

SCHOOL OF SCIENCE  
Department of Industrial Chemistry “Toso Montanari”

Second cycle degree in

# Low Carbon Technologies and Sustainable Chemistry

Classe LM-71 - Scienze e Tecnologie della Chimica Industriale

Life cycle assessment of nutrient recovery from  
the liquid fraction of pig manure digestate via  
struvite precipitation

Experimental degree thesis

**CANDIDATE**

Federico Bedogni

**SUPERVISOR**

**Chiar.mo Prof.** Fabrizio Passarini

**CO-SUPERVISOR**

**Dott.ssa** Arianna Pignagnoli, CRPA Soc.Cons.p.A.



# Contents

Abstract.....	5
1. Introduction.....	6
1.1. Aim of the work.....	6
1.2. The phosphorous resources shortage.....	6
1.3. Livestock concentration.....	8
1.4. Livestock and manure management emissions.....	12
1.4.1. Methane (CH <sub>4</sub> ).....	13
1.4.2. Nitrous oxide (N <sub>2</sub> O).....	14
1.4.3. Ammonia (NH <sub>3</sub> ).....	15
1.5. Manure management: anaerobic digestion.....	16
1.6. Struvite: a renewable fertilizer.....	18
1.7. Life Cycle Assessment (LCA): a tool for the sustainability.....	21
2. Materials and methods.....	24
2.1. Case study: recovery of nutrients from the liquid fraction of pig manure digestate via struvite precipitation.....	24
2.2. Chemical and physical analysed parameters, sampling points and analytical methods.....	28
2.3. Life Cycle Assessment (LCA).....	29
2.3.1. Functional unit.....	29
2.3.2. System Boundaries.....	30
2.3.3. Data Inventory Analysis.....	31
2.3.4. LCIA: Life Cycle Impact Assessment.....	33
2.3.4.1. Liquid fraction treatment phase.....	36
2.3.4.2. Atmospheric emissions of by-product streams.....	39
2.3.4.3. Emission savings from struvite utilization.....	48
2.3.4.4. Atmospheric emissions of the control system.....	50
3. Results and discussion.....	52
3.1. Chemical analysis results.....	52
3.2. Life Cycle Assessment (LCA) results.....	55
3.2.1. Climate Change.....	55
3.2.2. Freshwater Eutrophication.....	58

3.2.3. Terrestrial Acidification.....	61
4. Conclusions.....	63
5. References.....	66
6. Acknowledgments.....	74
ANNEX 1 Data, calculation and tables about input and output of prototype system in the LCA analysis.....	75
ANNEX 2 Data, calculation and tables about output of control system in the LCA analysis...	79
ANNEX 3 Chemical analysis results, design and management information and materials calculations.....	81
ANNEX 4 Results of Climate Change, Eutrophication and Acidification.....	84

## Abstract

In this work, the environmental performance of a prototype designed by Centro Ricerche Produzioni Animali – CRPA, which allows the nutrient recovery (N and P) from the liquid fraction of pig manure digestate, has been monitored through a Life Cycle Assessment (LCA). The process is born to solve the problem of the surplus of nutrients in zones rich in livestock and its expensive transportation to more needful areas. The reduction of nutrients in the effluents allows farmers to spread higher amounts of manure on the crop with lower emissions and ecosystem contamination. The recovered fraction consists of a Struvidic mud ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), which can be used as a fertiliser replacing synthetic fertiliser, decreasing the impact due to their production. The impact categories analysed are Climate Change, Eutrophication, and Acidification for the prototype system and the control system. The second one represents the already existing manure management system in the livestock. The environmental analysis shows an impact of 18.60 kg  $\text{CO}_2$  eq, 0.034 kg  $\text{PO}_4^{3-}$  eq and 0.211 kg  $\text{SO}_2$  eq for these categories regarding the prototype system, measured with respect to 1  $\text{m}^3$  of liquid fraction. Regarding the same FU, the control system's impact result is 27.66 kg  $\text{CO}_2$  eq, 0.035 kg  $\text{PO}_4^{3-}$  eq and 0.177 kg  $\text{SO}_2$  eq. The chemical analysis results show that a more nutrient-concentrated fraction was obtained during the process, and the reduction of nutrients in the others leads to a decrease in GHGs and contaminants emissions during the storage period.

# 1. INTRODUCTION

## 1.1 Aim of the work

The aim of this work is the environmental assessment, through a Life Cycle Assessment (LCA) analysis, of a process designed for the recovery of nutrients from digestate via struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) precipitation. This project, which is called Operational Group for Innovation – Manure and digestate treatment to reduce emissions and produce Struvite “GOI Struvite”<sup>1</sup>, was born by the partnership between a pig farm located in Formigine (MO) and Centro Ricerche Produzioni Animali – CRPA Soc.Cons.p.A., localized in Reggio Emilia (RE). The prototype that made the process and the process itself were designed to meet several needs and difficulties that many farmers encountered. The first problem is the limited amount of manure and organic fertilisers that can be spread on the field; with the nutrient recovery and precipitation, the resulting fraction should present a lower concentration of them, allowing farmers a higher application for crop amendment and to get rid of it without a large impact on the environment. The second problem is the geographical concentration of nutrients (N and P) due to the geographical distance of livestock and cropping. Most manure-producing zones in which the nutrients are contained need a more efficient and economical methodology of nutrient transport to cropping zones. Struvite, whose production could contribute to solving both problems, can replace synthetic fertiliser, making this process more sustainable. These issues must then be framed within a broader spectrum of aspects to be considered, such as the scarcity of resources from which synthetic fertilisers are obtained and the atmospheric emissions that result from this entire supply chain.

## 1.2 The phosphorous resources shortage

Since the birth of agriculture, man has sought technologies, techniques and substances to increase the yield of the fields and decrease the necessary energy and work. In this sense, there was a breakthrough in Western European and U.S. agriculture at the end of the Second World

---

<sup>1</sup> Gruppo Operativo per l'Innovazione STRUVITE - Trattamento degli effluenti e digestati zootecnici per ridurre le emissioni e produrre Struvite,- realizzato nell'ambito del Programma di Sviluppo Rurale 2014-2020 della Regione Emilia-Romagna — Tipo di operazione 16.1.01 — Gruppi operativi del partenariato europeo per la produttività e la sostenibilità dell'agricoltura — Focus Area 5D - Ridurre le emissioni di gas a effetto serra e di ammoniaca prodotte dall'agricoltura, <http://struvite.crpa.it/>

War, the so-called “green revolution”, where the first application of P fertilizers, obtained from guano and fossil phosphorites, contributed to a rapid growth of production and productivity [1]. The high availability of fossil phosphates, the increase in animal products and the division of animal farming and cropping in different geographical areas decreased the efficiency of agricultural nutrient recycling, including P, in industrializing countries during the 20<sup>th</sup> century [2]. P is often defined as a limiting nutrient because the input due to the natural deposition and de-sequestration in the soil system is relatively small if compared to the overall demand needed by the crop; in addition, the combination of abiotic weathering, the activity of microorganism, atmospheric deposition, erosion and crop removal tends to lower the total P stocks [3]. Despite phosphorous resources also have other applications, the use of these substances dominates traditional fertilization. Nowadays, more than 90% of the current usage of phosphorous resources (and more than 80% of fossil P resources) is involved in agricultural fertility. The raw material from which phosphate fertilizers are obtained is phosphate rock, whose major exporters are Morocco and China, with more than 70% of the overall terrestrial reservoirs and 57% of the global extraction, 220Mt in 2022 [4]. In 2020, 45Mt phosphorous fertilizers have been produced [5]. Thanks to the driving demand by developing countries such as India, Brazil, Indonesia and African states, extraction is estimated to increase to 260Mt in 2024 [6]. It has been predicted that phosphate rock reserves have entered a depletion cycle and will be fully run out by the end of the century [7]. Furthermore, the current elaboration and use of P lead to negative environmental impacts due to the pollution of P nutrients, which lead to eutrophication and soil acidification, and fossil P resource contaminants, with consequences on human health and ecosystem quality.

Since inorganic sources of P are going to exhaust, decreasing P rock utilization must pass through the efficiency and recovery of its major organic sources to feed the fast-growing world population, managing and optimizing crop production and human consumption. Several secondary organic phosphate resources have been detected over the years, such as human and animal excrements, harvest residues, organic wastes, and ashes that can help in feeding phosphorous, reducing nutrient loss and other environmental benefits (e.g., contaminants, pathogens, heavy metals).

Other important secondary sources particularly evaluated in the last years are municipal, industrial and livestock wastewater. Some studies suggest that removing 93% of P through struvite (magnesium ammonium phosphate, MAP) crystallization from wastewater is possible [8]. Using MAP as fertilizer would help in reducing the application of rock phosphate in the

agricultural sector. It is simultaneously beneficial for humanity by providing a slow nutrient release and reducing the risk of soil and water pollution by recovering the P from wastewater [9].

The P shortage situation is even made more difficult by the rough and inefficient use and recovery process done on one of the already available secondary organic resources: livestock effluents. The following paragraph presents the distribution of the existing farms and livestock in Italy and Emilia Romagna, it will explain how this affects the nutrient economy and the reason for the necessity to improve it in this geographical area.

### 1.3 Livestock concentration

The following images show the livestock density of pigs (Figure 1), cattle (Figure 2) and poultry (Figure 3) for each Italian province and Emilia-Romagna region.



Figure 1: pigs' density for each Italian province (head/Km<sup>2</sup>) [10].



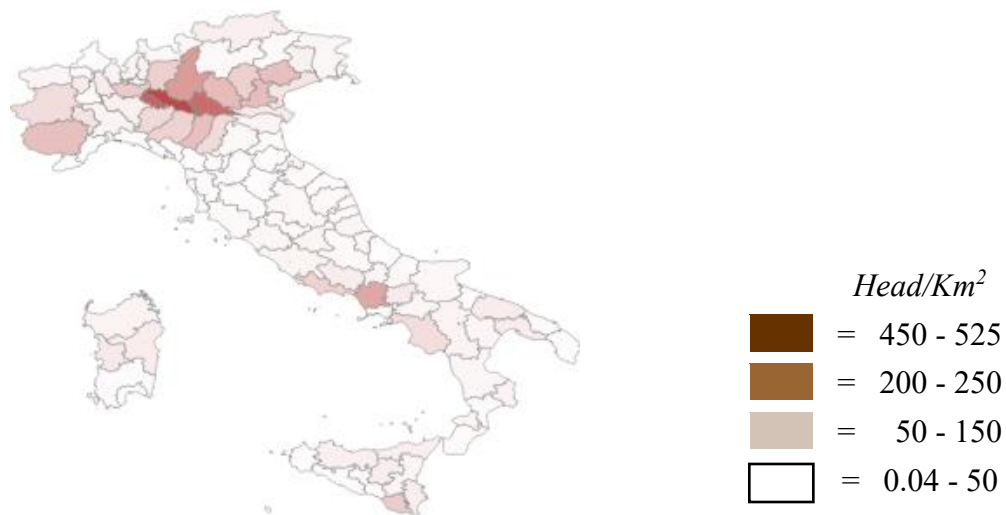


Figure 2: cattle density for each Italian province (head/Km<sup>2</sup>) [10].

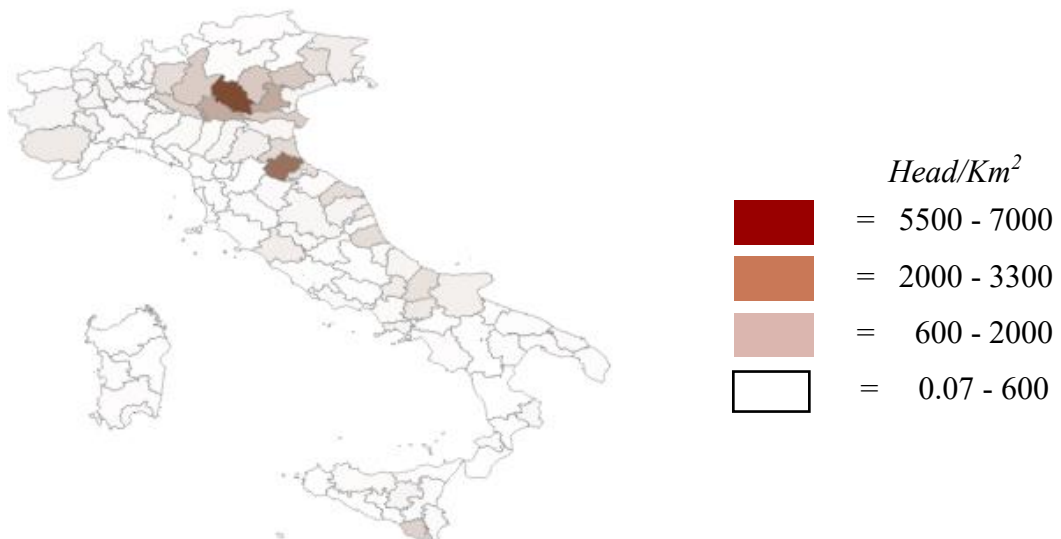


Figure 3: poultry density for each Italian province (head/Km<sup>2</sup>) [10].

From the previous figures, we can observe a high concentration of livestock in very limited areas, mostly placed in the northern regions: Lombardy, Emilia Romagna, Veneto and Piedmont. Also, within each of these regions, there is a very different density localization depending on the province and type of livestock.

- Regarding **pigs**, these four regions have 85% of the total population, and the first five provinces for density (Cremona, Mantua, Lodi, Brescia and Cuneo) have 52% of the total.

- Regarding **cattle**, these four regions have 61% of the total population, and the first ten provinces for density have 42% of the total.
- Regarding **poultry**, these four regions have 71% of the total population, and the first seven provinces for density have 49% of the total.

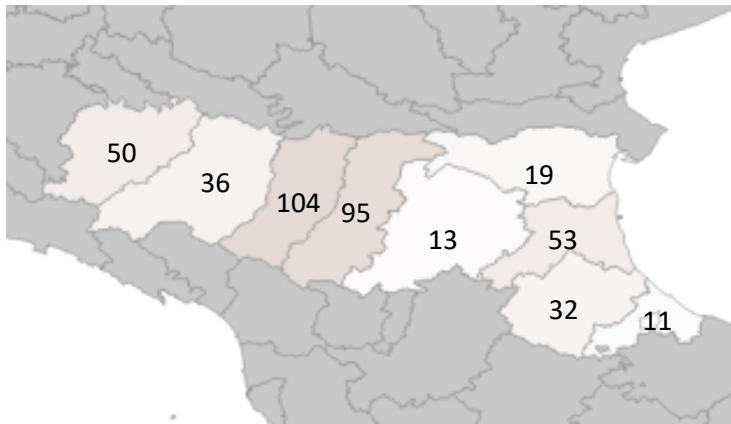
Farmers, sectorial studies and institutional organizations report a huge overproduction of livestock effluents rich in nutrients (P and N) in these areas due to the high concentrations of animals. These effluents can be recycled and directly applied to the field following the modes and the times needed by the crop and under strict law limits set by “EU Nitrates Directive” in 1991 [11], listed in the following table:

Type of zone	Limit
Not sensible zone	340 kg N/ha
Sensible zone	170 kg N/ha

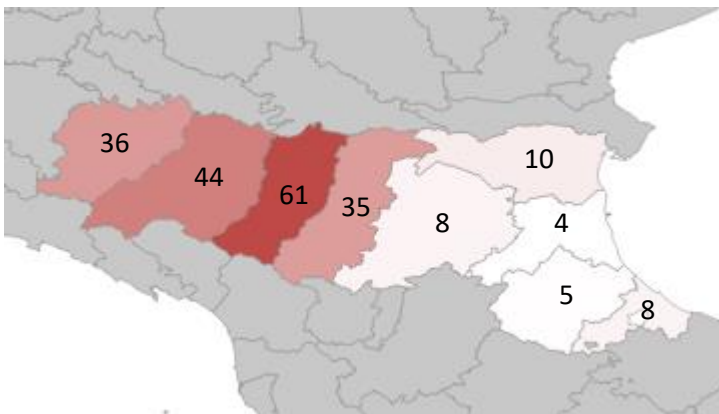
Limits of effluents application set by EU Nitrates Directive.

The overproduction occurring in these zones makes necessary the transport and delocalization of manure in areas where they are more needed and unavailable, such as cereal-producing areas, to avoid overapplication that can lead to eutrophication and soil acidification. Many technologies and treatments are being developed to make this more efficient process and the following application in the field. Some examples can be the concentration of ammonium nitrogen ( $\text{NH}_4^+$ ), N form directly available for plants, in a certain fraction or the decrease in volume of the nutrient fraction (palletization).

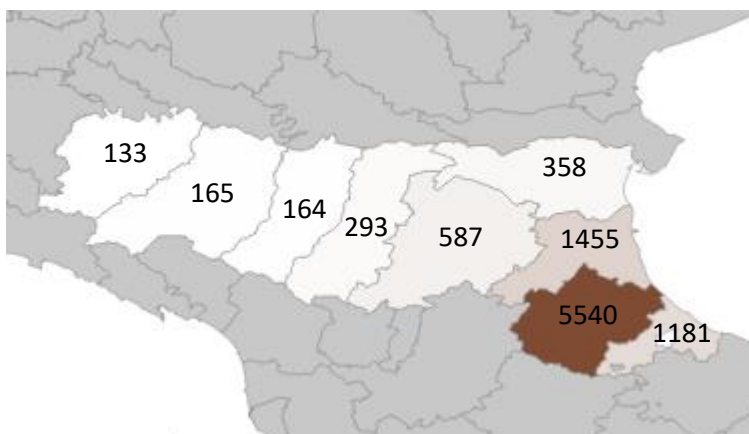
The same problem exists in the Emilia Romagna region, where there is a higher density of animals in certain provinces and a focus on cropping for others. The following images show the density of pigs (Figure 4), cattle (Figure 5) and poultry (Figure 6).



**Figure 4:** density of pigs in Emilia Romagna provinces (head/Km<sup>2</sup>) [10].



**Figure 5:** density of cattle in Emilia Romagna provinces (head/Km<sup>2</sup>) [10].



**Figure 6:** density of poultry in Emilia Romagna provinces (head/Km<sup>2</sup>) [10].

While there is a notable difference in livestock density in Italy along the north-south axis, in Emilia Romagna the differences are detected along the east-west axis. In order to analyze the situation, it is advisable to divide the Region into two different areas: the first composed of the western four provinces (Emilia) and the second composed of the others (Romagna). 73% of the total pig population and 85% of the cattle one is localized in the Emilia area, while 91% of the total poultry population is localized in the Romagna area.

This concentration of animals in a limited area is born to reduce production costs [12]. Still, it also leads to an over-application of nutrients on agricultural soils, resulting in water and soil pollution and eutrophication. This is not the only problem provoked by animal effluents; another very impacting one is atmospheric emissions.

#### 1.4 Livestock and manure management emissions

In global terms, agriculture is a significant contributor to GHG emissions. The IPCC report estimates that agriculture causes 14.5% of total GHG emissions, also considering Land Use and deforestation [13]. In 2018, the total contribution of the sector was 9.3 billion tons of CO<sub>2</sub>eq, where a major part of non-CO<sub>2</sub> emissions is released by enteric fermentation, livestock manure and its management [14]. All the studies agree that 65-77% of the total GHG emitted at the global level by livestock farming is due to cattle [13]. In Italy, the agricultural sector accounts for about 7% of national greenhouse gas (GHG) emissions, with 79% contribution by livestock. Apart from CO<sub>2</sub>, which is usually released during the use of machinery and farm processes, the other gases involved in the global warming process are methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O). Ammonia (NH<sub>3</sub>), even if it is not a greenhouse gas, represents the main pollutant linked to agricultural practice, and it leads anyway to important consequences on the environment, human health and biodiversity. In 2018, livestock was responsible for 78% of NH<sub>3</sub> emissions in Italy, with an 80% contribution by manure emissions [15]. About 30% of the total GHG production of the agricultural sector at the global level is attributed to manure management [16]. These gases can be released during storage, treatment and application. The release depends on several factors: characteristics of the manure (that can vary between different species but also between the same animal of different countries, farms, animal feed, water consumption and seasons), temperature, humidity, weather and amount of manure. The following paragraphs will explain in detail each gas involved in this process.

### 1.4.1 METHANE (CH<sub>4</sub>)

The methane concentration in the atmosphere has doubled compared to the one before the Industrial Revolution, with an annual increase of 1.0-1.3% in the last decade. In 2022, the total global methane emissions were about 355Mt with a 40% contribution by agriculture (47% for Italy) [17]. Methane is a particularly effective and dangerous GHG due to its high absorptivity potential. The IPCC Fourth Assessment Report (2007) estimated its global warming potential (GWP) as 25 times higher than the one of CO<sub>2</sub>, usually taken as a reference. Fifth Assessment Report (2014) estimated that value as 28 times higher, confirming the expectation. GWP (Global Warming Potential) is a crucial parameter because it expresses a substance's impact and specific contribution to global warming. Unlike CO<sub>2</sub>, the absorption zone of methane (8-13 μm, far-infrared zone) is not already saturated hence, an increase in concentration corresponds to a following increase in absorption since its zone does not overlap with the absorption zone of CO<sub>2</sub> and water vapour, the other most important GHGs. All these considerations take to conclude that even a small increase in the atmospheric methane concentration leads to an extremely strong effect on global warming.

This compound is mainly produced through the anaerobic digestion performed by microorganisms that transform the organic matter contained in the faecal material of livestock into a mixture of methane (55-80%) and carbon dioxide (20-45%). This process, which occurs under strictly anaerobic conditions and low redox potential conditions, is composed of four successive biological steps, each performed by a different micro-organism, where more complex macromolecules are degraded into simpler compounds through hydrolysis, acidogenesis, acetogenesis and methanogenesis [18].

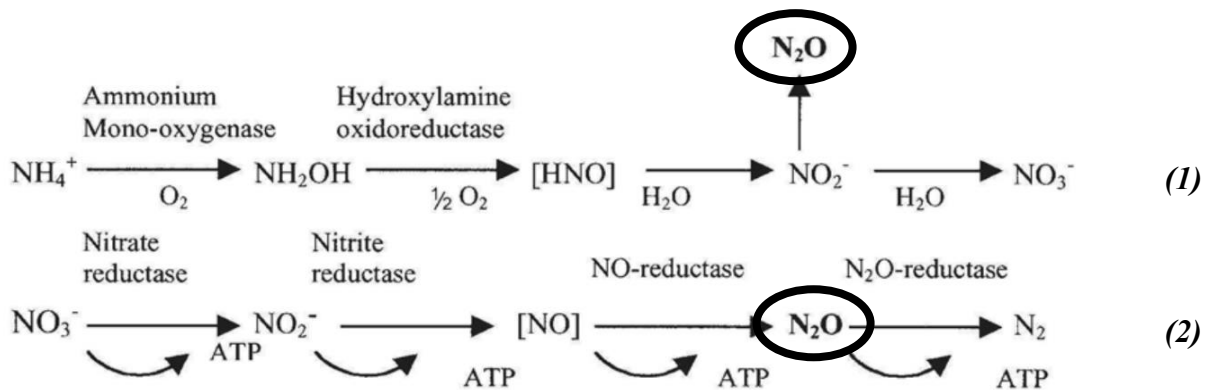
- 1) *Hydrolysis*: biological polymers (sugars, lipids and proteins) are broken into monomers (glucose, fatty acids and amino acids) by hydrolytic microflora that can be aerobic, facultative or strictly anaerobic.
- 2) *Acidogenesis*: production of volatile fatty acids (FAs), alcohols, H<sub>2</sub> and CO<sub>2</sub> starting from monomeric compounds; performed by fermentative microflora, which can be facultative or strictly anaerobic.
- 3) *Acetogenesis*: transformation of CO<sub>2</sub> and H<sub>2</sub> into acetate and vice versa; performed by homoacetogenic and syntrophic microflora.
- 4) *Methanogenesis*: production of CH<sub>4</sub> from CO<sub>2</sub> + H<sub>2</sub> and acetate by methanogens.

The most dominant factors that influence CH<sub>4</sub> emissions are the feed ratio (the amount of effluent), the amount of degradable organic matter and temperature; methane production

increases with increasing temperature, assuming that other parameters are held constant. The amount of emission also depends on the matrix that has produced the manure: cattle's manure can release about 3.5-4.5 times the amount released by pig's manure per head, depending on temperature. In both cases, the worst possible scenario, the most impacting one, is the manure storage in open lagoons [19]. During anaerobic fermentation, it is possible also to obtain several byproducts such as  $N_2$  and  $H_2S$  [20].

### 1.4.2 NITROUS OXIDE ( $N_2O$ )

Agricultural and farming sectors contribute about 65% of the total  $N_2O$  emissions of the planet. Nitrous oxide is mainly produced during aerobic storage, treatments and land spreading of animal excreta through the microbial process of nitrification (R.1) and denitrification (R.2) [16].



Nitrification is a process performed by aerobic micro-organisms such as bacteria (Nitrosomonas, Nitrospirota, Nitrospinota) and archaea (Nitrososphaerota) through which ammonia is oxidized, before into nitrite ( $NO_2^-$ ), and then into nitrate ( $NO_3^-$ ), getting available for plants nutriment. During denitrification, facultative anaerobic bacteria, using soil organic matter as electron donors, reduce nitrates into molecular nitrogen ( $N_2$ ) through several gaseous nitrogen oxide intermediates. The  $N_2O$  emission may occur in two different phases of the manure management system [21]:

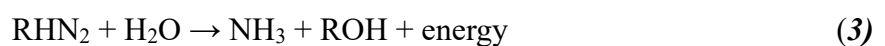
- 1) *Manure storage and processing.* The most impacting factors in this phase are the type of storage, in which aerobic conditions promote and increase  $N_2O$  emission, and the manure characteristics, where emissions are promoted by a high concentration of C, N and DM (dry matter).
- 2) *Manure spreading on the field.* The main factor affecting the  $N_2O$  emission in this phase is the manure or fertilizer's nitrogen availability ( $NH_4^+$  and  $NO_3^-$ ). In addition, all the factors

that affect soil chemical and physical characteristics such as T, pH, cation exchange capacity (CEC), plant coverage, soil moisture, texture, organic C, aeration and soil water content may influence, as a consequence, the emissions; this comprehends all soil management practices (tillage, soil compaction, irrigation, drainage) and manure application methods. In the end, also seasonal environmental conditions, such as air temperature, wind velocity and rainfall, may alter the emissions [22].

Analysing TPFE (treated piggery farm effluents) in average conditions, about 0.01-2.0% of the total nitrogen applied on a field is calculated to convert into N<sub>2</sub>O which has a huge global warming potential (GWP): 298 times higher than CO<sub>2</sub> according to the Fourth Assessment Report (2007) of IPCC and 265 according to the Fifth Assessment Report (2014). It also contributes to stratospheric ozone layer depletion [23].

### 1.4.3 AMMONIA (NH<sub>3</sub>)

Ammonia emissions into the atmosphere are considered a threat to the environment and legislation is increasingly limiting them. Livestock farming is the major source of atmospheric NH<sub>3</sub> in Europe and field-applied manure and slurry contribute significantly to this process [24]. Ammonia is produced through an enzymatically metabolized process starting from simple N molecules, such as amino acids and amines, derived from N organic macromolecules, such as proteins, degraded through hydrolysis performed by heterotrophic microorganisms. For example, amines undergo an ammonification reaction (R.3):



Also, urea (CO(NH<sub>2</sub>)<sub>2</sub>), the main component of synthesis fertilizers contained in animal manure, undergoes the ammonification reaction, releasing ammonium (NH<sub>4</sub><sup>+</sup>) ions (R.4):



This reaction, also known as urea hydrolysis, is catalyzed by urease, a powerful enzyme produced by practically all microbial and plant species. It is coupled with the release of hydroxyl (OH<sup>-</sup>) ions, leading to an increase in soil pH, affecting ammonia volatilization [25]. Ammonia volatilization, controlled by Henry's law, is favoured by alkaline conditions where ammonium ions are dissociated into gaseous NH<sub>3</sub> according to the following formula (R.5):



The key factors that determine the extent of ammonia release are those that affect the equilibrium between the species, regulated by  $K_a$  ( $pK_a=9.24$ ) and those that affect the mass transfer of gaseous ammonia between soil solution and atmosphere, such as temperature, air velocity and emitting surface area. Several features can control these two aspects when manure is spread on the field: soil pH, soil moisture, soil texture, soil cation exchange capacity (CEC), temperature, and wind velocity [20]. The pH and cation exchange capacity (CEC) are the most important soil properties controlling  $NH_3$  volatilization. A strong exponential relationship between ammonia volatilization and the pH of the soil has been shown [26]. It is observed that soils with low CEC are more prone to  $NH_3$  volatilization than others since the CEC of soils influences its concentration through the binding of the negatively charged cation exchange sites with  $NH_4^+$  ions [27]. The ammonia emission from manure already starts from housing, where floor type and climate conditions are the most influencing factors. The crucial floor characteristic that affects ammonia volatilisation is drainage, influenced by material properties, slat design and width of the opening: good drainage capacity decreases  $NH_3$  emissions. Although concrete replacement is rarely applicable due to cost and technical limits, it is not an ideal material to reduce ammonia emissions since it affects that process negatively. A good design of the slats' profile and an opening size increase can help reduce emissions. Concerning the housing environment conditions: high temperatures, humidity and ventilation rate negatively affect ammonia emissions [28]. Manure characteristics derive from the diet followed by the animal: it has been observed that an addition of 1% of benzoic acid in the diet decreases emissions by around 40% [29].

## 1.5 Manure management: anaerobic digestion

As mentioned, livestock geographical concentration and the following manure concentration can lead to the overapplication of these substances on the field, which can provoke eutrophication, soil acidification and gas emissions ( $NH_3$ ,  $CH_4$  and  $N_2O$ ). Many treatments and processes are born to solve this problem, to make transport and spread to the crop more efficient: from collecting nutrients to reducing GHG emissions. One of the most common and worldwide used is anaerobic digestion.

Anaerobic digestion (AD) is an engineered methanogenic decomposition of organic matter under anoxic conditions involving different species of anaerobic microorganisms that transform complex organic molecules into biogas through the mechanism already mentioned in the previous chapters.



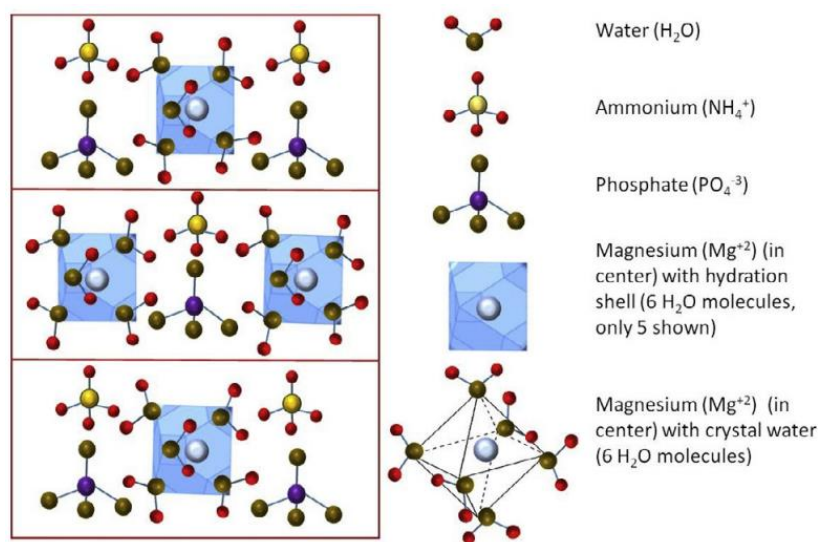
This process is successfully used for the treatment of municipal sludge, animal manure, industrial sludge, and industrial and municipal wastewater [30], and it was reported that AD has the lowest impact on global warming, eutrophication and acidification compared to other treatments, such as incineration and composting [31]. AD produces biogas at average rates of 0.2-0.4 L/g Volatile Solids (VS) from swine manure, decreasing GHG emissions released in the following steps and the field decomposition, producing renewable energy easily available for ongoing technologies. AD makes effluents better balanced and adapts to meet crop needs than raw manure slurry removing 0.80-0.90 of soluble chemical oxygen demand (SCOD) and 0.83 of total chemical oxygen demand (TCOD) thanks to the reduction of organic content in manures (about 70% or more), reducing the risk of eutrophication [32]. In addition, some types of anaerobic digestors, with some precautions, can eliminate zoonotic pathogens and parasites from manures such as Escherichia Coli, Salmonella, Streptococci and coliforms [33][34]. The resulting effluents, called digestate, can be spread on the field thanks to the high content of ammonium N (0.8-5.0 g/L) and P ( $\approx$ 1.21 g/L), directly available for plants, reducing the use of synthetic fertilizers and their impact due to the chemical production and the emissions from the field [35][36][37]. Some studies found that digested manure has lower NH<sub>3</sub> emissions than undigested ones and synthetic fertilizers [38]. A reduction in odour emissions has also been registered, usually due to a complex mixture of volatile organic compounds (VOC) and H<sub>2</sub>S [39]. Despite digestate being widely applied, in particularly intensive livestock regions, this cannot always be done due to the risk of overapplication. In these cases, AD is used to recycle and promote the efficient use of nutrients (N and P) since it facilitates their mobilization from organic matter into the liquid phase [40]. Further post-treatments were designed to help in this process: one of the most common is the separation of the solid and the liquid fraction: resulting in two different matrices that can be treated independently [41]. The solid fraction can be transported through longer distances thanks to the reduced water content or can undergo further treatments to produce bio-products such as compost and organic fertilizers, while the liquid fraction can be treated to satisfy the crop requirements or to recover valuable nutrients (N and P) [42].

## 1.6 Struvite: a renewable fertilizer

Struvite is a crystalline substance composed of magnesium, ammonium and phosphorus (MAP) in equal molar ratio and hexahydrate, formed according to the following reaction (R.6):



Struvite precipitation is nowadays successfully exploited as a sustainable and economical alternative for phosphorous recovery from several feedstocks such as animal manure and industrial, municipal and farm wastewater [43]. The different ions' structures (tetrahedral phosphate, octahedral magnesium water complex and tetrahedral ammonium ion) are linked by hydrogen bonds within the crystal, which also affect the bond distances and stability of the forming structure shown in the following image (Fig. 7) [44]:



*Figure 7: Struvite crystal structure [44].*

Due to the scarcity of  $\text{Mg}^{2+}$  in the usual feedstocks, the solution usually requires the addition of  $\text{MgCl}_2$  or  $\text{Mg}(\text{OH})_2$  to reach the same molar ratio (1:1:1) of ions required for the ideal precipitation of the crystals, which presents as a white powder with very different possible dimensions and shapes depending on the precipitation conditions. Despite the deficiency of Mg, digestate (liquid fraction) is an interesting feedstock due to the higher availability of N, P and Mg compared to undigested manure, thanks to the hydrolysis and mineralization of organic nutrients that occurred during the digestion [45]. The mechanism and the reaction of precipitation can change depending on the ions' availability in the solution at a certain pH, in

particular, ammonium and phosphorous ions, which are sensitive to pH variations and affect the solubility product. At alkaline pH, where the precipitation occurs, the reaction can follow two different pathways:

- In a slightly alkaline solution (R.7):



- In a strongly alkaline solution (R.8):



Struvite crystallization is considered a reversible reaction, and the maximum yield, represented by the equilibrium conversion, is affected by temperature: the struvite solubility product increases with temperature, but pH remains the most impacting factor on precipitation [46]. Another obstacle in this process could also be other dissolved ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$  typically present in wastewater which can provoke the precipitation of different salts rather than struvite [47]. However, the optimum pH to avoid the production of other salts and maximize the yield is reported between 8 and 9 [48].

Struvite is universally recognized as a less soluble slow-release fertilizer. It provides a longer-term source of P for crop growth than others and more easily soluble synthesis fertilizers such as ammonium phosphate and superphosphates. This peculiar feature, due to low water solubility, has many consequences [49]:

- Better matching with higher plant demand of P during the growing season and consequently more efficient use.
- Reducing the energy-intensive apparatus aimed at soil P absorption (extra root growth).
- Reducing the amount of fertilizer and nutrients adsorbed in the soil, decreasing the eutrophication risk due to land runoff.

The release of nutrients also depends on the size of the crystal: it has been found that smaller particles release more N than coarser ones in the first 3-6 weeks thanks to a higher surface area; after 6-9 weeks, the N release stabilizes for all particles size [50].

Many studies confirm that the main soil factor affecting struvite solubility is pH. While the final equilibrium of P concentration is not affected, the initial solubility of struvite is increased by lower pH. This characteristic makes acidic soil an ideal environment for struvite fertilization and particularly adaptable for those plant species with a root system that exudes large quantities

of organic acids [51]. Other environments where struvite is more effective than traditional phosphate rock fertilizers are those where fertilization is performed once every several years, like grasslands and forests. Also, semiarid environments are quite interesting destinations for struvite because many of those are characterized by calcareous soil, which contains high concentrations of Ca phosphate that decreases the solubility of common fertilizers, manure and compost; higher yield was found in struvite-applied plants in these regions [52]. Another characteristic that makes struvite an efficient fertilizer is the presence of Mg in its composition because it is noted that Mg deficiency in the soil causes a decrease in P uptake [53]; this situation could be made even more challenging by the presence of plant species with a high Mg and P requirement such as ornamental, medicinal plants and sugar beet. Struvite has been demonstrated to have higher P uptake and nutrient concentration in plants than other fertilizers in both cases [54].

Since the feedstocks used for struvite production (manure and wastewater) usually contain notable amounts of heavy metals, it makes sense to investigate their concentration in the final product to ensure the avoidance of contamination risk or a decrease in crop yield. Heavy metals can be incorporated into the crystalline structure during nucleation and crystal growth steps; in fact, struvite often contains heavy metals, but the concentration is perfectly under the legal limit for fertilizers [55]. However, pretreatments with membrane filtration are effective in the prevention of heavy metal struvite contamination. The process of precipitation also allows obtaining a product almost free of hormones and pharmaceuticals.

Struvite could have a positive impact on the dosing of the applied fertilizer. It has been reported that in the case of overapplication or overdosing, even 2-10 times higher than the normal application, this did not cause any problems (inhibition of sprouting, burning plant roots, etc.) on the plant growth thanks to the limited solubility [53]; on the contrary, some studies demonstrated several benefits (increase in fresh-dry weight and fresh height, high uptake of nutrients, fast-growing, early blooming) of struvite extra-dosing shown by different plant species such as broad bean, maize, tomato [56] and pepper.

Despite these numerous advantages, struvite alone does not allow sufficient early crop P uptake in most cases. The combination of struvite with other more soluble P-source fertilizers (ammonium phosphates) can lead to multiple advantages. Early and rapid P release by soluble fertilizer further postpones the struvite dissolution, elongating the nutrient application period for the crop and allowing a good peak of nutrient uptake during the growing season [57].

Considering the already mentioned aspects, the absence of odour, the reduced weight and volume, the easier transportation and storage thanks to the granular form, and the already successful use with tens of plant species, struvite represents a valuable and sustainable alternative or integration in the fertilizers sector [58]. Unfortunately, however, several obstacles are currently preventing the full development of this substance and this process; there are currently no functioning plants with sustainable costs. Furthermore, struvite does not have a real market, so it is not yet clearly defined within a legislative framework.

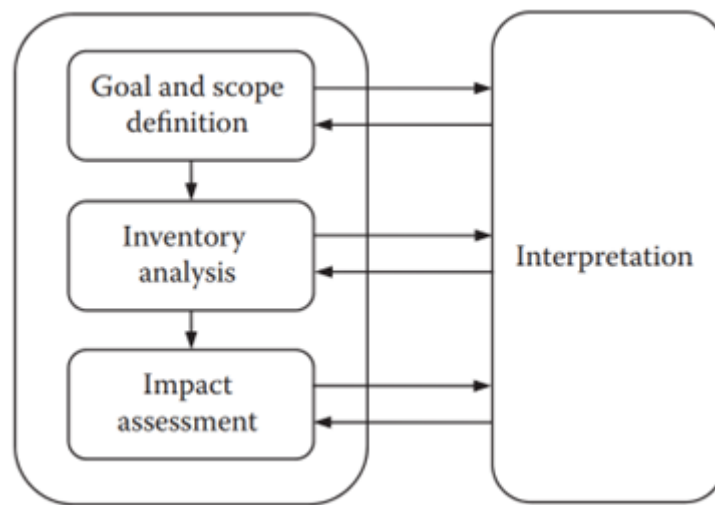
The following chapters will analyse the different impacts of struvite production from pig manure digestate using the Life Cycle Assessment (LCA) method.

## 1.7 Life Cycle Assessment (LCA): a tool for the sustainability

Life Cycle Assessment (LCA) is a technique that evaluates a product or service's potential environmental impact [59]. This assessment can be performed for the achievement of several possible purposes. It can identify opportunities to improve the environmental aspects of products at various points in their life cycle, helping in the decision-making process in industry, governmental or non-governmental organizations regarding strategic planning, priority setting, product or process design and marketing.

LCA has many peculiarities that deserve to be highlighted. Primarily, this method implements a life cycle perspective to identify and prevent the burden-shifting between life cycle stages or processes, creating further problems. For the same reason, the analysis covers a very broad range of environmental issues (up to eighteen). These issues include climate change, freshwater use, land occupation and transformation, aquatic eutrophication, toxic impacts on human health, depletion of non-renewable resources and eco-toxic effects from metals and synthetic organic chemicals. This approach allows to avoid unintentional increases in other types of environmental impacts during the efforts of decreasing one of them. Data used in the analysis are generally based on measurements, and models of the relationships between emission (or resource consumption) and impact are based on proven causalities. This quantitative nature of LCA allows the comparison of environmental impacts of very complex product systems made up of hundreds of flows and processes, making it possible to assess which products or systems are better for the environment and spot the processes that contribute the most to the overall impact and therefore should receive attention [60].

The life Cycle Assessment's fundamental structure was established for the first time in the International Organization for Standardization (ISO) standards 14040 in 1997 [61]. Many methodological aspects and procedures were further refined in the ISO LCA standards (ISO 2006a, b) [62] and in the European ILCD guidelines for LCA (EC-JRC 2010) [63], but many of them are still under discussion, and development continues today. According to the definitions provided in the ISO standards and by the Society of Environmental Toxicology and Chemistry (SETAC), an LCA consists of four different phases: goal and scope definition, inventory analysis, impact assessment, and interpretation of results (Fig. 8).



**Figure 8:** The four phases of Life Cycle Assessment [64].

#### *a. Goal and Scope Definition.*

This is the first phase of LCA, where the goals, the principles and the framework are defined. The reason for carrying out the study, the intended audience and how the results are intended to be communicated are made explicit in this phase. The studied scenario and system are described thanks to the definition of some key elements such as the function of the system, the functional unit, which is the quantified performance of a product system taken as a reference unit during the study and the system boundaries that determine which unit processes shall be included within the LCA [61].

The assessment parameters, the impacts that shall be analyzed and the geographical and temporal boundaries are also selected in this phase.

### *b. Inventory Analysis*

This analysis consists of the collection of information about the physical flows in terms of input of resources, materials, semi-products and energy and the output of emissions, waste, and valuable products for the product system. The analysis studies all the processes that were identified within the boundaries and scale every measure by the reference flow of product that was set by the functional unit. For comprehensiveness and simplicity, many data deriving from standardized and complex processes, such as the production of a material or the generation of heat and electricity, can be collected from databases that are made available. The outcome of the inventory analysis is the life cycle inventory, a list of quantified physical elementary flows for the product system correlated with the reference flow expressed by the functional unit [60].

### *c. Impact Assessment*

The impact assessment translates the life cycle inventory and the physical flows into impacts on the environment using knowledge and models from environmental science. The selection of impact categories was performed in the scope definition phase. Every elementary flow is translated and quantified into a contribution to each impact category according to its ability to impact (classification and characterization). Every contribution is aggregated into one score, representing the total impact that the product system has for that category, which has its own common metrics and unit of measure. The final score is then modified depending on the relative magnitude, taking a common set of reference impacts of a determined geographical area (normalization). These final scores (damage category) are then ranked according to their perceived severity or weighted using weighting factors that give a quantitative expression of how severe each impact category is in comparison to the others [60].

### *d. Interpretation*

The results of the study are interpreted to answer the questions posed during the goal definition phase. Sensitivity analysis and uncertainty propagation are calculated, and critical studies are performed to evaluate the influence of the chosen boundaries and hypotheses.

## 2. Materials and Methods

### 2.1 Case study: recovery of nutrients from the liquid fraction of pig manure digestate via struvite precipitation

All the processes and activities described in this case study were performed on a pig livestock in Formigine (MO). This farm took part in the Goi Struvite project with Centro Ricerche Produzioni Animali – CRPA S.p.A. (RE), which is responsible for the analysis and supervision of the precipitation plant. The goal of this project, financed by Regione Emilia Romagna and the European Union, is to decrease the nitrogen, phosphorous and total solid (TS) content in pig manure digestate to reduce the atmospheric emissions of  $\text{NH}_3$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  during storage, treatments and application phases of these fractions. The struvite produced in this process will be able to replace synthesis fertilizer, reducing the impact of their production and favouring the translocation of the surplus of nutrients from areas with high concentrations of livestock to regions with higher demand of nutrients due to cropping [65].

The pig livestock analysed has almost 15,000 fattening pigs distributed in nine different barns with a total meat production of  $100 \text{ m}^3$  of manure per day. All the organic wastes produced in the barns are collected and brought to the anaerobic digester, where they undergo this process for 40-60 days. The anaerobic digestion involves the mineralization of part of the organic N fraction into ammonium nitrogen ( $\text{N-NH}_4$ ) and part of the organic phosphorous fraction into orthophosphate ( $\text{PO}_4^{3-}$ ), optimizing the stream's characteristics for the struvite precipitation.

To achieve a fair degree of purity and high efficiencies in the crystallization and precipitation of the struvite, an effluent as free as possible of suspended material and solid particles must be loaded into the crystallization reactor in the second section of the plant (Figure 9). The only process of mechanical solid-liquid separation already implemented in the farm is not sufficient to achieve this. Therefore, before the crystallization/precipitation reactor, an innovative microfiltration system at  $50 \mu\text{m}$  (MFT Microfilter produced by WAMGROUP) already tested by CRPA in previous experiments and deemed suitable from a cost-benefit point of view was installed [66]. An operational rental is envisaged since this equipment is already on the market. Microfiltration will make it possible to obtain a microfiltered fraction with a low solid and organic substance content, therefore with reduced greenhouse gas emission potential (carbon dioxide, methane and nitrous oxide) and a reduced-volume dense fraction that acidified results in reduced emissions of both ammonia and methane.



Figure 9 has reported a schematic representation of the studied plant structure; some information clarifies the context and the surroundings in which this plant is located:

- The flow *Liquid fraction* comes from the mechanical solid-liquid separator already implemented in the farm for the digestate treatment;
- The flows *Thickened fraction* and *Clarified fraction* are rejoin to the existing liquid fraction treatment pathway already implemented in the farm (lagoons stock);
- The *Struvitic mud* represents the desired product which will be used as fertilizer, replacing synthesis fertilizers;

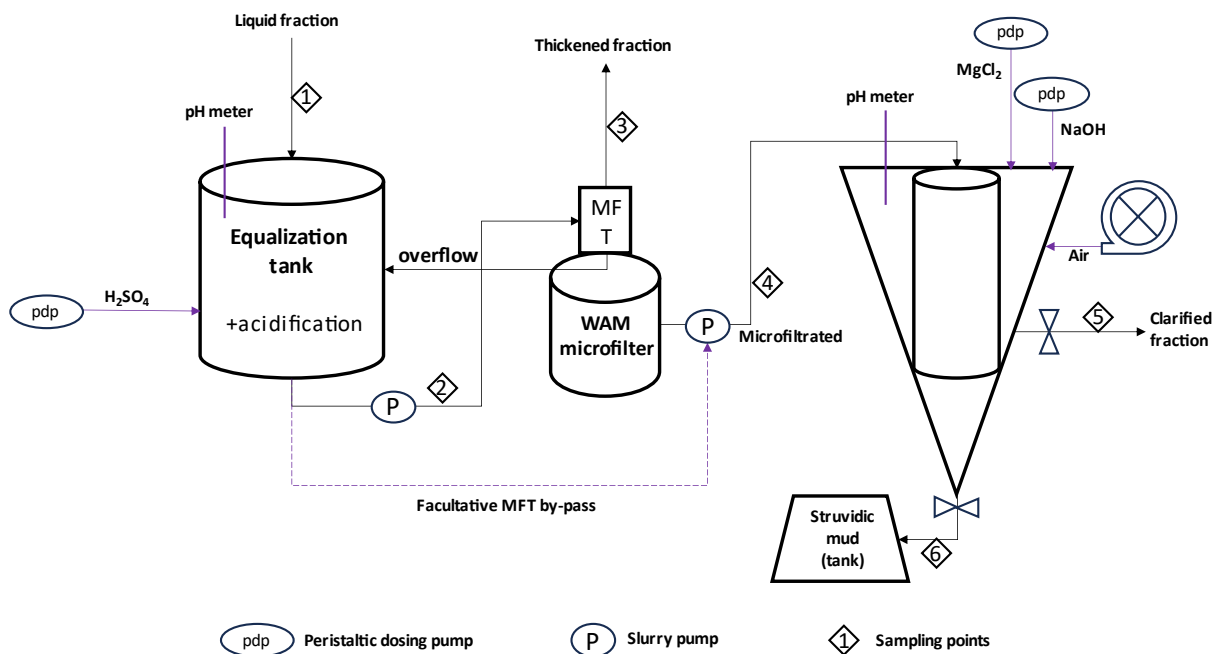


Figure 9: Scheme of the studied plant for the liquid fraction treatment [65].

The plant is composed of two sections:

1. Equalization tank both for storing the digestate to be treated and for its eventual conditioning with acid.
2. Reactor for crystallisation and separation of the precipitate (struvite - magnesium ammonium phosphate hydrate with chemical formula  $MgNH_4PO_4 \cdot 6H_2O$ ).

The main technical characteristics of the first section of the plant are as follows:

- Volumetric electric pump of the single-screw type to take the clarified fraction of digestate produced on the farm and load it into the equalization tank;
- Flow meter serving the loading pump to quantify the flow handled by the plant;
- Equalization reaction tank, made of polyethylene with a volume of 1-2 m<sup>3</sup> and complete with vertical-axis agitator for mixing the effluent and electronic level sensor for managing the loading and unloading of the effluent;
- pH control unit comprising a pH meter and a pump for dosing the chemical reagent (acid) for pH correction and transformation of the organic form of phosphorous into the more soluble and mineral form of orthophosphate, precipitable as struvite, compared to organic phosphorous.

The main technical features of the second section of the plant are as follows:

- Single screw volumetric pumps for taking the effluent from the first section and loading it into the reactor for crystallisation and precipitation of struvite, with the possibility of temporary storage in a polyethylene tank with a volume of 2 m<sup>3</sup>;
- The struvite crystallisation and precipitation reactor, with a capacity of 1 m<sup>3</sup>, is made of stainless steel AISI 305, of vertical conical shape and complete with an agitator for mixing the effluent during the reaction phase; a valve for separating the struvite salt precipitated during the sedimentation phase; weir for the clarified effluent with low nitrogen and phosphorous content; internal recirculation with pump;
- In the crystallisation reactor is planned to blow air through a blower to stripe out the CO<sub>2</sub> present in the digestate, thereby promoting the natural raising of the pH to 8.5-9;
- Serving the crystallisation/precipitation reactor, there is a pH control unit that includes a pH meter and a pump for dosing the basic chemical reagents, in case it is necessary to slightly raise the pH to promote crystallisation;
- Device for dosing magnesium salts to the crystallisation reactor to achieve the correct N:P:Mg molar ratio of 1:1:1 and thus promote struvite crystallisation;
- Two polyethylene containers with a volume of 100 litres for preparing and dosing the chemical reagents necessary;
- Polyethylene container with a volume of 500 litres for collecting precipitated and separated struvite;

- System to discharge slurry with reduced nitrogen and phosphorous content once the plant has treated it.

The plant can treat between 1 and 5 m<sup>3</sup> of digestate per day [65]. Pictures of the whole plant and the microfilter are available below (Pic.1) (Pic.2):




Picture 1: plant belonging to the case study [67].



Picture 2: microfilter belonging to the case study [67].

## 2.2 Chemical and physical analysed parameters, sampling points and analytical methods

Strategic and practical sampling points are studied and set on the plant for direct measurement or sample extraction (for instance,  in Fig.9). Physical parameters, such as volumetric flow rate and chemical parameters, are analysed for chemical identification and quantification.

For the stream of *liquid fraction* (sampling point n.1), the *thickened fraction* (sampling point n.3), the *clarified fraction* (sampling point n.5) and the *Struvidic precipitate fraction* (sampling point n.6), the following parameters have been monitored:

- Volumetric flow rate: volume of stream per unit of time;
- pH;
- Total Solids (TS): sum of the dissolved solids and precipitated solids (g/L);
- Volatile Solids (VS): sum of the solids which evaporate below 600 °C (g/L);
- Total Kjeldahl Nitrogen (TKN): sum of organic nitrogen, ammonia (NH<sub>3</sub>), and ammonium (NH<sub>4</sub><sup>+</sup>) (mg/L);
- Nitrogen Ammonium Fraction (N-NH<sub>4</sub><sup>+</sup>) (mg/L);
- Total phosphorous content (P<sub>tot</sub>), (mg/L);

These parameters are necessary for calculating the plant's performance and the methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) emissions of the *thickened fraction* and *clarified fraction* storage in lagoons.

- Total Kjeldahl Nitrogen (TKN) is essential for the calculation of direct and indirect N<sub>2</sub>O emissions during lagoon stock. This parameter is measured by converting organic nitrogen and free ammonia into ammonium using H<sub>2</sub>SO<sub>4</sub>, potassium sulfate (K<sub>2</sub>SO<sub>4</sub>), and cupric sulfate (CuSO<sub>4</sub>) catalyst. After the addition of the base, the ammonia is distilled from an alkaline medium and absorbed in boric or sulfuric acid. The ammonia may be determined colorimetrically by an ammonia-selective electrode or by titration with a standard mineral acid [68].
- The Nitrogen Ammonium Fraction (N-NH<sub>4</sub><sup>+</sup>) necessary for the calculation of waste streams' ammonia (NH<sub>3</sub>) emissions has been measured as follows. 5 grams of wet sample are treated with a KCl solution then mixed and separated by centrifugation. 1g of MgO and water is added to the extracted fraction. Separation by distillation is performed by collecting the

distillate in a solution of boric acid and 2 drops of indicator. The concentration of ammoniacal nitrogen is then obtained by colourimetric or potentiometric titration [69].

- Volatile Solids (VS) is a crucial value for the assessment of the methane emissions from the storage of waste fractions. Their measurement occurred as follows. VS is calculated as the difference between the dry residue determined after drying at 103-105°C for 12h and the total fixed solids determined after incineration at 550°C for 2h [70].
- The total phosphorous content ( $P_{\text{tot}}$ ) has been measured in order to establish the P recovery efficiency of the process and stabilize the quantity of synthetic fertiliser that can be replaced. The procedures utilized for its measurement are those provided by the US Environmental Protection Agency (EPA 3051A) and by the American Public Health Association (SM 4500-P-C) [71].

## 2.3 Life Cycle Assessment (LCA)

The following is the preliminary phase of the LCA study: the definition of the functional unit and system boundaries on which the subsequent stages of inventory analysis and impact assessment are dependent.

### 2.3.1 Functional unit

According to ISO 14044 (2006), the functional unit (FU) is the “quantified performance of a product system for use as a reference unit”. This measure includes the description of the system’s function and its quantification. This concept is born to satisfy the need to compare different systems, ways or scenarios to provide the same function; the same functional units allow the comparison between different systems.

The FU must be quantifiable and additive, which means that the FU and the impact are directly proportional: doubling the FU will also double the impact.

LCA studies regarding processes and techniques for nutrient recovery through struvite precipitation at the pilot scale are scarce; they are mostly concerned with laboratory-scale plants. The functional unit (FU) of this study is 1 m<sup>3</sup> of liquid fraction of digestate. This is one of the most common functional units to evaluate slurry, wastewater and general liquid fraction environmental burdens. This FU will allow the comparison of the impacts between the studied plant and the already existing liquid fraction management of the farm (lagoons stock).

### 2.3.2 System Boundaries

The system boundaries determine which unit processes are included within the system studied in the analysis. Several factors, such as the aim of the study, cut-off criteria and data availability, influence the determination of the system boundaries. They should ideally include all the required processes to fulfil the function, with a cradle-to-grave approach, analyzing the entire life cycle of the system. Unfortunately, this is sometimes impossible, and different strategies and approaches are implemented.

For this study case, the system boundary (shown in Fig.10) comprises the processes, energy and materials needed to treat the FU (1 m<sup>3</sup> of liquid fraction) with a cradle-to-grave approach. This LCA analysis system comprehends all the productive units belonging to the plant, from the feed of digestate liquid fraction to the production of struvite and all the reactants and materials needed during the process, also accounting for the impact of their production. The greenhouse gas (GHG) emission from by-product flows stock in lagoons is also accounted for. Since pig livestock is placed in a Nitrate Vulnerable Zone (NVZ) and does not cultivate perennial crops, according to Regional directives, these fractions must be stored for 180 days before the field application. Finally, GHG emission savings from replacing synthetic fertilizer with struvite were also considered.

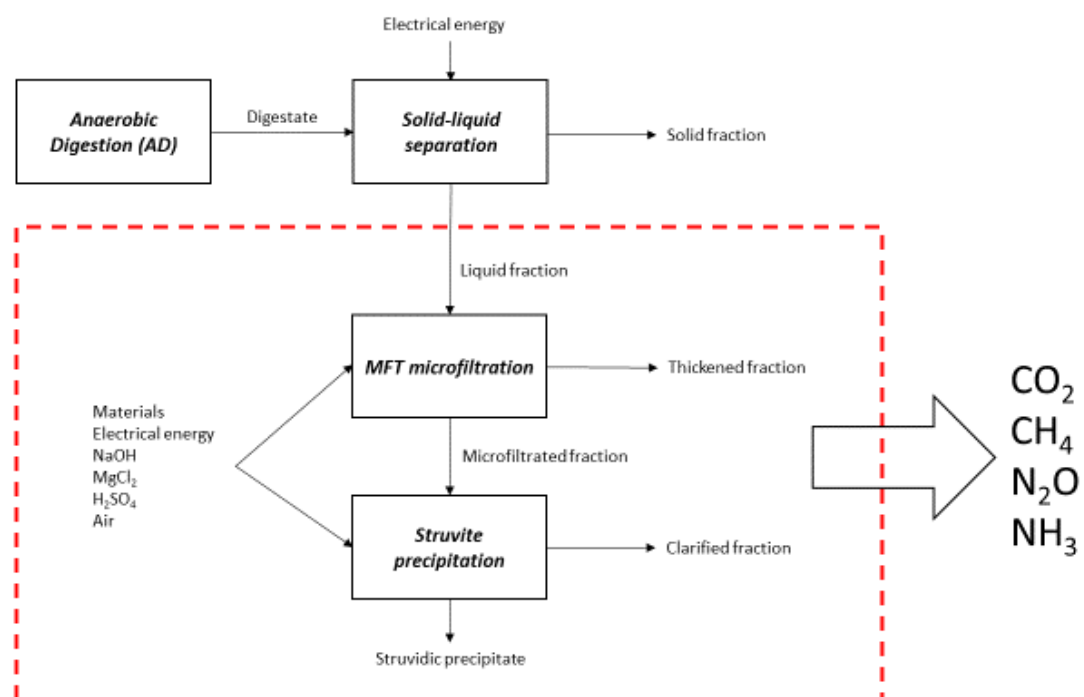


Figure 10: Schematic representation of the system boundary considered in the study.

The impact of this system will be compared with one of the already existing digestate liquid fraction management systems of the pig livestock (Fig.11), which consists of lagoon storage. The emissions due to field application are not accounted for in both systems. This system's impacts will be calculated using the same methodology framework followed for the studied system.

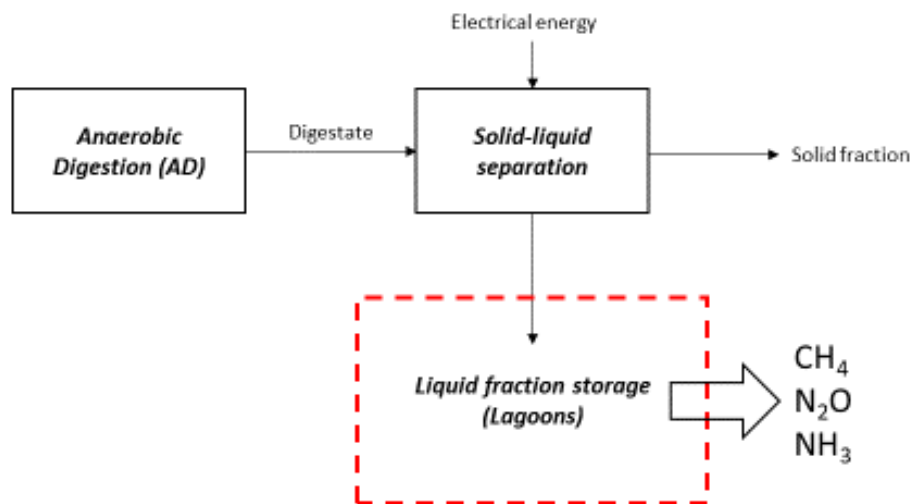


Figure 11: Schematic representation of the existing liquid fraction management system boundary.

### 2.3.3 Data Inventory Analysis

This phase comprehends all the data collection and compilation activity regarding elementary flows within the boundary system. This inventory lists the quantitative description of flows of matter, energy and pollutants that cross the system boundary and includes quantified input and output of used resources and substances released in the atmosphere, water and soil, representing the basis for the subsequent life cycle impact assessment phase. This is usually the most time-consuming and resource-intensive step.

ISO standards accurately plan this phase due to its crucial role in the analysis, which is subdivided into four main steps:

- *Identifying processes for the system model:* An identification process of the physical and energetic flows into details, usually starting from the reference flow with its upstream and downstream gradually widening to comprehend the entire system.

- *Planning and collecting data*: Planning is advisable to balance the effort of data collection with their relevance. The aim is to avoid wasting time collecting high-quality data with a low relevance for the results or spending too little time on collecting highly relevant data for the study.
- *Quality checking and allocation procedures*: The data already collected should represent the entire operating cycle of the process. Since the data type can vary, it is essential to ensure that they are in the form of flow with a unit that matches one of the characterisation factors and is scaled to 1 unit of reference flow. Allocation procedures are needed when dealing with co-products or by-products within the production process. These procedures aim to equally distribute the environmental emissions and resource consumption among the products analyzed and others obtained. In this study, it was decided to attribute the environmental impact contribution of each product according to its specific weight percentage of the total mass of the products obtained.
- *Calculation and reporting*: Calculations are performed, and the results are exposed in the documentation, which also reports the assumptions for each life cycle stage and all the passages to make the process replicable.

Thanks to on-site visits and technical reports drawn up by CRPA, it has been possible to understand the flow sheet and the structure of the plant. Several types of data have been collected directly in the field, such as energy consumption of the pumps and engines within the plant.

The CRPA analysis laboratory provides the data regarding the chemical-physical characterisation of the product and by-product streams.

The data not directly collectable are then retrieved by *databases*, created to obtain reliable inventory data, clearly described and regularly updated, usually geographically, temporally and technologically dependent. In this study, Agribalyse, ELCD (European Reference Life Cycle Database) and Environmental Footprint (EF) have been utilized for the collection of data.

Agribalyse is a French LCI database for the agriculture and food sector created in 2003. This database, elaborated by ADEME (Agence de la transition écologique), provides reference data on the environmental impacts of 2600 agricultural and food products produced and consumed [72]. Agribalyse uses a methodology co-developed by an extensive partnership between public



and private research institutes following key international guidelines as much as possible (ISO, LEAP, PEF) [73].

The European Reference Life Cycle Database (ELCD) is a database developed by the European Commission – Joint Research Centre which comprises Life Cycle Inventory (LCI) data from front-running EU-level business associations and other sources for key materials, energy carriers, transport, and waste management [74].

The Environmental Footprint (EF) database is part of the European Commission’s Single Market for Green Products Initiative. It is designed to support the use of product environmental footprint category rules (PEFCR) and organization environmental footprint sector rules (OEFSR). It offers life cycle datasets and LCIA methods compatible with European Union directives [75].

#### 2.3.4 LCIA: Life Cycle Impact Assessment

During the life cycle impact assessment, each elementary flow of the life cycle inventory is translated into its environmental impact contribution, aiming to evaluate the potential environmental impact of the process. At this point, it is essential to agree on an unambiguous definition of environmental impact: a set of environmental changes, positive or negative, due to human intervention. The ISO 14040/14044 standards (ISO 2006a, b) distinguish mandatory and optional steps for the LCIA phase.

Mandatory steps:

- **SELECTION:** the choice of the impact categories to investigate, category indicators and characterization models. This choice should guarantee non-redundancy, completeness and traceability, avoiding double-counting,
- **CLASSIFICATION:** The elementary flows of the LCI are assigned to the impact category to which they contribute. The LCA software usually performs this task automatically because it requires considerable knowledge of environmental science based on classification tables.
- **CHARACTERIZATION:** The environmental impact contribution of all elementary flows is calculated, resulting in an Impact Score (IS) that represents the magnitude of the environmental change provoked by the sum of the contributions regarding a single impact category.

The impact score (IS) of a specific impact category is obtained through the following equation:

$$IS_c = \sum_i (CF_i \cdot E_i)$$

where  $E_i$  represents the elementary flow, and  $CF_i$  represents the contribution per quantity to a specific environmental impact (category) for an elementary flow.

Impact categories, also called *midpoint categories*, group together all the changes having similar effects on the environment. There exist 18 midpoint categories, each with its characterization factor and unit. Depending on the method used, these midpoints can be further grouped into more general classifications, called *endpoint categories*, depending on the different Areas of Protection (AoP), representing human and ecosystem interests that must be protected. These categories are Human Health, Ecosystem Quality and Resource Depletion, each with its indicator name and unit.

A crucial characteristic of an environmental impact and, as a consequence, of its assessment is the scale on which this impact acts. There are three different geographical scales: local, regional, and global, depending on the mechanism and the effects of each impact [59]. Some midpoint impacts, such as climate change and ozone layer depletion, are classified as global because their environmental mechanism is the same regardless of where the emission occurs. This is not the case with local or regional ones such as freshwater eutrophication and terrestrial acidification, which strictly depend on the territory's characteristics where the emissions occur (waterbody presence, ion exchange capacity of the soil, etc.....). For this reason, analysing and understanding the surrounding ecosystem by studying the diffusion mechanisms and transformations these substances undergo is fundamental to giving significance to these results.

The impact categories chosen in this study are Climate Change (CC), Terrestrial Acidification (TA) and Freshwater Eutrophication (FE).

The CC category accounts for all the greenhouse gases emitted during the process under study; the quantity is expressed in Kg of CO<sub>2</sub> equivalents (CO<sub>2eq</sub>) thanks to standardisation, where IPCC calculates the global warming potential (GWP) for every gas. The GWP referring to a substance is its potential contribution to global warming compared to the one given by the same mass of CO<sub>2</sub> according to its thermal radiation absorption and time of residence in the atmosphere. The IPCC 2013 GWP 100a has been adopted as the LCIA method in this analysis.

This methodology expresses the GWP in Kg of CO<sub>2eq</sub>, considering the potential over a 100-year time horizon stabilised by the Fifth Assessment Report (AR5) of the Intergovernmental Panel on Climate Change (IPCC). The characterisation factors of N<sub>2</sub>O and CH<sub>4</sub> are 265 and 28, respectively [76].

Acidification of soil or aquatic ecosystems accounts for all the substances that lead to a decrease in a system's acid-neutralizing capacity (ANC). This can be due to the addition of hydrogen ions or specific cations collectable from the system. The most common and impacting substances belonging to this category are sulfur oxides (SO<sub>x</sub>), nitrogen oxides (NO<sub>x</sub>), ammonia and strong acids (H<sub>2</sub>SO<sub>4</sub> or HCl). This type of contamination leads to forest decline, aquatic fauna death and rapid corrosion of exposed metallic surfaces. Its characterisation factor, the terrestrial acidification potential (TAP), is expressed as the ratio between the potential released number of H<sup>+</sup> ions for a substance and the potential released number of H<sup>+</sup> ions for the same mass of SO<sub>2</sub>, the reference substance.

Eutrophication is the process of enrichment of the aquatic environment with nutrient salts (N and P-based) that leads to an increase in biomass production by planktonic algae and aquatic plants, which results in water quality degradation. The decreased dissolved oxygen concentration, caused by its consumption by dead algae decomposition, results in biodiversity loss and the proliferation of toxic organisms. The units usually used are kg P-eq or kg PO<sub>4</sub><sup>3-</sup>eq and they are calculated by summing all the contributions of the possible degrading mechanism measuring the Chemical Oxygen Demand (COD) parameter.

Acidification and eutrophication potentials are calculated with EPD 2018 as the LCIA method. This method assesses the acidification potential (AP), expressed in kg SO<sub>2eq</sub>, by assigning a characterisation factor to each contaminant contributing to this impact. Ammonia (NH<sub>3</sub>), nitrogen oxides (NO<sub>x</sub>) and sulfur oxides (SO<sub>x</sub>) have respectively 1.88, 0.70 and 1 as characterisation factors.

Also, for the eutrophication potential (EP) assessment, measured in kg P-eq, this method assigns a characterisation factor that indicates the specific contribution to the impact of each contaminant. Phosphorous, phosphate, and phosphoric acid have 1, 0.33 and 0.32 as characterisation factors [77].

OpenLCA 1.11.0 is the software version used to elaborate the data collected in the Data Inventory Analysis.

In addition to these three main steps defined by ISO standards, the LCIA can include other optional techniques to help understand and present the results obtained; *normalisation* and *weighting* are presented below.

- **NORMALISATION:** It allows the expression of the contribution of an impact indicator compared to the annual quantity in a determined geographical area, and it is calculated as the ratio between the impact score and the normalisation factor.
- **WEIGHTING:** This step must be applied after the normalisation step. It allows the prioritisation of impact categories by applying different or equal weights to each category indicator, determining which impacts are most important and how important they are. There is no scientific or objective basis for this step, and the adopted criteria can vary depending on the goal and audience to which this technique is applied.

#### 2.3.4.1 Liquid fraction treatment phase

In calculating the impact of the solid fraction treatment phase in the plant, all potentially impacting elements belonging to this phase and its preparation were considered. The main input categories can be resumed as follows:

- *Materials:* for plant production, whose impact was appropriately distributed along all the service time (20 years).
- *Electrical energy:* used by the pumps to inject the precise amount of reactant needed, air pump, impeller engine, main feeding pump and microfilter pump to treat the functional unit.
- *Reactants:* H<sub>2</sub>SO<sub>4</sub> for converting organic P into orthophosphate, NaOH for creating an advantageous reaction condition for struvite precipitation and MgCl<sub>2</sub> to regulate the ideal Mg<sup>2+</sup> ion concentration.

The amount of materials (kg) (Tab.1), that can be assumed as steel and polyethylene, and the quantity of reactants (kg) (Tab.2) are caught by the reports of preliminary studies which aimed to design and choose the proper plant characteristics and precipitation conditions. In order to calculate the impact of materials for 1m<sup>3</sup> of liquid fraction, the weight is divided by the expected lifetime (15 years) and the annual volume of the fraction treated (m<sup>3</sup>/year). The power of each pump and engine was calculated as instant power (kW) reported on each label and technical manual, multiplied by the day-work time (h) and then divided by 24 (h/day) to obtain the electrical energy (kWh) necessary for the treatment of the functional unit (Tab.3). Each value

was associated with the most suitable product flow from the databases and assigned as input in the analysed process (Tab.4).

All data entered in this way and the corresponding units of measurement can be found in the following tables:

material	Weight (kg)	Lifetime (years)	Production (m <sup>3</sup> /year)
steel	872	15	1600
polyethylene	140	15	

**Table 1:** Amount of materials and lifetime of the plant.

reactant	Weight (kg)	Conc. (kg/L)	Flow rate (L/h)	Time (h)
NaOH	3	0.3	2	5
H <sub>2</sub> SO <sub>4</sub>	8.75	0.5	3.5	5
MgCl <sub>2</sub>	3.75	0.15	5	5

**Table 2:** Quantity of reactants necessary for FU treatment.

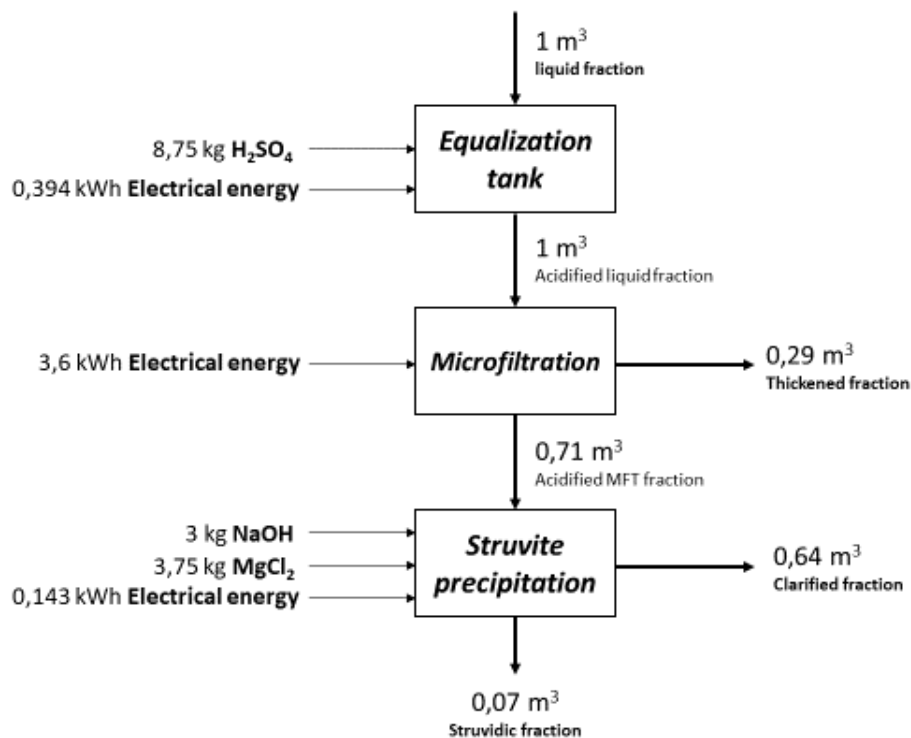
item	Power (kW)	Time (h)	Energy (kWh)
H <sub>2</sub> SO <sub>4</sub> pump	0.0239	24	0.5736
MgCl <sub>2</sub> pump	0.0239	24	0.5736
NaOH pump	0.0239	24	0.5736
Impeller engine	0.37	24	8.88
Main pump	1.1	24	26.4
MFT pump	10	6	60
Air pump	0.095	24	2.28
compressor	0.15	24	3.6
TOTAL			102.8808

**Table 3:** Total and specific energy required for FU treatment.

INPUTS		
Flow	Amount	Unit
Steel	0.0363	Kg
Polyethylene	0.0058	Kg
NaOH	3	Kg
H <sub>2</sub> SO <sub>4</sub>	8.75	Kg
MgCl <sub>2</sub>	3.75	Kg
Electricity	4.29	kWh

**Table 4:** Input flows for the LCA of the studied system.

A schematic overview of the process with the respective quantity of materials, energy and fraction treated is provided below (Scheme.1):



*Scheme 1:* Schematic overview of the process with relative quantity.

### 2.3.4.2 Atmospheric emissions of by-product streams

Thickened and clarified fractions are identified as by-product streams, and their storage impact in the lagoons is considered within the system.

It was impossible to accurately measure these waste fractions' emissions with field experiments because they would have to last several weeks. It was therefore decided to use the standard methodologies provided by the IPCC for these cases to calculate the emissions from manure management. The reference text for this study is the “2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories” [78]. This document is the updated version of the previous one, which provides standard methodologies for estimating national inventories of anthropogenic emissions by sources and removals by sinks of greenhouse gases.

As outlined in previous chapters, it has been observed that several greenhouse gases and contaminants are produced and released into the atmosphere during the storage and processing of pig manure; this can result in both methane ( $\text{CH}_4$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ) emissions, and the document provides guidance on methods to estimate them from the manure management system.

These methodologies are classified into three categories depending on the accuracy and approximation grade applied in the system's modelisation and data: Tier 1, Tier 2 and Tier 3. Our methodology will be derived from adapting the equations used in the Tier 1 and Tier 2 framework to our case study, as we have several experimental data and some country-specific factors at our disposal.

#### - *Methane ( $\text{CH}_4$ ) emissions*

Methane emissions are usually associated with manure management operations handled in a liquid-based system (e.g., in lagoons, ponds, tanks, or pits), as in this case study, under anaerobic conditions. The main factors affecting  $\text{CH}_4$  emissions are the amount of manure produced, its retention time, the content of degradable organic matter and temperature.

$\text{CH}_4$  yearly emissions produced by waste fraction storage are calculated according to the following equation (Eq.1):

**Equation 1**

$$EF_{CH_4} = VS \cdot B_{0(T)} \cdot 0.67 \cdot MCF_{(S,k)} \cdot AWMS_{(T,S,k)}$$

where

$EF_{CH_4}$  = methane emission factor, kg CH<sub>4</sub> /m<sup>3</sup>

$VS$  = volatile solids, kg dry matter /m<sup>3</sup>

$B_{0(T)}$  = maximum methane-producing capacity of the manure produced by livestock category T, m<sup>3</sup> CH<sub>4</sub> /kg VS

$0.67$  = conversion factor of m<sup>3</sup> CH<sub>4</sub> to kg CH<sub>4</sub>

$MCF_{(S,k)}$  = methane conversion factors for each manure management system S by climate region k

$AWMS_{(T,S,k)}$  = fraction of livestock manure handled using animal waste management system S in climate region k

Volatile solids (VS) values of the two examined fractions are measured in CRPA analysis laboratories through the procedure reported in Chapter 2.2 and they are available in Chapter 3.1. The B<sub>0</sub> value represents the maximum methane-producing capacity of the manure and varies by species and diet. This calculation is based on total excreted VS. Since Italy is considered in the Western Europe Region, and the study deals with swine, IPCC guidelines suggest adopting a value of 0.45 as B<sub>0</sub>. Since only one flow at a time is considered in the study, the value of AWMS is 100%.

The value of MCF is determined for a specific manure management system and represents the degree to which B<sub>0</sub> is achieved. It is affected by the extent of anaerobic conditions present, the temperature of the system, and the retention time of organic material in the system. Average regional MCF values for a specific system will largely be determined by the quantity of VS in the storage system during peak temperature periods [79]. All these parameters are summarized and considered, differentiating and categorizing MCF values by climate zone and months of storage. Following the IPCC Guidelines, considering that the case study consists of a



Liquid/Slurry storage system and a retention time of 6 months, the estimated value of MCF is 0.41.

At last, each  $EF_{CH_4}$  ( $\text{kg CH}_4/\text{m}^3$ ) is multiplied by the fraction volume ( $\text{m}^3$ ) to obtain the contribution of each fraction and the sum of the emissions of waste streams' storage ( $\text{kg CH}_4$ ) related to the functional unit (FU).

A last consideration must be done for calculating the thickened fraction emissions since the solution undergoes an acidification process before leaving the plant. It is widely reported in the literature that this process can decrease emissions of several harmful gases, including methane, by different types of manure and digestate fractions. The extent of this reduction may depend on many factors, such as pH, acid used and other chemical-physical characteristics of the fraction. This phenomenon is assumed to be related to the suppression of *methanogens* activity due to their vulnerable characteristics under acidic conditions and the accumulation of fermentation products [80]. The effect of this process in atmospheric emissions accounting is quantified by multiplying the theoretical emission by a correction factor which accounts for this phenomenon. Following a literature search on the subject [81], it was decided to adopt 0.273 as a correction factor.

A table summarizing all the values used, the units of measurement and the operations performed can be found below (Tab.5); Tab.6 also shows the output insert in the LCA analysis:

	operation	value	u.m.
$VS_{\text{thickened\_fraction}}$	$38.5*290/1000$	11.165	$\text{Kg VS}/\text{m}^3$
$VS_{\text{clarified\_fraction}}$	$25.3*290/1000$	16.192	$\text{Kg VS}/\text{m}^3$
$CH_4_{\text{thickened\_fraction}}$	$11.165*0.45*0.41*100\%*0.67*0.273$	0.376	$\text{Kg CH}_4/\text{m}^3$
$CH_4_{\text{clarified\_fraction}}$	$16.192*0.45*0.41*100\%*0.67$	2.002	$\text{Kg CH}_4/\text{m}^3$

**Table 5:** Values of methane ( $\text{CH}_4$ ) emission of waste fraction during storage.

The yearly emission found must be expressed with respect to the meantime of storage of the fractions in the storage location (90 days):

OUTPUT			
Flow	Operation	Amount	unit
Methane (CH <sub>4</sub> )	$(0.376+2.002)*90/365$	0.586	kg

**Table 6:** Output flow inserted in LCA analysis representing methane emission during the storage of waste stream.

### - *Direct nitrous oxide (N<sub>2</sub>O) emissions*

This section describes how the direct N<sub>2</sub>O emissions produced during the storage of thickened and clarified fractions are estimated.

Nitrous oxide emissions from manure management vary significantly between the management systems used, the nitrogen content, and the storage duration. Direct N<sub>2</sub>O emissions occur via combined nitrification and denitrification of nitrogen contained in the manure according to the mechanisms shown in Chapter 1.3.2. Nitrification (oxidation of ammonia nitrogen into nitrates) is a prerequisite for the emission of N<sub>2</sub>O from stored animal manures and occurs only under sufficient oxygen supply provision. Nitrites and nitrates are then transformed into N<sub>2</sub>O and molecular nitrogen (N<sub>2</sub>) during the naturally occurring denitrification process under anaerobic conditions. The production and emission of N<sub>2</sub>O from stored liquid fractions require the presence of both aerobic and anaerobic environments in addition to favourable conditions that prevent the reduction of N<sub>2</sub>O into N<sub>2</sub>, such as a low pH.

Regarding the case study, these conditions are fulfilled if a floating crust is formed on the surface of stored fractions. This phenomenon promotes the establishment of a peculiar environment's characteristics: a shallow oxygen-rich layer in which nitrification occurs and a deeper anoxic layer where denitrification is favoured. Many factors and parameters can determine the formation or not of the floating crust. The presence of straw bedding in manure, the high content of dry matter and a fibre-rich diet of livestock promote this phenomenon [82]. Due to its chemical characteristics, pig manure is usually less prone to crust formation. The fractions being considered have also undergone a process of anaerobic digestion and solid-

liquid separation that further inhibit and decrease the favouring factors. It can be assumed that thickened and clarified fractions do not undergo crust formation during storage.

This represents a crucial feature for nitrous oxide emissions counting since it influences the value of the emission factor for direct N<sub>2</sub>O emissions (EF<sub>3</sub>).

The calculation of direct N<sub>2</sub>O emissions from manure management is based on the following equation (Eq.2):

***Equation 2***

$$N_2O_{D(mm)} = N_{tot} \cdot EF_3 \cdot \frac{44}{28}$$

where

N<sub>2</sub>O<sub>D(mm)</sub> = direct N<sub>2</sub>O emissions from Manure Management, kg N<sub>2</sub>O/m<sup>3</sup>

N<sub>tot</sub> = total N content in the fraction, kg N/m<sup>3</sup>

EF<sub>3</sub> = emission factor for direct N<sub>2</sub>O emissions from manure management system, kg N<sub>2</sub>O-N /kg N

44/28 = conversion of N<sub>2</sub>O-N<sub>(mm)</sub> into N<sub>2</sub>O<sub>(mm)</sub> emissions

For those fractions which do not present a floating crust, like the ones in this case study, IPCC guidelines suggest adopting a null value as emission factor (EF<sub>3</sub>=0), resulting in no direct N<sub>2</sub>O emissions from storage of thickened and clarified fractions.

- ***Indirect nitrous oxide (N<sub>2</sub>O) emissions***

There may be other forms of nitrogen loss which can result in indirect N<sub>2</sub>O emissions. IPCC guidelines suggest considering two types of nitrogen losses with the following production of nitrous oxide: nitrogen loss from leaching and volatilisation. Leaching refers to the loss of N due to seepage into the soil and transport carried out by water flow (runoff). The study does not consider this contribution since the field application phase is not considered, and the storage point's retaining walls are impermeable, avoiding any sort of leak in the soil. Volatilisation contribution must be considered since thickened and clarified fractions undergo open-air storage. Volatized nitrogen, in the form of ammonia and NO<sub>x</sub>, may be deposited at sites downwind from manure storage areas and contribute to indirect N<sub>2</sub>O emissions according to the following equation (Eq.3):

***Equation 3***

$$N_2O_{G(mm)} = (N_{\text{volatilization-MMS}} \cdot EF_4) \cdot \frac{44}{28}$$

where

$N_2O_{G(mm)}$  = indirect N<sub>2</sub>O emissions due to volatilization of N from Manure Management, kg N<sub>2</sub>O/m<sup>3</sup>

$N_{\text{volatilization-MMS}}$  = amount of manure nitrogen that is lost due to volatilization of NH<sub>3</sub> and NO<sub>x</sub>, kg N/m<sup>3</sup>

$EF_4$  = emission factor for N<sub>2</sub>O emissions from atmospheric deposition of nitrogen on soil and water surfaces, kg N<sub>2</sub>O-N/kg NH<sub>3</sub>-N + NO<sub>x</sub>-N volatilized

44/28 = conversion of N<sub>2</sub>O-N<sub>(mm)</sub> into N<sub>2</sub>O<sub>(mm)</sub> emissions

IPCC guidelines suggest EF<sub>4</sub>, which represents the fraction of volatilised N that redeposit and undergoes an N<sub>2</sub>O transformation, a value of 0.010.

The amount of manure nitrogen that is lost due to volatilisation of NH<sub>3</sub> and NO<sub>x</sub> (N<sub>volatilization-MMS</sub>) is obtained by multiplying the amount of nitrogen in the fraction and the fraction of volatilized nitrogen which can be obtained according to the following equation (Eq.4):

***Equation 4***

$$N_{\text{volatilization-MMS}} = N_{\text{tot}} \cdot \text{Frac}_{\text{GasMS}}$$

where

N<sub>tot</sub> = total N content in the fraction, kg N/m<sup>3</sup>

Frac<sub>GasMS</sub> = fraction of managed manure nitrogen that volatilises as NH<sub>3</sub> and NO<sub>x</sub>

N<sub>tot</sub> values, available in Chapter 3.1, are measured in CRPA analysis laboratories according to the framework and methodology shown in Chapter 2.2 and it is expressed as Total Kjeldahl Nitrogen (TKN). The fraction of managed manure nitrogen that volatilises as NH<sub>3</sub> and NO<sub>x</sub> (Frac<sub>GasMS</sub>) depends on the type of manure management the case study deals with. Since the investigation concerns a Liquid/slurry typology without natural crust cover, IPCC Guidelines suggest 0.48 as its value. Since the thickened fraction undergoes an acidification process, the nitrous oxide emission must be adjusted by multiplying it for a correction factor (CF=0.5) found in literature, as in the case of methane [81].

A table summarizing all the values used, the units of measurement and the operations performed can be found below (Tab.7). Tab.8 also shows the output insert in the LCA analysis:

	<b>operation</b>	<b>value</b>	<b>u.m.</b>
N <sub>tot</sub> <sub>thickened_fraction</sub>	4587*290/1000000	1.33	Kg N/m <sup>3</sup>

Ntot <sub>clarified_fraction</sub>	$4025*640/1000000$	2.576	Kg N/m <sup>3</sup>
N <sub>2</sub> O <sub>thickened_fraction</sub>	$1.33*0.48*0.01*44/28*0.5$	0.005	Kg N <sub>2</sub> O/m <sup>3</sup>
N <sub>2</sub> O <sub>clarified_fraction</sub>	$2.576*0.48*0.01*44/28$	0.0194	Kg N <sub>2</sub> O/m <sup>3</sup>

**Table 7:** Value of nitrous oxide (N<sub>2</sub>O) emission of waste fraction during storage.

The yearly emission found must be expressed with respect to the meantime of storage of the fractions in the storage location (90 days):

OUTPUT			
Flow	Operation	Amount	unit
Dinitrogen monoxide (N <sub>2</sub> O)	$(0.005+0.0194)*90/365$	0.0244	kg

**Table 8:** Output flow inserted in LCA analysis representing N<sub>2</sub>O emission during the storage of waste stream.

### - *Ammonia (NH<sub>3</sub>) emissions*

This section describes how the ammonia (NH<sub>3</sub>) emissions produced during the storage of thickened and clarified fractions are estimated.

The accounting of ammonia atmospheric emissions is related to its role in the ecosystem acidification and water eutrophication processes, both originated by its deposition on sensitive environments and being a precursor to atmospheric particulates, causing a high incidence of respiratory diseases [83].

Despite being most recommended, it was chosen to postpone field measurements of ammonia emissions from waste fractions because of the excessively long time it would have required. It was therefore decided to use the standard methodologies provided by the European Monitoring and Evaluation Programme (EMEP) of the European Environment Agency (EEA). In particular, the reference text for this study is the “*EMEP/EEA air pollutant emission inventory guidebook (2019)*” [84], which provides guidance on estimating emissions from both anthropogenic and

natural emission sources [85]. According to the guidelines inserted in the reference document, the ammonia emissions are calculated as follows (Eq.5):

***Equation 5***

$$\text{NH}_{3\text{g}(\text{mm})} = \text{N-NH}_4^+ \cdot \text{EF}_s \cdot \text{CF}_{\text{NH}_3/\text{N-NH}_3}$$

Where

$\text{NH}_{3\text{g}(\text{mm})}$  = emissions of ammonia from Manure Management, kg  $\text{NH}_3/\text{m}^3$

$\text{N-NH}_4^+$  = nitrogen ammonium fraction, kg  $\text{N-NH}_4^+/\text{m}^3$

$\text{EF}_s$  = emission factor for ammonia volatilisation from storage, kg  $\text{N-NH}_3/\text{kg N-NH}_4^+$

$\text{CF}_{\text{NH}_3/\text{N-NH}_3}$  = conversion factor for ammonia production per nitrogen volatilised, kg  $\text{NH}_3/\text{kg N-NH}_3$

Nitrogen ammonium fraction ( $\text{N-NH}_4^+$ ) values, available in Chapter 3.1, are measured in CRPA analysis laboratories according to the framework and methodology shown in Chapter 2.2. EMEP/EEA guidelines suggest a value of 0.11 for  $\text{EF}_s$  since the study is dealing with swine. The standard conversion factor for producing ammonia from the volatilised ammonium nitrogen ( $\text{CF}_{\text{NH}_3/\text{N-NH}_3}$ ) is 17/14, equal to 1.2143.

As in the previous cases, the ammonia emission value of the thickened fraction must be adjusted with the most adapt correction factor ( $\text{CF}=0.2326$ ) according to the pH of the fraction [81].

A table summarising all the values used, the units of measurement and the operations performed (Tab.9) and a table showing the output chosen for the LCA analysis (Tab.10) can be found below:

	operation	value	u.m.
N-NH <sub>4</sub> <sup>+</sup> thickened_fraction	2851*290/1000000	0.77	kg N-NH <sub>4</sub> <sup>+</sup> /m <sup>3</sup>
N-NH <sub>4</sub> <sup>+</sup> clarified_fraction	3140*640/1000000	2.01	kg N-NH <sub>4</sub> <sup>+</sup> /m <sup>3</sup>
NH <sub>3</sub> thickened_fraction	0.77*0.11*1.2143*0.2326	0.024	kg NH <sub>3</sub> /m <sup>3</sup>
NH <sub>3</sub> clarified_fraction	2.01*0.11*1.2143	0.268	kg NH <sub>3</sub> /m <sup>3</sup>

**Table 9:** Value of ammonia (NH<sub>3</sub>) emission of waste fraction during storage.

The yearly emission found must be expressed with respect to the meantime of storage of the fractions in the storage location (90 days):

OUTPUT			
Flow	Operation	Amount	unit
Ammonia (NH <sub>3</sub> )	(0.024+0.268)*90/365	0.292	kg

**Table 10:** Output flow inserted in LCA analysis representing NH<sub>3</sub> emission during the storage of waste stream.

### 2.3.4.3 Emission savings from struvite utilization

This section describes how carbon dioxide (CO<sub>2</sub>) emission savings due to struvite utilisation are calculated.

The recovery of nitrogen (N) and phosphorus (P) nutrients from the liquid fraction of digestate is one of the main scopes this plant and project are designed for. Struvite represents a renewable and sustainable fertiliser that can replace synthetic fertiliser, decreasing the impact of the greenhouse gas released during their production. In order to calculate the carbon savings, the Joint Research Centre's Reports and proposals have been consulted [86, 87].

The JRC guidelines suggest adopting the following savings factor due to avoided synthesis fertiliser production (Tab.11):



<b>nutrient</b>	<b>Savings factor</b>	<b>u.m.</b>
Phosphorous (P)	1.24	Kg CO <sub>2</sub> eq/kg P <sub>rec</sub>
Nitrogen (N)	4.57	Kg CO <sub>2</sub> eq/kg N <sub>rec</sub>

**Table 11:** Carbon Savings Factors due to avoided production of synthesis fertiliser per unit of nutrient recovered.

The amount of P and N recovered is calculated by multiplying the concentration of the nutrients and the volume of the struvidic precipitate.

The efficiency in nutrient recovery has been calculated as the ratio between the total amount of nutrients in the final struvidic precipitate and the total amount of nutrients in the entering liquid fraction. These values (N<sub>tot</sub> and P<sub>tot</sub>) are available in Tab.17 and Tab.18.

A table summarising all the values used, the units of measurement and the operations performed can be found below (Tab.12):

<b>nutrient</b>	<b>operation</b>	<b>Amount recovered (kg/m<sup>3</sup>)</b>	<b>Recovery efficiency</b>
Phosphorous (P)	2964*70/1000000	0.20748	16%
Nitrogen (N)	5798*70/1000000	0.40858	9%

**Table 12:** Amount of P and N recovered in the Struvidic precipitate and their recovery efficiency.

The following table (Tab.13) shows the operations used to calculate the specific and total carbon savings due to nutrient recovery and the subsequent output adaptation adopted to include this aspect in the LCIA analysis:

<b>parameter</b>	<b>operation</b>	<b>Carbon savings (kg CO<sub>2</sub>eq/m<sup>3</sup>)</b>
Phosphorous (P)	0.20748*1.24	0.2572
Nitrogen (N)	0.40858*4.57	1.8549

OUTPUT			
flow	operation	amount	unit
CO <sub>2</sub> (carbon savings)	0.2572+1.8549	-2.1121	Kg

**Table 13:** Specific and total carbon savings due to nutrient recovery.

#### 2.3.4.4 Atmospheric emissions of the control system

The atmospheric emissions assessment of the control system, which represents the already existing manure management in the pig livestock, adopted the same framework and equations adopted in Chapter 2.3.4.2 for the calculation of the other fractions. This management system stores the liquid fraction leaving the solid-liquid separator in open-air lagoons in the same conditions presented in the previous chapter for the thickened and clarified fraction. National and Regional directives stabilise a mandatory storage period of 180 days for these fractions before the field application since pig livestock is placed in a Nitrate Vulnerable Zone (NVZ) and does not cultivate perennial crops. The same factors and parameters, due to atmospheric, climatic and storing conditions, are adopted for this fraction. Methane (CH<sub>4</sub>), direct and indirect nitrous oxide (N<sub>2</sub>O) and ammonia (NH<sub>3</sub>) emissions are calculated through Eq.1, Eq.2, Eq.3 and Eq.5, respectively. The volatile solids (VS), N<sub>tot</sub> (total nitrogen) and ammonium nitrogen (N-NH<sub>4</sub><sup>+</sup>) values, available in Chapter 3.1, are measured at CRPA analysis laboratories according to the procedure shown in Chapter 2.2. In order to compare the results of this system with those of the case study, all the values obtained are referred to the functional unit (FU), 1 m<sup>3</sup> of liquid fraction.

A table summarizing all the values used, the units of measurement and the operations performed (Tab.14) and a table showing the output chosen for the LCA analysis (Tab.15) can be found below:

	Operation	Value	u.m.
VS <sub>liquid_fraction</sub>	$30.2 \cdot 1000 / 1000$	30.2	Kg VS/m <sup>3</sup>
CH <sub>4</sub> <sub>liquid_fraction</sub>	$30.2 \cdot 0.45 \cdot 0.41 \cdot 100\% \cdot 0.67$	3.733	Kg CH <sub>4</sub> /m <sup>3</sup>

$N_{tot_{liquid\_fraction}}$	$4291*1000/1000000$	4.291	Kg N/m <sup>3</sup>
$N_2O_{liquid\_fraction}$	$4.291*0.48*0.01*44/28$	0.032	Kg N <sub>2</sub> O/m <sup>3</sup>
$N-NH_4^+_{liquid\_fraction}$	$2851*1000/1000000$	2.851	Kg N-NH <sub>4</sub> <sup>+</sup> /m <sup>3</sup>
$NH_3_{liquid\_fraction}$	$2.851*0.11*1.2143$	0.381	Kg NH <sub>3</sub> /m <sup>3</sup>

**Table 14:** Values of methane, nitrous oxide and ammonia emission from liquid fraction storage in the control system.

The yearly emission found must be expressed with respect to the meantime of storage of the fractions in the storage location (90 days):

<b>OUTPUT</b>		
<b>Flow</b>	<b>Amount</b>	<b>unit</b>
Methane (CH <sub>4</sub> )	0.92	kg
Dinitrogen monoxide (N <sub>2</sub> O)	0.008	kg
Ammonia (NH <sub>3</sub> )	0.094	kg

**Table 15:** Output flows inserted in LCA analysis representing the control system emission.

### 3. Results and discussion

#### 3.1 Chemical analysis results

The tables below show the values of the fractions' volumes (Tab.16), pH (Tab.16), Total Kjeldahl Nitrogen (TKN) (Tab.17), Nitrogen Ammonium Fraction (N-NH<sub>4</sub><sup>+</sup>) (Tab.17), volatile solids (VS) (Tab.18), total phosphorous content (P<sub>tot</sub>) (Tab.18) and their unit of measurement. These values are measured directly on the plant or through the laboratory techniques presented in Chapter 2.2.

	volumes		pH
	litre	[% input]	
Liquid fraction	1000	100%	8.3
Thickened fraction	290	29%	7.0
Microfiltrated fraction	710	71%	7.0
Clarified fraction	640	64%	9.0
Struvidic precipitate	70	7%	8.5

**Table 16:** Volumes and pH values of the fractions belonging to the system.

	TKN		N-NH <sub>4</sub> <sup>+</sup>	
	[mg/L tq]	[%ST]	[mg/L tq]	[%TKN]
Liquid fraction	4291	9,2	2851	66,5
Thickened fraction	4587	7,7	2658	58,0
Microfiltrated fraction	4108	10,2	3012	73,3
Clarified fraction	4025	10,7	3140	78,0
Struvidic precipitate	5798	7,6	3266	56,3

**Table 17:** Total Kjeldahl Nitrogen (TKN) and Nitrogen Ammonium Fraction (N-NH<sub>4</sub><sup>+</sup>) of the fractions belonging to the system.

	VS		P <sub>tot</sub>	
	[g/L tq]	[%ST]	[mg/L tq]	[%ST]
Liquid fraction	30,2	64,9	1281	2,8
Thickened fraction	38,5	64,8	1843	3,1
Microfiltrated fraction	25,8	64,0	1010	2,5
Clarified fraction	25,3	67,4	829	2,2
Struvitic precipitate	41,8	54,7	2964	3,9

**Table 18:** Volatile solids (VS) and total phosphorous content (P<sub>tot</sub>) of the fractions belonging to the system.

The case study and its analysis are designed to investigate this prototype's possibility and usefulness in solving two main problems for farmers: the geographical concentration of nutrients and their content in the spreading fractions. The chemical analyses carried out on the fractions resulting from the process reveal important implications from this point of view.

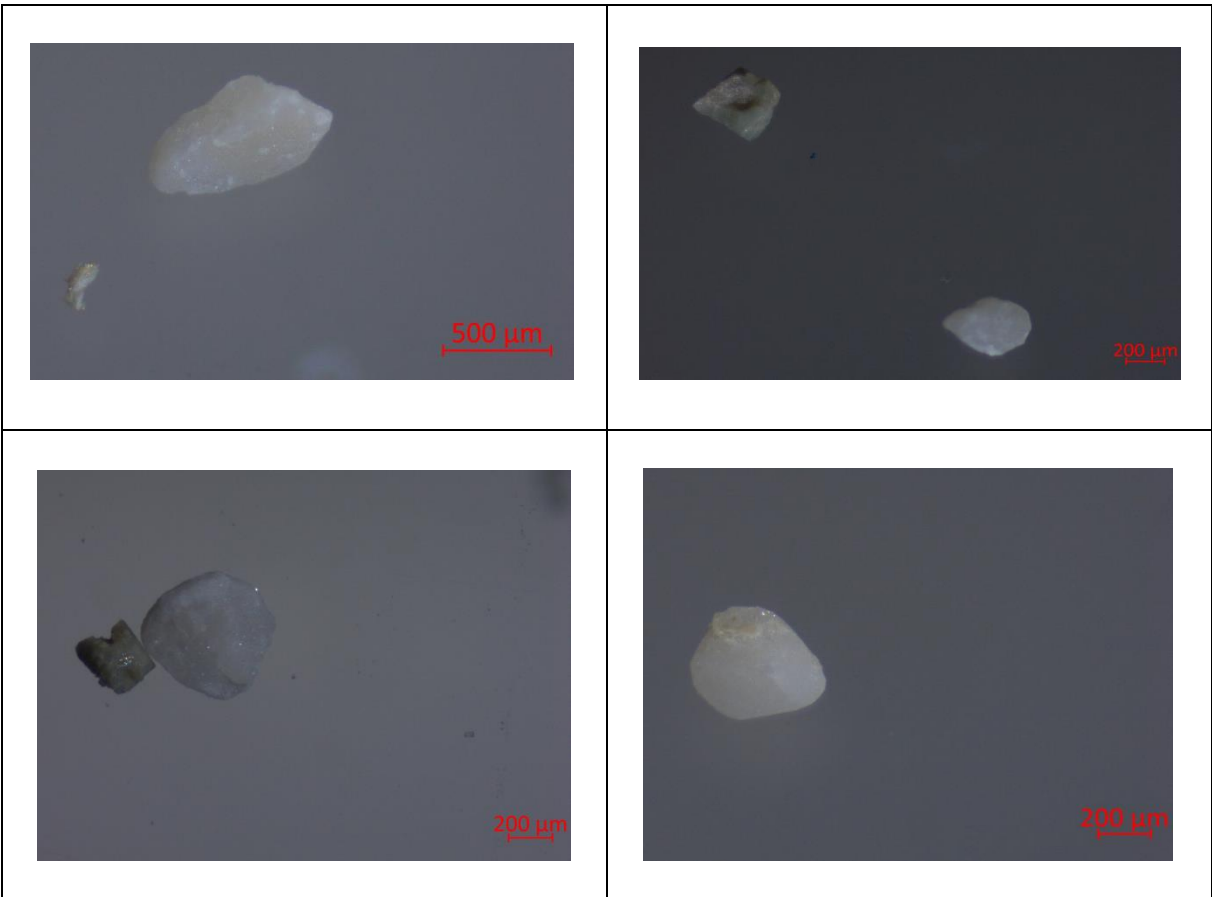
It can be seen that there is a higher concentration of nutrients in the struvitic precipitate than in the incoming liquid fraction: with a change from 1281 mg/L to 2964 mg/L for the total P content (+57%), from 4291 mg/L to 5798 mg/L for the total nitrogen content (+26%), from 2851 mg/L to 3266 mg/L for the ammonium nitrogen content (+13%). As also outlined above, this fraction can be used as a fertiliser replacing a synthetic fertiliser, thus reducing its environmental impact due to production. As can be seen in chapter 2.3.4.3, this reduction is 2.11 kg CO<sub>2</sub>eq for each m<sup>3</sup> of liquid fraction treated. The crystals of struvite (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O) formed during the precipitation step, which characterize this fraction, are shown in Figure 12. In addition to being a valuable nutrient recovery process, with a recovery efficiency of 9% for N and 16% for P, this fraction can also allow more efficient and less economically and environmentally costly transport of nutrients.

The nutrient reduction of the resulting fractions (thickened and clarified fractions) can have several positive consequences on the management of these effluents. A lower content of nitrogen and volatile solids results in lower greenhouse gas and ammonia emissions during the storage period. The lower nutrient content of these manure residues will allow them to be spread more widely in the fields. The disposal of these fractions is, in fact, a major problem for farmers, who are forced to dispose of them either by spreading them on their crops or by paying for their transport to more lacking geographical areas with fewer livestock farms in the vicinity.

The livestock under examination is in an even more particular and delicate situation than the average since being located in Formigine (MO), it falls within a Nitrate Vulnerable Zone (NVZ), within which the spreading of effluents on the crop is even more strictly monitored and limited. The value set as a limit by the “EU Nitrates Directive” published in 1991 for the application in these zones is:

**170 kg N/ha**

The areas identified by this directive are characterised by a strong presence of groundwater and watercourses and low clay content in the soil, which promotes soil permeability and facilitates its contamination by fertiliser nutrients. In Emilia Romagna, these areas are particularly concentrated in the Apennines foothill areas.



**Figure 12:** Struvite crystals present in the Struvitic mud at optic microscope.

## 3.2 Life Cycle Assessment (LCA) results

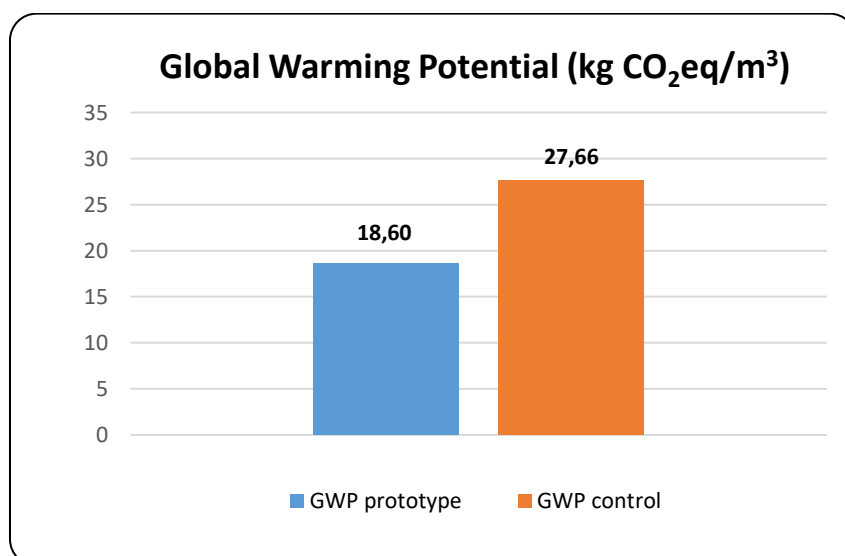
In this section, the results obtained by OpenLCA calculations will be displayed and commented on. The impact categories examined are Climate Change (CC), Freshwater Eutrophication (EU) and Terrestrial Acidification (AC).

### 3.2.1 Climate change

This impact category includes the emissions of all those substances that contribute to global warming, known as greenhouse gases (GHGs). Their contribution is expressed in terms of global warming potential (GWP) and is measured in kg CO<sub>2</sub> eq using the values set out in section 2.3.4

The emissions of methane, nitrous oxide and carbon dioxide were identified in the system examined (prototype system) and compared to those of the control system representing the management of digestate already existing on the livestock (control system).

The GWP of the system representing the prototype under evaluation resulting from the calculation is 18.60 kg CO<sub>2</sub> eq for the treatment of 1 m<sup>3</sup> of liquid fraction. The GWP of the control system results 27.66 kg CO<sub>2</sub> eq.



*Figure 13: Global warming potential of prototype system and control system.*

An overall decrease in greenhouse gas impact of 33% was therefore observed.

Going on to analyse more in details the data for the system representing the prototype examined, the analysis returns the results of the contributions of the individual phases and flows used during treatment. The most impacting phase results in the storage of thickened and clarified fraction, which was measured as 15.76 kg CO<sub>2</sub> eq; the second one is the production of the electricity used during the treatment, which results in 1.76 kg CO<sub>2</sub> eq, and the third most impacting factor is the production of the sulfuric acid used to acidify the liquid fraction which results in 1.01 kg CO<sub>2</sub> eq per m<sup>3</sup> treated.

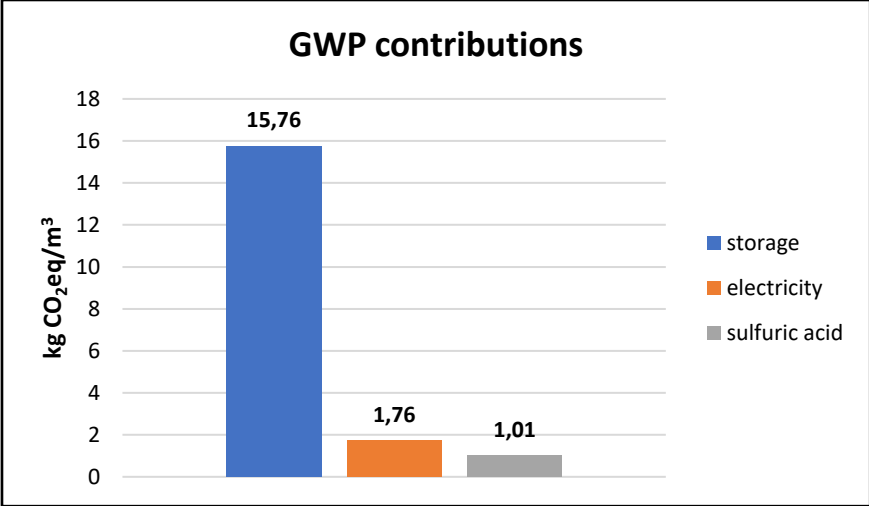


Figure 14: Specific contribution to GWP of prototype system.

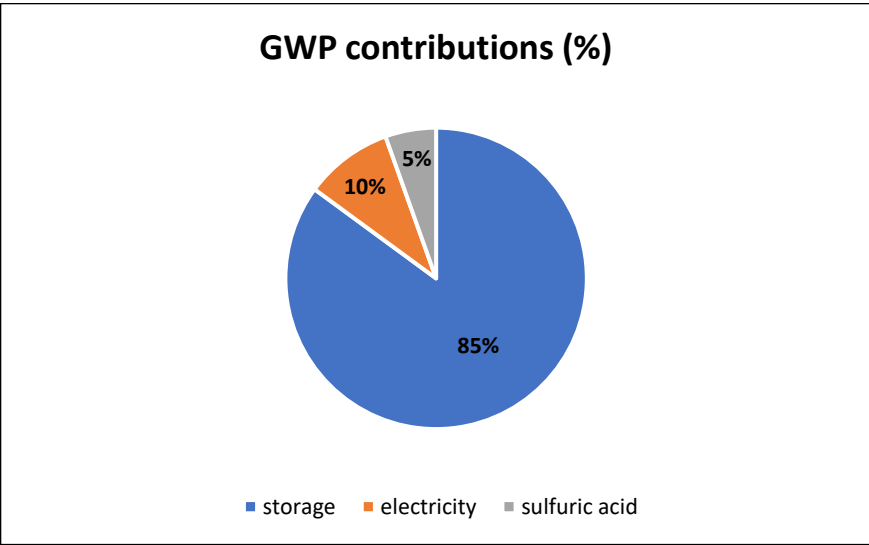


Figure 15: Percentage contribution to GWP of prototype system.



Since the storage phase is by far the most impactful, it is worth pausing to analyse it further; from the analysis, it was possible to obtain the contribution that each greenhouse gas made to the overall impact of this phase. The results (Figure 16) report that methane (CH<sub>4</sub>) is responsible for 91% of the impact due to the storage phase with an absolute value of 16.27 kg CO<sub>2</sub> eq, while nitrous oxide (N<sub>2</sub>O) is responsible for 9% with an impact of 1.59 kg CO<sub>2</sub> eq. This information can be particularly useful because it can be understood which gases and, thus, which precursors contained within the digestate could act to further reduce emissions from these fractions.

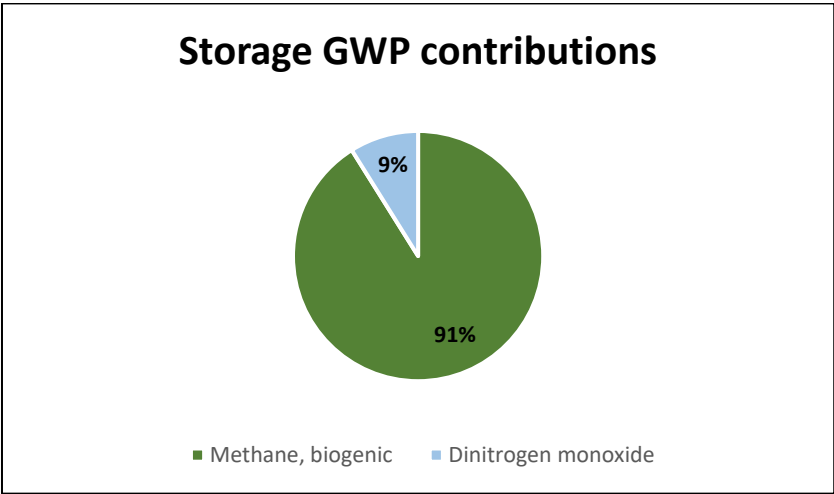


Figure 16: Percentage contribution of each GHG to storage GWP.

Other useful information can be obtained by investigating how each fraction affects the total emission of the storage phase; this will allow a better decision on which fraction to act on in order to achieve a more efficient reduction of emissions. The results show that the clarified fraction is responsible for 84% of the impact while the thickened one only for 16%. This difference is mainly due to the fact the thickened fraction did undergo an acidification process which drastically decreases its atmospheric emissions as observed in agricultural literature [81].

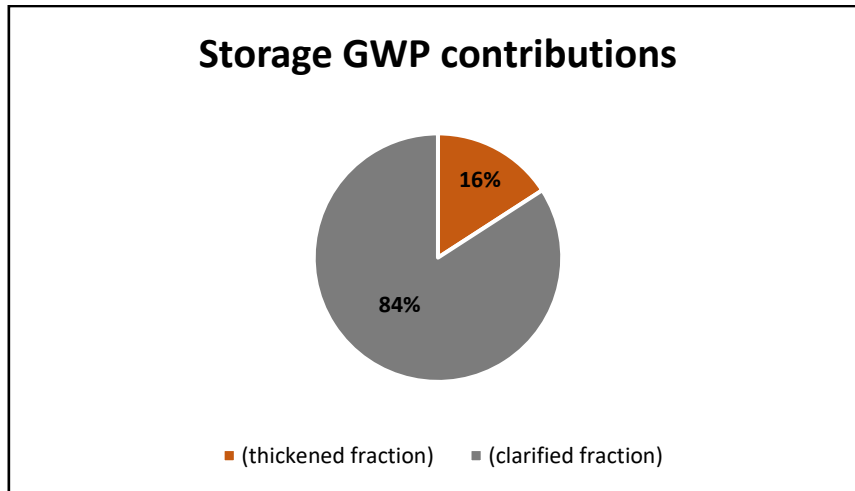


Figure 17: Percentage contribution of each fraction to storage GWP.

Finally, a 2.11 kg CO<sub>2</sub> eq reduction in the prototype system's emissions was observed due to the recovery of N and P nutrients through the precipitation of struvite, which will replace synthetic fertiliser; the carbon savings value obtained refers precisely to the lack of production of the latter.

For what concern the control system, all emissions and related impacts are due to the storage phase of 1 m<sup>3</sup> of liquid fraction. The percentage values expressing the contribution of each GHG to the impact of this phase that were obtained are very similar to those obtained from the prototype system.

### 3.2.2 Freshwater Eutrophication

Freshwater eutrophication is a phenomenon whereby there is a high concentration of nutrients (P and N) in surface water. The main sources of this contamination are industrial and urban wastewater and fertilisers used in agriculture. The excessive presence of these nutrients causes uncontrolled growth of phytoplankton, which can obstruct the sunlight irradiation of deep water, and aquatic plants which, if too dense, risk consuming all the oxygen dissolved in the water, representing a threat to animals and the biodiversity of these ecosystems.

In this case study, the eutrophication potential is expressed as kg PO<sub>4</sub><sup>3-</sup> eq.

The eutrophication potential of the prototype system resulted in 0.034 kg PO<sub>4</sub><sup>3-</sup> eq, while one of the control system resulted in 0.035 kg PO<sub>4</sub><sup>3-</sup> eq, both with respect to the functional unit (FU) of 1 m<sup>3</sup> of liquid fraction.

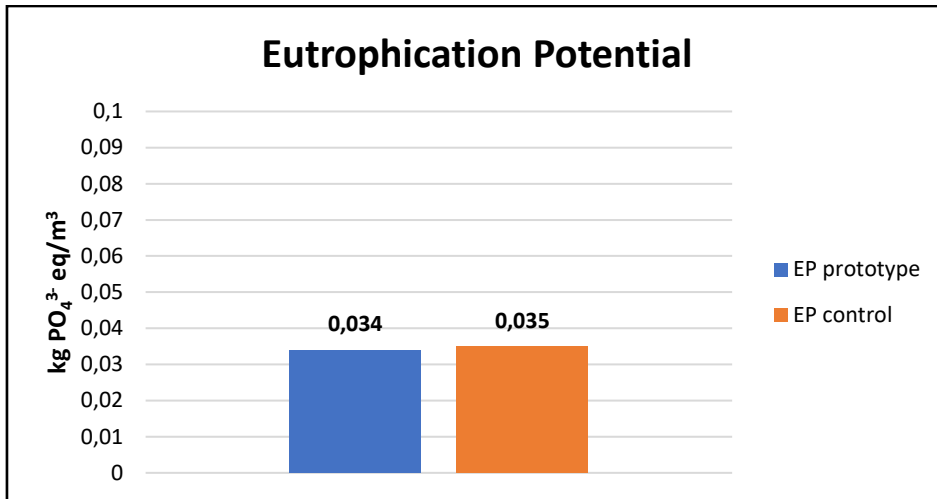


Figure 18: Eutrophication potential of the prototype system and control system.

Analysing the prototype system, an underlighting of the contribution of each phase was possible. The calculation attributed to the storage phase 0.027 kg PO<sub>4</sub><sup>3-</sup> eq, which represents 79% of the total prototype system impact. There are then electricity and sulfuric acid production with 0.0036 kg PO<sub>4</sub><sup>3-</sup> eq (11%) and 0.0035 kg PO<sub>4</sub><sup>3-</sup> eq (10%), respectively.

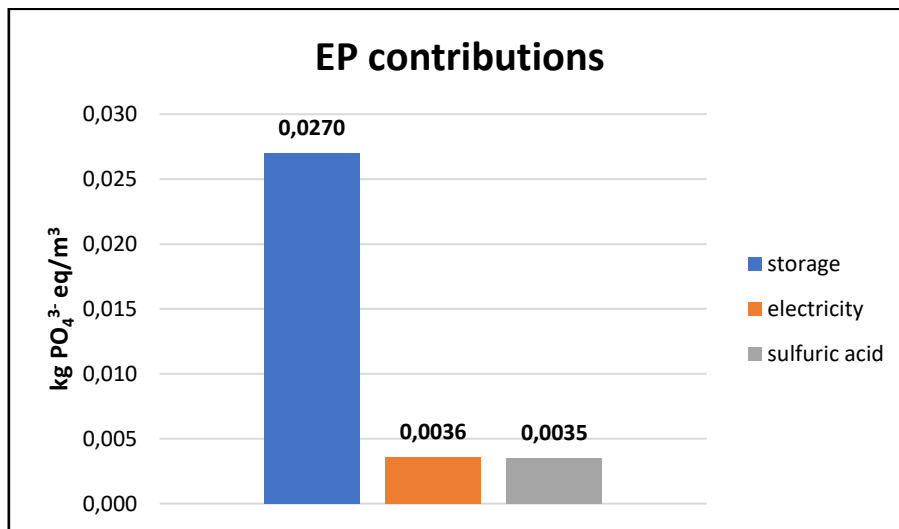


Figure 19: Specific contribution to EP of prototype system.

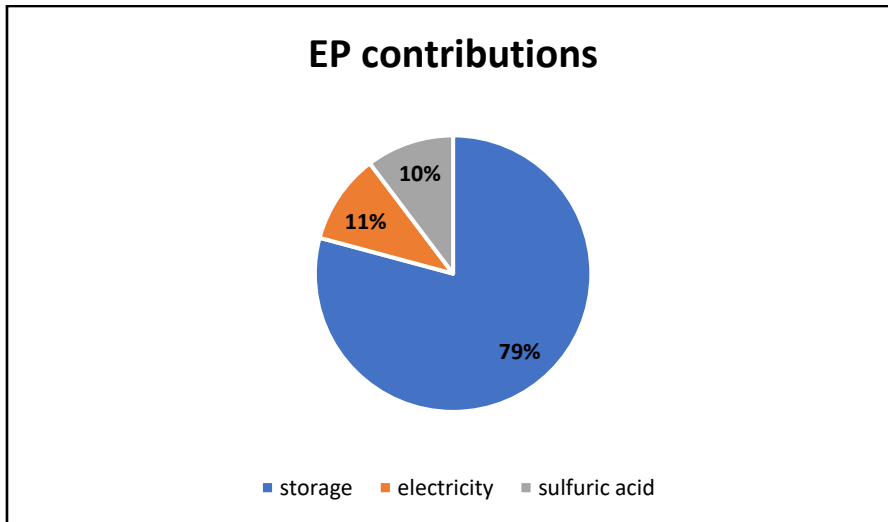


Figure 20: Percentage contribution to EP of the prototype system.

Very similar behaviours and values were recorded regarding the specific contributions of each fraction and each gas to this impact category; a decidedly predominant impact on the part of ammonia and the clarified fraction was therefore recorded.

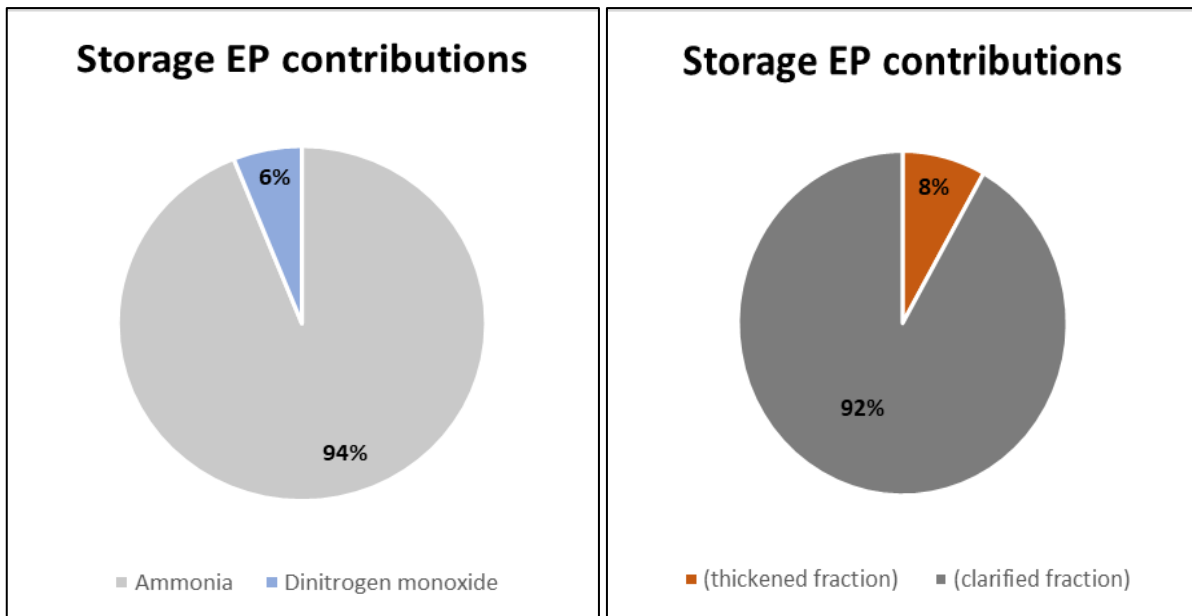


Figure 21: Percentage contribution to EP of each contaminant and each fraction.

The values of the percentage contribution to eutrophication potential (EP) of each contaminant during the storage period in the control system are identical to the ones regarding the prototype system.

It can be observed, like in the case of global warming potential, that the most impacting phase is the storage of the thickened and clarified fraction. In particular, the last cited is by far the most impacting one due to the acidification process done on the other. Both contaminants analysed in this category derive from the nitrogen contained in the fractions; it can be deduced that future nutrient recovery efficiency enhancements can contribute to decreasing its content in the resulting fractions, which undergo storage.

### 3.2.3 Terrestrial Acidification

Terrestrial acidification consists of releasing acidifying substances that can be deposited on the ground or in a water body, decreasing the pH of the environment or the ecosystem where they are. These changes severe biodiversity and ecosystem services, provoking forest decline, aquatic fauna death and rapid corrosion of exposed metallic surfaces. The acidification potential is expressed as kg SO<sub>2</sub> eq.

The acidification potential (AP) of the system representing the prototype under evaluation resulting from the calculation is 0.211 kg SO<sub>2</sub> eq for the treatment of 1 m<sup>3</sup> of liquid fraction. The AP of the control system results in 0.177 kg SO<sub>2</sub> eq.

An increase of 19% for the prototype system in this impact category has been observed. This is due to the treatments made on the fraction within the prototype because considering only the emissions due to the storage period of both systems, the less impacting one is the prototype. Indeed, the impact attributed to the storage phase for the prototype system is 0.135 kg SO<sub>2</sub> eq, all due to ammonia (NH<sub>3</sub>). This phase is the most impacting of the system (64%), followed by sulfuric acid production (29%) and electricity production (7%). As in the case of eutrophication potential, the clarified fraction is responsible for 94% of the ammonia emission. The acidification process of the thickened fraction allows a drastic decrease in its emissions, accounting only for 6%, as already documented.

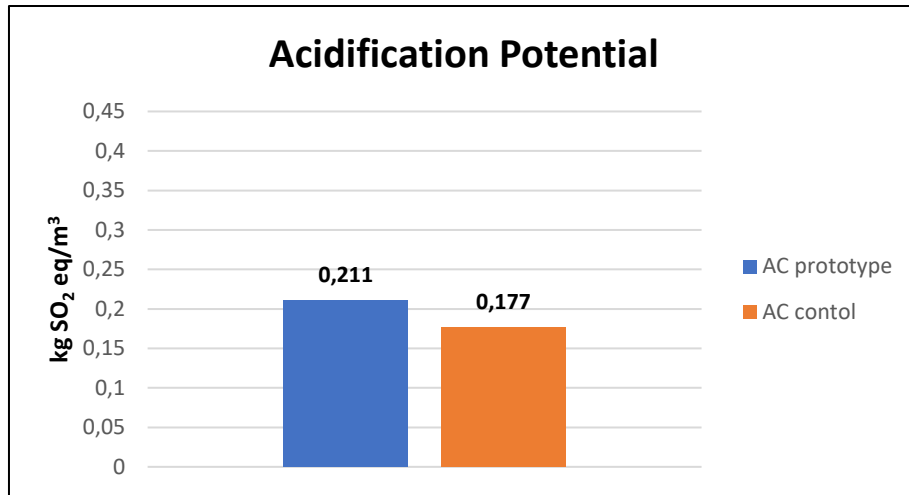


Figure 22: Acidification potential of the prototype system and control system.

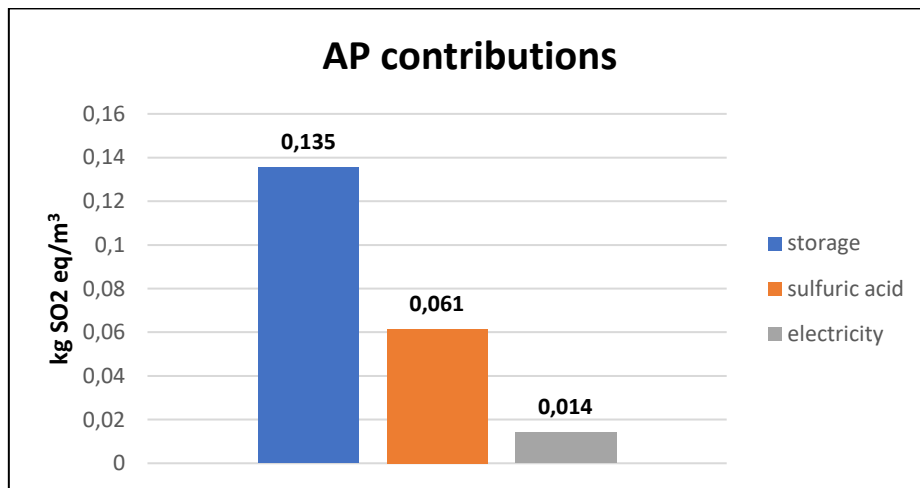


Figure 23: Specific contribution to AP of prototype system.

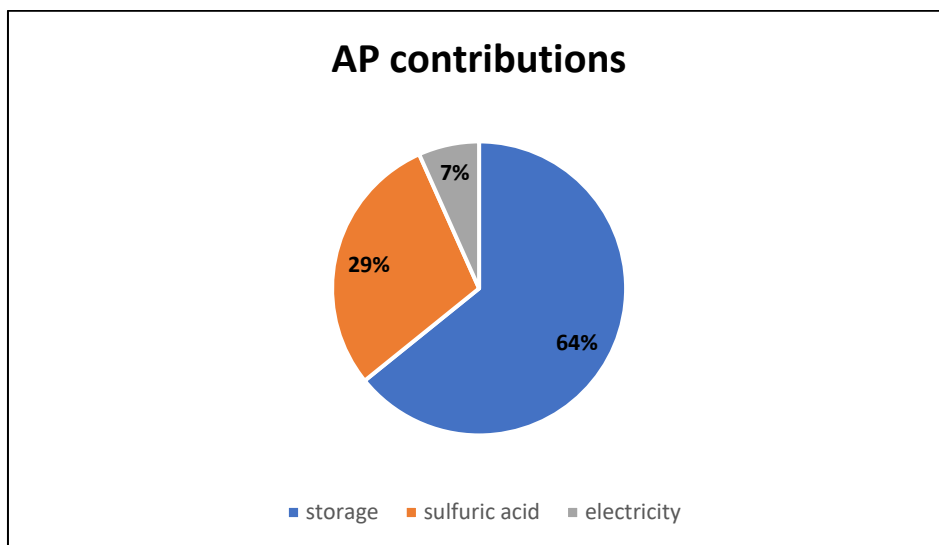


Figure 24: Percentage contribution to AP of the prototype system.

## 4. Conclusions

The aim of this work is the assessment of the environmental impact of the recovery of nutrients (N and P) from the liquid fraction of pig manure digestate via struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) precipitation.

All the activities and the processes regarding the case study took place in a pig livestock in Formigine (MO). The analysis of the effluents, the environmental assessment, the design and the management of the prototype were entrusted to Centro Ricerche Produzioni Animali – CRPA Soc.Cons.p.A., localized in Reggio Emilia (RE). These two realities collaborate in the pursuit of the project GOI Struvite, promoted by Regione Emilia Romagna and the European Union, which aims to decrease the nitrogen (N), phosphorous (P) and Total Solid (TS) content in pig manure digestate to reduce the atmospheric emissions of  $\text{NH}_3$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  during storage, treatments and application phases of these fractions. The struvite produced in this process will be able to replace synthesis fertilizer, reducing the impact of their production and favouring the translocation of the surplus of nutrients from areas with high concentrations of livestock to regions with higher demand of nutrients due to cropping [65].

The prototype fits into a manure management system already present on the farm.

The pig manure is collected from the nine barns of the livestock, which contains almost 15,000 fattening pigs, with a total meat production of  $100 \text{ m}^3$  of manure per day. The manure undergoes anaerobic digestion for 40-60 days. The digestate is then separated through mechanical solid-liquid separation: the solid fraction is left to dry while the liquid fraction can be stored in open-air lagoons or fed to the prototype.

The liquid fraction entering the prototype is acidified with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) to promote the transformation of organic phosphorous compounds into orthophosphates ( $\text{PO}_4^{3-}$ ). The solution is microfiltrated to decrease the solid particle content, which risks interfering with the precipitation mechanism. The stream thus reaches the crystallisation tank which undergoes air stripping of  $\text{CO}_2$  to increase the pH and basification with NaOH in order to obtain the ideal reaction condition for the struvite precipitation. For the same reason,  $\text{MgCl}_2$  is added, obtaining the ideal molar ratio of N:P:Mg of 1:1:1. The precipitated struvite is collected from the bottom of the tank and stored.

The waste fractions are collected and stored in open-air lagoons like the liquid fraction of the already existing manure management system.

The environmental impact of the systems just explained is assessed thanks to a Life Cycle Assessment (LCA) analysis.

In this case study, 1 m<sup>3</sup> of liquid fraction was chosen as the functional unit (FU). This choice allows the comparison between the prototype system and the control system, representing the already existing manure management system in the livestock. All the processes and materials used from the entrance of the liquid fraction in the plant till the finish of the storage period (180 days) of the waste fractions are accounted for within the system.

Materials, electrical energy consumption and reactant needed for the treatment of the functional unit have been quantified. The “2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories” has been used as reference text for the quantification procedure of greenhouse gasses (GHGs), such as methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O). The standard methodologies provided by the European Monitoring and Evaluation Programme (EMEP) of the European Environment Agency (EEA) have been used for the calculation of the ammonia (NH<sub>3</sub>) emission. The same methodologies and framework have been used for the control system emissions quantification. The environmental impact of Climate Change (CC), Eutrophication (EU) and Acidification (AC) has been assessed using OpenLCA as analytic software.

The results of the LCA analysis regarding the Climate Change (CC) impact category showed a GWP of 18.60 kg CO<sub>2</sub> eq for the prototype system against a value of 27.66 kg CO<sub>2</sub> eq for the control system. 85% of the total impact of the prototype system is due to the emissions during the storage phase, indicating that the treatment phase is carried out under environmentally acceptable conditions and values. These emissions are mainly due to clarified fraction (84%) because the thickened fraction did undergo an acidification process which drastically decrease its atmospheric releases. The most impacting GHG results are methane (CH<sub>4</sub>), representing 91% of the contribution.

The results of the LCA analysis regarding the Eutrophication (EU) impact category showed an eutrophication potential (EP) of 0.034 kg PO<sub>4</sub><sup>3-</sup> eq for the prototype system against a value of 0.035 kg PO<sub>4</sub><sup>3-</sup> eq for the control system. 79% of the total impact of the prototype system is due to the emissions during the storage phase of waste fractions, again mainly due to clarified fraction (92%). The most impacting contaminant results in ammonia (NH<sub>3</sub>), representing 94% of the contribution. It has been observed an enhancement in the emissions from fractions storage, but this value is compensated by the impact of the treatments the liquid fraction undergoes within the plant.



The results of the LCA analysis regarding the Acidification (AC) impact category showed an acidification potential (AP) of 0.211 kg SO<sub>2</sub> eq for the prototype system against a value of 0.177 kg SO<sub>2</sub> eq for the control system. 64% of the total impact of the prototype system is due to the emissions during the storage phase of waste fractions, mainly due to clarified fraction with the same values as in eutrophication since the emissions are almost the same. This evaluation calculates that the prototype has a worst overall impact for the acidification impact category.

All the detailed impact values and insides are available in Chapter 3.2. They can be summarized as follows: 33% of reduction in the Climate Change impact, 3% of reduction in the Eutrophication Potential and 19% of increase in the Acidification Potential.

It has been observed that the storage of the waste fractions is always the most impacting phase of the prototype system according to each impact category. It follows that their treatment could also be the focus of further future research in this field. Since the most impacting gasses are methane (CH<sub>4</sub>) and ammonia (NH<sub>3</sub>), future research could focus on the removal or recovery of their precursors, which are volatile solids (VS) and ammonium nitrogen (N-NH<sub>4</sub>). The acidification of these fractions could decrease their emissions or, even better, higher nutrient recovery efficiency and yield. The enhancement in the recovery performance will decrease the risk of nutrient over-application on the field and the concentration of ammonia, nitrous oxide and phosphate precursors. It also follows an increase in carbon savings due to the substitution of synthetic fertiliser with struvite. Today, the prototype has a fairly low efficiency in nutrient recovery as we are dealing with an experimental project that is still in the implementation phase. Project development, financing and production monitoring will continue throughout 2024 with the aim of increasing efficiency.

A phase that unfortunately could not be included in this environmental analysis is that of spreading. This phase needs many weeks of measurements and monitoring to be thoroughly analysed. Many factors, such as humidity, temperature, wind speed and soil characteristics, influence its emissions and ecosystem contamination. It is hoped that research will progress in this field as well.

At the end of the process, a struvitic fraction with higher nutrient concentration than the initial liquid fraction and a decrease in the nutrient content of spreadable fractions are obtained. These results will allow farmers to spread and dispose of a higher amount of digestate. This fraction may be spread with a lower risk for the environment while a more economical and efficient translocation of the nutrient surplus may be implemented.

## References

- [1] Van Zanden JL., *The first green revolution: the growth of Production and Productivity in European Agriculture, 1870–1914*. Econ Hist Rev 1991.
- [2] Bateman A, van der Horst D, Boardman D, Kansal A, Carliell-Marquet C. *Closing the phosphorus loop in England: the spatiotemporal balance of phosphorus capture from manure versus crop demand for fertilizer*. Resour Conserv Recycl 2011.
- [3] Ngoze S, Riha S, Lehmann J, Verchot L, Kinyang J, Mbuga D, et al. *Nutrient constraints to tropical agroecosystem productivity in long-term degrading soils*. Global Change Biol 2008.
- [4] U.S. Geological Survey, *Mineral Commodity Summaries*, January 2023.
- [5] Food and Agriculture Organization of the United Nations (FAO), Dataset, *Fertilizers by nutrients*, <https://www.fao.org/faostat/en/#data/RFN/metadata>
- [6] U.S. Geological Survey, *Mineral Commodity Summaries*, January 2021.
- [7] Cordell, D., Drangert, J.O., White, S., 2009. *The story of phosphorus: global food security and food for thought*. Global Environ. Change 19, 292–305.
- [8] Rahman, M.M., Liu, Y.H., Kwag, J.H., Ra, C.S., 2011. *Recovery of struvite from animal wastewater and its nutrient leaching loss in soil*. J. Hazard. Mater. 186.
- [9] Md. Mukhlesur Rahman, Mohamad Amran Mohd. Salleh, Umer Rashid, Amimul Ahsan, Mohammad Mujaffar Hossain, Chang Six Ra, *Production of slow-release crystal fertilizer from wastewaters through struvite crystallization – A review*, Arabian Journal of Chemistry (2014) 7.
- [10] Sistema Informativo Veterinario – Statistiche, [https://www.vetinfo.it/j6\\_statistiche/#/](https://www.vetinfo.it/j6_statistiche/#/)
- [11] *COUNCIL DIRECTIVE of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources (91 / 676 /EEC)*, Official Journal of the European Communities, No L 375 / 1.
- [12] Tregaro, Y., Lossouarn, J., 2004. *Dynamique de la production porcine mondiale et européenne: enjeux de localisation et de relations au territoire*. In: Séminaire Porcherie Verte, 7–8 décembre, La Rochelle, France (in French).
- [13] IPCC 2019, *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories*, Calvo Buendia, E., Tanabe, K., Kranjc, A., Baasansuren, J., Fukuda, M., Ngarize S., Osako, A., Pyrozhenko, Y., Shermanau, P. and Federici, S. (eds). Published: IPCC, Switzerland.

- [14] FAO. 2020. *Emissions due to agriculture. Global, regional and country trends 2000–2018*. FAOSTAT Analytical Brief Series No 18. Rome.
- [15] ISPRA - Institute for Environmental Protection and Research, *Italian Greenhouse Gas Inventory 1990-2021 National Inventory Report 2023*.
- [16] Steinfeld, H., Gerber, P., Wassenaar, T., Castel, V., Rosales, M., de Haan, C., 2006. *Livestock's long shadow – environmental issues and options*, FAO, p. 390.
- [17] IEA, *Greenhouse gas emissions from energy*, 2021.
- [18] Le Mer, J. L.; Roger, P. 2001: *Production, oxidation, emission and consumption of methane by soils: a review*. European Journal of Soil Biology 37: 25-50.
- [19] IPCC (2021) *Summary for policymakers*. In: Masson-Delmotte V, Zhai P, Pirani A, Connors SL, Péan C, Berger S, Caud N, Chen Y, Goldfarb L, Gomis MI, Huang M, Leitzell K, Lonnoy E, Matthews JBR, Maycock TK, Waterfeld T, Yelekçi O, Yu R, Zhou B (eds) *Climate Change 2021: the physical science basis. Contribution of Working Group I to the sixth assessment report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge.
- [20] Surinder Saggarr, N. S. Bolan, R. Bhandral, C. B. Hedley & J. Luo, *A review of emissions of methane, ammonia, and nitrous oxide from animal excreta deposition and farm effluent application in grazed pastures*, New Zealand Journal of Agricultural Research, 47:4, 513-544.
- [21] Yong Hou, Gerard L. Velthof, Jan Peter Lesschen, Igor G. Staritsky, and Oene Oenema, *Nutrient Recovery and Emissions of Ammonia, Nitrous Oxide, and Methane from Animal Manure in Europe: Effects of Manure Treatment Technologies*, Environ. Sci. Technol. 2017, 51, 375–383.
- [22] J Lia, J Luoa, Y Shib, D Houlbrookea, L Wangb, S Lindseya and Y Li, *Nitrogen gaseous emissions from farm effluent application to pastures and mitigation measures to reduce the emissions: a review*, New Zealand Journal of Agricultural Research, 2015 Vol. 58, No. 3, 339–353.
- [23] Richard S Stolarski, Anne R Douglass, Luke D Oman and Darryn W. Waugh, *Impact of future nitrous oxide and carbon dioxide emissions on the stratospheric ozone layer*, Environ. Res. Lett. 10 (2015).
- [24] S.G. Sommer, N.J. Hutchings, *Ammonia emission from field applied manure and its reduction—invited paper*, European Journal of Agronomy 15 (2001) 1–15.

- [25] Freney, J. R.; Simpson, J. R.; Denmead, O. T. 1983: *Volatilization of ammonia*. In: Freney, J. R.; Simpson, J. R. ed. *Gaseous loss of nitrogen from plant-soil systems*. The Hague, Martinus Nijhoff/Dr W. Junk Publishers. Pp. 1-32.
- [26] Selvarajah, N.; Sherlock, R. R.; Smith, N. P.; Cameron, K. C. 1989: In: Currie, L. D.; Loganathan, P. ed. *Proceedings of the Workshop on Nitrogen in New Zealand Agriculture and Horticulture*. Palmerston North, Massey University. Pp. 145—156.
- [27] Whitehead, D. C.; Raistrick, N. 1990: *Ammonia volatilization from five nitrogen compounds used as fertilizers following surface application to soils*. *Journal of Soil Science* 41: 387-394.
- [28] Francois-Xavier Philippe, Jean-Francois Cabaraux, Baudouin Nicks, *Ammonia emissions from pig houses: Influencing factors and mitigation techniques*, *Agriculture, Ecosystems and Environment* 141 (2011) 245-260.
- [29] Daumer, M.L., Guiziou, F., Dourmad, J.Y., 2007. *Effect of dietary protein content and supplementation with benzoic acid and microbial phytase on the characteristics of the slurry produced by fattening pigs*. *Journées de la Recherche Porcine* 39, 13–22.
- [30] Ann C. Wilkie, *Anaerobic digestion: Biology and Benefits*, In: *Dairy Manure Management: Treatment, Handling, and Community Relations*. NRAES-176. Natural Resource, Agriculture, and Engineering Service, Cornell University, Ithaca, NY, 2005.
- [31] Oldfield, T.L., White, E., Holden, N.M., 2016. *An environmental analysis of options for utilising wasted food and food residue*. *J. Environ. Manag.* 183, 826–835.
- [32] Massé, D.I., Patni, N.K., Droste, R.L., Kennedy, K.J., 1996. *Operation strategies for psychrophilic anaerobic digestion of swine manure slurry in sequencing batch reactors*. *Can. J. Civ. Eng.* 23, 1285–1294.
- [33] Duarte, E.A., Mendes, B., Oliveira, J.S., 1992. *Removal of Salmonella, Streptococci and coliforms in pig breeding effluent by anaerobic mesophilic digestion*. *Water Sci. Technol.* 26, 2169–2172.
- [34] Kearney, E.T., Larkin, M.J., Frost, J.P., Levett, P.N., 1993. *Survival of pathogenic bacteria during mesophilic anaerobic digestion of animal waste*. *J. Appl. Bacteriol.* 75, 215–219.
- [35] Sogn TA, Dragicevic I, Linjordet R, Krogstad T, Eijsink VGH, Eich-Greatorex S (2018), *Recycling of biogas digestates in plant production: NPK fertilizer value and risk of leaching*. *Int J Recycl Org Waste Agric* 7: 49-58.
- [36] Limoli A, Langone M, Andreottola G. *Ammonia removal from raw manure digestate by means of a turbulent mixing stripping process*. *J Environ Manag.* 2016; 176:1–10.

- [37] Nkoa R. *Agricultural benefits and environmental risks of soil fertilization with anaerobic digestates: a review*. *Agron Sustain Dev*. 2013;34(2):473–92.
- [38] Wagner, C., Nyord, T., Vestergaard, A.V., Hafner, S.D., Pacholski, A.S., 2021. *Acidification effects on in situ ammonia emissions and cereal yields depending on slurry type and application method*. *Agriculture* 11, 1052.
- [39] Yolanda M. Lemes, Tavs Nyord, Anders Feilberg, Sasha D. Hafner, Johanna Pedersen, *Effect of anaerobic digestion on odor and ammonia emission from land-applied cattle manure*, *Journal of Environmental Management* 338 (2023).
- [40] Mehta CM, Khunjar WO, Nguyen V, Tait S, Batstone DJ. *Technologies to Recover Nutrients from Waste Streams: A Critical Review*. *Crit Rev Environ Sci Technol*. 2014.
- [41] Tambone F, Terruzzi L, Scaglia B, Adani F. *Composting of the solid fraction of digestate derived from pig slurry: Biological processes and compost properties*. *Waste Manag*. 2015; 35: 55–61.
- [42] Nges IA, Wang B, Cui Z, Liu J. *Digestate liquor recycle in minimal nutrients-supplemented anaerobic digestion of wheat straw*. *Biochem Eng J*. 2015; 94: 106–14.
- [43] Sampriti Katak, Helen West, Michèle Clarke, D.C. Baruah, *Phosphorus recovery as struvite from farm, municipal and industrial waste: Feedstock suitability, methods and pre-treatments*, *Waste Management* 49 (2016) 437-454.
- [44] Berrin Tansel, Griffin Lunn, Oscar Monje, *Struvite formation and decomposition characteristics for ammonia and phosphorus recovery: A review of magnesium-ammonia phosphate interaction*, *Chemosphere* 194 (2018) 504-514.
- [45] Dolores Hidalgo, Francisco Corona, Jesús M. Martín-Marroquín, Josué del Álamo & Alicia Aguado (2016) *Resource recovery from anaerobic digestate: struvite crystallisation versus ammonia stripping*, *Desalination and Water Treatment*, 57:6, 2626-2632.
- [46] D. Crutchik, J.M. Garrido, *Kinetics of the reversible reaction of struvite crystallization*, *Chemosphere* 154 (2016), 567-572.
- [47] Guangan Jia, Hu Zhang, Joerg Krampe, Tim Muster, Baoyu Gao, Nanwen Zhu, Bo Jin, *Applying a chemical equilibrium model for optimizing struvite precipitation for ammonium recovery from anaerobic digester effluent*, *Journal of Cleaner Production* 147 (2017) 297-305.
- [48] He, G.X., He, L.H., Zhao, Z.W., Chen, X.Y., Gao, L.L., Liu, X.H., 2013. *Thermodynamic study on phosphorus removal from tungstate solution via magnesium salt precipitation method*. *Trans. Nonferrous Met. Soc. China* 23, 3440e3447.

- [49] Withers PJA, Sylvester-Bradley R, Jones DL, Healey JR, Talboys PJ (2014b), *Feed the crop not the soil: rethinking phosphorus management in the food chain*. Environ Sci Technol 48: 6523–6530.
- [50] Md. Mukhlesur Rahman, Mohamad Amran Mohd. Salleh, Umer Rashid, Amimul Ahsan, Mohammad Mujaffar Hossain, Chang Six Ra, *Production of slow release crystal fertilizer from wastewaters through struvite crystallization – A review*, Arabian Journal of Chemistry (2014) 7, 139-155.
- [51] Peter J. Talboys & James Heppell & Tiina Roose & John R. Healey & Davey L. Jones & Paul J. AWithers, *Struvite: a slow-release fertiliser for sustainable phosphorus management?*, Plant Soil (2016) 401:109–123.
- [52] Massey, M.S., Davis, J.G., Ippolito, J.A., Sheffield, R.E., 2009. *Effectiveness of recovered magnesium phosphates as fertilizers in neutral and slightly alkaline soils*. J. Agron. 101, 323–329.
- [53] Kaan Yetilmezsoy, Emel Kocak, Havva Melda Akbin & Didem Özçimen (2018): *Utilization of struvite recovered from high-strength ammonium-containing simulated wastewater as slow-release fertilizer and fire-retardant barrier*, Environmental Technology.
- [54] Bashan, D.L.E., Bashan, Y., 2004. *Recent advances in removing phosphorus from wastewater and its future use as a fertilizer (1997– 2003)*. Water Res. 38, 4222–4246.
- [55] Liu, Y.H., Rahman, M.M., Kwag, J.H., Kim, J.H., Ra, C.S., 2011. *Eco-friendly production of maize using struvite recovered from swine wastewater as a sustainable fertilizer source*. Asian-Aust. J. Anim. Sci. 24, 1699–1705.
- [56] Uysal A, Demir S, Sayilgan E, Eraslan F, Kucukyumuk Z. *Optimization of struvite fertilizer formation from baker's yeast wastewater: growth and nutrition of maize and tomato plants*. Environ. Sci. Pollut. Res. 2014;21(5):3264–3274.
- [57] Hertzberger AJ, Cusick RD, Margenot AJ. *A review and meta-analysis of the agricultural potential of struvite as a phosphorus fertilizer*. Soil Sci. Soc. Am. J. 2020;84:653–671.
- [58] Judit Nagy, Anna Mikola, Surendra K. Pradhan, Anikó Zseni, *The Utilization of Struvite Produced from Human Urine in Agriculture as a Natural Fertilizer: A Review*, Periodica Polytechnica Chemical Engineering, 63(3), pp. 478–484, 2019.
- [59] Gian Luca Baldo, Massimo Marino, Stefano Rossi, *Analisi del ciclo di vita LCA, Gli strumenti per la progettazione sostenibile di materiali, prodotti e processi*, Edizione Ambiente, 2008.

- [60] Michael Z. Hauschild, Ralph K. Rosenbaum, Stig Irving Olsen, *Life Cycle Assessment: Theory and Practice*, Springer International Publishing AG 2018, pp. 4; 30-32; 75-78.
- [61] ISO 14040: 1997(E), *Environmental management - Life cycle assessment - Principles and framework*.
- [62] ISO 14040:2006, *Environmental management – Life cycle assessment – Principles and framework*.
- [63] European Commission, *European Platform of LCA (EPLCA), ILCD International Life Cycle Data system*, 2010. <https://eplca.jrc.ec.europa.eu/ilcd.html>
- [64] Olivier Jolliet, Myriam Saadé-Sbeih, Shanna Shaked, Alexandre Jolliet, Pierre Crettaz, *ENVIRONMENTAL LIFE CYCLE ASSESSMENT*, CRC Press (2016), pp. 39-40.
- [65] Giuseppe Veneri, Giuseppe Moscatelli, Sergio Piccinini, *Trattamento degli effluenti e digestati zootecnici per ridurre le emissioni e produrre Struvite*, 23 novembre 2020.
- [66] Paolo Mantovi, Arianna Pignagnoli, Fabio Verzellesi, *Liquami e digestati microfiltrati utili e convenienti per fertirrigare*, L'informatore Agrario 11/2022.
- [67] [https://struvite.crupa.it/nqcontent.cfm?a\\_id=24715&tt=t\\_bt\\_app1\\_www](https://struvite.crupa.it/nqcontent.cfm?a_id=24715&tt=t_bt_app1_www)
- [68] APHA (2005) *Standard Methods for the Examination of Water and Wastewater*. 21st Edition, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC.
- [69] *METODI DI ANALISI DEI COMPOST, Determinazioni chimiche, fisiche, biologiche e microbiologiche*, COLLANA AMBIENTE, Torino, 1998.
- [70] IRSA-CNR, Quaderni N°64 (1983-85) Metodi di analisi per i fanghi.
- [71] APHA (2005) *Standard Methods for the Examination of Water and Wastewater*. 21st Edition, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC.
- [72] <https://simapro.com/products/agribalyse-agricultural-database/>
- [73] <https://nexus.openlca.org/database/Agribalyse>
- [74] <https://ghgprotocol.org/Third-Party-Databases/ELCD>
- [75] <https://simapro.com/products/environmental-footprint-database/>
- [76] Stocker, T.F.; Qin, D.; Plattner, G.K.; Tignor, M.; Allen, S.K.; Boschung, J.; Nauels, A.; Xia, Y.; Bex, V.; Midgley, P.M. (Eds.) IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change; Cambridge University Press: Cambridge, UK; New York, NY, USA, 2013; p. 1535. Available online:

- [https://www.ipcc.ch/site/assets/uploads/2018/03/WG1AR5\\_SummaryVolume\\_FINAL.pdf](https://www.ipcc.ch/site/assets/uploads/2018/03/WG1AR5_SummaryVolume_FINAL.pdf) (accessed on September 2023).
- [77] <https://www.environdec.com/resources/indicators>
- [78] IPCC, 2019: Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, *CHAPTER 10: EMISSIONS FROM LIVESTOCK AND MANURE MANAGEMENT*, P.R. Shukla, J. Skea, E. Calvo Buendia, V. Masson-Delmotte, H.-O. Pörtner, D. C. Roberts, P. Zhai, R. Slade, S. Connors, R. van Diemen, M. Ferrat, E. Haughey, S. Luz, S. Neogi, M. Pathak, J. Petzold, J. Portugal Pereira, P. Vyas, E. Huntley, K. Kissick, M. Belkacemi, J. Malley.
- [79] Hambaliou Baldé, Andrew C. VanderZaag, Stephen D. Burt, Claudia Wagner-Riddle, Anna Crolla, Raymond L. Desjardins, Douglas J. MacDonald, *Methane emissions from digestate at an agricultural biogas plant*, *Bioresource Technology* 216, September 2016, pp. 914-922.
- [80] Sang-Ryong Shin, Seongwon Im, Alsayed Mostafa, Mo-Kwon Lee, Yeo-Myeong Yun, Sae-Eun Oh, Dong-Hoon Kim, *Effects of pig slurry acidification on methane emissions during storage and subsequent biogas production*, *Water Research* 152 (2019) 234-240.
- [81] Giuseppe Moscatelli, Laura Valli, *Acidificare il digestato per ridurre le emissioni, terra e vita*, n.35-2020, 20 novembre 2020.
- [82] M. J. Aguerre, M. A. Wattiaux, J. M. Powell, *Emissions of ammonia, nitrous oxide, methane, and carbon dioxide during storage of dairy cow manure as affected by dietary forage-to-concentrate ratio and crust formation*, *J. Dairy Sci.* 95:7409–7416.
- [83] Giovanni Lonati, Stefano Cernuschi, *Temporal and spatial variability of atmospheric ammonia in the Lombardy region (Northern Italy)*, *Atmospheric Pollution Research* 11 (2020) 2154–216.
- [84] European Environment Agency, EMEP/EEA air pollutant emission inventory guidebook 2019. Technical guidance to prepare national emission inventories, EEA Report No 13/2019.
- [85] <https://www.eea.europa.eu/themes/air/air-pollution-sources-1/emep-eea-air-pollutant-emission-inventory-guidebook>
- [86] Bellan, E., Toth, G., Mccafferty, E., Kennedy, P., Kreysa, J. and Al Khudhairi, D., editor(s), Triollet, R., *JRC Annual Report 2017*, EUR 29171 EN, Publications Office of the European Union, Luxembourg, 2018, ISBN 978-92-79-91274-0 (online), 978-92-79-91273-3 (print), 978-92-79-91265-8 (ePub), doi:10.2760/138436 (online), 10.2760/664225 (print), 10.2760/20110 (ePub), JRC111359.



[87] Huygens D, Saveyn HGM, Tonini D, Eder P, Delgado Sancho L, *Technical proposals for selected new fertilising materials under the Fertilising Products Regulation (Regulation (EU) 2019/1009)*, European commission, JRC SCIENCE FOR POLICY REPORT.

## Acknowledgements

*I would like to thank all the teaching staff who accompanied me on my degree course, especially Chiar.mo Prof. Fabrizio Passarini, who, with competence, professionalism, politeness and patience, followed and helped me during this internship.*

*I would like to thank all the CRPA staff who provided analysis, data and help, particularly Dott.ssa Arianna Pignagnoli, who, despite her busy work schedule, managed to accompany, help and support me throughout the work.*

*I thank all my fellow students for all the help they have given me over the years. Without their company, support and presence, I would hardly have been able to reach this milestone.*

*I thank all my friends who, over the years, have never failed to give me their support and backing, with the smiles, the laughter, the days and nights spent together; it is also thanks to them that I have been able to get this far.*

*Finally, I would like to thank my family, who, with enthusiasm and happiness, have always approved and encouraged my every choice and decision, spurring me to improve and do my best.*

*My heartfelt thanks to all of you,*

*Federico*

## ANNEX 1

Data, calculation and tables about input (Table A.1) and output (Table A.2) of prototype system in the LCA analysis:

<b>TABLE A.1</b>					
<b>INPUT</b>					
<b>Materials</b>					
<b>parameter</b>	<b>values</b>	<b>u.m.</b>			
<b>Struvite reactor</b>	<b>0,0363</b>	<b>kg</b>			
<b>polyethylene</b>	<b>0,0058</b>	<b>kg</b>			
life time	15	y			
production	1600	m <sup>3</sup> /y			
<b>Electrical energy</b>					
<b>parameter</b>	<b>values</b>	<b>u.m.</b>	<b>time</b>	<b>u.m.</b>	
H <sub>2</sub> SO <sub>4</sub> pump	0,5736	kWh	24	h	
MgCl <sub>2</sub> pump	0,5736	kWh	24	h	
NaOH pump	0,5736	kWh	24	h	
impeller engine	8,88	kWh	24	h	
Main pump	26,4	kWh	24	h	
MFT pump	60	kWh	6	h	
air pump	2,28	kWh	24	h	
compressor	3,6	kWh	24	h	
TOT <sub>gg</sub>	102,8808	kWh/gg			
<b>TOT</b>	<b>4,2867</b>	<b>kWh</b>			
<b>Reactants</b>					
<b>parameter</b>	<b>values</b>	<b>u.m.</b>	<b>conc. (m/v)</b>	<b>flow rate (L/h)</b>	<b>time (h)</b>
<b>NaOH</b>	<b>3</b>	<b>kg</b>	0,3	2	5
<b>H<sub>2</sub>SO<sub>4</sub></b>	<b>8,75</b>	<b>kg</b>	0,5	3,5	5
<b>MgCl<sub>2</sub></b>	<b>3,75</b>	<b>kg</b>	0,15	5	5

**TABLE A.2**

<b>OUTPUT</b>		
<b>Emissions - Thickened fraction</b>		
<b>CH<sub>4</sub></b>		
<b>parameter</b>	<b>values</b>	<b>u.m.</b>
VS	11,165	kg VS/ m <sup>3</sup>
B <sub>0</sub>	0,45	m <sup>3</sup> CH <sub>4</sub> /kg VS
MCF	0,41	
AWMS	100%	
pH	7	
correction factor	0,273	(acidification)
TOT	0,3764	kg CH <sub>4</sub> / m <sup>3</sup> y
storage time	0,2466	years
<b>TOT</b>	<b>0,0928</b>	<b>kg CH<sub>4</sub>/ m<sup>3</sup></b>
<b>N<sub>2</sub>O</b>	<b>direct</b>	
<b>parameter</b>	<b>values</b>	<b>u.m.</b>
EF <sub>3</sub>	0	kg N <sub>2</sub> O-N/kg N
N	1,33023	kg N/m <sup>3</sup>
AWMS	100%	
pH	7	
correction factor	0,5	(acidification)
<b>TOT</b>	<b>0</b>	<b>kg N<sub>2</sub>O/ m<sup>3</sup> y</b>
<b>N<sub>2</sub>O</b>	<b>indirect</b>	
<b>parameter</b>	<b>values</b>	<b>u.m.</b>
EF <sub>4</sub>	0,01	kg N <sub>2</sub> O-N
FRAC <sub>gasm</sub>	0,48	
N	1,33023	kg N/m <sup>3</sup>
AWMS	100%	
N <sub>volat</sub>	0,6385	
pH	7	
correction factor	0,5	(acidification)
TOT	0,0050	kg N <sub>2</sub> O/ m <sup>3</sup> y
storage time	0,2466	years
<b>TOT</b>	<b>0,0012</b>	<b>kg N<sub>2</sub>O/ m<sup>3</sup></b>

<b>NH<sub>3</sub></b>		
	<b>direct</b>	
parameter	values	u.m.
N-NH <sub>4</sub>	0,77082	kg N-NH <sub>4</sub> /m <sup>3</sup>
EF <sub>storage</sub>	0,11	kg N-NH <sub>3</sub> /kg N-NH <sub>4</sub> <sup>+</sup>
Fattore di conversione	1,2143	kg NH <sub>3</sub> /kg N-NH <sub>3</sub>
corr. factor	0,2326	(acidification)
TOT NH <sub>3</sub>	0,0239	kg NH <sub>3</sub> /m <sup>3</sup> y
storage time	0,2466	years
<b>TOT</b>	<b>0,0059</b>	<b>kg NH<sub>3</sub>/m<sup>3</sup></b>
<b>Emissions - Clarified fraction</b>		
<b>CH<sub>4</sub></b>		
parameter	values	u.m.
SV	16,192	kg VS/ m <sup>3</sup>
B <sub>0</sub>	0,45	m <sup>3</sup> CH <sub>4</sub> /kg VS
MCF	0,41	
AWMS	100%	
TOT	2,002	kg CH <sub>4</sub> / m <sup>3</sup> y
storage time	0,247	years
<b>TOT</b>	<b>0,494</b>	<b>kg CH<sub>4</sub>/ m<sup>3</sup></b>
<b>N<sub>2</sub>O</b>		
parameter	values	u.m.
EF <sub>3</sub>	0	kg N <sub>2</sub> O-N/kg N
N	2,576	kg N/m <sup>3</sup>
AWMS	100%	
<b>TOT</b>	<b>0</b>	<b>kg N<sub>2</sub>O/ m<sup>3</sup> y</b>
<b>N<sub>2</sub>O</b>		
parameter	values	u.m.
EF <sub>4</sub>	0,01	kg N <sub>2</sub> O-N
FRAC <sub>gasm</sub>	0,48	
N	2,576	kg N/m <sup>3</sup>
AWMS	100%	
N <sub>volat</sub>	1,2365	
TOT	0,0194	kg N <sub>2</sub> O/ m <sup>3</sup> y
storage time	0,2466	years
<b>TOT</b>	<b>0,0048</b>	<b>kg N<sub>2</sub>O/ m<sup>3</sup></b>

<b>NH<sub>3</sub></b>	<b>direct</b>	
parameter	values	u.m.
N-NH <sub>4</sub>	2,0096	kg N-NH <sub>4</sub> /m <sup>3</sup>
EF <sub>storage</sub>	0,11	kg N-NH <sub>3</sub> /kg N-NH <sub>4</sub> <sup>+</sup>
Fattore di conversione	1,2143	kg NH <sub>3</sub> /kg N-NH <sub>3</sub>
TOT NH <sub>3</sub>	0,2684	kg NH <sub>3</sub> /m <sup>3</sup> y
storage time	0,2466	years
<b>TOT</b>	<b>0,0662</b>	<b>kg NH<sub>3</sub>/m<sup>3</sup></b>

<b>Emission savings - struvite</b>				
parameter	values	u.m.		
<b>CO<sub>2</sub></b>				
			kg CO <sub>2</sub> eq/kg nutrient	TOT spec. (kg CO <sub>2</sub> eq/m <sup>3</sup> )
P	0,21	kg P/m <sup>3</sup>	1,24	0,26
N	0,41	kg N/m <sup>3</sup>	4,57	1,85
<b>TOT Savings</b>	<b>2,11</b>	<b>kg CO<sub>2</sub>eq/m<sup>3</sup></b>		

## ANNEX 2

Data, calculation and tables about output (Table A.3) of control system in the LCA analysis:

<b>TABLE A.3</b>		
<b>OUTPUT</b>		
<b>LIQUID FRACTION</b>		
<b>CH4</b>		
<b>parameter</b>	<b>values</b>	<b>u.m.</b>
SV	30,2	kg VS/ m <sup>3</sup>
B0	0,45	m <sup>3</sup> CH <sub>4</sub> /kg VS
MCF	0,41	
AWMS	100%	
TOT	3,733	kg CH <sub>4</sub> / m <sup>3</sup> y
storage time	0,247	years
<b>TOT</b>	<b>0,921</b>	<b>kg CH<sub>4</sub>/ m<sup>3</sup></b>
<b>N2O</b>		
<b>direct</b>		
<b>parameter</b>	<b>values</b>	<b>u.m.</b>
EF3	0	kg N <sub>2</sub> O-N/kg N
N	4,291	kg N/m <sup>3</sup>
AWMS	100%	
<b>TOT</b>	<b>0</b>	<b>kg N<sub>2</sub>O/ m<sup>3</sup> y</b>
<b>N2O</b>		
<b>indirect</b>		
<b>parameter</b>	<b>values</b>	<b>u.m.</b>
EF4	0,01	kg N <sub>2</sub> O-N
FRACgasm	0,48	
N	4,291	kg N/m <sup>3</sup>
AWMS	100%	
Nvolat	2,0597	
TOT	0,032	kg N <sub>2</sub> O/ m <sup>3</sup> y
storage time	0,247	years
<b>TOT</b>	<b>0,008</b>	<b>kg N<sub>2</sub>O/ m<sup>3</sup></b>
<b>NH3</b>		
<b>direct</b>		
N-NH <sub>4</sub>	2,851	kg N-NH <sub>4</sub> /m <sup>3</sup>
EFstorage	0,11	kg N-NH <sub>3</sub> /kg N-NH <sub>4</sub> <sup>+</sup>
Fattore di conversione	1,2143	kg NH <sub>3</sub> /kg N-NH <sub>3</sub>

TOT NH3	0,3808	kg NH <sub>3</sub> /m <sup>3</sup> y
storage time	0,2466	years
<b>TOT</b>	<b>0,0939</b>	<b>kg NH<sub>3</sub>/m<sup>3</sup></b>



## ANNEX 3

Chemical analysis results, design and management information and materials calculations:

	Flussi		pH
	<i>m3</i>	<i>[% Input]</i>	<i>[-]</i>
Frazione chiarificata del digestato	1000	100%	8,3
<b>Frazione densa da Microfiltrazione</b>	<b>290</b>	<b>29%</b>	<b>7</b>
Frazione microfiltrata da Microfiltrazione	710	71%	7
<b>Surnatante</b>	<b>640</b>	<b>64%</b>	<b>9</b>
Precipitato con Struvite	70	7%	8,5

	ST	
	<i>[g/kg tq]</i>	<i>[%tq]</i>
Frazione chiarificata del digestato	46,6	4,7
<b>Frazione densa da Microfiltrazione</b>	<b>59,4</b>	<b>5,9</b>
Frazione microfiltrata da Microfiltrazione	40,3	4
<b>Surnatante</b>	<b>37,5</b>	<b>3,8</b>
Precipitato con Struvite	76,4	7,6

	SV	
	<i>[g/kg tq]</i>	<i>[%ST]</i>
Frazione chiarificata del digestato	30,2	64,9
<b>Frazione densa da Microfiltrazione</b>	<b>38,5</b>	<b>64,8</b>
Frazione microfiltrata da Microfiltrazione	25,8	64
<b>Surnatante</b>	<b>25,3</b>	<b>67,4</b>
Precipitato con Struvite	41,8	54,7

	NTK	
	<i>[mg/kg tq]</i>	<i>[%ST]</i>
Frazione chiarificata del digestato	4291	9,2
<b>Frazione densa da Microfiltrazione</b>	<b>4587</b>	<b>7,7</b>
Frazione microfiltrata da Microfiltrazione	4108	10,2
<b>Surnatante</b>	<b>4025</b>	<b>10,7</b>
Precipitato con Struvite	5798	7,6

	<b>N-NH4+</b>	
	<i>[mg/kg tq]</i>	<i>[%NTK]</i>
Frazione chiarificata del digestato	2851	66,5
<b>Frazione densa da Microfiltrazione</b>	<b>2658</b>	<b>58</b>
Frazione microfiltrata da Microfiltrazione	3012	73,3
<b>Surnatante</b>	<b>3140</b>	<b>78</b>
Precipitato con Struvite	3266	56,3

	<b>Ptot</b>	
	<i>[mg/kg tq]</i>	<i>[%ST]</i>
Frazione chiarificata del digestato	1281	2,8
<b>Frazione densa da Microfiltrazione</b>	<b>1843</b>	<b>3,1</b>
Frazione microfiltrata da Microfiltrazione	1010	2,5
<b>Surnatante</b>	<b>829</b>	<b>2,2</b>
Precipitato con Struvite	2964	3,9

<b>PESO e MATERIALI</b>		
<b>Plastica</b>		
Plastica dei quadri elettrici	25	kg
serbatoio capacità 3000 lt blu	115	kg
<b>totale</b>	<b>140</b>	<b>kg</b>
<b>Acciaio</b>		
serbatoio piccolo preparazione reagenti e miscelato	30	kg
pompa monovite + motore	40	kg
motori miscelatori	10	kg
Compressore + soffiante	9	kg
Metallo nei quadri elettrici e di comando + pompe dosatrici	25	kg
Reattore di cristallizzazione e precipitazione		
densità acciaio	8000	kg/m <sup>3</sup>
cilindro esterno		
diametro	1,25	m
Altezza	2	m
spessore	0,005	m
Peso lamiera acciaio	314	kg
Cilindro concentrico		
diametro	0,6	m

Altezza	1,25	m
spessore	0,005	m
Peso lamiera acciaio	94,2	kg
Peso skid acciaio	350	kg
<b>totale</b>	<b>872</b>	<b>kg</b>
<b>ORE ANNO SERVIZIO</b>	8000	h/anno
<b>DURATA PILOTA</b>	15	anni

## ANNEX 4

Results of Climate Change (Table A.4), Eutrophication (Table A.5) and Acidification (Table A.6):

<b>TABLE A.4</b>				
Name	Inventory result	Unit	Impact result	Unit
<b>Prototype_system</b>			<b>18,60</b>	kg CO <sub>2</sub> eq
<b>emissioni da stoccaggio</b>			<b>15,76</b>	kg CO <sub>2</sub> eq
Methane, biogenic	0,5864	kg	16,27	kg CO <sub>2</sub> eq
<i>(thickened fraction)</i>	0,093	kg	2,53	kg CO <sub>2</sub> eq
<i>(clarified fraction)</i>	0,493	kg	13,43	kg CO <sub>2</sub> eq
Dinitrogen monoxide	0,00602	kg	1,59	kg CO <sub>2</sub> eq
<i>(thickened fraction)</i>	0,0012	kg	0,32	kg CO <sub>2</sub> eq
<i>(clarified fraction)</i>	0,0048	kg	1,27	kg CO <sub>2</sub> eq
Carbon dioxide	-2,112	kg	-2,11	kg CO <sub>2</sub> eq
TOT (thickened fraction)			2,85	kg CO <sub>2</sub> eq
TOT (clarified fraction)			14,71	kg CO <sub>2</sub> eq
<b>market for steel, low-alloyed - GLO</b>			<b>0</b>	kg CO <sub>2</sub> eq
<b>market for electricity, low voltage - IT</b>			<b>1,756</b>	kg CO <sub>2</sub> eq
<b>polyethylene production, low density, granulate - RER</b>			<b>0</b>	kg CO <sub>2</sub> eq
<b>market for sulfuric acid - RER</b>			<b>1,01</b>	kg CO <sub>2</sub> eq
	Inventory result	Unit	Impact result	Unit
<b>liquid fraction_CONTROL - emissioni da stoccaggio</b>			<b>27,66</b>	kg CO <sub>2</sub> eq
Methane, biogenic	0,937	kg	25,54	kg CO <sub>2</sub> eq
Dinitrogen monoxide	0,008	kg	2,12	kg CO <sub>2</sub> eq

<b>TABLE A.5</b>				
Name	Inventory result	Unit	Impact result	Unit
<b>EUTROPHICATION_prototipo</b>			<b>0,034</b>	kg PO <sub>4</sub> <sup>3-</sup> eq
<b>liquid fraction_prototype</b>			<b>0,0270</b>	kg PO <sub>4</sub> <sup>3-</sup> eq
Ammonia	0,072	kg	0,0252	kg PO <sub>4</sub> <sup>3-</sup> eq
<i>(thickened fraction)</i>	0,0059	kg	0,0021	kg PO <sub>4</sub> <sup>3-</sup> eq
<i>(clarified fraction)</i>	0,0662	kg	0,0232	kg PO <sub>4</sub> <sup>3-</sup> eq
Dinitrogen monoxide	0,006	kg	0,0016	kg PO <sub>4</sub> <sup>3-</sup> eq
<i>(thickened fraction)</i>	0,0012	kg	0,0003	kg PO <sub>4</sub> <sup>3-</sup> eq
<i>(clarified fraction)</i>	0,0048	kg	0,0013	kg PO <sub>4</sub> <sup>3-</sup> eq
<b>market for steel, low-alloyed - GLO</b>			<b>0,0000</b>	kg PO <sub>4</sub> <sup>3-</sup> eq
<b>market for electricity, low voltage - IT</b>			<b>0,0036</b>	kg PO <sub>4</sub> <sup>3-</sup> eq
<b>polyethylene production, low density, granulate - RER</b>			<b>0,0000</b>	kg PO <sub>4</sub> <sup>3-</sup> eq
<b>market for sulfuric acid - RER</b>			<b>0,0035</b>	kg PO <sub>4</sub> <sup>3-</sup> eq
<b>EUTROPHICATION_controllo</b>			<b>0,035</b>	kg PO <sub>4</sub> <sup>3-</sup> eq
<b>liquid fraction_control</b>				
Ammonia	0,094	kg	0,033	kg PO <sub>4</sub> <sup>3-</sup> eq
Dinitrogen monoxide	0,008	kg	0,002	kg PO <sub>4</sub> <sup>3-</sup> eq

<b>TABLE A.6</b>				
Name	Inventory result	Unit	Impact result	Unit
<b>ACIDIFICATION_PROTOTYPE</b>			<b>0,2111</b>	kg SO <sub>2</sub> eq
<b>liquid fraction_prototype</b>			<b>0,1354</b>	kg SO <sub>2</sub> eq
Ammonia	0,072	kg	0,1354	kg SO <sub>2</sub> eq
thickened fraction	0,0059	kg	0,011	kg SO <sub>2</sub> eq
clarified fraction	0,0662	kg	0,124	kg SO <sub>2</sub> eq
<b>market for steel, low-alloyed - GLO</b>			<b>0</b>	kg SO <sub>2</sub> eq
<b>market for sulfuric acid - RER</b>			<b>0,0614</b>	kg SO <sub>2</sub> eq
<b>polyethylene production, low density, granulate - RER</b>			<b>0</b>	kg SO <sub>2</sub> eq
<b>market for electricity, low voltage - IT</b>			<b>0,0141</b>	kg SO <sub>2</sub> eq
<b>ACIDIFICATION_CONTROL</b>			<b>0,177</b>	kg SO <sub>2</sub> eq
<b>liquid fraction_control</b>				kg SO <sub>2</sub> eq
Ammonia	0,094	kg	0,177	kg SO <sub>2</sub> eq