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Livestock manure storage: assessment of natural permeable covers as possible ammonia emission mitigation strategies

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Tesi di dottorato di:

Antonio Mautone

Coordinatrice del corso

Prof. Albino Maggio

Tutor

Prof.ssa Stefania Pindozzi

Abstract

Ammonia (NH_3) emissions are responsible of negative impact on environment and human health. After the volatilization ammonia returns to soil by precipitation. Ammonia emissions and consequent deposition can lead to soil acidification, water eutrophication, and formation of particulate matter causing respiratory disease. Along with these environmental and health aspects, ammonia emission is responsible for large losses of nitrogen from the manure and thereby fertilizer value of the livestock manure significatively decrease. Ammonia emissions are mainly generated from livestock operations. Factors that affect ammonia emission are generally related to manure management, climatic condition and manure pH and characteristics. The influence that farms and manure management have on ammonia emission has been widely assessed. Farm management and structure including housing, storage and spreading systems can lead to the ammonia emission in many ways. Possible mitigation strategies to reduce ammonia emissions have been investigated. Each strategy can have benefits and disadvantages even when properly applied. This work focus on the manure storage phase and the possible ammonia mitigation techniques that can be applied during this step of the manure management chain.

In particular, an overview on the DATAMAN dataset have been carried out; the database collects detailed information on how manure is managed worldwide. The effect of different manure management and livestock systems on the Emission Factors from the poultry livestock systems have been analyzed. From the data collected in the database, and also from the missing one is possible to define and improve potential future research opportunities and improvements on manure management chain. Secondly under laboratory condition the phenomenon occurring during the storage phase and the effect of natural permeable cover application on liquid digestate surface have been studied. The investigated covers are natural crust, straw, clay, and biochar. The overall emissions reduction observed ranged between about 7% up to 78%. The resulting data from this thesis can therefore provide the basis for a better understanding on manure storage, cover application as mitigation strategies to deeper the knowledge on manure management and possible mitigations techniques.

1 The ammonia emission issue

Ammonia (NH_3) is the primary form of reactive nitrogen in the environment released into the atmosphere (Sutton et al., 2013). Nitrogen losses are mainly generated from the agricultural and livestock systems. In particular, steps leading to NH_3 loss in the environment are the application of fertilizer to crops, animal excretion, housing systems, manure storage and manure application. Manure is defined as animal feces and urine plus bedding materials and water (Pain & Menzi, 2011). Agriculture activities are responsible for 81% of the total global ammonia emissions together with livestock excretion while livestock emissions represent itself around 35% of estimated N emissions from the agricultural sector (Wyer et al., 2022) (Uwizeye et al., 2020). As ammonia is a volatile compound, it is emitted as a gas from livestock manure slurry and it is responsible for atmospheric and environmental quality depletion (Sigurdarson et al., 2018). Ammonia deposition has negative repercussions on the environment, contributing to the acidification and eutrophication of terrestrial and aquatic ecosystems. Moreover, it's the biggest contributors to the formation of secondary particulate matter (PM2.5) in the atmosphere, when reacts with sulphuric and nitric acids (Erisman & Schaap, 2004). Particulate matter exposure can cause illnesses, in particular cardiovascular diseases such as chronic obstructive pulmonary disorder (COPD) and lung cancer. The concentrations of NH_3 and NH_4^+ are often summed together and defined as total ammoniacal nitrogen (NH_4-N). Chemical and physical conditions of the manure are the characteristics that define the concentration of NH_3 at the liquid surface. The NH_3 fraction of the total ammoniacal nitrogen is the only fraction that volatilizes from the manure. The concentration of NH_3 in the air layer close to the manure surface is in equilibrium with the dissolved NH_3 and when transported away to the atmosphere by turbulent air diffusion results in an increase of emission (Génermont & Cellier, 1997). The volatilisation rate depends on the NH_4-N concentration in the solution, pH, emitting surface area, temperature and air velocity over the emitting surface (Hendriks et al., 2016). Ammonia emission from agriculture and the fate of reactive nitrogen after emissions are also strongly dependent on meteorological conditions (Schauberger et al., 2018). Ammonia volatilization is climate and temperature sensitive, and the overall emissions can increase up to 42% for warming of 5 °C, therefore global warming will exacerbate the NH_3 volatilized from the livestock agricultural sector (Sutton et al., 2013). The ammonia volatilization rate follows a defined pattern: it gradually increases and after reaching a peak starts to decrease at a slower rate when ammonia formation has stopped or when is slower than the volatilisation rate (Elzing & Monteny, 1997). An additional factor that affects the ammonia pollutant effect is the constant growth and intensification of the livestock and agricultural sector making this gaseous emission a real concern for human health (Grossi et al., 2019). Areas, where the agriculture sector is run more intensively, have as consequence higher ammonia concentration compared to others, and a higher livestock density also increases the volumes of manure produced and stored (Hendriks et al., 2016). Considering the wide range of parameters that influence nitrogen losses, several differences are recorded between Northern and Southern Europe. Southern Europe registered higher NH_3 emission factors for field-applied manure. In contrast, the N leaching factor in Northern Europe was higher than in the South (Hendriks et al., 2016).

1.1 Ammonia emissions along the manure management chain

1.1.1 Housing

Gas emissions from livestock buildings are a product of gas concentration and ventilation rates. Two categories of emissions can be identified: gross (based on the gas concentration inside the building) and net (based on the difference between the gas concentrations inside and outside the building) (Rzeźnik & Mielcarek, 2016). The produced gases within animal buildings are directly generated by animal's digestive system or decomposition of animal manure and when the ventilation is insufficient, the produced gasses tend to accumulate inside the buildings (Mostafa et al., 2020). In cold rooms since ammonia dissolves in cold and humid environment, it can accumulate on surfaces as well as in wet bedding material. Regardless of the structural characteristics of the barn, the animal diet is a fundamental factor that can influence the ammonia production. Farms rearing highly productive animals will generate more ammonia as a consequence of a more intensive feeding strategy (Bougouin et al., 2016). Feeding strategies is in fact part of the manure management chain affecting the quality and nutrient composition of excreta (Petersen et al., 2013). The main variables influencing NH_3 and GHG emissions from livestock buildings are barns structure, housing system, manure management activities, season and climatic condition (Viguria et al., 2015). Also, a combination of these variable can increase or decrease the emissions, for instance manure removal systems and floor type can affect barns and manure temperature itself and consequently influence the gaseous emission. The information regarding the emission from cows' barns not always refers to the same building typology since Northern Europe and Southern Europe generally have different building characteristics. In Northern Europe, for instance, loose housing with cubicles is common. The animals are usually kept in a closed barn divided into rows of single cubicles, feeding and walking alleys (Mosquera et al., 2014). On the other hands in Southern European and other countries with Mediterranean climate and hot summer the housing structure are generally open, with no perimetral walls, and usually the cooling systems are integrating with the natural ventilation (D'Urso et al., 2022). Open-lot barns are generally more influenced by weather conditions such as wind, moisture, and ambient temperature, all of which are important factors that influence NH_3 emissions (Bougouin et al., 2016). Measurements of gasses in different types of building make necessary the application of different approaches and techniques. The measurements of inlet and outlet concentrations of gases in naturally ventilated barns are more challenging compered to mechanically ventilated barns. Namely, naturally ventilated barns, do not have defined point inlets and outlets but have a wider area defined by open walls or roof chimneys (Joo et al., 2014). To define an average values for NH_3 emission from dairy barns is extremely challenging since there are many factor that can affect NH_3 volatilization rates (Hristov et al., 2011). Farms and buildings' characteristics also influence the manure management. When the manure is removed from the barn floor or when the urine is removed and separcated from the faces a decrease of the NH_3 is expected (Mostafa et al., 2020). On the contrary other studies showed how the emission factors were higher in farms equipped with scrapers. As a matter of fact, with this cleaning method, the thin layer of slurry generally remaining on the floor can sensibly increase the NH3 emission (Sommer et al., 2006). Pavement characteristics can modulate ammonia emissions as well. In particular when floor types allow instantaneous contact of urine and feces, NH_3 emissions are expected to be higher in building (Hristov et al., 2011). Moreover texture and porosity of the floor influence the amount of urine present on the surface after urination, therefore the percentage of urea converted into ammonia resulting in a higher NH_3 emissions in farms equipped with solid floors. A validated strategy to lower the emissions could be the installation of slatted floor or flushing system for manure removal or the aeration of the slurry under the floor also associated with an acid scrubber (Mostafa et al., 2020) (Baldini et al., 2016). In sum, not only the single characteristics of the building are factors having effect on nitrogen losses but also the relationships among housing solutions, floor type, manure collection and storage systems are variables that influence NH_3 and GHGs emission (Baldini et al., 2016).

1.1.2 *Storage*

The characteristics of manure storage mainly depends on farm management. The main difference consists in the management of solid and liquid manures. Adequate storage facilities are necessary to handle the larger volumes of slurry, save nutrients and reduce environmental risks. Slurry, depending on the region and country, must be kept for long periods in storages, ranging from 3 to 9 months (Sørensen et al., 2013). Storages for liquid slurry can be tank or lagoon. Lagoon is a large rectangular or square structure with sloping earth bank walls, more developed on the surface than in depth The depth of the storage is an important parameter, because deeper is the storage minor will be the surface exposed to the atmosphere. For tanks the depth can vary from 3 to 5 m, whereas for lagoon is generally lower, with a depth around 2-3 m (Kupper et al., 2020), reason why it is now dismissed in many regions. Data on tank operations such as manure agitation and storage emptying, (how often and how they are carried out) from the literature are anyway scarce. During the assessment of ammonia emissions, the interactions between the meteorological conditions and store operations must be considered and measurement must be conducted for an adequate time period. Even if of extremaly informative content, analysis carried out in laboratory scale rarely can create meteorological conditions equivalent to the real-world (Kupper et al., 2021) (Baldé et al., 2018). Factors responsible for changes in ammonia emission of stored manure are storage characteristics, manure management, temperature, and climatic condition. Being temperature sensible, ammonia emission is registered to be higher during warm season when also a bigger emission variability is detected compared to cold season (Kupper et al., 2021). A diurnal emission pattern is also highlighted, showing particularly high emission between sunrise and sunset specifically in the early afternoon (Baldé et al., 2018) (McGinn et al., 2008). Other events related to the season are the slurry agitation performed in the spring and preceding the spreading. Slurry agitation, destroying the eventual superficial crust and increasing the manure temperature also leads in an increase of emissions (Kupper et al., 2021). Moreover the manure spreading implies a lower depth of the stored manure and consequently the tank walls could have the effect of windbreaks (Baldé et al., 2018). Other seasonal phenomena affecting ammonia emission are the precipitations. When these events occur, sorption of NH3 onto wet areas and dilution of the TAN concentration at the emitting surface results in a lower emission related to rain intensity (Kupper et al., 2021). Manure temperature leading to a higher or lower emission aren't just a consequence of weather condition. Tanks and lagoon storage location and exposition affect the stored manure temperature. When measuring the lagoon surface temperature with infrared thermometer (McGinn et al., 2008) registered significant difference between the surface temperatures measured at various locations around the lagoon. It follows that reducing wind speed by sheltering the storage, or decreasing the surface temperature by shading it, could be and efficient strategies to reduce NH_3 emissions (McGinn et al., 2008).

1.1.3 *Spreading*

Land spreading of animal manure contributes to global N losses through atmospheric emissions of nutrients, accounting for roughly one-third of the ammonia (NH_3) emission from the agricultural sector (T. H. Misselbrook et al., 2000). Ammonia volatilization after manure application, in fact, involves nutrient losses up to the 70% of the total ammonium N content of the manure. The implementation of proper spreading techniques can be effective in reducing ammonia emission following the application of manures to land (Maguire et al., 2011). For these reasons the application of effective techniques to reduce ammonia emission after the spreading is already a national and international priority (Webb et al., 2010). In Europe although the annual emissions generated from manure application are lower than those from livestock housing, the limited time period of manure land application make these emissions more dominant. Some studies comparing different spreading methods showed that 72 h after the application to soil the amounts of ammonia concentrations were reduced by about 75 % for all the evaluated technologies (Lovanh et al., 2010). Other studies carried out by (Bittman et al., 2005) reported that when dairy manure was applied with surface-broadcast and banded to tall fescue 85% of NH_3 volatilization occurred within 24 h. The various ranges of outcomes is a reflection of the variable that influence ammonia emission such as weather conditions, application rates, and slurry and soil characteristics (Huijsmans & Schils, 2009). Between the established spreading techniques, incorporation of slurry into soil reduces NH_3 emissions. This effect is the consequence of reduced time of contact of manure with air and the transfers of volatile compounds to the atmosphere (Maguire et al., 2011) (Viguria et al., 2015). Studies assessing the efficiency of the injection techniques reported interesting results about this application methods. An ammonia reduction of 69% was registered when the digestate was applied with the injection compared to a superficial application (Riva et al., 2016). Also Maguire et al. 2011 reported that injection technologies can reduce NH_3 emission by 40 to almost 100% compared with broadcast application. In particular, manure incorporation with tillage can substantially reduce nitrogen gaseous losses, especially if the tillage is rapidly performed. Anyway, when tillage is not possible, injecting the liquid manure can be an method of reducing NH_3 volatilization in most situations (Maguire et al., 2011). These mentioned data indicate, that the correct use of slurry or digestate to avoid ammonia volatilization and to preserve fertilizer value is, as expected, injection into the soil (Riva et al., 2016). Techniques to reduce NH_3 emissions generated by the manure spreading have been defined as the most cost-effective measures available to farmers to reduce NH3 emissions (Webb et al., 2010).

1.2 Ammonia mitigation strategies

Several researches have been conducted with the aim to find an efficient way to mitigate gas emissions generated from livestock and agricultural sector (B. Chen et al., 2021). Manure storage is a critical step since during this phase up to 50 % of the initial total nitrogen N can be lost (Shah et al., 2012). The mitigation of the environmental impacts generated from the livestock production is a challenge not only for farmers but also for the public and regulatory agencies (Maurer et al., 2017) (Shah et al., 2012). Solutions that consider technical and socioeconomic factors are needed as well as the assessment of efficient techniques to manage livestock manure (Maurer et al., 2017).

1.2.1 Slurry acidification

The pH value has a strong effect on gaseous emissions from slurry stores (Sommer et al., 2013). A method to reduce NH_3 emission from livestock manure is to lower the manure pH to create higher NH4 +/NH3 ratio (Kai et al., 2008). Until now, in some European countries this method is already been tested and developed for over 30 years (Fangueiro et al., 2015). Slurry acidification can take place during manure storage when the additive is applied inside the tank or lagoon previous mixing. Foam formation and its consequent removal, and risks related to the acids use represent some of the limitations in the use of this additive. When acidification takes place directly in the barns, is necessary to perform aeration to avoid foam formation (Fangueiro et al., 2015). Although more full-scale studies are needed to define the best pH values, a pH range between 5.5 and 5.8 is suggested to reach an effective NH_3 emission reduction. When short-term effects is needed, a lower pH value is recommended over a higher one (Dai & Blanes-Vidal, 2013). Ammonia volatilisation starts to decreases below pH 7 and around a pH of 4.5, there is almost no measurable free ammonia (Ndegwa et al., 2008). The lowest pH values tested range from 4.0 to 4.5. At these values, less than 1% of the ammonium nitrogen was emitted to the air, compared to non- acidified slurry (Fangueiro et al., 2015). Other studies regarding the acidification of livestock manure have registered an ammonia emission reduction from 70% to 85% when applied to pig slurry by decreasing the slurry pH to 5.5 with the application of sulfuric acid (H2SO4) (Kupper et al. 2020,A lower pH value can increase the efficiency of the treatments, mitigating the emission and showing a prolonged period with low and stable emissions (Dai & Blanes-Vidal, 2013). The effect of acidification on gaseous losses can be as much efficient as the utilization of some impermeable covers and permeable covers such as PVC cover, leca pebbles, straw, natural surface crust (Kai et al., 2008). In sum, it must be considered that the effect of the acid on reducing N losses is related to several parameters regarding the manure and the used additive such as: target pH, treated slurry, and step in the slurry management chain (Fangueiro et al., 2015) (Ndegwa et al., 2008).

1.2.2 Additive

Biological additives are one of the mitigation technologies consisting of the alteration of the microorganisms crucial in minimizing the environmental impacts associated with slurry management. Slurry additives, biological or chemical, are substances applied to slurry to reduce the emission problems associated with slurry management. These additives can affect both chemical and biological composition and may be expected to influence gaseous emission patterns when applied to slurries. Biological additives consist of microorganisms or enzymes specifically designed to improve biological degradation of organic materials in slurries. These treatments are generally considered feasible and economically viable by the farmers when compared to other advanced treatment technologies. Generally manure additives are also well researched in comparison to other mitigation technologies, particularly at the farm scale (Maurer et al., 2017) (Owusu-Twum et al., 2017) . The effect and the efficacy of additives depends on several factors that influence the microbial activity. These factors include temperature, pH, dissolved oxygen concentration, nutrient availability, and microbial resistance to potential toxins (Provolo et al., 2016). A variety of additives have been applied and tested to reduce emissions from livestock manure. The composition and mechanism of the emission reduction of some additives are known. Other information related to commercial additives are not available because of confidentiality and limits in the literature (Peterson et al., 2020). The evaluation of the effectiveness of additives for reducing ammonia emission from different slurry type not always registered differences between treated and untreated samples In general, applying additives to slurry did not result in a significant decrease in NH_3 volatilization (Rahman et al., 2011) (Van der Stelt et al., 2007). In some cases after the additive application to the slurry an increasing trend in NH_3 volatilization was registered (Owusu-Twum et al., 2017). Other investigation registered a decreasing in ammonia emission from 45.9% up to 100% (Peterson et al., 2020) (Borgonovo et al., 2019). The conflicting results obtained in various study confirm the need to test the effect of additives in different conditions because the additives are likely to have different activities in different environments (Provolo et al., 2016).

1.3 Permeable covers

Manure covering can be set up with natural or synthetic materials of the effluent surface. The application of the cover has the effect to reduce ammonia emission decreasing the surface area where emissions can take place, minimize the air and wind disturbances, offer resistance to the transfer of NH_3 from the effluent surface to the overlaying air, thereby retaining ammoniacal nitrogen in the manure (Nartey et al., 2021)(Holly & Larson, 2017) (Bittman, S., Dedina, M., Howard C.M., Oenema, O., Sutton, 2014)The presence of a physical barrier on the surface of a manure storage is a method used to reduce NH3 emissions. Covers can be added to existing farm-infrastructure, and therefore have potential to be widely used. Synthetic covers are long-lasting and unlike natural covers do not mix with the slurry causing potential problem with the pumping. Permeable materials allow precipitation to seep through the cover, with the logistic benefit of not requiring water removal from the covers' top. Organic cover can be subject to weather and climatic condition, drifting for the wind action or sinking and mixing because of the rain effect. As consequence of the sinking, cover material could block the drainage system and the contact with the slurry could lead to a chemical or biological degradation. These are practical limitation already highlighted in various studies (Nartey et al., 2021)

(Guarino et al., 2006). Despite the above disadvantages, natural and permeable floating covers can be inexpensive and have proven to be a valid emission abatement system limiting the diffusivity of NH_3. natural materials tested to reduce emission include sawdust, straw, wood prunings, clay, corn stalks, biochar and natural crust (Nartey et al., 2021).

1.3.1 *Natural crust*

A number of studies showed that the floating natural crusts forming on liquid manure results is an NH_3 emission reduction comparable with other natural covers. Since crusting is effective in reducing emissions, should be established parameters defining what constitutes an efficient crust and how crust formation can be implemented. In laboratory scale is difficult to create realistic conditions that manage to represent on-farm storages including manure loading, surface crusting, solar radiation, and wind speed (Baldé et al., 2018). There is also need to pay attention on how to manage the crust considered that usually the store are emptied about once a year (Smith et al., 2007). It has been defined that an adequate completely crusted surface corresponds to at least 10 cm of thickness and a reduction in NH_3 emissions is more pronounced when the crust thickness increased (Tom H. Misselbrook et al., 2005) (Kupper et al., 2021). Several manure management practice and livestock feeding strategies can influence the crust formation and durability. Manure agitation is the most relevant factor for crusting since it destroys the natural crust together with tank filling and emptying destroy the natural crust (Kupper et al., 2021). Anaerobic digestion combined with solid separation indirectly increase NH_3 emissions during storage. These techniques increase TAN and pH and make more difficult the formation of a solid surface crusts (Baldé et al., 2018). Slurry Dry Matter content was identified to be a major factor influencing crust formation. Generally when Dry Matter content is below 1% the crust formation doesn’t occur (Tom H. Misselbrook et al., 2005). Different studies assessing the efficacy of the crust in reducing ammonia emissions have demonstrated how the crust reduced the mean NH_3 emission rate by ca 60% up to 80% compared to uncrusted stored slurry (Smith et al., 2007). The presence of crust allows to slurry to retaining more ammonium in the slurry solution (T. Misselbrook et al., 2016). Anyway crusts left for long periods can reduce the capacity of the store and may become very difficult to break (Smith et al., 2007).

1.3.2 *Biochar*

The word “Biochar” refers to a material obtained from biomass, any biomass is in fact suitable to produce biochar included animal manure or even sewage sludge (Kalus et al., 2019). Properties and characteristics of the biochar are related to the starting material used, and pyrolysis condition, in particular temperature and duration of the process. The pyrolyzed biomass is anyway the variable that affect the most the biochar properties. The most studied pyrolysis parameters, are peak temperature and heating rate (Aller, 2016). Generally with an increase of the pyrolysis temperature, resulting biochar is characterized by higher C content, porosity and surface area (Kalus et al., 2019). Biochar have become more popular in the past years because of its capacity to improve soil health, carbon sequestration, and crop productivity when applied to the soil (Jindo et al., 2020). Besides the beneficial effect after soil application, it is being studied for its capacity to reduce NH_3 emissions when applied on the surface of stored livestock manure (Scotto di Perta et al., 2020) (Aller, 2016). As a matter of fact, the application of biochar as manure cover can reduce the ammonia emission acting as physical barrier and performing an adsorption effect. Biochar structure contains different chemical functional groups that can influence the capacity to adsorb NH_3 compounds while porosity and surface area are effective for ammonium ion (NH4+) adsorption (Holly & Larson, 2017). With its high porosity and large surface area can be an excellent adsorbent, retaining pollutants or other microelements (Aller, 2016). Hydrophobicity is a characteristic to consider when assessing the biochar sinking or floating capacity, since it enables biochar to float decreasing its liquid absorption. Another parameter that could affect biochar floating on top of manure are the manure characteristics (Meiirkhanuly et al., 2020)(Dougherty et al., 2017). Several studies have been conducted regarding the use of biochar as a bio-cover or bio-mix. The studies investigated the capacity of biochar to reduce ammonia volatilization; its susceptibility to weather conditions when applied to full scale; the changing in biochar effect and characteristic when is produced by different bioproducts and with different pyrolysis methods (Meiirkhanuly et al., 2020) (Scotto et al. 2022). A biochar cover was assessed to significantly reduce ammonia emission by 33%, when applied to swine manure (B. Chen et al., 2021). Other studies assessing the difference in the biochar characteristics shown an ammonia reduction ranging from 4~78% (Di Perta et al., 2020)(Meiirkhanuly et al., 2019). Biochars with different physicochemical properties should be studied to define the changing in mitigation of specific gases (B. Chen et al., 2021).

1.3.3 *Clay*

Clay is a low-cost and widely distributed porous mineral which is mainly composed by montmorillonite and kaolinite generally in form of light and resistant granules (H. Chen et al., 2018) (Guarino et al., 2006). Clay granules consist of a porous material made from clay and coated with waterproof material. Clay granules are often used as insulating material and its physical properties allows it to float on a liquid surface such as slurry (Balsari et al., 2006). It can be also considered as biofilter, due to its capacity to trap and bio-transform N. Light expanded clay aggregates (LECA) granules is defined as low-cost cover (Ndegwa et al., 2008). The efficacy of clay granules to reduce ammonia emission from slurry have shown contrasting results. The granules seems to be able to reduce ammonia emissions exclusively at greater thickness (Guarino et al., 2006). On the other hand thin layer seems to be less effective or even result in an increase in NH_3 volatilization (Nartey et al., 2021).When a 10 cm layer was applied to pig slurry an ammonia emission reduction was registered up to 87% compared to the control group (Balsari et al., 2006)(Guarino et al., 2006). The inefficacy of the cover was registered when 5 cm of LECA during the storage formed surface crust. The gaps between the LECA and the low layer thickness allowing NH_3 release (Nartey et al., 2021). Moreover, microbes find an ideal structure for their activity on the granules surface. This microbe's proliferation can cause degradation of organic matter and leads to the increasing of NH_4^+ release and NH_3 emission. The presence of microbial growth could lower LECA performance due to bio-plugging of the LECA itself (Nartey et al., 2021)(Vander Zaag et al. 2005).

1.3.4 *Straw*

Crop residues are readily available on-farm generally at a low cost. Straw, as well as other materials, including corn stalks, corn cobs, and rice hulls as cover, have been tested as manure cover (VanderZaag et al., 2005). A wide and promising range of ammonia emission reductions have been observed when straw was applied on the manure surface. Significantly reduction of ammonia emission was register when the straw was used as cover as untreated material and also when used in addition of lactic acid its mitigation effect resulted improved (Scotto di Perta et al., 2020)(Berg et al., 2006). When added to manure during the composting process, a reduction of ca. 12 % was registered when reed straw was applied. This effect is probably due to the fact that straw is an easily decomposable, N-poor material and can lead the immobilization of ammonia (J. Z. Wang et al., 2012). Several studies have assessed the attitude of this material to reduce ammonia emission when used as cover but an important parameter to test is the floating attitude. Since straw is a light material, it is very susceptible to wind and rain damage and rapidly sink (Guarino et al., 2006). Resistance to sinking is parameter that must be considered when looking at an efficient and cost-effective cover. It can be stated that the capacity of floating and staying relatively still on the slurry surface can also depend on the dry matter content of the manure may improve flotation. Some studies assessed that to avoid straw to sink in the stored slurry a manure with 4% total solids was necessary (Guarino et al., 2006). During future studies that may be carry out it is necessary to better understand the effects on air quality when straw covers are used in addition to the optimal amount of straw used to optimize the straw affect (VanderZaag et al., 2009).

1.4 Research goals and overview of the chapters

Livestock production systems around the world generate a large amount of slurry that need to be managed. Slurry storage is mandatory and necessary to supply the manure nutrients to the crops when needed the most. To store the manure, a major part of the slurry is moved from the housings to an outdoor storage facilities such as tanks or earthen lagoons (Kupper et al., 2020). During the storage the greatest losses of N from are represented by gaseous emissions; NH_3 in particular is emitted in the largest amounts (Webb et al., 2012). Ammonia has a large variety of negative environmental impacts on quality of air, soil and water, ecosystems and biodiversity (N. Zhang et al., 2021). The heterogeneity of the agricultural sector needs to be considered when defining the most suitable mitigation strategy. As been assessed that to achieve the best results in mitigation strategies different factors must be taken into accounts, for example livestock systems, species, and climates conditions. Moreover a combination of more mitigation measures could be a better option to reach a more satisfying result (Grossi et al., 2019).

Since NH_3 emissions from industrialized systems have become considerable requiring mitigation, the aim of this research is to assess the efficiency of different mitigation method to apply during the manure storage. Different materials for covering liquid manure storage facilities to reduce gaseous ammonia emissions have been investigated, in particular natural permeable covers.

The second chapter will focus on the description of the poultry-based component of the DATAMAN (Beltran et al., 2021). The analysis on CH_4, N_2O and NH_3 emission factor for manure storage defines how the different handling methods of broiler manure influence gaseous emissions and manure properties. In the following chapter (Chapter 3) will be assessed the superficial application of straw cover to reduce ammonia emission and alongside the effect of the natural crust and the digestate characteristics leading to its formation are studied. Thereafter, a chapter (Chapter 4) will be dedicated to a focus on the biochar effectiveness in reducing ammonia emission when applied to the stored liquid digestate. This chapter, divided in three sections will: (i) demonstrate the biochar efficacy in reducing the emission; (ii) define between different application methods the most effective one; (iii) investigate the attitude to mitigate ammonia emission of two type of biochar produced with two different pyrolysis methods. In the last chapter (Chapter 5) the already separately tested cover materials in the previous chapters are compared among them in a new experimental setup. Uncovered buffalo digestate, digestate covered with straw, biochar and clay will be tested to assess the most effective cover under laboratory scale condition.

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2 Preliminary ammonia emission factors for poultry manure storage from the DATAMAN database

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2.1 Introduction

As the need of protein increase, the intensification of poultry production meets the need of affordable, quality food products (Awasthi et al., 2020). Poultry production, expanding in developing countries, produce a massive amount of manure that when stocked and treated is responsible for environmental damage (Williams, 2013)(Nahm, 2003). Poultry manure consists not only in bird excrement, but also in bedding materials that differs according to the farming techniques. Bedding material can be made of sawdust, wood shavings, straw and peanut or rice hulls (Williams, 2013). In poultry and livestock production facilities, different variables greatly influence gas emissions during the housing and during the manure storage (Liang et al., 2005). House ventilation system, management of water drinkers, bird stocking density and flocking behavior can influence the gas production and distribution inside the poultry houses (Brouček & Čermák, 2015), while manure management such as the duration of the storage period, the configuration of manure heap, can influence the chemical composition of manure and therefore affect the gas emission rat e(Awasthi et al., 2020) (Alberdi et al., 2016). Nutrient losses from poultry manure during storage and after spreading are not often investigated resulting in a poor knowledge about this topic (Rodhe & Karlsson, 2002). Moreover, few studies focus on the effect of different manure management and livestock systems on emission factors (EFs), representing the fraction of N applied as manure that is emitted as either N_2O or NH_3 or the amount CH_4 emitted per kg manure-VS. More information about manure management and storage are needed to gain a deeper knowledge on gaseous emissions driving factors, a key element when proposing mitigation strategies that would better adapt to specific conditions (Alberdi et al., 2016) (Naylor et al., 2016). For this reason, the global DATAMAN database was created to overcome this gap in knowledge collecting data and information about livestock production and manure management. The collected data are thereafter analyzed and studied thanks to the MELS project. In this paper a description of the poultry-based component of the DATAMAN database was carried out focusing on CH_4, N_2O and

NH_3 for manure storage and investigate if different handling methods of broiler manure affect gaseous emissions and manure properties.

2.2 Materials and methods

2.2.1 DATAMAN description

Livestock manure management systems are important sources of greenhouse gas and NH_3 emissions, for this reason the international project DATAMAN was created to develop a global database on harmful gasses emitted from the manure management chain. The DATAMAN database was created to collect CH_4, N_2O, and NH_3 emissions relating to livestock activities including housing, storage, and field application of manure. This database has the purpose to improve and facilitate the study of variables that can influence the gaseous emission during the manure management systems to better understand and possibly predict GHG and NH_3 emissions from manure management. The DATAMAN project aims to relate key variables with emissions and to refine emission factors. The database is disaggregated into (a) housing, (b) storage, and (c) field-based emissions(Beltran et al., 2021). In this study, the storage section of the database was taken into account focusing on the poultry species.

The statistical analysis of the collected data excluded all the studies published before the 2000 and all the paper where the measurements techniques of gaseous emissions were not specified were excluded because considered not reliable. Another criterion of selection was the ammonia experimental conditions measurement techniques. As a matter of fact, ammonia emissions can be measured with static and dynamic techniques. With the first method the NH_3 is captured passively, in the second one the air flow over the emitting surface is allowed. In this work, only measurements performed with dynamic techniques were analysed, because as stated by van der Weerden et al. 2021 the mean NH_3 Emission Factor (EF) values are significantly lower from static techniques when compared with dynamic techniques. Hence, when carried out statistical analysis these encompasses data on NH_3 poultry manure storage from 10 publication; data on N_2O poultry manure storage from 6 publications; data on CH_4 storage from 5 publications, all published between 2002 to 2020.

2.2.2 Description of the Data

2.2.3 Manure storage-poultry

In the DATAMAN database the total recorded observations regarding the manure storage of poultry species are 216. Within the poultry species three subcategories are identified: broilers, layers, and ducks; respectively 80, 134, and 2 observations. The measured gases are CH_4, N_2O, NH_3, CO_2, H_2S, odour. Those with a larger number of records are CH_4, N_2O and NH_3 with 44, 50 and 97 observations covering about the 88% of the total data. Gaseous CH_4 emissions in 97% of the case refers to layers (43 observation for layers, 1 for duck). Observation on N_2O and NH_3 concern layers and broilers with no distinction. On a total of 216 observation, 97 are gas mitigation studies, 83 are not mitigation studies, the remaining 36 observations are categorised as unsure. The measurement techniques collated into the database are dynamic enclosure, static enclosure, micro meteorological. The dynamic enclosure, with 88 observations represent the 45% of the recorded measurement techniques; 78 observations are recorded as other, representing around the 40%. The days of measurement vary between 3 and 330 days. To broilers and duck corresponds the data with the highest and lowest value, respectively 169 days and 3 days of measurement.

The observations reporting Emission Rate or Cumulative Emission are 154, these data have different measure units. Between them only one is a negative value: -0.000811808 g $N_2O.m^{-2}.d^{-1}$, corresponding to an N_2O measure to layer manure. The CH_4 Emission Factor values refer exclusively to layers with a total of 22 observations. The NH_3 and N_2O Emission Factor data are 107 corresponding to layers, broiler, and duck.

The EFs referring to the subcategories broilers and layers, show difference in ammonia NH_3 and nitrous oxide N_2O emissions, to layers always correspond significatively higher values ($p<0.05$). These EFs values however is not affected by the dry matter content of the manure. The manure type section has two categories: layer manure and broiler litter. The two typologies of manure differ in dry matter content, where broiler categories show a significatively higher value of dry matter. These differences observed between the two animal subcategories and manure characteristics may depend on several factors. Broilers and layers differ between them in several aspect such as breeding system, seasonality, breed type and production group (Agnew & Fonstad, 2005). The lack of the other recorded manure characteristics represent a limitation, and despite manure volatile solids content is a fundamental parameter to evaluate CH_4 emissions, this value is provided only six times for CH_4, NH_3 and N_2O observations.

Regarding the manure aspects, storage activities are categorized with the following techniques: manure heap, pit, slurry tank. Pit and slurry tank have respectively 6 and 12 observations. Pit observations are referred to broilers and duck, while the slurry tank observations are only referred to layers. The most represented storage method is the manure heap with 105 observations. Different manure treatments are reported: anaerobic treatment, enlisted for layers only in two observations; composting, referring almost exclusively to layers; "no treatment" are used for broiler and layer independently. Even if manure drying systems have become more common worldwide for egg and laying hen housing industry (Zheng et al., 2020), in the dataset the drying method corresponds only for layers, and all the collated studies have been carried out in Japan. Composted manure represents the 40% of the observations, categorized as heap storage or unsure. Not well represented are the manure covers. The cover identified as floating are 5 corresponding to manure heap and pit. Only one study reports natural crust as cover, and it refers to broiler. Thirteen studies don't report any cover, the rigid covers observations are 23, 87% of them corresponds to layer. Straw and sawdust are the two products recorded as bedding material enlisted 27 and 39 times. The only case where no bedding material is used refers to layers and no Emission Factor is reported; broilers only show the use of sawdust. Analyzing the different typologies of bedding materials, it has been found that, the materials don't affect manure dry matter content. Data regarding manure the dry matter content are divided in dry matter start and end of the storage. Data referring to the start have 96 observations, the one recorded at the end of the storage are 46, less than 48% on the initial data. The difference between the final and the initial dry matter is always positive in layer manure showing an increment of dry matter, broilers on the other hand show a reduction in dry matter after the storage. The pH data are recorded as follows: pH start of storage, pH end of the storage, pH average. The number of the observations are respectively 119, 59, 36. The lowest pH value at the start of the storage is 6.02 referring to duck and doesn't have a corresponding value at the end of the storage; the highest pH value at the start of the storage is 8.79, at the end of the storage the value is 8.69, it corresponds to layers manure.

The registered climate zones are divided in temperate wet and temperate dry. In the last case, 83% of the observations are relative to layers. Countries enlisted in the database are Sweden, France, Netherlands, United Kingdom, Australia, Canada, United States, Japan, China, but not all the mentioned country show EF values; there are no reported EF values for studies carried out in France and Australia studying respectively CH_4 and NH_3, N_2O and CH_4 and NH_3. All the studies on CH_4 reporting emission factors values have been carried out in China and Japan and they only refer to layers. In accordance with (Alberdi et al., 2016) most of the research on the emission of NH_3 from poultry, housing in particular, has been done in Central and Northern European countries and USA. Generally, different countries not only have different environmental conditions but also different production systems, leading in various gas emissions. In tropical countries, for instance, production facilities are mainly open, with natural ventilation systems; in Northern European countries, poultry facilities are usually closed and insulated (Oliveira et al., 2021). Also, studies on long time measurement about the air quality in laying hen houses are still lacking. Compared to NH_3, fewer studies on CH_4 and N_2O emissions have been done as stated by (Alberdi et al., 2016). In the DATAMAN database we observed this phenomenon as well, where the NH_3 observations represent the 51% of the total observation. Ammonia is the most environmentally harmful gas produced at poultry farms it may be the reason why ammonia is the focus of many research investigating gas emissions. Moreover, poultry are monogastric animals and produce only slightly amounts of CH_4, a bigger quantity of methane is usually generated in animal house, during the manure storage or when manure is applied to the soil (Brouček & Čermák, 2015). In the database there are no data regarding studies carried out in the USA about CH_4 emission, and only three observations (concerning the same study) are registered from Canada, and it refers to layers.

It must be considered anyway that from one study reported in this database there are more observation that can correspond to more treatment. These observations may have different Emission Factors but the same initial characteristics of the manure (Dry Matter or Total Nitrogen Content e.g.) and the same experimental conditions. As it can be understood from the database description above, none of the variable defined in the dataset are given in all publications and not all the parameters are suitable to make a detailed and informative analysis.

Overall, there are no variables corresponding to animal description such as breeding techniques, productions and characteristics of animal diet and feed intake.

2.3 Conclusions

This paper is a contribution to the ongoing discussions about livestock production and manure management influence to nitrous oxide (N_2O), ammonia (NH_3), and methane (CH_4) emissions. The importance of the DATAMAN database lies in the opportunity to collect detailed information on how manure is managed worldwide, while the MELS project additionally increase the knowledge of EF values for manure sources and evaluating mitigation strategies along the manure management chain. From the data collected in the database and from the missing one is possible to define potential future research opportunities and improvements. With the ongoing and future work, more data, from different range of rearing systems will be included in the database, with the possibility to fill the knowledge gaps about feeding strategies, manure storage and treatments, and countries with different climates conditions poorly represented

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3 Influence of Treatments and Covers on NH_3 Emissions from Dairy Cow and Buffalo Digestate Storage

The present Chapter is based on the following article:

- Scotto di Perta, E., Mautone, A., Oliva, M., Cervelli, E., & Pindozzi, S. (2020). Influence of treatments and covers on NH3 emissions from dairy cow and buffalo manure storage. *Sustainability*, *12*(7), 2986.

3.1 Introduction

During the storage of animal manure produced by livestock activities, airborne pollutants can be emitted. Although the manure storage is a required and generally compulsory step, if the storage is not properly managed an increase of pollutants gasses can be enhanced (Dougherty et al., 2017). In particular, ammonia volatilization occurring from storage tanks is caused by the microbial decomposition of nitrogen compounds mostly present in the urine (Hartung & Phillips, 1994). Studies have assessed that 20-40% of the initial total nitrogen content in stored manure can be lost as NH_3 (Kirchmann 1985). As response for these gas volatilization, new limits have been established to control the emission of pollutant gasses with the execution of the National Emissions Ceiling Directive (NECD). This directive aims to mitigate the effect of gasses such as NH_3 and makes necessary the assessment of practices capable to reduce gaseous emissions (Scotto di Perta et al., 2019) (Pedersen et al., 2018). Considered that Dry matter (DM), organic matter (OM), Total Ammoniacal Nitrogen (TAN), and Total Kjeldahl Nitrogen (TKN) content and pH are characteristics influencing ammonia emissions (Dinuccio et al., 2019), manure treatments designed to modify manure composition can be effective in reducing ammonia volatilization. Although the effect and the efficiency of the manure treatment are often satisfying, the application of these treatments on livestock manure still interest less than 8% of total livestock manure produced in the EU (di Perta et al., 2020). Manure treatments can be identified as: preliminary treatments like solid–liquid separation (SLS); secondary treatments like anaerobic digestion (AD); tertiary or finishing treatments like constructed wetlands. Each level of the mentioned treatments has an higher effect in reducing nitrogen concentration (Errico et al., 2019). Generally, AD and SLS are sequentially applied (Errico et al., 2019). Among the effects that AD has, can be mentioned: the stabilization of the manure, the reduction in volume and odor emission, the production of renewable energy (Scotto di Perta et al., 2019) (Ariunbaatar et al., 2015). Moreover, AD treatment enhances the availability of N when the processed manure in used as fertilizer for field application (Sommer, S. G., Christensen, M. L., Schmidt, T., & Jensen, 2013)As already investigated, SLS and AD can decrease manure organic matter, and therefore lower CH_4 emissions during the storage (Amon et al., 2006). On the other hand, AD may increase NH_3 emissions. This effect is due to the higher TAN value of the anaerobic digestate, consequent to the mineralization of organic nitrogen into ammonia (Fiorentino et al., 2018). As mentioned in the above chapter several studies have assessed the possibility to reduce ammonia emission of stored manure, with the application of different type of floating covers, temporary or permanent (VanderZaag et al., 2005) (Clanton et al., 2001). The development of the natural crust on manure surface is one of the studied covers since can lead to the same reduction efficiency of other cover type (Tom H. Misselbrook et al., 2005) (Rotz, 2004). Between the other studied covers, straw (an easily decomposable, nitrogen-poor material), could have the peculiarity of immobilizing NH_3 (H. Kirchmann & Witter, 1989). Generally covers can influence in three way the gas emission from the stored manure: (i) modifying the manure pH and consequently the chemical equilibrium; (ii) promoting the activity of bacteria responsible for the gas consumption; (iii) reducing the gas transfer into the atmosphere reducing the emitting surface (VanderZaag et al., 2005). As previously discussed, the disadvantages related to the natural cover application and maintenance, have made the utilization of this specific mitigation techniques not particularly common within the livestock farms. Specifically, the susceptibility to weather condition makes the cover sensible to the risk of surface cracks or sinking, in addition of being sometimes expensive (Rotz, 2004) (Dougherty et al., 2017). It also must be considered that as assessed by several studies, the manure characteristics can influence the effectiveness of the cover (Finzi et al., 2019).

This chapter aims to study the impact on ammonia emissions during the storage of two manure type treated differently. The simulated small-scale storage was carried out under laboratory condition in a climate-controlled room to compare the results under the same conditions. With two experimental trial, emissions mitigation techniques were studied. In trial 1 was assessed the efficacy in reducing the ammonia volatilization following the development of natural crust on raw cow slurry (CS) and liquid cow manure digestate (LFD). In trial 2 was compared the efficacy in reducing the emission from a straw layer cover and the natural crust development on buffalo raw slurry.

3.2 Materials and Methods

Two experiments were carried out independently. To simulate the storage condition cylindrical glass vessels (16 cm diameter) were filled with 1 liter of manure. Three replicates for each sample were set up. During the trial, the vessels were left open in a room with constant temperature and relative humidity. These parameters were recorded during the whole storage period. Water evaporation from

vessels was not considered in this preliminary study to avoid animal manure dilution and to investigate ammonia emissions from various kinds of manure characteristics and covers.
The experimental setup is summarized in Table 3-1.

Table 3-1. Experimental setup of the carried out analysis. AD = Anaerobic Digestion; SLS = Solid Liquid Separation

Trial	Monitoring period	Manure Applied	Treatment	Storage cover	Emissions	Temperature (◦C)
1	26 days	Cow raw slurry Liquid fraction of cow manure digestate	AD+SLS	Natural crust	NH_3	18
2	20 days	Buffalo raw slurry	-	Straw	NH_3	19.5

Manure characteristics were measured defining the following parameters: total solids (TS), volatile solids (VS), total Kjeldahl nitrogen (TKN), and total ammonia nitrogen (TAN). The characterization was performed according to the standard methods (APHA, 2005).

3.2.1 *Trial 1: Natural Crust Formation*

During Trial 1, ammonia emissions from stored cow raw slurry (CS) and liquid fraction of manure digestate (LFD) were measured for 26 days. Three replicates of each manure type for a total of six cylindrical glass vessels were filled with CS and LFD, respectively. Samples' characteristics are reported in Table 3-2. Ammonia emissions were measured once a day. During the trial the formation of natural crust was observed.

Table 3-2. Manure characteristics DM = Dry Matter; OM = Organic Matter; TKN = Total Kjeldahl Nitrogen; TAN = Total Ammoniacal Nitrogen.

	Raw Slurry		Liquid Fraction Digestate	
	mean	SEM	mean	SEM
DM ($g \times kg^{-1}$)	83.17	1.97	54.36	2.04
OM ($g \times kg^{-1}$)	67.72	0.26	37.53	0.23
TKN ($g \times kg^{-1}$)	3.82	0.13	4.15	0.01
TAN ($g \times kg^{-1}$)	1.85	0.16	2.46	0.04

3.2.2 *Trial 2: Effect of Straw cover*

During trial 2, was measured ammonia emission from buffalo row slurry with a straw cover (BSWS), and buffalo row slurry with no cover (BS). Two straw applications of 5 g each (corresponding to a layer of 1 cm) were made. The first application was performed the first day of the trial; the second one was performed one week later, respectively. Ammonia emissions were measured once a day.

3.2.3 *Manure Sampling*

The manure used for the experiments was collected in two livestock farms located within Caserta province (Campania region, Italy). For Trial 1, cow slurry (CS) and liquid fraction of manure digestate (LFD) were collected in a dairy cow farm from the tanks placed upstream and downstream the anaerobic digester plant, respectively, therefore before and after the treatment process. For trial 2, the slurry was collected in a buffalo dairy farm. In order to define the manure characteristics representative samples were taken to analyze dry matter (DM), organic matter (OM), Total Ammoniacal Nitrogen (TAN), and Total Kjeldahl Nitrogen (TKN) content.

3.2.4 *Measurement Method*

To perform the gaseous fluxes measurement was used the dynamic chamber technique (E. S. Di Perta, Cervelli, Faugno, et al., 2020). The gas measure of each vessel was done once a day for five days per week. For the whole duration of the trial the vessels filled with manure were stored with no lid in the climate room. To perform the measurement, the vessels were closed with a lid with two openings on it: one opening for the air inlet, the other opening connected with a Teflon tube to an expansion chamber. The expansion chamber was then connected to a gas sensor. The air circulation was provided through a vacuum pump and a flow meter. The air exchange was regulated to be 1.5 l min^{-1} (Figure 3-1).

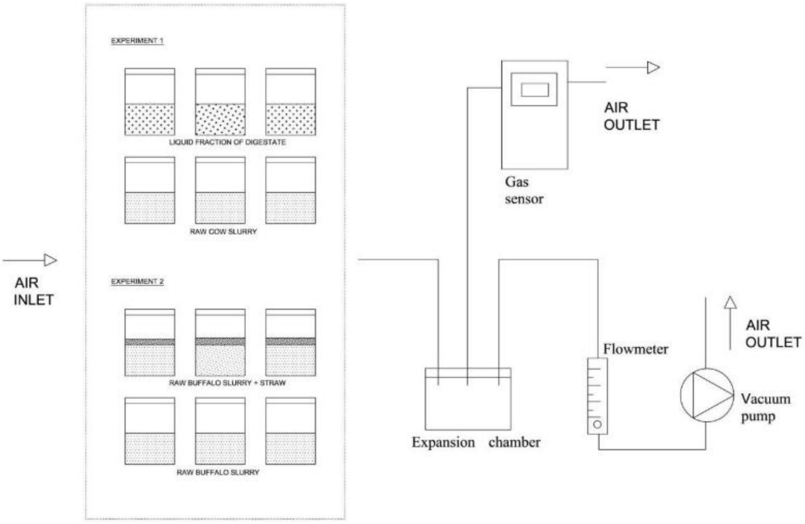


Figure 3-1. Experimental setup used to measure gaseous emissions

Each vessel was close and then ventilated for 20 min to achieve steady conditions inside the expansion chamber. The air was then sampled for 16 min and analyzed using a gas-sensitive semiconductor and electrochemical sensor (Aeroqual, series 500) to detect the real-time NH_3 concentration. The gaseous emission fluxes were measured using the following formula:

$$\mathrm{F} = \frac{\mathrm{Q(Cout - Cin)}}{A}$$

C_{in} is the gas concentration of air inlet into the chamber in mg m^{-3}; C_{out} is the gas concentration of air outlet from the chamber in mg m^{-3}; Q is the airflow rate through the chamber in m^3 h^{-1}; A is the circular area of the emitting surface in m^2. Cumulative emissions from each sample were evaluated by averaging net flux rates between two sampling points and by multiplying by the time interval between sampling points (Pampuro et al., 2016).

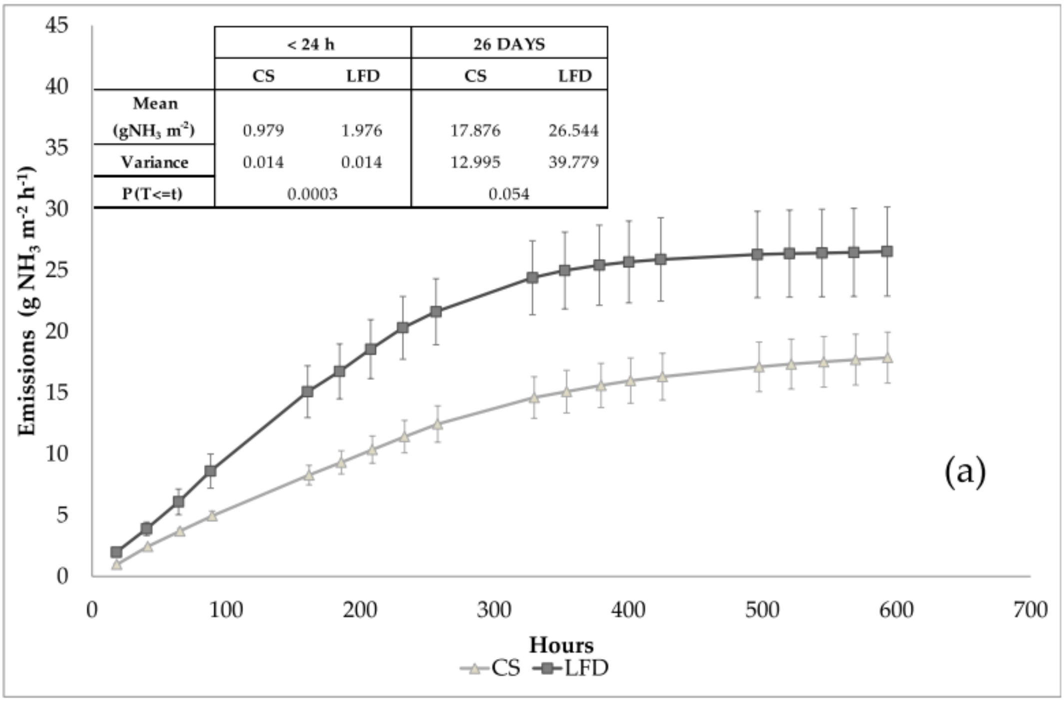
3.2.5 Statistical Analysis

Mean cumulative NH3 emissions within 24 h and over the whole measurement period were compared using a t-test at a significance value α = 0.05.

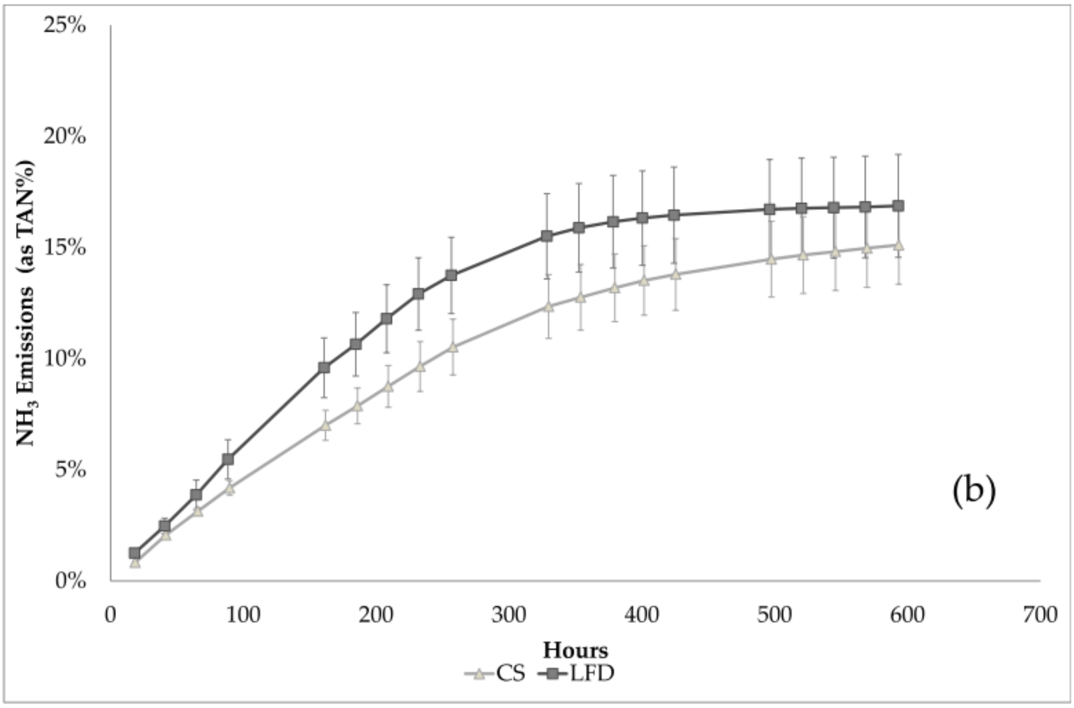
3.3 Results

3.3.1 Trial 1: Natural Crust Formation

The analyzed manure type showed differences in terms of DM and OM contents at the beginning of the trial. These differences are due to the treatments received from the manure. The DM content of LFD was ca. 35% lower than CS. The OM content in LFD (37.53 g kg^{-1}) is lower than 45% of CS. Differences in nitrogen content are also detected. Contents of TKN (4.15 g kg^{-1}) and TAN (2.46 g kg^{-1}) in LDF are 8% and 25% higher than CS. The higher DM content of CS is an effect of the presence of the straw used as bedding material that can facilitates the formation of an air-dried crust. A visual observation of CS showed how the crust started to develop during the first week of the trial. Throughout the trial changes in CS and LFD composition occurred, also as reported by (Scotto di Perta et al., 2020). The increase in DM content is the consequence of the water evaporation. The registered content reductions in OM, TAN, and TKN for CS were 1.6% and 5.2%, 46.4%; LDF reduction for the same parameters were and 88.9%, 39% and 74%. Figure 3-2 shows the cumulative ammonia emissions detected during the manure investigated. During the first days of measurement most of the NH_3 emissions occurred. Specifically, LFD emitted more than CS until the day 15. The cumulative NH_3 emissions was significantly higher from LFD than CS ($p < 0.05$) in the first 24 h. It was not significantly different over the 26th day of the measurement period (Figure 2a). It was observed a decreasing trend of NH_3 emissions in all the monitored samples. Mainly, this phenomenon was observed during the last week of the storage period. Regarding the cumulative NH_3 emission, CS emitted 33% less than LFD. In particular, the cumulative emissions accounted for 17.9 g NH3 m^{-2} (15% as TAN and 7% as TKN) and 26.5 g NH3 m^{-2} (17% as TAN and 10% as TKN) for CS and LFD, respectively.



	< 24 h		26 DAYS	
	CS	LFD	CS	LFD
Mean ($gNH_3\ m^2$)	0.979	1.976	17.876	26.544
Variance	0.014	0.014	12.995	39.779
P(T<=t)	0.0003		0.054	



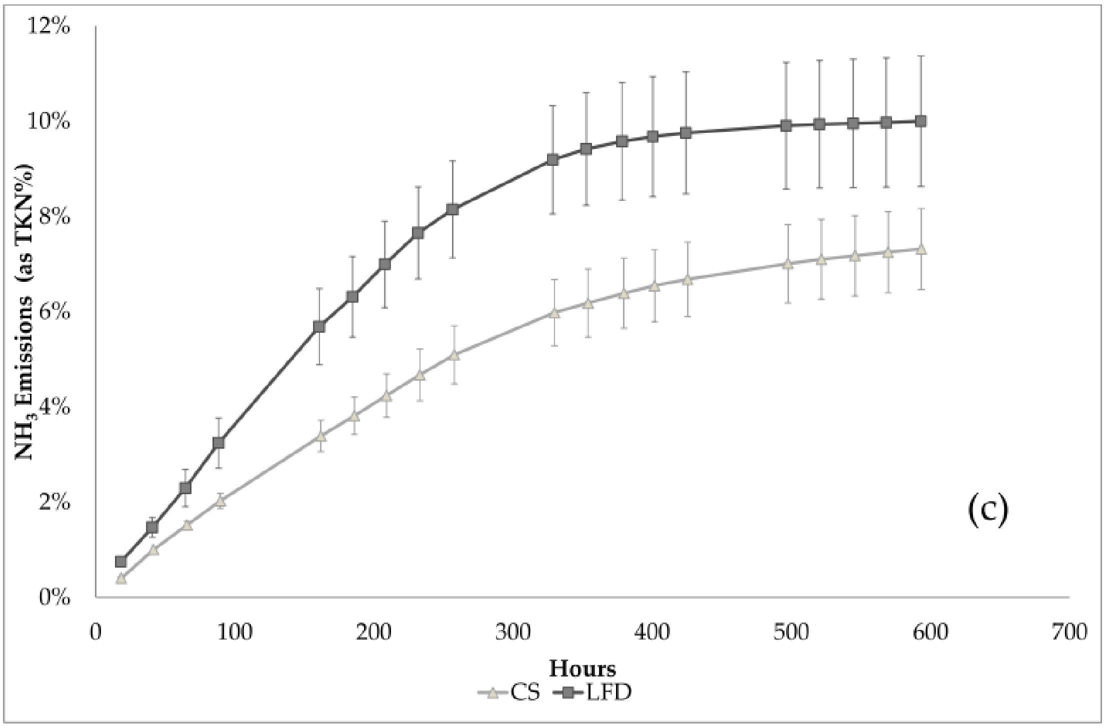


Figure 3-2. Cumulative ammonia emissions measured during storage (a), as TAN% (b), and as TKN% (c). Error bars indicate SEM (n = 3). CS = Cow slurry; LFD = Liquid fraction of manure digestate. (Di Perta et al., 2020)

3.3.2 Trial 2: Effect of Straw cover

The composition of the buffalo raw slurry was evaluated before and after the storage period. The manure characteristics are summarized in Table 3-3.

Table 3-3. BS = buffalo raw slurry; BSWS = buffalo raw slurry with straw; DM = Dry Matter; OM = Organic Matter; TKN = Total Kjeldahl Nitrogen; TAN = Total Ammoniacal Nitrogen.

	Before storage		After storage		After storage	
	BS		BS		BSWS	
	Mean	SEM	Mean	SEM	SEM	SEM
DM ($g \times kg^{-1}$)	19.62	0.51	58.31	0.51	24.17	0.69
OM ($g \times kg^{-1}$)	11.66	0.48	36.19	0.61	14.22	0.60
TKN ($g \times kg^{-1}$)	1.10	0.01	1.72	0.02	0.95	0.02
TAN ($g \times kg^{-1}$)	0.57	0.00	0.31	0.02	0.18	0.01

The storage period affected the buffalo manure characteristics. The DM content increased mostly for BS; specifically, it accounts for 3 times the value recorded at the beginning of the storage; the OM content followed the same trend as well. After the trial, TKN and TAN content both for BS and BSWS decreased. TAN contents were for BS and BSWS 46% and 68% less than the values recorded at the beginning of the storage. The TKN content of BS increased by 56% compared to the initial value. On the other hand, the TKN content of BSWS decreased by 14% during the storage period. Both values refer to DM content of the samples. TKN values referred to DM content proved to be 29.5 and 39.3 $g \times kg^{-1}$ DM for BS and BSWS, respectively, decreasing by 47.3% and 29.8%. Additionally, TAN referred to DM content as well and is 5.4 and 7.5 $g \times kg^{-1}$ DM for BS and BSWS, respectively. Thus, TAN values referred to DM content and showed a reduction of 74% and 81.4% for BSWS and BS, respectively. From Figure 3, ammonia emission fluxes can be observed. The day after the straw application, BSWS ammonia emission accounted of 8 mg NH_3 m^{-2} h^{-1}; the emission related to BS was 17.3 mg NH_3 m^{-2} h^{-1}. BS showed within 24 h, a mean cumulative NH_3 emissions significantly higher than BSWS ($p < 0.05$) (Figure 3-2 a). The following days, an increasing ammonia emission trend was assessed; for this reason, a new application of straw was performed at the beginning of the second week of monitoring. After the straw reapplication an ammonia emission reduction of 77% was registered in the BSWS samples. After 400 h, both emission curves followed a decreasing pattern, trending to values close to zero. The overall reduction in terms of NH_3 emissions associated with the straw application was 7.3%. Specifically, the cumulative emissions of BSWS accounted for 2.632 g NH_3 m^{-2} (8% as TAN and 4% as TKN). The cumulative emissions for BS accounted for and 2.839 g NH_3 m^{-2} (7% as TAN and 3.7% as TKN). Six days after the second straw application on the 18th day of the measurement, the mean cumulative NH_3 emissions were not significantly different between the two groups (Figure 3-2 a).

3.3.3 Discussions

The reported emissions could be used to assess the differences in terms of emissions between different manure treatments or covers application during the storage period. This aspect is fundamental for planning future research and field studies.

3.3.3.1 Trial 1: Natural crust formation

During the Trial 1, the cover effects of the crust formation were observed. The formation of a natural air-dried crust occurs mainly when the straw or other bedding materials are present in the raw slurry, especially if not treated with solid–liquid separation. The crust formation that consequently occurs have the capacity to reduce the NH_3 emissions (Aguerre et al., 2012). The efficacy of the crust cover has been reported to be able to reduce ammonia emission up to 60% (Smith et al., 2007). Crust formation is however dependent to the slurry DM content. Has been established that under 1% of DM there is no crust formation of the stored slurry (Tom H. Misselbrook et al., 2005). As stated above are the reason why in this test we assisted to the formation of CS first and afterwards for the LFD. Regarding the slurry crust formation, it can also be enhanced by the gaseous losses (CO_2 and CH_4) that generally occur during the storage as a consequence of the anaerobic environment that develops during the storage (Smith et al., 2007). Indeed, in our study, we assessed that some particles were raised up to the surface by bubbles formation.

The higher TAN (2.46 against 1.85 g kg^{-1} of CS) and the higher pH value (7.9 instead of 7 of RS) could be the reason why an higher NH_3 emission was detected for the LFD at the beginning of the storage (Finzi et al., 2019) (Baldé et al., 2018). However, a decreasing ammonia emission pattern was registered in both the examined manure groups. We hypothesized that this phenomenon could be consequent to the natural crust formation and the reduction of TAN content, considering that no other manure adding was provided during the study. The reported data implies that the development of naturally air-dried crust is an effective way to mitigate ammonia emissions during the manure storage. Anyway crust formation could also be influenced by manure characteristics in particular dry matter content, content and livestock diet (grass silage) (Smith et al., 2007). Considered the above-mentioned parameters, crust formation does not occur with the same timing and compactness for all the manure types.

3.3.3.2 Trial 2: Effect of straw cover

The application of the straw cover influenced the DM content at the end of the storage (Table 3). This difference is probably a consequence of the different water evaporation of the samples. Ammonia volatilization occurred, leading to a reduction of TKN and TAN content found in both BSWS and BS. An important implication of the reported data is that the observed ammonia emission reductions possibly happened because the straw layer applied on the manure surface absorbed the ammonia. The reduction of ammonia volatilization from manure was already observed when straw cover was applied in the manure surface. This effect can be addressed as the consequence of the nitrogen immobilization performed by microorganism as described by (H. Kirchmann & Witter, 1989) (Sommer & Møller, 2000). The DM content of the slurry can also influence the straw performances when this material is applied on the stored manure surface. In fact has been shown that when applied on the surface of pig manure with low DM content, the straw mitigation effect registered was poor (Finzi et al., 2019). With particularly low dry matter content the straw could sink more easily, as happened during the first week of the monitoring period. Since a reapplication of the cover have already been assessed that can improve the cover efficacy (Smith et al., 2007), we reapplied a second layer of 1 cm of straw after 142h. The cover decomposition could be another reason of its short time duration and effectiveness in reducing ammonia losses (Dougherty et al., 2017). Previous research has documented that a significant emission reduction was achieved when a thicker layer of wheat straw was applied to the slurry. The straw was therefore an efficient natural cover reducing the emissions from 58.6% to 100%. In the same study was also assumed that during the storage of pig slurry a thin cover did not contribute to a reduction in emission because of the straw characteristics that get easily soaked (Guarino et al., 2006). Oher studies indicate that straw was also efficient in reducing ammonia emission at the storage when applied to duck manure. Its reduction efficiency was higher when combined with other material such as zeolites. In particular a reduction of 12% and 36% in terms of cumulative NH3 was registered when a single layer of each material or a combination of them was applied (J. Z. Wang et al., 2012). These findings suggest the possibility to increase the straw reducing emissions effect by combining it with other materials.

3.4 Conclusions

The two trials carried out, demonstrated how manure treatments such as SLS and AD can change the manure characteristics. The change in manure characteristics consequently have an influence on the gaseous emissions during the storage. Anaerobic Digestion seems to have increased the NH_3 emissions during storage (48.5% more than RS), in reason of the higher TAN content of LFD at the beginning of the storage. The higher OM content in RS, mainly associated with the straw bedding in the manure, was a characteristic that helped the surface crust formation that started from the first days of the storage. The straw application, assessed in this experimental trial, have shown an interesting implication not only for the capacity to reduction the ammonia emissions during storage phase but also for the possible capacity of absorbing the nitrogen fraction from the slurry. Certainly, this aspect could also affect the slurry application to the field. The findings of this research suggest that this approach could also be useful for the validation of these results in full scale. Further study on other cover materials singularly or in combination with straw could improve the performances and the practical utilization of the bio-covers as well as the economic aspect. In conclusion, different natural covers could be used during manure storage, but the emissions mitigation effect is affected by the characteristics of the manure, including the same type of slurries.

3.5 References

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4 Biochar cover as possible ammonia emissions mitigation during the storage of liquid buffalo digestate. Effect of applications methods and pyrolysis process parameters

This chapter in based on the following papers:

- Scotto di Perta, E., Giudicianni, P., Mautone, A., Caro, S., Cervelli, E., Ragucci, R., & Pindozzi, S. (2020, November). Is the biochar an effective floating cover for manure storage to reduce ammonia emissions, adsorbing nitrogen at the same time. In *2020 IEEE International Workshop on Metrology for Agriculture and Forestry (MetroAgriFor)* (pp. 44-48). IEEE.
- Scotto di Perta, E., Giudicianni, P., Grottola, C. M., Mautone, A., Cervelli, E., Ragucci, R., & Pindozzi, S. (2022, November). Biochar covering to mitigate the ammonia emissions from the manure storage tank: Effect of the pyrolysis temperature. In *2022 IEEE Workshop on Metrology for Agriculture and Forestry (MetroAgriFor)* (pp. 43-47). IEEE.
- Scotto di Perta, E., Giudicianni, P., Mautone, A., Grottola C.M., Cervelli, E., Ragucci, R., & Pindozzi, S. Biochar application rate and adsorption capacity effects on NH3 losses mitigation from buffalo digestate storage. *Journal of Environmental Management.* Submitted paper.
- Scotto di Perta, E.; Giudicianni, P.; Mautone, A.; Grottola, C.M.; Cervelli E.; Grieco, R.; Ragucci, R.; Pindozzi S. (in press). The application of biochar as strategy to reduce NH3 emissions from manure storage tank: effect of the biochar characteristics. *In XX CIGR World Congress 2022.*

4.1 Introduction

The optimization of stored manure management is an important issue considered the large ammonia emission generated form the livestock activities. For several years great effort has been devoted to the study of different floating covers to apply on stored manure to limit these gaseous losses (di Perta et al., 2020). Different materials such as plastic, fabric or organic are defined suitable to be used as manure cover. The evaluation of various cover types, has been carried out under different laboratory condition as well as open field. The subject of the cover assessment is not only their efficacy in reducing gas emissions, but also the life span of the different covers when applied in open field. During the last few years considerable attention has been paid to biochar as possible cover, for its capacity to mitigate ammonia emission and its potential to absorb nutrients (Dougherty et al., 2017)

(B. Wang et al., 2015)(Ghezzehei et al., 2014). As already detailed described in the introduction chapter, biochar is a carbon-rich material that is obtained from a pyrolysis process conducted under strict oxygen conditions (Mandal et al., 2018). Various studies have focused the attention on the utilization of biochar to reduce ammonia volatilization from the livestock sector (Ro et al., 2020). Other investigated aspects are also the possible reduction of gasses and improvement of the compost process when biochar is added as bulking agent (W. Chen et al., 2017). Already well known is also biochar capacity of absorbing ammonium in aqueous solutions and lowering the nitrogen losses when applied to the soil is (Taghizadeh-Toosi et al., 2012). Pyrolysis condition such as temperature and the material used to produce the biochar can affect its physical and chemical properties, in particular pore volumes, surface areas, functional groups, pH. This characteristics can consequently affect biochar performances in reducing ammonia emissions (Mandal et al., 2018) (J. Zhang & Wang, 2016). Considerable attention has been paid to biochar but there is still poor information about the use of biochar in reducing emissions from the manure storage tanks. Previous study has already shown the capacity of biochar in reducing ammonia (NH_3) emissions for manure storage up to ca. 58% (Di Perta et al., 2020). However, aspects regarding biochar application method and cover layer thickness besides the most efficient way to produce it concerning material and pyrolysis method, still need further investigation. Based on the promising findings presented in the literature, work on the remaining issues is needed.

For this purpose, based on the hypothesis that biochar addition is a valid mitigation technique when used during manure storage, this work explore possible biochar application modulate according to different amount and application method. This chapter aims to give an overview of the biochar utilization when used as cover to reduce ammonia emission. Trial 1 investigate whether biochar is efficient in reducing ammonia emission from the stored buffalo digestate. Once we assessed its efficacy, on Trial 2 we investigated which was the best way to apply this material, as cover or mixed inside the buffalo digestate. On Trial 3 the effect of two different pyrolysis type were tested to study the performances of two different biochar when used as mitigation strategies.

4.2 Material and methods

4.2.1 Trial 1: Biochar effectiveness as cover

Digestate storage were simulated in laboratory condition. 6 glass containers with 5 l capacity were placed in a climate-controlled room. Temperature and humidity were set at a defined temperature and monitored daily, during the whole trial. The glass containers were filled with 3.5 l of buffalo digestate. A group of three replicates were covered with 2 cm of commercial biochar, other three replicates with no cover were considered as control.

4.2.2 *Trial 2: Biochar application rates and modalities*

Manure storage were simulated in laboratory condition. Glass containers with 5 l capacity were filled with 3.5 l of buffalo digestate. Biochar was applied in all the replicates to assess which was the best way to apply it. 2 cm of biochar were applied as cover (2B); the equivalent of 2 cm of biochar were mixed inside the manure (Bm); 1 cm of biochar was applied as cover on the manure surface. Three replicates for each treatment were stored in a climate- controlled room. Temperature and humidity were set at a defined temperature and monitored daily, during the whole trial.

4.2.3 *Trial 3: Effect of different temperature of pyrolysis*

This experiment wants to investigate the effectiveness of two different biochar as a storage cover material and to compare the ammonia emissions consequent with its application. The biochar was produced conducting a pyrolysis with different temperatures starting from poplar pellets. Three replicates for each treatment were set up for a total of 6 manure container filled with 3.5 l of buffalo digestate stored in a controlled temperature room. The trial lasted 55 days. During the first 3 weeks, the gaseous emissions were measured once a day. Afterwards, as the emissions started to decrease the measurement were carried out two days per week.

4.2.4 *Measurements techniques*

Ammonia emission and pH measurement were carried out undertaking the same methodology for all the three trials.

The dynamic chamber technique defined by (Scotto di Perta et al., 2019) was used to measure methane and ammonia emissions. The manure containers were generally stored open. When the gas measurement was performed the containers were closed with a specific lid drilled in two points. One of the access points on the lid was assigned to the air inlet. Through the open access point the lid was connected to the expansion chamber. The expansion chamber was then connected to the sensor and to the vacuum pump, which regulate the air exchange to 1.5 l min^{-1} through a flow meter. After closing the manure container, the manure was ventilated for 20 min to achieve steady conditions inside the chamber. After the ventilation, the air was sampled for 16 minutes and analysed using a gas-sensitive semiconductor and electrochemical 'sensors (Aeroqual, series 500) to detect the real-time NH3. The fluxes were evaluated as follows:

$$F = \frac{Q(Cout - Cin)}{A}$$

C_{in}: the gas concentration of air inlet into the chamber in mg m-3; C_{out}: gas concentration of air outlet from the chamber in mg m^{-3}; Q: airflow rate through the chamber in m^3 h^{-1}; A: area of the emitting surface in m^2. pH, NH_3 emissions were monitored for the whole observing period. pH was measured with a portable pH meter (MT51302523, Mettler Toledo). To avoid surface perturbation when the pH meter sensor was used, a column of access was fixed on the glass container walls. Through the column sensor was insert into the manure without disturb eventual crust formation (Figure 4-1).

Figure 4-1. From the left. Glass vessels. Biochar cover with column access

4.2.5 Manure characteristics

The stored manure used in the laboratory test was liquid digestate collected from an anaerobic digestion plant located in Southern Italy (Caserta province, Campania region, Italy). The digestion plant treats Buffalo manure collected from surroundings livestock farms. Before the storage simulation digestate samples were collected to be characterized and assess the following parameters: pH, Dry Matter (DM), Total Ammoniacal Nitrogen (TAN) and Total Kjeldahl Nitrogen (TKN). Table 4-1. shows the parameter of the manure used for the 3 trials.

Table 4-1. Manure characteristics DM = Dry Matter; TKN = Total Kjeldahl Nitrogen; TAN = Total Ammoniacal Nitrogen.

	pH	DM (g/kg^{-1})	TKN (g/kg^{-1})	TAN (g/kg^{-1})
Trial 1	8.6	81.73	3.26	1.84
Trial 2	8.1	46.22	2.19	0.95
Trial 3	8.6	79.97	2.92	1.65

4.2.6 Biochar characteristics trial 1 and trial 2

The biochar for the trial 1 e 2 was acquired from Nera Biochar Srl. It was produced via pyrolysis (30 minutes) at a temperature of 550 ° C. The used feedstock was a mix of wood chips from Piedmont: Elm tree, Ash tree, Chestnut and conifers. The technical specifications provided by the biochar producer reported a C, H, N and ash content equal to 74.6, 2.0, 0.7, and 3.4 wt%, respectively. Oxygen content, calculated as difference, was 19.3 wt% db, whereas pH was ∼10 and BET surface was 350 m^2/g. The concentration of total OH groups, measured adopting the Bohem titration procedure, was 0.0697mmol/g (Scotto di Perta et al., 2020).

4.2.7 Biochar characteristics Trial 3

Pyrolysis experiments for biochar production were carried out in a fixed bed reactor at a heating rate of 7 °C/min, and at a constant flow rate of nitrogen 12.5 Nl/m up to 285°C and 450°C. Biochar referred to as B-285 and B-450 were respectively produced at 285 °C and 450°C. Wood pellets of Poplar tree (Populus nigra) were used as feedstock (Figure 4-2). The layers of biochar, used to cover the digestate, were in both cases posed in 2 cm of thickness.

Figure 4-2. From left Biochar at 285 °C and Biochar at 450°C

4.3 Results and discussions

4.3.1 Trial 1

The mean storage temperature and humidity were 18.6 °C and 71.25 %. At the end of the trial, representative samples of each vessel were collected and characterized in three replicates.

Table 4-2. Manure characteristics at the end of the trial. DM = Dry Matter; TKN = Total Kjeldahl Nitrogen; TAN = Total Ammoniacal Nitrogen.

	DM ($g\ kg^{-1}$)	TAN ($g\ kg^{-1}$)	TKN ($g\ kg^{-1}$)
Control	92.73	1.34	3.45
Biochar	100.74	1.58	3.44

Changes in digestate composition were detected from the beginning of the storage. A reduction of the water content occurred, especially for the control samples. The different water evaporation amount led to an increase of dry matter content for both control and digestate covered with biochar.

The biochar cover layer showed the capacity to reduce ammonia emission up to 78% as reported in Figure 4-3

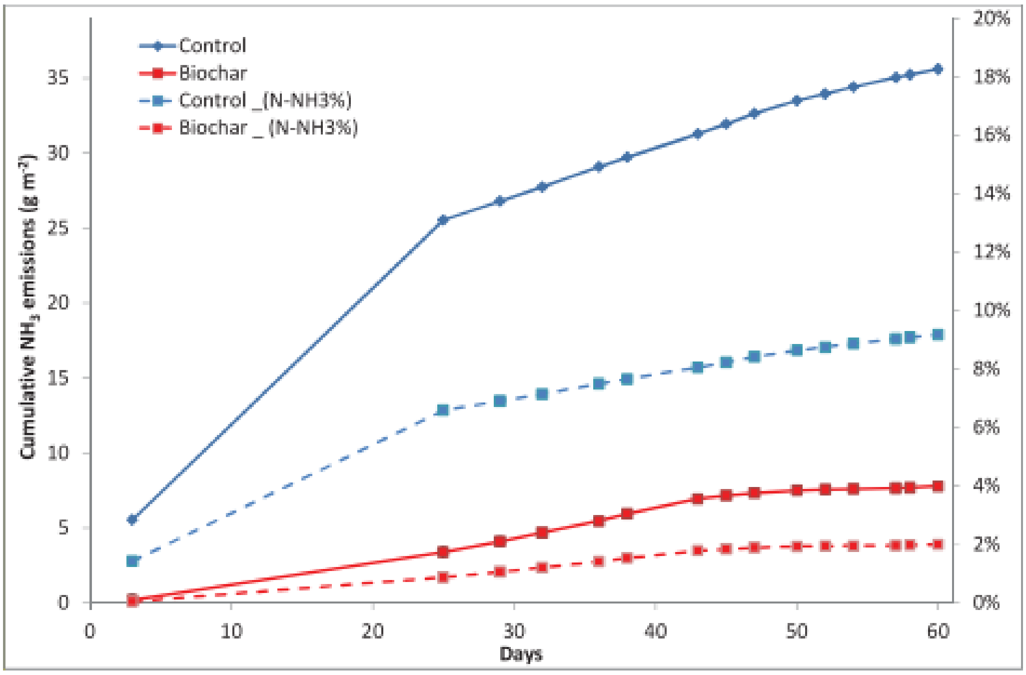

Figure 4-3. Cumulative ammonia emission. (Scotto di Perta et al., 2020)

In particular, the registered cumulative emissions were 35.61 g m^{-2} for the control and 7.78 g N m^{-2} for the digestate covered by biochar. The highest ammonia emission rates occurred during the first 3 days of the trial. The first measurement day, the control emission flux was 177.3 mg m^{-2} h^{-1} against 2.6 mg m^{-2} h^{-1} for the covered digestate. After 29 days the ammonia emission rates between the two samples started to show little differences: 12.5 and 7.6 mg m^{-2} h^{-1}, respectively. Digestate pH and biochar cover affected the ammonia emission flux. In detail, during the day 38th and 50th, a decrease in pH to the value 8.4 for the control determined a consequent reduction in terms of ammonia emission rates. The maximum emission reduction was detected right after the beginning of the trial. The covered samples emitted less than the control suggesting that the biochar cover limited the emissions acting as a barrier. The gas-film resistance to transport was the principal mechanism involved (B. Wang et al., 2015). Floating covers can reduce emissions of soluble gas decreasing the wind effect or the surface heating (VanderZaag et al., 2005). Biochar has also the capacity to adsorb the ammonia (NH_3(g)). This adsorbing effect is anyway related to the different characteristics of the biochar type (Ro et al., 2020). Is already well known that the application of biochar as cover can contribute to a great amount of ammonia emission reduction into the atmosphere (E. S. Di Perta, Cervelli, Di Nardo, et al., 2020). A previous study assessing the same type and the same amount of biochar (as used in the current experimental set up) applied on the surface of buffalo manure show how the biochar application reduced substantially the ammonia volatilization (E. S. Di Perta, Cervelli, Di Nardo, et al., 2020). In the current study a reduction of 78% was detected; during the previous study a reduction of 59% compared to the control group was detected. These differences could be consequence of different measurement operation. During the second trial the biochar cover was carefully handled to avoid any cracking of the biochar surface and thus increasing the cover efficiency. Biochar mitigation ability was observed and determined also when used to mitigate ammonia emissions from stored pig manure. However, the resulting obtained performance, didn't show a good mitigation capacity, probably, because of a significantly lower biochar application rate (4.57 vs 6.73 kg m^{-2} used in the current experimental setup) (Maurer et al., 2017).

4.3.2 *Trial 2*

Different biochar application methods were investigated to better understand the mechanisms involved in the mitigation of ammonia emissions in presence of biochar. It was assessed that the lowest NH_3 emissions were related to 2B (2 cm biochar layer). 1B (1 cm biochar layer) and Bm (biochar mixed with digestate) emitted 74% and 44% more than 2B. Manure characteristics after the trial are reported in Table 4-3. In Figure 4-4 the NH_3 emissions rates are presented together with the pH variations.

Table 4-3. Digestate characteristics at the end of the trial. DM = Dry Matter; TKN = Total Kjeldahl Nitrogen; TAN = Total Ammoniacal Nitrogen.

	DM ($g\ kg^{-1}$)	TAN ($g\ kg^{-1}$)	TKN ($g\ kg^{-1}$)
2B	62.05	0.65	2.44
1B	66.78	0.44	2.52
Bm	79.84	0.61	2.68

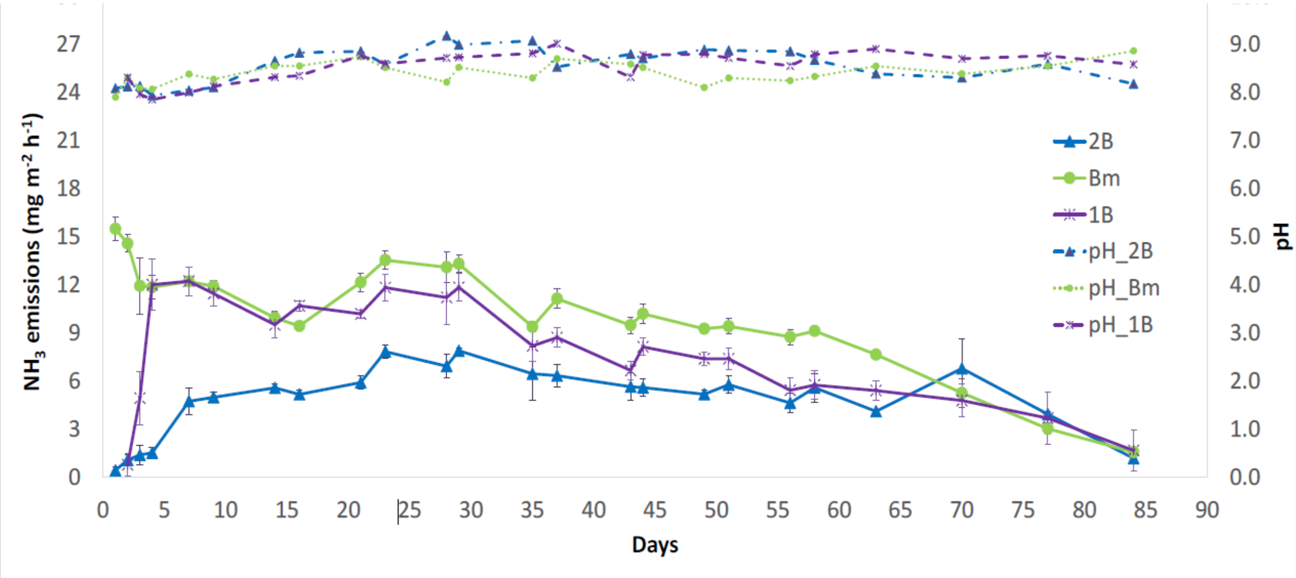

Figure 4-4. NH_3 emissions and pH variations. (Scotto di Perta et al. 2022 submitted)

Ammonia emission rates gradually decreased, tending to zero in all the treatments approximately after 84 days of trial. After the first 5 days from the cover application, emissions measured from 2B were very close to zero, showing a strong effect of the biochar in reducing gaseous exchange. In the case of 1B, the barrier effect lasted only for the first day, as shown in Figure 4-5.

Figure 4-5. From the left. Formation of biochar crust in the sample 1B. Volume reduction followed the storage period.

After 48h, was reported an increase in emission rate, specifically from 0.8 to 12 mg NH3 m^{-2} h^{-1}, reaching the same value of NH_3 emissions reported for Bm. Higher emissions since the beginning of the trial with a gradual decrease over time was detected from Bm. These data clearly show that the biochar cover, as well as the layer thickness, positively influence the ammonia retention. Different biochar application and quantity affected water evaporation, as well as the initial characteristics of the digestate. The dry matter of Bm resulted in the highest increase, followed by 1B. Concerning N content, the final values of concentrations are in good accordance with the emissions measured. The lower N reductions in terms of TAN and TKN were identified for 2B and1B. These findings show how a thicker cover layer acting as physical barrier enhance the mitigation of N losses. The long lasting of 2B layer was confirmed also by the monitoring of the surface during the trial. As reported by Rotz (Rotz, 2004) covers are able to reduce emissions if the sealing on the manure surface is kept undamaged. In the case of surface cracks, the cover efficacy decreases. Ammonia emissions monitoring showed how NH_3 emissions were significantly influenced by the biochar application method. The results obtained are in good accordance with Covali (Covali et al., 2021). Specifically, in their work was found thar biochar mixed in the digestate allowed a higher increase in ammonia emissions rate few hours after the application. At the same time, when biochar applied on the surface, emissions occurred later and slowly. Different aspects should be considered, to discuss the possible occurring mechanisms. First, it is well known that biochar acts as a barrier to gas transport at the air-liquid interface, as suggest by Wang (B. Wang et al., 2015) and Vanderzaag (A. C. Vanderzaag et al., 2010). More in deep, this last indicated that floating covers applied on a storage tank decrease the turbulent transport due to the reduced effect of wind and temperature on the surface. Another aspect to be considered, is the biochar NH_4^+ potential adsorption capacity, to understand which behavior is predominant.

In our work, during the monitoring of the surface conditions, significant differences and changes were noticed throughout the trial. The first cover group that started to show alteration of was the 1B. The biochar cover of one of the replicates cracked in the middle after 21 days. Since the cover was rather thin and less robust, we attributed the poor performances to the physical characteristic of the cover. Following the cover's crack an increase in ammonia emission was observed. Thereafter, also the other replicates of 1B showed cracks on the biochar cover. At day 21 in Bm was observed the development of a crust formed by the floating biochar mixed in the manure at the beginning of the trial. The crust appeared to be every day more tick and solid. Manure level in Bm decreased as consequence of the water evaporation, in fact also the DM value increased at the end of the storage (Figure 4-5).
The 2B cover remained almost intact didn't showing any crack on the surface. 2B always had the lowest emission rate. On week 9 a pick of 6.8 mg NH3 m^{-2} h^{-1} was observed. After week 9 the biochar cover lowered the level and appeared wet. The group 2B showed the lowest cumulative ammonia emission (10.38 g NH_3 m^{-2}). Reported cumulative NH_3 emissions are 14.98 gNH3 m^{-2} for 1B and 18.08 gNH3 m^{-2} for Bm. All treatments showed significantly different ammonia emissions ($p < 0.05$).

4.3.3 Trial 3

The Figure 3 shows the trend of the ammonia emission rate throughout the trial of the two tested samples. As it is possible to observe B-285 proved to emit less than B-450. Since the beginning of the monitoring period B-450 (2.38 mgNH_3 m-2 h-1) emissions were higher compared to B-285 (0.2 mgNH_3 m^{-2} h^{-1}). The different emissions amount may be due to the higher pH value of the B- 450 (~ 10); biochar pH also affected the pH of the underlying stored digestate. The average pH for B-450 was 8.92 ± 0.30 and 8.80 ± 0.28 for and B-285. Generally, emission trends followed the percentage of free ammonia in the liquid solution, which depends on pH and temperature. As a matter of fact, the higher the temperature, the greater the dissociation constant is, moving to the left the equilibrium between ammonia and ammonium and increasing the percentage of free ammonia in the solution (Yao et al., 2017). In both tested samples, ammonia emissions had an increasing trend. The maximum reached values of were 11.3 mgNH_3 m^{-2} h^{-1} for B-285 and 15.7 mgNH_3 m^{-2} h^{-1} for B-450. From the 30th day of monitoring the emitting trend started to reverse. Results of the emission monitoring are in good accordance with the N content of the digestates after the storage, shown in Table 4-4. Both the studied group showed TAN reduction, but the greater reduction was observed in B-450.The ST content after the storage period showed that the amount of evaporated water was close to zero in both groups. This result demonstrated the capacity of biochar to reduce water evaporation from the stored manure. These results have clearly showed that biochar reduced the ammonia volatilization acting as a physical barrier. In this study the more effective biochar was produced at a lower temperature.

Table 4-4. Digestate characteristics at the end of the trial. DM = Dry Matter; TKN = Total Kjeldahl Nitrogen; TAN = Total Ammoniacal Nitrogen.

	DM (g kg-1)	TAN (g kg-1)	TKN (g kg-1)
B-450	79.37	1.13	3.12
B-285	81.46	1.18	3.25

4.4 Conclusions

From the research that has been performed, it is possible to demonstrate that:

- biochar has a good attitude as a physical barrier to reduce ammonia emission. Specifically, in trial 1, the cumulative NH3 emissions were 35.61 g m^{-2} and 7.78 g N m^{-2} for the control sample and digestate covered by biochar, respectively; corresponding to a reduction of 78%.

-When the biochar is applied as a floating layer and compact, it introduces an additional resistance to the gas transfer. This aspect is even more impacting than the NH_3 adsorption in the NH_3 emissions reduction.

- pyrolysis temperature affected not only the biochar physical-chemical characteristics but also the effectiveness of biochar in reducing the ammonia emissions from the digestate storage. Specifically, in trial 3 B-285 emitted 42 % less NH3 than the other one. Also, in this case was demonstrated that the greater effect of the biochar in reducing NH3 emissions can be attributed to a "lid" action which constitutes a greater resistance to gaseous exchange.

These findings make biochar an interesting application as a cover for manure storage from the emission reduction point of view. Nonetheless, a common issue related to the covers, in wider terms, is their cost and the maintenance of their action over a long period. Unfortunately, biochar cost expressed as €·m^{-2} is still considerable. A possible way to make biochar attractive no also from the investment point of view is reducing the application cost, mainly cutting the cost related to the feedstock. For this purpose, considering farm waste such as agricultural materials, crop residues or animal manure could be a solution for reducing feedstock purchase and transportation costs and promoting a circular economy.

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5 Assessment of natural permeable cover to reduce ammonia volatilization from stored buffalo digestate

5.1 Introduction

Intensive livestock farming and the consequent management of animal waste may lead to adverse impact on the environment even when properly managed (Wheeler et al., 2011). As already discussed in the introduction chapter, livestock sector is responsible for a great sources of gaseous emission into the atmosphere, in particular ammonia (NH_3) (Kupper et al., 2021) (Smith et al., 2007). Manure storage is not considered the main cause of NH_3 volatilization within the livestock activities. However, the storage is often the focus of studies regarding emission mitigation strategies because is considered as a punctual source of emissions compared to wider areas, it is similarly managed worldwide, and since it is an emissions source relatively easy to monitor (A. Vanderzaag et al., 2015). Several factors can influence the gas emissions generated from the stored manure, for instance manure composition, manure storage, livestock farm typology and location. In particular, manure characteristics such as the concentration of urea in urine and total ammoniacal nitrogen (TAN) in the slurry, pH and slurry temperature (Portejoie et al., 2003). In addition to manure characteristics also the stored volume, the emitting surface, the air velocity, and climatic condition have effect on ammonia volatilization. Generally, influence of gaseous emissions also arise from the farm typology and location (Wyer et al., 2022)(Varma et al., 2021) (Sørensen et al., 2013). Besides the well-known negative impact of ammonia emissions on the environment, nitrogen losses are also responsible for particulate matter formation. This last can impacts human health causing respiratory and cardiovascular disease and is also potentially responsible for the diffusion of COVID-19 (Conticini et al., 2020). What derives from the potential ammonia emissions from manure management, is the necessity for the farmers to implement solutions, sometimes expensive, to follow the European Community rules (Scotto di Perta et al., 2019). Many studies have investigated possible NH_3 mitigation techniques to apply during the slurry storage. In particular organic cover have shown good reduction efficiency, up to 87% of reduction (Guarino et al., 2006). Between organic cover can also be included the biochar, a material that has recently gained interest as reduction techniques. Biochar have showed in previous studies its capacity to reduce ammonia emissions up to 78% (Scotto di Perta et al., 2020). To this purpose, this study aimed to evaluate the efficiency of three natural floating covers in reducing ammonia emission from stored buffalo digestate. Straw, clay LECA, biochar, and uncovered manure were monitored to assess their efficiency under laboratory condition. All the tested covers had the same thickness. The results showed how the biochar was the most effective cover reducing the emission of 67% compared to the control samples. LECA cover had the worst performance between the tested cover showing an increase in ammonia emissions probably due to an inadequate layer thickness. Further research will focus on the application on large scale and the susceptibility to the weather condition and durability of the cover when applied outdoor and in real scale.

5.2 Material and methods

Each experimental unit, used to simulate the average storage conditions of farm tanks, consisted in 5 l glass bucket, with a height of 25 cm and diameter of 16 cm. Each bucket was filled with 3 l of liquid fraction of digestate. The livestock liquid digestate was collected from an anaerobic digestion plant that treats buffalo manure collected from several buffalo farms. The consortium plant is located in the Caserta province. Three cover type were tested and applied to the digestate surface. For each treatment were set three replicates for a total of 12 experimental units. Three experimental unit were set up with straw cover (2 cm), three with the biochar (2 cm), three with clay LECA (2 cm), three were set up without any covering, as control (Figure 5-1). Previous studies on biochar effect showed that a layer of 2 cm was efficient on ammonia emission reduction when applied as cover (Scotto di Perta, et al., 2020). Considering this result, we compared other materials well-known to be able to reduce ammonia emission, to biochar, using the same layer thickness.

Respectively 12.8 g of straw, 84 gr of biochar, 180 gr of clay Leca. The cover materials were manually applied to ensure even and homogenous layers on the manure surface. All the covering materials were air dried at 105° for 24 hours to accurately standardize them. After this step the material were weighted and applied to the manure surface. The different covers were brought to room temperature before the application. The cover efficiency was tested for a period of four weeks. The pH and the manure temperature were monitored every measurement day before the gas measurement occurred. To avoid disturbance of the sample surface when the pH sensor was insert in the digestate sample, a plastic tube has been applied to the jar wall before the jar was filled with digestate, to create an easy access.

Figure 5-1 Tested cover on digestate surface. From the left: clay, straw, biochar, control, respectively

To define the effect of different treatments on gaseous emissions during digestate storage, under standardized experimental conditions the ammonia emissions were measured following the dynamic chamber method described by Berg et al. (2006). Accordingly, the digestate were stored in open vessels with no lid in controlled temperature room. Before starting the measurements, each vessel was closed with an air- tight lid provided with two air input. The air inlet port was connected with a flow meter and a compressor. The headspace between the stored digestate surface and the lid was then ventilated with compressed air to create an airflow through the dynamic chamber. The air exchange inside the chambers was adjusted by the flow meters and was set to make the air in the headspace to changed once per minute. The computer registered one value each minute for 15 minutes.

Samples of the digestate were taken before it was stored to analyse chemical and physical digestate properties, such as pH, Dry Matter (DM), Organic Matter OM, Total Ammoniacal Nitrogen (TAN) and Total Kjeldahl Nitrogen (TKN) (Table 5-1). Samples were also taken at the end of the storage period.

Table 5-1. Digestate characteristics at the beginning of the trial. DM = Dry Matter; TKN = Total Kjeldahl Nitrogen; TAN = Total Ammoniacal Nitrogen.

	DM (g kg^{-1})	TAN (g kg^{-1})	TKN (g kg^{-1})	pH
Digestate	66.66	1.66	3.5	8.2

To define if any significant differences in ammonia emission occurred within the treatments were investigated using the ANOVA procedure. For all the statistics, a significance level of p = 0.05 was applied.

5.3 Results

5.3.1 Digestate composition

During the storage period, water evaporation occurred and a consequent decrease in weight and digestate level was registered in all the samples. The cover applications influenced the evaporation from the manure and the final Dry matter content. At the end of the experiment Dry matter values had increased in all the tested sample. The highest increase of DM was registered in the control group, the lowest in the clay group. The average increase compared to the beginning of the storage was 22% for control and 10% for clay. Between the covers, the DM content didn't seem to be related to the decrease of the digestate level or weight.
At the beginning of the experiment the pH of the untreated buffalo digestate was 8.3. The lowest value of pH was detected the 16^{th} day of storage; the decrease occurred in all the samples, but clay showed the lowest value. The same day was also registered a decrease in temperature. On the 30^{th} day the highest peak of pH occurred in all the monitored samples, shifting from a mean of 8.5 to a mean of 8.92. All the change in pH were related to a change in the digestate temperature. Generally, digestate covered with clay had the lowest pH values. Total N content decreased in all the samples at the end of the experiment. The highest change in initial TKN occurred in the control and straw group. The lowest amount of initial TKN remained in the digestate covered with LECA; it tended to be 15.0% higher compared with uncovered digestate. Initial TAN content varied inconsistently between the groups. Digestate characteristics are reported in Table 5-2.

Table 5-2. Digestate characteristics at the end of the trial. DM = Dry Matter; TKN = Total Kjeldahl Nitrogen; TAN = Total Ammoniacal Nitrogen.

	DM (g/kg^{-1})	TKN (g/kg^{-1})	TAN (g/kg^{-1})
Control	81,32	2,93	1,15
Biochar	76,22	2,91	1,31
Straw	75,00	2,90	1,12
Clay	73,43	3,06	1,38

5.3.2 Emission

The cumulative emissions showed Figure 5-2 in accounted for 924.4 g m^{-2} for the biochar; 1798.9 g m^{-2} for the straw, 3186.7 g m^{-2} for the clay; for 2812.5 g m^{-2} for the control.

Biochar was the most effective material emitting 67% less than the control group. During the trial, the biochar cover remained intact with no cracks on the cover surface. The ammonia reduction efficiency and the emission pattern appeared to be consistent throughout the trial. After two weeks from the application, the char cover slowly started to sink, showing an uneven thickness but it never completely sank.

Straw cover showed an emission reduction of 58% compared to the control on the first day. The straw cover, compacted by pressing before the application on the manure surface, started after the first week to decrease in density showing on the second week a different distribution on the surface. Just the layer in contact with the manure surface appeared to be wet, but the cover didn't sink before day 23.

Clay cover at the beginning of the storage reduced the emission of 38% compared to the control, the lowest emission reduction between the treatments on the first day. From day 2 to day 13 the clay cover effectiveness continued to decrease. After the 13th day, the emission rate was always higher than the control. For almost all the monitoring period clay and straw cover showed the same emission pattern. Clay cover was the only one to remain stable for all the trial, this is because its capacity to float wasn't affected from the contact with the digestate and always showed a part of its surface under the digestate level and another part above the manure surface. The applied granules, managed to totally cover the digestate surface with a single layer of LECA sphere. Throughout the trial the granules were incorporated in the digestate surface creating a solid cover, less mobile than the other tested. The control group, set without any cover on the manure surface, showed emissions ranging from 7.8 g m^2 h^{-1} to 2.4 g m^2 h^{-1}. The first day occurred the maximum emissions that started to decrease from day 2 not maintaining a stable trend. From the day 13 a superficial floating crust starting to form in all the replicate. The crust was nonhomogeneous and cracked very easily but did not sink. The minimum temperature between all the tested group was registered in the control group. Figure 5-2 shows the cumulative ammonia emissions measured throughout the trial.

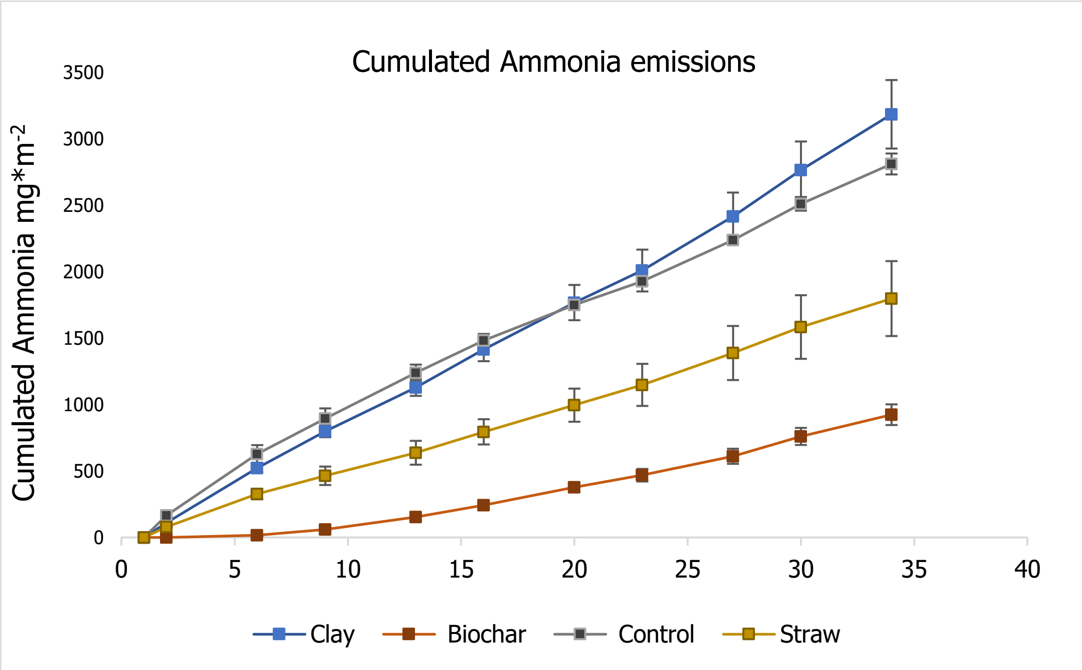

Figure 5-2. Cumulative ammonia emissions measured during storage

5.4 Discussions

5.4.1 Biochar

Biochar cover showed a significatively emission reduction compared to the uncovered sample. The data obtained are broadly consistent with the major trends showing that biochar cover has a great efficacy in mitigating NH_3 emissions. Since biochar effectiveness was already assessed, showing a capacity of mitigate ammonia emission up to 78%, other studies have investigated if the best biochar performances were registered when used as cover or mix inside (Scotto di Perta et al., 2020). Recently an investigation on the utilization of biochar as cover and mixed inside the digestate was carried out. Superficial biochar application and mixed biochar were able to reduce the cumulative ammonia emissions by 48% and 52% compared with the control. The reduction effect of application and the mixed biochar was not significantly different ($p = 1.00$) (Covali et al., 2021). In other studied, since the temporal effect of the biochar, the possibility to make a second application was investigated (Meiirkhanuly et al., 2020). A reapplication of biochar resulted in a much higher percentage reductions statistically significant (B. Chen et al., 2021).

5.4.2 LECA

Clay application increased the cumulative ammonia emissions compared with the control by ca. 13%. This result were consistent with a previous study also reporting an increase of the emissions of the covered manure compared to the control when 5 cm of clay was used as fresh dairy manure cover in a field trial (Nartey et al., 2021). Significant reduction of ammonia volatilization was assessed only when a thicker clay cover corresponding to 14 cm layer (Berg et al., 2006). For a thinner cover of 7 cm a reduction of 16.81% compared to the control was assessed but was not defined significant (Guarino et al., 2006). Even when LECA cover formed a firm surface crust, the gaps between the granules allows NH_3 volatilization making ineffective the superficial cover application (Nartey et al., 2021).

5.4.3 Straw

Straw cover reduced the ammonia emissions compared to the storage significatively. Several other authors confirmed the ability of straw cover in reducing the ammonia emission when this material was used as cover, both when pre-treated with other material such as lactic acid or when used untreated (Berg et al., 2006) (Guarino et al., 2006). Not only during the manure storage but also during the composting process, straw showed to be effective in mitigate ammonia emission also in combination with zeolites (J. Wang et al., 2014). When a layer of 30 cm was applied on the manure surface during a field treatment, after 122 day of storage, the cumulative emissions were reduced 90% compared to the control (VanderZaag et al., 2009). Although different straw types have been assessed in literature such as reed straw, wheat straw, rice straw, a comparison between the different aptitude and efficacy in reducing the emission between these different materials haven't been assessed yet.

5.5 Conclusions

The utilization of mitigation strategies to minimize NH_3 emissions during the manure storage has become fundamental. The application of floating cover has been assessed to be an efficient mitigation method. In this study we compared three cover material, biochar, clay LECA, straw. From the outcome of our investigation, it is possible to conclude that in a controlled environment biochar is the most effective cover material. In fact, the highest mitigation effect has been registered when the biochar was used as cover showing an overall reduction of cumulative emissions of 67%. Other results obtained suggest that to have proper reduction in term of ammonia mitigation when using LECA cover a thin layer is not sufficient, causing in this study an enhancement of the ammonia volatilization compared to the control. Clearly, further research will be needed to understand logistics and management aspects. The behaviour of biochar must be studied to better understand how to proper manage a cover when applied in an open field storage since this material is sensible to the weather condition. Further studies are also needed to investigate the main physical properties of biochar in relation to the pyrolysis process and how the production techniques can influence the gaseous mitigations.

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6 General conclusions

As widely assessed, livestock sector is a hotspot source of ammonia (NH_3) emissions. To avoid depletion of water, soil, and air quality, related to ammonia volatilization and deposition, mitigation strategies must be implemented. It has been previously discussed that mitigations strategies are suggested to be applied in all the livestock farming activities. Nitrogen losses can't be solved with one single solution, but an integrate strategy involving the whole manure management chain is needed to avoid the stored N to be lost downstream. This thesis work provides an overview on manure storage phase and the possible methodologies to apply in order to reduce ammonia emissions. Covers applied on the stored manure seems to be effective in reducing gas emissions, for this reason different techniques have been investigated. Many works have demonstrated the feasibility of using different covers, highlighting, and identifying the limitation, the strengths and the aspect that still need to be studied and developed. Covering manure storages is a mitigation strategy suitable for different manure type. Different covers can be combined and can be applied to raw slurry and to treated manure as well. Materials suitable to this use are many but we focused our interest on natural permeable floating cover. As largely described and defined in the literature, natural cover when properly installed and handled can be efficient in reduce NH_3 emissions by over 70%. Among the materials used as natural cover, biochar can be included. Biochar, a material made from pyrolyzed biomass has gained popularity because of its beneficial effect when applied to soil and its potential to sequestrate carbon. Recently biochar has also gained importance because of its capacity to reduce ammonia volatilization.

Our research focused on a variety of natural covers generally indicated as good emission reduction strategies, additionally this work deals with gas pollutant emissions throughout the manure management chain of poultry. In Chapter 2 a description of the poultry based component of the DATAMAN databased was carried out focusing on CH_4, N_2O and NH_3 generated from manure storage, moreover investigate if different handling methods of broiler manure affect gaseous emissions and manure properties. The chapter gives its contribution to the current investigations focusing on the livestock production and manure management impact to nitrous oxide (N_2O), ammonia (NH_3), and methane (CH_4) emissions. The DATAMAN database gives vast and detailed informations on how manure is handled worldwide. With the research on the collected data a deeper knowledge on EF values for manure sources can be gained and a more accurate evaluation mitigation strategies along the manure management chain can be carried out. In Chapter 3 storage tests showed how natural crust proved to be effective in reducing ammonia emissions of 33% compared to uncovered manure. In the same chapter an investigation on straw cover showed that this material was efficient in reducing emission for a short time period so a second application of the material was tested. In both experiments cover efficiency and durability was related to DM content. A biochar analysis carried out in Chapter 4 highlighted how the best way to apply the biochar is with a superficial application showing an ammonia emission reduction was up to 78%. The cover efficiency was related to its thickness, in fact a biochar cover thick 2 cm was more efficient in reducing the ammonia emission compared to a 1 cm cover and the equivalent of 2 cm mixed inside the buffalo digestate. Also the pyrolysis method was demonstrated to be a parameter influencing the mitigation capacity of biochar an in particular has been demonstrated how a pyrolysis conducted under lower temperature could represent a more efficient biochar. This result can be very interesting when the economic effectiveness of the covers is taken into account. In Chapter 5 biochar still proved to be the most effective cover material when compared with straw clay and a control, resulting the most efficient in reducing ammonia emission.

In this work all the investigate cover are natural material. The main reason is because the natural covers could give the possibility to be applied to soil together with the manure when is applied as fertilizer without the necessity to previously separate them from the slurry. Other cover type as clay pebbles, instead could be suitable for a second utilization, after a hypothetical separation from the slurry they may be applied on the digestate again. From the outcome of our investigation, general conclusions valid for natural floating covers can be defined. Cover thickness was assessed to be an important parameter to consider, in fact when applied in larger quantity or reapplied, many cover materials showed a higher effectiveness in reducing NH_3 emissions. Moreover, when covers are carefully handled, avoiding surface cracking, or sinking, it enhances the mitigation effect, keeping effective the resistance to ammonia volatilization or by decreasing the digestate emitting area. The next stage of the research on the emission abatement may be related to investigation on the already tested materials or new materials and possible combinations and treatments. Despite these rather encouraging results, there are some management aspects that still need to be thoroughly analyzed. The limitation of the studied cover type is their susceptibility to weather condition such as precipitation and windspeeds. To the authors´ knowledge open field trial and studies to possibly increase the covers floating aptitude and durability have been scarcely investigated. Moreover, farms byproducts and feedstock could be reutilized and applied as covers once treated for instance with a pyrolysis process.