UNIVERSITAT POLITÈCNICA DE VALÈNCIA

MÁSTER EN PRODUCCIÓN ANIMAL

FACTORS AFFECTING CH_4 AND NH_3 EMISSIONS FROM PIG SLURRY IN COMMERCIAL FARMS

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A todos vosotros GRACIAS

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Title: Factors affecting CH_4 and NH_3 emissions from pig slurry in commercial farms

Abstract:

Today there is an awareness of the environmental effects in the livestock, which is an important source of ammonia (NH_3) and greenhouse gases such as nitrous oxide (N_2O) and methane (CH_4) to the atmosphere. An important part of these environmental effects are produced in pig production, which is associated to high generation of slurries. The objective of this paper is to determinate the principal factors of the slurries which are involved in the emissions of NH_3 and CH_4 in commercial pig farms. To determine this relationship, 79 samples of feed and slurry were taken from different productivity orientation (gestation, maternity, weaners and growing pigs) in different commercial farms. Samples were chemically analysed for dry matter, ash content, volatile solids, protein, fibre, ether extract, ammonium and volatile fatty acids. Also, NH_3 and CH_4 emission potentials were determined in laboratory. As a result, slurry composition was highly affected by the productivity orientation (gestation, maternity, weaners and growing pigs). Growing pigs emitted more NH_3 than the rest of orientations, whereas CH_4 emissions were higher for weaners and growing pigs. However, we found no relationship between these two emissions. There are some elements very related to the production of CH_4 emission like ether extract, volatile fatty acid and of course total biogas production, but different types of fibre were negatively correlated. For NH_3 emission this was different, the parameter more related to the potential emission of NH_3 it was the initial ammonium content in the slurry. After all this analysis, equations were obtained to predict the emission of NH_3 and CH_4 with the components of the slurries.

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Títol: Factors que afecten a l'emissió de metà i amoníac en els purins de porcs de granges comercials

Resum:

Hui en dia hi ha encara mes preocupació per els possibles perills mediambientals, provocats per la ramaderia. La ramaderia es una important font de gasos contaminants a la atmosfera com el amoníac (NH_3) i els gasos d'efecte hivernacle com l'òxid nitrós (N_2O) i el metà (CH_4). Una part molt important d'aquestos efectes mediambientals provenen de la ramaderia porcina, directament relacionada amb la producció de purins. El objectiu d'aquest estudi es determinar el principals components del purí que provoquen emissions de NH_3 y CH_4 en les granges comercials de porcs. Per a poder determinar aquesta relació es varen tomar un total de 79 mostres de purí de granges comercials amb diferents orientacions productives (gestació, maternitat, transició i porcs d'engreix). Els components del purí analitzats varen ser matèria eixuta, cendres, sòlids volàtils, proteïna, fibres, extrac eteri, amoni i àcids grassos volàtils. També varen ser analitzades en el laboratori les diferents emissions de NH_3 i CH_4. Els resultats obtinguts varen ser, que la orientació productiva (gestació, maternitat, transició i porcs d'engreix) estigueren molt correlacionades amb les emissions produïdes per els purins. Els purins provinents de les granges de porcs d'engreix varen ser els que més NH_3 produeixen, mentre que les emissions de CH_4 principalment provenien de les granges de transició i de porcs d'engreix. Es va realitzar un anàlisis de les dos emissions per si hi havia una relació directa entre les dos tipus de emissions, però la seua correlació va ser molt baixa. Els components del purí més relacionats amb l'emissió del CH_4 varen ser el extracte eteri, els àcids grassos volàtils i per descomptat la producció de biogàs, mentre que es va trobar una correlació negativa amb les fibres. Per l'emissió del NH_3 els components del purí mes relacionats varen ser, la conductivitat elèctrica del purí i el contingut del amoni dissolt en la mostra. Després de haver relacionat tots el paràmetres del purí es varen formular unes equacions de predicció per a cadascuna de les emissions.

Título: Factores que afectan a la emisión de metano y amoniaco en los purines de cerdo de granjas comerciales

Resumen:

Hoy en día cada vez hay más preocupación sobre los posibles efectos medioambientales provocados por la ganadería. La ganadería es una importante fuente de gases contaminantes a la atmósfera como el amoníaco (NH_3) y los gases de efecto invernadero como el óxido nitroso (N_2O) y el metano (CH_4). Una parte muy importante sobre los efectos medioambientales en la ganadería están asociados a la producción porcina, directamente relacionada con la generación de purines. El objetivo de este estudio es determinar los principales componentes del purín que provocan emisiones de NH_3y CH_4 en las granjas comerciales de cerdos. Para poder determinar esta relación se tomaron un total de 79 muestras, tanto de los piensos como de los purines de granjas comerciales con diferentes orientaciones productivas (gestación, maternidad, transición y cebo). Las muestras fueron analizadas en materia seca, cenizas, sólidos volátiles, proteína, fibra, extracto etéreo, amonio y ácidos grasos volátiles. También se cuantificaron en el laboratorio las emisiones de NH_3 y CH_4. Los resultados obtenidos fueron que la orientación productiva (gestación, maternidad, transición y cebo) estaba muy correlacionada con las emisiones producidas por los purines. Los purines provenientes de las granjas de cebo eran los que más NH_3 emitieron, mientras que sobre las emisiones de CH_4, los purines provenientes de las granjas de transición y cebo era las que más CH_4 producían. Se realizó un análisis entre las dos emisiones por si había una relación directa entre ellas pero su correlación fue muy baja. Los componentes del purín más relacionados con la emisión de CH_4 fueron el extracto etéreo, los ácidos grasos volátiles y por supuesto la producción de biogás, aunque también hubo correlaciones negativas con las fibras. Para la emisión de NH_3 los componentes del purín más relacionados fueron la conductividad eléctrica y el contenido de amonio disuelto en el purín. Después de haber relacionado todos los componentes del purín se obtuvo una ecuación de predicción para cada una de las emisiones.

1. - Introduction

It is widely known that animal production may be a relevant source of pollutants to soil, water and the atmosphere, even for extensive production. The wastes from the pig farms are associated with atmospheric emissions like ammonia (NH_3), nitrous oxide (N_2O) and methane (CH_4); these gases contribute to a deterioration of the environment (FAO, 2013*)*. The consequences of NH_3 emissions on the environment are related to the eutrophication of water and the acidification of soils (Konarik, 2006), but it also affects the health and wellbeing of animals (Blanes-Vidal *et al.*, 2007). The emissions of CH_4 and N_2O contribute to the global warming, because their relative global warming potentials are 21 and 310 compared to carbon dioxide (CO_2), respectively (Solomon *et al.*, 2007).

The slurries produced by pig farms can be applied to land as fertilizers. To this aim, reducing NH_3 emissions increase the nitrogen content of slurries applied to crops (Konarik*, 2006*). This additional nitrogen incorporated in the soil it is quickly metabolized by plants and used as a nutrient. However, pig production in Spain has increased in the last years: in the last five years, the number of animals has raised by almost one million. In 2012 there were about 25 million pigs registered in Spain, including all types of animals. The region with more animals was Cataluña, with almost seven million pigs (Magrama, 2013). The most important type of animals is growing pigs from 50 to 109 kg (40%), followed by piglets (27%), growing pigs from 29 to 49 kg (23%), and reproductive animals (9%). Comparing with other European countries, Spain is the second pig producer after Germany (FAOSTAT, 2013). This increase of pig production has been a consequence of the better use of the resources and the improvement in production systems, but has also had negative environmental consequences (Magrama, 2011). In fact, there are regions where the swine production is very concentrated and there is not enough crops surface to use slurry as a fertilizer. Also, it is common that farmers prefer solid manure to pig slurry to be applied to crops, although there are not significant differences in pH, total nitrogen (N) contents and C:N ratios (Ndayegamiye, 1988).

The agriculture and livestock production contribute to the global warming. According to the Intergovernmental Panel on Climate Change (IPCC, 2007), the 13.5 % of the greenhouse gases are produced by the agricultural and livestock sectors, whereas total CH_4 emissions correspond to the 14.3% of the total greenhouse gases emissions (IPCC, 2007). In livestock production there are two main ways to produce CH_4: enteric fermentation and manure fermentation. The enteric fermentation is very important in the ruminants; this type of animal generates CH_4 in the rumen which is then directly expelled to the atmosphere (Carmona *et al.,* 2005). However, this pathway is not very important in monogastric animals such as pigs. Most of the CH_4 produced in pig production is generated by the fermentation of slurry, which is an excellent substrate to produce CH_4. This aptitude of slurry is closely related to their composition: their principal component it is water (which ensures anaerobic conditions in the substrate), it has a buffering effect and has all the nutrients that the microorganisms need to develop (Campos *et al*., 1999).

This potential of pig slurries to produce CH_4 can be exploited by means of controlled anaerobic digestion. This is a complex process by which a mixture of CH_4, CO_2 and other trace gases are produced. The percentage of CH_4 produced varies according the organic matter in the slurry (Martínez-Almeda and Barrera, 2004). The potential production of CH_4 depends on multiple factors: pH, temperature and physicochemical characteristics (Jarret *et al.,* 2010).

All the processes leading to NH_3 and CH_4 emissions from livestock production are directly or indirectly related to animal nutrition. It has been demonstrated that the emissions of these gases are directly related with the composition of the diet the animals receive. More quantity of crude protein in the diet has been associated to higher emissions of NH_3 (Le *et al*., 2008). When the animals metabolize their rations they excrete nitrogen as faeces and urine, which are the substrate for NH_3 emission. It has been described that a reduction of crude protein in the diet decreases nitrogen excretion in urine, whereas nitrogen excretion in faeces remains almost constant (Portejoie *et al*., 2004). The urea in the urine is converted rapidly into NH_3 by the urease enzyme produced by microorganisms in the faeces (Cahn *et al*., 1997). Contrarily, the organic nitrogen excreted in the faeces is decomposed more slowly and this process is mainly carried out by microorganisms of the soil (Powell *et al*., 1999). Therefore, a reduction of crude protein in diets is directly associated to lower emissions in animal buildings and slurry storage systems. Also, the increase of fermentable carbohydrates in the diet has been related to a lower pH in the digestive tract, which is also associated to reduced NH_3 emissions; at same time a slight increase in CH_4 production was detected for growing pigs (Aarnink and Verstegen, 2007).The potential of this slurry to produce emissions also depends on the kind of animal and the environment.

The main objective of this paper is to study the different factors that contribute to the potential emission of CH_4 and NH_3 produced by the slurry in commercial pig farms. More precisely, we aimed to:

- Determine differences between the type of animals are used in the study (gestation, maternity, weaners or growing pigs)
- Quantify changes in the emission of these gases according the characteristics of the slurry and diet

2. - Material and methods

2.1. – *Sampling of feedstuffs and slurries*

The different samples were taken from commercial pig farms in the East and Centre of Spain. In each farm, representative samples of slurry and feedstuff were taken for laboratory analysis and emission measurements. The commercial pig farms included all the types of animals (growing pigs, piglets, gestation and lactation). A total of 79 samples were taken including 32 of growing pigs, 17 of weaners, 15 of gestating sows and 15 of lactating sows. The distribution of samples in different zones, seasons and productive orientations is shown in Table 1.

Table 1 Origin of the slurry and feedstuff samples according to productivity orientation, farm location and season

<table>
<tr><th>Productivity orientation</th><th>Farm location</th><th>Season</th><th>Number of samples</th><th>Total samples</th></tr>
<tr><td rowspan="4">Gestation</td><td rowspan="2">Centre Spain</td><td>Summer</td><td>4</td><td rowspan="4">14</td></tr>
<tr><td>Winter</td><td>3</td></tr>
<tr><td rowspan="2">East Spain</td><td>Summer</td><td>4</td></tr>
<tr><td>Winter</td><td>3</td></tr>
<tr><td rowspan="4">Maternity</td><td rowspan="2">Centre Spain</td><td>Summer</td><td>3</td><td rowspan="4">14</td></tr>
<tr><td>Winter</td><td>4</td></tr>
<tr><td rowspan="2">East Spain</td><td>Summer</td><td>4</td></tr>
<tr><td>Winter</td><td>3</td></tr>
<tr><td rowspan="4">Weaners</td><td rowspan="2">Centre Spain</td><td>Summer</td><td>4</td><td rowspan="4">14</td></tr>
<tr><td>Winter</td><td>3</td></tr>
<tr><td rowspan="2">East Spain</td><td>Summer</td><td>4</td></tr>
<tr><td>Winter</td><td>3</td></tr>
<tr><td rowspan="4">Growing pigs</td><td rowspan="2">Centre Spain</td><td>Summer</td><td>7</td><td rowspan="4">37</td></tr>
<tr><td>Winter</td><td>11</td></tr>
<tr><td rowspan="2">East Spain</td><td>Summer</td><td>8</td></tr>
<tr><td>Winter</td><td>11</td></tr>
</table>

The sampling was made in commercial pig farms previously selected for similar housing and slurry management but different feedstuff supplier to generate variability in diets. Manure pits were cleaned before the entrance of a new group of animals and samples were taken at the end of the occupation period. Other factors of the installations (type of ventilation, slatted surface, and number of feeding phases) were fixed for the different animal categories. On the contrary, different kinds of animals (growing pigs, weaners, gestating sows and lactating sows) were considered. Additionally, farms were selected for differences in diet characteristics. The objective was to achieve a great variability in terms of diet composition to evaluate potential changes in slurry composition and emissions. Therefore, farms with similar diets were excluded from this study.

The slurries samples were collected according to the following protocol: to obtain representative samples slurry pits were completely emptied. Samples were taken at the closest register point to the manure pit in five different moments (2L in each moment) during the emptying process and mixed in a plastic jar (10 L of capacity). A representative sub-sample of 6 L was taken and cooled (4ºC) for all analysis. A representative feed sample of approximately 500 g was collected from different feeders where slurry was sampled.

Slurry samples were divided in the laboratory for the different analysis. Half of the collected volume (3 L) was separated in two containers, frozen and sent to the Universidad Politécnica de Madrid (UPM). The other half of the collected slurry stayed in the Institute of Animal Science and Technology at the Universitat Politècnica de Valencia (UPV) and was divided in aliquots for the NH_3 (2 L) and CH_4 (1 L) analysis. A small aliquot (50 mL) was acidified with HCl for determination of ammonium content.

2.2. - Chemical analyses

The analyses of the animal diets and slurries were conducted in the Department of Animal production at the UPM. Feed samples were analysed for dry matter (DM), ash, organic matter (OM), crude protein (CP), ether extract (EE), starch, neutral detergent fibre (NDF), acid detergent fibre (ADF) and acid detergent lignin (ADL), insoluble nitrogen (NDIN and ADIN). The samples of slurry were analysed for total solids (TS), volatile solids (VS), NDF, ADF, ADL and NH_4-nitrogen.

Chemical analyses of samples were conducted in duplicate. Procedures of AOAC (2000) will be used to determine the concentrations of dry matter and ash. Feed and freeze-dried slurry samples were ground to pass through a 1-mm mesh screen (Cyclotec 1093 Sample Mill, Foss Electric A/S, Denmark). NDF, ADF and ADL were determined sequentially by using the filter bag system (Ankom Technology, New York) according to Mertens (2002), AOAC (2000; procedure 973.187) and Van Soest et al. (1991), using heat stable amylase (A3306, Sigma) and sodium sulphite, and expressed without residual ash. For N fractionations in slurry samples, concentration of NH_3 (NH_4-N) were determined by steam distillation using an automatic analyzer (2300 Kjeltec, Foss Analytical, Hilleroed, Denmark). Ammonium nitrogen in the slurry was determined before and after the emission test (ini_NH_3 and fin NH_3) using a NH_3 electrode (Orion High Performance NH_3 Electrode, model 9512HPBNWP, Thermo Scientific, USA).

Volatile Fatty Acids (VFA) were determined in the UPV as follows. The sample was subjected to a pre-treatment consisting in a centrifugation at 3500 rpm during 20 minutes, after which 0.9 mL of the supernatant were taken and placed in an Eppendorf containing 0.1 mL of internal pattern (4-metil-valeric) and 1 mL of distilled water. After that a second centrifugation at 14400 rpm during 10 minutes, the supernatant was filtered with a cellulose acetate filter and 220 µL were deposited in chromatograph vials for analysis. The vials were frozen at -30 ºC until the analysis was performed by means of gas chromatograph. A gas chromatograph (Fisons 8000 Series, Fisons, Milan, Italy) was used, including a detector FID and injector in split mode. The identification of the different VFA was made by comparison with retention times of a VGA standard (46975-U de Supelco®, PA, USA). The volatile acids analyzed were: acetic acid, propionic acid, isobutyric acid, butyric acid, isovaleric acid, n-valeric acid, caproic acid and heptanoic acid. Total VFA were determined as the sum of these individual VFA.

2.3. - Measurement of potential NH_3 emissions

Potential NH_3 emissions were determined in a laboratory test following the methodology described by Portejoie *et al*., (2004). For each slurry sample, two measurements were made.

The experiment consisted in 16 measurement units, and therefore, 8 samples with 2 repetitions each could be measured simultaneously. The samples (0.6 L each) were placed in a 1 L closed chamber, and the air was extracted at an airflow rate of 1.2 L/min. A critical orifice allowed a constant pressure of the airflow, and this parameter was controlled daily. As shown in Figure 1, the air was forced to pass through 2 impingers in serial with an acid (100 mL of H_2SO_4 0.1 N). Most of the NH_3 was captured in the first impinger. The second impinger collected the NH_3 not retained by the first one. As a verification, it was checked that less than 5% of total emitted NH_3 was collected in the second impinger. A third cooled impinger was placed to remove the moisture from the air to protect the pump. The measures had a duration of 15 days, and every day the acid was changed. After the experiment the content of each emitting source was analyzed to determine the NH_3 content remaining in the sample.

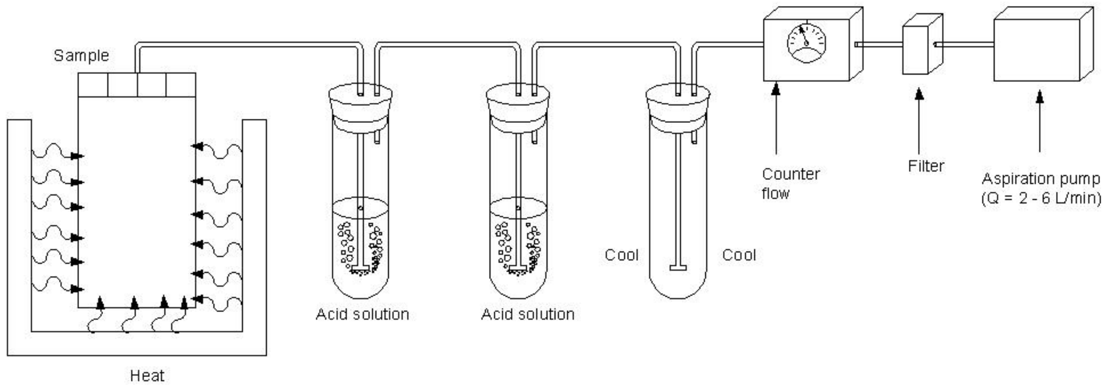

Figure 1 Process to recuperate the slurry NH_3

The ammonium retained in the acid traps was quantified using a NH_3 detection electrode (Orion High Performance NH_3 Electrode, model 9512HPBNWP, Thermo Scientific, USA). At the beginning of each series of measurement the electrode required a calibration with known solutions of ammonium. Two calibration curves were obtained, one for a high range corresponding to the first impinger (where most of the emitted NH_3 was retained) and another one for a low range corresponding to the second impinger. In each measurement, sodium hydroxide (NaOH) was incorporated to the sample to increase the pH up to 12 to convert all ammonium to NH_3, which can be detected by the electrode. After each analysis the electrode was cleaned with water before analysing the next sample.

2.4. - Measurements of potential CH_4 emissions

Potential CH_4 emissions were determined in a laboratory test following the methodology described by Verdenne *et al.*, (2008). This procedure determines the maximum CH_4-producing capacity (B_0) of wastes (also known as ultimate CH_4 productivity). For B_0 determinations, crystal bottles (120 mL) were filled with a variable amount of slurry and inoculum. To ensure anaerobic conditions, the headspace was filled with N_2 and hermetically closed with a septum. The composition of the mixture (inoculum:sample) depended on the concentration of the slurry in volatile solids. For each slurry sample, three replicates were made and the duration of the test was 100 days at 35^oC. Depending on the biogas production, one to two times per week the pressure generated in the headspace was measured using a manometer model HD 9220

(Delta Ohm, Barcelona, Spain) and the gases generated in the bottle were extracted until the returned to the atmospheric pressure. A sample of the gases generated was collected for CH_4 determination. The analysis of the CH_4 was made once a week using the gas chromatograph model 8000 (Fissons, Milan, Italy) equipped with a FID dectector and injector in split mode. The dispositive quantified the CH_4 presents in the gases and the results were checked before extracting the gases from the bottles.

2.5. - Data analysis

The data were analysed using Statgraphics Centurion XVI Version 16.1.11. An analysis of variance was conducted to evaluate the effects of productivity orientation, zone and season on the different measured parameters, using the following model:

$$X_{ijz} = m + PO_i + Z_j + S_z + \varepsilon$$

Where X_i is the variable studied, and the others are the different effects: PO_i is the productivity orientation is (gestation, maternity, weaners and growing pigs); Z_j is the zone (East and Centre of Spain) where the samples were taken, and S_z indicates in which season was taken the sample (winter, summer).

A possible relation between the emissions of CH_4 and NH_3 was explored using a linear regression:

$$CH_4 = a + b \cdot NH_3 + \varepsilon$$

Where "a" corresponds to the intercept and "b" corresponds to the slope.

To describe how the variables are related with the distinct emissions, correlation coefficients were determined.

$$r_{xy} = \frac{\sigma_{xy}}{\sigma_x \cdot \sigma_y}$$

Where:

r_{xy}= Correlation coefficient between the variables x and y

σ_{xy}= Covariance of the variables x and y

σ_x and σ_y= Standard deviation of variables x and y, respectively.

The final analysis consisted in describing an equation to predict the emission of CH_4 and NH_3. A multiple regression "stepwise" was used, where the dependent variable was the emission of CH_4 and NH_3 and the components of the diet, slurries and the slurry properties were used as independent variables:

$$E_x = B_0 + B_1 \cdot Y_1 + B_2 \cdot Y_2 + B_n \cdot Y_n + \varepsilon$$

Where E_x is the emission of NH_3 or CH_4, B_0 is the intercept, $B_1 \ldots B_n$ are the regression coefficients, $Y_1 \ldots Y_n$ are the independent variables and ε is the model error.

3. - Results and discussion

3.1. - Ration and slurry description

In Table 2 it is shown the characteristics of the different rations in the commercial farms studied. The data are organized as a function of the productivity orientation.

Table 2 Description of the commercial rations

Analytical parameter [1]	Productivity Orientation			
	Gestation	***Maternity***	***Weaners***	***Growing pigs***
DM (%)	89.6 ± 1.65 (86.9-92.48)	89.4 ± 1.57 (86.4-91.7)	89.9 ± 1.53 (87.4-92.6)	89.6 ± 1.20 (86.7-92.1)
Ash (% DM)	6.25 ± 1.04^{bc} (4.43-7.99)	6.54 ± 0.56^{c} (5.56-7.51)	5.90 ± 0.49^{b} (5.00-6.97)	5.17 ± 0.76^{a} (3.06-6.58)
CP (%DM)	14.9 ± 1.48^{a} (12.6-17.5)	17.9 ± 1.54^{bc} (15.7-21.6)	18.9 ± 1.51^{b} (16.9-21.5)	17.1 ± 1.52^{c} (13.7-19.9)
NDF(%DM)	22.6 ± 2.71^{d} (19.4-29.3)	19.0 ± 3.01^{c} (14.6-24.5)	14.0 ± 1.48^{a} (11.3-16.2)	16.7 ± 1.94^{b} (11.9-20.5)
ADF(%DM)	8.45 ± 2.1^{d} (4.12-11.8)	6.57 ± 2.26^{c} (2.19-10.5)	3.80 ± 0.7^{a} (2.90-5.38)	5.27 ± 1.31^{b} (2.82-8.94)
ADL(%DM)	2.28 ± 0.73^{d} (1.23-3.77)	1.79 ± 0.58^{c} (1.01-2.70)	0.91 ± 0.37^{a} (0.39-1.58)	1.31 ± 0.51^{b} (0.41-2.51)
EE(%DM)	4.93 ± 1.48 (2.23-7.57)	5.85 ± 1.24 (3.49-8.01)	5.47 ± 1.86 (2.26-7.72)	5.47 ± 1.73 (1.71-9.16)

[1] DM= dry matter, CP= crude protein, NDF= neutral detergent fiber, ADF= acid detergent fiber, ADL= acid detergent lignin, EE= ether extract.
Different letters indicate statistical differences among productivity orientations ($p<0.05$)

The quantity and composition of the pig diet is a very important factor in the characteristics of slurry and quantity of the emission produced (MTD MAPA 2006). In the Table 2 it is shown that there is a large variability for all the components except the dry matter which is around 89%. This variability was expected because of the selection procedure of farms according to different feedstuff supplier.

Analyzing all the components separately, statistically significant differences ($p<0.05$) in crude protein were found for the different productivity orientations. As expected, lactating sows, weaners and growing pigs have more nitrogen needs, for milk production (maternity) and animal growth (growing pigs and weaners) than gestating sows. The levels of crude protein are very similar to the recommended values in MTD MAPA (2006), being for gestation sows 14.9% of CP (recommendation 13 - 16%), for maternity 17.9% (16 - 18%), for weaners 18.9% (17 – 21%) and for the growing pigs 17.1% (14 – 18%). The needs of crude protein in growing pigs also depend on the production objectives (more lean or fatty), which is reflected in the high variability of CP found for these animals.

The adequate fibre content for each animal is more difficult to determine. In the gestation sows it is necessary to increase the fibre content to increase the digestive welfare (intestinal health and feeling satiated), so there is a recommendation for the gestation sows of 14% NDF. For lactating sows, however, the recommended content of fibre in the diet reduces to 13 – 14% NDF (FEDNA, 2006). In our study, however, fibre contents were considerably higher than these recommendations. For weaners, this depends of the animal weight, it is necessary a minimum content of fibre NDF for a proper development of the intestine, but not too much because it can produce a toxaemia in the animals. The recommendation is 7 – 13% of NDF in the diet, but in the study they are a little bit higher (14% of the diet). The content of fibre in the growing pigs affects in the palatability and in the digestibility of the diet, so when the diet has less fibre, the animals grow more. However, a minimum of fibre is necessary for the digestive welfare of the animal (less ulcers and better intestinal transit) so the recommendation of fibre for growing pigs are 11 – 17% (the value in the fibre analysed in the paper average 16.7%).The fibre is the parameter with more variability in the diet, and differences were statistically significant ($p<0.05$) among all the productivity orientations.

The energy needs are supplied basically by fats and carbohydrates. The ether extract is more important for maternity to produce milk and also for weaners and growing pigs to fatten. The recommendation of FEDNA (2006) for the gestating animals is 2.6% EE (in the commercial farms we found an average of 4.93%). For lactating sows, the minimum quantity of ether extract must be between the interval 4 – 6%; in the commercial pig farm data it averages 5.85% so it fits nutrient recommendations. Weaners and growing pigs have the same quantity of ether extract in their respective diet (5.47%). However, the recommendations for weaners are higher (5 – 9%) than for growing pigs (4 – 9%) but both orientations fitted the recommendations. There are no statistically significant ($p<0.05$) differences in ether extract among the productivity orientations, the value of each ration was also very variable.

In the Table 3 it is shown a measure of the different components of the slurries for all pig farms analysed. The data are organized as a function of the productivity orientation.

It can be observed that the TS (total solids), VS (volatile solids) and N (nitrogen content in the slurries) had statistically non-significant differences between the productivity orientations. These values presented low variability.

In the other side the rest of the components of the slurry presented statistically significant differences ($p<0.05$) among the productivity orientations. The whole group of fibres (NDF, ADF and ADL) of reproduction animals (gestating and lactating sows) have a higher content of the fibres in the slurry, because these animals can tolerate more quantity than the animals dedicated to fattening (weaners and growing pigs).

The component of the ether extract presented clear and statistically significant differences ($p<0.05$). Proportionally, the needs of energy in the gestation animals are the lowest, and thus the content of this component in the slurry is also the lowest (6.94%) in the other side, weaners have the highest recommendation of ether extract in the ration, so in the slurry content of ether extract they have the highest value (13.0%). The maternity sows and growing pigs are in an intermediate situation, they need high content of energy in their ration to produce milk (maternity sows) and keep fattening (growing pigs) but it is not necessary a ether extract content as high as for weaners. The ether extract presented values of 9.32% for maternity sows and 10.9% for growing pigs.

Table 3 Description of the slurries

Analytical parameter [1]	Productivity Orientation			
	Gestation	***Maternity***	***Weaners***	***Growing Pigs***
TS (%)	5.86 ± 5.27 (0.49-15.5)	3.58 ± 2.23 (0.86-7.58)	3.72 ± 2.42 (0.57-9.72)	5.38 ± 4.08 (0.75-17.7)
VS (%)	4.31 ± 3.97 (0.28-12.0)	2.62 ± 1.70 (0.49-5.54)	2.70 ± 1.86 (0.36-7.24)	4.08 ± 3.28 (0.43-14.5)
N(%TS)	13.1 ± 9.09 (4.12-37.4)	10.9 ± 5.58 (6.02-24.5)	11.3 ± 4.68 (5.62-23.0)	12.8 ± 5.16 (4.18-28.0)
NDF(%TS)	39.5 ± 15.2[b] (17.34-59.6)	38.7 ± 7.81[ab] (24.36-48.9)	29.5 ± 13.2[a] (3.79-48.0)	34.5 ± 12.4[ab] (5.25-56.62)
ADF(%TS)	20.8 ± 9.28[b] (8.08-36.3)	19.6 ± 4.82[b] (12.3-27.5)	12.6 ± 6.52[a] (1.07-21.2)	16.6 ± 7.52[ab] (2.24-36.2)
ADL(%TS)	8.96 ± 3.55[b] (4.46-14.1)	8.88 ± 2.66[b] (5.43-16.1)	5.12 ± 2.73[a] (0.39-10.2)	6.78 ± 3.57[a] (0.59-18.3)
EE(%TS)	6.94 ± 2.76[a] (3.58-12.2)	9.32 ± 3.56[ab] (4.03-15.5)	13.0 ± 4.31[c] (6.23-18.8)	10.9 ± 4.03[bc] (2.93-24.9)
pH	7.76 ± 0.13[b] (7.53-8.03)	7.6 ± 0.33[ab] (6.98-8.16)	7.35 ± 0.57[a] (6.34-7.92)	7.42 ± 0.41[a] (6.41-8.05)
EC(mS/cm)	22.04 ± 8.15[ab] (10.1-44.6)	15.6 ± 5.90[a] (6.26-25.6)	19.8 ± 11.3[ab] (2.65-46.6)	24.5 ± 13.5[b] (6.58-53.4)
NH_3 (mg/L)	2853 ± 1101.3[ab] (1255-4740)	1995.5 ± 886.6[a] (800-3351)	2223.2 ± 1497.2[a] (397-5247)	3428.5 ± 2207.9[b] (612-11950)
VFA total (mg/L)	2512.7 ± 2213.1[a] (266.6-5393.6)	2372.5 ± 2504.4[a] (98.9-8410.2)	6044 ± 5453.4[ab] (697.9-16902.3)	6597.3 ± 6246.3[b] (56.46-21696.7)

[1]TS= total solids, VS= volatile solids, N= nitrogen, NDF= neutral detergent fiber, ADF= acid detergent fiber, ADL= acid detergent lignin, EE= extract ether, EC= electrical conductivity, NH_3= initial ammonia in sample, VFAtotal= the total volatile fatty acid
Different letters indicate statistical differences among productivity orientations ($p<0.05$)

The case of the pH is very interesting because, as reported in the literature, it is much related to NH_3 emissions (Cahn *et al.,* 1998), and a location effect on pH was detected. The pH could vary depending on the zone, because the water in the east of Spain is more basic than the obtained in the centre of Spain, so the pH of the slurries would be presumably higher. Another factor that can be related with the pH is the VFA (volatile fatty acids) content. When there is a higher of volatile fatty acids dissolved in the slurry the pH is lower like in the weaners and growing pigs. Figure 2 shows the variation of the pH as a function of the quantity of VFA.

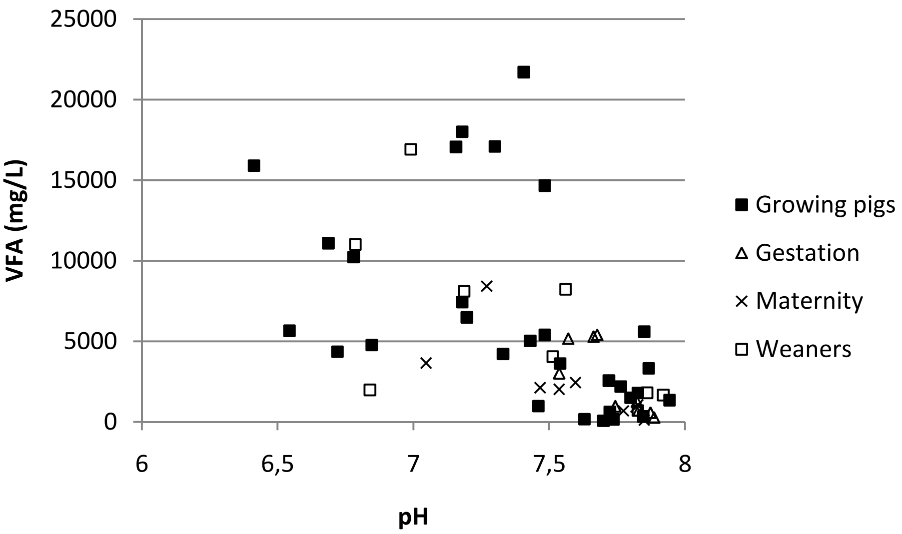

Figure 2 Relationship between pH and volatile fatty acids

The pH values differed statistically among orientation. The higher values of pH corresponded to the gestation sows (7.76) and maternity (7.60) that at the same time have the lowest content of VFA (2513 mg/L for gestation sows and 2373 for maternity sows). In growing pigs and weaners is the opposite situation is found and their pH value is on average lower: 7.42 for growing pigs and 7.35 for weaners, whereas the quantity of VFA is higher (6597 for growing pigs and 6044 for weaners).

The electrical conductivity can have also an explication; the lowest value is found in the maternity sows. This parameter followed a similar tendency to NH_3 content in the slurry. A possible explanation for this is that the conductivity depends on the amount of cations and anions dissolved in the slurry, and the production of milk entails high needs of cations like Ca^{2+}. Therefore, in the slurry the quantity of these components is expected to be lower, as well as the electrical conductivity (15.6 mS/cm). The weaners have also high needs of cations, but less than the maternity, and the values of the electrical conductivity is also low (19.8 mS/cm). This parameter is statistically significant ($p<0.05$) for productivity orientation.

3.2. – Emissions of NH_3 and CH_4

After describing all the diet and slurry characteristics, the next step was to quantify the emission of CH_4 and NH_3 of the samples, which is shown in Table 4.

The emission of NH_3 depended on the productivity orientation. In the growing pigs the value of this emission are the highest, in fact there are statistically significant differences ($p<0.05$) with the others productivity orientations (gestation maternity and weaners). The value of the emission of the growing pigs is 118.5 mg/L/day, for the other categories are gestation 87.6 mg/L/day, weaners 77.6 mg/L/day and maternity 66.8 mg/L/day. As for slurry composition, a very high variability was found for NH_3 emissions.

Table 4 Emission of NH_3 and CH_4

Analytical parameter [1]	Productivity Orientation			
	Gestation	***Maternity***	***Weaners***	***Growing Pigs***
E NH_3 (mg/L/day)	87.6 ± 16.2^a (57.9-122.1)	66.8 ± 21.9^a (34.9-100.9)	77.6 ± 46.6^a (15.4-155.9)	118.5 ± 54.7^b (27.2-237.2)
B_0 (mL CH4/gSV)	234.3 ± 148.6^a (52.2-517)	179.4 ± 80.2^a (25.9-327)	350.6 ± 137.7^b (96.8-572)	343.9 ± 155.0^b (36.6-589)

[1]E NH_3= ammonia emission, B_0= potential emission of methane
Different letters indicate statistical differences among productivity orientations ($p<0.05$)

According to MTD MAPA (2006), NH_3 emission depends on the chemical composition of the slurry, the physic chemical characteristics of the slurry, the surface of emission and the environmental conditions. Therefore, factors related to the productivity orientation may be affecting slurry composition and thus NH_3 emissions. The NH_3 dissolved in the slurry is in equilibrium with the ammonium. This equilibrium changes at high pH values, turning in NH_3 and causes a higher emission (Cahn *et al.,* 1998). However, in our study growing pigs presented the highest emissions despite having lower average pH than other animal types. The NH_3 content in the slurry, which is the source of NH_3 to the atmosphere, was higher for fattening animals, with is in accordance with the previous theory. This study agrees with the data reported by MTD MAPA (2006) where growing pigs is considered the productivity orientation with more emission in comparison with other productivity orientations.

The potential emission of CH_4 also differed among productivity orientations. The animals emitting more CH_4 to the atmosphere were weaners (350.6 mL CH_4/gSV) and growing pigs (343.9 mL CH_4/gSV). The sows produced less CH_4 and there was a statistically significant difference ($p<0.05$) with the other group. The emission of the gestation sows is 234.3 mL CH_4/gSV and the maternity sows emit 179.4 mL CH_4/gSV.

It is important to remark that the units of emission are not the same in the literature, both for NH_3 and CH_4. In our study, results are presented relatively to slurry volume, whereas in many studies it is presented on animal place basis. In the study by Coma and Bonet (2004) the CH_4 emission by reproductive sows (21.1 kg/animal/year) are higher than the maximum emission of growing pigs (11 kg/animal/year). Also, there is a similar case with the NH_3 emission found by Groot Koerkamp *et al.* (1998). The results of that study indicate that sows produce more NH_3 on animal place basis (503 mg/h per animal) than finishing pigs (185 mg/h per animal). However, when expressing emissions per animal weight, reproduction sows in slatted floor (1049 mg/h/500kg live weight) emit less NH3 than finishing pigs (2592 mg/h/500kg live weight). Therefore, similar results can be found in our study: growing pigs produce more NH_3 emission than the sow per production unit (volume of slurry).

All the data of this study have a huge variability, because samples were collected from commercial farms, with different origin of the animals, different environmental ambient, different quality of water (lower or higher levels of calcium carbonate). Also, although farms were selected according to similar management, small differences in management could increase this variability.

Figure 3 shows the relation between CH_4 and NH_3 emissions. Different productivity orientations (growing pigs, gestation, maternity and weaned) are distinguished. The equation relating both variables is CH_4 (mL CH_4/g SV) = 211 + 0.89·NH_3 (mg/L/day). This relationship was significant ($p=0.016$), but poorly relevant ($R^2 = 0.0769$). This means that there is a weak relationship between B_0 and the NH_3 emission and therefore, emission mitigation techniques could reduce emissions of both gases independently.

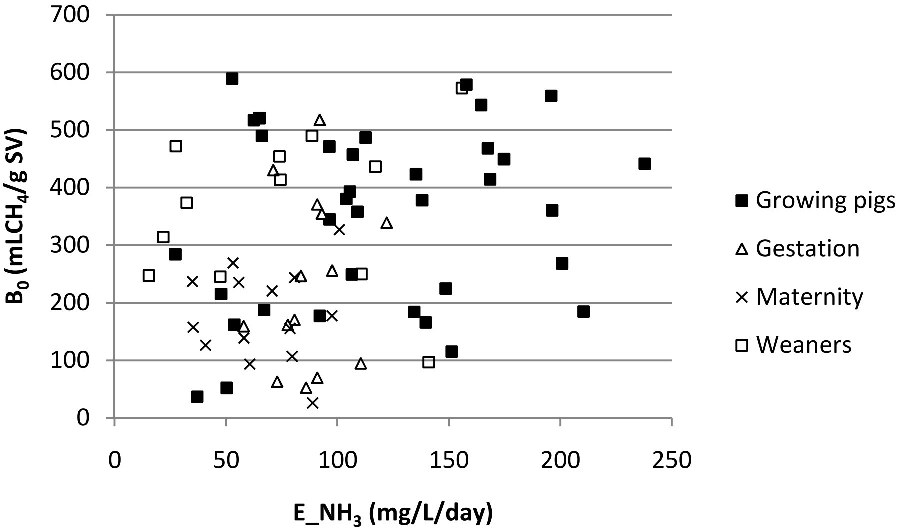

Figure 3 Relation between NH_3 and CH_4 emissions

3.3. – Factors affecting gas emissions

The second analysis of the data is the correlation coefficient between the variables with the emissions. In Table 5 the correlation between the variable and the different parameter and the p-value are shown.

The parameters most correlated to the more emission of NH_3 in this study were: the ammonium dissolved in the slurry (r=0.69) and electrical conductivity (r=0.58). This indicates that when a sample of slurry has a higher ammonium dissolved, the emission of NH_3 to the atmosphere is higher. The same was found for electrical conductivity, which is probably related to the close relationship between EC and NH_3 in slurry (r=0.86, $p<0.001$). Cahn *et al.* (1998) indicated that lowering the crude protein is an effective way to reduce NH_3 concentration and slurry pH, and consequently to reduce NH_3 emission. Although in our study no clear relationship between NH_3 emission and crude protein is found, the ammonium dissolved in the slurry was considered the best parameter to predict the emission of NH_3.

If the content of crude protein in the diet increases, the content of ammonium in the excretion also increases (Vu *et al.,* 2009). It has been reported that this increase has much more importance in the urine than in the faeces. This situation can cause then the positive relation between the C/N ratio in faeces material, which can stimulate CH_4 gas production (Jogensen, 2007). However, in our study the ammonium content in the slurry is not statistically correlated to the accumulated potential production of CH_4.

Table 5 Correlation of the NH_3 and CH_4 emission with the different parameters of slurry

Analytical parameter [1]	B_0			Emission NH_3		
	r	n[2]	P-value	r	n[2]	P-value
pH	-0.51	78	<0.001		77	NS
EC	0.23	78	0.041	0,58	77	<0.001
DM		78	N.S.	0,29	77	0.011
VS		78	N.S.	0,29	77	0.009
NDF	-0.43	78	<0.001		77	NS
ADF	-0.53	78	<0.001		77	NS
ADL	-0.64	78	<0.001		77	NS
EE	0.54	78	<0.001		77	NS
N		78	N.S.	0,23	77	0.047
NH_3		78	N.S.	0,69	77	<0.001
Biogas	0.92	78	<0.001		77	NS
VFAtot	0.63	58	<0.001	0,36	58	0.006

[1]EC= electrical conductivity, DM= dry matter, VS= volatile solids, NDF= neutral detergent fiber, ADF= acid detergent fiber, ADL= acid detergent lignin, EE= ether extract, N= nitrogen, NH_3= slurry ammonium, VFAtot= total volatile fatty acid
[2] Number of measurements

The content of fibre in the slurries had a negative influence on CH_4 emission. When the quantity of fibre in the slurry increases, then the emission of CH_4 decreases. For that reason, in diets with lower proportion of fibres (growing pigs and particularly weaners) the production of CH_4 emission would be higher. The correlations of each type of fibre with B_0 were: NDF (r=-0.43), ADF (r=-0.53), ADL (r=-0.64). This correlation decreases in order to how difficult is to metabolize the substance. The lignin is a structural polymer that the pigs cannot metabolize and to the microorganism is very inaccessible. However the structure of hemicelluloses is simpler so the microorganisms can use them to obtain energy and their coefficient is lower.

In relation to volatile fatty acids (VFA), there is high correlation with the potential CH_4 emission, because microorganisms can obtain energy easily from these substances. The correlation coefficient is 0.63 so it means that when the VFA are presents the emission of CH_4 is enhanced. However, other studies (Vedrenne *et al*., 2008) stated that there could be an inhibition of the methanogenesis (production of CH_4 by the microorganism), because VFA can acidify the environment and thus inhibit the CH_4 production. However, as it said (Verdrenne *et al.,* 2008) the buffering capacity of the slurry is normally high enough to handle with this.

The correlation coefficient of the ether extract with B_0 is very high (0.54). As indicated by other studies (Nallatambi, 2009) fat is one of the nutrients used by methanogenic bacteria. The explanation of this is because the fat is an easy way to obtain energy for microorganisms; they can easily ferment the substrate and produce CH_4.

After the calculation of the correlation coefficients, the statistically significant parameters ($p<0.05$) were be used in a stepwise regression of CH_4 and NH_3 emission. The first analysis of multiple regressions was with the B_0. The parameters which were correlated with statistical significance ($p<0.05$) with CH_4 emission were used in this calculation: pH, EC, NDF, ADF, ADL, EE, and VFAtotal. The parameter biogas was not used because it has a strong relation between with the CH_4 emission because CH_4 is a main part of the biogas.

In the Table 6 it is shown the parameters which are necessary to explain the variability of the CH_4 emission.

Table 6 Multiple regression of B_0 as a function of slurry characteristics

Analytical parameter [1]	***Standard T***			
Parameter	***Estimate***	***Error***	***Statistic***	***P-Value***
CONSTANT	1343.2	335.4	4.00	0.0002
pH	-118.3	44.1	-2.68	0.0097
ADL (% TS)	-29.0	4.8	-6.01	0.0000
VFAtot (mg/L)	0.013	0.003	3.90	0.0003
[1]ADL= acid detergent lignin, VFAtot= total volatile fatty acids				

The analysis of stepwise multiple regression chose the parameters: pH, ADL and VFAtot to build the prediction equation for the variable CH_4 emission. This election makes sense because all the parameters chosen are very related with the variable. As it was said before, the fibre component is negativity related with the emission of CH_4, because the microorganisms cannot use that component to obtain energy, since the lignin is not degradable, the B_0 is negatively related with the ADL (Triolo *et al*., 2011). The volatile fatty acids are positivity related with the CH_4 emission because the microorganisms are able to use these components to obtain energy from the slurry (unlike fibre), and the pH are very related to the volatile fatty acids, because this components acidify the slurry ambient Therefore, probably the pH has no direct cause and effect relationship with CH_4 emission. Surprisingly, the ether extract was not included in the prediction equation although it was highly correlated with B_0. It can be because the other parameters already included in the model (e.g. ADL) already explain the variability that the ether extract explains.

These parameters explain the 69% of the variability of the CH_4 emission with this equation:

$$Bo\ (mL\ CH_4/g\ SV) = 1343.22 - 118.3 \cdot pH - 29.0 \cdot ADL(\%\ TS) + 0.013 \cdot VFAtot\ (mg/L)$$

The second analysis with the multiple regressions will be the NH_3 emission. The parameters which were correlated with statistical significance ($p<0.05$) with NH_3 emission were used in this calculation: EC, DM, VS, Ini_NH_3, Fin_NH_3 and VFAtot. In the Table 7 it is shown the best parameters to define the variability of the NH_3 emission.

Table 7 Multiple regression of emission NH_3 as a function of slurry characteristics

Analytical parameter [1]	***Standard T***			
Parameter	***Estimate***	***Error***	***Statistic***	***P-Value***
CONSTANT	33.39	8.97	3.72	<0.001
EC (mS/cm)	1.46	0.67	2.17	0.034
Ini_NH$_3$(mg/L)	0.03	0.004	7.12	<0.001
Fin_NH$_3$ (mg/L)	-0.02	0.004	-6.09	<0.001
[1]EC= electrical conductivity, Ini_NH$_3$= initial ammonia, Fin_NH$_3$= final ammonia				

The analysis of multiple regression "stepwise" chose the parameters: electrical conductivity, the initial ammonium dissolved in the slurry and the final ammonium in the slurry to build the prediction equation of the variable NH_3 emission. The initial NH_3 was positively related with the NH_3 emission because the more ammonium dissolved in the slurry the higher potential NH_3 to be emitted. In the opposite case the final ammonium was negativity related with the NH_3 emission because the more ammonium dissolved at the end of the test means that this ammonium is retained by different substances and therefore not emitted to the atmosphere. However, this variable cannot be used to predict NH_3 emission because it corresponds to the end of the emission study. The electrical conductivity has a direct relationship with the ammonium dissolved in the slurry (Table 5) because it is an ion and the ion increases the electrical conductivity. However, in the prediction equation it was incorporated as a negative term, probably due to collinearity with the ammonium in the slurry.

The next equation explains the 48 % of the variability associated to the NH_3 emission:

$$ENH_3\,(mg/L/day) = 46.25 - 0.29 \cdot EC\,(mS/cm) + 0.02 \cdot Ini\_NH3\,(mg/L)$$

This study evidences that the diet is a very important variation factor, because slurry composition (and therefore gaseous emissions) depends directly in the ration of each animal. In this study it has been demonstrated that there are significant differences among productivity orientations in terms of diet, slurry and emissions. In diets, important differences are found in fibre content. A fibrous ration and an adjusted ration in protein (gestation sows) seems to be linked to lower emissions of CH_4 and NH_3. In the opposite case, an energetic diet and animals with high needs of protein (growing pigs) generates higher CH_4 and NH_3 emissions. Therefore, changing the nutritional components of the diets, the emission can also be modified.

In this study, almost 70 parameters (ration components, slurry components and properties) have been analysed as they could influence in the CH_4 and NH_3 emission. After analysing all of these parameters the most important for the NH_3 emission were the electrical conductivity and the ammonium dissolved at the initial and at the final of the emission test. For CH_4 emission the important factors were the pH the fibre (above all the ADL content) and the volatile fatty acids. All of these parameters were combining to build an equation to predict the different emission analysed. A further study could quantify how different components of slurry (organic nitrogen, carbohydrates and fat) contribute to the potential CH_4 emissions, as they are primary energy sources for methanogenic populations. To reduce the environmental effects, it seems that rations must be more fibrous (being aware the digestive welfare limits). However, to increase the B_0, to obtain CH_4 and use it for energy production, it seems that using slurries from weaners and growing pigs is may be the most appropriate.

4. - Conclusions

From this study we obtained the following conclusions:

- In commercial farms there exists variability in feedstuffs and slurries. This involved variable emissions of NH_3 and CH_4. To reduce these emissions, it seems that there is possibility for improvement by means of feeding strategies.
- The emissions of NH_3 and CH_4 were poorly correlated between them, which may suggest independent emission mechanisms and abatement techniques.
- Growing pigs emitted more NH_3 than the other productivity orientations, per unit of slurry produced. Sows produced the lowest CH_4 emissions.
- Slurry fibre was inversely correlated with CH_4 emission, whereas fat content was directly related. Both parameters could be used to predict the parameter B_0.
- The dissolved ammonium and electric conductivity of slurry were directly correlated with NH_3 emission. Therefore, they seem to be appropriate parameters to estimate potential NH_3 emission.

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