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Application of ion-exchange-based additive to control ammonia emissions in fattening pig barns with slatted floors

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ABSTRACT

The intense productivity related to the livestock sector has led to the development and application of different technologies and procedures to mitigate, mainly, NH_3 emissions. The addition of ion-exchange-based additives, such as Active NS, is one of the practices that may help reducing nitrogen emissions. In this study, the use of Active NS to mitigate NH_3 emissions in pig barns with slatted floor has been assessed during three pig fattening cycles. Two naturally ventilated identical barns were used to carry out the experiments at full-scale. Active NS was only applied in one of the barns while the other one was used as a reference to compare ammonia emissions between both barns during a 1-year monitoring campaign. The concentration of ammonia in the air at different points of each barn besides the ammonia emission rate generated directly from the slurry were measured monthly. The maximum reduction of ammonia emission (ranging from 17.6% to 38.3%) was systematically obtained at mid fattening cycle, where the concentration of Active NS in the slurry was between 40 and 45 g m^{-3} . The retention of ammonium into Active NS structure caused an increase of total nitrogen in the slurry of 19.6% compared to the control barn. This result indicated that the application of Active NS promoted better nitrogen retention in the slurry, thus avoiding its loss by volatilization during the storage of slurry. Lab-scale experiments were additionally performed in order to validate the results observed at full-scale under controlled conditions resulting in similar findings and confirming the adequacy of Active NS optimal dosage.

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1. Introduction

Ammonia (NH_3) is a hazardous compound that contributes to acid deposition and eutrophication. Moreover, NH_3 reacts with atmospheric acids (sulfuric, nitric, and hydrochloric acids), forming (secondary) particles that contribute significantly to the burden of particulate matter in the atmosphere (Webb et al., 2005). In addition, NH_3 is also well-known for its toxicity, which converts this compound into a potential health hazard for human beings and animals' welfare. Specifically in livestock housing, NH_3 represents a health risk for animals and humans since long term exposures to NH_3 combined with dust cause severe lung diseases (Seedorf and Hartung, 1999). It has also been reported that prolonged exposure to atmospheric NH_3 affects absolute blood cell counts, lymphocytes, and monocytes, for NH_3 concentrations up to 35 ppm_v .

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Anomalous serum haptoglobin and serum cortisol concentrations besides less feeding behavior have also been found in animals exposed to 50 ppm_v of NH₃ (Von Borell et al., 2007).

The agricultural sector is currently responsible for the vast majority of ammonia emissions in the European Union (2015). The EU legislation restricts ammonia emissions since 2010, targeting an ammonia emission reduction of 15% by 2030 (European Environment Agency, 2019a). Due to the lack of emission reduction efforts in the sector, over the period 2014–2017 the overall increase was 2.5% (European Environment Agency, 2019b). Agriculture was responsible for 94% of EU-28 NH₃ emissions in 2011 (EAA, 2017), and particularly in 2013, the agricultural activities in the EU-28 resulted in the emission of 3.6 Mt of ammonia to the atmosphere (European Union, 2015). The European Pollutant Release and Transfer Register shows that the largest portion, by far, of ammonia emissions generated in industrial sectors has its origin in the intensive rearing of poultry or pigs (E-PRTR, 2017). The annual consumption for pork products averages around 40 kg per capita in EU, a level that is higher than the overall poultry, cattle, sheep and goat products consumed (European Union, 2011). Following the intensive production of pigs, in 2017, the number of pigs in the EU achieved almost 148M head (FAOSTAT, 2017) and the total ammonia emissions for the whole European pig sector were estimated to be 606 Kt of nitrogen per year (Santonja et al., 2017).

The intense productivity related to livestock sector has led to the development and application of different technologies and procedures to mitigate, mainly, NH₃ emissions. The techniques to reduce NH₃ emissions from livestock housing can be separated into three general categories: (1) nutritional measures to reduce the amount of manure and its nitrogen content (2) utilization of physical and chemical additives and (3) optimization of livestock housing design and storage covering. Potential control strategies for NH₃ emission from animal production facilities include changing animal diet, redesigning or renovating barns, cleaning the exhaust air from buildings, treating manure, and improving the application of manure to land. In practice, to achieve optimal NH₃ volatilization abatement in animal production operations, the combination of these control strategies is frequently performed (Ndegwa et al., 2008). At full scale level and for the purpose to moderate the emissions from livestock housing, one of the best available techniques (BAT) to avoid NH₃ emissions from pig slurry consists of the slurry acidification (Kai et al., 2008; Misselbrook et al., 2016). The acid is added to the slurry in order to lower the pH to about 5.5 in the slurry pit (Santonja et al., 2017). Slurry acidification to pH values below 6.0 can be very effective to reduce NH₃ emissions, resulting in reductions over 99%, due to its pK_a of 9.26, compared with untreated slurries with typical pH values ranging from 7.0 to 8.0 (Kai et al., 2008; Petersen et al., 2012). However, the main drawbacks of this technique consist of personnel risks for concentrated acid management, high cost of the acid, corrosion and CO₂ and H₂S emissions generated (Fangueiro et al., 2015). Another example of BAT consists of installing cooling pipes in contact with pig slurry in order to decrease the temperature and prevent the volatilization of ammonia (usually less than 12 °C). Cooling intensities ranging from 10 W m⁻² to 50 W m⁻² are usually required for gestating sows and fattening pigs housed on partly slatted floors (Santonja et al., 2017). Apart from slurry acidification or cooling, the application of ion-exchange-based additives (IEbA), such as natural zeolites, activated zeolites or clay minerals, is one of the strategies that may help reducing nitrogen emissions. Moreover, the addition of IEbA to the pig slurry diminishes notably the high costs associated to the acidification and cooling strategies. High affinity to ammonia ions is a well-known feature of IEbA (Rhodes, 2010); they remove NH₃ from slurry by trapping and exchanging it in its crystalline structure. As an example, zeolite is a kind of mineral with an open reticular structure which allows the entrapment or release of various cations as a consequence of cation exchange mechanisms (Venglovsky et al., 2005) and adsorption (Bernal et al., 1993; Venglovsky et al., 2005). Zeolites are naturally occurring three-dimensional, microporous, hydrated aluminosilicate minerals characterized for showing high internal surface areas (Bíreš et al., 2005). Additionally, zeolites have been proven, at lab-scale, to enhance nitrogen retention in the solid fraction of pig slurry when added previously to the solid-liquid separation stage (Vargova et al. 2002). Taking into account the adsorption property of IEbA, many studies have also investigated the influence of this additives on NH₃ and nitrogen retention during waste treatments, such as composting (Cao et al., 2019; Giacomini et al., 2014; Li et al., 2012; Wang et al., 2017) and thermal drying (Liu et al., 2019). IEbA have been even tested as a dietary supplement to improve pigs' welfare but this practice could also mitigate ammonia emissions once pig slurry is excreted (Kim et al., 2005; Milic et al., 2005; Tatar et al., 2012). Even with these positive precedents, to the best of our knowledge, the use of IEbA, such as zeolites or clay minerals, as physical additives in the slurry has not been investigated up to date in full-scale pig farms.

Besides the abovementioned procedures and additives applied to directly reduce the emissions released from the slurry pit, many other additives have been used to mitigate the emissions of NH₃ associated to slurry management and treatment activities, especially during composting. As an example, biochar has been widely cited as one of the most convenient additives to mitigate NH₃ emissions during pig slurry composting, being used as a single additive (Liu et al., 2017; Steiner et al., 2010) or combined with other additives such as zeolites (Awasthi et al., 2016) or commercial bacteria (Mao et al., 2018). Sulfur has also shown effectiveness to mitigate NH₃ and odor emissions during composting (Li et al., 2020; Gu et al., 2018) as well as the application of enriched ammonia oxidizing-bacteria, which has been mainly used for nitrogen retention purposes resulting in the mitigation of the emissions both during storage and composting of pig slurry (Zhang et al., 2016a). Combined use of nitrification inhibitor and struvite crystallization (Jiang et al., 2016) and pyrogorskite addition to composting (Pan et al., 2019) have been also implemented to mitigate NH₃ emissions.

Considering the overview about the best available techniques and additives used to mitigate ammonia emissions from pig slurry, the present study aimed to demonstrate the environmental and economic feasibility specifically associated to the application of ion-exchange-based additives to pig slurry stored under slatted floor pig barns. This study focuses on the reduction of ammonia emissions directly from the slurry pit, which turns it into a pioneer solution applied to mitigate the emissions in pig housing systems and to favor the nitrogen retention in pig slurry post-treatment activities.

2. Materials and methods

2.1. Farm monitoring (in-situ)

2.1.1. Farm description

Full-scale testing and monitoring developed in this study was carried out in a pig fattening farm located in Catalonia (Spain). The farm had two identical fattening pig barns with a slatted floor system and a slurry pit underneath. The barns had a dimension of $33 \times 10 \times 10$ m, with a pig capacity of 400 pigs/barn. The slurry pit of each barn had a volume of 198 m^3 , that was designed considering the daily increase in the level of slurry ($< 198 \text{ m}^3$ by the end of each cycle). The slurry level was identical in both barns and followed the same increase rate since the number of pigs remained similar in all the cycles. The average evolution of the slurry level along the cycles is given in the Supplementary Material (Table S3). The lateral and roof windows positions were identical and following the same orientation, to ensure an identical natural ventilation inside the barns. Windows were fully or partially open depending on the season. One of the barns (Barn 1, as B-1) was used as a control and the second barn (Barn 2, as B-2) was used for testing (application of a commercial ion-exchange-based additive).

2.1.2. Fattening cycles description

Three pig fattening cycles were monitored in this study. Each cycle lasted 4 months, resulting in a 1-year monitoring campaign, thus, covering seasonal variability. Cycles were distributed as follows: cycle 1 (C-1) from Sept. to Jan. (fall-winter, first year); cycle 2 (C-2) from Feb. to May (winter-spring, second year); cycle 3 (C-3) from Jul. to Sept. (summer, second year). At the beginning of each cycle, the following actions were performed: (1) the slurry was removed as much as possible from the pit down to one third of the total capacity; (2) addition of a commercial ion-exchange-based additive (IEbA) (Active NS, FCSI, Denmark) to the remaining slurry in the experimental barn; (3) 400 piglets (25–30 kg) were located into each barn and were fattened up to 110–120 kg.

The supplier of the commercial IEbA, Active NS, recommended a concentration of 20 g m^{-3} to reduce ammonia emission. Active NS powder is a 100% natural product primarily composed of three different types of pre-processed clay minerals. The unique blend gives the product an exceptionally high ion-exchange effect and a binding capacity of 60 g of ammonium in 1 g of Active NS. The porous substances in the powder are structured as an open lattice of tetrahedrons with inner cavities capable of adsorbing and releasing ions, essentially operating as a molecular sieve. The adsorbent works according to the principle of exchanging negatively and positively charged ions.

Therefore, the amount added in the testing barn was calculated to achieve a concentration of 20 g m^{-3} of Active NS by the end of the cycle considering the daily dejections of pigs to the slurry pit. In this study, at the beginning of each cycle, 4 kg of Active NS were mixed with a small amount of water, and this mixture was added through the slatted floor at different points of the barn.

Monthly monitoring and sampling activities were performed in both barns along each fattening cycle (D1, D2, D3, D4). Ammonia emission rates ($\text{NH}_3\text{-ER}$) generated directly from the slurry stored in the slurry pit were monitored in one specific location of each barn (near the geometric center), as shown in Fig. 1. Pig slurry was also sampled from the same sampling point for further physical and chemical analyses. $\text{NH}_3\text{-in-air}$ maps (named air mapping in the present study) were also created by measuring the ammonia concentration in the air, at 21 evenly distributed points inside the barns as illustrated in Fig. 1. Further details about the performance of monitoring and sampling activities are given in the following sections.

2.1.3. Indoor air ammonia concentration: Air mapping

The concentration of ammonia in the air was measured using a multiparametric portable analyzer (MultiRAE Lite, RAE Systems, Spain) equipped with an electrochemical sensor for NH_3 analysis. The ammonia detection range was from 0 to 100 ppm_v , with 1 ppm_v increments. The air mapping represented the ammonia distribution pattern at surface level in each of the barns under study. As mentioned above, 21 points were measured to construct air maps. Besides the concentration of NH_3 , the air velocity and temperature were also measured using a thermal anemometer (Testo Ltd Testo –425, Alton Hampshire, UK) with a measuring range from 0 to 20 m s^{-1} , a resolution of 0.01 m s^{-1} and an accuracy of $\pm 0.015 \text{ m s}^{-1}$ for the air velocity, and a measuring range from 5 to $65 \text{ }^\circ\text{C}$, a resolution of $0.1 \text{ }^\circ\text{C}$ and an accuracy of $0.03 \text{ }^\circ\text{C}/^\circ\text{C}$ for the temperature. Both monitoring devices (MultiRAE and anemometer) were manually moved from one point to other, held in a fixed position by the operator until the stabilization of the displayed values. Both devices were placed 1 m above the slatted floor of each barn. Prior to each sampling day the sensors of the MultiRAE were calibrated using a calibration ammonia-nitrogen mixture cylinder of 50 ppm and an accuracy of $\pm 5\%$ (RAE Spain SL).

2.1.4. Ammonia emission rate

During C-1 the effect of the IEbA application on the pig slurry was evaluated in terms of average concentration of NH_3 in the air and % of N reduction, comparing Barn 1 (control) and Barn 2 (addition of Active NS). Pig slurry was also characterized. However, air ammonia concentration inside the barns is highly dependent on meteorological conditions and was not enough to assess the mitigation effect of the IEbA on ammonia released from the slurry pits due to its high dependence on meteorological conditions. Then, further information was required to clearly assess the mitigation effect

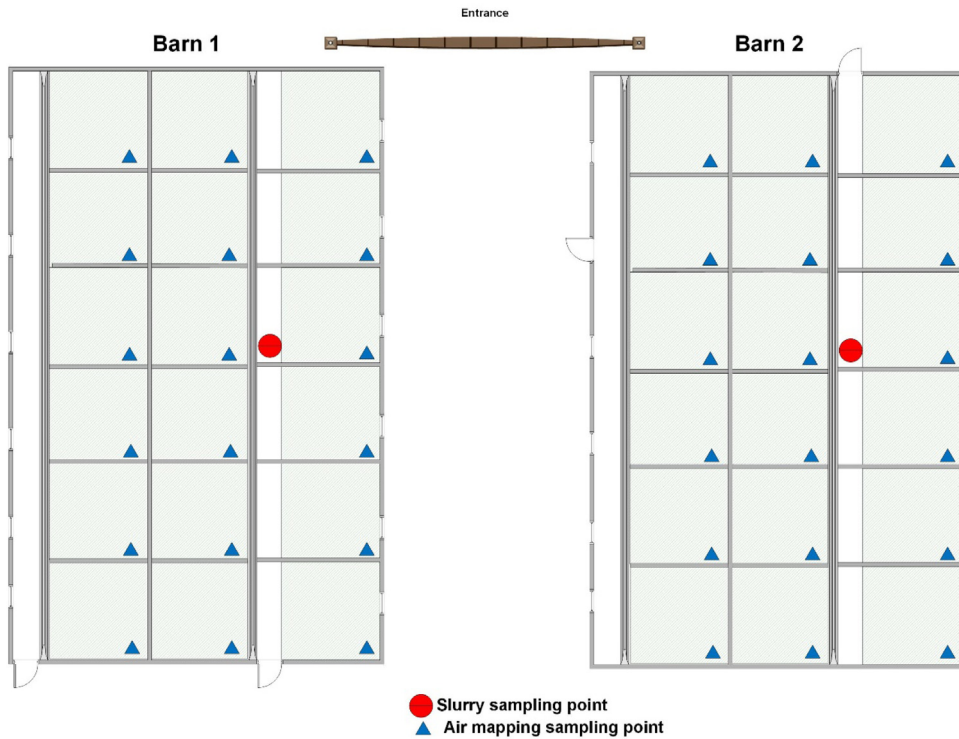


Fig. 1. Scheme of the barns used to carry out the study including air and slurry sampling points.

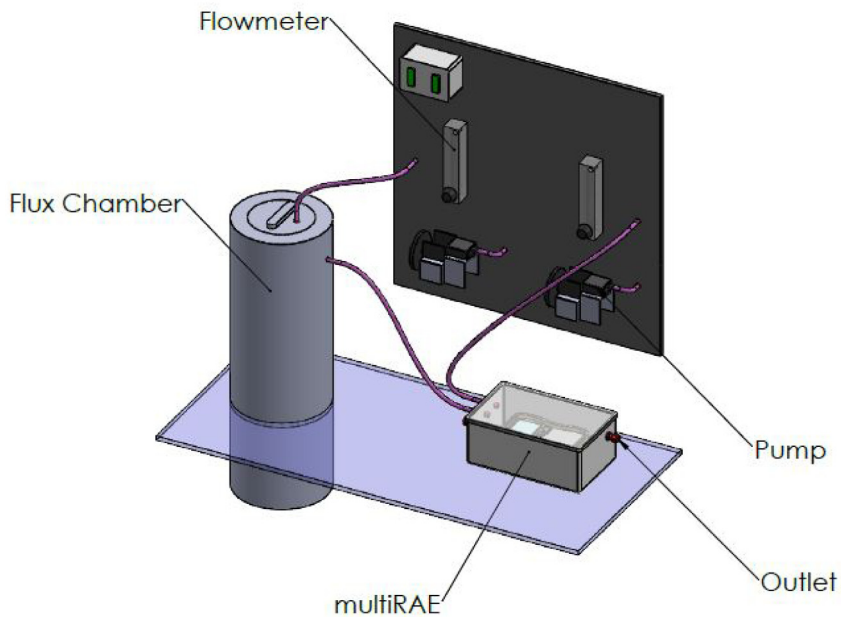


Fig. 2. Flux chamber set used to measure the ammonia emission rate generated from the pig slurry stored under the slatted floor of each barn.

of IEbA on ammonia released from the slurry pits. For this reason, a dynamic flux chamber (DFC) (Fig. 2) was designed and constructed to directly measure the ammonia emitted to the air from the pig slurry stored under the slatted floors. The implementation of the dynamic flux chamber in C-2 and C-3 helped complementing the study with more accurate data.

Fig. 2 shows the scheme of the DFC (200 mm Ø with 640 mm length). The use of a DFC has been considered by other authors (Blanes-Vidal et al., 2007) as a reliable method to assess the reduction of NH₃ emissions from this

type of waste. The enclosure of the DFC was effectively isolated from external conditions (such as wind velocity and temperature) avoiding the effect of meteorological factors on the measurements. Prior to the set-up of the DFC, the slurry was thoroughly mixed to obtain an integrated homogeneous sampling area (manually and identical procedure for both barns). Afterwards, the DFC was placed directly on the pig slurry, located 20 cm above the pit bottom. The headspace of the DFC allowed circulating air and extracting a dynamic flux of ammonia. To this aim, a clean air flow ($<1 \text{ ppm}_v$ of NH_3) of 4 L min^{-1} was introduced through a Teflon pipe via a lateral window of the barn into the DFC headspace to obtain a steady flux of ammonia from the pig slurry to calculate the NH_3 -ER. Exhaust air was released from the DFC and vented to a monitoring box. An additional flux of clean air was connected directly to the monitoring box to dilute the exhaust gas. Dilution ratios of 1:4–1:5 (exhaust air: total) were usually applied to prevent the saturation of the NH_3 sensor. The concentration of ammonia in the monitoring box was analyzed with the MultiRAE (Fig. 2). Air flow rates were controlled by two rotameters (Cole Parmer, USA). NH_3 emitted from the DFC was monitored until the concentration was steady (around 1 h). The NH_3 -ER was calculated through Eq. (1).

$$\text{NH}_3 - \text{ER} = C \cdot F_{\text{air}} \cdot A^{-1} \quad (1)$$

Where NH_3 -ER is the NH_3 emission rate ($\text{mg m}^{-2} \text{ min}^{-1}$), C is the NH_3 concentration in the exhaust air from the DFC (mg m^{-3}), F_{air} is the exhaust air flow rate ($\text{m}^3 \text{ min}^{-1}$), A is the mass transfer area (DFC section in m^2).

2.1.5. Nitrogen balance

The nitrogen balance assessment was evaluated using the nitrogen content in the slurry and slurry characterization. The nitrogen retained in each barn (Kg N /barn) was calculated by the mean of the emission rate calculated from the flux chamber, also considering the total nitrogen in the slurry at each sampling day. Thus, the difference of retained nitrogen in both barns for the performed cycles. The nitrogen calculations are more detailed in Supplementary Material (S3).

2.2. Lab-scale tests

A lab-scale experiment was also carried out to assess the mitigation of ammonia emissions, resulting from the addition of Active NS to pig slurry, under controlled conditions (Figure S1).

Lab-scale tests targeted the verification of Active NS optimal concentration recommended by the supplier. To this aim, a concentrated solution of zeolites was added to 0.4 L of raw pig slurry to set a final concentration of $20 \text{ g Active NS m}^{-3}$ slurry. A control test without the addition of Active NS was also included. The temperature was controlled at $20 \text{ }^\circ\text{C}$ through a thermostatic water bath. Once the Erlenmeyer flasks containing pig slurry were closed, an airflow of 10 mL min^{-1} was supplied to the headspace of the flask with airflow controllers (Bronkhorst, NL). The flask outlet was connected to a measuring graduated cylinder containing 0.2 L of boric acid (3%) with a mixed indicator (15 mL/L of the solution: 2 g methyl red + 1 g methylene blue in 1 L of ethanol 96%). The stripping of ammonia was induced during this process, thus, NH_3 was trapped by the acid and accumulated in the cylinders for two weeks. Samples of the acid were tested four times along the experiment and titrated using Hydrochloric acid (HCl 0.1 N). Lab-scale tests were carried out per triplicate.

2.3. Analytical methods

Slurry samples were stored at $4 \text{ }^\circ\text{C}$ before analysis and were analyzed in the first 7 days after sampling. The analyses of ammonium NH_4^+ and Total Kjeldahl Nitrogen (TKN) of the slurry were determined according to Standard Methods (APHA, 2005). All the measurements were performed per triplicate. TKN contained in solid and liquid fractions of the pig slurry was also analyzed. The sample was centrifuged at 4200 rpm for 10 min for the separation of solid and liquid fractions, the supernatant corresponding to the liquid fraction and the pellet to the solid fraction.

2.4. Statistical analysis

Statistical data analysis was carried out using U de Mann–Whitney and T student function on SPSS software, between Barn 1 (control) and Barn 2 (Active NS treatment). The level of significance was determined for each sampling day of cycles C-2 and C-3. The statistical significance ($p < 0.05$) was used for the data recorded from the DFC for C-2 and C-3 using U de Mann–Whitney. The T student function was used in the three cycles for the air mapping method to assess the difference of air inflow inside the barns.

3. Results and discussion

3.1. Air mapping at full-scale

Air mapping was performed to assess ammonia concentration in the indoor air of barns with and without the application of the ion-exchange-based additive. The average concentration of NH_3 in B-1 was higher than in B-2 uniquely in half of the sampling days (Table 1). Barns were naturally ventilated, and although they were located at the same farm and evaluated at the same time, differences in air inflows to the barn were detected, in C-2 (spring) and C-3 (summer).

Table 1
Average and maximum NH₃ concentration in the indoor air of B-1 and B-2 monitored along the cycles.

Cycle	Sampling day	Barn 1		Barn 2		NH ₃ emission reduction (%)	Airflow difference (%)
		[NH ₃] _{avg} (ppm _v)	[NH ₃] _{max} (ppm _v)	[NH ₃] _{avg} (ppm _v)	[NH ₃] _{max} (ppm _v)		
Cycle 1	D1	31 ± 9	47	30 ± 6	46	3.0	12
	D2	29 ± 7	41	19 ± 8	31	34	30
	D3	31 ± 5	38	15 ± 3	21	51	-10
	D4	18 ± 2	19	14 ± 2	18	22	6.0
Cycle 2	D1	41 ± 5	50	38 ± 2	40	8.4	29
	D2	11 ± 6	28	11 ± 5	22	-4.0	n.a. ^a
	D3	28 ± 8	41	27 ± 2	30	3.2	-7.3
	D4	7 ± 3	13	10 ± 2	13	-35	63
Cycle 3	D1	16 ± 9	32	17 ± 4	23	-5.0	48
	D2	10 ± 5	23	18 ± 5	25	-87	84
	D3	9 ± 4	19	10 ± 3	16	-11	55
	D4	13 ± 5	22	24 ± 8	45	-86	66

^aEquipment issue.

The windows of the barns were partially to fully open respectively during C-2 and C-3 to keep the barns aerated on hot seasons for animal welfare reasons. Instead, during the first cycle C1 (autumn-winter) the lateral windows of both barns were closed or partially opened (to prevent heat loss in the barn and a reduction of indoor temperature) making the airflow variations less evident and facilitating the interpretation of the results. The high variations in terms of air flowing into the barns caused a hindrance to obtain representative air maps. The NH₃ concentrations were highly influenced by the end of C-2 and C-3 (diluted), as the reduction of NH₃ in air concentration was not achieved as shown in Table 1. This could be justified by the abovementioned reason (windows closed in winter and partially to fully open in spring and summer cycles). Fig. 3 shows the NH₃ concentration distribution in the air (air mapping) inside the barns during the first fattening cycle (C-1). As can be observed in Fig. 3, NH₃ concentrations were clearly higher in B-1 compared to B-2, while similar air velocities were registered in both barns. Regarding the ambient temperature of the barns, similar to equal values were measured in all the cycles and for the four sampling days (detailed data is presented in Table S2 of the Supplementary Material).

The measured differences on airflows between the barns with and without the IEbA Active NS are shown in Table 1. For C-1 the difference of air velocities inside the barns was still significant ($p = 0.024$), however the NH₃ concentrations in B-2 was lower than B-1. During C-2 the difference started to be higher and more influencing; the p -value calculated for the measured air velocities was $p=0.006$. Likewise, the air velocity was statistically lower in B-2 with a $p = 0.001$ (precision of 95%) in the case of C-3, where the air flowing towards both barns was the leading cause of the limitation of the air mapping technic for the cycle. The average airflow difference between the barns from C-1 to C-3 was almost three times higher as 84% difference was recorder in C-3, that corresponded to -87% of NH₃ emission reduction (0.20 versus 0.03 m s⁻¹).

The interpretation of Active NS application influence on the ammonia indoor air concentration should be associated with a homogeneous ventilation to prevent any accumulation of particles. However, in the present study, the opening and closing of the windows was uncolorable, as the performance of the cycle must be carried out according to the typical conditions of a fattening cycle.

3.2. Ammonia emission rate at full-scale

NH₃-ER directly generated from the pig slurry stored under the slatted floor of the barns was estimated using a DFC. Mixing of slurry before setting up the DFC and the circulation of a fresh air flow through its headspace, forced the emission of ammonia and resulted in the appearance of a concentration peak (that lasted on 20 min in average), followed by decreasing and stabilization phases. After approximately 1 h, the steady NH₃ concentration monitored indicated the achievement of the mass transfer equilibrium. Table 2 shows the NH₃-ER calculated from the DFC data obtained, from both barns, during C-2 and C-3. In general, B-2 (the barn containing Active NS in the pig slurry) presented lower values ($p < 0.05$) of NH₃-ER than B-1 (control barn). Uniquely two exceptions were recorded, the sampling day D4 of C-2 and the sampling day D1 of C-3. The last sampling day of the second cycle there were 109 pigs more in B-2 than in B-1, the difference in the last days of the cycle is because the pigs were already being sent to the slaughterhouse which affected the reduction in terms of ER. The first sampling day of the last cycle there was a cleaning event in B-1 causing a decrease of the NH₃-ER. These are typical events that may inevitably occur at full-scale experimentation and highlights the complexity and value associated to the present study; however, despite NH₃-ER was higher in B-2 as an average, the recorded concentrations were not statistically significant ($p < 0.05$). Similar NH₃-ER trends were observed along cycles C-2 and C-3, reaching values up to 38.0% and 38.3%, respectively, the second sampling day. From the statistical analysis, it has been also determined that there is a significant difference between the emissions of ammonia in B-1 and B-2, in C-2 and in C-3. This indicates

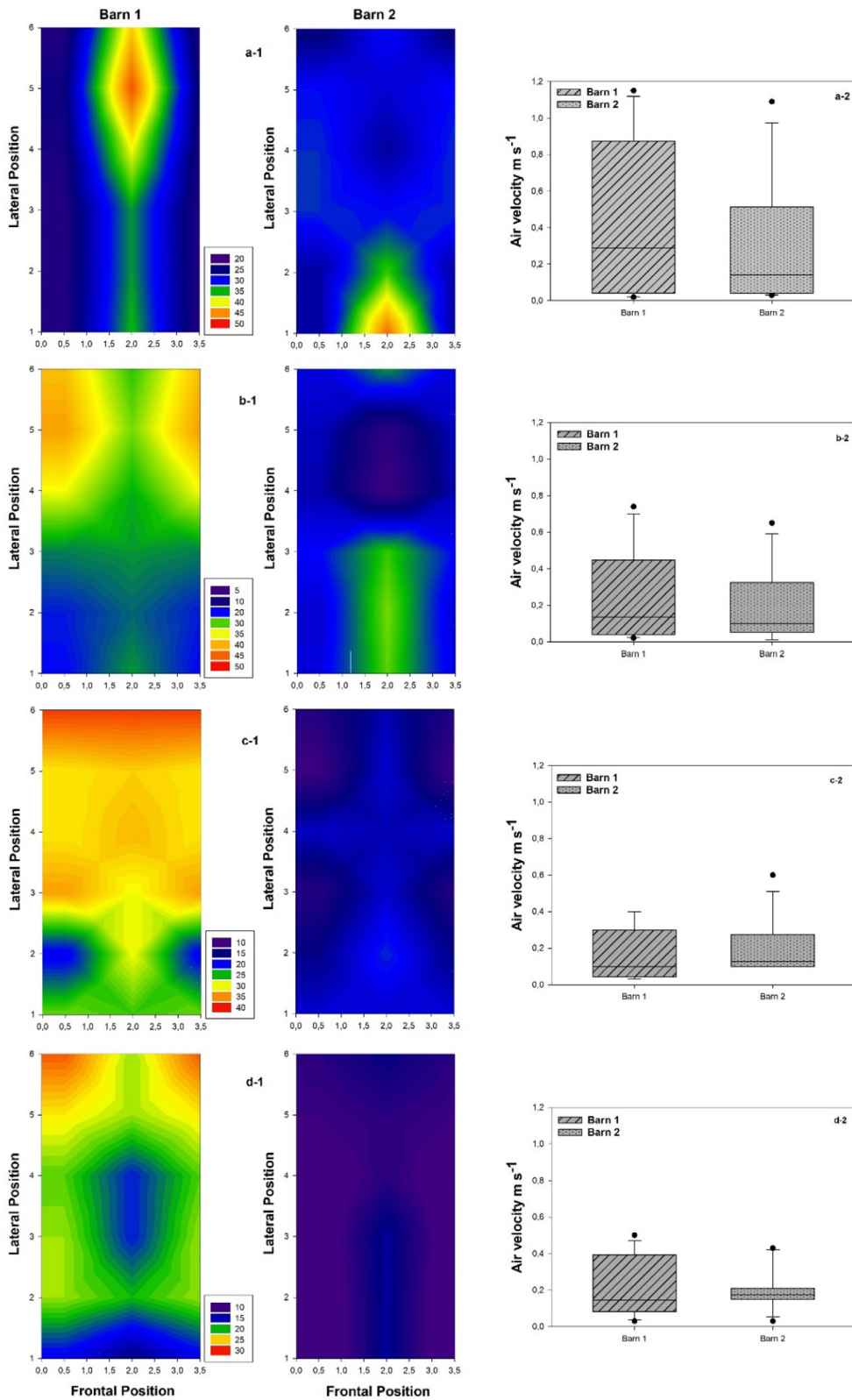


Fig. 3. Air mapping (charts on the left; in the legend the concentrations of NH₃ in ppm_v) and air velocity average and variation (charts on the right) corresponding to sampling days D1 (a-1, a-2), D2 (b-1, b-2), D3 (c-1, c-2) and D4 (d-1, d-2) of the first fattening cycle (C-1).

Table 2

Ammonia emission rate calculated from the dynamic flux chamber for cycles 2 and 3.

Cycle	Sampling day	Emission rate in B-1 (g N d ⁻¹)	Emission rate in B-2 (g N d ⁻¹)	Emission reduction (%)
C-2	D 1	179	148	17.6
	D 2	306	190	38.0
	D 3	706	495	29.8
	D 4	31.0	44.3	-43.0
C-3	D 1	358	432	-20.0
	D 2	906	559	38.3
	D 3	1014	870	14.0
	D 4	935	764	18.0

Table 3

Nitrogen balance in both barns during the fattening cycle.

	Cycle 1		Cycle 2		Cycle 3	
	B-1	B-2	B-1	B-2	B-1	B-2
Gas phase						
Total Emission Rate (kg N d ⁻¹)	n.a.		0.51 ± 0.3	0.34 ± 0.2	0.80 ± 0.3	0.66 ± 0.2
Total N emitted (kg N)	n.a.		60.7	41.1	96	79
N emitted from total N (%)	n.a.		5.9	3.9	10.2	8.1
Reduction of total N emitted (%)	n.a.		0	32.3	0	18.4
Slurry						
Total N increase (kg N)	510	540	471	551	345	429
Total N increase in the slurry (%)	0	5.6	0	14.7	0	19.6

Values shown in the table have been calculated as the averages of each cycle monitored.

that the concentration of NH₃ recorded from B-1 and B-2 are significantly different, that implies the validation of the influence of addition of Active NS on the slurry pit for NH₃ mitigation.

The addition of Active NS directly to the slurry pit exhibited successful performances in cycles C-2 (winter–spring) and C-3 (spring–summer). Experimental results at full-scale indicated that the application of this product is a cost-effective strategy to efficiently mitigate ammonia emissions regardless the seasonality. Then, the present study confirms for the first time, at full-scale and under seasonal influence, the proven benefits of Active NS application to pig slurry at lab-scale.

3.3. Nitrogen balance in the slurry

Apart from the monitoring of ammonia emitted from the DFC and the air mapping, samples of pig slurry (extracted from B-1 and B-2 each monitoring day) were characterized to assess the nitrogen balance in each cycle (Table 3).

Overall results indicated that B-2 emitted less ammonia to the atmosphere, in terms of NH₃-ER and total N. The application of Active NS engendered a total reduction in ammonia emissions of 32.3% and 18.4% in cycles C-2 and C-3, respectively. As expected, these reduction values (%) were aligned with the N emitted from total N contained in the pig slurry, which at the same time were of about 2-fold in C-3 (hottest season) rather than in C-2. As an example, N emitted (from total N in the pig slurry) in B-2 during C-3 was 8.10%, meaning a reduction of 20.4% with respect to B-1 for the same cycle, and 2.08-fold higher than in a colder season (3.89% in C-2). Results obtained herein indicate that the dosage of Active NS should be further optimized to target similar NH₃-ER along the year since ammonia generation rate increases with temperature, causing higher emission rates during hot seasons (Nimmermark and Gustafsson, 2005). As can be observed from Table 3, similar amounts of total nitrogen were retained in the pig slurry stored in B-2 for cycles C-2 and C-3 (19.6 kg N and 14.7 kg N, respectively), probably indicating the achievement of near-to-maximal retention capabilities of the Active NS applied.

Regarding the slurry analysis, the amount of total nitrogen in the slurry containing Active NS increased by 5.6%, 14.7% and 19.6% in C-1, C-2 and C-3, respectively. Fig. 4 represents the evolution of the total N remaining in the slurry along each fattening cycle. In C-1 the nitrogen available in the slurry, for both barns, is relatively similar along the whole cycle; then, by mid C-2 (D2 of C-2), the influence of Active NS was more effective regarding nitrogen retention in the slurry of B-2 compared to the slurry from B-1. In C-3 the effect of Active NS showed the same trend as in C-2, nevertheless, this last cycle showed less total nitrogen content than the previous cycle. Overall, at the beginning of all cycles the total nitrogen content (kg) in the control barn (B-1) was always higher than in B-2. Afterwards, Active NS started mitigating NH₃ emissions by blocking the nitrogen inside its tetrahedra structure, which allowed better retention of nitrogen in the pig slurry of B-2. By the end of the cycles, nitrogen retention was always higher in B-2.

Bíreš et al. (2005), among other authors, reported that IEbA, such as zeolites, remove ammonia from slurry by trapping and exchanging it in its crystalline structure. However, without elaborating a nitrogen mass balance, it is complex to confirm and assess the retention capability of IEbA, especially at full-scale, by uniquely analyzing ammonia in air and

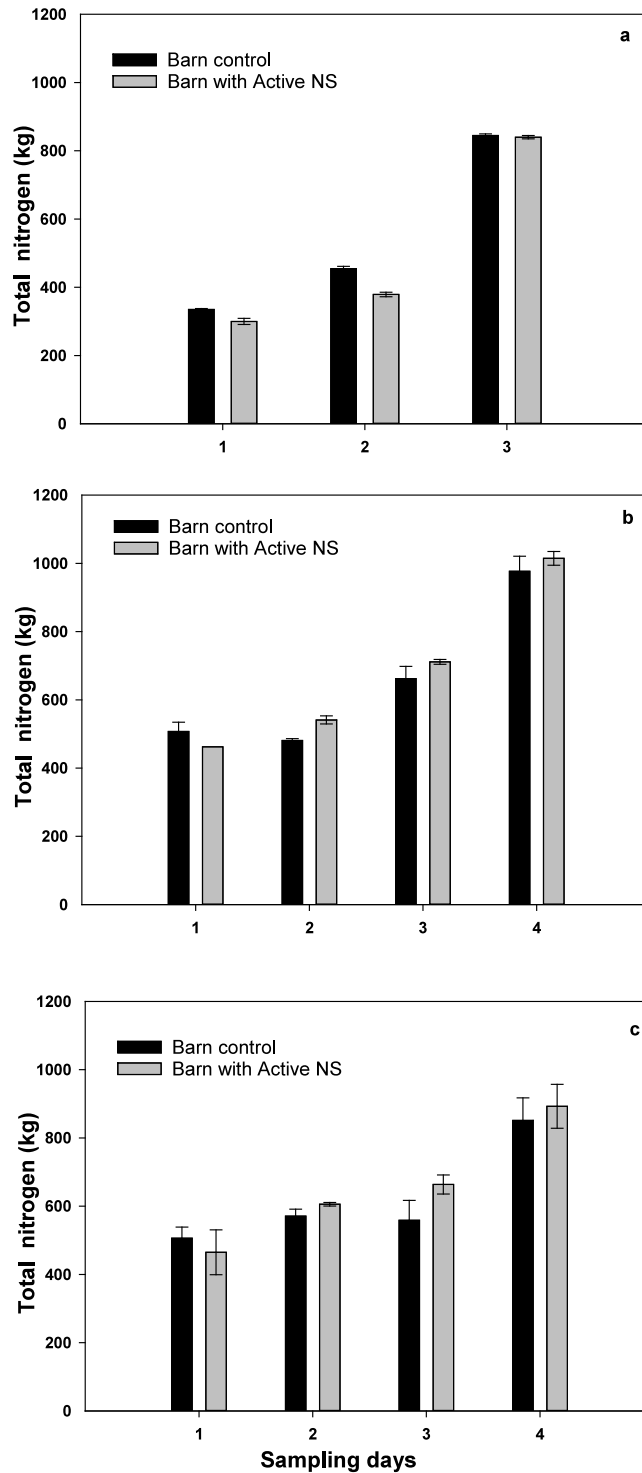


Fig. 4. Nitrogen retention in the slurry pit along the monitored cycles (a) C-1 (b) C-2 and (c) C-3.

ammonium in pig slurry. In the present study, the concentration of $N-NH_4^+$ in the slurry was quite stable and similar for both, the control barn and the barn with IEbA, for all the fattening cycles. The addition of Active NS did not show any effect during any of the fattening cycles in terms of $N-NH_4^+$ contained in the slurry. However, ammoniacal nitrogen is continuously generated enzymatically, from the urea, once excreted (Blanes-Vidal et al., 2007), underlining the importance

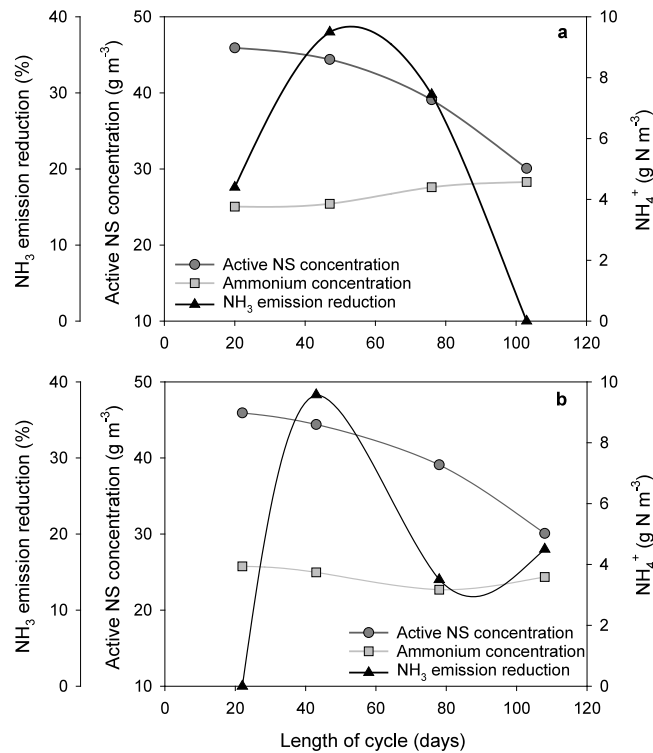


Fig. 5. Evolution of NH₃-ER, Active-NS concentration and ammonium concentration along cycles (A) C-2 and (B) C-3.

of analyzing the content of TKN in the pig slurry to clearly evaluate the effect of IEbA addition through the N balance. In this sense, Table S1 (shown in the Supplementary Material) summarizes the results obtained from the characterization of pig slurry, sampled from both barns during all the fattening cycles, where both NH₄⁺ and TKN are considered.

Fig. 5 represents the evolution of NH₃-ER, Active NS concentration and ammonium concentration along cycles C-2 and C-3. As mentioned in previous sections, the commercial IEbA was dosed at the beginning of each cycle, taking into account the final volume that should be achieved at the end of the cycle and the dosage recommended by the supplier (20 g Active NS m⁻³ pig slurry). The concentration of Active NS along each cycle was calculated by considering the initial amount added and the pig slurry volume accumulated each monitoring day. In Fig. 5 it can be observed that the maximum NH₃-ER was achieved almost two months after the cycle initialization, when the IEbA concentration was between 40 and 45 g m⁻³. The recommended concentration of IEbA was never achieved by the end of the studied cycles although Active NS effectiveness was already decreasing at mid-cycle, when its concentration was 2-fold the dosage recommended by the supplier. These results again indicate that the dosage of Active NS at full-scale and for long-term cycles should be still optimized. It has already reported that the saturation of adsorption sites of physical additives limits the adsorption capacity of N-NH₄⁺ and NH₃, and the NH₃ emission mitigation potential (Kastner et al., 2009). Moreover, the adsorption effect of NH₃ into acidic sites (Kastner et al., 2009) and N-NH₄⁺ onto negatively charged sites (Agyarko-Mintah et al., 2017) could also explain the loss of IEbA effectiveness with such a high dosage (45 g m⁻³ at the beginning of the cycles).

An optimization of the application of Active NS could be implemented in the farms, which consist of a weekly or monthly application of the optimum concentration to maximize the reduction, depending on the increase of the slurry inside the pit. The increase of the level of the slurry in the pit of the barns is represented by Eq. (2). At the beginning of the cycle, the level of the slurry rapidly increased with the pig growths to become uniform increase by the end (the level of the slurry is given in Table S3 of the Supplementary Material). Thus, a first application on the beginning of the cycle followed by another one by the middle of the cycle (after two months) could enhance the performance of Active NS and give better results.

$$S_i(\%) = 21.6 \cdot \ln(V_i) - 5.15 \quad (2)$$

Where V_i represents the existing volume of the slurry on the sampling day i ($i=1, 2, 3, 4$), and S_i the increase of pig slurry stored in the barn at the day i .

The addition of 4 kg of Active NS at the beginning of the cycle in order to achieve (20 g m⁻³) is a good compromise for the farmers, since the application is unique, however a good balance of Active NS addition and ammonia reduction should be taken into consideration.

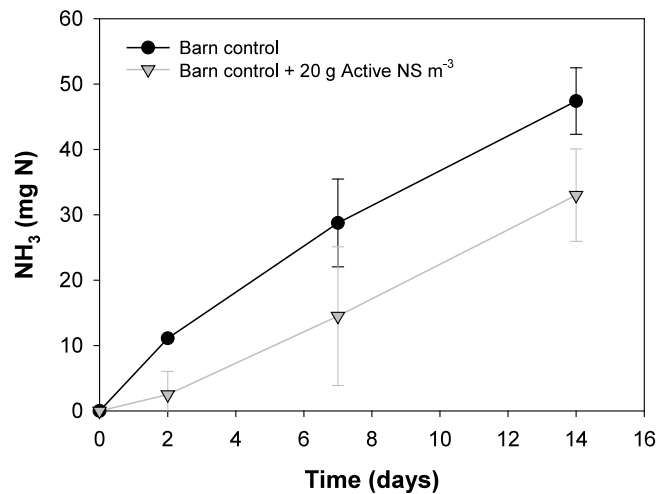


Fig. 6. Ammonia emission profiles obtained from Active-NS testing performed at lab-scale.

Regarding previous results reported in the literature it must be mentioned that, many studies have proven the benefits of IEbA application for nitrogen conservation and ammonia emission mitigation during the treatment of different wastes, such as composting of municipal solid waste (Ergun and O.N., 2014) or composting of sludge (Zhang et al., 2016b). Other studies also investigated the use of IEbA during the composting of pig manure in order to prevent nitrogen loss and to moderate the NH_3 emission during the process (Giacomini et al., 2014; Li et al., 2012; Wang et al., 2017). However, the evaluation of ammonia emissions mitigation and total nitrogen conservation, through the application of IEbA to the pig slurry at full-scale, has never been investigated to the authors' knowledge.

Other additives different than IEbA have also shown promising results during post-treatment activities of pig slurry, indicating that a proper combination of IEbA with them could result in the maximization of N emissions mitigation along the whole livestock manure management and treatment chain. As an example, Pan et al. (2018), reported that the acidic additives on sewage sludge composting had no negative effect of the quality of the compost, yet the conservation of N was improved during the process, elemental sulfur and phosphoric acid had the lower NH_3 volatilizations among the studied additives (0.80% and 0.98% of initial N, respectively). Tu et al. (2019) from the other side stated that the combination of biochar and microbial inoculation added to pig manure compost results on the increase of 59% of TKN through the reduction of NH_3 volatilization and N_2O production. Which is higher than the use of single biochar or microbial inoculation. Likewise, combined use of nitrification inhibitor and struvite crystallization to reduce the NH_3 emissions during composting showed promising results, significantly reduced NH_3 losses by 45%–53% (Jiang et al., 2016).

3.4. Ammonia emission rate at lab-scale

Tests performed at lab-scale, for 2 weeks and under controlled conditions revealed that an NH_3 -ER of 35% could be achieved applying 20 g Active NS m^{-3} of pig slurry (Fig. 6). This result confirmed the mitigation of ammonia emissions through the addition of such a low dosage of IEbA.

As can be observed in Fig. 6, the effect of Active NS was noted from the beginning of the experiment with higher percentages of NH_3 -ER associated than those obtained at full-scale. This result once again demonstrates the importance of testing this mitigation strategy at full-scale to clearly assess the performance under uncontrolled and variable conditions. The lack of IEbA mixing with pig slurry or the age of the pig slurry are two of the several variables affecting its effectivity. Even so, the effective mitigation of NH_3 emissions achieved linked to such a low dosage of additives to the slurry converts the application of IEbA into a successful alternative to other expensive or harmful strategies currently followed at full-scale. It must be pointed out that the average concentration of IEbA used for composting ranges between 1% to 10%, which is much higher than the dosage of IEbA required in the present study. Moreover, the use of acids directly to the slurry pit requires between 4 to 6 kg of acids to achieve a pH of 5.5 for 1 m^3 of pig slurry (MAPA, 2015). Portejoie et al. (2003) achieved 71% of NH_3 -ER reduction from a covered pig slurry storage applying zeolites, which is 86% higher than that obtained herein. However, these studies were performed at lab-scale, under well controlled conditions.

3.5. Economic approach of active NS addition for ammonia mitigation

An economic approach has been performed to evaluate the economic benefits associated to the application of Active NS to the pig slurry as an alternative to acidification, both considered efficient strategies to mitigate ammonia emissions in pig farms.

Regarding acidification, to achieve a pH of 5.5 for pig slurry, between 4 to 6 kg of concentrated sulfuric acid (95%–98% H₂SO₄) should be added to 1 m³ of pig slurry. The cost associated to the addition of sulfuric acid for treating pig slurry, include the acid cost, energy consumption and the maintaining cost, which are 0.72 € m⁻³, 0.17 € m⁻³ and 0.29 € m⁻³, respectively (Santonja et al., 2017). In addition, the application of this type of harmful products must be performed by trained staff (due to the level of safety required and the corrosive nature of the additive) and requires of maintenance activities over the time. This fact causes difficulties for the implementation of the acidification strategy by farmers.

Advantageously, due to the efficiency of the Active NS, a very low amount was required to mitigate the ammonia emissions. In the case studied, it was only necessary the addition of 4 kg of Active NS, in a barn of approximately 200 m³, at the beginning of each fattening cycle. The average price of IEbA similar to Active NS on the market is around 90 to 150 € tn⁻¹ depending on the supplier. Based on this value, the application cost of the IEbA is below 0.6 € in each fattening cycle, considering that the present method does not require maintaining cost nor energy consumption. Thus, the cost of the recommended concentration was 0.003 € m⁻³ and the optimum concentration found in the same study was 0.006 € m⁻³.

Regarding the cooling of the slurry as a technology for ammonia mitigation, the economic assessment was not performed to be compared due to the huge operational cost of the technology, moreover, the cooling pipes are more efficient in forced ventilated housing, which is not the case of the present study.

Hence, this study confirms that the application of an IEbA, such as Active NS, to pig slurry at full-scale is not only a successful strategy but economically more advantageous than other strategies applied to mitigate ammonia emissions, however achieving only the half of the efficiency than the acidification technique. Besides this, the use of pig slurry with zeolites could also improve the carbon footprint of its post-treatment.

4. Conclusions

The present study has proven that the addition of an ion-exchange-based additive (IEbA) to pig slurry stored in slatted floor barns is an environmentally friendly and economical and technically feasible strategy to mitigate ammonia emissions from livestock housing. Ammonia emissions and nitrogen balance were assessed along three pig fattening cycles, performed along 1 year at full-scale, using data from air mapping, dynamic flux chamber emissions and pig slurry characterization. The concentration of ammonia in the air inside the barns was highly influenced by air velocity, which required the use of a dynamic flux chamber. This methodology was guaranteed as the most adequate method for the assessment of ammonia emission rates in naturally ventilated housing systems. Data obtained from the DFC indicated that a dosage of 45 g m⁻³ of pig slurry of the commercial IEbA, Active NS, reduced up to 38.3% the ammonia emitted in comparison with the control barn. The analysis of pig slurry also revealed that a maximum increase of 19.56% total nitrogen was achieved in the pig slurry where Active NS was applied. A decrease of the additive effectiveness was observed by the end of the fattening cycles, indicating the saturation of the IEbA, applied at the beginning of each cycle. It was concluded that the dosage of Active NS should be further improved to optimize the mitigation of ammonia emissions in pig farms, recommending the addition of 20 to 45 g Active NS m⁻³ to the slurry pit on a monthly basis is to obtain optimal results.

CRedit authorship contribution statement

Imane Uald Lamkaddam: Investigation, Writing - original draft, Writing - review & editing. **Enric Blázquez:** Investigation, Writing - original draft, Writing - review & editing. **Lara Pelaz:** Conceptualization, Investigation. **Laia Llenas:** Resources, Funding acquisition, Project administration. **Sergio Ponsá:** Resources, Funding acquisition, Project administration. **Joan Colón:** Conceptualization, Investigation, Writing - review & editing, Project administration, Supervision. **Esther Vega:** Writing - review & editing, Supervision. **Mabel Mora:** Investigation, Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.eti.2021.101481>.

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