	7.44	7.66	3.89	9.09	1.04	25
		NH4-N, g/kg	*	*	*	*	*	0
		P-total, g/kg	4.31	4.29	3.04	6.60	0.75	25
		ortho-P, g/kg	*	*	*	*	*	0
		K-total, g/kg	4.16	4.57	0.49	7.78	1.67	25
		Mg-total, g/kg	2.88	2.98	0.32	5.03	0.97	25
		Ca-total, g/kg	6.32	6.68	0.60	12.54	2.39	25

Product	Step	Parameter	Average	Median	Minimum	Maximum	Standard-deviation	Count
Effluent of ammonia stripper	5	Dry matter, %	2.27	2.19	0.46	3.75	0.89	9
		Organic matter, % in the dry matter	48.08	48.30	30.00	63.78	8.88	9
		Volumetric mass, g/L	1005	1006	993	1014	7.39	9
		pH	8.85	8.96	8.19	9.05	0.27	9
		N-total, g/kg	1.85	1.95	0.37	2.77	0.63	9
		NH4-N, g/kg	1.05	1.05	0.36	1.38	0.32	9
		P-total, g/kg	0.42	0.37	0.01	0.99	0.35	9
		ortho-P, g/kg	*	*	*	*	*	0
		K-total, g/kg	2.93	3.22	0.49	3.66	1.01	9
		Mg-total, g/kg	0.22	0.12	0.05	0.60	0.21	9
		Ca-total, g/kg	0.60	0.40	0.25	1.44	0.44	9

Product	Step	Parameter	Average	Median	Minimum	Maximum	Standard-deviation	Count
Acid liquid fraction	7	Dry matter, %	2.30	1.30	0.81	5.39	1.27	28
		Organic matter, % in the dry matter	57.4	57.4	52.4	62.5	7.16	2
		Volumetric mass, g/L	1008	1009	991	1029	10.2	26
		pH	5.73	5.74	4.60	6.76	0.46	28
		N-total, g/kg	1.31	0.98	0.34	2.83	0.83	28
		P-total, g/kg	0.60	0.53	0.33	1.10	0.23	28
		ortho-P, g/kg	0.49	0.46	0.22	0.92	0.20	26
		K-total, g/kg	1.27	0.52	0.37	2.91	1.43	3
		Mg-total, g/kg	0.41	0.41	0.27	0.54	0.13	3
		Ca-total, g/kg	0.79	0.69	0.60	1.08	0.26	3

Product	Step	Parameter	Average	Median	Minimum	Maximum	Standard-deviation	Count
Organic soil amendment, P depleted	8	Dry matter, %	30.38	31.01	24.50	35.43	3.06	28
		Organic matter, % in the dry matter	92.40	92.71	89.54	95.08	1.55	28
		Volumetric mass, g/L	753	735	539	989	142.71	26
		pH	6.37	6.43	5.47	6.98	0.37	28
		N-total, g/kg	4.01	4.05	3.10	5.20	0.61	28
		P-total, g/kg	1.13	0.91	0.40	4.72	0.94	28
		ortho-P, g/kg	*	*	*	*	*	0
		K-total, g/kg	2.16	2.06	0.13	5.08	1.27	27
		Mg-total, g/kg	0.90	0.77	0.08	2.41	0.54	27
		Ca-total, g/kg	4.05	3.55	0.89	11.56	2.12	27

Product	Step	Parameter	Average	Median	Minimum	Maximum	Standard-deviation	Count
Recycled water	11	Dry matter, %	1.57	1.21	0.41	3.90	1.11	29
		Organic matter, % in the dry matter	35.19	35.97	20.44	50.36	7.82	27
		Volumetric mass, g/L	1003	1002	992	1020	7.85	27
		pH	8.67	8.58	7.81	9.70	0.45	29
		N-total, g/kg	1.07	0.78	0.27	2.60	0.72	29
		P-total, g/kg	0.11	0.01	0.00	0.84	0.26	29
		ortho-P, g/kg	0.006	0.006	0.002	0.009	0.005	2
		K-total, g/kg	1.47	1.05	0.37	3.42	1.04	29
		Mg-total, g/kg	0.47	0.40	0.19	1.17	0.28	29
		Ca-total, g/kg	1.04	0.81	0.19	3.41	0.89	29

Product	Step	Parameter	Average	Median	Minimum	Maximum	Standard-deviation	Count
Calcium phosphate	12	Dry matter, %	6.04	3.53	0.38	83.44	14.44	31
		Organic matter, % in the dry matter	45.87	46.31	24.44	56.97	6.90	31
		Volumetric mass, g/L	1010	1010	981	1039	13.00	27
		pH	8.55	8.55	7.76	9.78	0.47	31
		N-total, g/kg	2.19	1.27	0.42	22.42	3.84	31
		NH4-N, g/kg	1.05	1.00	0.37	1.80	0.49	21
		P-total, g/kg	2.79	1.16	0.06	49.25	8.66	31
		ortho-P, g/kg	*	*	*	*	*	0
		K-total, g/kg	1.56	1.04	0.13	4.12	1.29	31
		Mg-total, g/kg	1.07	0.60	0.11	12.96	2.24	31
		Ca-total, g/kg	5.99	3.58	0.22	63.13	12.21	31

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