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SEASONAL CHARACTERIZATION OF PIG SLURRY IN LAGOONS WITH EBD SYSTEM AT A FARM IN PULPI, SPAIN - EFFECT ON GREENHOUSE GASES AND AMMONIA.

FINAL REPORT

Contents

1. Pig production: Emission of Greenhouse Gases and Ammonia

Livestock production in Spain has undergone an intense process of specialization and concentration. This process has brought important advantages in the efficiency of the production process, but it also has potential drawbacks. The most important have been the environmental alteration that the concentration of animals can entail. The environmental pollution derived from pig farms is situated at several levels: that of the soil (organic or mineral), the water, and the air.

Livestock is one of many sources that contribute greenhouse gases to the atmosphere. The gases emitted by livestock are predominantly nitrous oxide (N_2O) from the soil with and without fertilizer application, methane (CH_4) from enteric fermentation, and both N_2O and CH_4 from manure management. In addition, during storage, manure emits considerable amounts of ammonium (NH_4+). The emission of ammonia (NH_3) occurs naturally during storage and the emission rate is governed by the existing ammonium: total ammonia nitrate (NH_4 +: NH_3) ratio.

Most of the gases produced by livestock are generated as a consequence of natural processes such as animal metabolism and the degradation of slurry or manure. Their emission depends on different factors associated with the design and maintenance of the facilities, as well as the management that is carried out during the storage, treatment, and agricultural recovery processes of the slurry or manure.

CH_4 emissions:

Methane originates as a consequence of the anaerobic processes that occur both in the digestive tract of animals and during the storage of manures (primarily slurry lagoon). The amount of CH_4 produced by the animal depends largely on the characteristics of the ingredients in the diet. Manure from all animals can produce CH_4 as long as it is stored under anaerobic conditions. Only facilities that handle liquid manure are capable of sustaining anaerobic conditions (e.g. Lagoons, pits and tanks). When manure is handled dry or deposited by grazing animals while it is in contact with the air, significant amounts of methane are not produced.

In the CH_4 production processes we must distinguish a double origin:

i) Enteric **-** in which the microbial consortium that participates directly or indirectly in the production of CH_4 will interact with the digestive system of the host animal by incorporating various substances or eliminating them through absorbing processes.

ii) Outside the body -for example, during storage or manure application.

In the case of enteric production, the absorption of usable substrates by the methanogenic consortium will limit the CH_4 synthesis processes, which in turn will show different intensities depending on the fermentation compartment in which the fermentation processes take place. In the case of outside of the body production we can see a complete degradation of organic matter with the consequent synthesis of CH_4. When said degradation is complete and the substrate methanization is complete, we can distinguish a sequential series of chemical processes (some of which are minimal in live production) in each of which various microbial populations that act synchronously are involved. The fermentation process would start with, I) Enzymatic hydrolysis of the more complex compounds (i.e. proteins and carbohydrates, lipids); II) Acidogenesis, degradation of different compounds (i.e. hexoses) to volatile fatty acids, H_2 and CO_2; (III) Acetogenesis (acetate synthesis); volatile fatty acids are transformed into acetic acid, in this phase homoacetogenic bacteria acquire special relevance, generating acetate from CO_2 and H_2; and finally (IV) methanogenesis, acetic acid is reduced to CH_4 and CO_2 by acetoclastic methanogens and hydrogen trophic archaea that are capable of reducing CO_2 to CH_4 using the H_2 from the medium.

NH_3 Emissions:

The agricultural sector is the largest source of ammonia emissions into the atmosphere: 80-90% of the total. The increase in the use of fertilizers and nitrogen contributions to livestock through feed has caused a large increase in ammonia emissions in the last 50 years. Ammonia can damage habitats sensitive to high nitrogen levels and cause acidification and eutrophication. Since emissions of other pollutants responsible for acidification, such as sulfur oxide and nitrogen oxides, have been reduced (40-80% in recent years), the relative importance of ammonia has increased. Several national and international agreements have been signed in which the commitment to reduce ammonia emissions has been established. In the process of synthesis and volatilization of ammonia different strategies can intervene more easily than for other gases, which facilitates the implementation of reduction strategies. Ammonia is also one of the main components associated with bad odors that cause discomfort to nearby populations. Ammonia comes from the breakdown of urea in urine. The process of decomposition of urea occurs when urine comes into contact with feces where there are microorganisms that generate the enzyme urease.

In the case of pig slurry, more than half of the nitrogen contained therein is of the ammonium type. The ammonium ion is in chemical equilibrium with ammonia, which, being a gas, can easily be released into the atmosphere by volatilization. This process occurs continuously from the moment it is generated and throughout the collection, storage, and agricultural application processes. The main factors that affect this balance are the slurry temperature, ambient temperature, ventilation, the pH of the slurry, its ammonium content, and the surface of the slurry. slurry-air contact. Ammonia remains for a relatively short period of time in the atmosphere, between 3 and 7 days, depending on weather conditions.

Considering the conditions necessary for NH_3 to be produced, either due to the enzymatic degradation of urinary urea (or uric acid) or due to the slower microbial degradation of organic nitrogen, the parameters that activate these processes will increase the levels of free ammonia in the slurry and therefore its emission, and vice versa. It has been shown that increases in aeration levels, high concentrations of urea or Carbon to Nitrogen ratio (C:N) rates in the medium and the microbial density will increase emission levels, while those that slow them down can be anaerobiosis, acidification of the medium, low temperatures or minimization of the contact surface.

Finally, it should be noted that the continuity of NH_3 emission in slurry after its application to the soil is also determined by a series of environmental factors related to the nature of the soil (pH, surface texture, profile characteristics and aeration) and climatic conditions (Levels of precipitation and temperature). Some human activities such as fertilization and the type of nitrogen fertilizer, quantity, time and form of application will also affect NH_3 emission levels. Other collateral factors also dependent on human activity, such as the management of crop residues, tillage, compaction, drainage, irrigation of the soil, as well as its changes in use and the livestock load will alter emission levels.

N_2O emissions:

In contrast to the production of CH_4 or NH_3, the emission of N_2O is enteric and comes from the management of the excrement and has less relevance. Its synthesis is not direct, N_2O can be generated from various compounds, or, in other words, it is an obligate intermediate in the nitrification and denitrification processes. The origin of the N that constitutes N_2O comes mainly from urea and uric acid previously degraded to ammonium (NH4+). However, other rapidly degradable sources of N may participate in its origin (synthetic fertilizers, manures [urine + feces]).

The nitrous oxide that is produced as part of the denitrification process occurs naturally in the soil itself under conditions of lack of oxygen (for example, in flooded soils, rice fields, ...) due to the action of anaerobic microorganisms that transform nitrates to reduced forms of nitrogen (N_2O and N2) that are eliminated into the atmosphere due to their volatile nature. This phenomenon not only affects the native nitrogen present in the soil but is also increased as a consequence of the application of nitrogen fertilizer compounds to the ground. Denitrification also occurs in livestock facilities and during slurry storage, but to a lesser extent than during the application of manure to the land. Denitrification is activated when the soil undergoes anaerobic processes. For this reason, the greatest losses occur in the days after irrigation or rain and are increased when applying nitrogen fertilizers together with organic matter.

CO_2 emissions:

Carbon dioxide is, together with CH_4 and N_2O, the third most important greenhouse gas caused by livestock. It is produced through aerobic processes of degradation of organic compounds (e.g. respiration, animal metabolism, composting or mineralization in soils). The amounts derived from biological activity are negligible on a global scale compared to those produced by other emission sources (combustion engines and industry). For this reason, in practice, the best way to influence the reduction of carbon dioxide emissions in livestock farms is through efficient energy use programs. The contribution of the poultry and pig sectors, including manure management, to the emission of greenhouse gases has been estimated, according to the national inventory of greenhouse gases, at just over 20% of total emissions from the agricultural and livestock sectors.

2. Emission Modifying Factors Legislation

Directive 2010/75 / EU of the European Parliament and of the Council, of November 24, 2010, on industrial emissions (integrated pollution prevention and control), and in particular its article 13, paragraph 5, and the published DECISION OF EXECUTION (EU) 2017/302 OF THE COMMISSION of February 15, 2017 establishing the conclusions on the best available techniques (BAT) regarding the intensive rearing of poultry or pigs (notified per C (2017) 688) requires the application of said BAT by 2020, and urges the competent authorities to set emission limit values that guarantee that, under normal operating conditions, emissions do not exceed the levels associated with the best techniques available that are set out in the BAT conclusions. In addition, Royal Decree 306/2020, of February 11, which establishes basic regulations for the management of intensive pig farms and modifies the basic regulations for the management of extensive pig farms, aims to reduce emissions in new installations through the adoption of BAT, which must reduce ammonia emissions by at least 80% with respect to the reference technique (open pits and without natural crust) by at least 40% in existing farms.

Royal Decree, Article 10 on reduction of emissions from pig production, states:

1. Newly installed pig farms, except for small ones and those for self-consumption, must adopt the Best Available Techniques (MTD) specified below:

a. Reduce total nitrogen excreted and ammonia emissions, as well as GHG emissions, while meeting the nutritional needs of the animals, they should use a nutritional strategy and feed formulation that reduce the crude protein content of the animal. feeding, and administering a multiphase feeding depending on the different nutritional requirements according to the productive stage.

b. Reduce ammonia emissions into the atmosphere of each building, as well as GHG emissions, a technique or a combination of techniques must be adopted that allow the reduction of ammonia emissions by at least 60% with respect to the technique reference (total grating, "U" pits and manure maintenance throughout the production cycle in the facilities pits).

c. Reduce ammonia emissions into the atmosphere during external storage of slurry, as well as GHG emissions, techniques that reduce ammonia emissions by at least 80% with respect to the reference technique (open pits and no natural crust).

2. Existing pig farms with a productive capacity greater than 120 Livestock Units (LSU) must adopt, in accordance with the terms established in the fourth final provision, a multi-phase feeding system, with reduction of the crude protein content, taking into account the needs of the animals as well as emptying the manure pits of the accommodation at least once a month. In addition, they must adopt at least one of the following techniques in their operation:

a. Emptying the manure pits of the accommodation at least twice a week, in order to reduce emissions of polluting gases by at least 30%, with respect to the reference technique.

b. Cover manure Lagoons, in areas where a crust does not form spontaneously that completely covers the surface, with techniques that reduce pollutant gas emissions by at least 40% with respect to the reference of a lagoon without crust. Any other technique, described as Best Available Technique, which guarantees a reduction in polluting gas emissions equivalent to that achieved through the techniques described in sections a) or b) and that contributes to minimizing GHG emissions from the farm.

Specifically, the conclusions on the best available techniques (BAT) in the framework of Directive 2010/75 / EU, for the reduction of emissions generated by the storage of slurry, the following MTDs are presented:

BAT16. To reduce ammonia emissions to the atmosphere from slurry storage, BAT is to use a combination of the following techniques:

a. Conduct proper design and management of slurry tanks, using a combination of the following techniques:

1. Reduce the coefficient between the emission surface and the volume of the slurry tank.

2. Reduce the wind speed and the air exchange on the slurry surface, reducing the filling level of the tank.

3. Minimize slurry agitation.

b. Cover the slurry tank. For this, one of the following techniques can be applied:

1. Rigid cover.

2. Flexible covers

3. Floating covers, for example: plastic pellets, light bulk materials, flexible floating covers, geometric plastic plates, pneumatic covers, natural crust, straw.

c. Acidification of slurry.

BAT 17. To reduce ammonia emissions to the atmosphere from a slurry basin, the BAT consists of employing a combination of the techniques below :

a. Minimize slurry agitation.

b. Cover the slurry basin with a flexible and / or floating cover, such as: flexible plastic sheets, light bulk materials, natural crust, straw.

BAT 18. In order to avoid emissions to soil and water from collecting and conveying slurry and from a slurry tank or basin, the BAT consists of employing a combination of the techniques below.

a. Use tanks that can withstand mechanical, chemical, and thermal stress.

b. Select a storage facility with sufficient capacity to conserve the slurry during periods when it is not possible to apply it to the field.

c. Build leak-proof facilities and equipment for the collection and transfer of slurry (e.g. pits, canals, drains, pumping stations).

d. Store the slurry in Lagoons with a waterproof base and walls, eg. ex. With clay or a plastic coating (or double coating).

e. Install a leak detection system, p. ex. A geomembrane, a drainage layer and a drainage duct system.

f. Check the structural integrity of the tanks at least once a year. Today's producers must understand that, in an increasingly demanding society like ours, reducing the emissions is of vital importance for maintaining their activity in the long term.

3. Basis and Operation of Environmental Balance Devices (EBD):

EBD devices are devices capable of balancing the oxide-reduction balance of the systems favoring the correct development of microbial populations which allows effective and consistent treatment of different environmental problems such as eutrophication in water, accumulation of pathogens, total solid increases. in suspension and of dissolved solids and other pollutants in effluents, among others. The application of EBD devices for the treatment of slurry is automatic and does not require chemicals, bacteria, electrical energy, filters, or other consumables. It is a quite functional system, since they can be installed around the storage tanks and along the conduction pipes affordably and with low maintenance. The specifications of each of the components of the different environmental balance systems are described below.

In order to understand the operation of EBDs, it is necessary to understand certain basic principles, one of them is that all matter on earth contains particles of positive and negative energy. On the other hand, it is known that wastewater contains elevated levels of negative energy particles (NEP-), and that these volumes of NEP- are excessive and therefore create “Reactive Oxygen Species” (ROS), a strong oxidant of free radicals that kill living organisms including microbes and their enzymes. The presence of ROS prevents microbial life from maintaining balanced population densities and varieties, so with the use of EBD devices it is possible to achieve a balanced state of particles (balance between positive (+) and negative (-) particles) to allow that the microorganism are metabolized and reproduced effectively which makes it possible for them to absorb, digest, secrete, excrete and decompose pollutants.

Reactive oxygen species are important oxidizing species that perform various functions within ecosystems, inducing oxidative stress and causing damage to organisms (Yu and Zhao, 2021). In addition, ROS have also been widely investigated for their antibacterial effect due to their powerful oxidative activity that has bactericidal effects (Shibata et al., 2010; Whan et al., 2019).

On the other hand, nanotechnology has been proposed as a possible solution to the treatment of wastewater and the remediation of contaminated sites. The oxidizing or reducing capacity of nanomaterials has been suggested as an alternative for the transformation of pollutants and toxic substances as well as to stimulate microbial growth (Vazquez-Duhalt, 2015). The use of bimetallic nanoparticles almost completely eliminates the production of these undesirable by-products (Wang et al., 1997). Nanoparticles that are activated by light such as titanium dioxide (TiO_2) and zinc oxide (ZnO) which are semiconductors with a wide forbidden band continue to be highly studied for the removal of polluting substances. These particles are cheap and can be produced in copious quantities in addition to being low toxicity (Fujishima et al., 2000). For example, ZnO nanoparticles are capable of sensing and of photocatalyzing the destruction of dangerous polychlorinated phenols (Kamat et al., 2002).

In this way the role they play in the elimination of microorganisms is justified, and in our case the ROS balance allows maintaining some of the microorganisms responsible for decomposing pollutants.

EBDs are installed on the perimeter of the area to be treated / remedied, a balanced energy state is emulated, allowing ROS electrons to pair with each other and greatly improving the quality of existing oxygen. Consequently, in a balanced energy environment indigenous microorganisms reproduce exponentially and totally eliminate the organic and inorganic contaminants present.

EBD units are placed around wastewater systems at equidistant intervals to attract and focus positive energy particles (PEP +) to the treatment zone. By creating a balance between positive and negative particles, the atomic frequencies of all the matter located around the area treated with the EBD units is naturally optimized, giving rise to the appearance of autochthonous microorganisms. i=In this way these microorganisms become more active and much more prolific.

For the selection of the type of devices, the number necessary will depend on the quality of the influent in question defined by the biological oxygen demand (BOD) it contains. If the BOD exceeds 80 mg / L, it will be necessary to reduce the intervals between the devices in the treated area; that is, the number of devices will be proportional to the BOD (the higher the BOD, the greater the number of devices).

For the installation it depends on the type of device (functionality and application), the type of wastewater to be treated, and the area where it is installed. The EBD WATER PACK, EBD AIR PACK, EBD MUD PACK and EBD SOIL PACK are the 4 treatment device types.

4. Objectives:

The general objective of this report is to conduct a physical-chemical and biological characterization of the slurry from the storage lagoons in which EBD (Environmental Balance Device Technology) devices were previously installed, as well as to quantify the emissions of greenhouse gases (N_2O, CH_4 and CO_2) and ammonia (NH_3) generated in them during all seasons of the year.

5. Experiment design:

The present study has been carried out in the Agrosolmen farm in Pulpí (Almeria, Andalucía Spain) located in polygon 10, parcel 117 whose surface is 11.47 ha (37 ° 22'25.1 "N 1 ° 43'58.6" W):

Figure 5.1. Aerial view location of the farm under study in Pulpí (Almería Spain).

It is an intensive farrowing pig farm with a total of 10,750 heads (8000 piglets, 2740 sows and 10 boars) integrated with the JISAP business group. Next to the warehouses there is a phase separator and 5 storage basins of variable dimensions. The whole set represents the treatment system present in the farm:

- **Lagoon 1:** Storage of raw slurry. EBD MUD, SOIL and WATER units are installed.
- **Lagoon 2:** Slurry storage after the phase separator with aeration system installed. EBD SOIL, WATER and AIR units are installed.
- **Lagoon 3**: Settling No. 1 (connected to Lagoon 2). EBD MUD units are installed.
- **Lagoon 4**: Settling No. 2 (connected to Lagoon 3). EBD MUD units are installed.
- **Lagoon 5**: Decanted slurry storage (connected to Lagoon 4). EBD MUD and WATER units are installed.

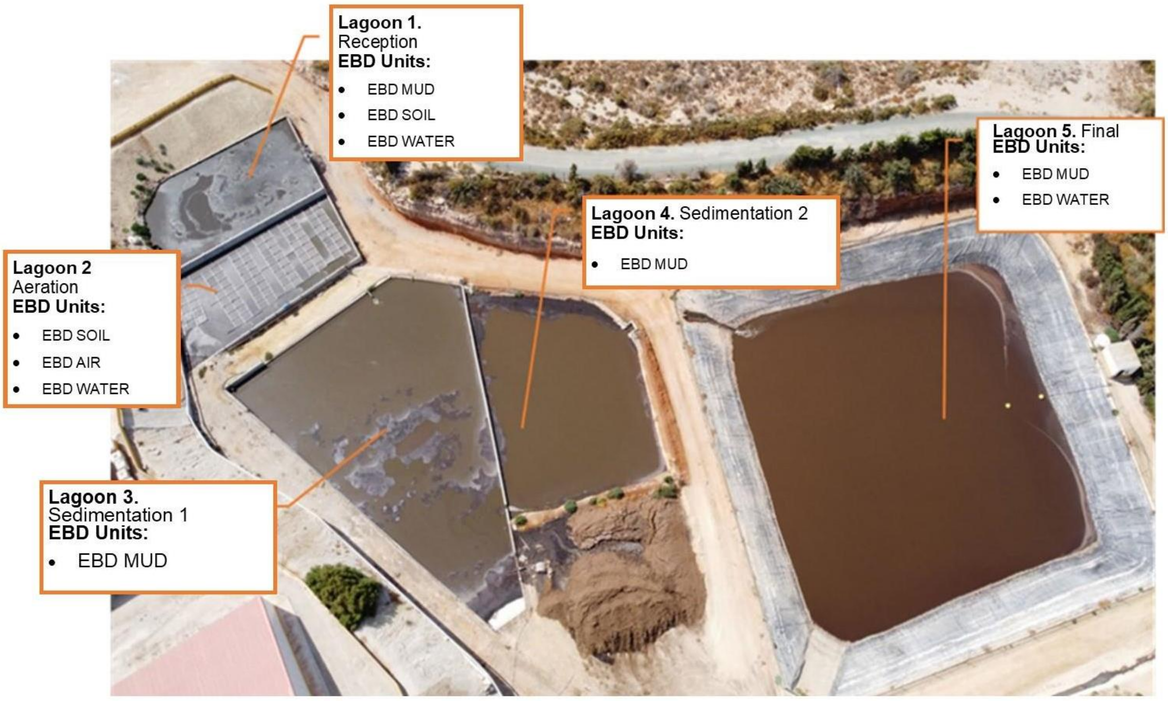


Figure 5.2 Arrangement of the 5 storage lagoons.

With seasonal frequency, the farm has been visited on 5 occasions by the staff of the Research Group on Management, Use and Recovery of Soils and Water of the Polytechnic University of Cartagena:

• June 28, 2020 (summer 2020). Slurry sampling.

• November 11, 2020 (Autumn 2020). Gaseous emissions sampling.

• March 16, 2021 (winter 2021). Sampling of slurry and gaseous emissions.

• May 27, 2021 (spring 2021). Sampling of slurry and gaseous emissions.

• June 21, 2021 (summer 2021). Sampling of slurry and gaseous emissions.

The following table, as a summary and for each station, shows the sampling points at which slurry samples have been collected (left column) and the sampling points at which the gaseous emissions measurements have been made:

Table 5.1 Sample points for collecting slurry samples and measuring gaseous emissions during each season

Sampling point	7/28/2020 (summer)		11/11/2020 (autumn)		3/16/2021 (winter)		5/27/2021 (spring)		6/21/2021 (summer)	
	Solid	Gas	Solid	Gas	Solid	Gas	Solid	Gas	Solid	Gas
Slurry pit	x	-	-	-	-	-	-	-	-	-
Slurry Lagoon 1	x	-	-	Gases	x	Gases	x	Gases	x	Gases
Slurry Lagoon 2	x	-	-	Gases	x	Gases	x	Gases	x	Gases
Slurry Lagoon 3	x	-	-	Gases	x	Gases	x	Gases	x	Gases
Slurry Lagoon 4	x	-	-	Gases	-	-	-	-	-	-
Slurry Lagoon 5	x	-	-	Gases	x	Gases	x	Gases	x	Gases
Sludge (Lagoon 3)	x	-	-	-	-	-	-	-	-	-
Slurry control (old Lagoon 4 enabled since June 2021)	-	-	-	-	-	-	-	-	x	Gases

Regarding Lagoon 4, it should be mentioned that since winter 2021 this lagoon was left in drying conditions in which it is not feasible to measure gaseous emissions due to the presence of crust. Likewise, since June 2021, Lagoon 4 has been enabled as a control lagoon for the storage of raw slurry in which there are no EBD devices installed.

The following figure shows the sampling points for each type of sample:

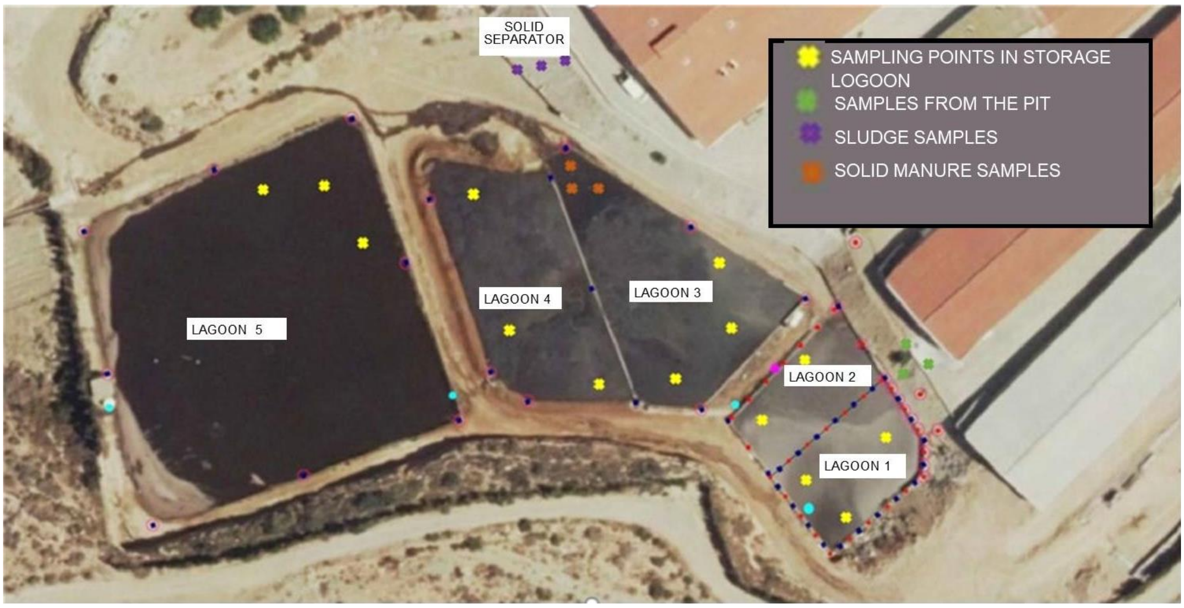


Figure 5.3 Location of slurry sampling points.

Below is a summary of the main analytical parameters determined in the different types of samples processed.

Parameters and analytical methods used in the slurry samples:

Temperature (T^a): It is determined in situ using a portable Hanna temperature probe (model, HI 9025).

pH: Crison GLP 21 equipment is used.

Electrical conductivity (CE): Crison GLP 21 equipment is used.

Total suspended solids (STS): Filtering the sample is done using a Vacuum Brand vacuum pump and a 0.45 µ Watman filter.

Kjeldahl Nitrogen (NK): Completed according to the Duchafour method (1970), taking between 1-5 mL of slurry for digestion.

Ammonia nitrogen (N-NH4 +): Distillation completed in a basic medium, collected in an acid medium and automatic titration.

Organic nitrogen (NO): Calculated by the difference between NK and N-NH4 +.

Analysis of ions, cations (Na +, K +, Mg2 + and Ca2 +) and anions (Cl-, SO42-, NO3-, NO2-, PO43-), using ion chromatography (Metrohm, model 850 Professional IC and model 815 Robotic USB Sample Processor (Metrohm Automatic Processor).

Chemical oxygen demand (COD): Macherey-Nagel GmbH & Co. KG. Nanocolor Test, Ref 985 028/29 are used.

Soluble Cu, Zn, Fe and Mn. With Agilent Technologies ICP-Mass Spectrometer. Model 7900 are used.

6. Greenhouse Gas and Ammonia Measurement Methodology:

Dynamic floating chambers are one of the most used systems to capture, and therefore be able to measure, greenhouse gases (N_2O, CH_4 and **CO**) and ammonia (NH_3) in slurry lagoons. The principle of this technique is to isolate a part of the surface where the slurry is stored and measure the change in concentration of the gases in the chamber over time. The results are expressed per unit area of slurry and per unit volume.

This method uses PVC plastic chambers to isolate part of the surface from which you want to know the emissions. For correct operation, an air pump with a known flow brings air to the dynamic chamber, while another second pump with a known flow is placed at the other end (outlet).

For the measurement of GHG and NH_3) emissions (F = flow measured with dynamic chambers), the emission concentration of the gases at the inlet (Ce) and at the output (Cs) in mg / m3, and multiplied by the air flow (Qa) of the dynamic chamber (m3 air / h) using the following relationship for each of the gases:

F= (Cs - Ce) * Qa

The analyzer used to measure gas concentrations both at the inlet and outlet quantifies the concentrations by infrared spectrometry.

The gas analyzer equipment allows the continuous measurement of gases. The gases are introduced into the analyzer through a tube, the internal pump extracts the gas sample through the instrument showing the measurements on the device. The analyzer measures and analyzes to an infrared spectrum of gas samples using a photo-acoustic sensor based on an optical microphone. This analyzer equipment identifies gases such as H2O, N_2O, CH_4,CO_2 and NH_3, and the units of measurement for the concentration of the gases are given in parts per million (ppm).

To implement this methodology, the principle described in “Vera of Environmental Technologies for Agricultural Production Test Protocol for Covers and other Mitigation Technologies for Reduction of Gaseous Emissions from Stored Manure” and the design according to “Reference procedures for the measurement of gaseous emissions from livestock houses and storages of animal manure” has been applied.

7. Arrangement of EBD devices in slurry storage lagoon:

The devices were previously installed in March of 2020 in each of the Lagoons where the measurements were conducted, detailed below:

Figure 7.1 Symbology used for each type of device.

In Lagoon 1 EBD MUD and SOIL units are installed on the right side, while the rest of the pool has the EBD MUD and SOIL units without burying. In addition, an EBD WATER unit was incorporated.

Figure 7.2. Arrangement of the devices on Lagoon 1.

In Lagoon 2 EBD SOIL, AIR and WATER devices are incorporated.

Figure 7.3. Arrangement of the devices on Lagoon 2.

In Lagoon 3 EBD MUD units are incorporated.

Figure 7.4. Arrangement of EBD MUD devices on Lagoon 3.

In Lagoon 4 buried and unburied EBD MUD units are incorporated.

Figure 7.5. Arrangement of EBD MUD devices on Lagoon 4.

In Lagoon 5 Buried EBD MUD and EBD WATER units are incorporated.

Figure 7.6. Arrangement of the devices on the Lagoon 5.

8. Results obtained in the autumn 2020 and winter 2021 seasons:

8.1 Slurry characterization

To conduct the evaluation of the emissions in the slurry storage lagoons, it is essential to always know the characteristics of the slurry, as well as in each of the lagoons with the different EBD units installed.

Tables 8.1.1 and 8.1.2 show the most relevant results of the physicochemical characteristics of the slurry for the summer 2020 and winter 2021 seasons.

Table 8.1.1. Characterization of the slurry in the summer period

Characterization of slurry in the summer period 2020							
Type of sample	**Slurry pit**	**Slurry Lagoon 1**	**Slurry Lagoon 2**	**Slurry Lagoon 3**	**Slurry Lagoon 4**	**Slurry Lagoon 5**	**Sludge Lagoon**
T^a (ºC)	24.4	27.9	26.0	26.6	29.0	27.0	24.0
pH	7.2	7.7	7.8	7.8	8.0	8.2	7.7
CE (dS/m)	11.7	15.9	15.0	13.1	15.0	14.1	20.9
STS (g/L)	95.0	95.0	0.0	95.0	91.7	0.0	100.0
COD (g/L)	33.3	11.8	7.9	30.3	13.0	6.1	74.7
NK (g/L)	2.7	2.2	1.8	3.3	2.2	1.2	5.3
$N\text{-}NH_4^+$ (g/L)	1.5	1.9	1.7	2.3	1.7	1.0	2.9
NO (g/L)	1.3	0.4	0.1	1.0	0.5	0.2	2.4
P total	353.6	213.5	106.3	529.1	336.3	42.0	1317.1
Cl^- (ppm)	916.9	1239.5	1008.3	1146.2	1254.5	1471.5	4614.8
NO_2^- (ppm)	LD < 0.07	LD < 0.07	LD < 0.07	LD < 0.07	LD < 0.07	LD < 0.07	LD < 0.07
NO_3^- (ppm)	40.5	41.1	38.7	42.7	41.2	37.1	99.1
PO_4^{3-} (ppm)	1071.4	647.1	322.0	1603.2	1019.2	127.1	3991.1
SO_4^{2-} (ppm)	84.4	72.5	75.0	85.9	74.7	57.1	179.4
Na^+ (ppm)	513.4	541.7	510.9	575.6	620.2	756.0	2454.9
K^+ (ppm)	915.0	1072.8	1049.2	1121.3	1225.1	1612.2	4815.4
Ca^{2+} (ppm)	592.0	553.4	403.8	555.6	503.7	268.6	1261.6
Mg^{2+} (ppm)	203.9	112.6	63.0	276.4	187.3	10.9	531.1
Cu (mg/L)	1.0	0.6	0.5	0.6	0.6	0.3	0.7
Zn (mg/L)	0.2	0.2	0.2	0.3	0.3	0.4	1.0
Fe (mg/L)	3.0	2.6	1.8	3.9	3.6	2.0	9.7
Mn (mg/L)	1.0	0.6	0.5	0.6	0.6	0.3	0.7

Table 8.1.2. Characterization of slurry in the winter period

Characterization of slurry in the winter period 2021				
Type of sample	Slurry Lagoon 1	Slurry Lagoon 2	Slurry Lagoon 3	Slurry Lagoon 5
T^a (ºC)	17.2	17.3	15.3	16.4
pH	7.8	7.91	8.02	8.27
CE (dS/m)	9.265	17.82	17.48	15.02
STS (g/L)	30.3	15.7	11.1	11.6
COD (g/L)	8.5	6.3	5.6	5.3
NK (g/L)	2.7888	2.0062	1.8242	1.3818
N-NH_4^+ (g/L)	1.2558	1.7206	1.6254	1.2614
NO (g/L)	1.533	0.2856	0.1988	0.1204
P total	654.3	154.0	107.8	38.1
Cl^- (ppm)	1150.12	1156.4525	1209.9775	1203.11
NO_2^- (ppm)	LD < 0.07	LD < 0.07	LD < 0.07	LD < 0.07
NO_3^- (ppm)	7.7911	16.71025	32.61525	23.04985
PO_4^{3-} (ppm)	2006.44	472.2425	330.645	116.864
SO_4^{2-} (ppm)	4478.93	53.397	34.37975	LD < 0.91
Na^+ (ppm)	LD < 0.03	LD < 0.03	LD < 0.03	LD < 0.03
K^+ (ppm)	2629.48	2375.04	2279.9175	1694.65
Ca^{2+} (ppm)	1230.76	1238.845	1243.6525	1217.99
Mg^{2+} (ppm)	415.056	197.08675	184.36575	143.96775
Cu (mg/L)	440.628	111.5145	65.12625	LD < 0.82
Zn (mg/L)	0.4502	0.6548	0.38473	0.33526
Fe (mg/L)	0.2748	0.3195	0.3456	0.3543
Mn (mg/L)	2.4523	4.1456	2.2633	2.2856

8.2 Evaluation of the first trial conducted in autumn 2020:

This project covers a wide spectrum, which includes the in-situ measurement of greenhouse gases and ammonia. The mean values obtained in each of the slurry storage lagoon during the autumn and winter periods are presented below. The values are expressed in g/m²/day, according to the transposition strategy used by the VERA protocol.

Methane (CH_4)

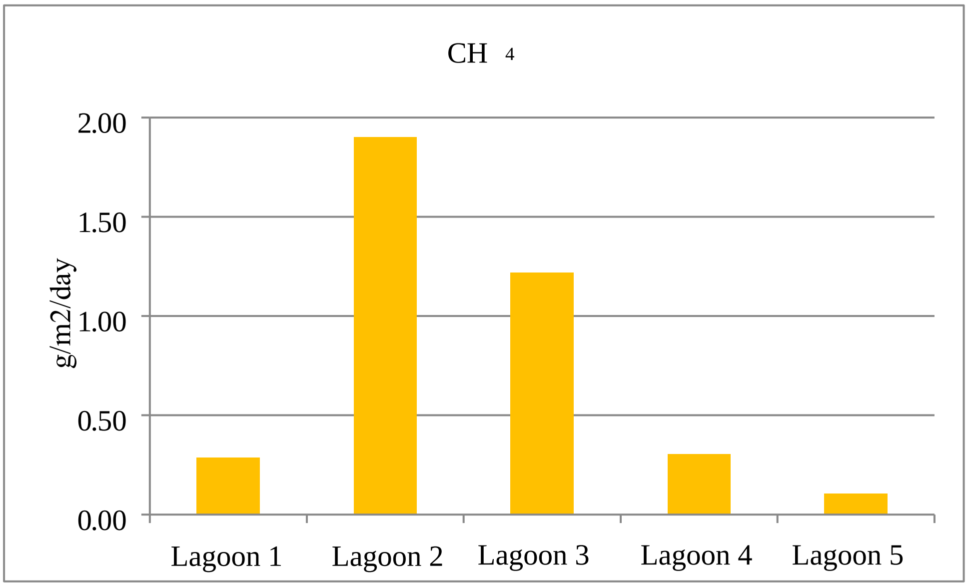


Figure 8.2.1 CH_4 emissions.

Lagoon 1 has the EBD MUD, EBD SOIL and EBD WATER units for treating the raw slurry. Among the functions of these devices are to favor the growth of microorganisms for the decomposition of organic pollutants, as well as elimination of bad odors, reduction of activated sludge, reduction of the solubility of phosphorus and nitrogen in water, reduction of COD values and value of BOD / Neutralization of water. When the density of the ultraviolet particles and the density of the infrared particles are balanced, the reaction of the radicals will decrease. It can be a way of preventing oxygen shortage, and the existing bacteria will act effectively on their own; therefore the nitrogen, phosphorus, and organic materials in the water will break down.

Methane concentrations, similar to most of the gases produced by microbial degradation in addition to the enzymatic degradation of urea (uric acid), in Lagoon 1 were also significantly reduced with further progression to Lagoons 2, 3, 4, and 5. This process could occur due to the beneficial effect of these devices.

Lagoon 2 contains slurry from the phase separator; therefore, it is slurry that has been treated prior to the devices installed in this lagoon which are EBD SOIL, EBD WATER and EBD AIR. The control of CH_4 emissions together with CO_2 have been affected by the action of bio-organisms, oxygen and natural energy provided by said devices for the treatment of slurry in a non-intrusive, natural, and sustainable way. In the specific case of the EBD AIR PACK, it would favor the reduction of CH_4 that originates as a consequence of the anaerobic processes that they occur during storage, so this device could have contributed to the decrease in the emission of this gas. From this pool, methane gradually decreased in the rest of the pools, which could be attributed to a reducing effect in sequence of study parameters defined.

In Lagoon 3, the EBD MUD PACK units are installed. The stored slurry comes from Lagoon 2, showing a decrease in relation to the previous pool, finding lower values than Lagoon 2 for CH_4 emissions. The EBD MUD PACK units could facilitate the lowering of CH_4 by activating microorganisms that would limit the degradation of various compounds involved in the methane synthesis process.

The devices installed in Lagoon 4 are exactly the same as those present in Lagoon 3. However, the stored slurry comes from Lagoon 3, which has undergone a previous settling. The comparison of this parameter demonstrates with the decrease in total suspended solids or total nitrogen, among others. The decrease in CH_4 emissions could be related to the decrease in the parameters due to the presence of the EBD MUD PACK units, which would intervene in this process in the same way as explained in the previous lagoon. This decrease contributed to Lagoon 5, where the lowest emission values of the entire treatment process can be noted, where the EBD MUD and EBD WATER units complement the slurry decontamination.

Carbon dioxide (CO_2)

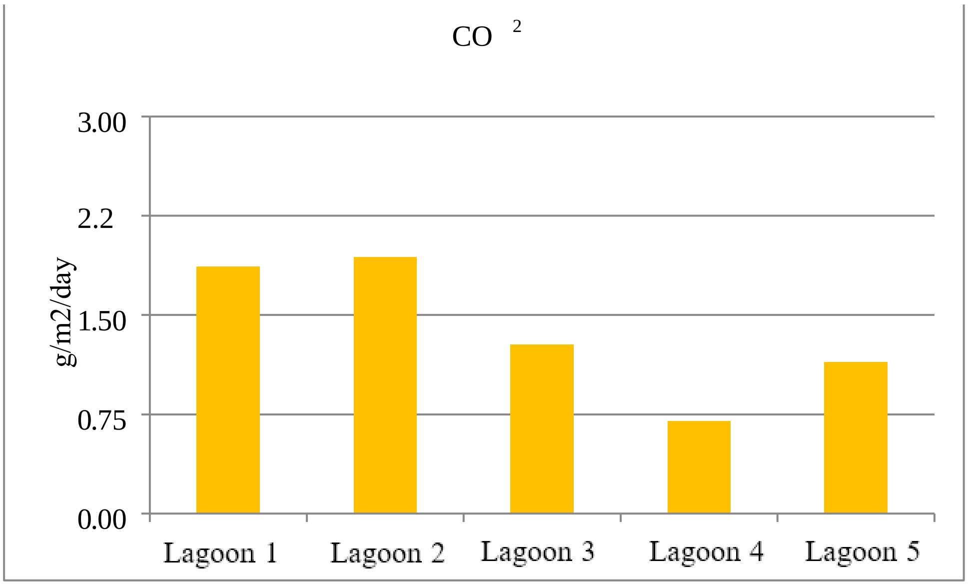


*Figure 8.2.2. **CO_2** emissions.*

In the autumn period, Lagoons 1 and 2 showed the highest CO_2 values in relation to the other lagoons, although in Lagoon 2 it receives the slurry with prior phase separator treatment or decanting. This increase can be justified because Lagoon 2 also has a treatment system with aeration, so that this biological transformation also results in the production of more CO_2 as a result of the activity of aerobic bacteria (oxygen consumption and CO_2 release).

Lagoons 3 and 4 saw the greatest decreases compared to the rest of the lagoons, with Lagoon 4 being the most benefited, because, although the 2 lagoons have the same devices (EBD MUD PACK), Lagoon 4 has them buried and unburied, in addition to the fact that the slurry treated in this lagoon is already decanted from Lagoon 3. In Lagoon 5 the CO_2 undergoes a slight rise in relation to the previous lagoons.

Nitrous Oxide (N_2O)

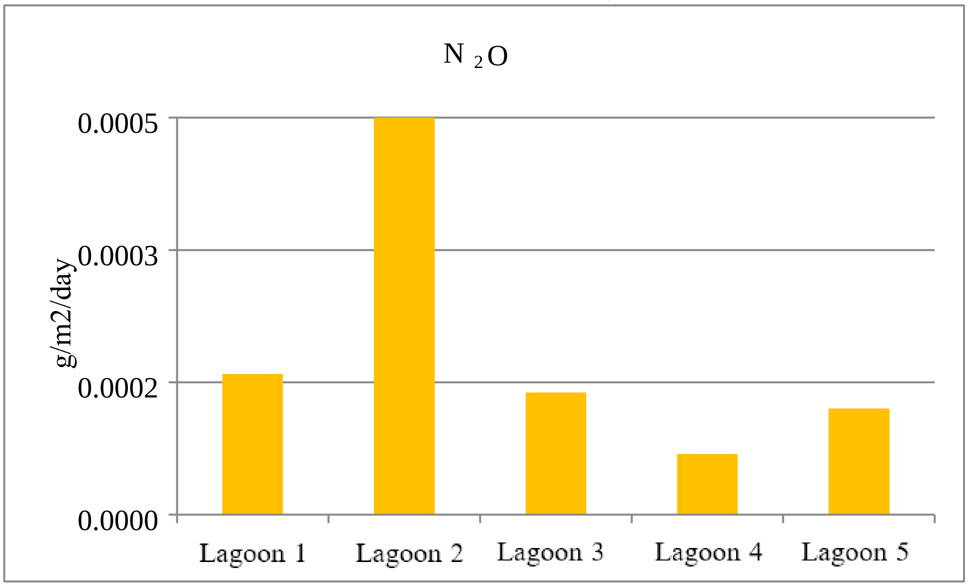


Figure 8.2.3. N_2O emissions.

In general, nitrous oxide in the **l**agoons showed values close to zero. The direct emission of nitrous oxide from slurry during storage and treatment depends on the nitrogen and carbon content of the slurry, and the duration of storage and the type of species or its treatment. Anaerobic conditions linked to the nature of slurry and manure sometimes inhibit ammonia nitrogen nitrification reactions that require strictly aerobic conditions, therefore, the presence of an additional source of carbon and the inherent moisture in these products favor denitrification processes.

The different devices incorporated in the lagoons were able to limit the nitrification reactions, preventing the transformation of ammonia into forms of NOx. It is also known that certain conditions of low pH or little humidity decrease the presence of N_2O, since it tends to be reduced to N_2, a condition that could be attributed to the EBD WATER PACK units. The content of N_2O emissions have been optimally reduced, due to the incomplete nitrification and denitrification process, since nitrification is a required prerequisite to the emission of N_2O due to the aerobic environment generated by the EBD AIR PACK units in reservoir 2.

Ammonia (NH_3)

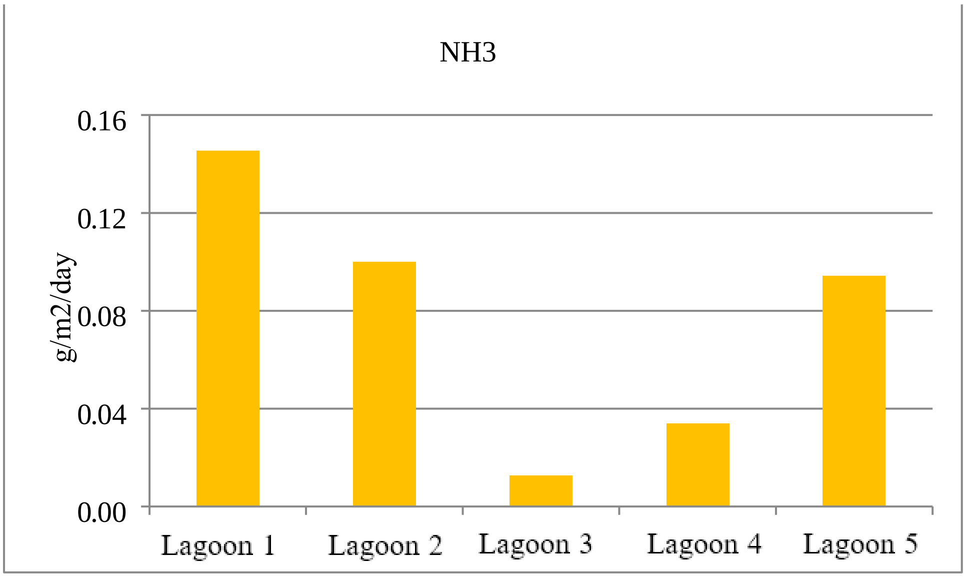


Figure 8.2.4. NH_3 emissions.

In Lagoons 1 to 3, a progressive decrease has been seen for ammonia, where an inverse relationship between nitrogen content and the emission of this gas could be observed at the same time. In the case of pig slurry, more than half of the nitrogen contained therein is of the ammonium type. The ammonium ion is in equilibrium with ammonia, which, being a gas, can easily be emitted into the atmosphere through volatilization. In this case, this equilibrium would be favored by the ammonium content.

On the other hand, the EBD WATER PACK units could positively affect the reduction of the strong odor produced by ammonia, as can be seen in Lagoon 3 of the graph. Likewise, it can be observed in Lagoon 5 that NH_3 undergoes a slight rise, which is not justified by the decrease in nitrogen in this lagoon and the slight increase in pH. The activation of microorganisms by MUD PACK could be intervening in this process.

8.3 Evaluation of the second trial conducted in winter 2021:

Methane (CH_4)

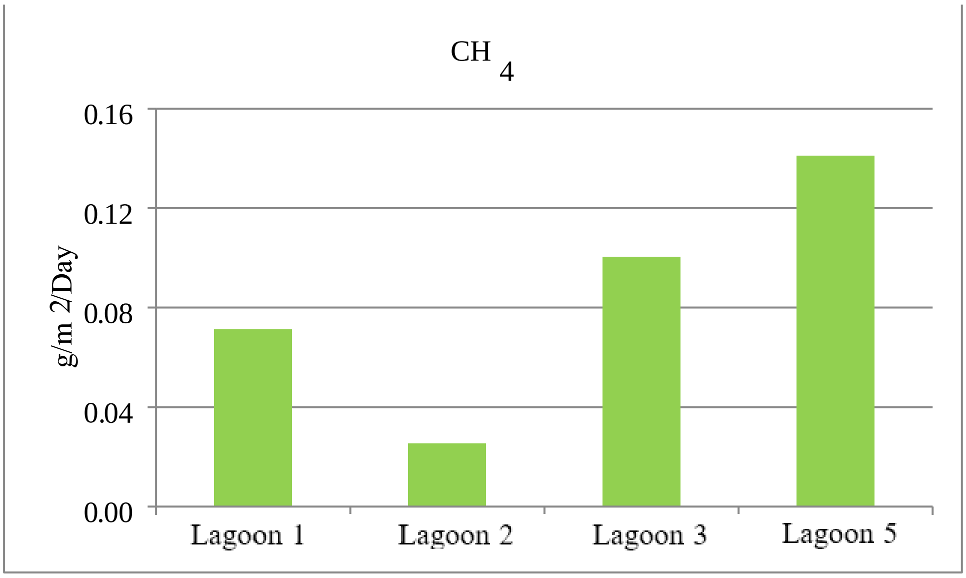


Figure 8.3.1. CH_4 emissions.

According to the values detected by the measurement equipment, the devices installed in Lagoon 2 (SOIL, WATER and AIR) to treat the liquid fraction of the slurry after having passed through a solid-liquid separator turned out to be the most effective. Many of the parameters analyzed in this lagoon show the decrease in pollutant load, as is to be expected in comparison to a slurry without any type of pretreatment.

Carbon dioxide (CO_2)

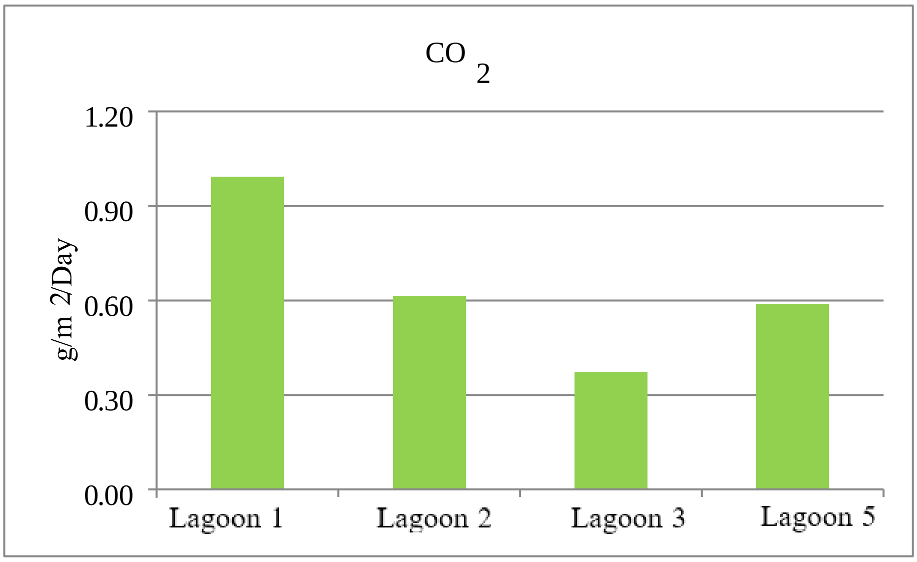


Figure 8.3.2. CO_2 emissions.

The CO_2 content has not been significant for any of the cases studied, since it is in ranges similar to those found in the "uncontaminated" atmosphere. The amounts derived from biological activity are negligible on a global scale compared to those produced by other emission sources (combustion engines and industry). For this reason, in practice, the best way to influence the reduction of carbon dioxide emissions in livestock farms is through efficient energy use programs.

However, the CO_2 emissions in winter from Lagoons 2, 3 and 5 evaluated presented lower emissions of this gas with respect to Lagoon 1, so the units installed (EBD SOIL, EBD WATER, EBD MUD and EBD AIR) in the Lagoons subsequently were more effective.

Nitrous oxide (N_2O)

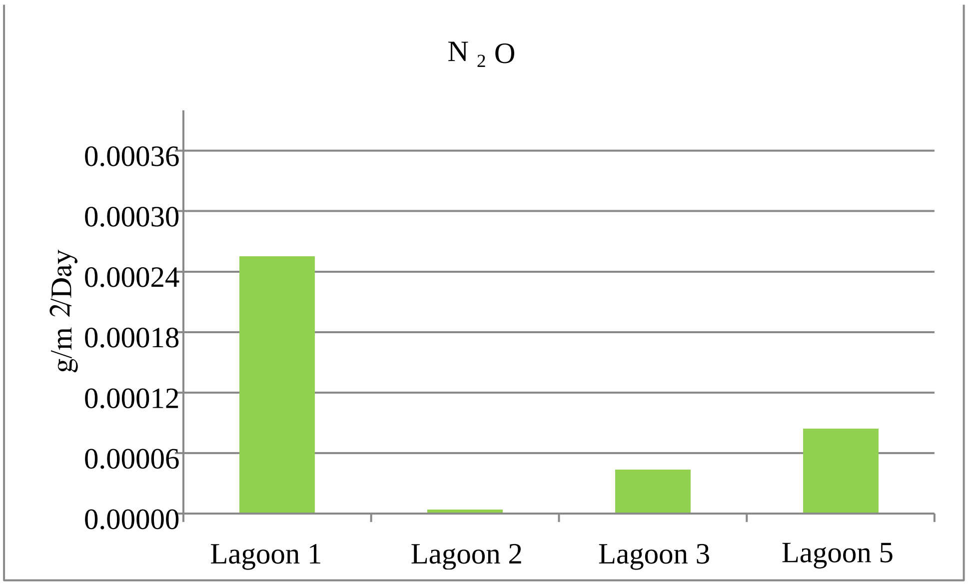


Figure 8.3.3. N_2O emissions.

Denitrification also occurs in livestock facilities and during slurry storage, but to a lesser extent than during the application of manure to the land. Nitrous oxide is produced as part of the denitrification process, which is negligible in the N_2O emissions recorded in storage Lagoons.

The installed devices have the power to reduce ammonia nitrogen solubility in slurry. In Lagoon 1 oxygen could be at the origin of the partial inhibition of nitrification and/or denitrification and therefore be the origin of N_2O. In Lagoon 2 there is a reduction of nitrous oxide, and this is explained by the success of the nitrification/denitrification due to the presence of oxygen together with the effect of the devices on the decomposition of organic matter and nitrogen.

The slurry in Lagoons 3 and 5 is considered as a more purified slurry and the solids located in Lagoons 3 and 5 compared to Lagoon 1 have generated a decrease of 93% and 61% respectively in N_2O. This explains the low nitrous oxide emissions in both lagoons.

Ammonia (NH_3)

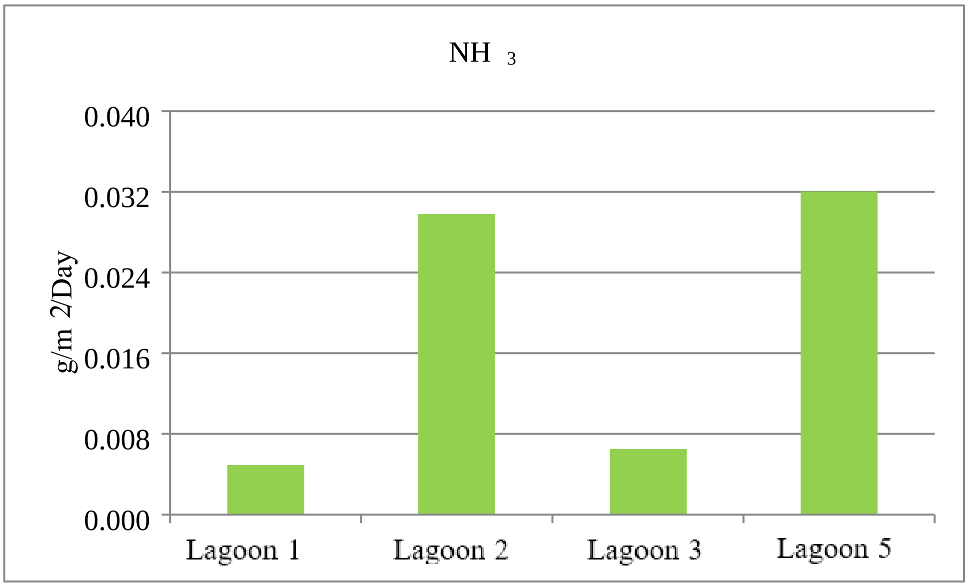


Figure 8.3.4. NH_3 emissions.

In Lagoon 1 the EBD MUD, EBD SOIL and EBD WATER units were able to limit NH_3 emissions. While in the second lagoon these emissions increased possibly due to the aeration contributing to the volatilization of nitrogen in the form of ammonia. However, in Lagoon 3 there is also a notable decrease in this parameter, in this Lagoon the pretreated slurry presented lower emission values which may be benefited by the increase in pH and the reduction of Total Suspended Solids and N, together with the effect of the EBD MUD device, which under these slurry conditions favored the quality of the slurry at the outlet and reduced NH_3 emissions in this lagoon.

In Lagoon 5 it can be seen that NH_3 rises, which, like the previous case, cannot be justified by the decrease in nitrogen in this Lagoon and the slight increase in pH. The activation of microorganisms by the MUD PACK device could be intervening in this process. In this lagoon, the organic pollutant load, as well as the nitrogen content, was significantly reduced (> 50%), an effect that could be attributed to on one hand the effect of the previous treatments (solid-liquid separation and decantation), and on the other hand, the action of the devices installed in this lagoon.

8.4 Conclusions of Fall 2020 and Winter 2021:

The emissions of CH_4 , CO_2, N_2O and NH_3 were lower in the winter period compared to those of autumn in the storage Lagoons, as expected due to the climatic conditions.

Contrary to what can be expected as it is a slurry without any type of pretreatment, the emissions in Lagoon 1, both of CH_4 in autumn and NH_3 in winter, have been reduced compared to the rest of the Lagoons. Therefore the efficiency of the devices installed both in number and variety in this lagoon with raw slurry for the reduction of emissions is highlighted and it can be considered that they could have an important effect in reducing these emissions in raw slurry.

9. Results Obtained in the Spring and Summer Seasons 2021:

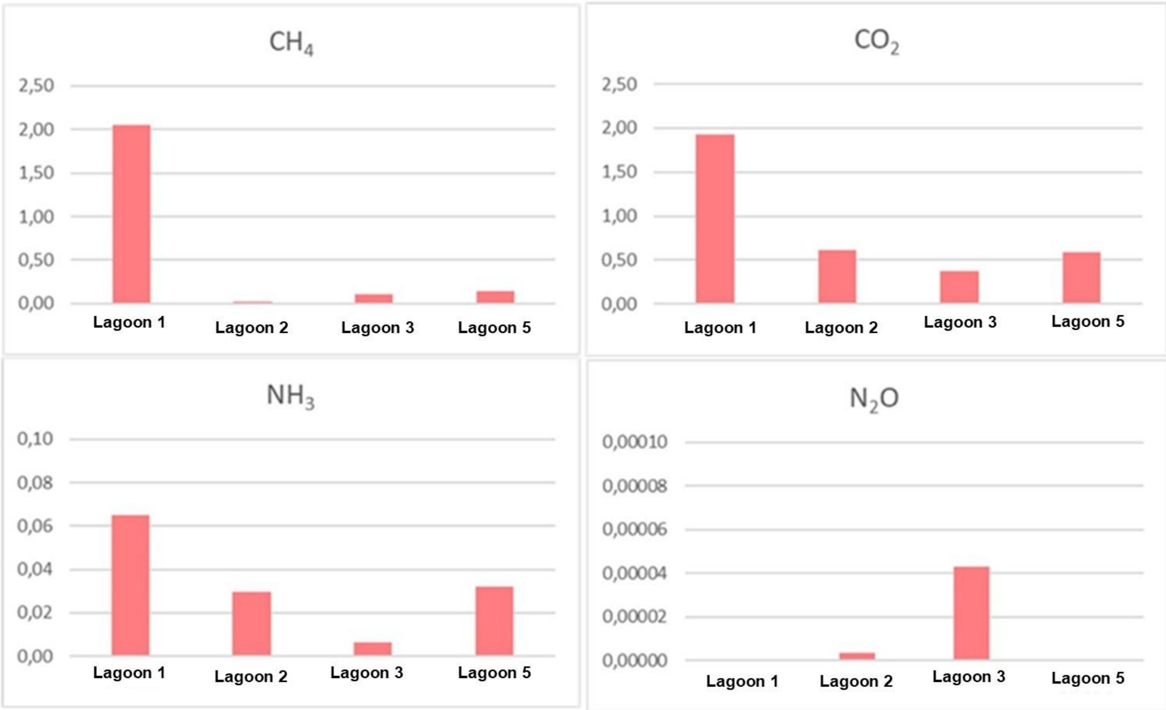
9.1. Evaluation of the Trial Conducted in Spring 2021:

Below, you can see the analytical results of the characterization of slurry in spring season 2021 in Lagoons 1 (crude slurry), 2 (slurry after phase separator with aeration), 3 (slurry settling No. 1) and 5 (decanted slurry storage lagoon). For most parameters, a slight decrease in the results can be seen from Lagoon 1 to Lagoon 5.

Table 9.1.1. Results of the physical-chemical and biological characterization of slurry in Lagoons 1, 2, 3 and 5 in the spring season 2021.

Characterization of Slurry in the Spring Period 2021				
Type of sample	Slurry Lagoon 1	Slurry Lagoon 2	Slurry Lagoon 3	Slurry Lagoon 5
T^a (ºC)	21.4	19.8	20.2	21.7
pH	7.66	8.12	8.11	8.24
CE (dS/m)	19.84	19.62	17.23	17.11
STS (g/L)	17	13.9	14.3	13.7
COD (g/L)	8.3	5.7	4.6	4.7
NK (g/L)	2.24	2.14	1.75	1.59
$N\text{-}NH_4^+$ (g/L)	2.10	2.09	1.53	1.43
NO (g/L)	0.14	0.05	0.22	0.16
P total	117.9	52.8	50.0	34.1
Cl^- (mg/L)	1250	1258	1772	1278
NO_2^- (mg/L)	LD < 0.07	LD < 0.07	LD < 0.07	LD < 0.07
NO_3^- (mg/L)	24.33	29.50	22.26	27.46
PO_4^{3-} (mg/L)	361.5	161.8	153.3	104.7
SO_4^{2-} (mg/L)	33.3	LD < 0.91	LD < 0.91	LD < 0.91
Na^+ (mg/L)	LD < 0.03	LD < 0.03	LD < 0.03	LD < 0.03
K^+ (mg/L)	2402.4	2240.2	2787.0	1755.1
Ca^{2+} (mg/L)	1337.8	1333.8	1901.2	1357.4
Mg^{2+} (mg/L)	170.7	115.2	145.1	127.0
Cu (mg/L)	75.3	26.5	38.4	LD < 0.82
Zn (mg/L)	0.76	0.68	0.70	0.67
Fe (mg/L)	0.28	0.39	0.38	0.35
Mn (mg/L)	3.54	4.49	3.63	4.12

Figure 9.1.1 Greenhouse gas emissions (CH_4, CO_2 and N_2O) and ammonia (NH_3) in Lagoons 1, 2, 3 and 5 of the Pulpí farm (Almería, Spain) during the 2021 spring season.



The results obtained for the emissions recorded at this station are shown below. As expected, for all the lagoons the most notable emissions are those of CH_4 and CO_2, followed by NH_3, and lastly by N_2O.

Methane (CH_4)

For CH_4 emissions, values between 0.03g m²/day (Lagoon 2) and 2.05g/m²/day (Lagoon 1) are observed, with the reduction between Lagoon 1 and the rest of Lagoons (Lagoon 2, 3 and 5), the reduction recorded can be associated with the values of STS and COD, as well as the presence of the EBD SOIL, WATER, AIR and MUD devices in Lagoons 2, 3 and 5:

STS (g/L): 17 (LLagoon 1), 13.9 (Lagoon 2), 14.3 (Lagoon 3) and 13.7 (Lagoon 5).

COD (g/L): 8.3 (Lagoon 1), 5.7 (Lagoon 2), 4.6 (Lagoon 3) and 4.7 (Lagoon 5).

Carbon dioxide (CO_2)

With respect to CO_2 values, a trend similar to that observed for CH_4 is observed, with values between 0.37g/m² day (Lagoon 3) and 1.93g/m²/day (Lagoon 1). On the contrary, for Lagoon 5 would normally expect CO_2 concentrations to be lower than those recorded (0.59g/m²/day) given that it is the final storage tank and it receives the most treated slurry, but nevertheless the lowest values are detected in Lagoon 3, possibly influenced by the suppression of aeration when going from Lagoon 2 to Lagoon 3, which does not favor CO_2 emissions. The concentrations can be related to the TOTAL SUSPENDED SOLIDS and COD values as well as to the presence of EBD units that could favor that the emissions recorded are lower than the emissions that would be recorded if the EBD units were not installed.

Ammonia (NH_3)

Concentrations between 0.01g/m²/day (Lagoon 3) and 0.07g/m²/day (Lagoon 1) are recorded, the range of values being quite low and narrow. These variations are associated with the concentrations of N-NH_4 + present in the slurry, but also with the rest of the fractions of the nitrogen cycle:

N-NH_4 + (g/L): 2.10 (lagoon1), 2.09 (Lagoon 2), 1.53 (Lagoon 3) and 1.43 (Lagoon 5).

NK (g/L) (g/L): 2.24 (Lagoon 1), 2.14 (Lagoon 2), 1.75 (Lagoon 3) and 1.59 (Lagoon 5).

NO (g/L): 0.14 (Lagoon 1), 0.05 (Lagoon 2), 0.22 (Lagoon 3) and 0.16 (lagoon5).

- (mg/L): all concentrations are below the detection limit of the measuring equipment (LD <0.07 mg/L).

NO3- (mg/L): 24.33 (Lagoon 1), 29.50 (Lagoon 2Lagoon 2), 22.26 (Lagoon 3) and 27.46 (Lagoon 5).

The fact that the lowest NH_3 emissions (such as CO) are detected in Lagoon 3 could be due to the decantation and sedimentation process under non-aeration conditions that the slurry receives in the presence of EBD MUD devices. Said slurry comes from Lagoon 2Lagoon 2 in which they have been subjected to an aeration process in the presence of EBD SOIL, WATER and AIR devices. When the aerated slurry from Lagoon 2Lagoon 2 to Lagoon 3 where the aeration is suppressed, anaerobic conditions are generated in the presence of EBD devices that could favor the reduction of emissions such as CO_2 and NH_3 linked to the decrease in COD values (5,7 g/L Lagoon 2Lagoon 2: 4.6 g/L Lagoon 3). Later, when the slurry passes from Lagoon 3 to Lagoon 5, the fact that emissions increase could be due to a greater presence of tight microorganisms in the final storage lagoon.

Nitrous oxide (N_2O)

N_2O emissions are zero in Lagoons 1 and 5. And in Lagoon 2 and 3 emissions are detected, although they are very low (Lagoon 2: 0.0000034 g/m²/day and Lagoon 3: 0.00004 g/m²/day). The increase from Lagoon 2 to Lagoon 3 is very low, perhaps it could be associated with the increase in nitrogen concentration organic from Lagoon 2 (0.05g/L) to lagoon3 (0.22g/L) and nitrate reduction (Lagoon 2: 29.50 mg/L; Lagoon 3: 22.26 mg/L). The aeration process to which the slurry from Lagoon 2 is subjected could favor an increase in the presence of nitrifying bacteria and therefore an increase in the concentration of nitrates present in this lagoon. And later in Lagoon 3 when the aeration is suppressed the concentration of nitrifying bacteria and the concentration of nitrates are reduced and the consequent increase in the organic fraction of nitrogen, which may come from nitrifying bacteria.

9.2. Results Obtained Summer Period

To conduct the evaluation of the emissions in the slurry storage lagoons, it is essential to know the characteristics of the slurry at all times, as well as in each of the lagoons with the different EBD devices installed.

Table 9.2.1 shows the most relevant results of the physical-chemical characteristics of the slurry at the time of conducting the registration of emissions of greenhouse gases and ammonia, during the summer period.

Table 9.2.1. Characterization of the slurry in the summer period

Characterization of slurry in the summer period 2021					
Type of sample	Slurry Lagoon 1	Slurry Lagoon 2	Slurry Lagoon 3	Slurry Lagoon 5	Control Slurry
Tª (ºC)	25	25.4	26.4	25.4	25.3
pH	7.54	7.93	8.13	7.53	8.12
CE (dS/m)	20.19	20.63	19.09	18.98	17.18
STS (g/L)	55.8	26.7	9.1	11.8	9.9
COD(g/L)	11	15	11.2	11.9	5
NK (g/L)	2.9274	2.7818	1.6702	1.694	1.4602
$N\text{-}NH_4^+$ (g/L)	1.8228	1.1004	1.6058	1.596	1.4168
NO (g/L)	1.1046	1.6814	0.0644	0.098	0.0434
P total	660.5	59.6	36.4	46.7	36.9
Cl^- (ppm)	1449.24	1488.43	1473.99	1627.10	1620.77
NO_2^- (ppm)	6.81	6.62	LD < 0.07	LD < 0.07	6.09
NO_3^- (ppm)	291.80	155.64	92.53	109.66	153.53
PO_4^{3-} (ppm)	2025.40	182.80	111.52	143.27	113.14
SO_4^{2-} (ppm)	LD < 0.91	LD < 0.91	LD < 0.91	LD < 0.91	LD < 0.91
Na^+ (ppm)	LD < 0.03	LD < 0.03	LD < 0.03	LD < 0.03	LD < 0.03
K^+ (ppm)	2235.32	2272.13	1964.31	2212.09	1724.83
Ca^{2+} (ppm)	1117.75	1392.10	1470.18	1516.03	1506.91
Mg^{2+} (ppm)	313.44	172.73	130.55	198.19	154.41
Cu (mg/L)	316.07	45.43	LD < 0.82	31.43	LD < 0.82
Zn (mg/L)	0.6052	0.4958	0.6259	0.3548	0.6742
Fe (mg/L)	0.2056	0.2357	0.2586	0.3596	0.3456
Mn (mg/L)	2.5025	2.1052	3.4563	2.3056	3.8456

9.3. Evaluation of Emissions to the Atmosphere in Slurry Lagoons and Influence of EBD Units:

This project covers a wide spectrum, which includes the in-situ measurement of greenhouse gases and ammonia. The mean values obtained in each of the slurry storage lagoons during the summer period are presented below. The values are expressed in g/m²/day, according to the transposition strategy used by the VERA protocol.

Methane (CH_4)

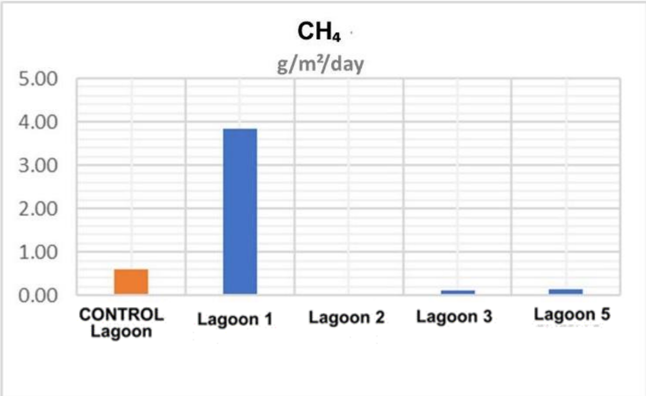


Figure 9.3.1. CH_4 emissions

The control lagoon (prior to Lagoon 1 treatment), which corresponds to the crude slurry storage lagoon was put into operation during the June 2021 period and it does not have any type of pretreatment. This is evidenced by the characterization of the slurry, where the values corresponding to the total solids and total nitrogen are higher in relation to the other lagoons. Regarding CH_4 emissions, the recorded values are lower than those corresponding to Lagoon 1. This could be due to the fact that the amount of storage time in the lagoon is relatively short compared to the other lagoons.

Lagoon 1 has the EBD MUD, EBD SOIL and EBD WATER units for treating the raw slurry. These devices can favor the elimination of bad odors, reduction of activated sludge, decrease of the solubility of phosphorus and nitrogen in water, decrease of COD and BOD/Neutralization values of the water. However, an increase in methane emissions are observed in this lagoon. This may be due to the fact that in the summer period the temperature values are higher and consequently, bacteria growth rate and emission production increases.

Lagoon 2 contains slurry from the phase separator. It is, therefore pretreated slurry. The devices distributed in this lagoon (EBD SOIL, EBD WATER and EBD AIR), turned out to be the most effective, according to the values detected by the measurement equipment. In the specific case of the EBD AIR device, this could favor the reduction of CH_4 that originates as a consequence of the anaerobic processes that occur during storage. Thus, this device could contribute to the decrease in the emission of this gas since the greatest decrease in this parameter is registered with respect to the other lagoons. Finally, it should be added that this lagoon also has an aeration system. In Lagoon 3 the EBD MUD PACK devices are installed. The stored slurry comes from the settling of Lagoon 2 and shows an increase in relation to the previous lagoon. This increase can be attributed to the increase in temperatures as a consequence of the time of year.

The devices installed in Lagoon 5 are EBD MUD and EBD WATER. The stored slurry comes from Lagoon 3, and has undergone a previous settling. CH_4 emissions show a slight increase in relation to the previous lagoon, with higher values than Lagoon 3 for CH_4 emissions, this increase can be attributed to the increase in temperatures as a consequence of the time of year, and to the increase registered in COD values.

Carbon dioxide (CO_2)

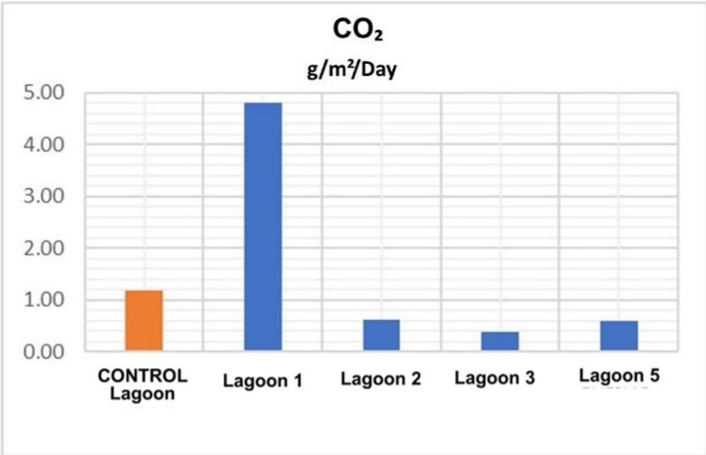


Figure 9.2.2. CO_2 emissions

In the summer period, the control lagoon and Lagoon 1 showed the highest CO_2 value in relation to the other lagoons, this increase can be related to the increase in the temperature value and the increase in the growth rate of the lagoon's bacteria, so this biological transformation also results in increased CO_2 production as a result of aerobic bacteria activity (oxygen consumption and CO_2 release). Lagoons 2, 3 and 5 saw the greatest decreases compared to the rest of lagoons, so the devices installed (EBD SOIL, EBD WATER, EBD MUD and EBD AIR) in subsequent lagoons were more effective, with the lowest values are detected in the Lagoon 3 possibly influenced due to the suppression of aeration when going from Lagoon 2 to Lagoon 3 which does not favor CO_2 emissions.

Nitrous Oxide (N_2O)

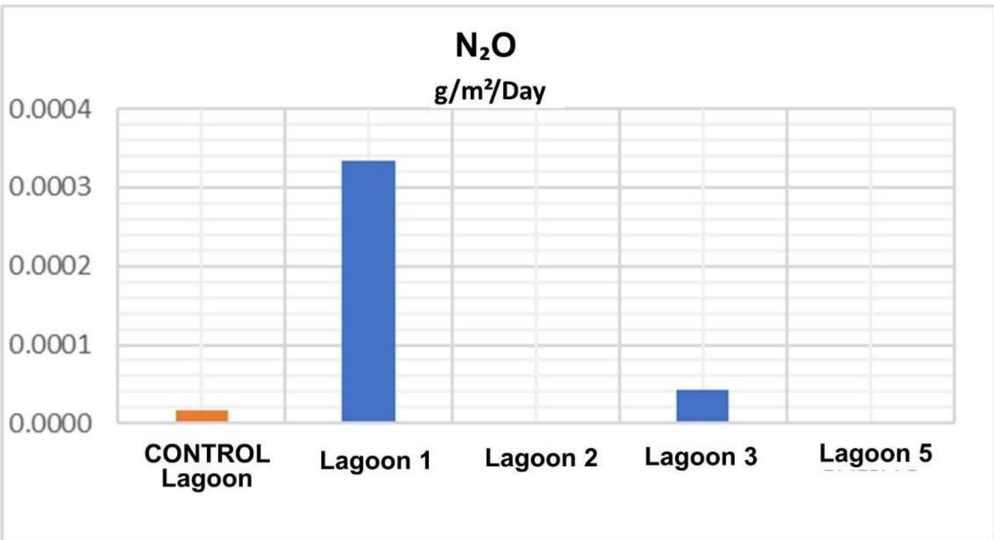


Figure 9.3.3. N_2O emissions

Nitrous oxide in the lagoons showed values close to zero. The direct emission of nitrous oxide from slurry during storage and treatment depends on the nitrogen and carbon content of the slurry, and the duration of storage and the type of species or its treatment. Anaerobic conditions linked to the nature of slurry and manure sometimes inhibit ammonia nitrogen nitrification reactions that require strictly aerobic conditions. Therefore the presence of an additional source of carbon and the humidity inherent in these products favor denitrification processes. Denitrification also occurs in livestock facilities and during slurry storage, but to a lesser extent than during the application of manure to the land. Nitrous oxide is produced as part of the denitrification process which is imperceptible in the N_2O emissions recorded in storage lagoons.

Ammonia (NH_3)

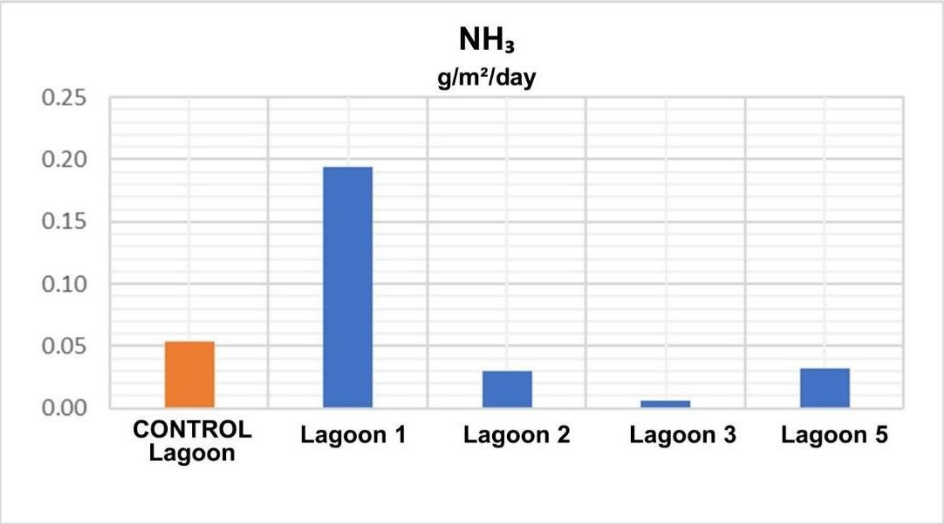


Figure 9.3.4. NH_3 emissions

In the case of pig slurry, more than half of the nitrogen contained therein is of the ammonium type. The ammonium ion is in equilibrium with ammonia, which can easily be released into the atmosphere by volatilization. In this case, this balance would be favored by the content of ammonia. Secondly, odor produced by the ammonia as can be seen in Lagoon 3 of the previous figure. The activation of microorganisms by EBD MUD could be intervening in this process.

Lagoon 3 shows a notable decrease in this parameter, in this pool the pretreated slurry presented lower emission values, which may be benefited by the increase in pH and the reduction of STS and N, together with the effect of the EBD MUD device. that under these conditions the slurry favored the quality of the slurry and decreased NH_2 emissions in this lagoon.

As can be seen in Lagoon 5 that NH_3 undergoes a slight rise, the activation of microorganisms by the MUD device could be intervening in this process. In this Lagoon, the organic pollutant load, as well as the nitrogen content, was significantly reduced (> 50%), an effect that could be attributed to the effect of the previous treatments (solid-liquid separation and decantation) and, on the other hand, the action of the devices installed in this lagoon.

9.4. Spring and Summer Conclusions:

The emissions of CH_4, CO_2, N_2O and NH_3 were lower in the spring period compared to the summer in the storage lagoons.

From the evaluation of the results of the emissions recorded in the spring and summer season it is concluded that lagoons 1, 2, 3 and 5 present the following quantitative emissions trend: CH_4 ~ CO_2>>NH_3>>N_2O. The analytical parameters associated with the emission results are STS and COD for CH_4 and CO_2, and nitrogen fractions (NK, N-NH_4 +, NO, NO_3- and NO_2-) and COD for NH_3 and N_2O. The aeration process to which the slurry is subjected in Lagoon 2 together with the presence of EBD SOIL, EBD WATER and EBD AIR devices could favor the reduction of CO_2 and NH_3 emissions in Lagoon 3, although it could also favor N_2O emissions by the possible development of nitrifying bacteria in the spring and summer period.

10. Seasonal Comparison:

Next, a comparison is made for each of the lagoons in which emissions have been recorded during all seasons (autumn, winter, spring, and summer):

Manure Lagoon 1

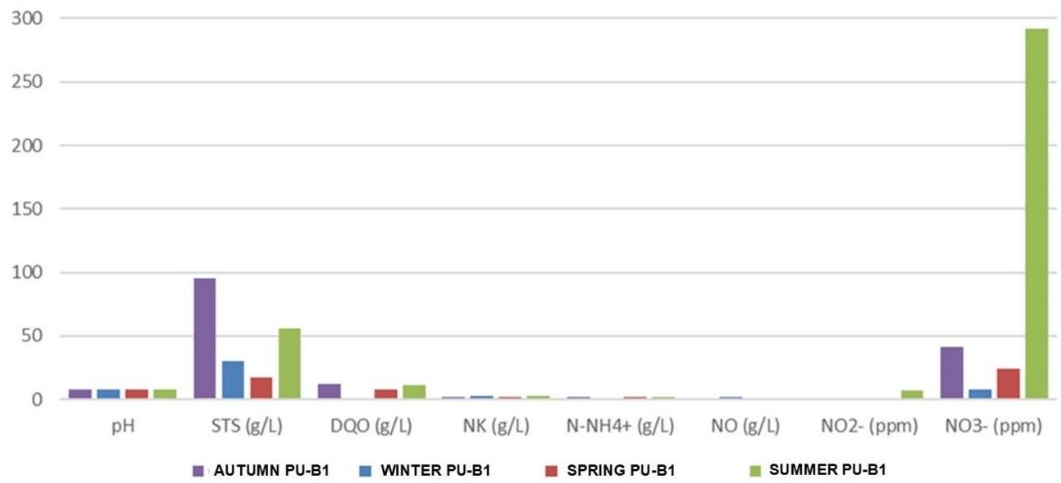


Figure 10.1. Comparison of manure Lagoon 1 characterization of manure

Manure Lagoon 1

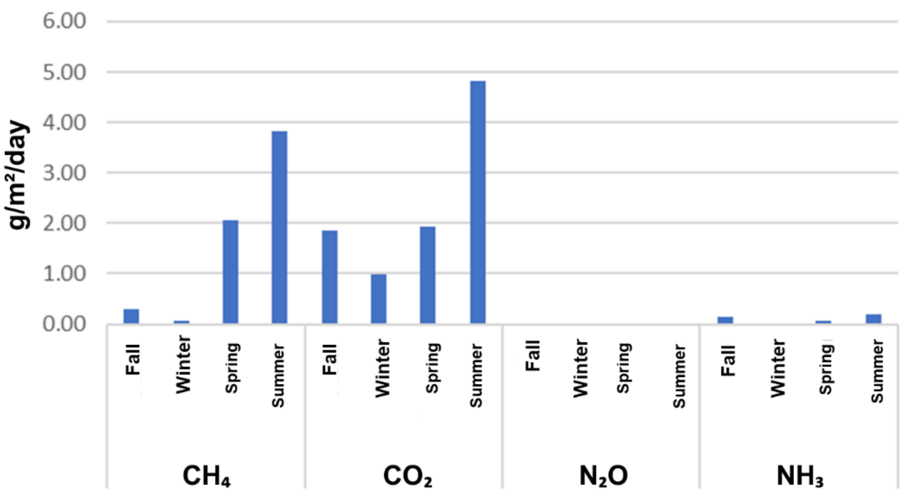


Figure 10.2. Comparison of manure Lagoon 1 registered emissions.

Lagoon 1 receives the raw slurry and has the EBD MUD, EBD SOIL and EBD WATER devices. It can be observed that the analytical results of the characterization of slurry show a slight decrease in spring compared to the other stations, which are reflected in the values corresponding to TOTAL SUSPENDED SOLIDS and COD for CH_4 and CO_2, and nitrogen fractions (NK, N-NH_4+, NO, NO_3- and NO_2-) and COD for NH_3 and N_2O.

The highest emissions recorded in Lagoon 1 correspond to the summer period. This may be associated with the increase in the value of the lagoon temperature that consequently increases the growth rate of bacteria and the production of emissions. Denitrification also occurs in livestock facilities and during slurry storage, but to a lesser extent than during the application of manure to the land. N_2O is produced as part of the denitrification process, which is imperceptible in the N_2O emissions recorded in storage lagoon. The installed devices have the power to reduce ammonia nitrogen solubility in slurry. In Lagoon 1, oxygen can be at the origin of the partial inhibition of nitrification and/or denitrification and therefore be the origin of N_2O.

Manure Lagoon 2

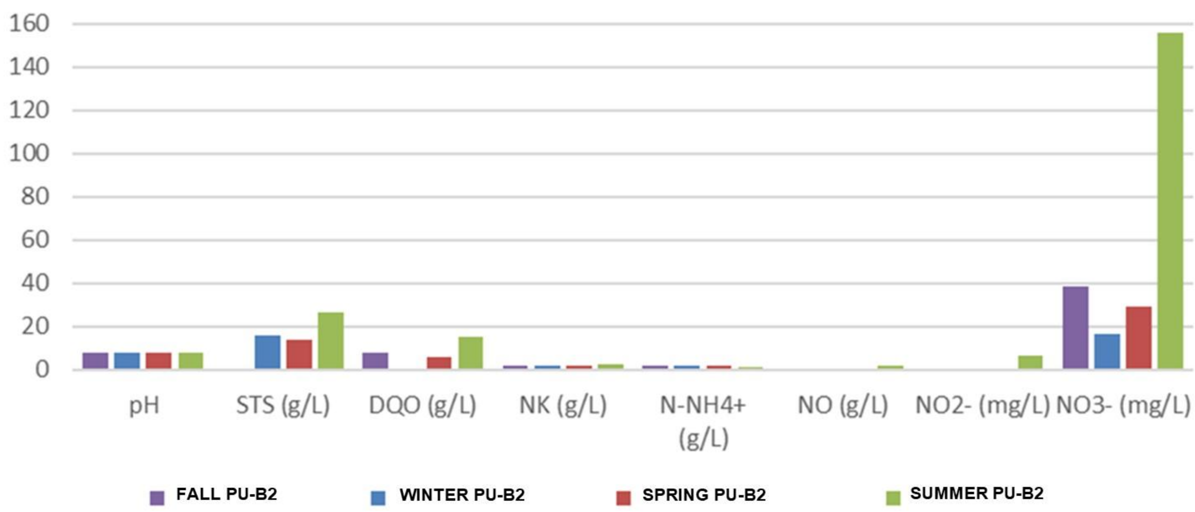


Figure 10.3. Comparison of manure Lagoon 2 characterization of manure

Manure Lagoon 2

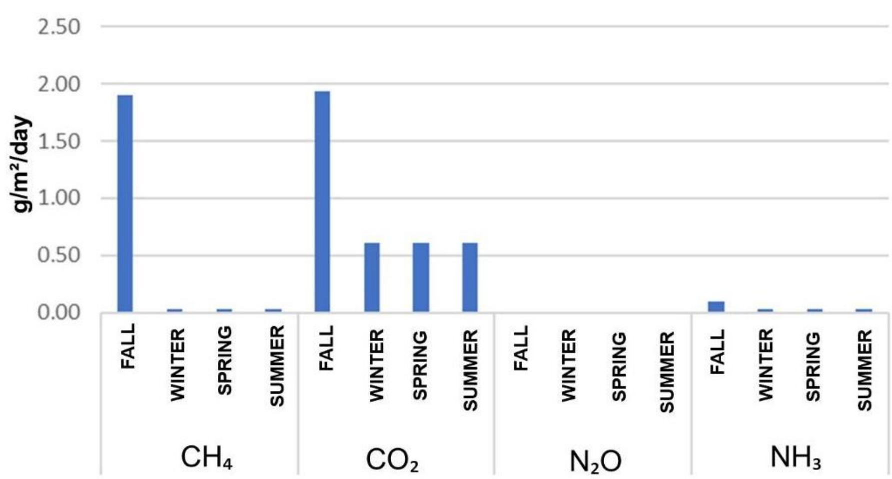


Figure 10.4. Comparison of manure Lagoon 2 registered emissions

The devices distributed in Lagoon 2 are EBD SOIL, EBD WATER and EBD AIR. In the specific case of the EBD AIR device, this would favor the reduction of CH_4 that originates because of the anaerobic processes that occur during storage, so this device has been able to contribute to the decrease in the emission of this gas since you can watch their descent in sequence for each season.

In the case of CO_2 emissions, this lagoon presents the highest emissions in the autumn period, this lagoon receives the slurry with previous treatment of phase separator and aeration, so this increase can be justified due to the treatment with aeration, so that this biological transformation also results in a higher production of CO_2, which is a result of the activity of aerobic bacteria (oxygen consumption and CO_2 release), however it is observed that for the other stations this value is considerably stable which can be attributed to the installed devices.

The N_2O emissions, for each of the stations measured in Lagoon 2, show values very close to zero, the different devices incorporated in the lagoons could limit nitrification reactions, preventing the transformation of ammonia into forms of NOx, it is also It is known that certain conditions of low pH or little humidity decrease the presence of N_2O, since it tends to be reduced to N_2, a condition that could be attributed to the EBD WATER device.

NH_3 shows a progressive decrease in this lagoon. In the case of pig slurry more than half of the nitrogen contained in it is of the ammonium type. The EBD WATER device can positively affect the reduction of the strong odor produced by ammonia as observed.

Together it can be observed in the analytical results of the slurry from the winter and spring stations 2021 show a slight decrease reflected in the values corresponding to TOTAL SUSPENDED SOLIDS and COD for CH_4 and CO_2, nitrogen fractions (NK, N-NH_4 +, NO, NO_3- and NO_2-) and COD for NH_3 and N_2O.

Manure Lagoon 3

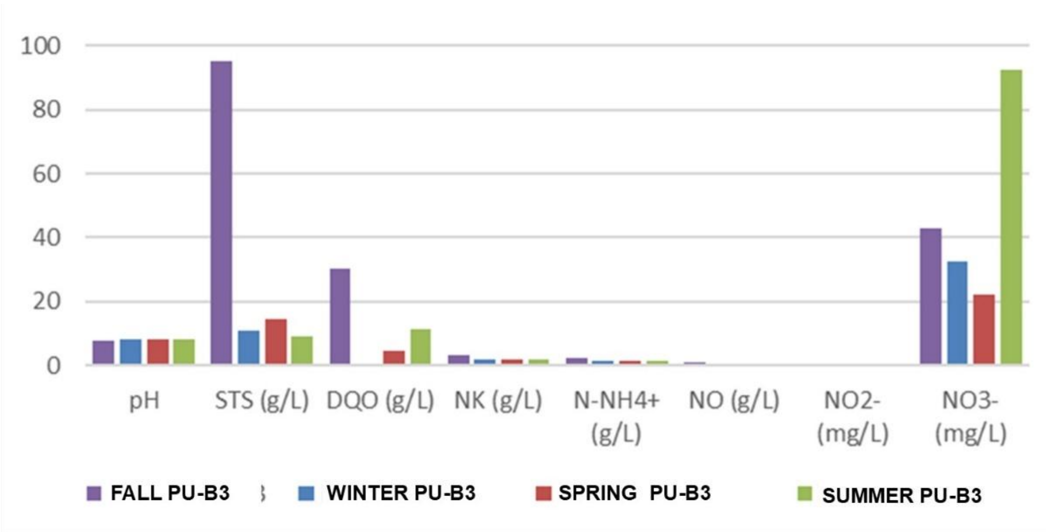


Figure 10.5. Comparison of manure Lagoon 3 characterization of manure

Manure Lagoon 3

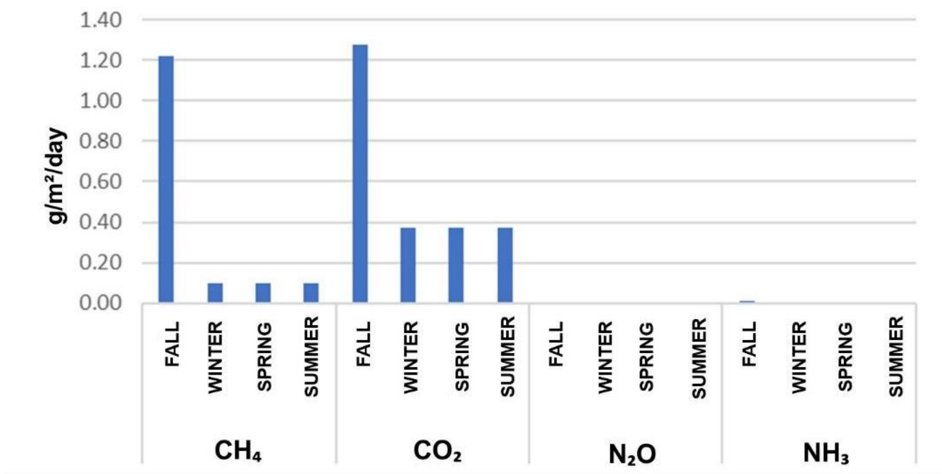


Figure 10.6. Comparison of manure Lagoon 3 emissions registered

In relation to the other lagoons, Lagoon 3 shows the greatest decreases in relation to the measurement of emissions. EBD MUD devices are installed in this lagoon. The stored slurry comes from Lagoon 2, showing a decrease in relation to the previous lagoons.

It is observed that the measurements made for CH_4 show a notable decrease between the autumn season and the other seasons, which could be attributed to the EBD MUD device since it could facilitate the decrease of CH_4 through the activation of microorganisms that would limit the degradation of various compounds involved in the methane synthesis process. With respect to CO_2 and NH_3 emissions, it is observed that these are higher in the autumn period, showing a notable decrease in the following seasons. This could be due to the decantation and sedimentation process in non-aeration conditions that the slurry receives in presence of EBD MUD devices. Said slurry comes from Lagoon 2 in which they have been subjected to an aeration process in the presence of EBD SOIL, EBD WATER and EBD AIR devices. When the aerated slurry from Lagoon 2 moves to Lagoon 3 where the aeration is suppressed, anaerobic conditions are generated in the presence of the EBD devices that could favor the reduction of emissions such as CO_2 and NH_3 linked to the decrease in COD values.

Manure Lagoon 5

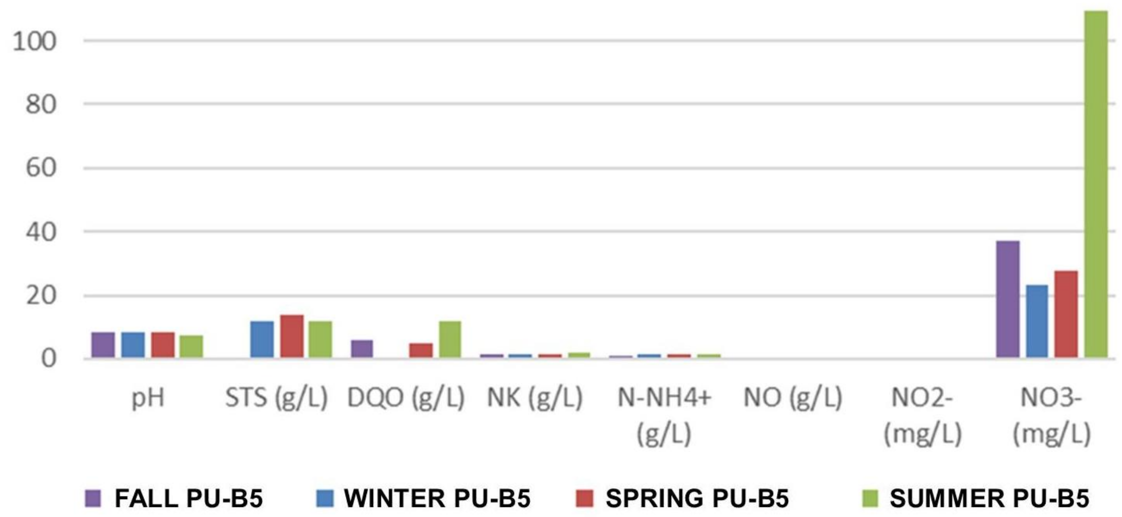


Figure 10.7. Comparison of manure Lagoon 5 characterization of manure

Manure Lagoon 5

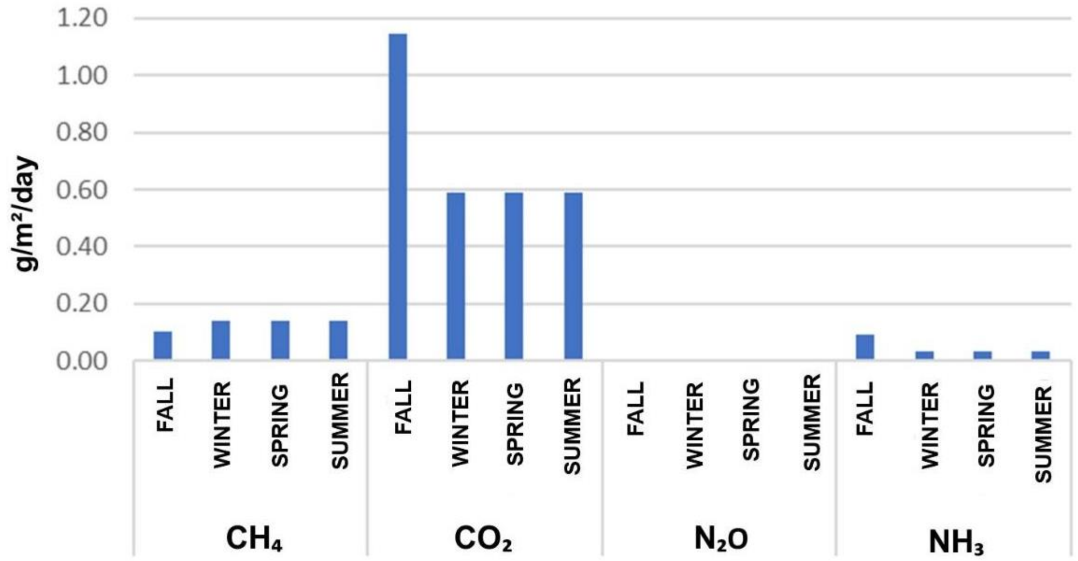
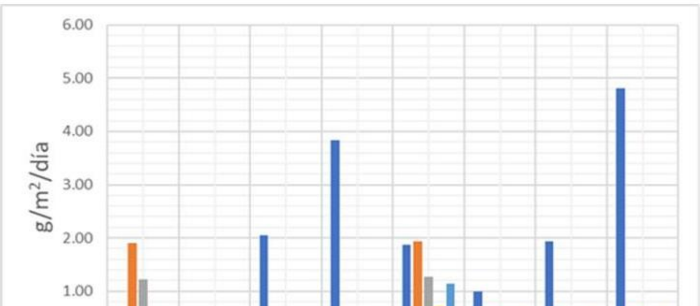


Figure 10.8. Comparison of manure Lagoon 5 emissions registered

The devices distributed in this lagoon are EBD MUD and EBD WATER. The detected N_2O emissions are very low (max: 1.1428 g/m²/day). The maximum is recorded in the autumn period, which could be associated with an increase in the concentration of organic nitrogen in the lagoon (0.2g/L) and a decrease in nitrates (37.1mg/L).

The NH_3 emissions, detected in the autumn, spring and summer periods, show a certain stability, which could be attributed to the settling process that the slurry receives under non-aeration conditions



In the following figure you can observe the emissions throughout all of the lagoons:

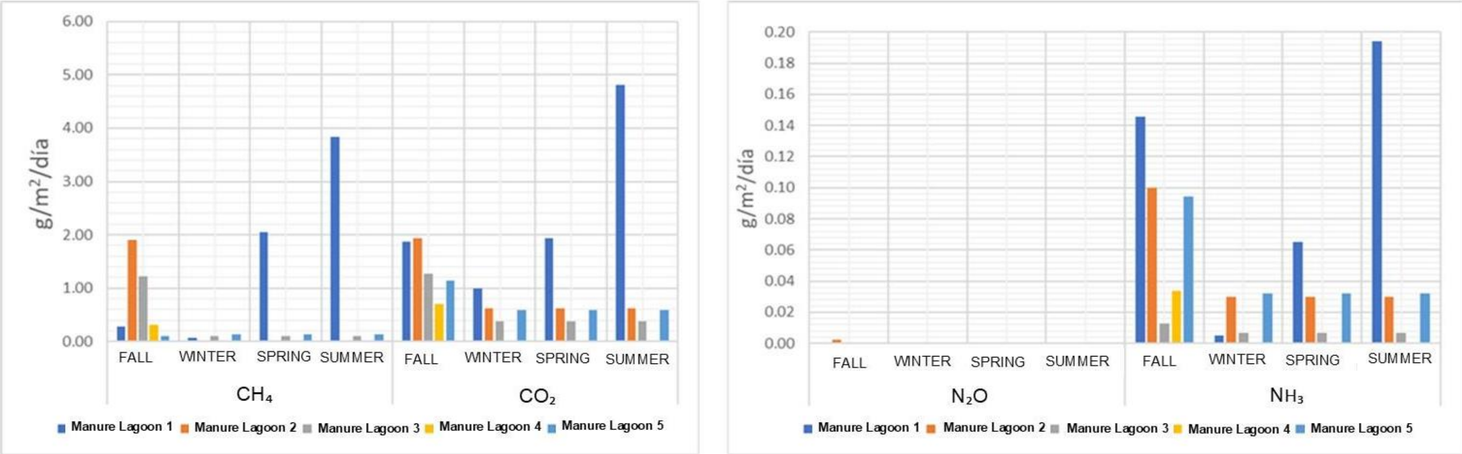


Figure 10.9. Results of the emissions recorded for each lagoon at each station

10.1. Comparison of the Emission Values Measured: Lagoons / MAPA Reference:

The emissions of ammonia and nitrous oxide from storage, according to the calculation tables of gas emissions from the livestock sector prepared by the MAPA for the State Registry of Pollutant Emissions and Sources (EPER-Spain), are those indicated in the following table

Table 10.1.1. Emission of ammonia and nitrous oxide due to volatilization from storage.

Categories	Ammonia emission (kgNH_3-N/Location and year	Nitrous Oxide emission (kg N_2O-N/Location and year)
Piglets from 13.3 to 44 lbs (6 to 20kg)	0.2969	0.000445
Pigs from 44 to 110.3 lbs (20 to 50kg)	14.992	0.002249
Pigs from 110.3 to 220.5 lbs (50 to 100kg)	21.261	0.003189
Pigs from 44 to 220.5 lbs (20 to 100kg)	18.137	0.002721
Sows with piglets from 0 to 13.3 lbs (0 to 6kg)	37.503	0.005625
Sows with piglets up to 44lbs (20kg)	45.004	0.006751
Replacement female pigs	21.261	0.003189
Sow in Closed Cycle	14.4007	0.021601
Boars	44.991	0.006749

Source: EPER-Spain. Livestock sector gas emission calculation tables calculated by MAPA

In methane emissions, according to the tables for calculating gas emissions from the livestock sector prepared by MAPA for the State Registry of Pollutant Emissions and Sources (EPER Spain), the emissions produced by manure management are jointly included (Code SNAP 97-2: 1005) without differentiating between storage and agricultural application. Considering that methane formation requires anaerobic conditions, such as those found in lagoons and slurry storage tanks, but not typically after agricultural application, it is expected that most methane emissions will occur during storage. Methane emissions from manure management are those indicated in the following tables.

Table 10.1.2. Methane emission from manure management

Categories	Average excretion of volatile solids (kg VS)	Specific weight of methane (kg/m²)	Potential production of methane (m³/kg VS)	Provincial methane conversion factor	Emission factor (kg CH_4/location)
	B	C	D	E	BxCxDxE
Piglets from 13.3 to 44 lbs (6 to 20kg)	28.93	0.67	0.45	Table 10.1.3	
Pigs from 44 to 110.3 lbs (20 to 50kg)	76.78	0.67	0.45	Table 10.1.3	
Pigs from 110.3 to 220.5 lbs (50 to 100kg)	166.92	0.67	0.45	Table 10.1.3	
Pigs from 44 to 220.5 lbs (20 to 100kg)	133.54	0.67	0.45	Table 10.1.3	
Sows with piglets from 0 to 13.3 lbs (0 to 6kg)	445.12	0.67	0.45	Table 10.1.3	
Sows with piglets up to 44lbs (20kg)	445.12	0.67	0.45	Table 10.1.3	
Replacement female pigs	178.05	0.67	0.45	Table 10.1.3	
Sow in Closed Cycle	1,185.14	0.67	0.45	Table 10.1.3	
Boar	445.12	0.67	0.45	Table 10.1.3	

Source: EPER-Spain. Livestock sector gas emission calculation tables calculated by MAPA

Table 10.1.3. Methane emission from manure management

Province	Methane Conversion Factor	Province	Methane Conversion Factor
La Coruña	0.19819	Soria	0.19562
Lugo	0.19603	Valladolid	0.19603
Orense	0.19602	Zamora	0.19600
Pontevedra	0.20033	Madrid	0.19818
Asturias	0.19682	Albacete	0.20034
Cantabria	0.19817	Ciudad Real	0.20037
Alava	0.19602	Cuenca	0.19680
Guipúzcoa	0.19819	Guadalajara	0.19601
Vizcaya	0.19687	Toledo	0.20049
Navarra	0.19683	Alicante	0.20773
La Riojo	0.19681	Castellón de la Plana	0.20345
Huesca	0.19602	Valencia	0.20741
Teruel	0.19684	Murcia	0.20770
Zaragoza	0.19827	Badajoz	0.20742
Barcelona	0.19830	Cáceres	0.20351
Girona	0.20031	Almeria	0.20750
Lleida	0.19604	Cádiz	0.21291
Tarragona	0.20338	Córdoba	0.20763
Balcares	0.21270	Granada	0.20038
Avila	0.19603	Huelva	0.21271
Burgos	0.19600	Jaén	0.20345
León	0.19562	Málaga	0.20759
Palencia	0.19550	Sevilla	0.21290
Salamanca	0.19683	Las Palmas	0.21970
Segovia	0.19602	Santa Cruz de Tenerife	0.21307

Source: EPER-Spain. Livestock sector gas emission calculation tables calculated by MAPA

The reference values in the following tables are based on the indicators prepared by MAPA for the State Registry of Pollutant Emissions and Sources (EPER-Spain) as indicated in the previous tables. The emission values for NH_4 have been calculated for the Region of Murcia. For its part, the reference values for CO_2 emissions are not considered by MAPA, therefore only the values measured directly in each of the lagoons in this study are shown.

Below is a summary table with the average emissions per lagoon/year (according to dimensions) and square/year (according to annual census), considering the measurement conditions constant. An annual average calculated from the autumn, winter, spring, and summer seasons has been considered, taking into account that the autumn and spring seasons correspond to periods of low emissions and the summer season to the period of high emissions according to the Vera Protocol.

Table 10.1.4. Annual average, minimum and maximum values of GHG (CH_4, CO_2 and N_2O) and NH_3 for the types of lagoons studied at the Agrosolmen farm in Pulpí, Spain (Lagoon 1: raw slurry (EBD MUD, EBD SOIL and EBD WATER), Lagoon 2: slurry After phase separator with aeration (EBD SOIL, EBD WATER and EBD AIR), Lagoon 3: settling No. 1 (EBD MUD), Lagoon 5: decanted slurry (EBD MUD and EBD WATER.)

Lagoon	Gas	kg/Lagoon (*)/year		kg/square/year		MAPA reference values	
		Media ± DE	Minimum	Maximum	Media ± DE		
Lagoon 1		214±240	0.0009	0.0488	0.0199±0.0224	1.8116 kg/year	Piglets 6-20 kg
Lagoon 2	CH_4	68±128	0.0003	0.0242	0.0063±0.0119	27.8741 kg/year	Mothers with piglets 0-6 kg
Lagoon 5		18±2	0.0013	0.0018	0.0017±0.0002		
Lagoon 1		329±228	0.99	4.81	2.4±1.66	Data not available	-
Lagoon 2	CO_2	129±91	0.61	1.94	0.94±0.66	Data not available	-
Lagoon 5		99±38	0.59	1.14	0.73±0.28		
Lagoon 1		0.0256±0.0197	0.000000	0.000333	0.000187±0.000144	0.0007 kg/square/year	Piglets 6-20 kg
Lagoon 2	N_2O	0.0738±0.1469	0.000000	0.002149	0.000539±0.001073	0.0088 kg/square/year	Mothers with piglets 0-6 kg
Lagoon 3		0.0078±0.0079	0.000003	0.000139	0.000057±0.000057	0.0106 kg/square/year	Boars
Lagoon 5		0.007±0.0083	0.000000	0.000120	0.000051±0.000061		
Lagoon 1		14±11	0.0049	0.1942	0.1024±0.084	0.3612 kg/square/year	Piglets 6-20 kg
Lagoon 2	NH_3	6±5	0.0298	0.1000	0.0473±0.0351	4.5622 kg/square/year	Mothers with piglets 0-6 kg
Lagoon 3		1±0	0.0065	0.0127	0.0081±0.0031	5.4732 kg/square/year	Boars
Lagoon 5		7±4	0.0320	0.0942	0.0476±0.0311		

(*) Lagoon 1: 375 m², Lagoon 2: 315 m², Lagoon 3: 860 m² and Lagoon 5: 2500 m².

According to the bibliography consulted, the hours in which the emission measurements were made between 9AM-12PM in the morning represent the average emissions in a day because they are hours that do not include the hours of maximum emissions (15:00-17:00) nor the hours of minimum emissions (from sunset to sunrise).

You can compare the average emissions in the Agrosolmen farm for a total of 10,750 boars (8,000 piglets 13.3-44 lbs (6-20 kg), 2,740 sows with piglets 0-13.3 lbs (0-6 kg) and 10 boars) and the MAPA reference emissions for CH_4 gases, N_2O and NH_3 (for CO_2 there is no comparison data available).

To make the comparison with the MAPA values, the experimental results shown previously (g/m²/ day) have been used and they have been converted into kg/lagoon/year multiplying by the surface of the respective Lagoon and 365 days. Subsequently, they have been divided by the total number of pigs (10,750 pigs) to obtain the results in kg/pig/year. It should be noted that in the data presented, no distinction has been made between animals because the storage systems are the same for all animals. The experimental results represent a mixed slurry from 13.3-44 lbs (6-20 kg) piglets, sows with 0-13.3 lbs (0-6 kg) piglets and boars and these values are compared with the referenced values for each type of animal.

The factors 1.2165 (ratio 17.031/14) have also been used to convert N-NH_3 into NH_3 and 1.5725 (ratio 44.03/28) to convert N-N_2O into N_2O respectively since this is how the values in the MAPA tables are shown.

In all cases, the real emissions of the farm under study are well below the reference values calculated by MAPA.

The reduction percentages determined from the experimental data obtained and the MAPA reference data can then be observed. For CH_4 the percentages of reduction of the farm are close to 100%, for N_2O they range between 23.00% (piglets, Lagoon 2) and 99.52% (boars, Lagoon 5) and for NH_3 they range between 71.64% (piglets, Lagoon 1) and 99.85% (boars, Lagoon 3).

Table 10.1.5. Reduction percentages determined from the experimental data with respect to the MAPA emission reference values.

Lagoons	Gas	% Reduction (vs. Piglets 6-20 kg)	% Reduction (vs. Mothers with	% Reduction (vs. boars)
Lagoon 1		98.90	99.93	99.93
Lagoon 2	CH_4	99.65	99.98	99.98
Lagoon 3		99.73	99.98	99.98
Lagoon 5		99.91	99.99	99.99
Lagoon 1		-	-	-
Lagoon 2	CO_2	-	-	-
Lagoon 3		-	-	-
Lagoon 5		-	-	-

Lagoon 1		73.27	97.88	98.24
Lagoon 2	N_2O	23.00	93.91	94.92
Lagoon 3		91.85	99.35	99.46
Lagoon 5		92.71	99.42	99.52
Lagoon 1		71.64	97.75	98.13
Lagoon 2	NH_3	86.90	98.96	99.14
Lagoon 3		97.77	99.82	99.85
Lagoon 5		86.82	98.96	99.13

These comparisons allow to denote the effectiveness of the EBD devices, thus it is evident how each of the processes to which the slurry has been subjected is complemented from the phase separator, decantation, aeration and the effectiveness of the devices for the treatment and remediation tasks, which create a state of energy balance. Consequently this shows the efficacy in the sufficient production of microorganisms capable of minimizing and in some cases eliminating the organic and inorganic pollutants contained in the slurry.

11. General Conclusions:

There is no single trend for CH_4, CO_2, N_2O and NH_3 emissions in the autumn, winter, spring and summer seasons. For some lagoons emissions were higher in the summer period compared to the other stations. This could be attributed to the increase in temperature with respect to other stations, since the increase in the value of the temperature, consequently, increases the growth rate of bacteria and the production of gaseous emissions.

The variety, distribution, and quantity of EBD devices in the lagoons have been sufficient to attribute an effect related to the reduction of greenhouse gas and ammonia emissions. Likewise, the devices could have a notable effect in reducing emissions when installed in slurry lagoon with some type of treatment (for example aeration) and without any type of pretreatment. However, it is recommended to implement the installation of devices in the final storage Lagoons to mitigate N_2O emissions.

It has been found that the emissions produced in all the lagoons of both GHG and ammonia are significantly below the reference values (MAPA), so that when comparing them with these reference values, reductions of over 95% are achieved in most of the cases.

In addition to the reduction of emissions into the atmosphere, the reduction in odors is also notable, especially related to ammonia, which is verified in the results obtained.

12. References:

- Duchaufour, P. H. 1970. Précis de Pédologie. Paris, France: Masson et Cie, 257-280.
- Environmental balance device technology (EBD). Raw sewage treatment. *https://www.freytech.com/environmental-balance-devices*. Freytech , inc,
- Fujishima, A., Rao, T. N., Tryk, D. A. (2000). Titanium dioxide photocatalysis. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 1, 1.
- Guide to the Best Available Techniques in the pig sector. 2010. Ministry of the Environment and Rural and Marine Affairs.
- Kamat, P. V., Huehn, R., Nicolaescu, R. (2002). A "Sense and shoot" approach for photocatalytic degradation of organic contaminants in water. Journal of Physical Chemistry B., 106: 788. ´
- Royal Decree 306/2020, of February 11, which establishes basic regulations for the management of intensive pig farms and modifies the basic regulations for the management of extensive pig farms.
- Shibata, Y., Suzuki, D., Omori, S., Tanaka, R., Murakami, A., Kataoka, Y., Baba, K., Kamijo, R., Miyazaki, T. 2010. The characteristics of in vitro biological activity of titanium surfaces anodically oxidized in chloride solutions. Biomaterials, 31-33, 8546-8555.
- Vazquez-Duhalt, R. 2015. Nanotecnología en procesos ambientales y remediación de la contaminación. Mundo Nano, 8-14.
- Wang, C., Zhang, W. (1997). Synthesizing nanoscale iron particles for rapid and complete dichlorination of TCE and PCBs. Environmental Science and Technology, 31: 2154.
- Wang, Y., Kadiyala, U., Qu, Z., Elvati, P., Atheim, C., Kotov, N.A., Violi, A., Stott VanEpps, J. 2019. Anti-biofilm activity of graphene quantum dots via self-assembly with bacterial amyloid proteins. ACS Nano 13-14, 4278-4289.
- Yu, W and Zang, L. 2021. Chemiluminescence detection of reactive oxygen species generation and potential environmental applications. *Trends in Analytical Chemistry 136, 116197*.

13. Photographs

45

EBD devices in slurry lagoon. Evaluation of results.

EBD devices in slurry lagoon. Evaluation of results.

47

EBD devices in slurry lagoon. Evaluation of results.

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EBD devices in slurry lagoon. Evaluation of results.