EIP-AGRI Focus Group - Nutrient recycling

Mini-paper – Available technologies for nutrients recovery from animal manure and digestates

David Fangueiro[1], Emilie Snauwaert[2], Giorgio Provolo[3], Dolores Hidalgo[4], Fabrizio Adani[3], Christian Kabbe[5], Augustus Bonmati[6], Jeanet Brandsma[7]

[1]LEAF, Instituto Superior de Agronomia, Universidade de Lisboa, Portugal

[2] vcm-mestverwerking, Belgium

[3] University of Milano, Italy

[4] CARTIF, Spain

[5]Berlin Centre of Competence for Water, Germany

[6]IRTA, Spain

[7]Netherland

1. Introduction

During many years, the main sources of plant nutrients at farm scale were organic materials provided by livestock production (solid manure) or some plant residue that were stored until soil application.

With the increase of mineral fertilizers utilization in the 70´s, the use of organic materials as source of nutrients strongly declined. There are several reasons for this, namely the intensification of crop production, the decoupling of arable and livestock farms and the need to produce more at a lower price.

Today, we are facing a new challenge: on one hand, raw materials for mineral fertilizers have a limited availability and such availability relies on geopolitical and economic conditions. Furthermore, mineral fertilizer synthesis has a strong impact on environment. As a consequence, a reduction of mineral fertilizers production might be expected for the next decades. On the other hand, large amounts of organic materials, namely animal manure and sewage sludge, become a problem for livestock farm and waste water treatment plants (WWTP) but also represent an available and renewable source of nutrients. Hence, it looks logical to increase the use of organic materials as fertilizers in arable farms.

Nevertheless, organic materials present several limitations in their use: high variability of composition (total concentration of N, P, K; imbalance N:P:K ratio), high moisture content, require specialized equipment for application.

Several technologies are available today for manure/digestate treatment, some to improve manure management and application, some to concentrate nutrients, some to produce energy. Detailed information about the best available techniques for manure and digestate treatment has been reported in several publication over the last years (Schoumans et al., 2010; Flotats et al., 2011; Foged et al., 2011; Frandsen et al., 2011; Egle et al., 2015; Kabbe et al., 2015; Camargo-Valero et al., 2015; Bamelis et al., 2015; Vaneeckhaute et al., 2016) and the Agro Technology Atlas (**http://www.agro-technology-atlas.eu**) is today one of the most resourceful database relative to manure treatment technologies. Furthermore, the "inventory of technology reviews" maintained by WETSUS available online on the ESPP website www.phosphorusplatform.eu under "downloads" provides a commented list of publications related with nutrient recovery technologies.

However, from all the available technologies, only a limited number is fully used at farm scale. Indeed, the amount of manure processed in Europe represent less than 8% of the total amount produced (Foged et al., 2011). The reluctance of farmers for some techniques relies on several parameters that vary depending on the European region considered.

In the present paper, we intend to give a brief overview of the available processing techniques for manure and digestate illustrated with some success stories of utilization at farm scale in order to clarify the gap existing between available technologies and farmers demands.

2. Available Technologies

1. Acidification

Animal manure is a rich source of nitrogen, namely ammonium (NH_4^+) that is directly available for plants. However, part of this ammonium nitrogen can be lost during storage or field application due to ammonia (NH_3) volatilization. Indeed, the equilibrium between NH_4^+ dissolved in the slurry and NH_3 can be easily disturbed leading to N losses to atmosphere (Fangueiro et al., 2015). NH_3 emissions are a severe environmental problem with impacts on humans and animal welfare. 80% of the total NH_3 emissions from agricultural activities are from barns and slurry stores represent up and more than 50% of the applied N can be lost by NH_3 emissions during and after slurry application to soil. Such losses led to two main problems in term of nutrients use efficiency: a decrease of the fertilizer value of slurry in terms of nitrogen and a significant variability of N concentrations in slurry during field application.

Slurry acidification is a simple solution to avoid NH_3 emissions but such technique is today used at farm scale exclusively in Denmark and in some countries of North and Eastern Europe. The main reason for this low implementation at farm scale in other European countries is probably the fear of farmers relative to the handling of concentrated acids (mainly sulfuric acid). Indeed, such operation has to be performed by trained staff and implies, in most cases, to rely on contractors. On the other hand, the acidified slurry has characteristics significantly different from raw slurry, namely in terms of buffering capacity, N and P speciation, electrical conductivity. Slurry acidification can also lead to significant CO_2 emissions during the process as well as H_2S emissions during storage. The consequences of long term application of acidified slurry to soil are still unclear and the decrease of soil pH and increase of S content in soil are often presented as the principal threat of acidified (H_2SO_4) slurry application to soil. Finally, tools for fast and accurate measurement of slurry pH are still missing what difficult oversight operation by authorities in farms using such technique.

Techniques are available for slurry acidification directly in slurry channels in the animal house, in the storage or during spreading in fields.

Acidification in slurry channels implies pumping the slurry to a process tank where the slurry is acidified and then, part of the acidified slurry is flushed back to the slurry channels while another part is pumped to a storage tank. A clear overview of the system proposed by JH Agro can be found at **https://www.youtube.com/watch?v=u_gjFt3Rk44**. Such solution is quite exclusive for new animal houses even if it can be adapted to existing animal houses.

funded by European Commission

Another alternative, more adapted to older livestock units, consists in acidifying slurry in the storage tank. Such process has to be performed by specialized staff and it might be necessary to repeat the process several times during the storage period to ensure minimum NH_3 losses. Another solution is to acidify the slurry in the storage tank only few days before slurry application in fields. From the 3 acidifying techniques proposed here, acidification in storage appears as the most easily to perform in any farm and should be, in the future, the most commonly used all around Europe.

Finally, acidification of slurry during spreading is also an option using the SyreN system that allows continuous acidification directly in the slurry tanker immediately before application. Full details about this solution can be consulted at **http://www.biocover.dk/home** and a full overview of the process can be seen at **https://www.youtube.com/watch?v=Evz6WbXssuQ**.

Table 1. Main characteristics of raw and acidified pig and dairy slurries (wet weight basis) - mean of 3 replicates. In each column and for each slurry type, values followed by different letters are significantly (P<0.05) different based on a Tukey test.

Treatment	DM	TOC	TN	N-NH_4^+	TP	P_{sol}	K
				(g Kg^{-1})			
Pig slurry							
RP	41.0^b	17.6^c	2.64^b	1.61^a	0.59^b	0.02^b	1.42^a
SP	44.8^b	19.3^b	2.74^b	1.71^a	0.55^b	0.41^a	1.43^a
AP	62.1^a	23.7^a	3.18^a	1.73^a	0.73^a	0.00^c	1.45^a
Dairy slurry							
RD	94.9^c	39.0^b	3.05^a	0.94^b	1.09^b	0.01^b	3.36^a
SD	106.3^b	43.3^a	3.10^a	1.33^a	1.29^a	0.37^a	3.17^a
AD	118.5^a	44.1^a	3.17^a	1.33^a	1.43^a	0.00^b	3.26^a

RP: Raw Pig Slurry; **SP**: Pig Slurry acidified with Sulfuric acid; **AP**: Pig Slurry acidified with Alum; **RD**: Raw Dairy Slurry; **SD**: Dairy Slurry acidified with Sulfuric acid; **AD**: Dairy Slurry acidified with Alum.**DM**: Dry Matter; **TOC**: Total Organic Carbon; **TN**: Total Nitrogen; **N-NH_4^+**: Amonium; **TP**: Total phosphorus; **Psol**: soluble phosphorus; **K**: Potassium; **C:N ratio**: Carbon to Nitrogen ratio.

A full technical description of all these techniques can be found in (Fangueiro et al., 2015) and (Sindhöj E. and Rodhe L., 2013).

Till now, the acidification agent used is exclusively sulfuric acid since it is the cheapest additive available and it requires generally less than 1 L of H_2SO_4 per cubic meter of slurry to decrease slurry pH from 8 to 5.5. On the other hand, it leads to slurry enrichment in terms of sulphur. This last point can be seen as an advantage in fields where sulphur contents are low since application of acidified slurry might replace synthetic S fertilizer. As previously referred the use of concentrated H_2SO_4 is one of the main limitation to a more extensive use of this technique at farm scale and some new additives as aluminium sulphate, elemental sulphur or weak acids have been tested. There is also a strong interest in promoting self-acidification but all these alternatives to sulphuric acid are still at research level. Another limitation of using H_2SO_4 is the fact that it cannot be used for solid fraction or solid manure since it will increase moisture content and lead to a heterogeneous acidification.

Slurry acidification is promoted to minimize N losses but it might also increase P plant availability since the amount of soluble P increase significantly when slurry is acidified with sulfuric acid (see Table 1). Nevertheless such effect relies on the slurry type with a stronger effect in pig slurry relative to dairy slurry.

The application of acidified slurry relative to non-acidified slurry might lead to an increase of yields and N uptake (Hoeve et al., 2016). Furthermore, acidified slurry has a higher proportion of dissolved P than non-acidified slurry. For this reason, some studies pointed out that it might be of interest to apply acidified slurry before maize since it could stimulate maize growth acting as a starter fertilizer.

A combination of acidification with other technologies as separation or composting is of interest and recently, Regueiro et al. (2016) showed that acidification has a positive impact on separation.

Several Danish farms are now using the system of slurry acidification in the animal house and during spreading. The main reason to use such systems is related with the request of local authorities to include, in any demand of animal farm expansions, the implementation of new measures to reduce ammonia emissions. By using such systems, farmers are then authorized to increase the number of animals at farm. Furthermore, the acidified slurry has a higher fertilizing value than raw slurry. Hence, even in arable farms where slurry is used as organic fertilizer, application of acidified slurry might be of interest.

The system of acidification in storage tank is used mainly in Denmark but also in Estonia where slurry acidification is performed, first to enrich slurry in terms of sulphur and secondly to minimize ammonia emissions. Indeed, farmers argue that sulphuric acid is cheaper than mineral S fertilizer and, with a single slurry application, most of the nutrients are applied to the soil with no need of extra mineral fertilizer application. It represents not only a significant decrease of costs associated to soil fertilization (energy, machinery etc.) but also a decrease of soil compaction and CO_2 emissions.

Also from Denmark, the SME Biocover developed a mobile slurry acidification and on-field spreading system called SyreN. More than 100 units have been sold in Denmark alone and market exploration in Europe is ongoing. **www.biocover.dk**.

2. Ammonia stripping

Ammonia can be stripped by air, steam or vacuum through the liquid fraction in a packed tower (See Figure 1). Ammonia stripping can be obtained directly from the manure or digestate or even from their respective liquid fraction by heating at 80 °C. Nevertheless, a pH lifting (with NaOH) up to 10.5 and temperature of 70 °C, allow 85-90% of ammonia to be stripped.

Literature reported that pH optimization has more importance than temperature. So, the N-recovery rate manly depends on the NaOH consumed for pH lift.

Stripped gas rich in ammonia is then recovered by washing air flux with strong acid solution (H_2SO_4), which produces ammonium sulfate (N = 3-8 % w/w). Besides H_2SO_4 as sorbent, also nitric acid (HNO_3) can be applied to obtain ammonium nitrate, as it is done at Oslo WWTP (Sweden) or at the Flemish company Detricon. Also capture of NH_3 in water yields in a commercial product – the ammonia water $NH_3(aq)$ with concentrations up to 25%.

Another solution is represented by "cold ammonia stripping" to be operated on mineral concentrate (see above). In this case N stripping can be operated at ambient temperature by adjusting pH with CaO (or similar). Performance reported for full scale plant are of 80-90 % of ammonia stripped.

Such technology has Technology readiness levels (TRL) of 9 and total cost for S/L separation and successive ammonia stripping (hot stripping) were reported for full scale plant between 3 to 6 € m^{-3}.

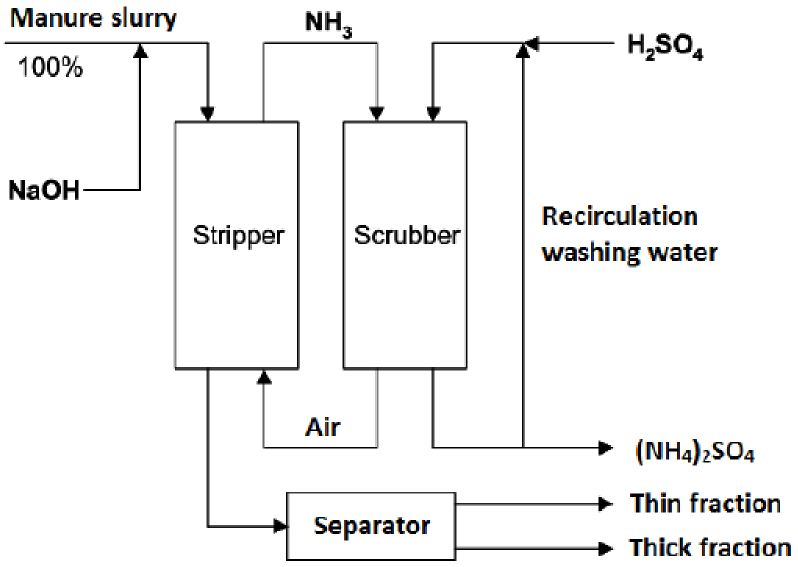

Figure 1. An ammonia stripping scheme (from: Biorefine, 2015)

3. Anaerobic digestion

During the various metabolic steps of anaerobic digestion (hydrolysis, acidogenesis, acetogenesis, methanogenesis) the organic matter is first degraded up to the obtaining of volatile fatty acids (mainly acetic acid), carbon dioxide and hydrogen. The latter are transformed from methanogenic bacteria by closing the fermentation cycle. The concentration of volatile fatty acids is therefore one of the key parameters to be taken under control for a correct evolution of the fermentation process.

During the anaerobic digestion the organic nitrogen is mineralised and at the end of the process the ratio of ammonia and total nitrogen may reach 70-80%. The increase of the ammonia nitrogen concentration also leads to an increase in pH usually between 8 and 9. However, the digestion process does not modify the total amount of nitrogen in the products.

The anaerobic digestion represents a potentially very effective treatment in reducing greenhouse gas emissions: in fact, during the process the majority of fermentable organic matter is degraded to methane and carbon dioxide, obtaining an effluent (digestate) having a lower GHGs emission potential than the incoming products. However, some studies have reported an increase in methane emissions during storage of digestate. This effect may be related to the hydraulic retention time in the digester that might be too short to complete the degradation of the material in the biogas plant and thus continues in the storage. In addition, significant biogas losses can occur even from the pipes and the covers of digesters that can easily reach 10% of the biogas produced.

This treatment may increase the ammonia emissions in the subsequent storage phase. The digestate is usually characterized by higher ammonia nitrogen content and pH than to the starting slurry, both factors that facilitate the volatilization of the ammonia process. Another factor that facilitates these emissions is the content and type of solids present in the digestate; these in fact are reduced in quantity and size because of degradation processes, features that do not facilitate the formation of a crust, which may represent an effective barrier to emissions.

Anaerobic digestion in addition to producing renewable energy allows for other benefits:

funded by European Commission

- Abatement of odours: the smelly substances that are formed during the process (hydrogen sulphide, mercaptans) are contained in the biogas and sent to the combustion.
- Stabilization of manure and co-substrates: the demolition of the carbonaceous organic load resulting from the anaerobic digestion gives the manure a sufficient stability in subsequent periods of storage; it causes a slowdown of the degradation and fermentation processes.
- Reduction of the pathogens: the anaerobic digestion in mesophilic environment (40 °C) can partially reduce the pathogenic charge in the manure. By operating in thermophilic conditions (55 °C) it is possible, instead, to get the full hygienization of the sewage with the total destruction of the pathogens.

Table 2 reports the content variations of the main parameters during the anaerobic process for manure.

The solids and nutrient variations of the co-substrates depend greatly from the products used and their degradability.

Table 2. Variation of the characteristics of the effluent during treatment of anaerobic digestion compared to the product inlet.

Type of manure	Total solids (%)	Volatile solids (%)	Total nitrogen (%)	Ammoniacal nitrogen (%)	P (%)	K (%)
Cattle slurry	- 15÷35	- 20÷40	none	+ 30÷60	none	none
Pig slurry	- 20÷70	- 25÷80	none	+ 20÷50	none	none
Poultry	- 35÷40	- 45÷50	none	+ 30÷50	none	none

The volume of the products decrease during the process due the mass loss of the gas that can be accounted considering the density of the biogas produced.

Anaerobic process has been widely applied in several countries (Figure 2). The diffusion has been influenced by the national or local legislations (especially related to the type of co-substrates and the land use of the digestate) and incentives, thus the diffusion is not homogenous in European countries. According to the European Biogas Association, there were more than 17,000 biogas plants in Europe at the end of 2014 (**http://european-biogas.eu/2015/12/16/biogasreport2015/**).

A description of the technology and economic indicators can be found at this link **http://agro-technology-atlas.eu/techdescs.aspx?techgroup=600.**

Figure 2. Anaerobic digestion system used in a swine farm in Northern Italy

4. Composting/biothermal drying/hygienization

Composting is a natural process where micro-organisms convert the fresh organic material under controlled conditions into a stable and humus rich product.
Biothermal drying of the solid fraction of pig manure is frequently carried out in order to pasteurize manure at 70°C for 1 hour without using external heat (Figure 3). It is a short, very intensive composting process that takes only a few days. The end-product is an organic fertiliser/soil improver suitable for export and use in agriculture.

Composting (self-heating) of the product at temperatures exceeding 70°C is only possible if a maximum of 30 wt% of solid fraction of pig manure is used. This can then be combined with the solid fraction of cattle slurry, cattle manure with straw, horse manure or poultry manure to obtain enough structure and an optimal C/N ratio. Some sites also add vegetal biomass or vegetable, fruit and garden (VFG) waste or green waste compost.

This mostly occurs in a closed shed consisting of several tunnels which can be closed off and aerated separately (large capacity). It can also be done by use of an aerated drum (feasible at farm scale level). The material can also be placed in rows on the floor and is turned over manually (extensive composting).

Farm-level composting could be used for optimisation of the quality of the solid fraction of manure as fertilizer/soil improver, and reduce nutrient losses during storage.

If a farmer has invested in a separation system (screw press), he can use the liquid fraction as an NK-fertiliser on his land, and can do a hygienisation of the solid fraction. In this way he obtains an organic fertiliser which can be exported outside the country, or can be sold to the private market (gardening, etc.). In the Netherlands, the pasteurised solid fraction is also used as bedding material for cows. This gives an extra guaranty that no infection will occur. In the Netherlands there are two companies who offer a decentralized (farm-scale level) aerated drum in which solid fraction of manure can be pasteurised. This is an aerated rotating drum in which manure/digestate is pasteurised without any

funded by European Commission

external heat. Because of the rotation, and the air that is blown with a ventilator into the drum, a natural composting process starts.

a) *Company 1*

The temperature of the solid fraction increases up to 60°C during several hours. This installation is already recognised in the Netherlands according to the EU 1069/2009. Pasteurisation of only pig manure can be difficult (low in fibres), so it is necessary to add other fibrous material (f.e. poultry manure) to increase the temperature in the pile. The residence time is about 15 to 24h (depending on the input material). The labour for the farmer is only 20 minutes a day. For dairy farmers, this system is available from 175 cows. Today, in the Netherlands, there are several installations running on digestate, cow manure and a mixture of pig, poultry and cow manure.

b) *Company 2*

The temperature increases up to 70°C or more, so the installation is recognised according to the EU1069/2009. The drum is covered by a container; in this way all safety procurements are met, and higher temperatures can be reached. The drum is made of plastic, so the drum remains in a temperature controlled environment, so the solid fraction can dry easier. The end product has a dry matter content of 42-47% (with input of 32-35% DM). The smallest drum has a capacity of 3.5-5 m³ solid fraction/h (manure of 200-220 cows).Today, in the Netherlands, already 7 installations are running (on cow manure or pig manure).

Figure 3. Aerated drum for biothermal drying on farm scale level

In Flanders first trials are running in practice for the use of a similar aerated drum. Especially farmers at the border with France are interested in this technique: by pasteurisation of the solid fraction, they can transport the solid fraction to their neighbouring French farmers (pasteurisation of pig/cow manure is needed for cross-border transport).

Farm-level composting is an extensive process, in open air, where no external aeration is used. To obtain a good composting process, it is necessary to have a good ratio of carbon-rich input materials and N-rich input materials. Also the temperature, CO2- and moisture content are important parameters.

To aerate and homogenise the pile it is necessary to turn it over from time to time. At farm level this can be done with a windrow turner. The follow-up and turning of the pile requires extra time and labour for the farmer.

The objective of extensive farm composting is to produce a homogeneous and stable product to apply on Flemish agricultural land; this for maintenance of the soil (application of OM). If the product can be pasteurised by the composting process, the end product can be exported.

In Flanders there is one installation who has an operational extensive composting plant (recognised according to the EU1069/2009), but different external input materials (mostly combination of poultry and pig manure) are needed to obtain the required temperature for pasteurisation. With input of only solid fraction of pig manure the needed temperature cannot be obtained.

5. Mechanical Solid-liquid separation

Mechanical separation of raw manure or digestate results in the concentration of nitrogen (and potassium) in the liquid fraction, and the concentration of phosphorus and organic material in the solid fraction.

This technique is mostly applied as pre-treatment for nutrient recovery techniques. However, separation can already be an interesting manure management technique. The liquid N-rich fraction, can be used on arable land/grassland on the farm to reduce the use of mineral fertiliser. The solid fraction contains a high concentration of phosphorus and is mainly used in regions with low P-soils and/or with a high demand of carbon. By concentration of P in the solid fraction, a high amount of P can be transported in a small volume (15-20% solid fraction).

Separation of manure can be achieved by different techniques as screw press, centrifuge or belt press (Figure 4) fully described by Hjorth et al. (2010). The choice of technique depends on the type of manure, the desired end product, the volume that needs to be separated (needed capacity), the investment- and operational costs, etc.

Recently, there is a renewed interest in (mobile) separation of manure (by screw press or centrifuge) in European countries as Denmark, Netherlands, Spain and Belgium, namely in Flanders. The advantage of separation is that the farmer can separate the on-farm produced manure and use the resulting N-rich liquid fraction (low in P; higher N:P ratio) on his proper farm, according to crop needs. The remaining part (15-20% solid fraction) can be transported/processed, so the transport and processing costs of the manure that needs to be disposed can be reduced. Moreover, as the liquid fraction aligns better with crop nutrient needs (N:P ratio), according to the Flemish fertilisation limits, higher volumes of animal manure can be spread on Flemish land, so the use of mineral fertiliser can be decreased. The solid fraction can be used on agricultural land (f.e. maize, potatoes) or in fruit farming (high demand of C); although the high P-content needs to be taken into account. The solid fraction can also be used as input material for co-digestion or can be processed on an external site (biothermal drying to obtain pasteurised fertiliser/soil improver for export/private market).

The main objective of pig farmers to separate manure is to dispose P from the farm (pig manure has a low N:P ratio) while, for cattle/dairy farmers, also the use of the liquid fraction on grassland/agricultural land (easy to spread, high N:P ratio) is a major motivation.

A centrifuge is more expensive (investment and operational cost) than a screw press and, as individual investment, a centrifuge is in most cases not feasible while a screw press, more adapted to moderate volumes of sludge or manure is more affordable. For this reason there are different dairy farmers in Flanders who have a stationary screw press and there are now 4 mobile separation systems, for separation of pig manure (centrifuge) and cow manure (screw press).

Figure 4. slurry separation devices used at farm scale (belt press and screw press)

6. Membrane and Ultrafiltration technique

Membrane (MF) and ultrafiltration (UF) techniques consist in physical separation by forcing stream input (i.e. liquid fraction of manure or digestate after decanter digestate centrifugation, through membrane by means of pressure (Figure 5). Membranes used to process digestate can be classified as in the following according to pore size: MF- (pores > 0.1 µm, 0.1-3 bar), UF- (pores > nm, 2-10 bar) and RO-membranes (no pores, 10-100 bar). Membranes used can be either organo-polymeric or ceramic. The first ones are less expensive but they are difficult to be cleaned and they do not support high pressure. Ceramic membrane, used above all for ultrafiltration, are easier to be cleaned (they have resistance to chemicals) and they allow higher performance because of high pressure used. Nevertheless, the higher the separation performance, the higher the energy consumption what might be the main limitation for the implementation of such technique.

Membranes operate a separation of the suspended solid fraction. This process is generally used as pretreatment of the reverse osmosis in a cascade modality. Reverse osmosis applied to the digestate consist in the MF or UF refining.

funded by European Commission

Figure 5. Ultrafiltration plant used for pig slurry treatment

Ultrafiltration + reverse osmosis, have been reported to be able producing mineral concentrate, i.e. 0.5-1 % w/w (95 % ammonia) to be used directly as NK-fertilizer. The permeate of RO, that still contains small ions, can be discharged, maybe after a 'polishing' step, or used as process water.

Mineral concentrate can be successively treated by N stripping technology to remove ammonia producing clean water to be directly discharged in shallow water and ammonia sulfate (7-8% N). This last configuration allows a total digestate volume reduction of 50-70 %. Technology readiness levels (TRL) of 9.

Total cost for centrifugation + UF + OI were reported for full scale plant between 4 to 12 € m^{-3}

Nevertheless, it is refer that membrane filtration systems have often suffered technical problems and are not today economically viable for digestate treatment (Vaneeckhaute et al. 2016). On the other hand full scale plant are actively running having good performances (Ledda et al., 2013)

funded by European Commission

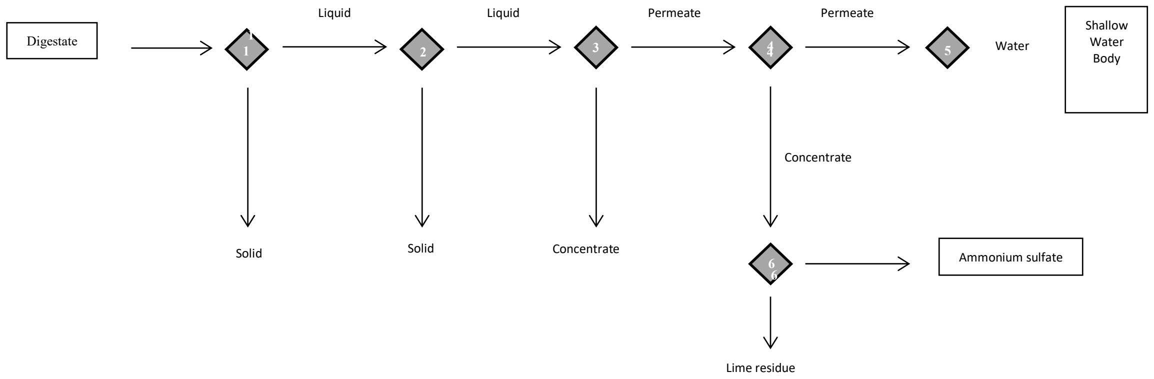

Figure 6. Simplified scheme of the membrane plant (1: Screw press separation, 2: Centrifugation, 3: Ultrafiltration - UF, 4: Reverse Osmosis - RO, 5: Zeolites refining, 6: Cold ammonia stripping)

Since 2009, the agricultural, economic and environmental effects of the production and use of mineral concentrates are studied in the Netherlands, with the approval of the European Commission. The mineral concentrates from this pilot can be applied as mineral fertiliser in Dutch agriculture. In 2011, 8 installations of the pilot had a processing capacity of 207.500 tonnes of manure. Meanwhile, different installations in the north of the Netherlands quited because of economical and technical reasons, but, in the south of the Netherlands, the pilot has extended to a capacity of 263.000 tonnes of manure at the 10 installations in use in 2014 (Luesink *et al,* 2016).

7. Microalgae cultivation

A potential method of nutrient extraction from organic wastes is the production of proteinaceous biomass by cultivating microalgae. This increases the value and manageability of the nutrients.

Recycling the nutrients from manure and assimilating them into algal biomass can result in high quality fertilizers without incurring the environmental and monetary costs of using chemical fertilizers while simultaneously remediating the waste effluent from this process. Manure digestate is an especially attractive feedstock to grow microalgae for biofertilizers production, as it is less contaminated than untreated effluents and rich in nitrogen and phosphorus. Microalgae could be used to recover nutrients from the liquid fraction of digestate and as microalgae incorporate these nutrients into their biomass, a fertilizer is created that is less prone to nutrient losses towards the environment. By reducing the volume of the liquid digestate, the nutrients become more manageable and some reclaimed water may be produced. Several authors have shown that dried algal biomass produced from the treatment of anaerobically digested manure could be a good substitute for commercial fertilizers (Mulbry et al., 2005; Uggetti et al., 2014; Veronesi et al., 2015). According these authors, dry algae do not contain free ammonia or nitrate that can leach into the environment or volatize at the time of application. Furthermore, concentration of heavy metals in microalgae grown on manure digestate are low enough not to reduce its value as soil or feed amendment.

Several studies have tested algal strains for the treatment of the manure. The results are still preliminary but promising. Scenedesmus sp. cultivation in fermented swine wastewater yielded good value added production in association with nutrient removal (Franchino et al., 2013). Several authors (Wang et al., 2010; Levine et al., 2011; Yang et al., 2011; Franchino et al., 2013) concluded that using microalgae may be an appropriate way of digestate treatment. These authors have studied the biomass growth and nutrient recovery by the green algae Neochloris oleoabundans and Chlorella sp. Results showed a high removal efficiency of main nutrients. Franchino et al. (2013) compare the behavior of three microalgae strains: Neochloris oleoabundans, Chlorella vulgaris and Scenedesmus obliquus, when cultivated on agro-zootechnical digestate concluding that the three strains almost completely remove different nitrogen forms and phosphate with C. vulgaris presenting the highest elimination capacity of ammonium. Bjornsson et al. (2013) showed that magnesium was critically limiting for algal growth in swine manure digestates. On the other hand, the digestate phosphorus concentration was found to have no impact on microalgae growth due to the phosphorus storage capacity of microalgae.

There is, thus, increased interest in creating improved fertilizer products from manure digestate, in order to increase its value, secure outlets and potentially generate an additional revenue stream for the biogas plant.

Living microalgae can also be used as a nitrogen fixator to bring atmospheric nitrogen into the soil and as soil conditioner. Microalgae can be also further processed (e.g. hydrolyzed) in order to obtain more elaborated biofertilizers and biostimulants.

8. Phosphorus precipitation

Another option to recover nutrients is to create the physical-chemical conditions in the bulk solution (pH, ion strength, etc.) to favour the formation of different salts with low solubility products, and its subsequent precipitation to recover them. Among others, magnesium ammonium phosphate, usually called struvite, is the most common salt enabling the recovery of phosphorous and nitrogen from wastewaters. Other salts that enables to recover phosphorus are calcium phosphate and K-struvite. Today, a large range of products based on struvite are commercially available (Figure 7).

Figure 7. Nutrient recycling products (Copyright: Kabbe 2016)

a) *Struvite recovery*

Struvite is a white crystalline substance, which is considered as a slow releasing and valuable fertilizer (5-28-0-10Mg), as it is sparingly soluble under neutral and alkaline conditions but readily soluble in citric acid. Struvite precipitation is produced in alkaline conditions when the concentration of Mg^{2+}, NH_4^+ and PO_4^{3-} exceeds the solubility product, according to the following reaction:

$$Mg^{2+} + NH_4^+ + H_nPO_4^{n-3} + 6\ H_2O \rightarrow MgNH_4PO_4 \cdot 6\ H_2O + nH^+$$

A combination of physical and chemical parameters controls the complex mechanism of struvite precipitation. One of the main factors is pH, as it changes the concentration of free ions available for reaction. When pH increases, Mg^{2+} and NH_4^+ concentrations decrease, as the first one complexes with hydroxides, and the second one increases its volatilization in the form of ammonia (NH_3). On the other hand, PO_4^{3-} concentrations increase as the pH increases. pH is also involved in controlling struvite solubility, being minimal with pH values between 9 and 10.7 (Doyle and Parsons, 2002). So, pH should be increased to favour struvite precipitation, generally using NaOH or $Mg(OH)_2$. Alternatively, CO_2 stripping can be used to reduce the consumption of alkali (Cerrillo et al., 2015).

Struvite recovery has been demonstrated at pilot and with more than 40 installations world-wide in full scale mainly with municipal sludge digester effluent and industrial wastewater using biological P removal (Figure 8). Limiting factor for implementation is a minimum concentration of 100 mg/l dissolved P (ortho-phosphate). At the moment only a few phosphate recovery techniques are developed for livestock manure treatment.

Figure 8. Crystal Green, the Ostara Struvite recovered at WWTP Amersfoort (Germany) (Copyright: Kabbe 2016)

The main hindrance of liquid manure to struvite formation are their high concentration of suspended solids and Ca^{2+}, high ionic strength, high alkalinity, and low soluble reactive P (Tao et al., 2016). These characteristics might vary depending on the type of the manure (pig, cow, etc.) and on the previous processing (mechanical separator, anaerobic digestion, etc.). Different strategies has been tested to overcome these constrains, microwave-based thermochemical treatment (Jin et al., 2009), Ca^{2+} chelation (Shen et al., 2011; Zhang et al., 2010), acidification to dissolve particulate inorganic phosphate (Massey eta al. 2010), etc., but none of them seems to be economically viable. More recently, a new P-precipitation system has been developed, tested and validated in Germany (Kupferzell). More information is available in the website: **http://www.bioecosim.eu**

b) Calcium phosphate and K-Struvite recovery

Calcium phosphate precipitation is very complex and involves various parameters. It depends on calcium and phosphate ions concentration, ionic strength, temperature, ion types and pH but also on time (Desmidt, et al., 2015). When calcium hydroxide ($Ca(OH)_2$) is added to the liquid fraction and the pH increases above 10, and temperature (70ºC), phosphorus precipitates as hydroxyapatite ($Ca_5(PO_4)_3OH$) or brushite ($CaHPO_4 \cdot 2H_2O$). Depending on dosage, three different Ca-phosphates can be obtained: the highly water-soluble mono-calciumphosphate (MCP), the citric acid soluble di-calciumphoshate (DCP) and the barely soluble tri-calciumphosphate (TCP). For fertiliser application, MCP and DCP are favoured.

Alternatively, K-struvite ($KMgPO_4 \cdot 6H_2O$) can be recovered form manures. It has a similar structure as struvite; the only difference is the replacement of NH_4^+ into K^+ ion. From their solubility constants, it can be stated that if both ammonia and potassium are present in excess, struvite will precipitate instead of K-struvite. Therefore, K-struvite will be only precipitate if the excess of potassium is much higher than ammonium (e.g. denitrified wastewaters).

funded by European Commission

3. Conclusions/Considerations

We described and discussed in the previous section several technologies useful to improve animal manure utilization as source of nutrients and it is clear that we have today solutions for most of the particular situations faced at farm scale. The integration of new technologies at farm scale is always the most difficult step in any technology development and probably the less considered in research plans. The main limitations for technologies at farm scale are: the acquisition costs, maintenance of equipment, and complexity in running operations. Implementation at farm level will only be successful if the technology is low in labour and easy to handle. The farmers has his own work, and does not have the time for extra work load. Especially high tech systems/biological systems ask for specific knowledge and follow-up. On the other hand, the volumes of manure to be treated at farm scale level are rather low in comparison to the capacity of the systems recently developed (or it is financially not interesting to have a small capacity system). Mobile systems (by contractor) or co-investment of different farmers can be a solution for this. Finally, the management of the by-products, not only the "high quality" product obtained (e.g. ammonium sulphate), but also the remaining processed slurry (e.g. liquid Fraction with less N and P) is one of the relevant issues that limits the implementation of these technologies.

Other aspects as national legislation, land price, farmer's motivation have also to be considered to understand why farmers are not using some of the available technique.

Several scenarios have to be considered:

1) Farmers subject to IED BAT for large piggeries and poultry farms
2) Farmers owning enough land area to apply all the raw slurry produced and not subject to legal constraints to minimize nutrients losses (gaseous emissions and/or leaching)
3) Farmers owning enough land area to apply all the raw slurry produced but subject to legal constraints to minimize nutrients losses, namely ammonia emissions at farm and field scale, or farms located in NVZ.
4) Farmers needing to decrease nutrient losses by leaching
5) Farmers needing to export manure due to legal constraints relative to slurry application
6) Farmers needing to decrease nutrient losses by gaseous emissions.
7) Farmers interested in having some profit with manure sub-products.

For operators of large poultry or piggery units, the BAT defined under the IED (Industrial Emissions Directive) must obligatory be applied.

For farmers of group 2, the advantages of slurry processing are not so obvious and should generally not be economically sustainable. The target audience for manure processing technologies are therefore farmers from other groups.

For farmers from 3, 4, 5 and 6, the first option is to export raw manure to other farms. To minimize, transport costs, farmers might be interested in manure separation to export only the solid fraction but they still need to deal with the liquid fraction.

Farmers of group 7 should be the most interested in recent and more complex technologies.

funded by European Commission

4. Proposal for potential operational groups

Based on our conclusions, we propose to new operational groups:

- Sustainable implementation and integration of most recent technologies for nutrients recovery from animal manure and digestates.
- Downgrade of some existing technologies to increase implementation at farm scale
- Valorisation of end-products (f.e. recognition as mineral fertiliser)

5. Proposals for (research) needs from practice

As referred above, the technology implementation at farm scale is the less successful step. Hence, what could be done by researchers to facilitate integration? A solution is certainly a stronger dissemination of new results and a stronger collaboration with farmers in projects of development of new technologies. The sub-products obtained after some slurry treatments as separation or P-precipitation are still seen as an animal product (legal constraint – see mini paper legislation) and new solutions for its valorisation are still needed. It is also of interest to develop some activities related to the assessment of the technologies in the whole farm cycle (including the utilisation of the end products) in order to evaluate the environmental and economic sustainability of the technologies not as stand-alone but when inserted in the farm context.

6. Bibliography

ARBOR Project: Techniques for nutrient recovery from digestate. ARBOR Interreg IVB project, with financial support of the Interreg IVB programme, the province of West-Flanders and the Flemish Commmunity. http://www.vcm-mestverwerking.be/publicationfiles/VCM001_Rapport_04_LR.pdf.

Biorefine. 2015. Recycling inorganic chemicals from agro- and bio-industrial waste streams Techniques for nutrient recovery from manure and slurry.

https://orbi.ulg.ac.be/bitstream/2268/194586/1/Manure-Slurry.pdf

Bamelis, L., Blancke, S., Camargo-Valero, M.A., De Clercq, L., Haumont, A., De Keulenaere, B., Delvigne, F., Meers, E., Michels, E., Ramirez-Sosa, D.R., Ross, A.B., Smeets, H., Tarayre, C., Tarayre, N., Williams, P.T., 2015. Techniques for nutrient recovery from digestate derivatives. Published by Biorefine

http://biorefine.eu/biorefine/downloads/report-techniques-nutrient-recovery-digestate-derivatives)

Bjornsson, W.J., Nicol, R.W., Dickinson, K.E., McGinn, P.J. 2013. Anaerobic digestates are useful nutrient sources for microalgae cultivation: functional coupling of energy and biomass production. J Appl Phycol 25(5): 1523-1528.

Camargo-Valero, M.A., De Clercq, L., Delvigne, F., Haumont, A., Lebuf, V., Meers, E., Michels, E., Raesfeld, U., Ramirez-Sosa, D.R., Ross, A.B., Schoumans, O., Snauwaert, E., Tarayre, C., Tarayre, N., Vandaele, E., Velthof, G., Williams, P.T., 2015. Techniques for nutrient recovery from manure and slurry. Published by Biorefine (http://biorefine.eu/biorefine/downloads/report-techniques-nutrient-recovery-manure-and-slurry)

Cerrillo, M., Palatsi, J., Comas, J., Vicens, J., Bonmatí, A. 2015. Struvite precipitation as a technology to beintegrated in a manure anaerobic digestion treatment plant – removal efficiency, crystal characterization and agricultural assessment. J Chem Technol Biotechnol. 90:1135-1143.

Desmidt, E., Ghyserlbrecht, Zhang Y., Pinoy, L., Van Der Bruggen, B., Verstraete, W., Rabaey, K., Meesschaert, B., 2015. Global Phosphorus Scarcity and Full-Scale P-Recovery Techniques: A Review. Crit. Rev. Env. Sci. Tec. 45:336-384.

Doyle, J. and Parsons, S. 2002. Struvite formation, control and recovery. Water Res. 36:3925-3940

Egle, L., Rechberger, H., Zessner, M. 2015. Overview and description of technologies for recovering phosphorus from municipal wastewater. Resour. Conserv. Recy. 105:325-346.

Fangueiro, D., Hjorth, M., Gioelli, F. 2015. Acidification of animal slurry: a review. J. Env. Manag. 149: 46-56;

Flotats, X., Foged, H.L., Bonmati Blasi, A., Palatsi, J., Magri, A., Schelde, K.M. 2011.Manure processing technologies . Technical Report No. II concerning "Manure Processing Activities in Europe" to the European Commission, Directorate - General Environment. 184 pp.

Foged, H.L.,, X. Flotats, A.B. Blasi, J.Palatsi, A. Magri. 2011. Inventory of manure processing activities in Europe. Technical Report No. III concerning "Manure Processing Activities in Europe" to the European Commission, Directorate-General Environment. 78 pp.

Franchino, M., Comino, E., Bona, F., Riggio, V.A. 2013. Growth of three microalgae strains and nutrient removal from an agro-zootechnical digestate. Chemosphere, 92(6): 738-744.

Frandsen, T.Q., L. Rodhe, A. Baky, M. Edström, I.K. Sipilä, S.L. Petersen, K. Tybirk. 2011. Best available technologies for pig manure biogas plants in the Baltic Sea Region. Published by Baltic Sea 2020, Stocksholm. 159 pp.

Hjorth, M., Christensen, K. V., Christensen, M. L., Sommer, S. G. 2010. Solid–liquid separation of animal slurry in theory and practice. A review. Agron. Sustain. Dev. 30: 153–180.

Hoeve, M.T., Nyord, T., Peters, G.M., Hutchings, N.J., Jensen, L.S., Bruun, S. 2016. A life cycle perspective of slurry acidification strategies under different nitrogen regulations, J. Clean. Prod. 127:591-599.

IEA Bioenergy, 2015. Nutrient Recovery by Biogas Digestate Processing.

http://www.iea-biogas.net/files/daten-redaktion/download/Technical%20Brochures/NUTRIENT_RECOVERY_RZ_web1.pdf

Jin, Y., Hu, Z., Wen, Z. 2009. Enhancing anaerobic digestibility and phosphorus recovery of dairy manure through microwave-based thermochemical pretreatment. Water Res. 43:3493-3502.

Kabbe C., Remy C., Kraus F. 2015. Review of promising methods for phosphorus recovery and recycling from wastewater, Proceedings International Fertiliser Society **763**, ISBN 978-0-85310-400-1

Ledda, C., Schievano, A., Salati, S., Adani, F. 2013. Nitrogen and water recovery from animal slurries by a new integrated ultrafiltration, reverse osmosis and cold stripping process: A case study Water Research 47:6157 – 6166.

Levine, R.B., Costanza-Robinson, M.S., Spatafora, G.A. 2011. Neochloris oleoabundans grown on anaerobically digested dairy manure for concomitant nutrient removal and biodiesel feedstock production. Biomass Bioenergy 35: 40-49.

Luesink, H., Postma, R., Smits, M-J, van Schöll, L. and de Koeijer, T. 2016. Effect afzet mestverwerkingsproducten bij wettelijke status kunstmest of EG-meststof. LEI Wageningen UR, Wageningen, mei 2016.

Massey, M.S., Ippolito, J.A., Davis, J.G., Sheffield, R.E., 2010. Macroscopic and microscopic variation in recovered magnesium phosphate materials: implications for phosphorus removal processes and product re-use. Bioresour. Technol. 101:877-885.

Mulbry, W., Westhead, E.K., Pizarro, E., Sikora, L. 2005. Recycling of manure nutrients: use of algal biomass from dairy manure treatment as a slow release fertilizer. Bioresour Technol 96:451-458.

Regueiro, I., Pociask, M., Coutinho, J., Fangueiro, D. 2016. Animal Slurry Acidification Affects Particle Size Distribution and Improves Separation Efficiency. J Environ Qual., 45(3):1096-103.

Schoumans, O.F., Rulkens, W.H., Oenema, O., Ehlert, P.A.I., 2010. Phosphorus recovery from animal manure; technical opportunities and agro-economical perspectives. Wageningen, Alterra, Alterra report 2158. 110 pages.

Schoumans, O.F., Bouraoui, F., Kabbe, C., Oenema, O. and van Dijk, K.C. 2015. Phosphorus management in Europe in a changing world, AMBIO, 44:180-192

Shen, Y., Ogejo, J.A., Bowers, K.E., 2011. Abating the effects of calcium on struvite precipitation in liquid dairy manure. T. ASABE 54:325-336

Sindhöj, E., Rodhe, L., 2013, Examples of Implementing Manure Processing Technology at Farm Level. Published by Baltic Manure (http://www.balticmanure.eu/download/Reports/bm_inno_web.pdf)

Tao, W., Fattah, K.P., Huchzermeier, P. 2016. Struvite recovery from anaerobically digested dairy manure: A review of application potential and Hindrances. J Environ. Manage. 169:46-57.

Uggetti, E., Sialve, B., Latrille, E., Steyer, J.P. 2014. Anaerobic digestate as substrate for microalgae culture: the role of ammonium concentration on the microalgae productivity. Bioresour Technol, 152:437-443.

Vaneeckhaute, C., Lebuf, V., Michels, E., Belia, E., Vanrolleghem, P.A., Tack, F.M.G., Meers, E., 2016. Nutrient Recovery from Digestate: Systematic Technology Review and Product Classification", Waste and Biomass Valorisation, http://dx.doi.org/10.1007/s12649-016-9642-x

Veronesi, D., Ida, A., D´Imporzano, D., Adani, F. 2015. Microalgae Cultivation: Nutrient Recovery from Digestate for Producing Algae Biomass. Chem Eng T 43

Wang, L., Li, Y., Chen, P., Min, M., et al. 2010. Anaerobic digested dairy manure as a nutrient supplement for cultivation of oil-rich green microalgae Chlorella sp. Bioresour. Technol. 101:2623-2628.

Yang, Y., Xu, J., Vail, D., Weathers, P. 2011. Ettlia oleoabundans growth and oil production on agricultural anaerobic waste effluents. Bioresour. Technol. 102:5076-5082.

Zhang, T., Bowers, K.E., Harrison, J.H., Chen, S., 2010. Releasing phosphorus from calcium for struvite fertilizer production from anaerobically digested dairy manure. Water Environ. Res. 82:34-42.