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ANALYSIS OF AMMONIA RELEASE AND BEST AVAILABLE PRACTICES TO SUPPORT FARM MANAGEMENT IN THE REDUCTION OF AMMONIA EMISSIONS IN DAIRY HOUSES

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CONTENTS

ABSTRACT

The objective of this thesis work was to verify the levels of ammonia concentrations in different functional areas of naturally ventilated dairy houses, through the measurement of the concentrations of ammonia at different heights from the floor of the breeding environment, also in relation to the main inside microclimatic variables and outside climate conditions.

The research activities were carried out in barns located in an area of the Province of Ragusa highly suited to livestock breeding, where are located most of the naturally ventilated barns present in Sicily (Italy).

In this work, issues of great interest which concern the protection of animal welfare, salubrity within the breeding environment, the operators' safety in the workplace and the environmental protection have been dealt with through the outcomes of this research which gave a contribution to the analysis of ammonia concentrations and microclimatic variables in breeding environments of dairy houses.

An experimental protocol for measuring ammonia concentration within the breeding environment at different heights from the floor and for the measurement of the main internal microclimate variables and the external climatic ones was proposed.

The ammonia emission values related to the cows housed in the Building A ranged between 0.44 and 0.14 kg/h whereas the values related to the HPU were between 0.31 and 0.10 kg/h/HPU. The Heat balance method yielded ammonia emission values ranging between 0.005 and 0.27 kg/h and 0.004 and 0.19 kg/h/HPU.

A technique for the ammonia emissions reduction has been tested, by using a processing residue of the coffee industry. This technique could be regarded as feasible in this field since the experiment showed a reduction of approximately 50% of the emissions and the choice of this dried vegetal material is suitable due to its easy availability in the territory.

Finally, indications have been obtained to support farmers' management choices in order to reduce ammonia emissions into the breeding environment. They are based on emission reduction techniques adapted to the specific case study.

1 INTRODUCTION

1.1 Preface

If not properly managed, intensive livestock farms have the potential to cause environmental pollution. Livestock installations and associated activities such as the application of manure on farmland are a significant source of different emissions into air, soil and water. Among gaseous emissions there are to mention unpleasant odours, ammonia, methane and nitrous oxide and dust. Emissions are mainly caused by the decomposition of animal waste (odour, ammonia, nitrous oxide), the digestion of ruminants (methane), the application of manure (ammonia, odour, nitrous oxide) and the feeding and bedding (dust) and barns management.

As regards ammonia (NH_3), agriculture is known as the major source of atmospheric NH_3, contributing to 50% of NH_3 emissions in the world (Bouwman et al., 1997), over 90% in Europe (EEA, 2011) and 95% in Italy (ISPRA, 2011). Of this 95% the livestock sector is responsible for about 77% (Buijman et al., 1999).

Ammonia emission from naturally ventilated dairy houses is difficult to be quantified due to the direct relation between the outdoor wind and indoor environment. Moreover, since outdoor wind has a turbulent and time-varying nature it is complex to accurately know where and when high or low velocity gradients are present in the different functional areas of the livestock building. As a consequence, it is not generally known which area of the barn floor covered by the manure is subject to high air velocity gradients.

Besides the effects of ammonia emissions on the environment, the importance of evaluating the ammonia concentrations in livestock buildings regards the necessity to ensure the operators' safety and animal welfare. In fact, high concentrations of NH_3 inside the animal houses also represent potential health hazards to humans and animals (Reece et al., 1980; Carr et al., 1990; Crook et al., 1991; Wheeler et al., 2000a). Chronic respiratory diseases of swine production facility workers have been attributed to dust and NH_3 (Donham et al., 1995). Animal respiratory diseases, such as sneezing, coughing, or pneumonia, increased when NH_3 concentrations were 20÷40 ppm as compared with 5÷15 ppm (Busse, 1993).

In general, the release of ammonia from manure deposited on building floors depends on the characteristics of the manure, livestock management practices, climatic conditions within the buildings, and animal behaviour. To compute ammonia emissions, knowledge of the ventilation rate is also required.

Although studies of agricultural NH_3 have increased in recent years, reliable field measurements of NH_3 at animal facilities (animal houses, and manure storage and treatment) are a major need. Understanding and control of NH_3 at animal facilities depend on sampling/measurement techniques, including devices, instruments, and procedures. Accurate and reliable techniques provide high quality data that are essential to research as well as abatement of NH_3 emissions.

In Italy, at present, few research studies, have regarded ammonia concentration surveys and the evaluation of how the different housing types and different techniques of manure management affect the emission of ammonia from livestock buildings, although ammonia concentrations in the breeding environment inside the barn could be of relevance and, as a consequence, ammonia emissions from livestock buildings.

1.2 Objective and limits of the study

The research study reported in this thesis work was carried out in an area of the Province of Ragusa (Sicily, Italy) which is one of the most important livestock breeding areas in the country. In this area, open or semi-open livestock buildings are widespread.

The main objective of this thesis work was to verify the levels of ammonia concentrations in different functional areas of barns for dairy cows, located in the considered area, through the measurement of the concentrations of ammonia at different heights from the floor of the breeding environment, also in relation to the main inside microclimatic variables and outside climate conditions.

The second objective regarded the computation of ammonia emissions from the breeding environment. Although some limits that are described below have affected this computation, an effort to seek for an approximate estimate of the ammonia release in the environment was performed.

An additional objective consisted in looking for possible “Best Available Practices” to support farm management in order to reduce ammonia emissions in the environment.

To achieve these objectives, a wide bibliographic research regarding measurement and computation methods of ammonia emissions in barns for dairy cows and methods of reducing emissions was carried out.

The limits of the work depending on the type of measurement instrument available for the trials can be summarised as follows:

- the measurements of gas concentrations inside the breeding environments were conducted as a succession of measurements on predefined points through the use of a portable measuring device. Therefore, it was not possible to carry out a continuous and simultaneous recording of data of the concentrations of ammonia in the barns;

- measurements of air velocity in a location inside the barn and wind speed in a location outside the barn were collected. Therefore, it was not possible to make an accurate assessment of air exchanges between the interior and the exterior of the buildings based on simultaneous multiple measurements at the defined inlets and outlets of the barn.

The measuring instruments used in the trials were simpler than the equipments used in the works reported in the literature. However, the simplicity, the lower cost in comparison to those equipments and the good accuracy of the measurements may constitute good characteristics for a tool which could be more easily used by a farmer to control ammonia level. This usage would be suitable especially for the control of the ammonia level in specific areas of the barn, both for animal welfare and for the safety of operator's work.

1.3 Work organization

In the second chapter of this thesis work, after a description of the molecular forms of nitrogen, the sources and the processes of ammonia emissions in the environment are described. Knowledge of ammonia production and the related release processe is of crucial importance to understand the distribution inside the breeding environments and suggest possible modifications in the barn management routines.

The third chapter of the thesis work gives an overview of the methods for measuring ammonia concentrations and computing ammonia emission rates. In detail, it describes a comprehensive review of ammonia measurement techniques and the models for NH_3 emission simulation, as well as the related state of the art in the application of these methods and models.

The fourth chapter describes the materials and methods of the research. In detail, it describes the breeding environments analysed and the method proposed for the sampling and measurements of ammonia concentrations in some functional areas of the barns under study.

The fifth chapter describes the results obtained from the application of the methods for ammonia concentration measurement and ammonia emission estimates, and provides a general discussion on these outcomes in relation to the observations provided by other researchers on similar experimental trials.

2 SOURCES AND PROCESSES OF AMMONIA EMISSIONS

2.1 The nitrogen and its molecular forms

Nitrogen (N), and its molecular form (N_2), is the most abundant element in the atmosphere, hydrosphere and biosphere. However, it is not directly usable by most organisms, due to the large energy required to break its ties (Galloway et al., 2003). The agricultural land is often lacking in N content which is needed to provide optimum levels of nutrition for the crop (Godwin and Singh, 1998). Since the biological fixation of nitrogen is not sufficient to cover the needs of the crops, N fertilizers are widely used in order to enhance the soil supply of such macroelement and to increase the food production.

Anthropogenic flows of N constitute the mayor component of the earth's nutrient cycles (Galloway, 2008), producing positive effects, as increase of yields, and negative effects as the release of reactive form of N (Nr) in the environment. In particular, significant fractions of the mobilized N are lost towards atmosphere by gaseous emissions of N compounds such as ammonia (NH_3), nitrous oxide (N_2O), oxidised nitrogen (NOx) and nitric acid (HNO_3), and through leaching and runoff losses of nitrate (NO^{3-}) to ground and surface waters (de Vries et al., 2001). Three N forms are mainly involved in the impact of the N excess on the environment: NOx mainly emitted by combustion processes; N_2O formed by nitrification and de-nitrification processes in the soil; reduced nitrogen, including NH_3 and ammonium (NH^{4+}), mainly formed by agricultural practices and from livestock farming.

2.2 Ammonia in the environment

Ambient NH_3 assumes an important role and growing interest among different atmospheric N species, as a key of the future negative impacts of N on terrestrial ecosystems (Sutton, 2006). In particular, the environmental issues due to NH_3 include mainly acidification of soils, eutrophication of water with loss of biodiversity, human health and the long-range transport of sulphur (S) and N (Sutton et al., 1993; Asman et al., 1998; Erisman et al., 2001; Harper, 2005). Moreover, by 2020 it is estimated that NH_3 will be the largest single contributor to acidification, eutrophication and formation of secondary particulate matter (Ammann et al., 2005).

Dry or wet deposition of ammonium particles to the ground contributes to soil acidification (van Breemen et al., 1982; Galloway, 2003), where NH^{4+} is nitrified in NO^{3-}, with the realising of protons (H^+). Soil pH will decrease when the buffer capacity of the soil is exhausted, causing changing in soil chemistry. In acidic soils elevate atmospheric deposition leads to nutrient imbalances since the uptake of base nutrients (Ca^{2+}, Mg^{2+}, K^{+}, P) is reduced (Erisman and de Vries, 2000; Galloway, 2003). This effect may be worsened in natural systems where N is a limiting nutrient, causing increasing growth of the vegetal species and increased demand of these base cations (van der Eerden et al., 1998). The excess of N supply in natural or semi-natural ecosystems influences their structure, competitive processes, sensitivity to stresses and functionality of vegetal species. Furthermore, NH_3 by means of NH^{4+} aerosol depositions, if not absorbed by the vegetation, may lead to increased environmental loads, such as NO^{3-} in the groundwater, and producing indirect greenhouse gas (GHG) emissions as nitrous oxide and ozone (O_3) (Galloway et al., 2008; Sutton et al., 2011).

Direct deposition of NH^{4+} aerosols to water contributes significantly to the eutrophication phenomenon, with consequent negative effects on aquatic life and biodiversity. Surface freshwater ecosystems (wetlands, streams, lakes and rivers) receive most of their N from atmospheric deposition and from biological nitrogen fixation (Galloway, 2003), where an increase in N deposition leads to degradation of the resource. Marine ecosystems, receiving N from freshwater, groundwater and from atmospheric depositions, result frequently in excessive algae growth with consequences on biota due to hypoxic status of water.

2.2.1 Particulate matter

Particulate matter (PM) is defined as particles of solid or liquid matter suspended in air. They are characterized by their origin (primary and secondary particles), their particle size, their composition and their potential physiological pathways.

Primary emissions are directly emitted by a source. Secondary particles are formed in the atmosphere by chemical reactions of certain gases that either condense or undergo chemical transformation to a species that condenses as a particle (Seinfeld, 1986). (The expression "secondary particle" is also sometimes used to describe redispersed or resuspended particles.)

Ammonia is a chemically active gas and readily combines with nitrate (NO^{3-}) and sulphate (SO^{4-}) in acid cloud droplets to form particulates (Asmanet al., 1998). The formation of particulates prolongs their existence in the atmosphere and therefore influences the geographic distribution of acidic depositions. The emitted NH_3 is subsequently deposited to land and water, either by dry deposition of NH_3 or by dry and wet deposition of ammonium (NH^{4+}) (Asman and Van Jaarsveld , 1991).

Atmospheric particles formed by the reactions of NH_3 in the troposphere, could interfere directly with radiation and energy balances through the increasing of earth albedo, or indirectly with clouds formation. Despite this effect cannot be quantified precisely, it contributes to a negative radiative forcing of about 1 W m^{-2}

(Schimel et al., 1996). Once released from the sources, NH_3 is rapidly dispersed in the turbulent atmosphere, going toward chemical reactions by forming ammonium aerosols and incorporating in precipitation. Approximately 50% of the NH_3 emitted does not react in atmosphere and returns as gas in dry deposition to natural surfaces, particularly wet surfaces and vegetation, within few kilometres (Asman, 1998; Ferm 1998).

Estimates of the atmospheric lifetime of NH_3 range from approximately 0.5 hours to 5 days (Fowler et al., 1997). This short lifetime is the result of rapid conversion of NH_3 gaseous to NH^{4+} on the liquid phase of atmosphere, causing wet deposition on surface.

PM_{10} is the fraction of suspended particulate matter in the air with aerodynamic diameters less than or equal to a nominal 10 µm. These particles are small enough to be breathable and could be deposited in lungs, which may cause deteriorated lung functions. In fact, particulate matter (PM) is considered to be a major threat to human health through respiratory cardiovascular disorders, especially by long term exposure of PM smaller than 2.5 µg ($PM_{2.5}$), according to WHO (2005). At the national level the incidence of agriculture in the formation of PM is about 4% of $PM_{2.5}$, and 11% of PM_{10} (ISPRA, 2011).

2.3 Ammonia produced from manure

Ammonia emission is the transfer function of NH_3 to the free air phase from the air-phase in immediate contact to the ammoniacal solution. The concentration of NH_3 in air close to the manure surface is in equilibrium with the dissolved NH_3 (Génermont and Cellier, 1997). As the air from the atmosphere passes over the manure surface, NH_3 from the manure surface is transported away horizontally by advection and vertically by turbulent diffusion.

Once manure is excreted, microbial processes begin to release manure nutrients in forms that can be taken up by plants or readily transported in the environment. Nitrogen is excreted in the form of urea and uric acid in the urine of mammals and birds, respectively. Conversion of nitrogen in the form of urea or uric acid requires the enzyme, urease, which is excreted in the feces. This conversion occurs rapidly, often within a few days. The breakdown of complex organic nitrogen forms in the feces occurs more slowly (within months or years). In both cases, the nitrogen that is released exists predominantly in the form of ammonium (NH^{4+}) under acidic or neutral conditions, or in the form of NH_3 at higher pH levels.

The relationship between NH^{4+}, NH_3, and pH (Fig.1) plays an important role in determining the fate of manure nitrogen because NH_3 is much less soluble in water than NH^{4+}. Therefore, NH^{4+} is not readily volatilized from manure, whereas NH_3 is rapidly converted to a gaseous form and emitted from manure. The rate of

NH_3 volatilization is influenced by the concentrations of manure NH_3 and urea, temperature, air velocity, surface area, and moisture.

Understanding how NH^{4+} and NH_3 are formed, the characteristics of these compounds, and the effects of various conditions on their environmental fate is the key to understanding how manure can be managed to minimize NH_3 emissions.

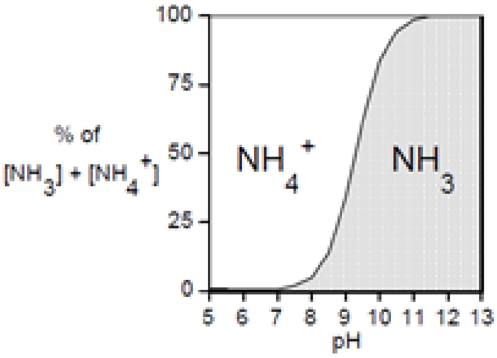


Fig.1 Relationship ammonia (NH_3) and ammonium (NH_4^+) as a function of pH. Source: G. Becker et al., 2001

2.3.1 Sources and processes related to nitrogen turnover

Ammonia originates from faeces and urine. Both the quantity and the composition of the faeces and urine are of interest when studying ammonia emission. Faeces are defined here as the fresh excreta from animals, while manure (solid) and slurry (liquid) are the mixture of faeces and urine as they are encountered in the animal house. Cows excrete their superfluous nitrogen as urea in the urine and undigested proteins in the faeces. Uric acid and undigested proteins are the main nitrogen components in the faeces, representing about 70% of the total nitrogen. Urea in urine and undigested proteins in faeces contribute also 70% to the total nitrogen excretion of cows, but this can vary considerably. The nitrogen components of uric acid, urea, ammonia/ammonium and undigested proteins are potential sources for ammonia volatilization.

2.3.1.1 Release of ammonia

Ammonia is mainly a product of the degradation of nitrogenous compounds. The biochemical degradation processes of uric acid (1), urea (2) and undigested proteins (3) are complex, but can be simplified as follows (Koerkamp et al., 1998):

$$C_5H_4O_3N_4 + 1.5O_2 + 4H_2O \rightarrow 5CO_2 + 4NH_3 \qquad (1)$$

$$CO(NH_2) + H_2O \rightarrow CO_2 + 2NH_3 \qquad (2)$$

$$Undigested \cdots proteins \rightarrow NH_3 \qquad (3)$$

All three processes are affected by microbial action. Various authors have described the aerobic decomposition of uric acid to ammonia (Eqn. 1). According to these descriptions, water and oxygen must be available, and ammonia and carbon dioxide arise as products of this degradation process. The enzyme urease, commonly present in microorganisms, is specific to this reaction with uric acid. The degradation of uric acid and proteins is positively influenced by temperature, pH and moisture content. The degradation process of urea (Eqn. 2) follows the law of Michaelis-Menten and is positively influenced by the urease activity, pH and temperature.

The enzyme urease is produced by microorganisms that are commonly present in manure. Elzing et al. (1992) described the breakdown of urea in cattle urine on a dirty slatted floor. They measured a total breakdown of urea within several hours under normal housing conditions.

Taiganides (1987) gives a scheme for the anaerobic degradation of organic material into N, C and S compounds. A review of microbial transformation of inorganic nitrogen is given by Painter. Three main processes can be distinguished. First, the fixation of dinitrogen (N_2) leading to ammonia production (aerobic or anaerobic). Second, due to nitrification (autotrophic or heterotrophic), ammonium can be converted to nitrite (NO_2^-) and hence nitrate (NO_3^-). Autotrophic nitrification is considered to be most important, in which case sufficient oxygen must be available. Third, nitrate can be utilized by microorganisms either for its nitrogen (assimilation-synthesis of N), or for its oxygen (dissimilation). For assimilation, ammonia is generally preferred to nitrate, since nitrate first has to be reduced to ammonia. The end product of the dissimilation can be nitrite (NO_2^-), nitric oxide (*NO*), nitrous oxide (N_2O) or dinitrogen (N_2). If any of the last three are formed, the process is called denitrification. For dissimilation the conditions must be anaerobic or nearly so.

2.3.1.2 Volatilization of ammonia

The ammonia in manure or litter is liable to volatilization to the surrounding air. Before being liberated into the air, ammonia is involved in equilibria in the liquid (l) and gas (g) phase, as in the Eqns (4)-(7):

$$NH_4^+(l) \Leftrightarrow NH_3(l) + H^+ \qquad (4)$$

The ammonium-ammonia equilibrium is influenced by temperature and pH. Below a pH of 7, nearly all ammonia is bound as ammonium and not liable to volatilization. Higher temperatures favour ammonia concentrations, because of the positive influence of temperature on the dissociation constant Ka, which is defined as:

$$K_a = [NH_3] \cdot \cdot [H_3O^+] / [NH_4^+] \qquad (5)$$

The volatilization equilibrium of ammonia to the gas phase, follows Henry's law for dilute systems,

$$NH_3(l) \Leftrightarrow NH_3(g) \qquad (6)$$

$$NH_3(g, manure) \Leftrightarrow NH_3(g, air) \qquad (7)$$

The partial pressure of gaseous ammonia, NH_3 (g) is proportional to the NH_3 (l) concentration. The volatilization of ammonia from manure to air, is defined as the mass flux. This flux is generally defined as the product of difference in partial pressure between the two media and a mass transfer coefficient. Higher partial pressure difference increases the flux. Mass transfer coefficients increase with increasing air velocity. The ventilation rate and pattern affect not only the global internal climate, but also the local climate above the manure and litter.

2.4 A review of ammonia concentration measurement techniques

Understanding and control of NH_3 at animal facilities depend on sampling/measurement techniques, including devices, instruments, and procedures. Accurate and reliable techniques provide high quality data that are essential to research as well as abatement of NH_3 emissions.

To obtain accurate information about NH_3 at animal facilities, suitable measurement techniques have to be adopted and one or more measurement variables have to be chosen depending on measurement objectives. These variables include NH_3 concentration, air exchange rate (or ventilation rate), air temperature, and air pressure.

Most NH_3 concentration measuring devices provide direct reading in volumetric concentrations. However, mass concentrations are required to calculate NH_3 emissions. The volume of gas depends on temperature and pressure and is therefore not constant. When converting from volumetric concentration to mass concentration, the volumetric concentration is multiplied by the molecular weight and the pressure, and divided by the gas constant and the temperature. Temperature and pressure therefore need to be known. However, although measurement of air temperature was often included in published works, air pressure measurements are seldom found. Atmosphere pressure varies between about 980 and 1040 mbar, a 6% variation, or a ±3% from standard atmosphere, which is often assumed. The measurements of temperature and air pressure are relatively easy with few technical challenges. Sampling and measurement methodologies applied at animal facilities are summarized in fig. 1 and some of them will be described in the following sections.

2.4.1 Ammonia Sampling

2.4.1.1 Location and time of sampling

The necessity of selecting location and time of sampling is obvious, because there are temporal and spatial variations of NH_3 concentration in animal buildings and open-air facilities for manure storage and treatment. An animal building is a ventilated and imperfectly mixed air space, where temperature and concentration gradients exist. Changes in room temperature and building ventilation usually follow diurnal and seasonal patterns. Although ventilation in the building creates air mixing, it can also increase the spatial concentration variations in situations when it dilutes NH_3 at some locations more than other locations. Field studies have confirmed non homogeneity of NH_3 concentrations in livestock houses (Krause and Janssen, 1990; 1991; Berckmans et al., 1994; Ni et al., 2000b).

	Sampling device	Converter Collection medium	Measuring device	
AMMONIA	Ferm tube	Aqueous acid trap	**Wet chemistry**	
			➢ Titrimetry ➢ Photometry & colorimetry ➢ Conductimetry	
		Distilled water	➢ pH paper ➢ pHdrion test strips ➢ Ammonia Quick Test	
			Gas detection tubes	
	Dynamic chamber		➢ Dragher tube ➢ Kitagawa tube ➢ Gastec tube ➢ Sensidyne tube ➢ MSA tube	
			FTIR spectroscopy	
		Open-path	➢ K300 ➢ M 2401 ➢ Bomen-100	
			Non-dispersive IR analyzer	
		Stream controller	➢ PAS Type 1302 ➢ Rosemount; Beckman	
	Dynamic chamber		**UV-DOAS system**	
		Open-pat Lindvall box	➢ Opsis monitor ➢ WSU system	
			CL NOx analyzer	
		Stream controller NH_3-NO converter	➢ Monitor-Labs analyzer ➢ THIS analyzer ➢ TEI analyzer ➢ API analyzer	
			Electrochemical sensor	
	Flux chamber		➢ Dragher sensor ➢ Quadscan gas monitor ➢ Twistik Transmitter	
			Chemcassette Monitor	
			➢ Single Point monitor	
			Solid-state sensor	
			➢ Solidox sensor ➢ IMEC sensor	
(Adapted from Ni et al., 2001)				

Tab.1 Overview of techniques for the measurement of ammonia concentrations (Source: Ni et al., 2001)

2.4.1.2 *Selection criteria of sampling techniques*

Three main sampling methods currently applied in field tests are closed, point, and open-path methods. The differences among the three methods are the spatial coverage by the sampling devices. The closed method collects samples from an enclosed surface area. The point method and the open-path method target air at certain points and in a narrow optical path within a three-dimensional zone, respectively. Depending on the sampling devices, the point sampling method can also be divided as two sub-methods: the passive exposure method and the active extraction method, which can be localized or centralized.

The **closed sampling method** involves a physical enclosure or chamber to create a limited headspace over a selected piece of NH_3 release surface. The ‘‘static’’ chamber does not have air exchange between the outside and inside of the chamber and has thus far only been used in investigations of NH_3 release from soil. The dynamic sampling chambers have an open bottom and are equipped with one or more air inlets and one or more outlets. The chamber is placed on the floors of animal buildings or on the surfaces of liquid or solid manure that releases NH3 thus isolating the release surface from its surroundings. The equipment and setup costs of the closed method are low, however, a sampling chamber is intrusive and alters the facility’s natural conditions and gas concentration profile.

Point sampling is the method in which samples are taken at a selected single point or at multiple points at animal facilities. Unlike closed sampling, the sampling location of this method can be at different heights from the NH_3 release surface or at the air inlet/exhaust of a building. Exposure sampling uses passive sampling devices or sensors and therefore does not require sampling pumps. It can be a simple procedure when using measuring devices, such as detection tubes, where sample air is diffused to passive NH_3 samplers/sensors for obtaining a small number of time weighted average (TWA) concentration data. The cost of point sampling varies greatly because this method has different variations. The exposure method can have very low equipment and setup cost due to its simplicity. However, it can also be very high if a complicated micrometeorological sampling system is involved. Point sampling can be used for different study objectives. Samplers and sampling probes can be easily located at the animal and human breath zones. The method is flexible for different sizes of studies, ranging from a small emission source to an entire commercial animal farm. This method is basically nonintrusive and does not disturb the NH_3 source and its surroundings. It is the most widely used sampling method in animal buildings.

Open-path sampling uses optical detection devices, which consist of an emitter telescope and a receiver/detector. The source light from the emitter, ultraviolet (UV) or infrared (IR), is beamed in one direction over a certain distance (hence an open path), which contains gaseous NH_3, to the receiver/detector. Its sampling equipment and setup cost can be from low to medium depending on the complexity of the research objectives. It is not intrusive to the system being measured and there is also no adsorption of NH_3 on sample transporting system (e.g., tubing and fitting). Large areas can be investigated and the detection limit is very low. However, different emission sources lying close to each other cannot be distinguished from each other, and in general it is not easy to use for animal exposure study inside the barns.

Sampling location and time are critical issues to obtain high quality data. Different sampling locations may result in wide variations in measurement data because of spatial NH_3 differences. Measurements of varying concentrations that cover excessively short periods produce data with serious temporal limitations. However, measurement objectives play an important role in selecting sampling location and time. For example, for animal or human exposure studies, sampling locations should be in animal or human respiration zones, whereas the best sampling locations are the building air exhausts for emission measurement.

In mechanically-ventilated negative-pressure animal houses, the sampling position can be chosen at the exhaust fans for emission study. The advantage of this technique is that the gas concentration in the exhaust represents the outgoing gas concentration. Since the ventilation rate can also be measured in the exhaust(s), it is favorable for obtaining relatively accurate gas emission data. This sampling technique was reported by Berckmans and Ni (1993), Hartung et al. (1997), and Heber et al. (2001).

In naturally-ventilated animal houses, since indoor ventilation is tightly connected to outdoor wind speed and direction, difficulties are encountered in identifying the openings as inlet or outlet and their changes with time. Therefore, the sampling positions are usually uniformly distributed points over the area of the openings.

The temporal variations of NH_3 concentrations demonstrated that it is important to select proper sampling time. Sampling time should be arranged to cover peak and valley concentrations during the day, especially when there are significant temperature and airflow rate fluctuations, to obtain daily mean concentration, whether short duration sampling (e.g. active gas detection tube) or long-duration sampling (e.g. passive gas tube or wet chemistry) techniques are used. Based on the same principle, sampling should be designed to cover the low concentration season (usually summer) and high concentration season (usually winter) if an annual mean concentration is to be obtained. (Ni et al, 2001)

It is clear that low frequency sampling results in poor representation of the true NH_3 fluctuation pattern and therefore unreliable mean NH_3 concentrations. The higher the sampling frequency is, the better the data resolution, and the more accurate the mean value. According to the Nyquist Theorem, the sampling frequency should be at least twice the maximum frequency of the signal that is being sampled (Finkelstein and Grattan, 1994). Of course, high frequency sampling is subject to some technical restrictions like the capacity and response time of the measuring device.

2.4.2 Measurement techniques of ammonia concentrations

2.4.2.1 Selection criteria of measurement techniques

Selection of measurement techniques should be based on research objectives, coupled with the existing capabilities of the research institution and the budget constraints of the research. Cost of the techniques is one of the most important factors to be considered in almost all research projects. Thus, capital and operating costs may need to be assessed with the performance of the technique. A single-use sensor can only provide one measurement although it is relatively inexpensive. If large number of measurement data is required, the cost per measurement using a high-priced instrument with multi-use sensors may be less expensive than using low-price single-use sensors. In many cases, small numbers of short-term samples cannot satisfy the accuracy requirements of a careful field investigation. Techniques that produce large quantities of data should therefore be considered. Some expensive instruments, like IR analyzers and NH_3 analyzers, are usually only used at institutions conducting intensive research on agricultural NH_3.

Standard wet chemistry requires analytical instruments that may already exist at many institutions. When the cost of analytical instruments does not need to be considered, wet chemistry methods are inexpensive and affordable techniques. They are especially useful with small sample numbers. The pH-paper-based test kits are appropriate for obtaining simple indications of in-building NH_3 concentrations when accuracy is not a priority.

Applications of high and low sensitivity measuring devices are generally related to indoor and outdoor NH_3 measurements, respectively.

Measuring devices with short response times (e.g. less than 2 min) are required to properly study the dynamic behavior and diurnal variations of NH_3 concentrations. Sensors with long response times, e.g. passive gas tubes, are very good when only TWA (time –weighted-average) data are needed.

2.4.2.2 Classification of measurement techniques

The different techniques are classified according to analytical methods (wet or dry), sensitivity, delivery of measurement results (direct or indirect readout) type of sensor use (single or multiple use), method of sampling air delivery (active or passive sampling), response time.

- Wet and Dry

According to Kamin et al. (1979), analytical methods of NH_3 can be classified as “wet method”, which uses an aqueous medium, and “dry method”, which is the method of direct analysis of NH_3 in the gas phase.

- Active and Passive Sampling

An active sampling technique needs a pump, whether hand or electric powered, to force the sample air flowing to the sensor. Techniques with active sampling also enable transportation of sample air through sampling tubing to realize multi-point measurements with a single set of measuring device.

A passive sampling technique lets air diffuse into the sensor, or lets air stay “as is” in the open measurement point, thus a pump is not required. Sensors for passive sampling need to be placed right at the sampling location during measurement. Passive sampling depending on diffusion takes longer to finish a measurement. Because of this, it can provide time-weighted-average (TWA) concentration in a single point measurement. Some active methods (e.g. wet chemistry using acid traps) also provide TWA concentrations.

- Readout

Direct readout is an important feature, especially for field measurements. Techniques with direct readouts provide an immediate visual display of NH_3 concentration right after the measurement is completed. Most of the reported techniques provide direct readout. Some of them are followed by automatic data retrieving and processing.

Techniques with indirect readout require a chain of procedures and devices; for example, trapping NH_3 in acid collection medium followed by laboratory analysis of the medium with wet chemistry methods. Compared with the direct readout, the indirect readout method takes more time to obtain results and is not suitable for large numbers of measurements.

- Sensor Life

The sensor in an NH_3 measuring device is the material or part that undergoes a physical or chemical change when exposed to sample air. Single measurement techniques adopt disposable sensor materials that cannot be re-used. The gas detection tube is a typical single use sensor. In wet chemistry methods, the NH_3 collection medium is used only once. Continuous measurement techniques can provide many concentration readings over time, usually in the form of electronic signals that can be easily recorded and processed. Sensor materials for these devices usually do not need to be replaced, with the exception of EC sensors (e.g.

Dräger unit that has a sensor life of 18 months). The cassette needed with the Chemcassette Gas Monitor is a single use sensor, although one cassette can provide multiple readings.

- Sensitivity

Sensitivity is the capability of a measuring device to discriminate between measurement responses representing different levels of a variable of interest. Sensitivity is determined from the value of the standard deviation at the concentration level of interest. It represents the minimum difference in concentration that can be distinguished between two samples with a high degree of confidence (USEPA, 1998).

Some of the techniques were reported to be highly sensitive, for example, the method of converting NH_3 to NO followed by NOx analysis is sensitive at the ppb level. Other techniques provide sensitivity at ppm level, e.g. NH_3 detection tubes. Sometimes high sensitivity techniques are called analytical techniques, which provide quantitative data, and low sensitivity ones are called detection techniques, which provide qualitative or semi-quantitative data.

- Response

Response is a measure to evaluate how quickly or slowly a measuring system can react to NH_3 and present correct concentration readings. Manufacturers use response time (TEI, 1995), time needed for an instrument to reach from 0 to 90% at zero to span difference in gas concentrations, to describe specifications of the instrument. The response of passive diffusion sampling can be as long as 8 or 24 h.

2.4.2.3 Analitical method and equipment description

The description of the analytical methodand equipment related to some **wet methods** is reported below.

- Colorimetry methods

These methods (e.g. Colorimetry-indophenol, Colorimetry-Nessler, Photometry, Conductimetry, Titrimetry Photometry- Nessler,) rely on collecting gaseous NH_3 into a suitable acid solution and then performing concentration determination. The volume of air passed through the scrubber is recorded and the NH_3 concentration in the air is calculated (Hashimoto, 1972). With wet methods, once valid samples of ammonium ions are obtained in solution, it is relatively simple to arrive at final analytical results in the laboratory. The most commonly used acid traps for measuring NH_3 at animal facilities include boric acid (H_3BO_3) (Curtis et al., 1975), sulfuric acid (H_2SO_4) (Valli et al., 1991; Krieger et al., 1993, Guingand, 1997; Pfeiffer et al., 1993; Jiang and Sands, 2000), and orthophosphoric acid (Asteraki et al., 1997; Kay and Lee, 1997; Misselbrook et al., 1998).

The ammonia captured in the acid can be assayed e.g. by colorimetry. The method is simple, cheap, reliable and suitable for low concentrations of ammonia in air, although only the average concentration over a long sampling time in hours may then be possible. The main drawback of the method is the high labor input and the fact that it is basically non-continuous.

- pH Test Paper Methods

Moum et al. (1969) developed a very simple method by employing pH test paper and neutral distilled water as an NH_3 trap. The measuring range was 0–100 ppm and the accuracy was ±5 ppm. One follow-up use was tested by Seltzer et al. (1969). The method is inexpensive and provides direct in-situ readout. However, it has low sensitivity and precision.

The description of the analytical method and equipment related to some **dry methods** is reported below.

- Gas Detection Tubes

Gas detection tubes are based on adsorption of tested air pollutant on solid surfaces accompanied by a color reaction. The most obvious advantage of the gas detection tube is its operational and functional simplicity. There are two types of disposable tubes: active sampling tube and passive sampling tubes. Tubes with different measurement ranges are available. Usually, the sensitivities of the tubes are too low for measuring outdoor NH_3 concentrations.

Active sampling involves a hand-pump that sucks a pre-defined volume of air per stroke. Both ends of the test tube are sealed when manufactured and are cut open just before measurement. The open-end tube is inserted tightly into the pump connector. By pumping the hand-pump, the air sample flows through the tube. The color that arises is evaluated to assess the NH_3 concentration. Active gas tubes from five different manufacturers have been used for NH_3 measurement at animal facilities. The Dräger Tube is probably the most widely used gas tube product.

Like the active tubes, the passive sampling tubes are also sealed before using. However, only one sealed end of passive tube is broken open to commence measurement. The opened tube is exposed at the selected sampling location for a specific time, usually several hours. The gas concentration indicated in the tube should be interpreted with the exposure time.

The diffusive sampler is direct-reading in the product of concentration and time of exposure (i.e. in p.p.m./h), but its lower limit of concentration is 1,8 mg/m^3 (2.5 p.p.m.) and its coefficient of variation (20÷25%) is higher than that of the long-term detector tube.

- Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy is a technique involving the interaction of IR electromagnetic radiation with the test sample. The technology has been called interferential spectroscopy; multiplex; Fourier spectroscopy; interferometric spectrophotometry, or Fourier transform spectroscopy through its development by physicists and manufacturers over the years. The acronym FTIR is almost universally used by chemists to refer to the technique (Johnston, 1991). The Fourier transformation is a mathematical manipulation that relates a signal, curve, or algebraic function to its frequency content. In Fourier spectroscopy, the output signal is known as an interferogram, and is produced by an interferometer. As the movable mirror of the instrument is gradually displaced, a cycle of maximum and minimum intensity recurs. It yields specific information about the chemical structure of organic and inorganic compounds based on the unique vibrational modes of different chemical bonds. The FTIR spectrum is rich with information because each vibrational mode absorbs a specific wavelength of IR radiation. Each bond within a molecule may have several vibrational modes. The FTIR absorption spectrum is a "fingerprint" for a particular molecule that can be compared with reference spectra of known compounds, thereby aiding in the identification of unknowns and providing unambiguous confirmation of the identity of "known" materials.

A few of the many models of FTIR spectroscopy have been used for NH_3 measurement at animal facilities. A FTIR Spectroscope K300 with a White-Cell was used in Germany (Neser et al., 1997). Air samples were pumped into or through a special optic cell (White-cell), which used a series of mirrors to create a lengthened light path of 8 m (Amon et al., 1997).

In FTIR, software is used to carry out Fourier transforms, in order to ‘unscramble' the absorption peaks from each gas in a mixture of gases (Kolb et al., 1995). Thus, for example, interference from water vapour can be overcome and a good measurement of ammonia concentration can be obtained (Krahl et al., 1996). Systems based on flow-through cells and on long open paths both exist. A reading can be obtained typically once every minute, or, with some sacrifice of accuracy, once every few seconds (Phillips et al., 2000). A detection limit for ammonia of 1.1 mg/m^3 (1.5 p.p.b.) has been reported (Biermann et al., 1988). Disadvantages include the high capital cost of a system and the need for very frequent and careful re-calibration with expensive standard gas mixtures and for an experienced operator (Phillips et al., 2000).

- Photo Acoustic Multi-gas Monitor

In Photo Acoustic Spectroscopy (PAS), the gas to be measured is irradiated by intermittent light of pre-selected wavelengths. The gas molecules absorb some of the light energy and convert it into an acoustic signal, which is detected by a microphone. The general principle of the PAS system is developed by Innova AirTech Instruments A/S, Ballerup, Denmark. The PAS monitor can automatically measure multiple gases with a single instrument. When gas samples are drawn from ambient air around the analyzer, the measurement time is approximately 30 s for one gas or water vapor, and about 120 s if five gases plus water vapor are measured. Increasing the length of the sampling tube increases the time required to pump in a new air sample and therefore increases the measurement time. The PAS requires less frequent calibration as compared with NOx analyzers. However, its investment is relatively high and it is subject to interference of water at high relative humidities (Ni et al., 2001).

C.K. Saha et al. (2013) carried out measurements on concentrations of carbon dioxide (CO_2), NH_3, CH_4, and N_2O which were measured continuously inside the barn at eight uniformly distributed points and outside the barn at four points (Fig. 2) for the specific periods. Gas concentrations were measured using an infrared photo-acoustic analyser (INNOVA 1312, Innova AirTech Instruments, Ballerup, Denmark) at 12 sampling points. The detection thresholds of the gases were: 1.5 ppm for CO_2, 0.4 ppm for CH_4, 0.2 ppm for NH_3 and 0.03 ppm for N_2O.

The results showed that NH_3 emission varied seasonally following outside temperature whereas CH_4 emission did not show clear seasonal trend. Daily variation of CH_4 emission was less pronounced than NH_3. The average NH_3 and CH_4 emissions between 6 a.m. and 6 p.m. were 66% and 33% higher than the average NH_3 and CH_4 emissions between 6 p.m. and 6 a.m., respectively for all seasons. The significant relationships ($P < 0.0001$) between NH_3 and influencing factors were found. They included outside temperature, humidity, wind speed and direction, hour of the day and day of the year. The significant effect ($P < 0.0001$) of climate factors, hours of the day and days of the year on CH_4 emission might be directly related to activities of the cows.

- Non-dispersive infrared (NDIR) analysers

This method measure the spectral absorption of a gas at one spectral band of the IR spectrum. The spectral dispersion of the absorption spectrum of the gas is not used (Phillips et al., 2000). In general, the instrument consists of an IR source, an absorption chamber with windows, and a radiation detector. The IR radiation absorbed is a measure of the gas concentration in the chamber. To enhance the selectivity and sensitivity of NDIR analyzers, many different ways of optimizing the IR light source, absorption chamber and detector have been developed (Janac et al., 1971).

- Ultraviolet Differential Optical Absorption Spectroscopy

In the ultraviolet differential optical absorption spectroscopy (UV DOAS) method, an emitter-receiver set creates a light path in a detection zone. Light is generated by a xenon lamp in the emitter and projected to the receiver. Each gas in the detection path absorbs different parts of the light spectrum in a unique way. The absorption is recorded using a spectroscope.

The detection limit depends on the length of the light path and the averaging time of the measurement. The detection limit for ammonia is (Mennen et al., 1996) approximately 1 p.p.m. The light source (high-pressure xenon lamp) emits radiation in the UV range which is focused on the receiver connected to a fast scanning spectrometer. These instruments use a database of calibrated absorption spectra of gases to interpret the differential absorption spectrum sampled. (Phillips et al., 2000). The calibrated absorption spectra should be produced on the instrument with which it is measured (Spellicy et al., 1991). If available, absorption spectra of interfering gases can be used for correction (Hollander, 1993b). The UV DOAS system uses narrow light beams, which makes keeping transmitter and receiver aligned a difficult job under field conditions (Klarenbeek et al., 1993). Under these conditions, the process of aligning the system should be automated.

- Chemiluminescence Analyzer

Chemiluminescence (CL) NH_3 analyzers involve an indirect measurement of NH_3 based on converting NH_3 to nitric oxide (NO) and then performing NO analysis by CL method. The NH_3 content is obtained by either chemical or mathematical subtraction of the background NO signal (Pranitis and Meyerhoff, 1987). This technique requires two instrument modules, an NH_3 converter and an NOx analyzer.

A chemiluminescence detector can be used to measure ammonia concentrations, provided ammonia is first oxidized to nitric oxide. When the nitric oxide is further oxidized within the instrument, using ozone, nitrogen dioxide is produced, in an excited state. The nitrogen dioxide molecules return to a lower energy state by releasing photons. This electromagnetic radiation has a wavelength around 1200 nm (Phillips et al., 2000).

- Electrochemical Sensor

Electrochemical (EC) NH_3 sensors consist of two electrodes and detects NH_3 with the following EC reactions:

on the measuring electrode,

$$2NH_3 \rightarrow N_2 + 6H^+ + 6e^-$$

and on the counter electrode,

$$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$$

Electrochemical sensors provide direct readout and continuous measurements. Several EC sensors have been tested or used at animal facilities. Hoy et al. (1992) and Hoy and Willig (1994) described a Series 6004 Quadscan Gas monitoring system, connected with a printer, for continuous measurement of NH_3. This system consists of two main components, the Series 6004 gas receiver and three Series 4485 NH_3 gas transmitters.

Heinrichs and Oldenburg (1993) used a Dräger apparatus for measuring NH_3 in a fattening pig house, but did not provide details of the system. A Dräger NH_3 sensor (Polytron 2, Dräger Safety, Inc. Pittsburgh, PA) connected to a data logger was used in broiler houses (Wheeler et al., 1998; 1999; 2000a). The sensor was battery powered. Its scale was 0÷300 ppm and its precision was ±3% or ±9 ppm. The sensor was successful at a reasonable cost for research or demonstration projects. The unit consisted of a multi-gas body (Polytron 2) with a sensing unit. The multi-gas body can be combined with specific sensor units to measure over 60 toxic gases including NH_3. The expected life of an NH_3 sensor is equal to or longer than 18 months.

- Gas chromatography and photo-ionization detectors

A gas chromatograph (GC) procedure has been reported (Yamamoto et al., 1994) in which ammonia is automatically collected from the air over a period of a few minutes in a tube containing alkalized Porasil B. The ammonia is desorbed thermally, dehumidified, separated on a GC column packed with 15% polyethylene glycol of mean molecular weight 6000 and 5% potassium hydroxide solution on Chromosorb 103, and detected by flame thermionic detection. The method has been demonstrated in a range of 1.4-70 $\mu g/m^3$ (2-100 p.p.b.), and has been used to make continuous ambient measurements in an urban atmosphere. A detection limit of 0.014 $\mu g/m^3$ (0.02 p.p.b.) was reported. Under particular circumstances, photo-ionization detectors can be used to determine concentrations of ammonia in air, although it must be borne in mind that such detectors are not inherently specific to ammonia.

In this type of detector, ultraviolet light ionizes the chemical and the ions formed are collected by electrodes, the current generated being a measure of the concentration. The UV ionizing lamp used in the detector is chosen to ionize selectively at the necessary potential. The ionization potential of ammonia is

10.15 eV, so a lamp of 10.9 eV is chosen. Typically, the detector is attached to a GC column in order to make the detector specific to NH_3.

- Solid State Sensor

The solid state or electronic NH_3 sensor is a relatively new measurement method. It benefits from the spread of the electronic sensor technology. There are several types of these sensors that are sensitive to NH_3 (Göpel and Schierbaum, 1991). There exist several advantages of solid state NH_3 sensors, including simplicity, low price, quick response, and automatic measurement. Their limitations include low accuracy, drift, and interference by humidity and other gases. Several types of NH_3 sensors have been tested in animal houses. However, they were still in the development stage. Krause and Janssen (1990; 1991) first used a chemical NH_3 sensor to measure NH_3 distribution in animal houses. The sensor had a detection range of 1–1000 ppm, a response time <1 s and an accuracy of ± 10% between 4÷500 ppm.

Berckmans et al. (1994) described a test of a solid state NH_3 sensor, developed by the Interuniversity Micro Electronic Center (IMEC), Belgium, in livestock buildings. The sensor had a detection range of 0÷100 ppm NH_3 and a response time of 10÷15 s. It was a thick film semiconducting metal oxide sensor consisting of a heater element, a dielectric layer, a contact layer, and a gas sensitive semi-conductive metal oxide layer. The conductivity of semiconducting metal oxide films at a certain temperature was influenced by the presence of NH_3 gas in the surrounding atmosphere. The sensor's optimum operating temperature was around 350÷400 °C. Hess and Hügle (1994) tested an NH_3 measuring system called SOLIDOX-NH_3, manufactured in Germany, in animal houses for a few times but with difficulties.

2.4.3 Techniques to measure ammonia emission rate in naturally ventilated barns

Most of the approaches to measure ammonia emission rates require the monitoring of building ventilation rates and airflow rates across slurry or manure stores. Three kinds of methods for monitoring such ventilation rate exist.

The first based on using a tracer gas, allows a direct measure of overall ventilation rate and thus, at least in principle, is applicable to both forced- and naturally ventilated buildings, as well as to airflows across slurry and manure stores. The tracer could be natural or artificial.

The second kind relies on measuring, in different locations, the airflow rates through all openings in a building and then summing these measures to obtain the overall ventilation rate of the building. This kind of technique is basically simpler, is readily applicable to force-ventilated buildings, but can only be applied to naturally ventilated buildings under particular circumstances, nor is it applicable to manure stores (Phillips et al., 2000).

The third kind of technique is based on the natural ventilation theory in which the air exchange rate is determined by buoyant forces and wind pressures at the ventilation openings.

2.4.3.1 Tracer gas methods for direct measurement of overall ventilation rate

The basic principle of tracer techniques for direct measurement of overall ventilation rate is to release a tracer at a known rate, monitor its concentration at downwind points and hence deduce the airflow necessary to reconcile the known rate of release with these measured concentrations. In the case of a livestock building, it is necessary to assume good air mixing inside. In practice, this may well not be the case, especially in naturally ventilated buildings, and errors in the ammonia emission rate may result (Barber and Ogilvie, 1982; Demmers et al., 1998).

The tracer gas may be carbon dioxide (CO_2) (Kittas et al., 1996), nitrous oxide (N_2O) or sulphur hexafluoride (SF_6) (Seipelt et al., 1999; Snell et al., 2003). Sulphur hexafluoride is probably the most widely used of gaseous tracers and has already been used to some extent with livestock buildings (Gustafsson, 1996; Marik & Levin, 1996; Seipelt et al., 1998), as well as in other source quantification problems (e.g. Lamb et al., 1986, 1995; Claiborn et al., 1995). Its concentration is best measured by gas chromatography, using an electron capture detector. This can be automated to allow samples to be taken sequentially every few minutes, and measured with a detection limit of order 1 p.p.t. (International Atomic Energy Agency, 1992): the current background is 3 or 4 p.p.t. in the northern hemisphere (Maiss et al., 1996). Sulphur hexafluoride absorbs strongly in the infrared and so its concentrations can also be determined by infrared methods, but with less sensitivity.

Sulphur hexafluoride is non-toxic and stable in air and at surfaces in normal circumstances. It is non-infiammable. The only hazards are asphyxiation (requiring concentrations of tens of percent) and avoidance of very hot surfaces (which cause decomposition to the toxic hydrofluoric acid). In practice, the amounts required for an experiment are so small that there is no possibility of either hazard being significant. One of the few drawbacks of using sulphur hexafluoride is that it is a very powerful greenhouse gas with a very long half-life in the atmosphere.

Demmers et al. (2001) stated that the constant release tracer gas method gives the most reliable estimates of ventilation rate. Brehme (2000) described the compartmentalisation method which was used for many measurements in dairy buildings. This tracer gas method (i.e. decay method) combines, through a dispersion mechanism, concentration measurements with air exchange measurements within which the volumetric flow rates are permanently fluctuating. The dependency of NH_3 emission mass flow has been derived in form of mathematical model as well as measured data or values.

An investigation was employed by S.Schrade et al., (2011) to determine emissions from two areas of different source intensity, with a tracer ratio method. A variety of accompanying parameters was used to characterise each measuring situation and to derive the relevant influencing variables. The daily average NH_3 emission across all farms varied from 31 to 67 g LU^{-1} d^{-1} in summer, from 16 to 44 g LU^{-1} d^{-1} in the transition period, and from 6 to 23 g LU^{-1} d^{-1} in winter (1 LU = 500 kg liveweight). From a linear mixed-effects model the wind speed in the housing ($p<0.001$) and the interaction of outside temperature and the urea content of the tank milk ($p < 0.001$) emerged as significant variables influencing NH_3 emission. A model-based calculation with bootstrapped variance components was used to calculate yearly averaged emission factors for two mountain and plain regions and two wind speeds (0.3 and 0.5 m s^{-1}).The model input was based on milk urea contents from commercial dairy farms and air temperatures over a five-year period. The calculated NH_3 emission factors, which thus accounted for regional differences due to climatic conditions and feeding levels, ranged between 22 and 25 g $LU^{-1}d^{-1}$.

Experiments were carried out by Samer et al. (2011) about air exchange rates (AER) occurring in naturally ventilated dairy buildings during summer seasons 2006 to 2010. A tracer gas technique (TG) for AER measurements was developed. The AERs were determined by decay of radioactive tracer Krypton-85, and CO_2 balance used as the reference method (RM). During each experiment, continuous measurements of gaseous concentrations (NH_3, CO_2, CH_4 and N_2O) inside and outside the building and 85Kr tracer gas experiments were performed. The combined factors investigated were released over feeding table or over the manure alley, average values of AER per second (s^{-1}) or the sum of impulses, selected radiation counts or all radiation counts. The results were compared using Pearson correlation analysis, developing a linear regression model, and testing the differences between the factor combinations and the RM using an ANOVA model. There were differences between impulses ($Pr > |t| = 0.0013$), where the sum of impulses showed better results than the average AER values. Although there was no difference ($Pr > |t| = 0.344$) between the readings of the radiation counts, it was considered that by using all the readings of the radiation counters it was more representative and easier to calculate the AER.

Natural tracers

In addition to releasable tracers, other naturally occurring tracers are available in livestock buildings: among them there are metabolic carbon dioxide, water vapour, and metabolic heat, produced by the livestock. Using one of these tracers requires not only the presence of animals inside the building, but also an accurate knowledge of the carbon dioxide, water vapour or heat production rate of these animals. A procedure is also needed for predicting the site of production of the tracer in the building or manure store. Several models exist (e.g. the model called STALKL, reported by van Ouwerkerk & Pedersen, 1994) which can predict the production rates of carbon dioxide, heat and humidity by housed livestock to within 20%, based on a knowledge of the feed composition, body weight, species etc.

CO_2 Balance

Carbon dioxide, formed by animal respiration and microbial degradation of faeces, can be used as a natural tracer gas. The ventilation rate throughout the building can be determined by calculating the mass balance of CO_2 flow. CO_2 balance is not in general terms used as reference method to measure air exchange rates.

The followin equation describes the relationship between the ventilation rate and the gas production rate assuming ideal mixing with the air inside the building:

$$V_{CO2} = \frac{n \cdot P_{CO2}}{C_i - C_0} \qquad (8)$$

where:

P_{CO2} (mg h^{-1} cow^{-1}) represents the excretion rate of CO_2 from one cow,

n is the number of cows housed inside the building,

$\dot{V}_{CO2}$ (m^3 h^{-1}) is the ventilation rate subject to CO_2 balance, and C_i (mg m^{-3}) and C_o (mg m^{-3}) are the concentrations of the gas inside and outside the building, respectively.

The air exchange rate can be then calculated by dividing the ventilation rate by the volume of the building.

This method requires valid heat production values for the animals and assumes that CO_2 production is solely from animal respiration. However, much of the heat production data was collected from 20 to 50 years ago and may no longer be valid due to advances in animal genetics and nutrition (Bicudo et al., 2002). Furthermore, measured CO_2 concentrations may include CO_2 from both animals and microbial activities related to manure decomposition. Therefore, building ventilation rates based on the building carbon dioxide (CO_2) balance method may lack the accuracy that is necessary to determine accurate ammonia emission rates.

Pedersen et al., (1997) compared three methods for the calculation of the ventilation rate in Northern European livestock buildings, on the basis of the balances of animal heat, moisture and carbon dioxide for fattening pigs, dairy cattle and laying hens. The results showed that for insulated buildings under conditions of relatively large differences between indoor and outdoor temperatures, absolute humidity and carbon dioxide concentration, ventilation rates over 24 h can be calculated from heat, moisture and carbon dioxide balances. For uninsulated buildings, only the carbon dioxide method is recommended because of the difficulties in estimating the heat transmission loss from the building. The CIGR equation for calculation of heat production is applicable for cattle if a suitable correction factor is used, but under summer conditions it underestimates the sensible heat production for fattening pigs and poultry. By fixing the sensible heat production at 61% of the total heat production for fattening pigs and at 68% for laying hens in cages, the ventilation rates calculated from heat and moisture balances are in good agreement over the temperature range from 15 to 25°C. A correction for evaporated water from feed and wet surfaces in cattle buildings can be made by multiplying the sensible heat production by a correction factor of 0.85, corresponding to a 15% conversion of the sensible heat into latent heat.

Bjerg et al. (2011) carried out experiments about determination of emission of contaminant gases as ammonia, methane, or laughing gas from natural ventilated livestock buildings with large openings. The close relation between calculated animal heat production and the carbon dioxide production from the animals have in several cases been utilized for estimation of the ventilation air exchange rate for the estimation of ammonia emissions. The results showed that the methane emission can be determined with much higher precision than ammonia or laughing gas emissions, and, for methane, relatively precise estimations can be based on measure periods as short as 3 h.

An investigation, by Zhang, Strom et al. (2005) was carried out to provide fundamental knowledge on gas emissions from naturally ventilated dairy cattle buildings with different floor types and manure-handling systems. Emission rates of NH_3, N_2O and CH_4 were determined from measured values of gas concentrations and calculated values of air exchange rates. The methods to determine the air exchange rates in the naturally ventilated buildings were presented and discussed on the basis of the tracer gas method and the CO_2 production model for the animals. The results showed that, in all cases, the NH_3 emission rate increased with temperature, but the increase was highly dependent on floor type and manure system. In most buildings under study, the emission level increased from about 10 to 30 $gHPU^{-1}$ d^{-1} as the temperature increased from 2°C to 20°C with a standard deviation from 0.5 to 9 $gHPU^{-1}$ d^{-1}. The highest emission rate measured was 75 gHPU at 22 °C with a standard deviation of 15 gHPU. This study demonstrated that the emission rates were dependent on floor type and manure-handling method. The lowest ammonia emission was found for buildings with solid floors with smooth surface, scraper and drain. For buildings with slatted floors, manure treatment with acid, scraper on the slatted floor surface or channel scraper are potential alternative methods for reduction of the ammonia emission.

Wentao Wu et al. (2012) performed measurements in two naturally ventilated dairy cattle buildings with different layouts, floor types and manure management systems during three periods covering winter and summer time. Air temperature and the three dimensional air velocities inside and outside the buildings were recorded over the course of summer period. Emission rates were determined by CO_2 production model. The results showed that the internal concentrations of NH_3, CH_4 and CO_2 were increased or decreased simultaneously. From multiple linear regression models, there was a significant linear relationship between NH_3 emission rates and climatic factors including the external wind speed as well as the air temperature ($P < 0.001$), but not with the external wind directions ($P > 0.05$).

H_2O Balance

The ventilation rate through out the building can be determined by calculating the *mass balance of H_2O flow*. The calculations of moisture balance were based on several studies (Albright, 1990; Hellickson and Walker, 1983). The following model describes the moisture balance:

$$\dot{V}_{H2O} \qquad \frac{M_W}{W_i - W_o} \tag{9}$$

$$M_W = n \cdot m_W \tag{10}$$

$$m_W = P_{H2O} \cdot M_{avg} \tag{11}$$

where

$\dot{V}_{H2O}$ ($m^3\ s^{-1}$) represents the ventilation rate subject to the H_2O balance,

v ($m^3\ kg^{-1}$ dry air) is the air specific volume,

W_i (g H_2O kg^{-1} dry air) is the humidity ratio inside the building,

W_o (g H_2O kg^{-1} dry air) is the humidity ratio outside the building,

M_W (g H_2O s^{-1}) represents the moisture produced by the cows housed in the building;

n represents the number of cows housed in the building,

m_W (g H_2O s^{-1}) is the moisture produced by one dairy cow,

M_{avg} (kg) is the average mass of the cow ,

P_{H2O} (g H_2O h^{-1} kg^{-1}) is the moisture produced by a dairy cow per mass unit, which is equal to 1.8 (Lindley and Whitaker, 1996).

Heat Balance method

In this method, the concept of energy conservation is applied to sensible heat. Hence, the heat balance addresses the sensible heat transfers. Albright stated that the control volume for the energy balance is the air within the space bounded by the walls, floor, ceiling and imaginary planes at the ventilation inlets and outlets of the building. The general form of an energy balance for a control volume is the difference between gains and losses and it is equal to the change of storage.

The heat balance was calculated as follows (Hellickson and Walker, 1983; Albright, 1990; Lindley and Whitaker, 1996):

$$\dot{V}_{HB} = \frac{q_s - (\Sigma UA + FB)\cdot(t_i - t_0)}{C_p \cdot \rho \cdot (t_i - t_o)} \qquad (12)$$

where:

$\dot{V}_{HB}$ (m^3 s^{-1}) represents the ventilation rate, subject to the heat balance;

q_s (W) is the sensible heat produced by the animals and is estimated using the energy calculation model (CIGR, 2002; Samer et al., 2011b);

U (W m^{-2} °C^{-1}) represents the overall heat transfer coefficient of the building component under consideration;

A (m^2) is the area of building component under consideration;

F (W m^{-1} °C^{-1}) represents the perimeter heat loss factor and was considered as 1.5 W m^{-1} °C^{-1} (Albright, 1990);

P (m) is the perimeter length of the barn;

C_p (J kg^{-1} °C^{-1}) represents the specific heat of the air which was considered as 1006 J kg^{-1} °C^{-1} according to Albright (1990);

ρ (kg m^{-3}) is the air density and is the inverse of the specific volume which was derived from the relations associated to the psychrometric charts using the dry-bulb temperature and the relative humidity;

t_i (°C) is the indoor air temperature;

t_o (°C) is the outdoor air temperature.

Calculation of total heat production (Φtot) from dairy cows is generally expressed in heat production unit (HPU), where one HPU is defined as a total heat production of 1000 W at 20°C (CIGR, 2002):

$$\Phi tot = 5.6\ m^{0.75} + 22Y_1 + 1.6\ 10^{-5}p^3\ , W \qquad (13)$$

where m is the cow weight (kg), Y_1 is the milk production (kg/day), and p the days of pregnancy.

Samer et al. (2012) carried out experiments and statistical analysis to study the ventilation rates (VRs) in a naturally ventilated dairy barn through four summer seasons and three winter seasons. VRs were determined using moisture (H_2O) balance, heat balance (HB), CO_2-balance and radioactive tracer gas technique (TGT). H_2O balance showed reliable results through winter and slightly acceptable results through summer. HB showed slightly acceptable results through summer and unsatisfactory results through winter. CO_2-balance showed unexpected high differences to the other methods in some cases. TGT show ed reliable results compared to all methods and is independent on physiological parameters.

2.4.3.2 Ventilation rate by summation of air-flows through individual openings

In this second kind of technique, some form of anemometer is generally needed, to measure the air velocity through each opening. Two basic types of vane anemometer are available. In the first, the diameter across the vanes is small compared with the size of the opening through which airflow is to be measured. Therefore, with this type it is necessary to measure the local air velocity at each of a series of sampling points within the opening and then to carry out a numerical integration across the whole opening. Standard procedures for these operations are available (British Standards Institution, 1980).

The second type of vane anemometer, which generally leads to a much more accurate measurement of airflow rate, is the ‘fan-wheel anemometer', in which the diameter across the vanes is only a few millimetres less than the diameter of the (circular) opening in which it is mounted (Phillips et al., 2000). An accurate but inexpensive design has been developed by Berckmans et al. (1991). The fact that this second type does need a more permanent installation is in some situations a disadvantage, especially if an adaptation is needed to a duct which was not originally circular in cross-section. Fan-wheel anemometers are much more suitable for use with force-ventilated than with naturally ventilated buildings, and are not useful for airflows around manure stores. Measuring ventilation rate by the summation of air-flows through individual openings, where it is feasible, has an inherent advantage over measuring a gross ventilation rate, namely that the more detailed picture of the ventilation which results may simplify the task of planning how to abate ammonia emissions from a building (Phillips et al., 2000).

2.4.3.3 Natural ventilation theory

Another method to obtain the ventilation rate from measurements is based on the natural ventilation theory. Natural ventilation is the movement of air through openings of a building due to the natural forces produced by wind and temperature difference; the air exchange rate is determined by thermal buoyancy forces and wind pressures at the ventilation openings. The difficulties in using this method are the uncertainties in determining the pressures at the openings and the need of acquiring extensive information of pressures in many positions.

The interaction of the air in the naturally ventilated livestock house and the external atmosphere causes the dispersion of ammonia and greenhouse gases from livestock buildings to the surrounding atmospheric environment. The key climatic factors influencing the gas emissions include the external air temperature, the external wind speeds and directions.

The thermal buoyancy occurs in naturally ventilated animal barns independently of the outside wind conditions. However, the actual VR from any opening is not equal to the sum of the two estimated quantities from wind effect and thermal buoyancy (Hellickson and Walker, 1983). It is also not linearly proportional to pressure difference (Albright, 1990). Field experience and comparisons with relatively elaborate natural ventilation computer models have shown that the net rate of ventilation can be approximately estimated by the following Equation (14) (Albright, 1990; Hellickson and Walker, 1983; Kittas, Boulard, and Papadakis, 1997):

$$V_{total} = \sqrt{\left(V_{wind\,forces}\right)^2 + \left(V_{thermalbuoyancy}\right)^2} \qquad (14)$$

where: V_{total} is the total VR (m^3/h); $V_{windforces}$ is the VR due to wind forces (m^3h^{-1}); $V_{thermalbuoyancy}$ is the VR due to thermal buoyancy (m^3/h).

Ventilation rate due to the wind forces

The fluctuation of outside conditions limits the adaptability of a theoretical equation for determining the VR due to wind forces (Nääs et al., 1997). In practice, the VR can be approximately estimated using empirical data in the following equation (Hellickson and Walker, 1983):

$$V_{wind\,forces} = 3600\ E\ A\ V \qquad (15)$$

where: $V_{windforces}$ is the VR due to wind forces (m^3h^{-1}); E is the effectiveness of the opening, a value of 0.35 is normally recommended for agricultural barns (Hellickson and Walker, 1983; Albright, 1990); A is the area of inlet opening (m^2); V is the wind speed ($m\ s^{-1}$).

The determination of the effectiveness of the opening for typical naturally ventilated agricultural barns is very difficult (Bruce, 1986; Naas et al., 1997). Pearson and Owen (1994) presented discharge coefficients (C_d) between 0.45 and 0.98 for side openings. Demmers (1997) estimated the C_d values for space boarding between 0.43 and 0.46 for high and low wind cases, respectively (Kiwan et al., 2012).

Ventilation rate caused by temperature difference forces

When the temperature inside a barn is different from that outside, pressure gradients are created because of a difference in air density. When the inside temperature is warmer, the warm air will be displaced upwards by a buoyancy force. In the literature, this is also known as the chimney or stack effect. The discharge velocity of air is directly proportional to the pressure difference and to the height between inlets and outlets. The pressure difference can be converted to a temperature difference according to perfect gas laws. Therefore, the discharge velocity resulting from thermal buoyancy can be calculated by the following equation (16) (Hellickson and Walker, 1983):

$$V_{discharge} = \theta \sqrt{\frac{2gH(T_i - T_o)}{T_i}} \qquad (16)$$

where,

$V_{discharge}$ is the discharge velocity ($m\ s^{-1}$);

θ is a reduction factor for losses due to friction of the air against the inside surface of the duct;

g is the acceleration of gravity ($m\ s^{-2}$);

H is the height difference between inlet and outlet openings (m);

T_i is the inside temperature (K);

T_o is the outside temperature (K).

Multiplying the velocity by the inlet area will produce the quantity VR due to thermal buoyancy Equation (17) (Hellickson and Walker, 1983):

$$V_{thermal buoyancy} = 3600 \times V_{discharge} \times A \qquad (17)$$

where,

$V_{\text{thermal buoyancy}}$ is the VR due to thermal buoyancy ($m^3\, h^{-1}$);

$V_{\text{discharge}}$ is the discharge velocity ($m\, s^{-1}$);

A is the area of the inlet opening (m^2).

Kiwan et al. (2012) carried out a comparison of the performance of the three methods of measuring ammonia emissions. Three different methods were investigated to estimate VR through naturally ventilated dairy barns: (i) the tracer gas technique, using radioactive isotope Krypton-85 (^{85}Kr), (ii) the measurement of the air velocity through the barn openings, and (iii) the natural ventilation method. For VR estimation based on air velocity measurements, it was concluded that it is more important to measure the air velocity at different points within an opening to obtain representative data for the whole opening than to measure at a high number of openings which are located in very similar positions. The three methods investigated showed a generally good correlation with each other (0.59÷0.86; $p \leq 0.03$). Only when the wind approaching the barn had to pass surrounding obstacles, there was nonlinear correlation between the air velocity measurements through the inlet openings and the tracer gas technique (0.56; $p = 0.06$; 0.06; $p = 0.85$, respectively). Air velocity measurements through the inlet openings of a naturally ventilated dairy barn are an option to estimate VR, but outside wind conditions have to be considered as well. They demonstrated that the radioactive tracer gas technique is promising for the estimation of VR through naturally ventilated dairy barns and merits further development.

2.5 Models of ammonia emission from naturally ventilated dairy houses

Measurements of variables involved in ammonia emissions from naturally ventilated dairy houses are also utilized to collect the dataset needed to validate models for predicting ammonia emissions.

A complete ammonia emission model involves different levels of description of the relations between the building and the environment (Bjerg et al, 2013a, 2013b, 2013c).

Models involving the processes taking place in the barn have been developed to predict ammonia evaporation from manure for different species, floor types, manure handling systems, manure properties and environmental conditions (Eltzing and Montent, 1997; Kroodsma et al., 1993; Monteny et al, 1998; Muck and Stenhuis, 1981; wang et al., 2006; Montes, Rotz, Chaoui, 2009).

Other models describe the interaction between the ventilation configuration of a building and the surrounding environmental conditions at a micro-scale level. They aim at predicting the distribution of climatic variables and pollution within a detailed geometrical model of a building (Banhazi, Rutley, Pitchford, 2010).

Finally, in other models the long-term climatic effects on building performance and emissions at a macro-scale level are considered (Liberati and Zappavigna, 2007).

The ammonia emission models are statistical empirical, or mechanistic. Empirical modelling involves specification of the correlation structure between variables and the use of a numerical technique to find the parameters for the structure that maximise the correlation between variables. This method is frequently used inrelation to field studies or experiments.The mechanistic models require fundamental process-level knowledge and understanding of the interactions between the process variables to define the model structure and experimental data are usually used to determine the parameters for such models.

Though some attempts have been made (Monteny, Schulte, Elzing and Lamaker, (1998); Wang, Li, Zhang, Rom and Strøm (2006)), further research is needed to validate the results obtained from emission sources used in the laboratories with the emission process from manure storage systems in field measurements within commercial livestock farms.

Pressure-based modelling refers to Bernoulli equation stating that air speed across an opening depends on pressure drop across the opening which can be generated by a temperature gradient between inside and outside air. In the literature, this effect is also known as buoyancy effect or the chimney or stack effect. When thermal buoyancy is a significant contributing factor it is necessary to calculate the global natural ventilation by calculating the energy balance of the building, which requires the inside temperature. In setting up the energy balance, there are various approaches presented in the literature. Regarding the thermal behaviour of the building envelope, some authors use steady-state models, with some including the effects of solar heat load. In other works thermal behaviour is modelled in a transient way (Axaopoulos,Panagakis, Pitsillis, Kyritsis, 1994; Liberati and Zappavigna, 2007). Furthermore, some researches consider also evaporation from manure removing in such way sensible heat from the ambient through latent heat (Axaopoulo, Panagakis, Kyritsis, 1992; Liberati and Zappavigna, 2007) or simulation of the internal surface temperatures including the floor (Liberati and Zappavigna, 2007). Wind inducted ventilation can be estimated by means of the wind pressure coefficients though this approach shows some weaknesses (Demmers, 2001).

Several researchers have suggested models that estimates air change over time by following a steady-state approach, with a time advancing update of the building heat and mass balances (van 't Ooster and Both, 1988; Axaopoulos et al., 1994; van't Klooster, Bontsema, Salomons, 1995; Cooper, Parsons, Demmers 1998; Liberati and Zappavigna, 2007).

Modelling of air change in natural ventilated buildings also require estimation, produced by empirical or semi-empirical deterministic approaches or stochastic processes, or data on the main external climatic parameters such as: solar radiation, air temperature and humidity, wind speed and direction.

2.6 Management practices to reduce ammonia emissions

Ammonia can be emitted at several different stages of livestock production. Although ammonia losses will vary significantly among farms due to differences in management practices, especially those used to collect, store, and/or treat slurry or manure are the most important to reduce ammonia emissions.

Meisinger and Jokela (2000) estimated that the greatest ammonia losses are expected to be associated with land application of manure (35-45%) and housing (30-35%). Significant losses can also occur during grazing (10-25%), if applicable, and manure storage (5-15%).

Two different strategies can be used to reduce the loss of ammonia from livestock: one approach is relation between ammonia release and diet, the second is slurry treatment by acidification.

Management practices that target ammonia generation can be divided into pre-excretion (e.g. nutritional) and post-excretion approaches during livestock housing (e.g. slurry acidification by chemical and biological amendments). While some of these management practices may be universally applicable, other approaches may be applicable only in certain cases, depending on manure characteristics, type of housing, and/or other factors.

2.6.1 Pre-excretion techniques

2.6.1.1 Relation between ammonia release and diet

Kebreab, France, Mills, Allison and Dijkstra (2002) developed a model that can be used for computation of N utilization in dairy cows and simulated the effects of energy concentration and level and degradability of protein in the diet on N output. Li et al. (2009) used two different diets for lactating dairy cows and found that reducing dietary crude protein (CP) reduced total Kjeldahl N in manure, but did not affect the total ammoniac N (TAN, total ammonia nitrogen) in manure and had no significant effect on the ammonia emission rates from the barn floor. Generally, characterisation of cattle manure mainly includes pH, TAN, and content of dry matter. Manure characteristics are related to the feeding, manure handling/treatment system in house and indoor thermal conditions. About 80% of dairy cattle N intake is excreted in urine and faeces (Vaddella, Ndegwa, Joo, Ullman, 2010). Urinary–N is about 75% urea, whereas faecal–N is mostly organic (Vaddella et al., 2010). Urinary–N (urea) can only be volatilized when it is hydrolyzed to ammonia (NH_3) in a process catalyzed by urease, which is predominantly found in faeces. Minimizing contact between urine and faeces may be an effective approach to reducing urea hydrolysis and subsequent NH_3 emissions (Vaddella et al. 2010). Burgos et al. (2010) attempted to assess the relationship between ammonia emissions from dairy cattle manure and milk urea N, and to test whether the relationship was affected by stage of lactation and the dietary CP concentration. They concluded that milk urea N concentration is one of several factors that allow prediction of ammonia emissions from dairy cattle manure.

De Boer, Smits, Mollenhorst, van Duinkerken and Monteny (2002) reported a study to predict urinary urea concentration of a cow using feed characteristics. They concluded that observed urinary urea concentration can be predicted with reasonable accuracy from existing models to predict urine volume and urinary N excretion using feed characteristics. The model for prediction of N excretion can be used by animal nutritionists and producers to determine diets that result in a reduced NH_3 emission. As another part of the study, Monteny, Smits, van Duinkerken, Mollenhorstand de Boer, (2002) reported the modelling approach to predict NH_3 emission from dairy barns for various diets, using feed characteristics, and climate, barn, and slurry related parameters. Further research is required to determine the daily distributions of urinations which contribute significantly to the fluctuations in the ammonia emission from animal buildings. Kulling et al. (2001) reported a 68% decrease in NH_3 volatilization from manure slurry (from lactating cows) when the dietary crude protein content decreased 30%. Comparable decreases in NH_3 volatilization with a decrease in the crude protein content of the feed were found by James et al. (1999) and Paul et al. (1998).

2.6.2 Nutritional techniques

Excretion of nitrogen supplied in feed cannot be avoided; however, careful control of dietary protein and aminoacids can be used to minimize the amount of nitrogen that ends up in manure and serves as a source of ammonia emissions.

Some techniques to reduce ammonia emissions by controlling animal feed, are shown in the following sub-sections.

2.6.2.1 Diet-BY-STEP

The diet by-step consists in following the cow ingestion capacity and the gradual decline of the ratio muscle/fat resulting in decreasing aminoacid requirements and diets with a lower protein content. In a first step, the ration is increased and, as a consequence, its aminoacid composition. As the digestive capacity of the animal increases the amount of food is increased in such a way as to provide a higher energy content. And finally, a ration with the same energy content but lower protein content is provided.

2.6.2.2 Reduction of dietary protein

The reduction of nitrogen in the diet is another strategy to reduce ammonia emissions. At present, the technique that makes it possible to have a significant nitrogen reduction consists in the administration of high protein digestibility to reduce nitrogen in the faeces. These techniques are based on the selection of very digestible raw materials or practicing enzymatic or technological treatments.

Smits, Valk Elzing and Keen (1995) reported the effect of protein nutrition on the urinary concentration of urea and subsequent emission of ammonia using a mechanically ventilated cubicle house containing 34 lactating dairy cows (cross bred Holstein Friesian and Dutch Friesian). Two silage-based diets with different amounts of rumen-degradable protein balance (OEB) were alternately fed during six 3-week periods. The decrease in urea concentration as a result of a lower OEB contributed substantially towards diminishing the emission of ammonia from cubicle houses for dairy cattle.

2.6.2.3 Integration with feed additives

Dietary manipulation of manure pH has been shown to reduce manure ammonia emissions. This is accomplished through the addition of acidogenic phosphorus sources and/or calcium salts to feed in order to counteract the pH increases that occur as a result of urea hydrolysis. The use of feed additives such as yucca plant extracts (Saponins, which are glycosides derived from the yucca plant, are supposed to bind or to convert) that purportedly inhibit urease activity may also be a useful pre-excretion strategy for reducing ammonia emissions. The use of substances with a probiotic action (regulatory enzymes of the intestinal fermentation) has the aim to reduce the quantity of feed ingested without reducing the increase in weight of the animals in the herd. With the improvement of the feed conversion it can be obtained about 3 to 5% less nutrients excreted.

Organic nitrogen associated with faeces is degraded more slowly than urea in the urine. Therefore, dietary changes that shift nitrogen from the urine to the faeces may reduce ammonia emissions. For example, inclusion of fermentable carbohydrates such as sugar beet pulp into swine diets increased faecal nitrogen at the expense of urinary nitrogen and decreased ammonia emissions.

2.6.3 Post-excretion techniques

In recent years, several techniques have been developed to reduce NH_3 emissions during livestock housing (e.g., automated scrapers, Phillips et al., 1999), during storage, (e.g., surface covers, Webb et al., 2005), and during application of slurry to the soil (e.g., trail-hoses or slit-injection, Huijsmans et al., 2001). Changing manure composition can also be an effective way to reduce NH_3 emissions (Børsting et al., 2003; Monteny et al., 2002).

In the Thematic Strategy on Air Pollution (CEC, 2005), the European Commission expressed the environmental objectives for 2020, aimed at reducing 27% of agricultural NH_3 emissions in the EU25 compared to 2000, approximately 23% of the reduction have to be met by introduction of specific abatement measures in agriculture. In order to reduce NH_3 emissions, different technologies have been developed (Ndegwaa et al., 2008). Among them, one of the effective mitigation strategies is slurry acidification, which has been approved as Best Available Technology (BAT) in Denmark (Kai et al., 2008). Previous studies have reported that about 70% to 85% of the NH_3 release from swine slurry can be reduced by decreasing the slurry pH to 5.5 through the addition of sulfuric acid (H_2SO_4) (Stevens et al., 1989; Frost et al., 1990; Kai et al., 2008). Acidification also improves the mineral N fertilizer equivalence (MFE) of the slurry by 25% (Sørensen and Eriksen, 2009).

Since the main manure characteristics that determine NH_3 volatilization are the total concentration of ammoniacal nitrogen, pH and dry matter content (Jarvis and Pain, 1990; Sommer and Husted, 1995), other post-excretion techniques were proposed to reduce the dry matter content of slurry by diluting slurry with water which resulted in lower NH_3 emissions, due to a lower TAN content and a decrease in pH (Sommer and Hutchings, 2001; Van der Stelt et al., 2005).

2.6.3.1 Chemical and biological amendments

The use of a variety of amendments, including aluminum sulfate (alum), ferrous sulfate, phosphoric acid, and proprietary products to acidify poultry litter and maintain ammonia in the non-volatile ionized form has been evaluated. Significant reduction in ammonia emissions following the addition of the acidifying agents has been observed. Furthermore, the addition of alum or ferrous sulfate may be beneficial because the metal ions form insoluble compounds with phosphorus, which help immobilize manure phosphorus. However, reductions in ammonia production are observed so long as pH levels remain low. If manure has sufficient buffering capacity, the pH may eventually increase, which results in a resumption of ammonia volatilization.

Chemical and biological amendments can be divided, according to their modes of action, into five groups (McCrory and Hobbs, 2001): (i) Digestive additives are amendments which enhance the biodegradation of manure and consists of microbial strains and/or enzymes. (ii) Acidifying additives lower the pH of manure, which will lead to a shift in the NH_3/NH_4^+ equilibrium towards a higher NH_4^+concentration, which concomitantly will lead to reduced NH_3 emissions (Dewes, 1996). (iii) Adsorbing additives, like zeolite (e.g., clinoptilolite) or peat, are involved in the binding of NH_3, NH_4^+, or both (McCrory and Hobbs, 2001; Lefcourt and Meisinger, 2001). Other adsorbents bind toxic substances in manure and thereby improve the conditions for micro-organisms to decompose manure slurry. (iv) Urease inhibitors prevent the breakdown of urea, which is a major source of NH_4^+/NH_{3aq} in manure (Sommer and Husted, 1995). However, the use of urease inhibitors is momentarily not profitable. (v) Saponins, which are glycosides derived from the yucca plant, are supposed to bind or to convert NH_4^+.

Although effect of acidification on NH_3 emissions has been known for many years, its implications on the emission of other compounds, such as CO_2 and H_2S, has not been fully documented in the literature. The release of dissolved gases from slurry is a function of the concentration of gas present in the slurry surface in a non-ionized form, which will be affected by the slurry surface pH. Therefore, a reduction of slurry pH favors the emission of weak acid forming gases such as CO_2 and H_2S. Furthermore, acidification by addition of H_2SO_4 may increase the concentration of inorganic sulfur in the slurry, which could potentially result in an increase of H_2S emission as a result of the additional sulfate provided as substrate to sulfate-reducing bacteria. However, the acidification may also inhibit the bacterial activities in slurry and limit the sulfate reduction (Eriksen et al., 2008).

2.6.3.2 Application of urease inhibitors

This technique, which implies, for instance, as the application of N-(n-butyl) thiophosphoric triamide, cyclohexylphosphoric triamide, and phenyl phosphorodiamidate to cattle and/or swine manure, has been shown to effectively limit urea hydrolysis in laboratory and field studies. Presumably, urease inhibitors would also be effective with poultry manures. However, these inhibitors are easily degraded and must be continuously applied to manure in order to reduce the production of ammonia from urea.

2.6.3.3 Separation of faeces and urine

This category includes all building structures such as slatted floor or floor with a slope of V, which allow the separation of feces and urine. Minimizing their contact may be an effective approach to reduce urea hydrolysis and, as a consequence, ammonia emissions (Vaddella et al., 2010). Similarly, maintaining low manure moisture content may slow the rate of reactions that lead to ammonia generation and may help to minimize ammonia volatilization.

2.6.3.4 Housing ventilation systems

Housing ventilation systems may be equipped with a variety of different filters or other treatment systems that remove ammonia using physical/chemical or biological mechanisms.

Some companies in Denmark produce a type of filters (Farm AirClean) for biological air cleaning in the barns. The system is based solely on biological air cleaning principles. These principles are effective when it comes to reducing odour, ammonia and dust. The content of ammonia in the outgoing air from the livestock house is reduced down to 1 ppm and the dust content in the outgoing air is reduced by 90%.

The livestock house air is led through two filters sprinkled with water. Ammonia and odorants are removed in both filters while most of the dust is removed in the first filter. The air cleaning process is a biological process. Biofilms of bacteria and other microorganisms are formed on the filters. Ammonia, odorants and dust are removed when the housing air gets into contact with the water and the biofilms in the filters.

2.7 Legislation

2.7.1 Overview on Legislation to reduce ammonia emissions

Environmental legislation comprises today some 300 legal acts, including directives, regulations, decisions and recommendations. To this come a large number of communications and other policy documents of relevance for EU environmental policy. As a consequence, European legislation has an increasing influence on the legislation in the Member States and over 80% of legal regulations that are relevant for the industry are of European origin. Legislation is chiefly concerned with limiting pollution by introducing minimum standards, notably for water pollution and air pollution. For example, to prevent water pollution a number of directives have been adopted by the Member States to introduce water quality standards (e.g. drinking water and bathing water directives), to reduce and avoid emissions (Nitrates Directive), to protect water resources and to monitor emissions of pollutants. A number of policies have been implemented within Europe that either directly or indirectly act to reduce emissions of ammonia. These include:

- the National Emission Ceilings Directive 2001/81/EC (NECD) which entered into force in the European Community in 2001. The NECD sets emission ceilings for four important air pollutants (NH_3, sulphur dioxide (SO_2), nitrogen oxides (NO_X) and non-methane volatile organic compounds (NMVOCs). The ceilings are designed to improve the protection of the environment and human health against risks of adverse effects arising from acidification, eutrophication and ground level ozone in the Community.

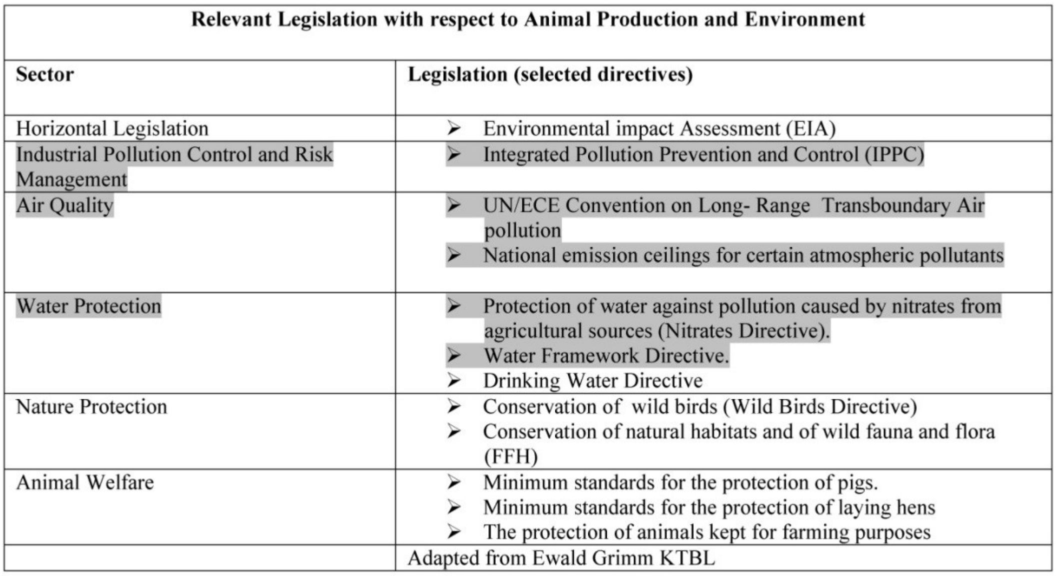
- The Gothenburg Protocol (1999) of the United Nations Economic Commission for Europe's (UNECE) Convention on Long-Range Transboundary Air Pollution (LRTAP Convention) to abate acidification, eutrophication and ground-level ozone. A key objective of the protocol is to regulate emissions on a regional basis within Europe and to protect eco-systems from transboundary pollution by setting emission reduction ceilings. Overall for the EU Member States, the ceilings set within the Gothenburg protocol are generally either slightly less strict or the same as the emission ceilings specified in the NECD.

- The Directive on Integrated Pollution Prevention and Control (96/61/EC) entered into force in 1999. It aims to prevent or minimise pollution to air, water or land from various industrial sources throughout the European Union. Those installations covered by Annex I of the IPPC Directive are required to obtain authorisation from the authorities to operate. New installations and existing installations, which are subject to 'substantial changes' have been required to meet the requirements of the IPPC Directive since 30th October 1999. The emission limit values outlined in the permit conditions must be based on best available techniques (BAT). The Commission has been undertaking a review of the IPPC Directive and related legislation on industrial emissions and on the 21st December 2007 adopted a proposal for a Directive on industrial emissions. The proposal recasts seven existing Directives relating to industrial emissions (including IPPC and the Large Combustion Plant Directive (2001/80/EC) into a single legislative instrument.

Apart from the NECD and Gothenburg Protocol and the IPPC Directive, there is currently no other EU legislation proposed or in force specifically aimed at reducing ammonia emissions. However, several regulatory instruments have influenced EU emissions of ammonia from the agriculture sector since 1990, such as:

- the Common Agricultural Policy (CAP);
- the Nitrate Directive (91/676/EEC);
- the Water Framework Directive (2000/60/EC);

These measures have had the indirect effect of changing agricultural practices across the EU, and have, for instance, led to a reduced use of nitrogenous fertilisers and to an overall decrease in cattle numbers, both of which affect the levels of ammonia emissions. The reforms of PAC, and specifically the removal of the link between farm production and payments, has also resulted in reduced livestock numbers across the EU and hence also will have indirectly contributed to the decrease in ammonia emissions observed (Tab. 2).



Relevant Legislation with respect to Animal Production and Environment	
Sector	**Legislation (selected directives)**
Horizontal Legislation	➢ Environmental impact Assessment (EIA)
Industrial Pollution Control and Risk Management	➢ Integrated Pollution Prevention and Control (IPPC)
Air Quality	➢ UN/ECE Convention on Long- Range Transboundary Air pollution ➢ National emission ceilings for certain atmospheric pollutants
Water Protection	➢ Protection of water against pollution caused by nitrates from agricultural sources (Nitrates Directive). ➢ Water Framework Directive. ➢ Drinking Water Directive
Nature Protection	➢ Conservation of wild birds (Wild Birds Directive) ➢ Conservation of natural habitats and of wild fauna and flora (FFH)
Animal Welfare	➢ Minimum standards for the protection of pigs. ➢ Minimum standards for the protection of laying hens ➢ The protection of animals kept for farming purposes
	Adapted from Ewald Grimm KTBL

Tab 2 – Rilevant Legislation with respect to animal Production and Environment (source: Ewald Grimm et al., 2010)

To combat global warming, national and international efforts are combined to reduce emissions of the gases responsible. The EU adopted the United Nations Framework Convention (1992) and the Kyoto Protocol (1997). To meet this target, strategies are developed by the Community at present. Up to now greenhouse gas emissions from animal husbandry are limited only as a side-effect by the legislation on air pollution control.

The Council Directive 91/676/EEC on the protection of waters against pollution caused by nitrates from agricultural sources (Nitrates Directive) has been necessary because the nitrate content of water in some areas of Member States was increasing and was already high as compared with standards laid down in Council Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water and Council Directive 80/778/EEC relating to the quality of water intended for human consumption. The objectives of the Directive are twofold (table 2):

- to reduce water pollution caused or induced by surplus nitrogen from agricultural sources (i.e. application and storage of inorganic fertiliser and manure on farmland);

- to prevent further pollution of this type both to safeguard drinking water supplies, especially to meet the standards of Directives concerning the quality of drinking water ($NO_3 < 50$ mg/m^3) and to prevent wider ecological damage in the form of the eutrophication of freshwater and marine waters.

With Directive 91/676/EEC, the EU has proposed to provide information on control and reduction of water pollution that derives from the use of excessive amounts of fertilizers and by the spreading of manure of farm animals.

These indications have been implemented by Italy with DM 7 aprile 2006, which indicates the regional criteria for identifying vulnerable areas, represented by the areas that drain directly or indirectly nitrogen compounds in waters already polluted, and the risk of pollution because of the use in agriculture of nitrogen fertilizers and livestock manure. The regions must also design and implement the necessary Mandatory action programs aimed at reducing, in vulnerable areas, water pollution from nitrogen compounds of farm origin. These action programs adopt measures which aim to limit the land-application of all fertilizers containing nitrogen and to establish specific restrictions in the use of organic fertilizers, these measures constitute mandatory intervention for all farms that fall, even partially, in the vulnerable areas.

To this aim Member States must identify waters affected by nitrate pollution and waters which could be affected by such pollution and designate them and all known areas draining into those waters as 'vulnerable zones'. In those zones there is conflict between arable and livestock production and the need for nitrate-free human water supplies. For ´vulnerable zones´ Member States must then establish and implement action programs to reduce and monitor the nitrate concentrations in groundwaters and surface waters as well as eutrophication in surface waters. In addition a code of good agricultural practice for the reduction of nitrate pollution in general should be introduced. The objective is to keep the nitrate concentration in drinking water supplies below a Maximum Allowable Concentration (MAC) of 50 ppm by reducing the ´residual nitrogen´, the amount of nitrate remaining in the soil and soil water after normal absorption by crops. The action programs mentioned above according to Annex III of the directive contain mandatory measures, including periods when the application of certain fertilisers is prohibited.

Regulations on the capacity of storage vessels for livestock manure should state that this capacity must exceed that required for storage throughout the longest period during which land application in the vulnerable zone is prohibited, except where it can be demonstrated to the competent authority that any quantity of manure in excess of the actual storage capacity will be disposed of in a manner which will not cause harm to the environment.

The limitation of the land application of fertilisers should be consistent with good agricultural practice and take into account the characteristics of the vulnerable zone concerned, in particular soil conditions, soil type and slope, climatic conditions, rainfall and irrigation, land use and agricultural practices, including crop rotation systems and to be based on a balance between the foreseeable nitrogen requirements of the crops and the nitrogen supply to the crops from the soil and from fertilisation corresponding to the amount of nitrogen present in the soil, the supply of nitrogen through the net mineralization of the reserves of organic nitrogen in the soil, additions of nitrogen compounds from livestock manure, and additions of nitrogen compounds from chemical and other fertilisers.

These measures shall ensure that, for each farm or livestock unit, the amount of livestock manure applied to the land each year shall not exceed 170 kg N per hectare.

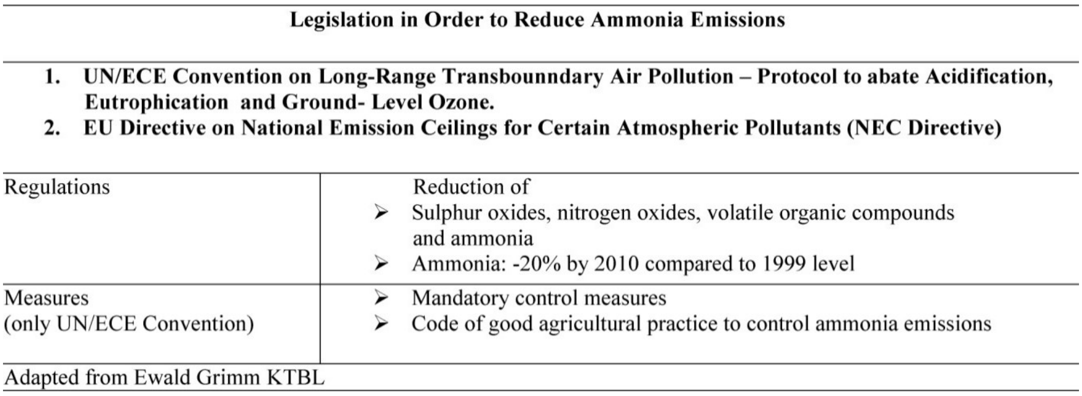
The codes of good farming practice, that have to be introduced into the vulnerable zones in order to keep the nitrates concentration below the MAC should take into account conditions in the different regions of the Community and certain provisions covering the following items according to Annex II of the directive:

- periods when the land application of fertiliser is inappropriate;
- the land application of fertiliser to water-saturated, flooded, frozen or snow-covered ground;
- the conditions for land application of fertilisers near water courses;
- the capacity and construction of storage vessels for livestock manure, including measures to prevent water pollution by run-off and seepage into the groundwater and surface water of liquids containing livestock manures and effluents from stored plant materials such as silage;
- procedures for the land application, including rate and uniformity of spreading, of both chemical fertiliser and livestock manure, that will maintain nutrient losses to water at an acceptable level. Member States may also include in their code(s) of good agricultural practices the following items:
- land use management, including the use of crop rotation systems and the proportion of the land area devoted to permanent crops relative to annual tillage crops;
- the maintenance of a minimum quantity of vegetation cover during (rainy) periods that will take up the nitrogen from the soil that could otherwise cause nitrate pollution of water;

- the establishment of fertiliser plans on a farm-by-farm basis and the keeping of records on fertiliser use;
- the prevention of water pollution from run-off and the downward water movement beyond the reach of crop roots in irrigation systems .

2.7.2 Legislation to reduce ammonia emissions

In order to reduce the emissions of sulphur oxides, nitrogen oxides, volatile organic compounds and ammonia a Protocol to Abate Acidification, Eutrophication and Ground-Level Ozone was signed under UN-ECE Convention on Long-Range Transboundary Air Pollution from 1999. In addition the Directive on National Emission Ceilings for Certain Atmospheric Pollutants (NEC Directive, 2001/81/EC), highlights the importance of reporting air pollutant emission data for assessing progress in reducing air pollution in the European Union region and for ascertaining the compliance of the Member States with their commitments (Tab. 3). As regards Italy, ISPRA (Istituto Superiore per la Protezione e la Ricerca Ambientale), each year, prepare a report on emissions.



Legislation in Order to Reduce Ammonia Emissions

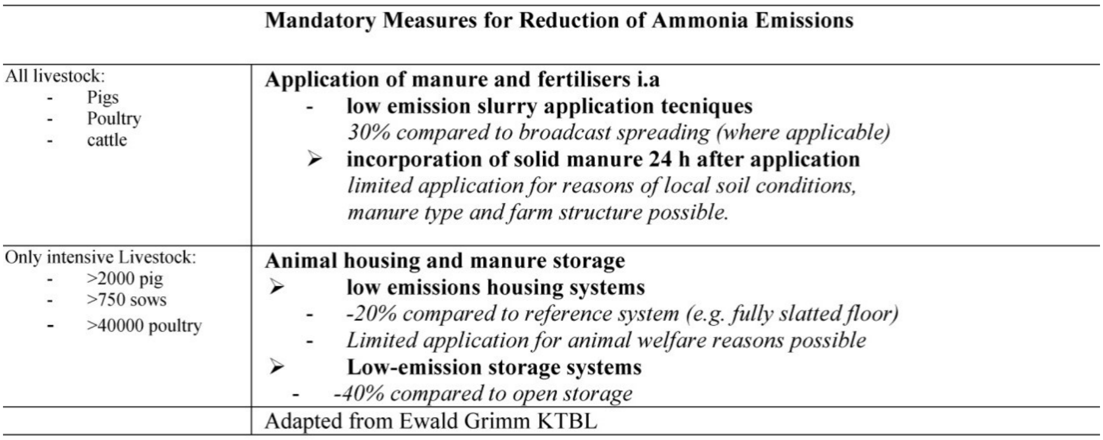
1. **UN/ECE Convention on Long-Range Transbounndary Air Pollution – Protocol to abate Acidification, Eutrophication and Ground- Level Ozone.**
2. **EU Directive on National Emission Ceilings for Certain Atmospheric Pollutants (NEC Directive)**

Regulations	Reduction of ➢ Sulphur oxides, nitrogen oxides, volatile organic compounds and ammonia ➢ Ammonia: -20% by 2010 compared to 1999 level
Measures (only UN/ECE Convention)	➢ Mandatory control measures ➢ Code of good agricultural practice to control ammonia emissions

Adapted from Ewald Grimm KTBL

Tab. 3– Legislation in Order to reduce Ammonia Emissions (source: Ewald Grimm et al., 2010)

Under UN-ECE Convention in each state mandatory control measures must be applied and a code of good agricultural practice to control ammonia emissions should be established. Mandatory measures include low emission application techniques for manure and low emission housing and manure storage systems particularly for intensive poultry and pig production. This also involves implementing best available techniques for livestock production. Further details are reported in Table 4. The code of good agricultural practice for ammonia abatement shall include provisions on nitrogen management in general (balanced N application), livestock feeding strategies (adapted, N-reduced feeding) and low emission techniques for manure storing, manure spreading and animal housing.



Mandatory Measures for Reduction of Ammonia Emissions	
All livestock: - Pigs - Poultry - cattle	**Application of manure and fertilisers i.a** - **low emission slurry application tecniques** *30% compared to broadcast spreading (where applicable)* ➢ **incorporation of solid manure 24 h after application** *limited application for reasons of local soil conditions, manure type and farm structure possible.*
Only intensive Livestock: - >2000 pig - >750 sows - >40000 poultry	**Animal housing and manure storage** ➢ **low emissions housing systems** - *-20% compared to reference system (e.g. fully slatted floor)* - *Limited application for animal welfare reasons possible* ➢ **Low-emission storage systems** - *-40% compared to open storage*
	Adapted from Ewald Grimm KTBL

Tab. 4 - Mandatory Measures for reduce Ammonia Emissions (source: Ewald Grimm et al., 2010)

2.7.3 Best Available Techniques (BAT)

The basic technology requirement to be reflected in IPPC integrated permits is the ‘Best Available Techniques’ (BAT).

“Best available techniques” shall mean the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole.

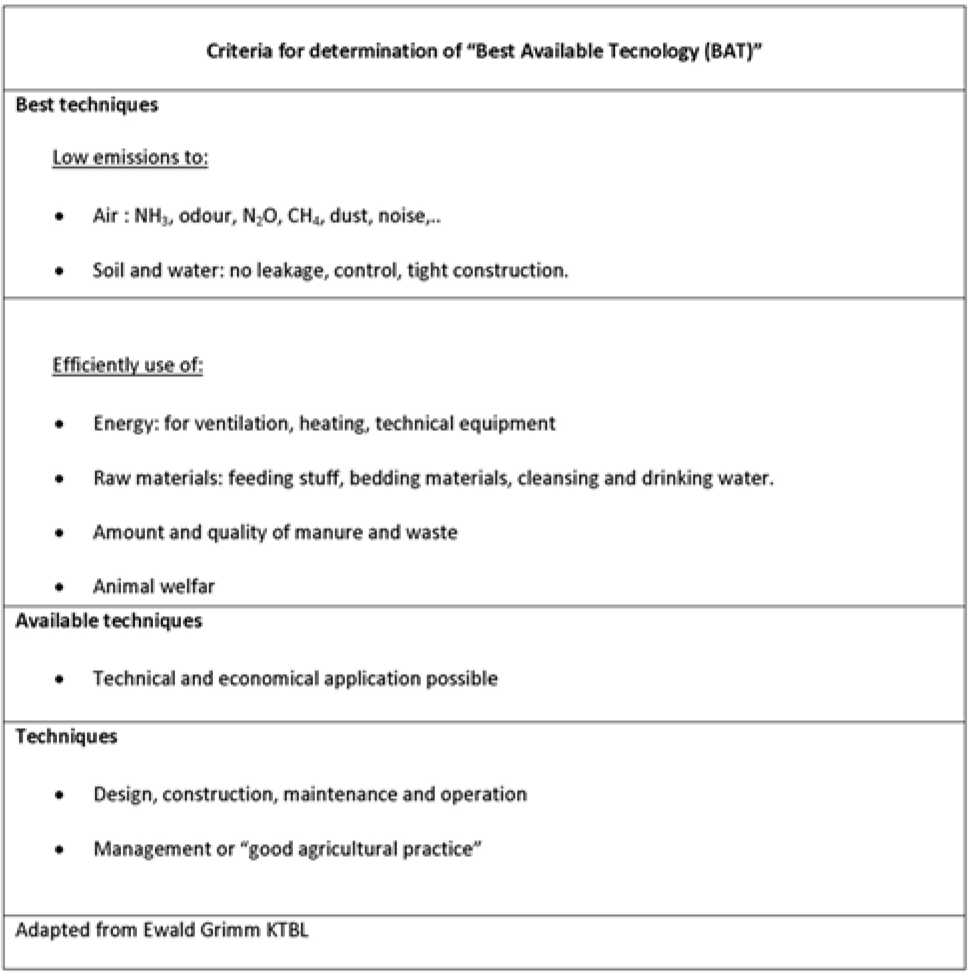
“Techniques” shall include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned.

“Available” techniques shall mean that they are developed on a scale which allows implementation in the relevant industrial sector under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator.

“Best” shall mean most effective in achieving a high general level of protection of the environment as a whole.

The application of BAT requires significant input of technical resources and a high degree of support for both the regulator(s) and industry. Comprehensive advice and guidance notes are essential for effective implementation of the integrated pollution control regime. The European IPPC Bureau (EIPPC) in Seville is charged with producing BAT Reference Documents (BREFs) for each of the categories of industrial activities listed in Annex 1 of the directive. The

BREFs will assist the regulatory authorities by describing reference techniques and reference levels for each sector (Table 5).



Criteria for determination of "Best Available Tecnology (BAT)"

Best techniques

Low emissions to:

- Air : NH_3, odour, N_2O, CH_4, dust, noise,..
- Soil and water: no leakage, control, tight construction.

Efficiently use of:

- Energy: for ventilation, heating, technical equipment
- Raw materials: feeding stuff, bedding materials, cleansing and drinking water.
- Amount and quality of manure and waste
- Animal welfar

Available techniques

- Technical and economical application possible

Techniques

- Design, construction, maintenance and operation
- Management or "good agricultural practice"

Adapted from Ewald Grimm KTBL

Tab. 5 - Criteria for determination of "Best Available Tecnology" (BAT) - (source: Ewald Grimm et al., 2010)

2.7.4 Threshold limits of ammonia (MAC: Maximum allowable concentration)

Concern about the effects of ammonia on man and livestock, and thus ammonia concentration as one of the parameters within livestock buildings, preceded the attention now given to ammonia emission and its effect on the environment. Acceptable levels of ammonia concentrations for the working environment of the stockman and/or the living environment of livestock lie below nationally defined and established maximum allowable concentrations (MAC values).

These levels vary from 20 to 50 p.p.m. depending on animal type, working time (exposure) and country. Several authors have shown that these levels are often exceeded in poultry and pig houses and concluded that efforts must be made to improve the living and working environment.

The definitions of threshold limits are shown below:

- TLV (Threshold Limit Value) express the airborne concentration of a material to which nearly all persons can be exposed day after day without adverse effects.

- TLV-TWA (Threshold Limit Value -Time Weighted Average) is the allowable concentration for a normal 8-hour work-day or 40-hour work week.

- TLV-STEL (Threshold Limit Value - Short Time Exposure Limit) is the maximum concentration for a continuous 15-minute exposure period (maximum of four such periods per day, which at least 60 minutes between exposure periods, and provided that the daily TLV-TWA is not exceeded).

- The Value Of Roof, TLV-C (Threshold Limit Values - Ceiling) it is absolute exposure limit that should not be exceeded at any time, it is a very important parameter for the irritants gas.

The threshold Limit Values (TLV) are indicated annually by the ACGIH (American Conference of Governmental Industrial Hygienists, 2007), and in Italy, are also recommended by 'Italian Association of Industrial Hygienists for Industrial Hygiene and Environment (AIDII). These threshold Limit Values are not a clear demarcation line between dangerous and non-dangerous concentrations, or a relative index of toxicity, however, they serve as a guideline for the prevention of health risks in the workplace (‘substances which may be present within confined spaces’) (ISPESL 2008).

TLV (threshold limit value)	Values		Source	Date of revision
	ppm	mg/m^3		
TLV TWA	20	14	Acros organics	May 2012
TLV STEL	50	36		
TLV CEILING	-	-		
TLV TWA	25	17	OSHA (Occupational safety & health administration)	October 2013
TLV STEL	35	24		
TLV CEILING	50	36		
TLV TWA	20	14	Inchem (Geneva)	1990
TLV STEL	-	-		
TLV CEILING	-	-		
TLV TWA	25	17	Ispels	2008
TLV STEL	35	24		
TLV CEILING	-	-		
Conversion factors: From ppm to a mg/m^3 * 0.71 From mg/m^3 to ppm * 1.41				

Tab. 6 - Ammonia threshold limits according to different sources.

2.7.4.1 *Chronic Adverse Health Effects of Ammonia in Humans*

Ammonia gas is normally absorbed by mucous membranes of the upper airways at ambient air concentrations, however, once adsorbed to respirable dust, ammonia can penetrate deeper into the lungs, increasing the risk of illness in the lower respiratory tract at low ammonia concentrations. In their review of agricultural lung disease, Kirkhorn and Garry (2000) argue that current occupational limits for ammonia (25 to 50 ppm, i.e., 17 mg/m^3 to 35 mg/m^3) are not appropriate for animal confinement workers, and recommend an ammonia limit of 7.5 ppm (5 mg/m^3), based on the work of Reynold et al. (1996). In addition to occupational risks, the authors raise concerns of respiratory health issues in areas neighboring animal confinement facilities (Kirkhorn and Garry, 2000).

3 MATERIALS AND METHODS

3.1 The livestock buildings under study

The barns under study were two naturally ventilated dairy houses. These livestock buildings were free-stall barns with a cubicle resting area. Both buildings, named Building A and Building B in the following, are the result of a functional rearrangement of the indoor areas modifying an old type of management which involved breeding on litter.

3.1.1 Building A

The building A was a free-stall barn open on three sides which is located in Contrada Pozzilli in the municipality of Vittoria (RG), at an altitude of approximately 230 m.

The building A was about 55.50 m long and about 20.80 m wide, had a ridge height of 7 m and an eave height of 4 m. Its bearing structure was made partly of reinforced concrete columns and beams and partly by steel pillars and trusses. The roof was symmetric with a central ridge vent, and composed by fiber-cement sheets supported by the bearing structure made of steel trusses and purlins.

The building was oriented to north-east. The sides facing to south-east, north-east and north-west were fully open, whereas the side to south-west was fully closed (Fig. 2).

At the centre of the barn, the feeding passage, 4.20 m wide, divided the barn in two symmetric areas: in one side there were boxes for calves and the farmer office, on the other side the cow functional areas. In detail, the feeding area was separated from the manger by the feed barrier composed of locking yokes, manually operated. Adjacent to the feeding alley, the resting area was made of a raised platform divided in 64 head-to-head cubicles (1.20 m wide and 2.15 m long) arranged in two rows and equipped with sand beds. A service alley was in the north-east side of the barn, adjacent to the resting area, and two side passages constituted walkways for the cows to move from the feeding alley to the service alley.

Inside the barn 45 dairy cows (Friesian) were bred. They were divided into three equal groups each consisting of 15 cows, grouped according to the stage of growth. The first group was composed of the cows at the end of their careers who have a lower lactation curve and daily production; the second group was composed of the primiparous cows, which often have problems with the milking and are not yet accustomed to the breeding routines; and the third group was composed of the cows on the 2nd, 3rd and 4th or highest pregnancy, representing the excellence of milk production for the farm.

The alleys, made of concrete, were cleaned by a mechanical tractor with scraper that was used by the operator once a day, at about 09:00 in the morning. In this scraper an hard rubber was applied to the blade to ensure a better cleaning effect (Fig. 2).

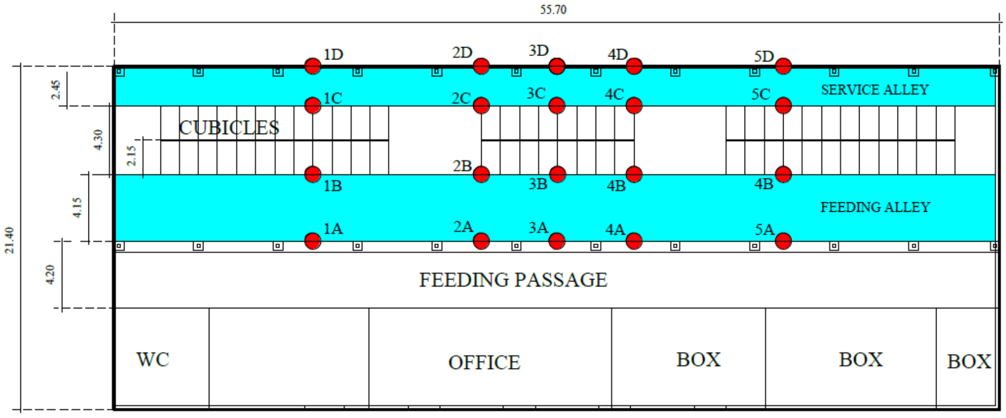


Fig. 2 – Floor plan of Building A and sampling points located in the functional areas.

The milking parlour was located in a specific building outside the barn. The first milking is carried out at 5.30 a.m. and the second one at 17.30 p.m.

The barn was also equipped with an external paddock in which heifers and dry cows are stabulated.

Above the feeding alley and resting area, fans were located at about 2.70 m height from the floor level, which were automatically operated when the temperature rised above 27°C and remained active for 5 minutes at intervals of 20 minutes. Another cooling system consisted of dispensers that atomize water at a pressure of 2 bar, located above the feeding alley, which were activated when the temperature exceeded 29°C. Measurements had no interference with daily cool and fan management, since these devices were switched off during the data acquisition.

3.1.2 Building B

The building B was a free-stall barn open on two sides which is located in c.da Castiglione (RG) at an altitude of approximately 330 m. The building had a rectangular plan, with a bearing structure composed of steel pillars and trusses. The roof was symmetric with a central ridge vent, and composed by fiber-cement sheets supported by the bearing structure made of steel trusses and purlins.

The building B was 65.0 m long and 23.0 m wide, and it was divided into two symmetric areas by the feeding passage, 5 m wide. On the north side, there is a set of multiple boxes in which calves until the age of about 1 year are housed, while on the other side there are the manger, the feeding alley, which is 4.30 m wide, and one row of cubicles, which are 1.20 m wide and 2.20 m long, equipped with straw beds.

Unlike the building A, building B had ventilation openings in the long walls at a 2.20 m height to prevent the air from going directly on the animals, whereas it is open in the other two sides to facilitate the passage of the bulldozer and the feed mixing truck.

The actual distribution of functional areas of the barn derived from a structural reorganization that, while maintaining unchanged the bearing structure, substituted the litter with one row of cubicles. In this new layout, the service alley is not accessible to the cows yet it is utilized only by the operators (Fig. 3).

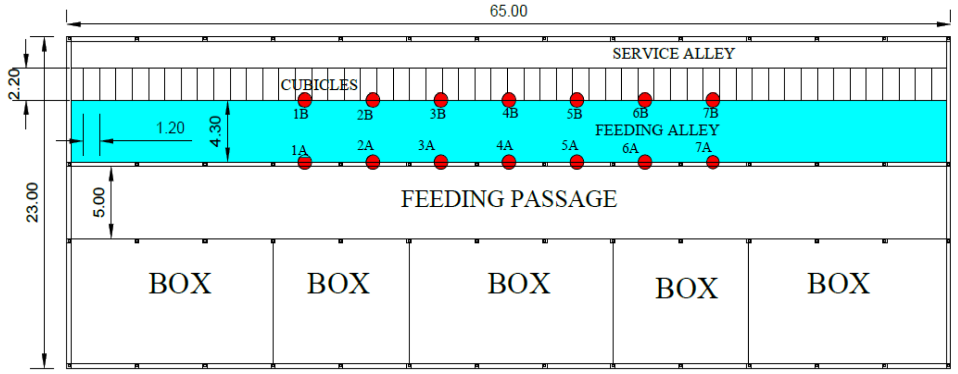


Fig. 3 – Floor plan of Building B and sampling points located in the functional areas.

In this barn fifty Friesian cows were bred, four of which belong to the Jersey breed. The farmer introduced these group of cow in the herd since the quality of the milk they produce has an index that is very high in protein and in fat, which is essential for making cheese.

In this building, cleaning is done twice a day: at approximately 09:00 am, after the first milking, and at approximately 19:00 pm, with some variations depending on the season. Although this routine results in a greater loss of time compared to that carried out in Building A, in which the cleaning was done only in the morning, this management choice is justified by the fact that the cows of Building B are not yet accustomed to the cubicles of the as rest area. As it is only 3 years since the breeding reorganization has been carried out, the cows often consider the feeding alley as a resting area, dirtying it with their own manure. The choice of providing the cubicles with straw bed was made to facilitate bed cleaning and make cows get accustomed to the new functional organization of the areas. The straw is also less expensive than sand, and such frequent replacement also avoids all the possible phenomena related to its condition of fermentable material.

In this barn, there are axial fans placed on the cubicles and the feeding alley in order to maintain the optimal internal microclimatic conditions. Also in this case, measurements were not interfered by the fan management, since these devices were switched off during the data acquisition.

3.2 Measurement setup

According to subsection 2.4.1.2, where criteria for selecting sampling method, location and time were described, measurement objectives played an important role. In this thesis work, ‘point sampling’ was the selected method in which samples are taken at a selected single point or at multiple points at animal facilities. In detail, sampling locations were fixed in animal and human respiration zones, since animal and human exposure were investigated. To compute ventilation rate, instead, within the objective of emission estimation, sampling location were fixed at the centre of the building and at the roof vent.

Sampling time for ammonia concentration depended on the time needed to perform manual collection of the data in the functional areas investigated and allowed measuring the variations in data because of spatial NH_3 differences. Microclimatic variables were continuously sampled for VR computation at the vents levels and manually acquired in a number of measurements carried out in the animal respiration zone.

Selection of measurement technique was based on research objectives, coupled with the existing capabilities of the research institution. A single-use sensor for ammonia concentration measurement, although it is relatively inexpensive, was not considered since it would have broaden the sampling time.

For ammonia concentration measurement, a dry method with a passive sampling technique was selected among those analysed in Section 2.4.2. The choice derived from the good precision of the method with a low cost of the device, which allows direct readout of measurements, good sensitivity and short response.

3.2.1 Portable measuring devices for ammonia concentration and microclimatic variables

A portable measurement device, **Dräger X-AM 5000** (Dräger, Germany)**,** was used for monitoring ammonia concentrations, within the functional areas examined. This instrument (Fig. 4) detects ammonia through an electrochemical sensor situated at the top. It has a detection range between -25 and 200 ppm of NH_3 and detects at temperatures between -20 and 50° C with an error of 2-3% on the data detected. The response, i.e., the time to perform the gas concentration measurement, varies from 1 to 30 sec.

Its dimensions are of a remote control and have ergonomic characteristics. It can measure independently five gases, depending on the Dräger sensors installed. The instrument has different types of components, as described in Figure 4, and in detail has a digital display which shows the gas concentration in ppm, the battery level, indications of anomalies, and alarm levels.

Fig. 4 - Portable instrument for the measurement of ammonia concentration (Dräger, Germany)

The instrument set has two alarm values for ammonia concentration (A1 and A2): in both cases the alarm signal is optical, acoustic and also shown by vibration. The alarm A1 activates at a concentration ≥20 ppm of NH_3, you will hear a sound and the indicator light flashes once, whereas the alarm A2 activates at a concentration ≥40 ppm of NH_3. When the instrument reaches or exceeds the concentration of 40 ppm it is displayed on the alarm A2 and a double beep is emitted and the indicator light flashes twice.

The measurements, during experimentation, were carried out manually, since it was necessary to detect the ammonia concentration in the sampling points within the functional areas where the cows developed their usual behaviours (feeding, lying, standing, etc.). After a first curiosity for the new operators, the cows got accustomed to the measurement operations.

As regards microclimate variables in the barn, the air temperature, the air relative humidity and air velocity were also measured in order to analyse the concentration of NH_3 in relation to microclimate variables at the ground level.

Fig. 5 - Portable instrument for the measurement of air velocity, air temperature and relative humidity (Marcucci, Italy).

In the trials a portable instrument, **AM-4205** (manufactured by Marcucci, Italy), was utilised to measure the air velocity (m/s), air temperature (°C) and relative humidity (Fig. 5).

Due to the suspension on a sapphire crystal, the fan allows achievement of an accurate reading of the measurement.

The relative humidity is measured by a thin film capacitive sensor. The device is also equipped with an incorporated precision thermistor for air temperature measurement.

Data recording is provided with the function of maintaining the data and recording of maximum and minimum values. The instrument accuracy is ± 2% for relative humidity and air velocity, and about 0.8 °C for temperature. The measuring interval of the air velocity was 0.4 – 25 m/s.

3.2.2 Instruments for continuous measurement of indoor microclimatic data and outdoor climatic data

In Building A, in addition to the instrumentation already described, a datalogger CR10X (Campbell, UK) connected to sensors of air temperature and relative humidity (Rotronic Italy srl., Italy) was utilised. Also connected to the datalogger were sensors for the measurement of velocity and direction of indoor air (anemometers WindSonic, Gill Instruments Ltd., UK), and wind speed and direction outside the barn.

The sensor of air temperature was a platinum thermoresistance (Pt 100 ohm 0°C) with a measure interval of -40°C÷60°C and precision of ±0.2°C (at 20°C). The hygrometer was a trasducer with a sensibility of ±0.04%RH/°C and precision of ±2% (a 20°C). This combined sensor was placed inside a shelter to avoid inaccuracies due to direct radiation on the sensor. The anemometers were bidimensional sonic sensors characterized by a measuring interval of 0÷60 m/s, a precision of ±2% (at 12 m/s), a resolution of 0.01 m/s, and a threshold of 0.01 m/s. The direction sensor had a measuring interval of 0°÷359°, a precision of ±3% (at 12 m/s), and a resolution of 1°.

The sensors inside the barn were located at a height of about 2.0 m, while outside it were at the ridge vent above the roof of the barn.

All the measured parameters were recorded at intervals of five seconds by the dataloggers that every five minutes computed the average values and stored them in memory locations.

3.3 Sampling

3.3.1 Sampling layout in the buildings analysed and data collection sessions

As regards sampling points, it was decided to work on representative points in relation to the areas in which animals deposited the most of their manure. The number of sampling points located in the functional areas of the two buildings were respectively 20 in Building A and 14 in Building B. The difference in the number of points fixed in the two barns was due to the presence of a single row of cubicles in the second barn (building B), compared to the first one (building A) which had two rows of stalls.

The position of the sampling points is illustrated on the floor plans of Figures 2 and 3. The measurements of ammonia concentrations were made at three different heights from the floor (10 cm, 20 cm and 40 cm) in order to analyze the presence of the gas at different levels from the floor. These levels represent the heights at which the animals breathe for most of the day, both in the phase of decubitus inside the cubicles and when they go to feed.

Sampling points, indicated by numbers, correspond to the edges of the walls of the feeding and service alleys and represent areas in which animals make their manure and cleaning may be less effective.

Measurements have been carried out during the daylight hours of the day in order to evaluate the daily trend of emission and their relationship with the microclimatic conditions.

In building A, the 20 points identified were grouped in sets of five points and arranged as follows:

- points A, located along the wall of the feed barrier;
- points B, positioned along the rear wall of the row of stalls, adjacent to the feeding alley;
- points C, situated along the rear wall of the second row of stalls, adjacent to the service alley;
- points D, positioned at the N-E open side of the barn.

In building B, the 14 points were grouped only in two sets of 7 points and arranged as follows:

- points A, located along the wall of the feed barrier;

- points B, at the same distance, positioned along the rear wall of the cubicles.

The points were placed at equal intervals of 5 m along the longitudinal direction of the barn (Fig. 2-3).

To facilitate the ammonia detection at fixed height from the ground, a wooden support with three cases at the three heights was specially constructed. The measuring instrument was placed in these cases in order to keep it fixed during each measure. It was decided to carry out four sessions of sampling within a day by choosing the most representative hours in relation to the internal microclimatic conditions and the cleaning operations of the barn.

The sessions were identified as follows:

- 1st session: at 08: 00, before barn cleaning operations;
- 2nd session: at 11:00, after the cleaning operations;
- 3rd session: at 13:00, which correspond to the hottest hours of the day;
- 4th session: at 17:00, during the second daily milking.

The sampling sessions, have undergone a change in the timetable, on certain days of trial, for logistical reasons.

3.4 Methods of computation of Ammonia Emissions

In naturally ventilated barns, as described in section 2.4.3 on the state of the art of research studies in the field, ammonia emissions can be calculated according to three methods: 1) the tracer gas technique, 2) the measurement of the air velocity through the barn openings, and 3) the natural ventilation method.

Since the measurement system utilized for this research work did not allow the application of the most utilised experimental protocols for estimating ammonia emissions from naturally ventilated barns, characterised by a semi-open envelope, it was decided to perform an estimation of ammonia emissions by applying the calculation of emissions through the relations shown in the first method (i.e., the tracer gas technique with natural tracers) and the third method.

Therefore, ammonia emissions were calculated according to the equation of Kiwan et al. (2012) as shown below:

$$E_{ammonia} = VR \times C_{NH3}$$

where:

VR is the ventilation rate (m^3/h);

C_{NH3} is the ammonia concentration (mg/m^3);

The VR was computed as $\dot{V}_{H2O}$ and $\dot{V}_{HB}$ as well as $\dot{V}_{total}$, following the methods described in sections 2.4.3.1 and 2.4.3.3.

The computation was carried out for building A where the measuring instruments of indoor and outdoor variables were provided.

To compute the total heat produced by the cows according to eqn.(13) and V_{H2O} according to eqn. (9) the live weight of the cows housed in building A was 650 kg, the milk production was 32 l/g and the number of days of pregnancy was fixed to 135 on average.

3.5 Statistical Analyses on collected data

Collected data were subject to statistical analyses. The analysis of variance (ANOVA) was performed. It is a test for difference in means based on the test of the null hypothesis: the means between treatments (i.e., factor levels) are equal.

One-way ANOVA compares three or more unmatched groups, based on the assumption that the populations are Gaussian. ANOVA partitions the variability among all the values into one component that is due to variability among group means (due to the treatment) and another component that is due to variability within the groups (also called residual variation). Variability within groups (within the columns) is quantified as the sum of squares of the differences between each value and its group mean. This is the residual sum-of-squares. Variation among groups (due to treatment) is quantified as the sum of the squares of the differences between the group means and the grand mean (the mean of all values in all groups). Adjusted for the size of each group, this becomes the treatment sum-of-squares. Each sum-of-squares is associated with a certain number of degrees of freedom (df, computed from number of subjects and number of groups), and the mean square (MS) is computed by dividing the sum-of-squares by the appropriate number of degrees of freedom. These can be thought of as variances. The square root of the mean square residual can be thought of as the pooled standard deviation.

The F ratio is the ratio of two mean square values. If the null hypothesis is true, you expect F to have a value close to 1.0 most of the time. A large F ratio means that the variation among group means is more than you'd expect to see by chance. You'll see a large F ratio both when the null hypothesis is wrong (the data are not sampled from populations with the same mean) and when random sampling happened to end up with large values in some groups and small values in others.

The P value is determined from the F ratio and the two values for degrees of freedom shown in the ANOVA table.

The calculated P value determines the significance of the test. If the value lies below 0.05 the test is significant at the 5% level and we would say there is evidence that the population means are not the same, i.e., the test is significant so we reject the null hypothesis of no difference in means. If the value is less than 0.1 but greater than 0.05 then there is weak evidence in favour of the alternative hypothesis. Finally, if the P value is greater than 0.1 then we would usually say there is no evidence to reject the null hypothesis that the population means are the same.

If the ANOVA result is significant, a post-hoc test is usually carried out. The reason for carrying out the test is to compare pairs of treatments (or factor levels) simultaneously, to gain more information as to why a significant result was obtained for the overall ANOVA. In fact, if the p-value is very low so that we reject the null hypothesis of no difference in means, this does not mean that the mean are all significantly different among them but it rather means that there is at least a couple of means which differs significatively. Therefore, it is necessary to identify which means are different among them by verifying the equality between all the possible couples of means through adequate tests. In these tests, named post-hoc tests, for each couple of means the null hypothesis is that the difference between these is equal to zero, whereas the alternative is that the two means significantly differs between them.

One of the post-hoc tests which perform multiple comparisons between the means and evaluate the confidence intervals for the differences is the Tukey Honest Significant Difference (HSD). If the confidence interval includes 0, the difference between the two means is not statistically significant.

The Tukey HSD simultaneous confidence intervals are calculated as:

$$\bar{Y}_{i.} - \bar{Y}_{j.} \pm Q_{1-\alpha,k,r}\sqrt{\frac{\mathrm{MSE}}{n}} .$$

where $\bar{Y}_i$ and $\bar{Y}_j$ are the sample averages of the two treatments *i* and *j*, ($Q_{1-\alpha,k,r}$) is the critical value, referred to the number of groups *k* and the degrees of freedom for the MSE *r*, and $Q_{1-\alpha}$denotes the $1 - \alpha$ percentile of the distribution of Q, α is the Family error rate, MSE is the mean square error, and *n* is the sample size per treatment. Tukey achieves at least 95% overall confidence. Tukey's HSD test accurately maintains alpha levels at their intended values as long as statistical model assumptions are met (i.e., normality, homogeneity, independence).

A number of other post-hoc procedures are available. There is Scheffe's procedures which is the most flexible, and the most conservative, the Tukey-Kramer procedure designed for the situation in which n-sizes are not equal. Brown-Forsythe's post hoc procedure is a modification of the Scheffe test for situations with heterogeneity of variance. Duncan's Multiple Range test and the Newman-Keuls test provide different critical difference values for particular comparisons of means depending on how adjacent the means are. Both tests have been criticized for not providing sufficient protection against alpha slippage and should probably be avoided.

In grouping information using Tukey Method, the means that do not share a letter are significantly different. In case of nonnormal distribution of the data, it is possible to transform non normal data with the Box-Cox method or the Johnson

Trasformation so that it follows a normal distribution. You can then use the transformed data with any analysis that assumes that the data follow a normal distribution.

Computation of percentiles and outliers values

Percentiles are utilized to compute outliers values of a group of data.

Let k be a number between 0 and 100. The k-th percentile is the value that separates the first k% of the data, which have to be ordered in growing sequence, from the remaining data.

The index of the k-th percentile is given by the following relation:

$$Ik = (n+1)\times k/100$$

By performing a linear interpolation, the precise value between the two data of the group, which have the index of the sequence equal to the integer number before and after Ik, is computed. Some software tools perform a simple mean of the two data, however the inaccuracy is negligible only if n is big.

The main percentiles are the following:

Q_1 is the first quartile or 25-th percentile.

Q_2 is the second quartile or 50th percentile (Median).

Q_3 is the third quartile or 75th percentile.

Q_3-Q_1 is the interquartile range (where 50% of the data are included).

The outlier values x are those abnormally too big or too small, which are too different from the rest of the data and are calculated as follows:

$$x \geq Q_1 - 1.5(Q_3 - Q_1) \quad \text{or} \quad x \geq Q_3 + 1.5(Q_3 - Q_1) \qquad (18)$$

The outlier is said “mild” if it satisfies the condition shown in eqn (19) or (20):

$$Q_1 - 3(Q_3 - Q_1) < x \leq Q_1 - 1.5(Q_3 - Q_1) \qquad (19)$$

or in the equation:

$$Q_3 + 1.5(Q_3 - Q_1) \leq x < Q_3 + 3(Q_3 - Q_1) \qquad (20)$$

The outlier is “strong” if satisfy the condition shown in the equation:

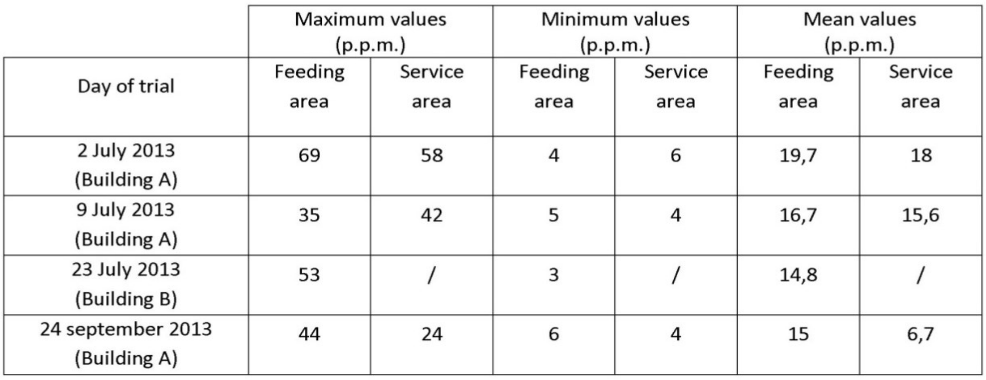
$$x \le Q_3 - 3\left(Q_3 - Q_1\right) \qquad (21)$$

or in the equation:

$$x \ge Q_3 + 3\left(Q_3 - Q_1\right) \qquad (22)$$

4 RESULTS AND DISCUSSION

In Table 7 the maximum values and the minimum values of all the measurements of ammonia concentrations in the feeding areas and the service area of the different buildings analysed, and the mean values of the ammonia concentrations computed for all sampling sessions at 10 cm from the ground, in each of the days of the trials, are reported. This table shows that the highest values were found on July 2, in the building A, within the feeding area. However, also in other days of the trials, values higher than the threshold of the MAC (maximum allowable concentrations) were found and, in particular, the highest values were found in the feeding area compared to the service area. This condition could be explained by the fact that the service area is more exposed to the air flows that are generated by natural ventilation, on the side of the barn which is fully open and, therefore, it causes the dispersion of the gas outside the barn. On the contrary, the feeding area is located in the central area of the barn and, therefore, is less affected by the movements of the air; also cows tend to stay for much time in this area of the barn, as they feed, so the manure accumulates in larger quantities.



	Maximum values (p.p.m.)		Minimum values (p.p.m.)		Mean values (p.p.m.)	
Day of trial	Feeding area	Service area	Feeding area	Service area	Feeding area	Service area
2 July 2013 (Building A)	69	58	4	6	19,7	18
9 July 2013 (Building A)	35	42	5	4	16,7	15,6
23 July 2013 (Building B)	53	/	3	/	14,8	/
24 september 2013 (Building A)	44	24	6	4	15	6,7

Tab. 7 - Maximum values and minimum values of all the measurements of ammonia concentrations in the feeding areas and in the service area of the different buildings analysed, and mean values of the ammonia concentrations computed for all sampling sessions at 10 cm above the ground, in each of the days of the trials.

In the analsis of the data, only two outliers values of ammonia concentration were found, according to the statistical analyses described in Section 3.5. They were found on 9 July (building A): an outlier with value 0 ppm at 11:00 and an outlier with a value of 32 ppm at 13:00.

According to the research scope declared in the introduction, the main objective of this work was to verify whether or not the levels of ammonia concentrations, in the naturally ventilated Sicilian barns, were higher than threshold values, which can be dangerous for workers who spend their working hours in the barns and for the animals which live in those breeding environments. To this aim Table 8 shows the number of times that the values of ammonia emissions are in four distinct ranges defined by the threshold values TLV-TWA, TLV-STEL, and TVL-C. The values of ammonia concentration, relative to all the sampling dates and within the two areas examined (feeding and service areas), were grouped into intervals according to the TLV. Values corresponding to less than 20 ppm are defined by the TLV-TWA (Threshold Limit Value - Time Weight Average), the values between 20 and 35 ppm are identified by the TLV-STEL (Threshold Limit Value - Short Time Exposure Limit), values between 35 ppm and 50 ppm are under the TLV-C (Threshold Limit Values - Ceiling), and finally values greater than 50 ppm, i.e., above TLV-C, represents dangerous values for health. These threshold values were selected on the basis of the analysis of the recommended limits for different work environments in European and foreign countries, as described in Section 2.7.4 (Tab. 6).

Date/Building	Ammonia (NH_3) (ppm)	Feeding area		Service area	
		N.	%	N.	%
2 July Building A	values < 20	28	56	30	60
	values 20≤x<35	14	28	13	26
	values 35≤x<50	7	14	6	12
	values ≥50	1	2	1	2
	TOT	50	100	50	100
9 July Building A	Values < 20	32	64	34	68
	values 20≤x<35	17	34	12	24
	values 35≤x<50	1	2	4	8
	values ≥50	0	0	0	0
	TOT	50	100	50	100
23 July Building B	values< 20	44	83,9	/	/
	values 20≤x<35	7	12,5	/	/
	values 35≤x<50	4	7,1	/	/
	values ≥50	1	1,8	/	/
	TOT	56	100	/	/
24 september Building A	values< 20	27	67,5	39	97,5
	values 20≤x<35	12	30	1	2,5
	values 35≤x<50	1	2,5	0	0
	values ≥50	0	0	0	0
	TOT	40	100	40	100

Table 8 - Number of times that values of ammonia concentrations (ppm) lie in the four distinct ranges defined by the threshold values TLV-TWA, TLV-STEL, and TVL-C.

From the analysis of Table 8 it was observed that, on July 2, 2013 in Building A, higher rates of gas concentration were found, with values greater than 35 ppm and in some cases higher than 50 ppm. A similar condition also occurs on July 23, 2013 in Building B while in the other days these values were much lower. Higher percentages of values above the TLV-TWA threshold were found in the feeding area compared to those in the service area, as already observed in Table 7 for maximum, minimum and mean values of ammonia concentrations. In Building A, the number of ammonia concentration values above TLV-TWA threshold were always higher than those found in Building B. These results could be related to the different microclimate conditions of the building environment which will be analysed in the following of the text and to the different amount of slurry production of the herd observed during the trials which, in turn, depended on the coe weight and the diet.

Figure 6 shows the trend of ammonia concentrations compared to the evolution of inside temperature on July 2, 2013. The ammonia concentration is inversely proportional to inside temperature, as in the warmer hours of the day the lowest values of ammonia are recorded. Similar results were found in the other days of trials (Figs. 11, 16, and 18). This is probably due to the buoyancy effect that determines an upward movement of the air which disperses the gas and to the effects of indoor air velocity during the central hours of the day, which is described in the following of the text.

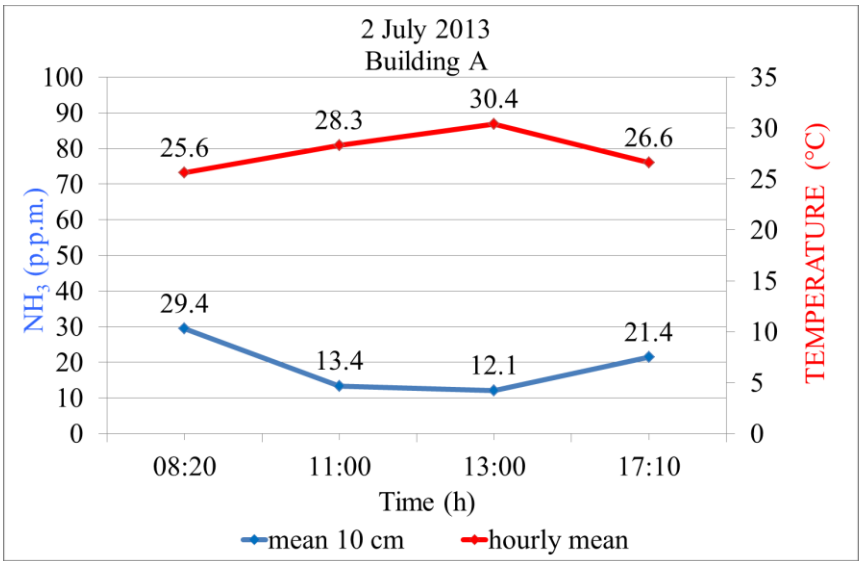


Figure 6- Indoor air temperature and ammonia concentration at 10 cm above the ground in the building A, on July 2, 2013.

Figure 7 shows the trend of ammonia concentrations compared to the evolution of inside relative humidity on July 2, 2013. The ammonia concentration tends to follow relative humidity. Similar trends were observed in the other days of the trials (Figs. 12, 17 and 19). In general, relative humidity should be kept between 50% and 70% in closed livestock environments. Lower relative humidities are likely to produce a dusty environment while higher relative humidities can lead to wet litter and high ammonia concentrations.

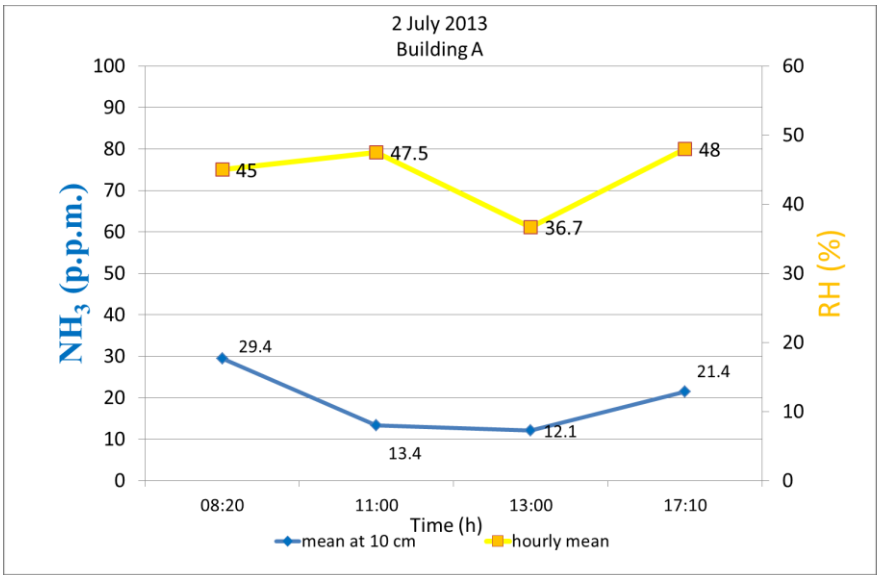


Fig. 7 - Indoor relative humidity and ammonia concentration at 10 cm above the ground in the building A, on July 2, 2013.

The graph of Figure 8 shows the trend of the ammonia concentration in relation to the velocity of indoor air. The concentrations of ammonia are lower during the central hours of the day corresponding to the maximum velocity of indoor air (approximately 1.3 m/s), which determines the dispersion of the gas from inside to outside due to the open sides of the barn.

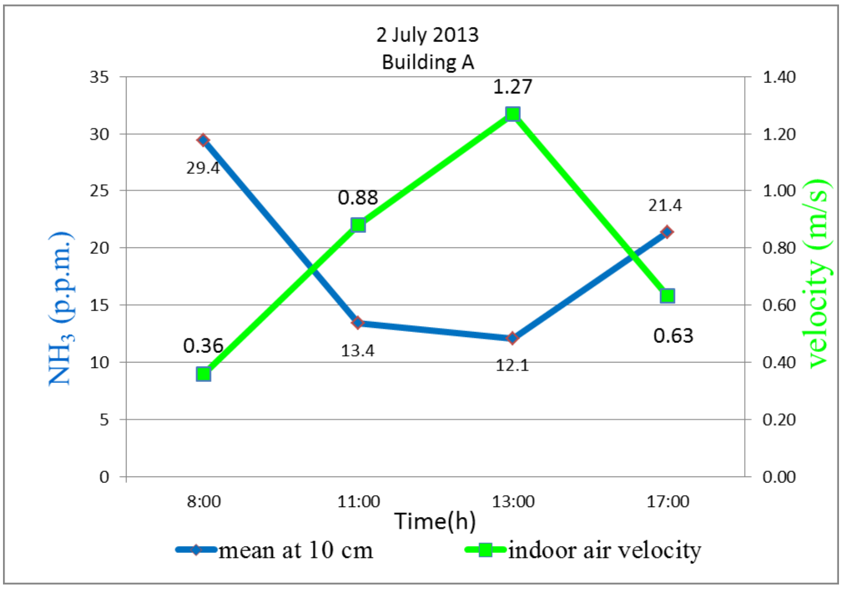


Fig. 8– Indoor air velocity and ammonia concentration above the ground in the building A, on July 2, 2013

In this day the ventilation effect is more evident during the warmest hours of the day than at lower temperatures, when the ammonia concentrations are higher, i.e., during the early hours of the day and the evening. A similar trend was observed on 9 July (Fig. 13). Although the values of outside air temperature recorded on July 2, 2013 (Fig. 8) were generally lower than those recorded on July 9, 2013 (Fig. 14), the inside air temperature inside the breeding environment of building A was higher on 2 July than on 9 July (Figs. 6 and 11).

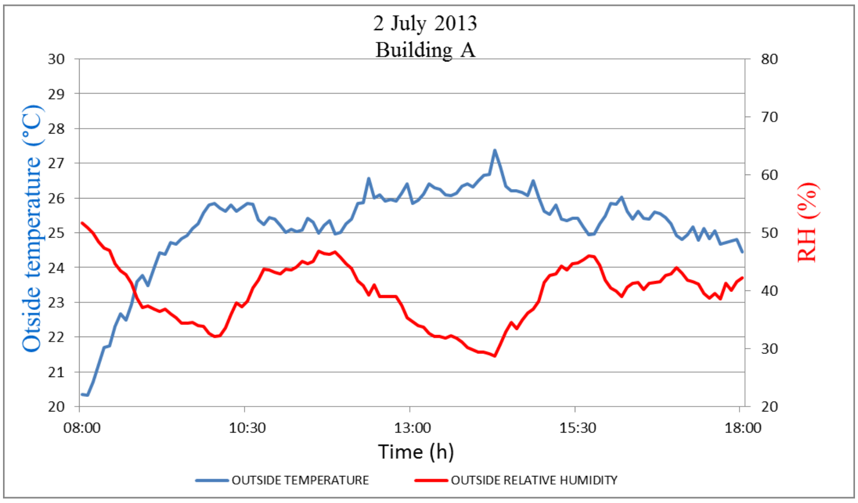


Fig. 9 - Outside temperature and outside relative humidity in the building A, on July 2, 2013

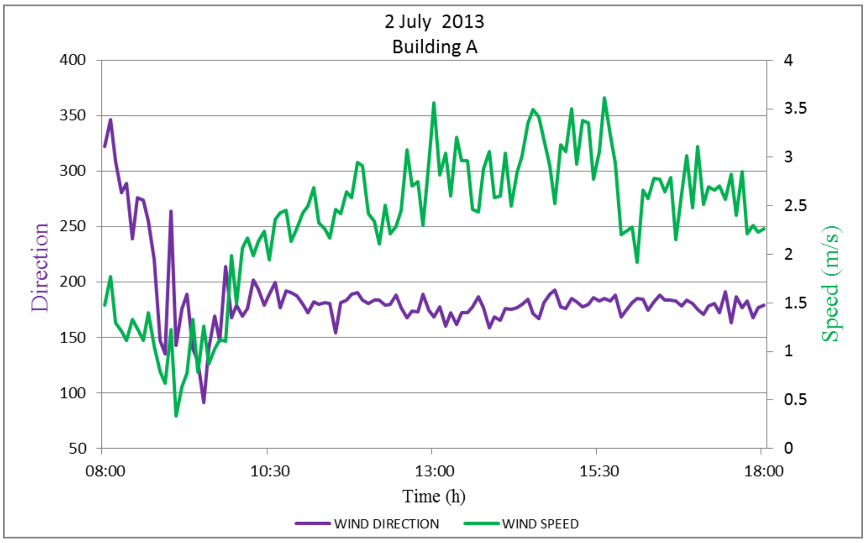


Fig. 10 - Wind speed and wind direction in the building A, on July 2, 2013.

Figure 10 shows the speed and the direction of the wind on July 2, 2013. The wind speed increases about from 10.30 to 15.30, while prevailing winds come from South.

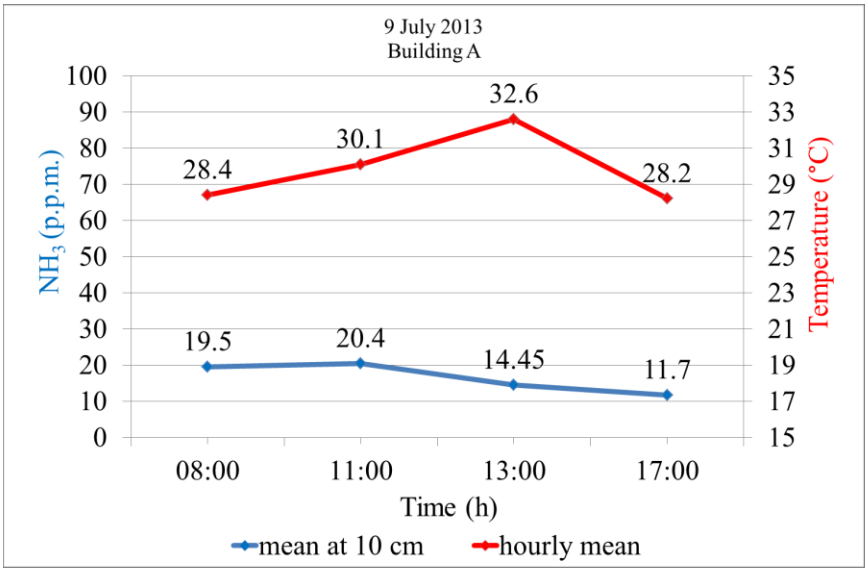


Fig. 11 - Indoor air temperature and ammonia concentration at 10 cm in the building A, on July 9, 2013.

Figure 11 shows the trend of ammonia concentrations compared to the evolution of inside temperature on July 9, 2013. The variations of temperature and ammonia are similar to those recorded of July 2, 2013 where an inverse proportionality was observed.

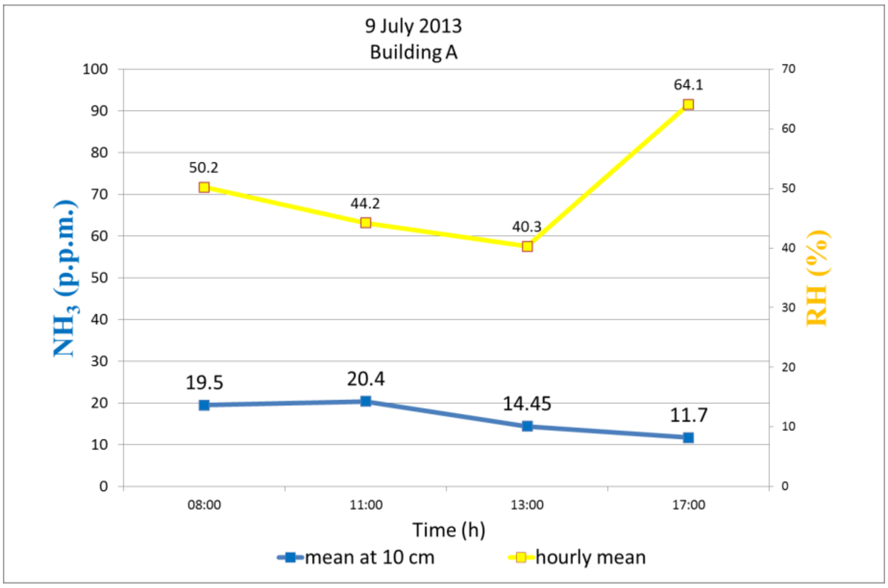


Fig. 12 - Indoor relative humidity and ammonia concentration at 10 cm in the building A, on July 9, 2013.

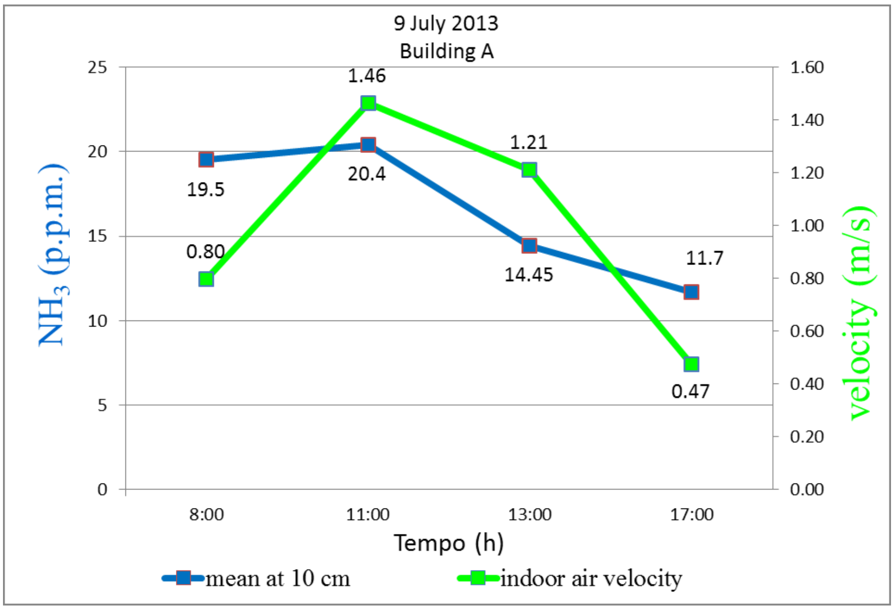


Fig. 13 - Indoor air velocity and ammonia concentration at 10 cm in the building A, on July 9, 2013.

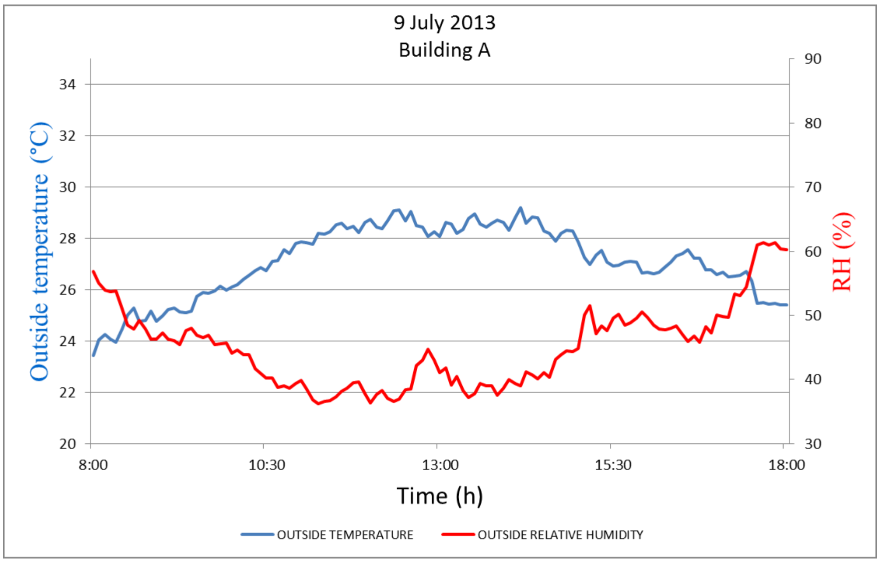


Fig. 14 - Outside temperature and outside relative humidity in the building A, on July 9, 2013

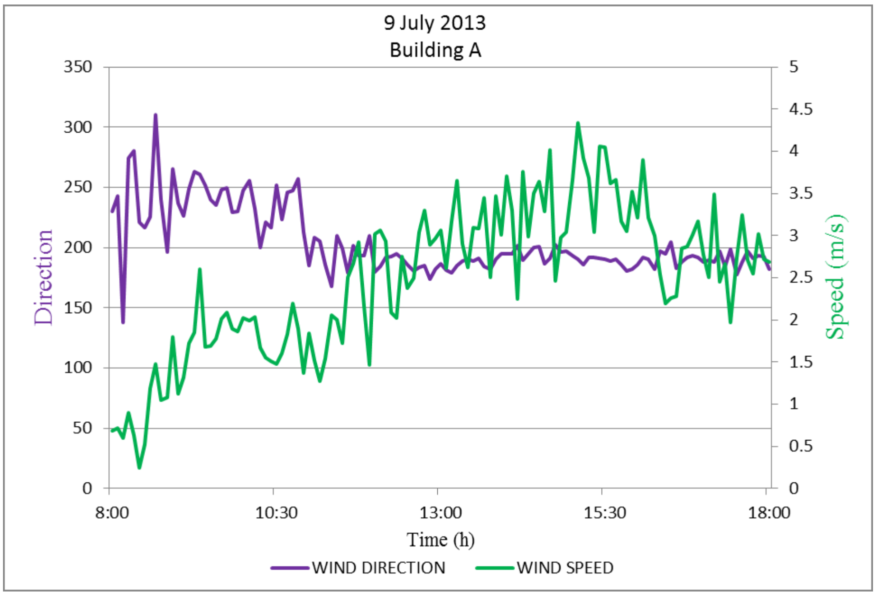


Fig. 15 - Wind speed and wind direction in the building A, on July 9, 2013.

Figure 18 shows the wind speed and the air direction on July 9, 2013. The wind speed increases about from 11.00 to 16.30, while prevailing winds come from South–West.

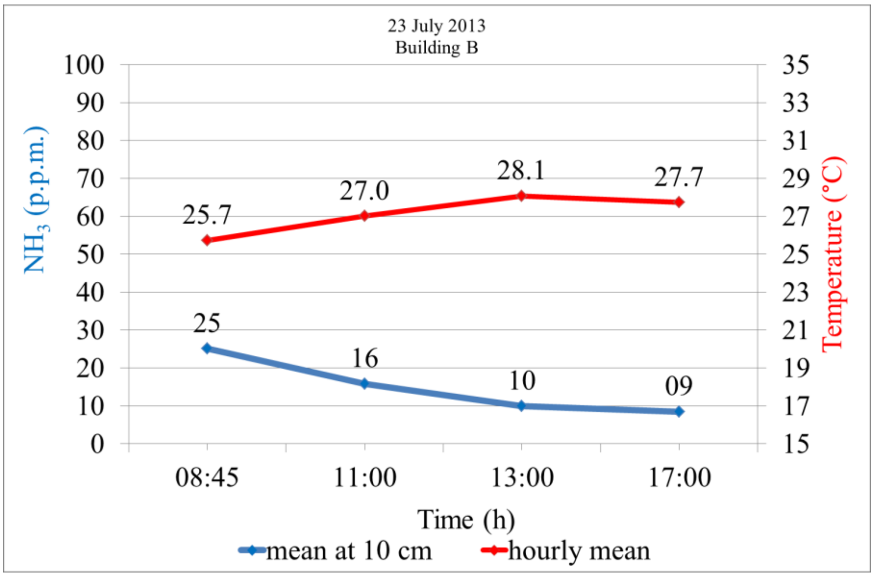


Fig.16 - Indoor air temperature and ammonia concentration at 10 cm in the building B, on July 23, 2013.

In Figures 17 and 18 the air relative humidity and the ammonia concentration measured at 10 cm inside the breeding enviroment of the two barns are shown. The values of relative humidity are almost constant at the ground level in building B (Fig. 17) whereas in building A a higher variation was recorded during the day, at the same height from the floor, on September 24, 2013 (Fig. 18).

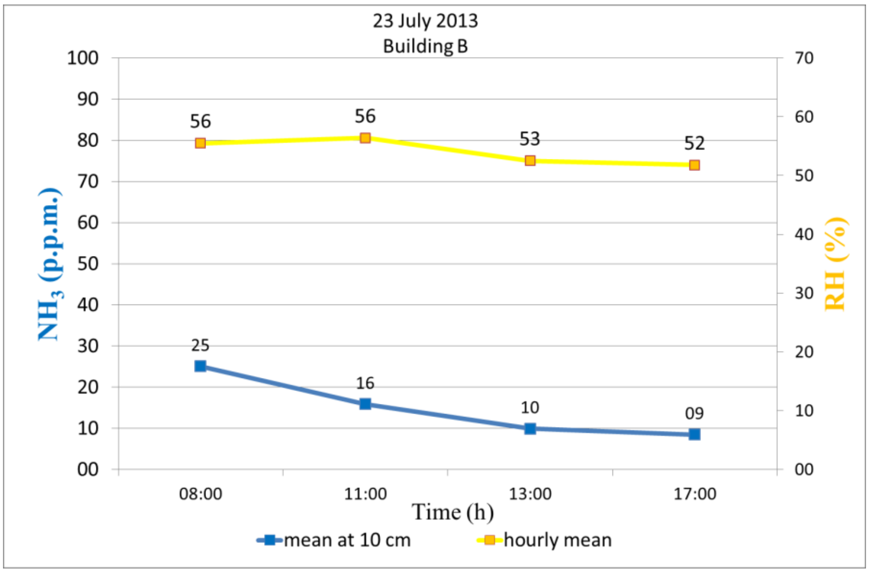


Fig. 17 - Indoor relative humidity and ammonia concentration at 10 cm in the building A, on July 23, 2013.

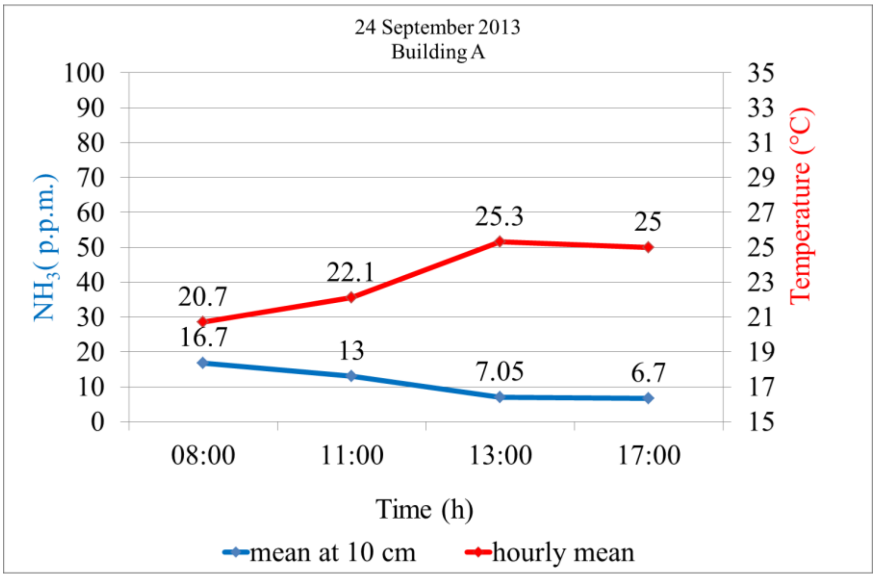


Fig. 18 - Indoor air temperature and ammonia concentrations at 10 cm in the building A, on September 24, 2013.

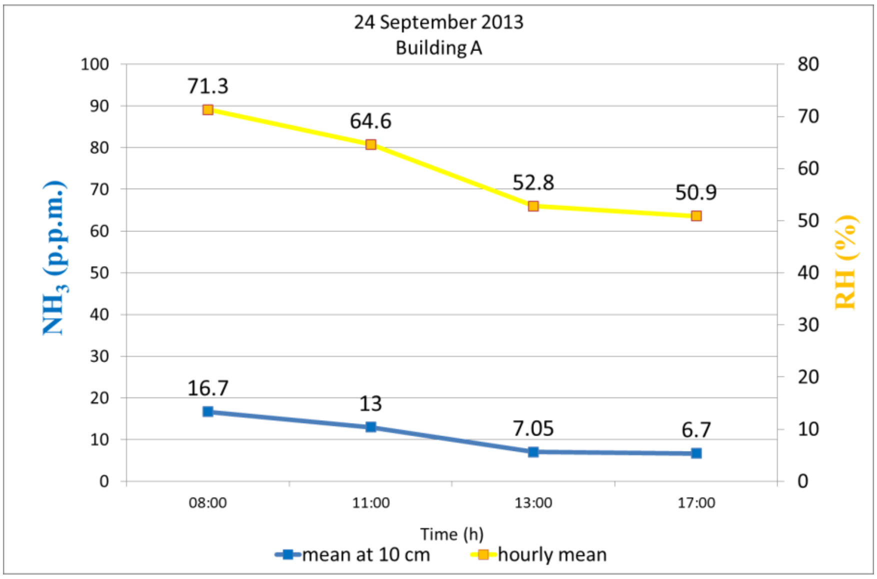


Fig. 19 - Indoor relative humidity and ammonia concentration at 10 cm in the building A, on September 24, 2013.

In Table 9, the maximum, minimum and mean values of the inside and outside air temperature and relative humidity are summarised for each day of the trials. By comparing the ammonia concentration values measured in the different days of the sampling sessions, reported in Tab. 7, with the microclimatic variables, reported in Tab. 9, a general decrease of ammonia concentration values is observed in relation to a natural decrease of inside air temperature from the summer season to autumn.

In Table 10, the maximum, minimum and mean values of the inside air velocity and outside wind speed, and the frequency of wind direction are summarised for each day of the trials. Outside variables were not recorded on 23 July and 24 September.

As previously observed, in the day of trial July 2, 2013 the highest concentrations of ammonia were observed. This outcome could be explained considering that air temperature was high and the air was more still inside the barn in comparison to July 9, 2013.

	Inside air Temperature (°C)		
Day of trial/Building	max	min	mean
2 July – A	30.7	25.0	27.7
9 July – A	33.0	27.5	29.8
23 July – B	28.8	25.2	27.1
24 September – A	27.3	18.9	23.3

	Inside air Relative Humidity (%)		
Day of trial/Building	max	min	mean
2 July – A	35.0	29.8	44.3
9 July – A	64.1	38.8	48.5
23 July – B	61.4	48.4	54.1
24 September – A	74	46.9	59.9

	Outside air Temperature (°C)		
Day of trial/Building	max	min	mean
2 July – A	26.4	20.3	24.5
9 July – A	29.0	23.4	26.9

	Outside air Relative Humidity (%)		
Day of trial/Building	max	min	mean
2 July – A	51.7	30.2	41.1
9 July – A	61.4	36.3	46.0

Table 9 - Maximum, minimum and mean values of inside and outside air temperature, and inside outside relative humidity of the air, in each of the day of trial.

The measurement reported for 23 July and 24 September showed that the air velocity near the ground is under 0.4 m/s, which is the threshold of the portable anemometer.

	Inside air velocity (m/s)		
Day of trial/Building	Max	Min	Mean
2 July – A	1.6	0.2	0.8
9 July – A	1.9	0.2	1,0
23 July – B	< 0.4	< 0.4	< 0.4
24 September – A	< 0.4	< 0.4	< 0.4

	Outside wind speed (m/s)		
Day of trial/Building	Max	Min	Mean
2 July – A	3.6	0.3	2.3
9 July – A	4.3	0.2	2.5

Frequency of wind direction				
Day/Building	0°-90° (N-E)	90°-180° (S-E)	180°-270° (S-W)	270°-360° (N-W)
2 July/ A	0	61	52	7
9 July/ A	0	6	111	3

Table 10 - Maximum, minimum and mean values of inside air velocity, wind speed, and frequency of wind direction, in each of the day of trial.

From Table 10 it comes out that the prevailing winds are from South–East as well as from South-West on 2 July whereas from South-West on 9 July. Hot and humid air was, therefore, released from Southern summer winds in that period. As a consequence the ventilation of the building A was generally along the longitudinal axis of the barn.

On the basis of the variables analysed above an estimation of the ammonia emission based on the relations described in Sections 2.4 and 3.4 was carried out.

As already found by Samer et al. (eqn. 9) the H_2O method gave unreliable results and it is not adequate for summer analyses. The methods referring to Natural ventilation theory and the Heat balance, instead, gave different but acceptable results which could be considered as estimates of the emissions from the breeding enviroment analysed.

In Fig. 17 the ammonia emission estimated by using the Natural ventilation method described in Section 2.4 is shown for the day July 2, 2013 in Building A.

The ammonia emission values related to the cows housed in the Building A ranged between 0.44 and 0.14 kg/h whereas the values related to the HPU were between 0.31 and 0.10 kg/h/HPU. The Heat balance method yielded ammonia emission values ranging between 0.005 and 0.27 kg/h and 0.004 and 0.19 kg/h/HPU. However, ammonia emission trend, which is reported in Fig. 18, showed that the lowest values are in the warmest hours of the day when ventilation is high. Since this trend highly follows the temperature difference between inside and outside, it could fit for closed breeding enviroments where the buoyancy effect is much higher than the wind effect. In semi-open barns, instead, ventilation is the main driving force. When the air velocity inside the barn increases, ammonia concentrations decrease whereas ammonia emission increases due to the high ventilation rates.

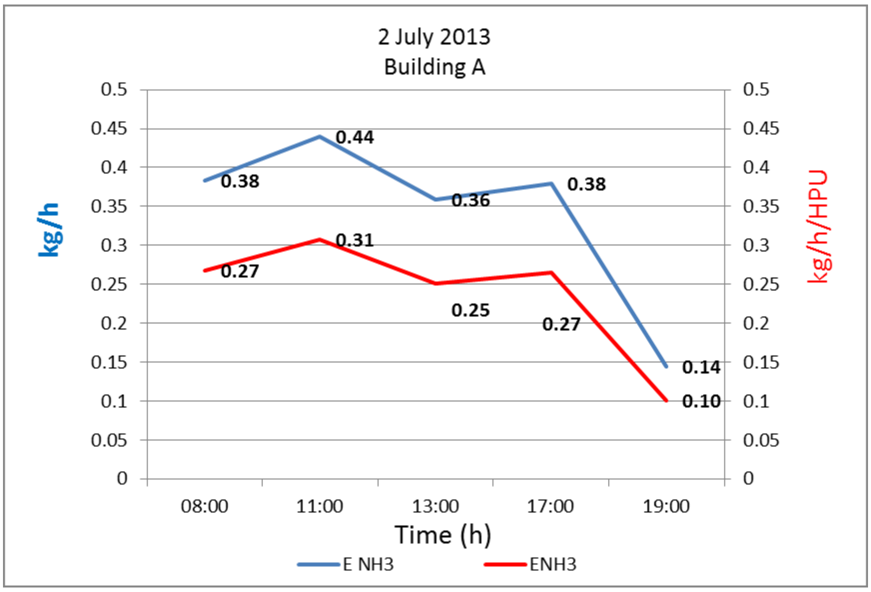


Fig. 17 - Ammonia emission estimated by using the natural ventilation method.

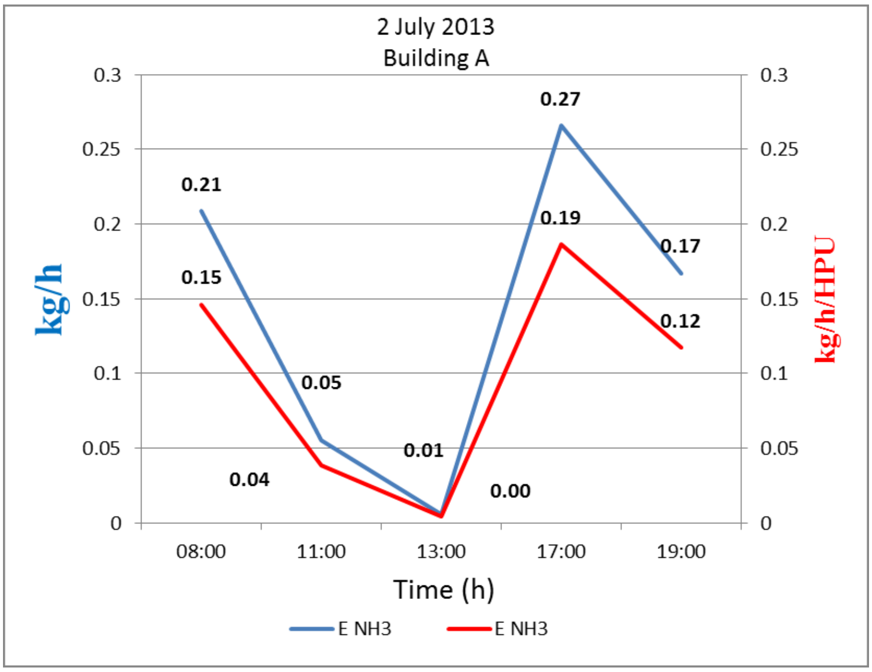


Fig. 18 - Ammonia emission estimated by using the Heat balance method.

In the following of the text, the results of the statistical analyses carried out on ammonia concentration data, collected in the breeding environments considered, are reported.

In detail, data means of ammonia concentrations were analysed and compared in different conditions:

- at different heights from the ground (i.e., 10 cm, 20 cm, and 40 cm);

- in the two different functional areas of the considered area of interest of the barn in building A;

- at the different hours of the sampling sessions in the two buildings analysed in order to compare measurements before and after cleaning operations.

In all these analyses, the p-values of ANOVA tests for difference in means resulted <0.05, therefore, the tests were significant at the 5% level and there was evidence that the population means were not the same.

Consequently, post-hoc tests were carried out to compare pairs of treatments simultaneously in order to investigate which data means were significantly different, as described in Section 3.5.

Sampling Sessions										
2 July	8:00		11:00		13:00		15:00		17:00	
	Mean	Group	Mean	Group	Mean	Group	Mean	Group	Mean	Group
10 cm	29.40	A	13.40	A	12.10	A	12.10	A	21.40	A
20 cm	19.00	B	8.90	A	5.05	B	15.05	B	10.70	B
40 cm	8.55	C	2.95	B	1.30	B	1.30	B	2.55	C

9 July	8:00		11:00		13:00		15:00		17:30	
	Mean	Group	Mean	Group	Mean	Group	Mean	Group	Mean	Group
10 cm	19.50	A	20.40	A	14.45	A	14.55	A	11.70	A
20 cm	14.70	A	11.80	B	6.05	B	8.55	B	6.70	B
40 cm	7.65	B	4.30	C	1.5	C	1.95	C	1.55	C

24 September	8:00		11:00		13:00		16:00	
	Media	Group	Mean	Group	Mean	Group	Mean	Group
10 cm	16.70	A	13.00	A	7.05	A	6.70	A
20 cm	9.70	B	4.85	B	2.30	B	1.35	B
40 cm	4.95	c	1.95	B	1.10	B	0.00	B

23 July	8:45		11:00		13:00		17:00	
	Media	Group	Mean	Group	Mean	Group	Mean	Group
10 cm	25.07	A	15.87	A	9.92	A	8.50	A
20 cm	17.86	AB	9.71	A	7.57	A	6.50	A
40 cm	8.43	B	2.14	B	0.85	B	1.07	B

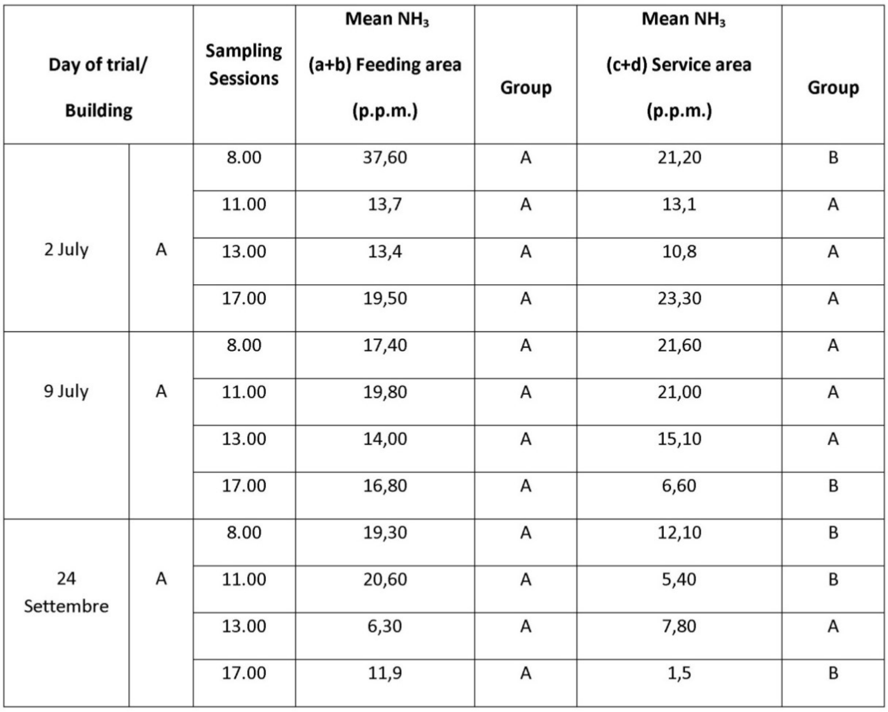
Tab. 11 – Statistical analyses on datasets related to ammonia concentrations at the heights of 10 cm, 20 cm and 40 cm from the barn floor.

In Table 11 statistical analyses on the three datasets related to ammonia concentrations at 10 cm, 20 cm and 40 cm of height from the barn floor were reported.

As regards the acquisitions carried out on 23 July, which are related to Building B, the statistical analyses showed that the mean of the measured ammonia concentrations at 10 cm and 20 cm were quite always significantly different from those at 40 cm.

In almost all the acquisitions carried out in the other days analysed, which are related to Building A, the mean of the measured ammonia concentrations at 10 cm were significantly different from those at 20 cm and 40 cm.

These results showed that there is a different influence on measured ammonia concentrations at the ground level determined by microclimatic variables. However, the measuring threshold of the instruments utilized did not allow for a precise analysis of changes in microclimatic variables: the air velocity recorded at 10 cm was always under the threshold of the instrument, equal to 0.4 m/s (Table 10). The dependence of ammonia concentrations levels on temperature was proved as ammonia concentration values decreased from 2 July to 24 September at decreasing of inside air temperature (Tabs 7 and 9).



Day of trial/ Building		Sampling Sessions	Mean NH_3 (a+b) Feeding area (p.p.m.)	Group	Mean NH_3 (c+d) Service area (p.p.m.)	Group
2 July	A	8.00	37,60	A	21,20	B
		11.00	13,7	A	13,1	A
		13.00	13,4	A	10,8	A
		17.00	19,50	A	23,30	A
9 July	A	8.00	17,40	A	21,60	A
		11.00	19,80	A	21,00	A
		13.00	14,00	A	15,10	A
		17.00	16,80	A	6,60	B
24 Settembre	A	8.00	19,30	A	12,10	B
		11.00	20,60	A	5,40	B
		13.00	6,30	A	7,80	A
		17.00	11,9	A	1,5	B

Tab. 12 - Statistical analyses on data of ammonia concentrations collected in the two functional areas: the feeding area (a+b) and the service area (c+d), at the different sampling sessions in building A.

From the statistical analysis performed on the data collected in Building A, the data means of ammonia concentrations collected in the two functional areas analysed, i.e., the feeding area (a+b) and the service area (c+d), resulted significatively different on 24 September, only at 8:00 (before the cleaning activity) on July 2, 2013, and on July 9 at 5:00 p.m. after the cleaning operations. Therefore, it appears that significant differences in data means occurred when there was a difference in the amount of manure deposited in the functional areas where the cows live.

Day of trial	Building	Sessions	Mean	Grouping	P-value
2 July	A	8:00	19,00	A	0,00
		11:00	8,90	B	
		13:00	5,05	B	
		17:10	10,70	AB	
		19:30	10,15	B	
9 July	A	8:20	19,50	A	0,01
		11:00	20,40	A	
		13.00	14,45	AB	
		15:30	14,55	AB	
		17:30	11,70	B	
23 July	B	8.45	25,07	A	0,00
		11.00	15,85	B	
		13.00	9,92	B	
		17.00	8,50	B	
24 Sept.	A	8.00	16,70	A	0,00
		11.00	13,00	AB	
		13.00	7,05	B	
		17.00	6,70	B	

Tab. 13 - Statistical analyses on data of ammonia concentrations collected in the different hours of the sampling sessions in the two buildings analysed.

Since the p-values reported in Table 13 are all less than 0.05, the values are highly significant. So we reject the null hypothesis of the means for the different acquisitions at different hours of the day being equal.

The post-hoc test performed for the two buildings showed the following results.

By applying the Tukey HSD test, the comparison between the measurements before and after cleaning operations showed that the effectiveness of the cleaning routine is statistically detected in building A on July 2 and in building B on July 23, while in the other two days there was not a significant difference between the means of the measurements before and after the cleaning operations.

5 GUIDELINES ON THE POTENTIAL APPLICATION OF DEVELOPMENT TECHNIQUES FOR REDUCING AMMONIA EMISSIONS IN EXISTING LIVESTOCK BUILDINGS

On the basis of the knowledge acquired in the trials carried out and described in this thesis work, in this section some guidelines to operators to control ammonia emissions will be given. As already discussed in sections 2.6.2 - 2.6.3 and their sub-sections, the techniques to reduce ammonia emissions may be grouped into two different typologies, i.e., pre and post-excretions techniques.

Reduction options developed in the past focuses on different floor constructive solutions. It's important to specify that in this section all the floor constructive solutions, such as the slatted floor or the V-shaped floor with a slope for the separation of the feces from the urine, will not be analysed since they may regard the design of new barns whereas for existing ones other solutions should be proposed.

The following recommendations relate to existing natural ventilated barns, characterized by a rather open envelope, which is provided with ventilation openings or it is completely open on two or three sides, and solid floor:

- Introduction of good management practices such as two cleaning operations (one in the morning and one in the evening) in the barn since in some cases it has been observed that just one in the morning is carried out.

- Introduction of a manual cleaning operation of the feed barrier to release the manure deposits, which could be carried out periodically, e.g., once a week because the feeding area is a critical point for the ammonia emissions. In the trials, it was observed, in fact, that the cleaning action of the tractor with scraper is not effective,

- Increased focus on nutritional techniques, for example, by replacing forage with maize, by utilizing highly digestible protein foods together with enzymes and/or additives that reduce the content of urea and, as a consequence, the ammonia emissions.

Apart from those above mentioned reduction option that have already been developed and assessed, there are some new possible promising reduction options that need further development and evaluation. These techniques also include those of slurry acidification and addition of urease inhibitors.

Within the techniques of slurry acidification, the use of a dried vegetal material, with high absorption power, such as wastes of the food industry could be recommended. This technique belongs to the group of new techniques which need to be developed and tested.

Within the trials carried out for the thesis work, on 24 September an experiment was carried out in the building A with the aim of applying a method for the reduction of ammonia emissions. This method had the purpose to acidify the slurry and to reduce the ammonia volatilization, through the high absorbent power of the dry material used. In the following of the text, the trial carried out is described in detail.

Criteria for the selection of the dried material

Among dried vegetal materials, a remnant of coffee industry processing was selected and, particularly, the husks (as parchment et silverskin) that are discarded during the roasting process. This compound has, in fact, the requirements characteristics to our usage. In particular:

- High level of absorption;
- Low pH (acidic);
- Readily available in the area and inexpensive.

A specific investigation showed that in Sicily there are about 18 companies in the coffee roasting activity and 4 of these are in the territory of Ragusa. The amount of this debris material that the companies produce is equal to about 20 kg/ton of green roasted coffee. These companies give the product, and they support these costs, to companies that use it for composting. For these reasons, the material chosen has the appropriate characteristics (feasibility and sustainability) to the considered utilization.

Acidification treatment

The dried vegetal material has been previously treated with a weak acid (acetic acid) in order to lower its initial pH (6.5) and to take to a value of about 5.5. This value does not damage the hooves of dairy cows which walk on it.

Distribution Procedure

The dried vegetal material was mixed with the weak acidic solution and spread over an area of about 20 m^2, after three hours from the operations of cleaning in the morning, along the feeding alley. The chosen area was near the feed barrier where they had created many urine puddles.

It was noted that:

- The cows have not shown discomfort in walking on the treated area;

- The puddles of urine were quickly absorbed.

Results:

After a few hours, the ammonia concentration was measured in two points within the treated area and it was found that there has been a reduction of approximately 50% of ammonia levels compared to the ammonia concentration recorded at the same points before the treatment.

Fig. 20 - The remnant of coffee industry processing

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Fig. 21 - Distribution of the material in the feeding area.

Fig.22 - Ammonia concentration measurement with the portable instruments placed in the wooden facility, before the treatment.

Fig. 23 - Ammonia concentration measurement with the portable instruments placed in the wooden facility, after the treatment.

6 CONCLUSIONS

In this thesis work, issues of great interest which concern the protection of animal welfare, salubrity within the breeding environment, the operators' safety in the workplace and the environmental protection have been dealt with through the outcomes of this research which gave a contribution to the analysis of ammonia concentrations and microclimatic variables in breeding environments of dairy houses.

The research activities of this thesis work were carried out in barns located in an area of the Province of Ragusa highly suited to dairy cows breeding, where are located most of the naturally ventilated barns present in Sicily (Italy).

Ammonia monitoring is important for the well-being of livestock. High ammonia concentrations can lead to poor feed conversions, reduced weight gains, and increased susceptibility to disease.

When a person is constantly exposed to ammonia, sense of smell is adversely affected and ability to detect ammonia decreases. With time, most growers are not able to detect ammonia by smell until the ammonia concentration has reached 50-60 ppm or higher, which are dangerous values for human health.

As regards the environment, the increase of the ventilation rate decreases the ammonia concentration in the premises, but maximizes the emission of ammonia.

The issue of ammonia emissions from livestock buildings has been reviewed by a wide literature search concerning the methods of measurement used in the barns and methods of emissions reduction.

An experimental protocol for measuring ammonia concentration within the breeding environment at different heights from the floor and for the measurement of the main internal microclimate variables and the external climatic ones was proposed.

Based on the research findings, data about the levels of ammonia concentrations in naturally ventilated barns, belonging to semi-open typology, the relationship between these levels and the internal microclimate variables, and the effectiveness of the cleaning routine were obtained.

Finally, indications have been obtained to support farmers' management choices in order to reduce ammonia emissions into the breeding environment. They are based on emission reduction techniques adapted to the specific case study.

In particular, for the thesis work, a technique for the ammonia emissions reduction has been tested, by using a processing residue of the coffee industry. This technique could be regarded as feasible in this field since the experiment showed a reduction of approximately 50% of the emissions and the choice of this dried vegetal material is suitable due to its easy availability in the territory.

All the limits of this research considered, which have been analyzed and described in the thesis work, this study contributes to the improvement of the knowledge basis regarding ammonia emissions within the breeding environments located in South-Eastern Sicily and lays the groundwork for further investigation in this field.

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