Development and evaluation of methods for the measurement of airborne emissions from animal houses

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Insanity: doing the same thing over and over again and expecting different results.

Albert Einstein

The most exciting phrase to hear in science, the one that heralds new discoveries, is not 'Eureka!' (I found it!) but 'That's funny.

Isaac Asimov

Con mis maestros he aprendido mucho; con mis colegas, más; con mis alumnos todavía más.

Proverbio hindú

Summary

Airborne emissions from livestock production are nowadays one of the major concerns of this activity. For this reason, the reduction of these emissions is a requirement in many countries. The development of abatement techniques for the reduction of emissions needs for accurate knowledge about their magnitude. Emission measurement techniques arise then as a key issue. The development of measurement techniques considering not only the accuracy of the results but also the optimization of resources is needed. In this sense, in this thesis a tool and three options for the rationalization on the use of resources when measuring airborne emissions are investigated. The tool is the uncertainty analysis and the three options are: downscaling measurements, indirect measurement of airflow rates and reduction of sampling rates. In this thesis, theoretical and practical studies were conducted to determine the suitability of these techniques to obtain reliable data from more rational measurements on airborne emissions. Firstly, an uncertainty model was developed in order to assess the trustworthiness of the results when determining N_2 and N_2O emissions from a biological scrubber using a combined N-balance in air and water. This model was later partially validated throughout an experimental work in a chemical scrubber. The uncertainty model and the experimental work agreed in the key results of both studies, finding that N-balances were not successful for the proposed aims. Secondly, a flux chamber for the measurement of gas emissions from rabbits was designed and built. A measuring protocol for gas emissions from both animals and their manure was also developed. This chamber was later used to determine the CO_2 emission rate from fattening rabbits during the whole fattening cycle. Using this CO_2 emission rate from fattening rabbits, the carbon dioxide balance was tested as an option to determine the ventilation rate from fattening rabbit houses. The results of these balances were compared with direct measurements of ventilation rates finding no statistical differences. Finally, the effect of reducing sampling when measuring ammonia emissions from livestock facilities was evaluated. Emissions calculated using semi-continuous measurements of NH_3 concentrations and airflow rates were compared with emissions calculated on 24-hour average values for these parameters. The error committed with these low time-resolution measurements resulted to be low in comparison with other error sources committed when measuring emissions from livestock facilities. The main conclusion of this work is that there are available techniques that allow optimizing the use of resources of measurement processes, by keeping the accuracy of the results.

Resumen

La emisión de contaminantes atmosféricos es uno de los principales problemas a los que se enfrenta actualmente la producción ganadera. Por ello, en muchos países se requiere tomar medidas para reducir estas emisiones. Para poder desarrollar técnicas de reducción es necesario disponer de información precisa acerca de la magnitud de las emisiones. En este sentido, las técnicas disponibles para la medición de emisiones se presentan como uno de los factores clave de estudio. Es necesario por lo tanto, desarrollar metodologías considerando no sólo la precisión de los resultados, sino también un uso racional de los recursos. Así, en esta tesis se han investigado tres opciones y una herramienta encaminadas a optimizar los recursos utilizados en la medición de emisiones. La herramienta investigada es el análisis de la incertidumbre, y las opciones señaladas son: reducción de la escala de las mediciones, determinación de la ventilación usando trazadores y reducción de la tasa de muestreo. En este sentido se han desarrollado estudios teóricos y prácticos sobre la aplicabilidad de estas herramientas para la obtención de datos precisos en la medición de emisiones. En primer lugar se ha desarrollado un modelo de incertidumbre para evaluar la verosimilitud de los resultados cuando se evalúan las emisiones de N_2 y N_2O en lavadores de aire biológicos utilizando balances de nitrógeno en agua y aire. Este modelo se ha validado parcialmente con un estudio práctico en un lavador de aire químico. Ambos estudios concluyeron que el uso de balances de nitrógeno no es una buena herramienta para determinar la eficiencia del sistema o las emisiones secundarias. En segundo lugar, se diseñó y construyó una cámara de flujo para determinar las emisiones procedentes de conejos y su estiércol. Se desarrolló también un protocolo para la realización de estas mediciones. Esta cámara se utilizó posteriormente para determinar las emisiones de CO_2 en conejos de cebo. Utilizando estos datos, se determinó la tasa de ventilación en una granja comercial de conejos de cebo a través de un balance de CO_2. Finalmente, se estudió el efecto de reducir la tasa de muestreo en la medición de emisiones de amoniaco en granjas. Se compararon los resultados de mediciones semi-continuas con medias diarias, llegando la conclusión de que el error cometido es bajo en comparación con otras fuentes de error cometidas al medir emisiones. La principal conclusión de esta tesis es que es posible racionalizar el uso de recursos, manteniendo la precisión de los resultados, en la medición de las emisiones de contaminantes atmosféricos procedentes de explotaciones ganaderas.

Resum

La emissió de contaminants atmosfèrics es un dels principals problemes als que s'enfronta la producció ramadera actualment. Es per això que en molts països es requereix prendre mesures per a reduir aquestes emissions. Per a poder desenvolupar aquestes tècniques de reducció, es necessari disposar d'informació precisa sobre la magnitud d'aquestes emissions. En aquest sentit, les tècniques disponibles per a la mesura d'emissions es presenten com un dels factors claus d'estudi en aquest àmbit. Es necessari, per tant, desenvolupar metodologies considerant tant la precisió dels resultats, com un ús racional dels recursos. Així, en aquesta tesi s'han investigat tres opcions i una eina encaminades a optimitzar l'ús de recursos en la mesura d'emissions. L'eina investigada és l'anàlisi de la incertesa, mentre que les opcions ressenyades son: reducció de l'escala de les mesures, determinació de la ventilació utilitzant traçadors i reducció de la taxa de mostreig. En aquest sentit, s'han desenvolupat estudis teòrics i pràctics sobre l'aplicabilitat d'aquestes eines per a l'obtenció de dades precises en la mesura d'emissions. En primer lloc s'ha desenvolupat un model de incertesa per a avaluar la versemblança dels resultats quan s'avaluen les emissions de N_2 i N_2O en rentadors d'aire biològics utilitzant balanços de nitrogen en aire i aigua. Aquest model s'ha validat parcialment amb un estudi pràctic en un rentador d'aire químic. Ambdós estudis van concloure que l'ús de balanços de nitrogen no és una bona eina per a determinar l'eficiència d'aquests sistemes ni les emissions secundàries. Posteriorment, es va dissenyar in construir una càmera de flux per a determinar les emissions procedents de conills i el seu fem. Es va desenvolupar també un protocol amb recomanacions pràctiques per a la realització d'aquestes mesures. Aquesta càmera es va utilitzar posteriorment per a determinar les emissions de CO_2 de conills d'engreix. Utilitzant aquestes dades, es va determinar la taxa de ventilació en una granja comercial de conills d'engreix mitjançant l'ús d'un balanç de CO_2. Finalment, es va estudiar l'efecte de reduir la taxa de mostreig en la mesura d'emissions d'amoníac en granges. Van comparar-se resultats de mesures semi-continues amb mitjanes diàries, arribant a la conclusió de que l'error és baix si es compara amb altres fonts d'error que es cometen en la mesura d'emissions. La principal conclusió d'aquesta tesi es que és possible racionalitzar l'ús de recursos, mantenint la precisió dels resultats, en la mesura d'emissions de contaminants atmosfèrics procedents d'explotacions ramaderes.

Table of contents

Chapter 1

Introduction. Resource optimization in the measurement of airborne emissions from animal houses

1.1. Introduction

1.1.1. General approach

According to the Food and Agriculture Organization of the United Nations (FAO), the livestock sector is a major stressor on many ecosystems and on the planet as whole (Steinfeld et al., 2006). In fact, nutrient losses from animal production are a major source of soil and water pollutants such as nitrates, phosphorous and potassium (Tamminga, 2003), The effect of nutrient excess in water and soil environments may lead to heavy leaching rates of elements such as nitrate, potassium, calcium, chloride, sulphate and heavy metals (Martinez and Peu, 2000). Environmental effects such as pollution and eutrophication occur then on surface and groundwater and soils. The contribution of this activity to anthropogenic airborne emissions cannot be neglected either. Livestock production is one of the major sources of ammonia emissions, contributing directly up to 62% of total European anthropogenic emissions (EEA, 2009a). Regarding to greenhouse gas emissions this sector is responsible of almost 48% and 9% of methane and of nitrous oxide emissions respectively in the EU-27 (EEA, 2009b). Other airborne pollutants coming from livestock production such as particulate matter (Cambra-López et al., 2010) and odour (Schiffman, 1998) must be also considered attending to their effects on humans and the environment.

Ammonia emissions are directly linked to acidification and eutrophication of soils and eutrophication of water courses, as well as alterations in the growth of plants (Krupa, 2003). Acidification or eutrophication processes due to nitrogen deposition affect ecosystems and can lead to potential negative effects on biodiversity and even on humans, because of the pollution of water resources (Heij and Erisman, 1997). Ammonia emitted to the atmosphere and subsequently derived NH_4^+ are removed from the atmosphere by dry and wet deposition. These deposition processes on the vegetation may cause several negative impacts such as toxicity, nutrient imbalance or even the death of the plant (Krupa, 2003). Carbon dioxide, methane and nitrous oxide are considered main contributors to the greenhouse effect (Seinfeld and Pandis, 1998). These greenhouse gases alter the Earth's radiation balance, affecting the climate with changes on global temperature, rainfall and sea level (IPCC, 2007). In this sense, a large number of regulations have been recently developed and implemented which aimed to reduce and control environmental impacts from livestock production (Jongbloed et al., 1999; Melse et al., 2009).

1.1.2. Airborne emissions from livestock production

The emission of gases from livestock production to the atmosphere can be explained by the relationship between livestock production and the global nitrogen and carbon cycles. Ammonia originates in the decomposition of nitrogenous compounds in the manure through ammonification being emitted later due to volatilization processes. Nitrous oxide originates through nitrification and denitrification of ammonium nitrogen during manure management and after its application to land (Tamminga, 2003). Finally, methane originates in the microbiological decomposition of certain organic compounds in anaerobic conditions. Therefore, animals emit methane as a sub-product of digestive processes (Crutzen et al., 1986). The anaerobic fermentation of volatile solids in manure (for example during manure storage in tanks and pits) is also an important source of this gas (Steed and Hashimoto, 1994).

There are many sources of particulate matter (PM) emissions identified in livestock houses. These sources usually differ among species and rearing systems. For instance, in pig production, the main sources of PM are feed, skin and manure, while litter material and fur can be main sources of PM in poultry and rabbits buildings respectively (Cambra-López et al., 2010).

The anaerobic degradation of organic compounds contained in manure results in the generation of odorous volatile compounds. When manure undergoing degradation has a surface exposed to the atmosphere, volatile products are emitted to the environment. These compounds are responsible of unpleasant odours (Mackie et al., 1998).

In livestock farms, airborne pollutants are emitted from both buildings and manure storage facilities. These emissions arise from the animals and their manure. ***Table 1*** presents a brief summary of different pollutants emitted from livestock production, classified according to their source.

Table 1. Classification of pollutants emitted from livestock production according to their source (animals and manure) for building and manure management).

Source	***Emissions from buildings***	***Emissions from manure management***
Animals	CH_4, PM	-
Manure	NH_3, N_2O, CH_4, PM and odour	NH_3, N_2O, CH_4, PM and odour

1.2. Measurement of airborne emissions from livestock production

1.2.1. General overview

There are two ways to determine the amount of airborne pollutants emitted from livestock production. The first one consists in measuring the emissions from each stage (buildings and manure storage facilities). The second option consists in quantifying the emissions generated from each source separately (animals and manure), and adding them up to obtain the total emission value. The first option is more adequate to determine emissions from a certain activity as a whole (for example, to obtain emission factors). Nevertheless, using the second option, emissions from each source can be determined separately and the influencing factors and possible mitigation techniques can be easily identified. This work is within the framework of the measurement of emissions from livestock houses.

1.2.2. Measurement techniques

There exist several methodologies for the determination of airborne emissions from livestock activities (Bunton et al., 2007; Ni and Heber, 2008; Phillips et al., 1998). These methodologies can be classified into three main groups of techniques: i) farm scale balances, ii) chambers and iii) micrometeorological techniques.

Farm scale balances are based on the mass conservation law. In an existing physically delimited system (e.g. an animal house), if stationary conditions are expected, the emission rate of any airborne pollutant can be determined as the difference between the inlet and outlet fluxes of this pollutant. Eq. 1 summarizes this calculation:

$$E_i = F \times \left(C_{s(i)} - C_{e(i)} \right) \qquad \text{Eq. 1}$$

where, E_i is the emission rate of the pollutant *i* (mg h^{-1}), $C_{s(i)}$ and $C_{s(e)}$ *are the* outgoing and ingoing pollutant concentration in the air (mg m^{-3}) respectively and *F* is the ventilation rate in the system (m^3 h^{-1}).

This technique has been widely used to determine emission factors of airborne pollutants (Bottcher et al., 2004; Groot Koerkamp et al., 1998).

Chamber techniques consist in enclosing a representative sample of the emitting source (animals or manure) in which a mass balance is established. Two types of chambers can be used, dynamic and static chambers. Dynamic chamber techniques use the same fundamentals as farm scale balances. In static chambers there is no airflow exchanged between the inside and outside of the chamber, thus the emission can be calculated from the increase of concentration of the pollutant in the chamber (Eq.2).

$$E_i = \frac{\delta C_{(i)}}{\delta t} \times V \qquad \text{Eq. 2}$$

where, t is the time (h), $\delta C_{(i)}/\delta t$ represents the variation of the pollutant i concentration during the measurement (mg m^{-3} h^{-1}) and V is the volume of the chamber (m^3).

Chamber techniques have been used to determine airborne emissions from separated emitting sources such as animals and manure (Estellés et al., 2009) and whole buildings (Amon et al., 2001).

Micrometeorological techniques measure the airborne flux from a surface without disrupting the measurement environment. They also allow measuring gaseous fluxes over a larger area than with chambers techniques. Emissions are calculated using concentrations and meteorological data such as wind speed profile, temperature, barometric pressure, etc. These techniques have been used to determine airborne emissions from animal houses (McGinn et al., 2006) and from manure in large surfaces (Misselbrook et al., 2005).

1.2.3. Selecting the appropriate measurement system

The first step to determine emissions is defining the aim of the measurement. In general terms, three main objectives can be considered: i) to determine an overall emission factor for one given specie in a region or country, ii) to characterize the emissions from a system or single livestock facility and iii) to evaluate the emissions from a single building during an isolated period. These objectives have different requirements in terms of the accuracy of the results. This is directly linked to the fact that the sources of variability and errors are also different for each case. For example, when a measurement is aimed to obtain an overall ammonia emission factor for poultry production in Southern Europe, it is not needed to determine ammonia concentrations with extreme accuracy, because the variability of emissions between different seasons and animal houses may be much more important for the global emission value (Ogink et al, 2008). ***Table 2*** summarizes the accuracy requirements and main sources of variability depending on the aim of the measurement.

Table 2. Accuracy requirements and main sources of variability when measuring emissions with different aims

Aim of the measurement	*Required accuracy*	*Main sources of variability*
To determine and emission factor for a region	Low accuracy for single measurements, high representation (more measurements)	Location, climate, season, management, type of animal,
To monitor a system or a livestock facility	Medium accuracy for single measurements and replication at different locations or moments	Location, climatic, seasonal
To obtain a single measurement for a given facility and moment	High accuracy for a single measurement	Hourly, spatial sampling,

Therefore, only after defining the objective of the measurement and the required accuracy of the results, a measurement method or technique must be chosen. As seen before, there are many available techniques for the measurement of airborne emissions from animal houses. Normally, for a given objective with its accuracy requirements, more than one technique may be applicable. The optimization of resources (e.g. manpower, time and costs) must be then used as the decision tool to select the most appropriate measurement methodology or technique.

This work is aimed to provide an overall view on the selection of measurement methods when determining airborne emissions from livestock houses, considering the three main principles: the aim of the measurement, the required accuracy of the results and the optimization of resources. In this sense a decision tool and three options aimed to optimize the resources when developing emissions measurement are discussed here in terms of accuracy and applicability to different measurement aims. The decision tool is the uncertainty analysis, and the three options are: downscaling measurements, airflow rates estimation using tracers and sampling rate reduction.

1.3. Alternatives for optimizing resources of emissions measurement

1.3.1. Uncertainty analysis

The aim of the measurements determines the required precision, and therefore a tool is necessary to estimate it to assess error sources. Each objective requires different levels of accuracy for the final results. The sources of error or variability of the results are also different depending on what is being measured, since different factors are involved in the measurement. In some cases, the simplification of the measurement process can be a

powerful tool in order to optimize the use of resources by keeping the accuracy of the results on the required levels.

For a defined scenario (for a known measurement aim and required accuracy) different procedures may be available to measure a variable (e.g. emissions). In this case it is needed to have decision tools, which provide information about the trustworthiness of the results obtained with each procedure. In addition, it is crucial to identify the main contributors to the measurement imprecision in order to put the efforts in improving their determination.

In this sense, uncertainty analyses provide a quantitative measure of the reliability and trustworthiness of a measurement. The uncertainty of a parameter is a combination of uncertainties of all measured values involved in its determination. For example, the uncertainty of a gas emission value when using stationary balances (mass balances in buildings or dynamic chambers), is composed by the uncertainty of the measured gas concentrations and ventilation rates. In practice, in order to obtain the uncertainty of a measured value, it is needed to know the uncertainty of all single parameters involved in the measurement and the relationship among them and with the final value (Cox and Harris, 2006). Sensitivity analysis is a parallel tool to the uncertainty analysis which allows determining the contributions of individual uncertainties in inputs to the uncertainty in results (Helton et al., 2006).

Therefore uncertainty analysis can help us to choose the appropriate measurement method or protocol attending to the desired reliability of results. By the other hand, by performing a sensitivity analysis, we can identify the main parameters introducing uncertainty in the final results, directing the efforts to improve their determination.

These uncertainty analyses can be useful for all defined scenarios. The previous knowledge about the accuracy of a method is helpful when determining emission factors, characterizing the emissions from a system or livestock house or even for single measurements. Uncertainty models, together with cost analysis, arise as one of the most powerful tools when selecting appropriate measurement techniques or methodologies for the measurement of airborne emissions from animal houses.

1.3.2. Downscaling measurements

When determining emissions from an activity in which various sources are involved, measurements can be conducted in two ways: measuring the whole system (e.g. a whole livestock building), and measuring the emissions from each single source (e.g. animals and manure separately) and adding them to obtain the whole emission rate. Normally, to obtain emission values from a livestock house, whole system methods are preferred

(Gates et al., 2006), nevertheless it is also possible to estimate the total emissions by adding the results from measurements of the representative components of the total process (Phillips et al., 2000).

When using methods that allow determining emissions from the whole system, information about the complete process is obtained. The use of these methods implies the simultaneous determination of ventilation rates and airborne concentrations in the air (Phillips et al., 1998). Nevertheless, it must be considered that measuring ventilation rates in livestock houses is one of the main challenges when determining airborne emissions, as it will be discussed later. Usually, the determination of airflow rates in large commercial farms is not possible due to physical or economic restrictions. For example, in open naturally ventilated livestock houses, such as some cattle buildings, where direct measurement of ventilation rates is not possible, and alternative methods for the measurement of emissions are needed. In addition, the measurement of ventilation rates is one of the main sources of uncertainty when determining airborne emissions from animal houses (Gates et al., 2009). This restriction may affect mainly to measurements aimed to determine the emissions at system level, but the measurement of ventilation rates in naturally ventilated houses, can also be a main constraint when the aim of the measurements is to obtain an emission factor.

By the other hand, obtaining an accurate value for the average pollutant concentration in a single building may be complicated, due to the spatial and time variability (Ni and Heber, 2008). For most cases measuring in the number of locations needed to obtain accurate values for average concentrations is often impractical due to the limitation of the budget, equipment, time and manpower (Ni and Heber, 2008). This fact is crucial when the aim of the measurement is to obtain a single emission value in a building or even when a system or animal house is being monitored.

The use of dynamic or static chambers for the measurement of emissions appears as an alternative when whole system measurement methods are not useful in practice. In addition, when very precise information about the individual emitting sources (animals and manure) is needed, the use of chamber methods can be a good choice.

1.3.3. Airflow rates estimation using tracers

Determining ventilation rates is crucial to measure airborne emissions from livestock houses (see section 1.2.2). Two main groups of techniques are available to monitor ventilation rates in animal buildings, direct and indirect methods (Phillips et al., 2001). The first ones rely on the measurement of airflow rates through all individual openings in the building and summing them up to obtain the overall ventilation rate of the building. The second one consists in determining indirectly the ventilation rate by using a tracer.

Knowing the release rate of the tracer in the building, the ventilation rate can be calculated by measuring tracer concentrations inside and outside the house, making use of the mass conservation law (see Eq. 1).

Big efforts have been done in order to develop techniques to directly measure ventilation rates in livestock buildings (Calvet et al., 2010; Gates et al., 2004; Berckmans et al., 1991). These techniques can be classified into two groups according to their nature: direct measurement of airflow rate using full size fan-wheel anemometers and determination by measuring the average air velocity through the fan.

The use of fan-wheel anemometers attached to the fans is considered as the reference method to determine the airflow rate in a fan (Demmers et al., 2000; Mosquera et al., 2005). The typical inaccuracy of this method is 5% over the measured value (Demmers et al., 1999). One of the main problems of this method is its associated economic cost. The use of fan-wheel anemometers may imply high costs, mainly in farms equipped with several fans since these devices should be installed in all of them. Even if the ventilation system follows a synchronized configuration in which various fans are simultaneously controlled, if fan-wheel anemometers are not installed in all fans, a significant error may be committed when determining the total airflow rate through the building. This is due to the different performance of fans (different dirtiness accumulation, power supply, etc.). In these cases, the sampling error can lead to errors up to 25% of the measured value according to Calvet et al (2010). In addition it must be considered that the pressure drop caused by the fan-wheel anemometer reduces the airflow rate, up to 5% (Berckmans et al., 1991). This is particularly important when not all fans are equipped with the fan wheel anemometer, thus, the measurement may lead to underestimate of the total airflow rate of the building.

Determining the airflow rate through the measurement of air velocities is also a standard procedure mainly in the United States (Gates et al., 2006). Knowing the open section of the fans and the average air velocity through them, the airflow rate can be easily calculated. The AMCA (1999) outlines a protocol to determine average velocities which involves measuring at least at 24 points in order to obtain reliable average values. Normally, air velocity is measured using hot-wire anemometers or Pitot tubes. The main drawbacks of this method are that the technician and measuring devices may interfere with the airflow, and these hand-held instruments are time-consuming and tedious in use. In order to avoid turbulence effects, it is also needed to obtain average velocity values for each point measurements, which leads to measurement protocols up to one hour when determining the airflow rate in a single fan (Simmons et al., 1998). The same authors developed a portable system based in the same principle that improved the measurements in terms of accuracy (6%) and time consumption. This system was later

optimized reducing its error to 3% (Gates et al., 2004). This system also interferes with the airflow, leading to flow underestimations for airflow rates higher than 30,000 m^3 h^{-1} (Gates et al., 2004). The main disadvantage of this system is that it cannot be used for continuous measurements of operating fans. The main aim of the system is obtaining calibration curves of the fans in the farm as a function of pressure drop. Later, instant values for airflow rates are obtained from indirect measurements of these parameters. It is known that the airflow rate of a single fan can vary strongly due to dirtiness accumulation, corrosion or punctual malfunctions (Casey et al., 2008). In addition, wind conditions in the outside can have an influence on the calibration measurements (Wheeler et al., 2002). Therefore, it is needed to repeat the calibration process frequently in order to obtain representative values.

Tracer balances can be considered an alternative to direct measurements. As explained before, the ventilation rate can be calculated by measuring the tracer concentration in the inlet and outlet of the building. The ideal characteristics of a released tracer include low and stable background level, no hazard, acceptability, ease of measurement, stability (in storage, in air and at surfaces) and low cost (Phillips et al., 2001). Many tracers can be used to this aim, and they can be classified according to their nature in artificially and naturally emitted in buildings. Artificially introduced tracers such as N_2O, SF_6 or radioactive tracers imply high costs due to the equipment needed for their accurate measurement, and have also negative effects on the environment and consequently should be managed carefully. Nowadays, balances are normally carried out using tracers that are naturally emitted in livestock buildings, such as carbon dioxide, humidity and sensible heat (Blanes and Pedersen, 2005). These methods are in general less accurate than direct measurements, but they can be powerful tools when direct measurements cannot be performed. By the moment, these balances are the most used techniques for the determination of ventilation rates in naturally ventilated buildings.

The use of these techniques for the evaluation of ventilation rates can be useful independently of the aim of the measurement. If the measurements are aimed to establish emission factors, the use of tracers can reduce the overall costs of the measurements, since the number of measurements to be done is high and the accuracy required at system level is not that high. When the aim of the measurement is to monitor a single system or building, or even obtaining a single emission value for a livestock house, the use of these tracer methods may be the only available technique in the case of naturally ventilated houses (when the emissions from the whole building are being measured, otherwise chamber methods can be used).

1.3.4. Sampling rate reduction

As discussed before, when determining airborne emissions from livestock production, both spatial and temporal variations must be considered in order to obtain representative results. At system level, if considering emissions from mechanically ventilated buildings, the spatial variability within the same barn can be neglected when there is a well-defined outlet in the barn. This is different for naturally ventilated houses with big opening surfaces, where emission fluxes are not controlled. This source of variability is very important when the measurement is aimed to monitor a single building. By the contrary, when the measurements are aimed to obtain emission factors representative of different locations, the main source of variability arises from differences between livestock houses (Ogink et al., 2008).

Attending to the temporal variations, three main factors cause differences in emissions: daily variations, seasonal variations and variations due to different stages of animals housed in the barn (Sun et al., 2010). The relative importance of each factor is closely related to the aim of the measurement, as seen in section 1.2.3. This variation sources originate random errors in measurements which can be reduced by repetition of measurements.

In terms of temporal variability, when measurements are aimed to determine emission factors or characterizing systems, the importance of variability factors such as seasonal patterns or different animals' stages is crucial. In this sense, most of the measuring protocols used nowadays include the measurement of emissions during long periods that can arrive up to 6 months of continuous measurements in pig production (Mosquera et al., 2005) in order to consider seasonal variations. These long term measurements are aimed to obtain representative results from the four seasons and different stages of animals. Even for animals with short time variations in terms of physiological stage such as poultry, measurements along different seasons have been traditionally made (Hayes et al., 2006). The cost of these high resolution measurements can arrive up to 50.000 € for each livestock facility measured (Dekock et al., 2009). Nevertheless, the results obtained from these high frequency measurements suffer from autocorrelation, since there is a close relationship among measurements that are near in time. In practice averaging the results at longer integration times, such as an hourly or daily basis, may solve this problem. That implies reducing the number of effective measurements with allows potential reductions of measuring costs. In this regard, intermittent independent sampling may give the same information by reducing the investment of the measurement campaign (Ogink et al., 2008).

If a measurement is aimed to obtain a representative emission value in a certain moment, it is important to pay attention to the daily variation of airborne emissions. Many studies have demonstrated that emissions follow daily patterns (Sun et al., 2008; Jacobson et al., 2005; Schauberger et al., 1999). These daily variations are mainly related to animal activity rates and climatic conditions, since ventilation rates are directly related to temperatures. This daily variation causes that most of the measuring protocols include high resolution measurements for the determination of daily emission rates, with sampling intervals varying from hours or minutes (Hinz and Linke, 1998; Mosquera et al., 2005; Phillips et al., 1998) to seconds (Heber et al., 2001). These high resolution measurements need the use of complex and expensive measuring devices such as photoacoustic, FTIR or chemiluminiscense monitor for gases, tapered element oscillating microbalance (TEOM) or isokinetic samplers for PM and frequent sampling for odour determination. In addition, these measurements require the installation of high resolution monitoring devices for ventilation rates, or using accurate data for indirect balances. This may be a restriction in naturally ventilated animal houses, where the determination of accurate ventilation rates is a challenging task moreover when high-resolution data are required.

Average daily emissions can also be determined using a simplified approach in which average daily values of gas concentrations and ventilation flows are measured. In this case, no attention is paid to daily variations of airborne pollutant concentrations or airflow rates. This approach allows the use of simpler and cheaper techniques for sampling airborne concentrations (e.g. wet chemistry based methods for determining ammonia concentration) and indirect method for the determination of airflow rates such as carbon dioxide balances. However, considering the daily variation of airborne concentrations and airflow rates, the product of 24-h average values for both terms may differ from the true daily emission, which is defined as the integration of concentration and flow over the day. This approach may be useful when the information about the daily variation is not needed. As explained before, that happens when measurements are aimed to determine emissions in a longer time-basis, such as emission factor or the characterization of systems.

1.4. Conclusions, research objectives and thesis structure

1.4.1. Conclusions and research objectives

As it was stated at the beginning of this chapter, before starting a measurement of emission from animal houses, a reflection is necessary concerning the aim of the measurement, the needs in terms of accuracy, and the best use of the resources. There are diverse technologies, techniques and strategies available for the determination of

emissions, but not all of them are always appropriate for all cases. In the previous section, four strategies aimed to optimize the resources when determining emissions have been analyzed.

The uncertainty analysis is potentially a powerful tool to evaluate the accuracy of different measurement technique. One of the main advantages of these analyses is that information can be obtained before making decisions. Uncertainty analysis can help us to identify the best way to obtain a reliable value from measurements when diverse methodologies are available. They also have demonstrated to be a robust tool to identify the main parameters introducing noise or uncertainty in the measurements. This strategy has been rarely used until the moment in the field of livestock and environment. From this point arises the first objective of this thesis that is:

- *To develop and test a methodology for the use of uncertainty analysis aimed to compare the accuracy of different methods for measuring emissions.*

Scaling down the measurements by using chambers is one of the possible techniques for the measurement of emissions in some cases (e.g. completely open naturally ventilated livestock houses), and can simplify the measurements in other cases (e.g. in large naturally ventilated houses where determining the ventilation rate is a challenging task). The use of chambers can also be used when deeper information about the individual emission sources (animals and manure) is needed, since both sources can be quantified separately. There is little information available about the use of these chambers in small animals such as rabbits. In addition, there is no agreement on general recommendations for the proper use of chambers. There is a need then to develop chambers useful for small animals, and to establish recommendations for its use. The second objective of this thesis is double and can be stated as:

- *To build up and test a flux chamber for the determination of emissions from rabbits and their manure. To develop a number of recommendations for its use.*

It has been described in the previous section that indirect methods such as carbon dioxide balances, are a powerful tool to determine ventilation rates in livestock buildings. In some cases these methods are the only available technique for the determination of ventilation rates (naturally ventilated buildings), but they can also be useful when other techniques are available, since they can imply lower investment by keeping the accuracy at the needed levels. These balances have been previously used to determine ventilation rates in most of the livestock species, but not in rabbit buildings. Due to this lack of knowledge, the third aim of this thesis is:

- *To set-up and test the use of carbon dioxide balances for the determination ventilation rates in rabbit buildings*

Finally, it has been explained before that, in some cases, reducing the intensity of the measurements, in terms of the sampling frequency, may provide accurate results at lower costs. This fact will always depend on the final aim of the measurement, but it can be a good strategy to optimize the resources in emission measurements. In this sense, few is known about the effect of using daily average measurements of emissions, instead of continuous or semi-continuous measurements, on the overall accuracy of the results. Therefore, the fourth objective of this thesis is:

- *To evaluate the effect of reducing the sampling frequency when determining ammonia emissions from livestock houses.*

In general terms this thesis deals with the development of tools for the optimization of resources when measuring emissions from livestock houses. This topic is afforded from a double perspective: the aim of the measurements and the required accuracy of the results.

1.4.2. Thesis structure

According to these objectives, a research work has been developed in this thesis. This work includes the development and evaluation of different techniques aimed to optimize the resources when measuring emissions. This PhD thesis is structured in eight chapters that are briefly described below.

Chapters 2 and 3 are aimed to deal with the use of uncertainty analysis as a previous step when planning emissions measurements. In order to determine the potential of uncertainty analysis as a tool for the selection of technologies or strategies for the determination of emissions from livestock houses, a theoretical uncertainty model was developed in a case study. This model was aimed to test two methodologies for the evaluation of the formation of N_2 and N_2O in biological scrubbers. This model is expected to allow evaluating the trustworthiness of the results as well as the relevance of each measured parameters on the result uncertainty (Chapter 2). A practical validation of the uncertainty model developed before was developed subsequently. To this aim, two methods aimed to determine the efficiency of a chemical scrubber were evaluated in terms of their reliability in a case study in a pig facility (Chapter 3).

For the evaluation of downscaling as a technique for the measurement of emissions, a flux chamber was designed and tested. Chapter 4 summarized the research developed for the design and construction of a dynamic flux chamber for the measurement of gas emissions

from rabbits. This study also included practical recommendations about the use of the chamber in order to optimize the measurements.

In order to test the usefulness of tracer balances for the determination of ventilation rates, two experimental studies were carried out in rabbit farms (Chapters 5 and 6), where there is not information about the use of this technique. Chapter 5 deals with the determination of CO_2 emissions from fattening rabbits. To this aim, the dynamic flux chamber developed in the previous chapter was used. This chapter can be considered therefore a practical and exhaustive validation of the chamber. The results obtained in this chapter were mainly aimed to provide information for the development of CO_2 balances. Since the use of CO_2 balances had not been used before for the determination of ventilation rates in fattening rabbit buildings, a practical validation of this methodology was carried out in Chapter 6. A flux chamber was also used in this study to obtain the CO_2 emission rate from rabbit's manure. The accuracy of the CO_2 balance method was then determined by comparing the results with direct measurements of ventilation rates.

Finally, with regard to the last strategy defined before aimed to optimize resources in emissions measurement, the effect on the accuracy of the results of reducing the time sampling rate when determining ammonia emissions was evaluated in Chapter 7. A wide database with high frequency measurements was evaluated in this work, comparing the results of using daily average values for the determination of emission rates to the use of hourly or bi-hourly measurements.

The last chapter of this thesis (Chapter 8) includes a summary of the main conclusions of this thesis, as well as a general discussion, relating the results obtained with the options aimed to the optimization of resources analyzed in this chapter. An analysis about the options for future research in both, general and specific terms is also included.

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Chapter 2

Evaluation of N_2 and N_2O formation in ammonia scrubbers: options for performance measurement

To be submitted as:

Estellés, F., Calvet, S., Melse, R.W. and Ogink, N.W.M. Evaluation of N_2 and N_2O formation in ammonia scrubbers: options for performance measurement.

Evaluation of N_2 and N_2O formation in ammonia scrubbers: options for performance measurement

Abstract

Biological scrubbers, aimed to the reduction of ammonia emissions, may emit N_2 and N_2O as a result of the nitrification and denitrificacion processes occurring in them. The direct measurement of these emissions is not possible nowadays due to the constraints of measuring N_2 concentrations. Determining these N losses in form of N_2 and N_2O throughout nitrogen balances in the system arises as an alternative. The main aim of this work was to provide a methodological framework for the development of N balances in biological scrubbers and for the study of the uncertainty associated. As a secondary objective an uncertainty model and a sensitivity analysis were run in order to analyse the magnitude of the uncertainty and to identify the main contributors to the final uncertainty. For a defined case study, the uncertainty of the results (released N in form of N_2 and N_2O) resulted in 132% of the measured value. The main contributors to the final uncertainty were the airflow rate and the water volume in the scrubber vessel. The uncertainty of the measurements of NH_3 concentrations in air and N ions in water had a low effect on the final uncertainty. According to these results, N balances cannot be recommended for the evaluation of the N_2 and N_2O formation in biological scrubbers, due to the high uncertainty of the results obtained.

Keywords: uncertainty, model, ammonia, scrubber, N_2, N_2O.

2.1. Introduction

Intensive livestock production systems, concentrated in several European regions, are responsible for environmental impacts such as atmospheric, soil and water pollution. The publication of laws, bindings and recommendations from public administration in this area has increased during the last years (Melse et al., 2009). Therefore, the development and implementation of techniques to reduce these impacts is crucial. Manure and exhaust air treatment technologies arise as key factors for a sustainable intensive livestock production (Melse and Timmerman, 2009).

Among the air treatment technologies available nowadays, air scrubbing systems are the most widespread in livestock houses, mostly in Northern European countries. Air scrubbers are mainly aimed to reduce ammonia concentrations in the exhaust air from farms, but they have also demonstrated to be a powerful tool to reduce dust and odour emissions (Busca and Pistarino, 2003). Scrubbers can be classified in two main groups according to their working principle: chemical and biological scrubbers. In the first ones ammonia is trapped in an acid solution in form of ammonium salts. In biological scrubbers, ammonia is nitrified by bacteria (mainly *Nitrosomonas* and *Nitrobacter* species) to nitrites and nitrates (Weckhuysen et al., 1994).

Despite achieving higher removal rates for odour than chemical scrubbers (Melse and Ogink, 2005) biological scrubbers may present inconveniences such as secondary nitrogen compounds formation. Here, one of the main concerns is the possibility of N_2O formation which is a greenhouse gas with a high global warming potential (IPCC, 2001). During biological removal of ammonia in air, nitrification processes occur since nitrites and nitrates are the main nitrogen species recovered in both trickling water and the packing material of the scrubber (Ramírez et al., 2009; Chen et al., 2005; Baquerizo et al., 2005). This process can be complemented with a denitrification in which nitrites and nitrates are converted into N_2 (Sakuma et al., 2008). During these processes, N_2O might be formed as a by-product of uncontrolled nitrification and denitrification processes that take place in the scrubber water (Trimborn, 2006). N-N_2O formation rates of 3-4% on the basis of the N-NH_3 inlet were measured in a pilot biotrickling scrubber (Hahne and Brandes, 2002; Hahne and Vorlop, 2004). Hahne and Vorlop (2004) suggest that N_2O formation starts after 100 days of scrubbing performance, with no water discharge or removal. In a full-scale biological scrubber placed in a pig house with weekly water renewal, the formation of N-N_2O was on average 1.2% of the N-NH_3 inlet (Aguilar et al., 2010).

Determining the amount of N_2 and N_2O that is being released from a biological scrubber is a challenging task. The most straightforward way to assess these emissions is measuring

gas concentrations before and after the scrubbing process. The measurement of N_2O is also difficult due to the low concentrations usually registered in the exhaust air from livestock buildings, and must be performed using accurate methods (e.g. gas spectroscopy or chromatography). Nevertheless, due to the high background concentrations of N_2 in air, and also the low reactivity of this molecule, determining the expected small differences of concentrations in scrubbers, is not possible in practice. Therefore since N_2 flows cannot be measured in the scrubber, direct measurements lead to an incomplete knowledge of the processes occurring in the system.

In order to avoid these expensive measurements, N_2O emissions can be also determined indirectly through a nitrogen balance considering all the processes occurring in the system and derived nitrogen forms (***Fig. 1***).

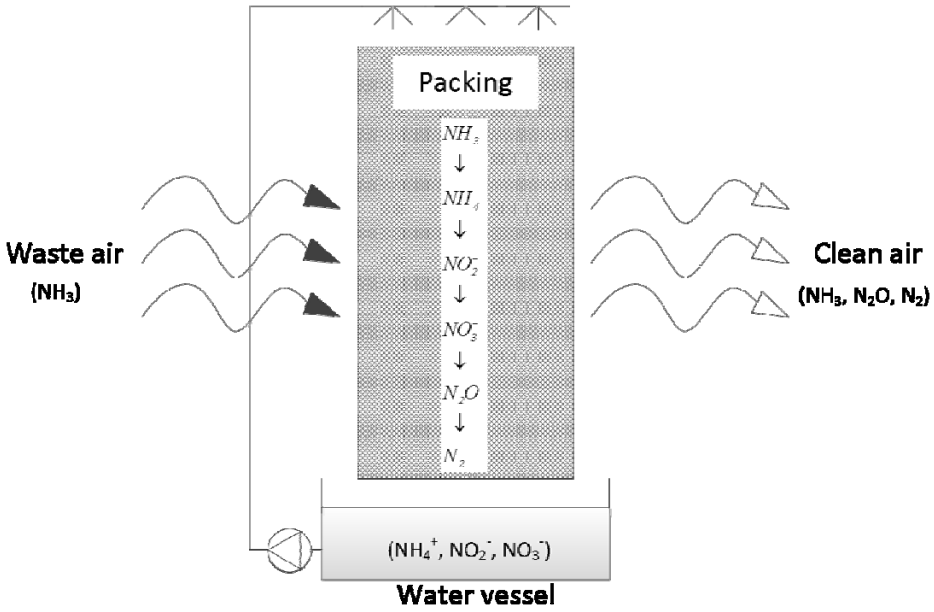

Fig. 1. Scheme of the working principle of ammonia removal in a biological scrubber

As explained before, in a biological scrubber NH_3 is nitrified and then denitrified, thus being the main source of N_2 and N_2O emissions. Thus, by measuring NH_3 fluxes in the inlet and outlet air of the scrubber as well as the amount of ammonia trapped in the scrubber (in the forms of NH_4^+, NO_2^-, NO_3^- and organic nitrogen), it should be possible to determine the amount of nitrogen released as N_2 and N_2O.

The measurement of ammonium, nitrite, nitrate and organic nitrogen concentrations can be achieved with high accuracy nowadays. Ammonia concentrations in air can be

determined with precisions below 1 ppb or 1% of reading using chemiluminiscence analysers (Ni and Heber, 2008). Nitrogen ions and organic nitrogen can also be determined in a water solution with accuracies from 1 to 3% of reading (APHA, 2005). However, performing nitrogen balances in biological scrubbers is difficult, not only due to the uncontrolled processes and also the pseudo-steady state occurring with low accumulation of substrates and metabolites in the packing (Sakuma et al., 2008), but also because airflow rates and water volumes must be determined accurately to develop the balance. In addition, it must be considered that all errors committed during the balance development (including measurement, sampling and modelling errors) are accumulated in the final result. In this sense, there is a need to investigate whether these N balances can be a tool for the determination of N_2 and N_2O in terms of accuracy.

The main aim of this work is to provide a methodological framework for the evaluation of N_2 and N_2O formation in biological scrubbers through N balances. In this sense the specific objectives of the work are:

1. To define exactly a method based in a N balance for the determination of N_2 and N_2O formation in biological scrubbers
2. To develop a model for the evaluation of the uncertainty associated to this balance
3. To provide a methodology for the determination of all individual uncertainties involved in the model
4. To apply a method for the identification of the parameters with large influence on the balance uncertainty (sensitivity analysis)

2.2. Balance definition

As seen before, when using a nitrogen balance to determine the amount of N_2 and N_2O being formed in a biological scrubber, it is needed to determine ammonia fluxes in the air as well as the amount of this ammonia recovered in water. Eq. 1 describes this calculation

$$N_{formed} = NH_{3\_inlet} - NH_{3\_outlet} - N_{recovered} \qquad \text{Eq. 1}$$

where, N_{formed} is the amount of N-N_2 and N-N_2O formed in the scrubber (g N), NH_{3_inlet} is the incoming N-NH_3 flow in the scrubber (g N), NH_{3_outlet} is the amount of N-NH_3 leaving the scrubber (g N) and $N_{recovered}$ is the nitrogen recovered in the system (g N).

To obtain the N-ammonia flux (NH_{3_i}) in the air in a location *i* (inlet and outlet) it is needed to know both the N-ammonia concentration in the air in this location as well as the airflow that went through during the considered period:

$$NH_{3\_i} = F \times [NH_3]_i \quad \text{Eq. 2}$$

where, F is the airflow (m^3) and $[NH]_i$ is the N-ammonia concentration (g N m^{-3}) in a location i.

The amount of nitrogen recovered in the system is composed of ammonium, nitrites, nitrates and organic nitrogen, trapped in the water of the system (both recirculated and discharged) and the packing material. Nitrogen fixed in the packing material can be dragged to the water vessel in the scrubber, finding then all the nitrogen dissolved in water. Therefore, the amount of nitrogen recovered in the system can be calculated following Eq. 3:

$$N_{recovered} = V_t \times \left([NH_4^+]_t + [NO_2^-]_t + [NO_3^-]_t + [N_{org}]_t \right) - V_0 \times \left([NH_4^+]_0 + [NO_2^-]_0 + [NO_3^-]_0 + [N_{org}]_0 \right) \quad \text{Eq. 3}$$

where, V_t and V_0 are the volumes of water (m^3) at the end and the start of the balance respectively, $[NH_4^+]_t$, $[NO_2^+]_t$, $[NO_3^+]_t$ and $[N_{org}]_t$ are the concentrations (g N m^{-3}) of ammonium, nitrite, nitrate and organic nitrogen respectively at the end of the balance and $[NH_4^+]_0$, $[NO_2^+]_0$, $[NO_3^+]_0$ and $[N_{org}]_0$ are the concentrations (g N m^{-3}) of ammonium, nitrite, nitrate and organic nitrogen respectively at the start of the balance.

2.3. Uncertainty model

When reporting results coming from experimental data, it is needed to provide not only the mean and its standard deviation, but also a measure or estimation of the reliability of the provided data (ISO, 1995). The uncertainty is defined by the ISO (1995) as a parameter (e.g. standard deviation or confidence interval) associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand.

To obtain the uncertainty of the final result of a measurement process, it is necessary to propagate all single uncertainties (from individual measurements or calculation processes) into the final result. That can be achieved using an uncertainty model (Sommer and Siebert, 2006).

The propagation of individual uncertainties through the model can be achieved using two different methods: the law of propagation of uncertainties, and the propagation of distributions (IPCC, 2000). The numerical propagation of distributions, following Monte

Carlo Methods (MCM), has been chosen in this work, because of their versatility and the possibility of reducing calculation times when using computers (Cox and Harris, 2006).

The first step when developing an uncertainty model is describing the measurement, identifying all variables taking part on it (measurand and measured parameters) as well as the measurement method (Sommer and Siebert, 2006). This has been defined in the previous section of that paper.

As a next step, in order to develop an uncertainty model for N balances in biological scrubbers, a cause-and-effect diagram in which all uncertainty sources are included has been developed (***Fig. 2***).

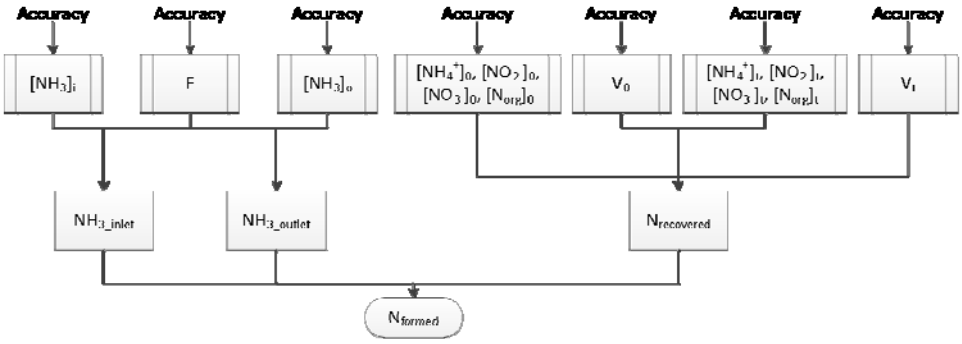

Fig. 2. Representation of the cause-and-effect relationship when determining N_2 and N_2O formation using a N balance in a biological scrubber, including uncertainty sources.

2.4. Determination of variables uncertainties

As seen before, an uncertainty model is aimed to obtain the uncertainty of a measurand by propagating all the individual uncertainties involved in the measurement.

All identified uncertainty sources for this model classified according to their origin can be found in ***Fig. 2***. Once identified the uncertainty sources it is needed to characterize them in order to introduce them in the model.

According to the ISO (1995), the knowledge about any quantity that influences the result of a measurement can be described by a probability density function (PDF). PDF of the variables may be inferred from either repeated measurements or scientific judgement based on all available information about the quantity.

Thus, to assign a PDF to each variable, general recommendations made by ISO (1995), JCGM (2006) and Cox and Harris (2006) were followed. When possible, PDF's were obtained from repeated measurements. If no experimental information was available the

next rules were applied: if errors were expected to be normally distributed and very accurate information about the variable was available, a Gaussian distribution N(μ,σ) was adopted. In those cases in which information was available only with regard to the lower (a) and upper limit (b), a rectangular distribution was used R(a,b), according to the principle of maximum entropy introduced by Jaynes (1957).

Correlations among parameters is not considered when measurements are independent among them (Payraudeau et al., 2007; Sommer and Siebert, 2006). This is the case of this work.

2.5. Sensitivity analysis

2.5.1. Methods

Obtaining information about the contribution of each individual uncertainty to the measurand uncertainty is crucial. In addition, knowing the effect on the final uncertainty of modifying the uncertainty of each parameter is also needed, since it may help to identify the most sensitive uncertainty sources.

In order to obtain the contribution of each parameter to the final uncertainty, two types of sensitivity analysis were evaluated. The approach used by Benke et al (2008) was adapted to this aim. The first sensitivity analysis is stochastic in nature. As seen before, the variance of the measurand error distribution depends on the variances of each parameter erro distribution. Therefore, if a parameter PDF is replaced in the model by a constant value its effect on the final uncertainty is removed. This process was followed individually with all parameters involving uncertainty. Therefore, starting with the full model, all parameters were held constant individually and MC simulations were run for each situation. The effect on the final uncertainty was then observed.

The second sensitivity analysis was performed in order to obtain the effect of the variation of individual uncertainties on the final uncertainty. To this aim, the individual uncertainty of each single parameter was modified from 0 to 200% of the initial value and the effect on the measurand uncertainty was observed.

To develop the uncertainty analysis it is needed to make some assumptions related to the parameters and their individual uncertainties that will be propagated through the model. A nitrogen balance will be established for a biological scrubber installed in a pig farm with 5,000 fatteners for a period of 24 hours. The average efficiency on ammonia removal of the scrubber is 70% (Melse and Ogink, 2005). It is expected that around 95% of the retained N-ammonia is converted into $N\text{-}NH_4^+$, $N\text{-}NO_2^-$ and $N\text{-}NO_3^-$ following a proportion 2:1:1 which is within the range described by Melse and Mol (2004), the rest of the

incoming ammonia is expected to be emitted as N-N_2O and N-N_2. There is no water discharge during the balance period. The amount of N_{org} in the system remains constant during the balance and no accumulation of nitrogen in the packing material is expected.

The average airflow rate in the building is established at 30 m^3 h^{-1} per animal (which is in the range determined by Seedorf et al (1998) for Northern European fatteners houses). The inlet ammonia concentration is considered to be 10 mg m^{-3} (Melse and Ogink, 2005). Water volumes in the vessel are considered to be constant during the balance and equal to 1.5 m^3. Ammonium, nitrite and nitrate concentrations at the beginning of the experiment can be considered at (1,000, 500 and 500 mg N l^{-1} respectively) which is also in the range proposed by Melse and Mol (2004).

NH_3 concentrations in air are determined using a chemiluminiscence analyser, with an accuracy of 1% of the reading (Ni and Heber, 2008). Airflow rates are measured using a fan-wheel anemometer installed in the farm exhaust. The inaccuracy of the system is 5% over the measured value (Mosquera et al., 2005). The accuracy of the water vessel volume measurement can be considered fixed at 0.1 m^3. The accuracy of the measurement method for nitrogen species in water can be established at 1% of reading for N-NO_2^- and N-NO_3^-, 2% of reading for N-NH_4^+ (APHA, 2005). ***Table 1*** summarizes the assumptions made in order to run the uncertainty model.

Table 1. Characterization of individual uncertainties

Variable	*Uncertainty source*	*PDF*	*Source*
$[NH_3]$	Accuracy of the measuring method	$N\left[\left[NH_3\right],0.01\times\left[NH_3\right]\right]$	Ni and Heber (2008)
F		$N\left[F,0.05\times F\right]$	(Mosquera et al., 2005)
$[NH_4^+]$		$N\left[\left[NH_4^+\right],0.02\times\left[NH_4^+\right]\right]$	(APHA, 2005)
$[NO_2^-]$		$N\left[\left[NO_2^-\right],0.01\times\left[NO_2^-\right]\right]$	(APHA, 2005)
$[NO_3^-]$		$N\left[\left[NO_3^-\right],0.01\times\left[NO_3^-\right]\right]$	(APHA, 2005)
V		$R\left[V-0.1,V+0.1\right]$	Own experience

For the propagation of the uncertainty the software RiskAMP Monte Carlo Add-In Lybrary version 2.7 for MS Excel (Structured Data, 2005) will be used. The number of iterations used will be $M=10^5$, which is the recommended value to obtain coverage intervals (Cox and Harris, 2006).

2.5.2. Results

The average value for N_{formed} (related to the $N\text{-}NH_3$ inflow) was 3.5% with a coverage interval at 95% of probability of [-6.11, 11.79]. ***Fig. 3*** shows the PDF of the measurand.

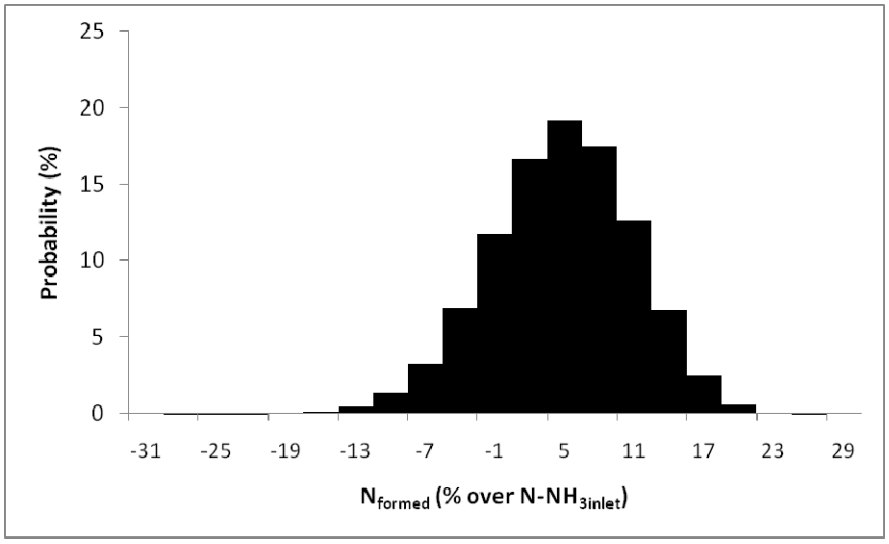

Fig. 3. PDF of the N_{formed} obtained with the uncertainty model

As expected, the average value obtained agrees with the theoretical expectation. Nevertheless, the uncertainty of this value (4.62) is high. This result implies that the formation of $N\text{-}N_2$ and $N\text{-}N_2O$ cannot be determined using the N balance method, considering the assumptions made in this work.

Regarding to the influence of individual uncertainties over the measurand uncertainty, ***Table 2*** summarizes the results of the first sensitivity analysis.

Table 2. Uncertainty of the measurand when deleting individual uncertainties from the model			
Variable	N_{formed}	$u(N_{formed})$	***Reduction of u with respect to the complete model (%)***
$[NH_3]$	3.50	4.52	2.16
F	3.50	3.17	31.34
$[NH_4^+]$	3.50	4.55	1.51
$[NO_2^-]$	3.50	4.63	0.00
$[NO_3^-]$	3.50	4.63	0.00
V	3.50	3.60	22.00
Complete model	3.50	4.62	0.00

It can be observed that the main contributor to the final uncertainty is the uncertainty of airflow measurement. The uncertainty of the water volume has also a clear effect on the final uncertainty. The rest of parameters uncertainties present minor (or null) effects on the final uncertainty.

The effect of modifying each individual uncertainty on the measurand uncertainty is shown in ***Fig. 4***.

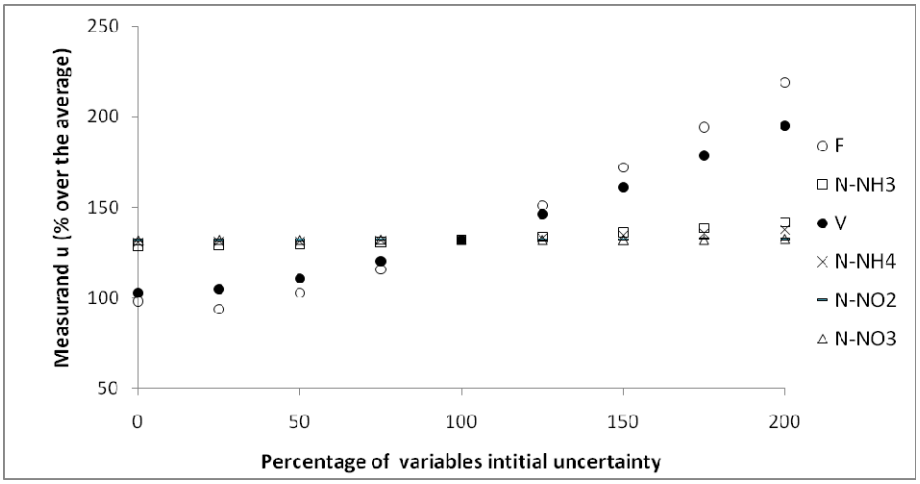

Fig. 4. Influence of variables uncertainties variation on measurand uncertainty

When representing the individual uncertainty variation (from 0 to 200% of the original value) against the uncertainty of the measurand (represented as % of the average value), the sensitivity of each parameter uncertainty can be clearly observed. As expected, the airflow rate and the water volume are the most sensitive parameters in the model. According to these results, reducing uncertainty of both factors at 50% over the initial

value leads to a reduction of the measurand uncertainty of 22.4% and 16.1% respectively. In general terms, the effect of reducing the uncertainty of the airflow rate reduces the measurand uncertainty 15% more than reducing the uncertainty of the water volume. It must be also noticed that the measurand uncertainty cannot be reduced below 100% of the average value in any case for model proposed here, which indicates that at least two of the parameters involved introduce a considerable amount of uncertainty in the final result.

2.6. Discussion

The model proposed in this work, in which a nitrogen balance in a biological scrubber is described, provides overall information about processes occurring in these systems. Nevertheless, in practice, is difficult to develop these balances. Due to the uncertainties of the measurements, identifying and quantifying all processes taking place in the system become a challenging task.

Uncertainty models have demonstrated to be a useful tool in the field of environmental protection. These models have been successfully developed before to assess the uncertainties in pollutant emission inventories (IPCC, 2000), measurement of emissions to air (Romano et al., 2004) and Lyfe Cycle Assessment (Payraudeau et al., 2007). The model developed in this work provides a methodological framework for uncertainty studies when evaluating scrubbers' performance. The methodology employed for the definition of individual uncertainties follows the ISO recommendations (ISO, 1995) and is similar to the one used in recent studies in the same field (Calvet et al., 2010; Gates et al., 2009).

The uncertainty model developed in this work aims to provide an insight in the uncertainty of nitrogen balances in biological scrubbers. The results derived from this model can be considered as a close approximation to the real processes, since the assumptions made in the case definition (e.g. ammonia concentrations, airflow rates, ions concentrations in water, etc.) are representative, and also the uncertainty of the variables is the result of a comprehensive bibliographic investigation.

In this sense, the uncertainty obtained for the measurand (over 132% on relative terms) is a clear indicator of the low trustworthiness of these measurements. It should be considered that this model does not include processes like the formation of organic nitrogen, accumulation of nitrogen in the packing or water discharge. These processes would introduce extra uncertainty in the model, increasing thus the uncertainty in the final result.

The most influencing parameters in the model (in terms of uncertainty) are those related to the measurement of fluxes (both airflow and water volumes). This fact is due to the

difficulty of measuring accurately these fluxes, as well as to the high influence of these values in the model (sees Figure 2). Gates et al (2009) also investigated the crucial effect of airflow measurements when determining gas emissions. It must be considered that this information is crucial to effectively improve the quality of the measurements and optimize measurement efforts for an expected measurement quality

In practical terms, according to these results, it may be recommendable not to use nitrogen or gas fluxes when evaluating the performance of scrubbers, for example when determining the ammonia removal efficiency the results will be less uncertain if only ammonia concentrations in the inlet and outlet of the system are measured, than if a complete nitrogen balance is carried out.

Finally, it has been observed that reducing the uncertainty of airflow rate and water volumes measurements would lead to a significant reduction on the final uncertainty. Despite of that, in practical terms, nowadays is hard to reduce these uncertainties (mainly the uncertainty associated to the measurement of airflow rates) at levels allowing accurate determinations of the N_{formed}.

2.7. Conclusions

A model for the development of nitrogen balances in biological scrubbers, aimed to determine the formation of N_2 and N_2O, has been defined in this work. In addition, an uncertainty balance has been defined and applied, including an analysis of sensitivity. The main conclusions that can be drawn out from this model are:

- The uncertainty of the determination of N_2 and N_2O formation in biological scrubbers using N balances is expected to be high (an uncertainty higher than 130% of the result was obtained in this work).
- The main contributors to this uncertainty are the uncertainties of the airflow rates and water volumes measurements.

According to these findings, and to the assumptions made in this work, the use of nitrogen balances for the determination of N_2 and N_2O formation in biological scrubbers, instead direct measurement of N_2O, is not recommended.

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Chapter 3

Evaluation of the NH_3 removal efficiency of a chemical scrubber using two methods: a case study in a pig facility

To be submitted as:

Estellés, F., Melse, R.W., Ogink, N.W.M. and Calvet, S. Evaluation of the NH_3 removal efficiency of a chemical scrubber using two methods: a case study in a pig facility.

Evaluation of the NH_3 removal efficiency of a chemical scrubber using two methods: a case study in a pig facility

Abstract

The use of air cleaning systems for the reduction of ammonia emissions from animal houses is increasing. These systems are normally used in order to comply with local or national regulations on ammonia emission. Therefore, accurate determination of the proportion of ammonia being removed by these systems is crucial. There are two main methods available for the measurement of ammonia removal efficiency in scrubbers, viz. air balances and combined water-air balances. The first ones are simpler to establish while the second ones might provide deeper information about the process occurring. The main aim of this work is to assess the use of these two methods for evaluation of the efficiency of a chemical scrubber on a pig farm, using the air balance method and the combined water-air balance method. These two methods will be evaluated in terms of the trustworthiness of the results. A chemical scrubber (70% NH_3 removal, Uniqfill, The Netherlands) was monitored during 10 complete 24-hours cycles for ammonia concentrations, airflow rates, and nitrogen accumulation in the water basin. The average efficiency calculated using the air balance was 71% (± 4%), close to the design value of 70%, while when using the combined water-air balance it was 255% (± 53%). According to these results, for chemical scrubbers as the one studied here it is recommended to use the air balance when determining the ammonia removal efficiency of the system. The variability of the results was much higher when using the combined water-air balance. The accumulation and precipitation of ammonium salts in the packing material seem to be the main cause of the high variability and inaccuracy of the combined water-air balance observed for this type of scrubber. According to the variability of the results observed in this work, when using the air balance to determine the ammonia removal efficiency of a chemical scrubber, at least 24 measurement days are needed in order to keep the error below 5%.

Keywords: ammonia, scrubber, chemical, efficiency, methods.

3.1. Introduction

Livestock production is one of the major contributors to ammonia, odour and particulate matter emissions in the agricultural sector. During the last years, international commitments (e.g. Kyoto Protocol, European Ceilings Directive 2000/81 CE) are binding the countries to reduce total emissions of atmospheric pollutants. The use of techniques to reduce emissions is playing a key role in several areas across Europe where livestock farming facilities are concentrated.

A large variety of techniques for the reduction of ammonia emission from animal houses are available. According to Ndegwa et al (2008) they can be classified in four main groups: reduction of nitrogen excretion, reduction of volatile nitrogen, building designs and manure management and emissions capture and treatment. Techniques for treatment of exhaust air from farms are included in this last group. These systems, also called "end-of-pipe systems", have become off-the-shelf techniques for the reduction of NH_3 emissions from pig and poultry houses in countries like The Netherlands, Germany and Denmark (Melse et al., 2009a).

An air scrubber is a reactor filled with an inert or inorganic packing material. This material is either continuously or intermittently sprayed with water to keep it wet. The exhaust air of the farm is driven through the scrubber. This process results in a contact between air and water, and enables a mass transfer from gas to liquid phase. A fraction of the trickling water is continuously recirculated, while another fraction is discharged and replaced by fresh water.

Air scrubbers can be classified in two main groups attending to their operation principle: chemical scrubbers and biofilters or biotrickling scrubbers. Chemical scrubbers (also called acid scrubbers) are based on the capture of ammonia in an acid solution that is being recirculated over the packed material. An ammonium salt is then formed, that will be discharged with a certain frequency. Sulphuric acid is commonly used and pH is kept between 2 and 4. Melse and Ogink (2005) reported an average ammonia removal efficiency of 96% in chemical scrubbers (ranging from 40 to 100%). Biofilters or biotrickling scrubbers work on the principle of the formation of a bacterial biofilm in the packing material. These bacteria degrade the water soluble components of the air that have been trapped in the water. Due to this bacterial activity, ammonia is converted into nitrites and nitrates. Nitrogen concentrations in the water are kept below inhibiting levels by regular discharge of the recirculation liquid. Average ammonia removal in these filters has been estimated in 70% (ranging from 0 to 100%) by Melse and Ogink (2005). One of the negative aspects of these systems may be the emission of N_2O in biological air treatment

systems, in which nitrification-denitrification (NDN) processes occur (Hahne and Vorlop, 2004).

As the ammonia removal efficiency of these systems is used for regulatory purposes, the measurement procedure and technique takes a crucial role. Two main techniques, based in mass balances, can be found (Shah et al., 2008; Manuzon et al., 2007). One of them is based on the measurement of the reduction of ammonia concentration in air, just by determining NH_3 concentrations before and after the scrubbing process (air balance). This is the most common technique and is used in all countries. The other technique consists in measuring the amount of nitrogen that has been recovered in the water, relating it to the total amount of ammonia entering the system (combined water-air balance). This combined water-air balance technique can be an additional requirement to the air balance measurements when certifying a scrubber, as it is in Germany. ***Fig. 1*** summarizes both measurement methods.

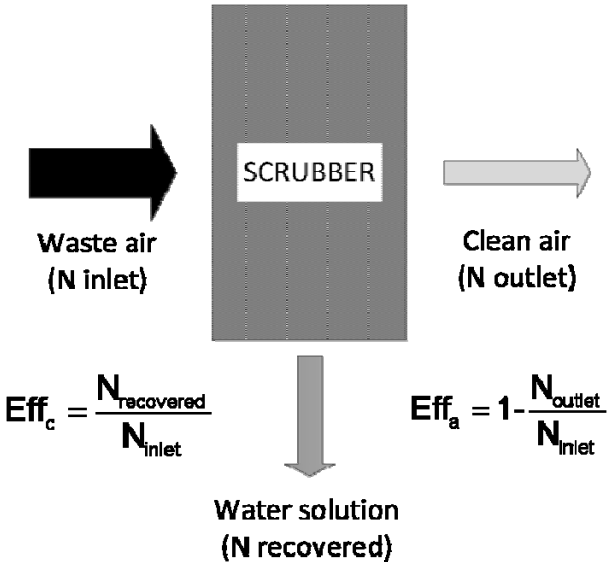

Fig. 1. Types of mass balances for the determination of ammonia removal efficiency in air scrubbers, with Eff_c representing the combined water-air balance and Eff_a the air balance.

The main advantage of the first technique is its simplicity because it is only needed to measure ammonia concentrations of the air, whereas the second technique requires not only the measurement of concentration in air and water but also determination of volumes and/or flows as well. On the other hand, the second technique might provide further information about the process and nitrogen fluxes, e.g. the occurrence of gaseous nitrogen emissions other than ammonia or nitrogen accumulation in the system. This

could lead e.g. to a better understanding of NDN processes in biological scrubbers. It also may help to explore precipitation of ammonium salts in the system.

One of the main constraints of the combined water-air balance approach is based on its accuracy. It is expected that the fact of measuring more parameters (e.g. air and water volumes) introduce extra measurement errors with respect to the air balance approach. This fact may lead to a lower overall accuracy of the nitrogen balance and consequently, of the determined ammonia removal efficiency. Estellés et al (2010a, 2010b), estimated in a theoretical study on a chemical scrubber, that the uncertainty associated with the efficiency measurement increases between 3 and 50 times (depending on the measurement methods and expected efficiency) when using the combined water-air balance instead of the air balance.

Therefore, there is a need to test whether these theoretical findings may be applicable in practice. For the purpose of validating these results, the two balance methods for the determination of scrubbers' efficiency were tested in a particular case in a chemical scrubber. A chemical scrubber was chosen to this aim in order to simplify the measurements by avoiding NDN processes in the system. It was considered that chemical scrubbers follow a straightforward operating principle in which all nitrogen fluxes can be accurately monitored.

The main aim of this work is to assess the use of two methods for evaluation of the efficiency of an acid scrubber on a pig farm, using the air balance method and the combined water-air balance method. These two methods will be evaluated in terms of the trustworthiness of the results.

3.2. Materials and methods

3.2.1. General approach

A single stage acid scrubber was chosen in order to simplify the measurements and to avoid possible biological activity that could lead to the loss of nitrogen in form of N_2O or N_2.

All measurements were conducted during a three weeks period in June 2009, resulting in 10 trials with a time basis of 24 hours. A graphical representation of the experimental calendar is presented in ***Fig. 3***.

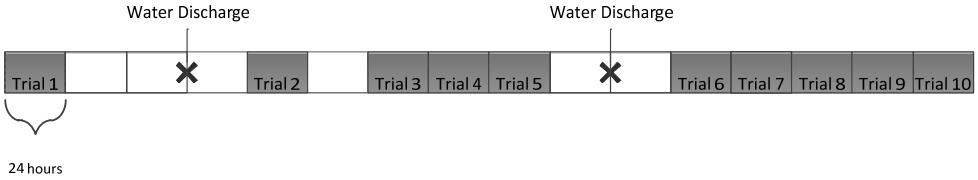

Figure 3. Time-line scheme of the experiment. Grey bars symbolize the measuring periods and white ones non-measuring periods

Relative humidity and air temperature were recorded each five minutes from both locations, before and after the scrubbing process using T/RH sensors (Hygroclip-S, Rotronic Instrument Corp., NY, USA). Data were collected using a data logger (CRX10, Campbell Scientific Inc., UT, USA).

3.2.2. Description of the scrubber

Measurements were taken from an acid scrubber (minimum required average NH_3 removal is 70%, Uniqfill Air BV, Meijel, The Netherlands) installed in a fattening pigs house with slatted floors (1180 animals) in Schijndel (The Netherlands). The house had a single air exhaust in which the scrubbing system was installed wit a maximum capacity of 90,000 m^3/hour (***Fig. 2***).

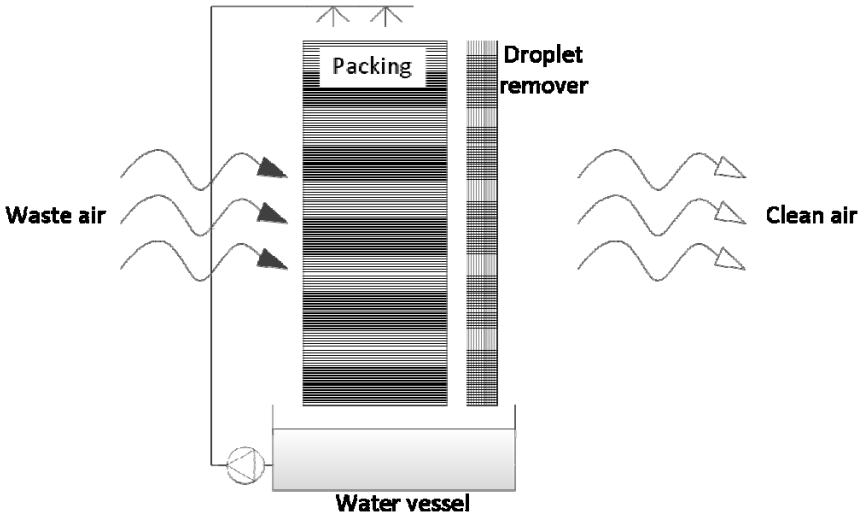

Fig. 2. Scheme of the chemical scrubber studied

The scrubber followed a cross flow configuration. The packing was formed by a stack of vertical ion-exchange fiber cloths, directed parallel to the airflow (4600mm width, 2010mm height and 500mm thickness) over which the acid solution was sprayed

intermittently (about 1 minute every 20 minutes). This means that the empty bed residence time at maximum air flow equals to 0.18 seconds. A plastic droplet remover (thickness: 150mm) was also present. A water collection basin (4600mm width, 450mm height and 950mm length) was installed below the packing unit. The acid solution was recirculated (1 m^3 h^{-1}) and pH was automatically controlled and kept below 4 and over 1.5, by means of addition of concentrated sulfuric acid to the system. Fresh water was continuously added to the system in order to compensate the volume of evaporated liquid. The acid solution of the basin was discharged weekly, but never at the time that a 24-hour measurement trial was being carried out. After the discharge of the acid solution, fresh water and sulfuric acid were added automatically to the system in order to achieve normal process operations again.

It is important to remark that the operating principle of this specific scrubber may not be representative of the common operation of chemical scrubbers. The packing material of chemical scrubbers is normally continuously wetted with an acid solution while in this case this fact happens intermittently. In addition, the packing material of the scrubber used in this work is formed by stacks of fiber cloths parallel to the airflow while normally it is formed by a structured plastic packed bed.

3.2.3. Air balance

General approach

To obtain the efficiency of the scrubber using the air balance method (Eff_a), both ammonia concentrations in the inlet ($[NH_3]_i$, mg m^{-3}) and outlet air ($[NH_3]_o$, mg m^{-3}) must be determined. The efficiency is calculated as follows:

$$Eff_a = 1 - \frac{[NH_3]_o}{[NH_3]_i} \qquad \text{Eq. 1}$$

Air ammonia concentrations

Ammonia concentrations in the air were determined daily using wet traps (impingers). Two sampling locations were defined (inlet air and outlet air). Two sampling lines per location were installed. Each sampling line was sub divided in two replicates, obtaining finally eight sampling points (four from the inlet and four from the outlet air). Two constant flow pumps were installed for air sampling. Critical orifices were used in order to obtain constant airflows (1 L min^{-1}) through the impingers. All sampling tubes were made of PFTE in order to avoid ammonia absorption (Philips et al, 1998). Two impingers containing a nitric acid solution (0,05 M) were located in series for each sampling point. The ammonia concentration in the air was calculated from the air sampling rate, the

nitrogen content of the acid solution in the bottles, which was determined spectrophotometrically (NEN, 2006), and the weight of the bottles before and after the sampling period to correct for volume increase due to water condensation. The air sampling rate of the impingers was determined by measuring the air flow twice, at the beginning and at the end of each measuring period by means the use of a flow meter (Defender 510, BIOS Int. Corp., NJ, USA).

Ammonia concentrations in the air were calculated as follows:

$$\left[NH_3\right] = \frac{N\text{-}NH_4^+ \times IM \times 17/14 \times D}{IA \times t \times 10^{-6}} \quad \text{Eq. 2}$$

where $N\text{-}NH_4^+$ (mg L^{-1}) is the ammonium concentration in the acid solution, *IM* (g) represents the impinger solution mass, *IA* (mL min^{-1}) is the average airflow rate through the impinger, *t* (min) is the sampling time, *D* is the density of the acid solution (10^3 g L^{-1}), 17/14 converts $N\text{-}NH_4^+$ into NH_3 concentration, and 10^{-6} is the conversion factor from mL to m^3.

3.2.4. Combined water-air balance

General approach

For the determination of the efficiency using the combined water-air balance method (Eff_c), it is needed to determine the ammonia flux coming in the scrubber through the air (ANH_3, mg) and the amount of ammonia recovered in the acid solution of the system (WNH_3, mg). Efficiency of the system can be calculated then following Eq. 3:

$$Eff_c = \frac{WNH_3}{ANH_3} \quad \text{Eq. 3}$$

Ammonia flux in the air

The determination of the amount of ammonia getting into the scrubber through the air was determined by multiplying the average ammonia concentration determined using the impinger method ($[NH_3]_i$) times the airflow rate gone through the scrubber (*F*, m^3 h^{-1}) during the studied period (*t*, min) following Eq. 4:

$$ANH_3 = \left[NH_3\right]_i \times \int \frac{F}{60} \times dt \quad \text{Eq. 4}$$

The airflow rate was determined by using four fan wheel anemometers (Fancom, BV, Panningen, The Netherlands) attached to the four exhaust fans of the building.

Anemometers were calibrated by the DLG in Germany (Ref 09-566). Airflow rates were recorded each five minutes using a data logger (CRX10, Campbell Scientific Inc., UT, USA).

Ammonia recovered in the water

The amount of ammonia recovered in the water is calculated as the increment of ammonia present in the vessel before and after the measuring period (Eq. 5). To obtain these values ammonium concentrations in water (WNH_4^+, mg mL^{-1}), as well as water volumes of the vessel (*V*, mL) at the beginning (*i*) and the end (*f*) of the experiment were determined.

$$WNH_3 = \left(WNH_4^+ \times V\right)_f - \left(WNH_4^+ \times V\right)_i \qquad \text{Eq. 5}$$

Duplicate water samples (100 mL) were taken from the vessel at the beginning and at the end of each sampling period. Later, they were analysed in the lab for ammonium concentration using spectrophotometric methods (NEN, 2006). EC and pH determinations were conducted as well. For consecutive sampling periods (Trials 3 to 5 and 6 to 10), it must be considered that the final sample of a period equals to the initial sample of the next period.

The volume of the solution in the water basin was determined by multiplying the water basin surface times the water height. The surface of the water basin was calculated using the manufacturer measurements. The measurement of the water height at each moment (this is at the beginning and at the end of the sampling process) was determined as follows: firstly, the recirculation pump of the scrubber was manually stopped if running, to allow stabilization of the water level. Then after five minutes without recirculation a calibrated ruler was introduced in the water basin and the water height was measured by triplicate. As explained before, it must be considered that for consecutive sampling periods, the final volume of a period equals to the initial volume of the next period.

3.2.5. Time scale

In order to evaluate the effect of the time scale of the measurements, the data obtained from daily measurements will be assessed in two ways. First of all, the daily variability of the air balances will be calculated. This value will be used as an estimator to determine the minimum number of daily measurements needed to obtain the average removal efficiency of the system with an error below 5%. The following expression will be used to this aim:

$$N \geq \left(t_{\alpha/2}\right)^2 \times \left(\frac{s}{\delta}\right)^2 \qquad \text{Eq. 6}$$

where, $t_{\alpha/2}$ is the upper critical values from a t distribution, being α the risk of rejecting a true hypothesis (0.05), s the standard deviation of the sample (the removal efficiency in this case) and δ the maximum relative expected error (5%).

As a second step, the time scale of the combined balance will be evaluated. These balances will be calculated both, in a daily basis and during a cycle. Considering that a cycle comprises consecutive measurements between water discharge processes. Therefore, this balance will be developed using the data of the last five trials (Trial 6 to 10).

3.2.6. Statistical analysis

The effect of inlet ammonia concentrations on outlet ammonia concentrations will be tested throughout a linear regression. In addition, in order to test the effect of inlet airflow rates, inlet ammonia concentrations and environmental conditions (inlet temperature and relative humidity) on the ammonia removal efficiency calculated using the air balance, a simple linear regression with each of the parameters was developed. The REG procedure of the statistical software SAS (2001) will be used to this aim, following the model described below:

$$Eff_a = \alpha + \beta \times X + \varepsilon \qquad \text{Eq. 7}$$

where, α is the intercept of the regression, β the slope, X the considered parameter (average pH, average EC, airflow rates, inlet ammonia concentrations, inlet T and inlet RH), and ε is the error of the model.

3.3. Results and discussion

3.3.1. Environmental conditions, airflow rates and water volumes

Average temperature and relative humidity registered during each trial are shown in ***Fig. 4***.

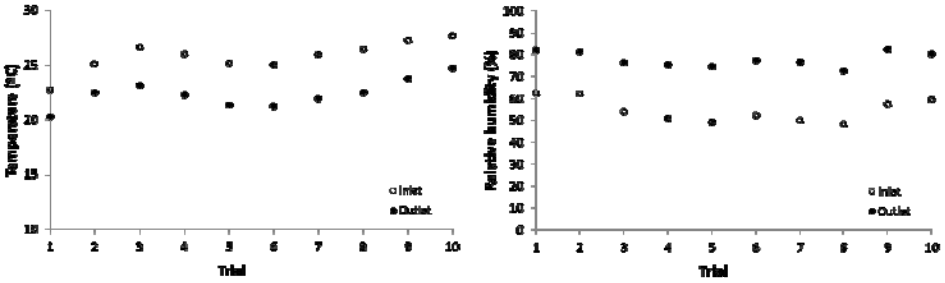

Fig. 4. Temperature and relative humidity registered during the experimental period in both, the inlet and outlet air

Average values for temperature (25.8±2.3 ºC) and relative humidity (54.5±7.3%) were in the range observed before by Seedorf et al (1998b) in fattening pigs farms during summer in Northern European buildings. As expected, an increase in the humidity content of the air (on average 21.8±5.5%), and subsequently a reduction of its temperature (averaging 3.2±0.9 ºC) was observed. This fact is due to the wetting effect of the scrubber, which is translated in average water content increase of the air was 1.9±0.42g H_2O kg air^{-1}.

The average airflow rate for the whole experiment was 41.9±6.6 m^3 h^{-1} $animal^{-1}$. The daily average value for each Trial is presented in ***Table 1***.

Table 1. Average values (± s.e.) for ammonia concentrations in the inlet ($[NH_3]_i$) and outlet ($[NH_3]_o$), ammonium concentrations in the water at the beginning (WNH_{4i}) and at the end (WNH_{4f}) of the trial, airflows and initial (V_i) and final (V_f) water volumes in the water basin, for each 24-hour trial (June 2009, Schijndel, The Netherlands)

Trial	$[NH_3]_i$	$[NH_3]_o$	Airflow	WNH_{4i}	WNH_{4f}	V_i	V_f
	mg NH_3 m^{-3}		m^3 h^{-1} $animal^{-1}$	kg N-NH_4 m^{-3}		m^3	
1	11.6±0.1	5.3±0.3	31.9±0.2	20.9±1.8	35.3±0.9	1.28±0.00	1.40±0.00
2	10.9±0.1	4.0±0.4	35.5±0.2	26.6±4.9	33.2±4.1	1.36±0.00	1.60±0.00
3	9.0±0.0	3.7±0.1	46.7±0.3	43.0±2.7	42.0±0.2	1.36±0.01	1.58±0.00
4	9.4±0.0	3.5±0.1	44.6±0.3	41.9±0.2	6.9±0.0	1.58±0.00	1.60±0.01
5	9.8±0.2	3.1±0.2	40.8±0.2	6.9±0.0	40.6±4.2	1.60±0.01	1.47±0.00
6	10.3±0.0	2.4±0.4	37.9±0.3	23.2±0.2	39.8±2.9	1.55±0.00	1.57±0.00
7	9.3±0.0	1.8±0.0	43.8±0.4	39.8±2.9	20.3±1.3	1.57±0.00	1.41±0.00
8	8.1±0.0	2.3±0.0	47.1±0.2	20.3±1.3	35.4±0.7	1.41±0.00	1.40±0.01
9	9.2±0.0	1.4±0.0	45.0±0.3	35.4±0.7	42.8±0.1	1.40±0.01	1.53±0.00
10	10.0±0.1	1.2±0.1	45.2±0.2	42.8±0.1	53.3±0.2	1.53±0.00	1.50±0.00
Avg.	9.8±0.2	2.9±0.2	42.0±0.1	30.1±2.7	34.9±2.9	1.47±0.12	1.51±0.01

This airflow rate is close to the average value for summer conditions obtained by Seedorf et al (1998a) in fattening pigs' facilities in The Netherlands, which was 42.7 m^3 h^{-1} $animal^{-1}$ with an average weight of 92 kg, which can be considered as normal values. The standard error of these measurements was 0.3% of the average value. This low value for the error is attributable to the high frequency of the measurements. This standard error must not be considered as an indicator of the measurement accuracy since it does not include any reference to the measurement device accuracy but its precision

Average water volumes in the basin for each trial are also shown in ***Table 1***. It can be observed that the variability of the water volume is low due to the automatic level control of the system. The water volume remained always below the maximum level of the water basin (1.97 m^3). Water level presented a low variability between different trials varying from 1.3 to 1.6 m^3.

3.3.2. Ammonia and ammonium concentrations

In ***Table 1*** it is shown the average inlet and outlet ammonia concentrations in air for each single measuring day. The average (± s.e.) inlet concentration for all balances was 9.8±0.2 mg m^{-3}. The variability of the inlet concentrations within days was low during the experiment, ranging from 8.1 to 11.6 mg m^{-3}. The average value is within the range reported by Melse and Ogink (2005) for the same animal category, and it is also very close to the average NH_3 concentration of 10.4 mg m^{-3} observed by Groot Koerkamp et al (1998) for the same animal category and management system in Northern European facilities. The standard error represented 1.6% of the average value, which is very close to the uncertainty calculated for this factor (1.2%) in the theoretical approach developed by Estellés et al (2010a;2010b).

Regarding to the outlet ammonia concentrations, they were on average (± s.e.) 2.9±0.2 mg m^{-3}, ranging from 1.2 to 5.3 mg m^{-3}. In this case, the variability of the data was higher and a clearly decreasing tendency as the experiment advanced can be observed, which means that the removal efficiency increased. The standard error (7.11% over the average value) is similar to the uncertainty value (3.9%) determined by Estellés et al (2010a;2010b) for this parameter in a theoretical framework. In this case the relative error is higher due to the lower absolute concentrations observed. There was no statistical relationship between inlet and outlet ammonia concentrations ($p>0.09$).

Measured ammonium concentrations in water during the experiment are shown in ***Table 1***. Ammonium concentrations varied from 6.9 to 53.3 g L^{-1}. It is not clear why WNH_{4i} of trial 5 is much lower than the other measurements. The variability of concentrations in the vessel for a given moment can be related to the standard error of the results, that represents 8.9 and 8.3% of the average value for initial and final concentrations

respectively. This adds an extra error source with respect to the theoretical model developed by Estellés et al (2010a;2010b).

With regard to the variability within days (deviation between replicated samples) ranged from 0.2 to 26% of the average observed value, being on average 8.7%. This is an indicator of the high variability of ammonium concentrations within different days in the water basin. This high variability could be also caused by the operating principle of this specific scrubber, since the discontinuous water recirculation and the packing material with sheets parallel to the airflow could favor the formation of ammonium salts in the packing.

Regarding the evolution of concentrations, an increase in the concentration over the time was not observed. A reduction in the ammonium concentration after water discharges (before balances 2 and 6, see Figure 3) was neither observed. In this sense, that may be caused by the partial and not fully discharge of the water contained in the water basin.

3.3.3. Removal efficiencies

The average NH_3 removal efficiency calculated using the air balance was 70.9±11.4 % over the inlet concentration, ranging from 54.5% to 87.9% (see ***Table 2***).

Table 2. Values for each component of the Nitrogen balance, initial and final pH and EC and calculated efficiencies for each trial

Trial	ANH_3	WNH_3	*pHi*	*pHf*	*ECi*	*ECi*	Eff_a	Eff_c
	kg N-NH_3	*kg N-NH_4*	*-*	*-*	*mS cm-1*	*mS cm-1*	*%*	*%*
1	8.7	22.8	1.9	2.5	145.5	182.8	54.5	263.3
2	7.5	16.9	1.5	2.1	192.6	>200	62.9	225.0
3	9.7	7.8	2.9	1.9	>200	>200	59.1	80.4
4	9.6	-55.0	1.9	2.0	>200	59.1	62.5	-571.8
5	9.2	48.5	2.0	1.4	59.1	>200	68.1	525.4
6	9.0	26.5	1.9	1.5	104.5	>200	76.9	294.2
7	9.4	-34.0	1.5	1.5	>200	137.8	81.7	-363.1
8	8.9	20.8	1.6	1.5	137.8	196.7	71.7	235.6
9	9.6	16.0	1.4	1.5	196.7	>200	84.5	165.8
10	9.3	14.7	1.8	1.6	>200	>200	87.8	157.9
Average (±s.e.)	9.1±0.2	8.5±9.6	1.8±0.2	1.8±0.1	163.6±15.9	177.6±14.5	70.9±3.6	254.5±52.5*

*The average value and its standard error have been calculated only for independent trials (that are 1, 2, 3, 5, 6, 8 and 10)

It can be considered that this value accomplishes with the specifications of the manufacturer (70% reduction) and the Dutch regulations (Melse et al., 2009b). The variations recorded within days on the system efficiency was reported before during the certification of the system by the DLG (2009). The average pH of each balance presented a significant effect ($p<0.01$) on the ammonia removal efficiency calculated using the air balance, with an intercept $\alpha=124.0\pm13.2$ ($p<0.001$) and slope $\beta=-29.7\pm7.3$ ($p<0.005$). The inlet temperature of the air also presented a significant effect ($p<0.05$) on the system efficiency. Nevertheless, the R^2 of the regression obtained was below 45%, thus further research is needed in order to confirm this relationship. There was no statistical effect of average EC ($p>0.4$), inlet ammonia concentrations ($p>0.3$), airflow ($p>0.2$) neither and relative humidity ($p>0.7$) on the calculated efficiency.

The efficiency calculations on a daily basis using the combined water-air balance resulted unsatisfactory, finding an average (±sd) of 254.5±139.0% (calculated only for independent trials), with values ranging from -571.8% to 525.4% (see Table 1). There was not observed any relationship among these results and the efficiencies calculated using the air balance. A random error is expected then from this method since systematic deviations between both methods are not observed.

Considering that no water was discharged during the trials and, ammonia concentrations in air, airflow rates and water volume measurements were trustworthy (very low variability), these errors may arise from the measurements of ammonium concentrations in the acid solution. The high variation observed in these concentrations may arise from accumulation and precipitation processes of ammonium salts occurring in the packing material. The DLG (2009) reported an accumulation of ammonium-N in the packing material of 16.3% over the inlet ammonia-N load, when testing a chemical scrubber of the same model than the one evaluated in this work. This accumulation and precipitation of ammonium salts may occur in all scrubbers (both chemical, forming ammonium salts, and biological, forming organic nitrogen floccules), nevertheless, the characteristics of this model (discontinuous wetting and with sheets placed in parallel to the airflow rate) make this process more frequent and significant.

Another explanation for this high variability is that, due to the on/off cycle of the pumps, of this specific type of scrubber, the mixing of the water in the water basin before sampling was not good, resulting in non-representative sampling.

3.3.4. Time scale

According to the calculated variability of the removal efficiency calculated using the air balance (s.d. was 16% of the average value), and following Eq. 6, to obtain the average efficiency of the system with a relative error below 5%, at least 23 daily measurements

must be performed ($p<0.05$). This variability between trials is slightly higher than the one reported by Melse and Ogink (2005) for different types of chemical scrubbers (in this work the standard deviation of the average efficiency ranged from 1 to 10% of the mean for different scenarios). Nevertheless, the number of measurements proposed in this work is within the range proposed by Melse and Ogink (2005) when monitoring the performance of chemical scrubbers in The Netherlands.

Regarding to the time scale of the combined water-air balance, during the period from Trial 6 to 10 (consecutive measurements without water discharge), the total ammonia recovered in the water was 44.1 kg $N\text{-}NH_4^+$, and the ammonia inlet was 46.14 kg $N\text{-}NH_3$, which equals a removal efficiency of 95.50%. This value is still different from the calculated on average for this whole period using the air balance (80.4%). This means that the results obtained with the combined water-air balance become better (considering the air balance as a reference), when longer integration times are used, i.e a number of consecutive measurements is performed. Nevertheless the accuracy of this method is low when compared to the air balance.

Attending to the results obtained in this case study the accuracy of the air balance is higher than the combined water-air balance. Since more parameters are involved when developing the combined water-air balance, the error sources also increase, leading to higher errors when determining the overall ammonia removal efficiency. These findings agree with the theoretical work previously developed by Estellés et al (2010a:2010b).

3.4. Conclusions

Ten complete 24-hour nitrogen balances have been carried out in order to determine the ammonia removal efficiency of the acid air scrubber system. The results obtained show that:

- The average (±s.e.) ammonia removal efficiency calculated using the air balance was 70.9±3.6%, this is the value that is normally used to assess the efficiency of a scrubber. Using the combined water-air balance which also takes into account the nitrogen recovery from the water phase, the calculated efficiency (average±s.e.) was 254.5±52.5%.
- The large variations that were found using the combined water-air balance might be explained by accumulation and precipitation of ammonium salts processes in the packing material, as well as not representative sampling of water due to incomplete mixing processes occurring in this type of scrubber (operating with discontinuous recirculation of water).

- 24-hour air balances arise as simple and stable (due to the low variability observed) tools to assess the ammonia removal efficiency in acid scrubbers, while combined water-air 24-hour balances are not recommended to this aim in scrubbers with the operation system described in this work, due to large variations that were found using this method.
- The variability of the removal efficiency within individual days (calculated using the air balance) observed for this case study makes recommendable to repeat the measurements at least 23 times in order to obtain a relative error lower than 5%.

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Chapter 4

Technical note: A flux chamber for measuring gas emissions from rabbits

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Technical note: A flux chamber for measuring gas emissions from rabbits

Abstract

Atmospheric pollution related to gas emissions from livestock production has become an issue of increasing interest. International commitments bind countries to provide annual reports on national emissions. However, there is a lack of information regarding the estimation of emissions from rabbit farms. There are several methodologies available to measure gas emissions, being the flux chamber technique one of the most commonly used. In this study, a flux chamber to measure emissions from small farm animals and their manure was designed. Likewise, the methodology to calculate ventilation fluxes appropriate for each experiment was also developed. After the chamber was constructed, two experiments were carried out to test the chamber's operation, as well as to check its design and construction. Firstly, carbon dioxide emissions from fattening rabbits were measured during 24 and 48 hours. Secondly, emissions from fattening rabbit manure were measured during one-hour periods. The operation of the flux chamber was satisfactory during both experiments, yet some considerations are noted to improve the performance through future research. Recommendations for its use are also summarized in this study.

Keywords: rabbits, emissions, ammonia, greenhouse gases, flux chamber.

4.1. Introduction

Ammonia and greenhouse gas emissions currently constitute one of the main environmental problems for livestock production (Owen, 1994). Some years ago, international agreements (e.g. Kyoto Protocol and European Ceilings Directive 2000/81/EC) began to require countries to report total emissions of greenhouse gases and ammonia, and to reduce them. Thus, national emissions inventories are, crucial to achieving these two goals.

In order to compile the national inventories in the livestock production sector, accurate data are needed to calculate the amount of gases the animals produce. Information is frequently unavailable for gas emissions from certain animal sources, for example those from species typically reared in the Mediterranean area. Rabbit production is one area in which there are little data related to ammonia and greenhouse gas emissions.

The two main sources of gas emissions from livestock production are manure management and enteric fermentation (IPCC, 2006). On the one hand, manure management is the primary source of ammonia and nitrous oxide emissions, as well as a critical source of methane and carbon dioxide. There are many studies about gas emissions from manure of many animal species (e.g. Wathes et al., 1998), but to our knowledge, no data are available on rabbit manure.

On the other hand, large amounts of methane and carbon dioxide are emitted as a result of the enteric fermentation process. These processes are crucial in ruminants, and therefore, they constitute the primary source of these gases. However, it has been traditionally accepted that some monogastric animals, such as pigs, horses or rabbits, also produce significant amounts of these two gases during their digestion processes (Crutzen et al., 1986).

As hindgut fermenters (Langer, 2002), rabbits produce considerable amounts of methane during digestion, mainly due to anaerobic decomposition reactions in the caecum. Although experiments have evaluated methane production using caecum cultures in vitro (Piattoni et al., 1996), there is little information from living animals and thus, these data are not really useful when estimating total methane emissions from reared rabbits.

Taking into account the increasing number of rabbits reared in Mediterranean countries, methane emissions from their production should be considered and included in the national gas inventories. Therefore, experimental measurements are essential to obtain estimations for rabbits and complete these gas emission inventories (IPCC, 2006).

Several methods are available to assess gas emissions from animals. Ni and Heber (2008) provided a comprehensive review of the most widespread methodologies used to measure emissions at animal facilities: static chambers, dynamic chambers, tracer methods and micrometeorological techniques. Static chambers are generally used to measure emissions from manure, whereas dynamic chambers are useful to measure emissions from both manure and animals. Tracer methods can be used to measure emissions from buildings and, in some cases, to quantify methane emissions from large animals (ruminants). Finally, micrometeorological techniques are widely used to obtain open-range emission data (Misselbrook et al., 2005).

Chambers offer four advantages: easy replication, comparison among treatments, no site restrictions, and relatively inexpensive cost (Shah et al., 2006b). These chambers usually enclose a small area (0.1 to 0.2 m2), which may be a restriction when studying heterogeneous emitting sources, for example, open field emissions (Meissinger et al., 2001).

The emissions from a dynamic chamber can be calculated according to the mass conservation law, which may be simplified for a stationary state as shown in Eq. 1:

$$E = \left(C_{inlet} - C_{outlet}\right) \times F \qquad \text{Eq. 1}$$

where, E is the emission rate (mg h^{-1}), C_{inlet} is the inlet gas concentration (mg m^{-3}), C_{outlet} represents the outlet gas concentration (mg m^{-3}) and F is the airflow exchange in the chamber (m^3 h^{-1}).

Dynamic chambers have been developed primarily to study emissions from large animals, such as sheep (Blummel et al., 2005) and cattle (Beauchemin and McGinn, 2005; Kurihara et al., 1999). These chambers have also been used to estimate poultry emissions (Wang and Huang, 2005). Kiwull-Schöne et al. (2001; 2005) used these chambers for nutritional studies with rabbits. Dynamic and static chambers are considered then, as a robust method to measure emissions from animals and their manure.

This research is aimed at adapting, designing and testing a flux chamber for small animals, principally rabbits, so as to accurately compile data for both their emissions and those from their manure. To this end, the standard methodology for its use will be described and basic recommendations will be provided. Obtaining experimental data on rabbit greenhouse gases and ammonia emissions will contribute to completing national emissions inventories and, subsequently, to implementing strategies to reduce the emissions themselves.

4.2. Materials and Methods

4.2.1. Chamber design

The basic structure of the chamber (60cm long x 40cm wide x 40cm high) was constructed with polymethyl methacrylate (PMMA) (0.5cm thick). The chamber did not have bottom side, so it was placed on a flat surface where it self-sealed with rubber. The air inlet and outlet were conducted through two lateral modules with a pyramidal shape finishing in a cube (10cm long x 5cm wide x 5cm high), constructed as well with PMMA. ***Fig. 1*** shows the constructive schema and shape of the chamber. The total volume of the chamber was 0.1705 m^3, and the area of the base was 0.24 m^2.

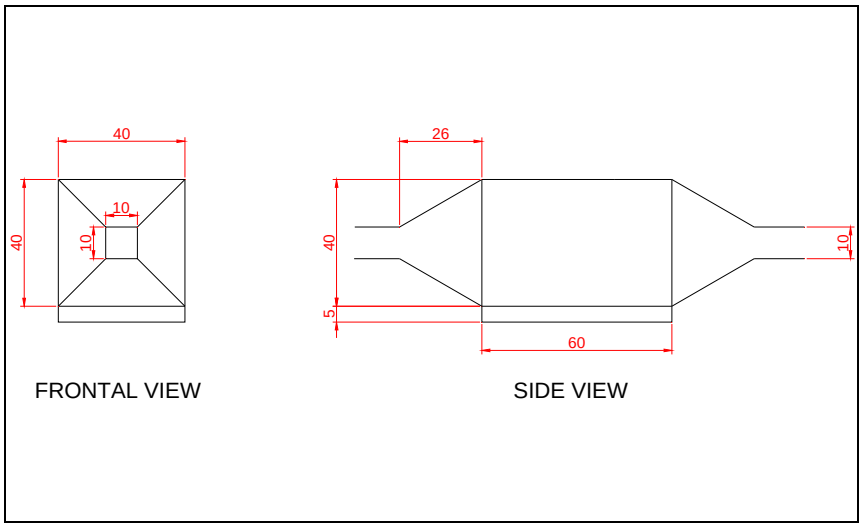

Fig. 1. Schema of the chamber (measurements in cm).

Flow rate

Gas emissions are directly conditioned by flow rate, as indicated in Eq. 1. Therefore, one of the main considerations when designing a chamber is to choose an appropriate flow rate. In addition, the air exchange rate directly influences the environmental conditions inside the chamber, such as relative humidity (RH) and temperature (t). For this reason, the ventilation flow required must be different considering the two possible emitting sources (animals or manure) and should be established during the experimental design. The main factors to be considered when calculating the airflow requirements are i) emission source needs, ii) environmental conditions and iii) sensor used to measure gas concentration.

i) Emission source needs. The optimal ventilation flow depends, mainly, on the temperature, humidity and carbon dioxide concentration produced by the animals themselves through their metabolism. A proper ventilation flow will prevent inadequate environmental conditions inside the chamber. When measuring animal emissions, ventilation flow should be calculated considering these three factors, by means of Eq. 2, Eq. 3 and Eq. 4, respectively. Finally, the highest ventilation flow will be chosen to account for the most restrictive factor.

$$V_{CO_2} = \frac{E_{CO_2}}{CO_{2\max} - CO_{2out}} \qquad \text{Eq. 2}$$

where, V_{CO2} is the flux needed to eliminate excess carbon dioxide ($m^3\ h^{-1}$), E_{CO2} is the CO_2 emission rate (mg h^{-1}), CO_{2max} is the maximum CO_2 concentration admissible for the animal (mg m^{-3}) and CO_{2out} is the CO_2 concentration of external air (mg m^{-3}).

$$V_{H_2O} = \frac{Q_l}{597 \times (w_i - w_o)} \times v_s \qquad \text{Eq. 3}$$

where, V_{H2O} is the flux needed to eliminate excess humidity ($m^3\ h^{-1}$), Q_l is the latent heat production (kcal h^{-1}), w_i is the internal air absolute humidity (kg water vapour kg dry air^{-1}), w_o is the external air absolute humidity (kg water vapour kg dry air^{-1}), v_s is the specific volume of air (m^3 kg air^{-1}) and 597 is the energetic value of water vapour (kcal kg water $vapour^{-1}$).

$$V_{Heat} = \frac{Q_s}{H_s \times (t_i - t_o)} \times v_s \qquad \text{Eq. 4}$$

where, V_{Heat} is the flux needed to eliminate excess heat ($m^3\ h^{-1}$), Q_s is the sensible heat production (kcal h^{-1}), H_s is the specific heat of air (kcal $Kg^{-1}\cdot ºC^{-1}$), t_i is the internal air temperature (ºC) and t_o is the external air temperature (ºC).

ii) Environmental conditions. Temperature and humidity inside the chamber can significantly affect manure and animal emissions and, as stated before, the air flow rate modifies environmental conditions. Therefore, ventilation inside the chamber should aim to obtain environmental conditions similar to those existing in animal buildings.

iii) Sensor used. It is necessary to consider the properties of the sensor used to measure gas concentrations. To determine an appropriate ventilation rate for the sensor two factors must be considered. The first consideration is sensor measuring range for each gas, which will determine the concentrations that can be measured in the chamber. Secondly,

it is necessary to estimate an approximate emission rate expected for each gas. Eq. 5 shows the calculation process for the ventilation rate according to the sensor measuring range.

$$C_{low} \leq \frac{E'}{F} + C_{inlet} \leq C_{up} \qquad \text{Eq. 5}$$

where, C_{low} is the lower threshold of the sensor (mg m^{-3}), C_{up} is the upper threshold of the sensor (mg m^{-3}) and E' is the expected emission rate (mg h^{-1}).

In brief, one of the main considerations to establish the ventilation flow, when studying manure as emission source, is the sensor measurement range (Eq. 5). By contrast, when animals are studied, their environmental needs must be taken into account (Eq. 2, Eq. 3 and Eq. 4), in addition to the sensor measurement range (Eq. 5).

4.2.2. Experimental tests

To test the performance of the designed chamber, two experiments were carried out. In the first experiment, carbon dioxide emissions from fattening rabbits were measured over 4 days. In the second experiment, ammonia and carbon dioxide emissions from manure were measured during three periods of approximately one hour each.

4.2.3. Carbon dioxide emissions from rabbits

In the first experiment, the chamber was placed in an experimental rabbit farm located at the *Universidad Politécnica de Valencia* (Valencia, Spain). Inside the chamber the following devices were installed: an air pump for ventilation (Resun® Silent-Pump AC-9002, 0.423 $m^3 \cdot h^{-1}$), a small fan to circulate the air inside the chamber (Power Logic PL80S12M), a water dispenser and a feeder. Outside the chamber a carbon dioxide sensor was placed (Vaisala GMT-222, 0-10,000 ppm), connected by means of a process adaptor (Vaisala 26150GM) to one of the exhaust tubes of the chamber. Data were recorded every minute with a data logger (HOBO H8 RH/Temp/Out, Onset Computer Corp., Pocasset, Mass.). Environmental conditions, including temperature and relative humidity, were measured using two data loggers (HOBO H8 RH/Temp, Onset Computer Corp., Pocasset, Mass.), one of them inside the chamber and the other one outside. The chamber is assembled as depicted in ***Fig. 2***.

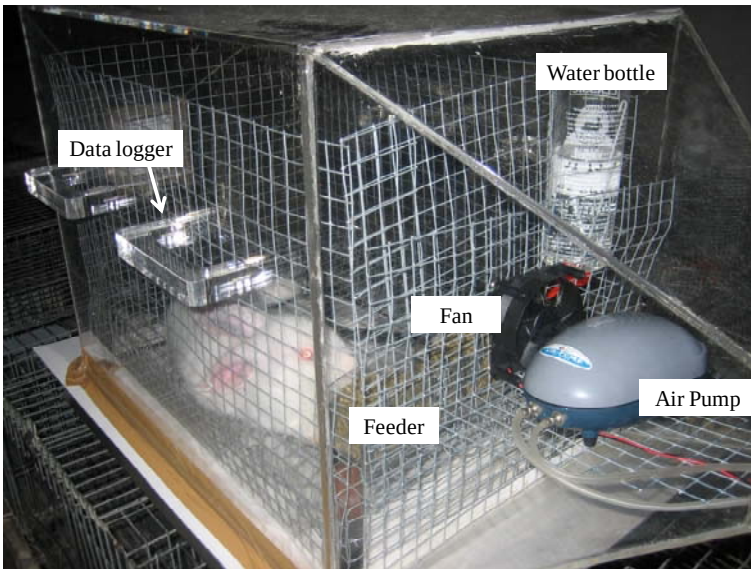

Fig. 2. Image of the chamber during animal emissions experiment.

Three 32-day old (one week after weaning) hybrid rabbits (New Zealand White x Californian) were selected for the study. The first experiment was designed as follows. During the first and second day, two of the three rabbits were placed in the chamber, individually, for 24-hours each (Trial-1 [24h] and Trial -2 [24h]). The third rabbit (Trial-3) was placed in the chamber during the third and fourth day (48h). This design allowed the study of the relative effect of the experiment length, particularly manure accumulation. Rabbits were weighed at the beginning and at the end of each trial. The feeder and the water dispenser were also weighed to assess feedstuff and water consumption. The data on rabbit performance for the different trials are summed up in ***Table 1***.

Table 1. Rabbit growth as well as water and feedstuff consumption during the experiment.

Animal	*Initial age*	*Entrance data*	*Time of permanence*	*Initial weight*	*Final weight*	*Water consumption*	*Feedstuff consumption*
(id)	*(days)*		*(h)*	*(kg)*	*(kg)*	*(L)*	*(kg)*
55531	32	6/08/07	24	0.980	1.040	0.220	0.080
56124	33	7/08/07	24	0.700	0.760	0.120	0.070
55304	34	8/08/07	48	0.780	0.860	0.180	0.150

Emissions were calculated on an hourly basis, using the general mass balance equation corrected by the metabolic weight (Eq. 6):

$$E_{MW} = \frac{\left(C_{outlet} - C_{inlet}\right) \times F}{LW^{0.75}}$$ Eq. 6

where, E_{MW} is the emission rate per kilogram of metabolic weight (mg·LW$^{-0.75}$·h^{-1}) and *LW* is the live weight of the animal (kg).

According to the expected relationship between carbon dioxide emissions and metabolic activity, emissions were corrected dividing them by the metabolic weight of the animals. To minimise the effect of the temperature, emissions were standardized at 20ºC using the CIGR algorithm (Eq. 7) to correct total heat production (CIGR, 2002), in which T is the measured temperature (ºC).

$$Conversion\ factor = \left[1 + 4 \times 10^{-5} \times \left(20 - T\right)^3\right]$$ Eq. 7

To determine the daily variation pattern, emissions were standardized dividing each value by the global mean, obtaining thus the relative emission for each measurement.

Mean emissions were obtained using PROC MEANS of SAS (2001). Daily variation of these data was studied and modelled by means of PROC NLIN of SAS (2001).

4.2.4. Emissions from manure

Three manure samples were taken from the experimental rabbit farm located in the *Universidad Politécnica de Valencia* (Valencia, Spain). Manure was sampled from the manure pits under the cages using three small boxes (15 x 15 x 5 cm) made with a mesh (4 x 4 mm orifices) and placed on the pits for one week. These sampling boxes were taken from the pit after the collection period and left on the ground to drain during approximately 15 minutes. Then, all sides and the bottom of the boxes were sealed with aluminium foil to prevent gas losses, allowing the emission to flow only from the top surface. Finally, they were individually introduced in the chamber for approximately one hour. After each measuring period, the chamber was opened to air for30 minutes.

Two devices were placed inside the chamber: an air pump for ventilation (Resun® Silent-Pump AC-9002, 0.552 m^3·h^{-1}) and a small fan to circulate the air inside the chamber (Power Logic PL80S12M). A multi-point sampling device was used to measure inlet and outlet gas concentrations by duplicate. Gas samples were conducted through Teflon tubes to a photoacoustic gas monitor (INNOVA 1412, AirTech Instruments), which measured gas concentrations (NH_3 and CO_2) in a 2-minute interval. Finally, average values for each location were used to calculate the emissions. The assembled chamber is depicted in ***Fig. 3***.

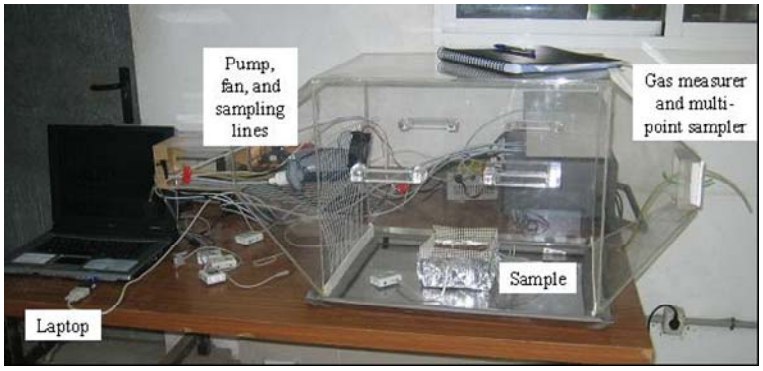

Fig. 3. Image of the chamber containing rabbit manure.

Emissions were calculated with the simplified mass balance equation in a stationary state using Eq. 1. It must be underlined that the initial minutes of a measurement with the chamber are subjected to a transitory regime. In this time, the concentration increases progressively from the initial value until it becomes stable, and only then can the emission be modelled as a stationary regime. In practice, it can be considered that the stationary regime is achieved when 95% of the equilibrium concentration is reached at the time given by Eq. 8.

$$t = -\frac{V \cdot Ln(1-0.95)}{F} \qquad \text{Eq. 8}$$

where, t is the time to achieve a practical equilibrium in the chamber (h), V is the volume of the chamber (m^3) and F is the air exchange rate ($m^3 \cdot h^{-1}$).

4.3. Results and Discussion

4.3.1. Experimental test 1 (animal emissions)

Table 1 shows the productive results obtained during the three trials in terms of animal age, initial and final weight, as well as water and feedstuff consumption. These results were similar to those obtained at the same experimental farm by Calvet et al. (2008) in a previous study. Therefore, it may be concluded that the animals were not affected by the chamber in terms of productive results.

The average carbon dioxide emission was 1.42±0.13 (L $CO_2 \cdot h^{-1} \cdot LW^{-0.75}$). This is a higher value than those reported by Kiwull-Schone et al. (2001; 2005), which ranged between 0.825 and 0.935 L $CO_2 \cdot h^{-1} \cdot LW^{0.75}$, respectively. This difference could be the result of the different methodology employed in those cases, in which animal emissions were

measured only during a 25-minute period, while in this experiment a longer period was used. In addition, no information is provided about the time when the experiment was carried out, so if measurements were done during the day, lower emissions can be expected. It is also higher than the value estimated according to the CIGR (2002) methodology, which is about 1 L $CO_2 \cdot h^{-1} \cdot LW^{-0.75}$. It is important to remark at this point that CIGR values are estimated and not measured, and this could be the cause of the observed difference.

A daily pattern of CO_2 emissions was identified, as reflected in the average hourly emissions graph (***Fig. 4***).

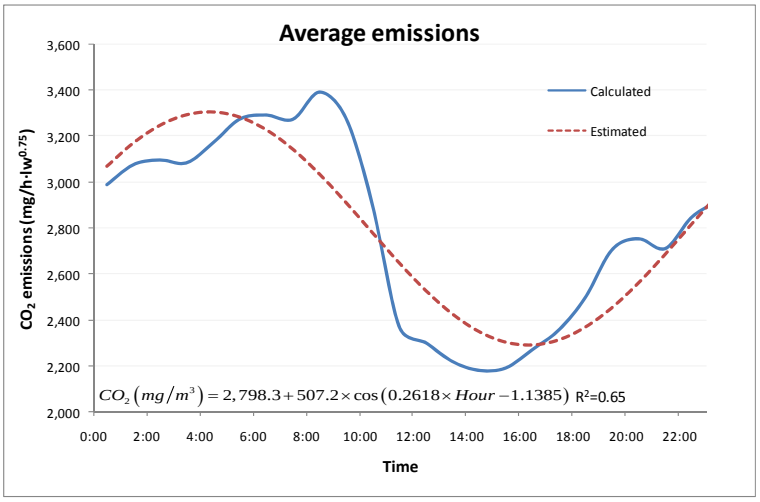

Fig.4. Average emissions and regression values.

Emissions were higher at night and in the early morning. During the third trial, the same emission pattern was observed although more emissions were observed during the second day than the first (***Fig. 5***).

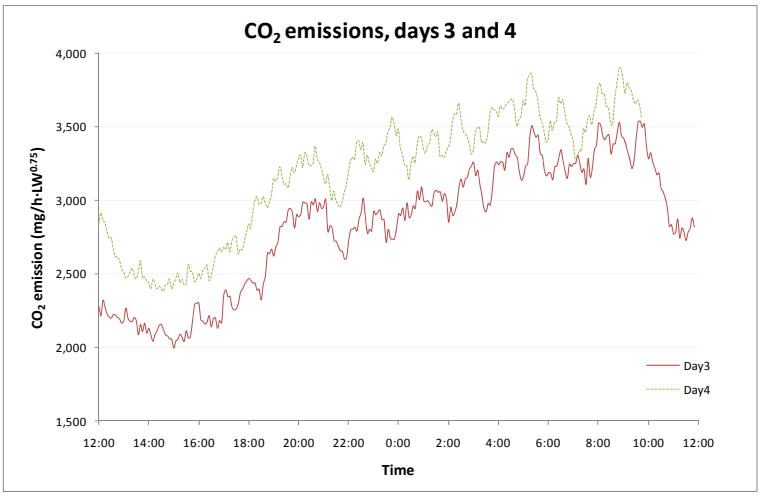

Fig. 5. Comparison of emissions, days 3 and 4 (Trial 3).

It can be concluded then that a 24-hour period is long enough to determine the daily emissions pattern. These higher emission values observed during the second day may be attributed to the accumulation of faeces in the chamber, and the subsequent increase of emissions from this source.

Ventilation flux was previously calculated using Eq. 2 to 5. Environmental conditions considered for the estimations were: outside air about 26ºC and 50% RH (normal data for this period in Valencia), the highest temperature and RH desirable inside the chamber, calculated according to CIGR recommendations (1992), were 30ºC and 60% RH. Values for CO_2, and heat emissions were taken from CIGR (2002), as well as maximum CO_2 concentration for the animals and CO_2 concentration in the inlet air. Ventilation flows were estimated as 0.078 $m^3 \cdot h^{-1}$, 0.074 $m^3 \cdot h^{-1}$ and 0.009 $m^3 \cdot h^{-1}$ for Eq. 2, to 4, respectively. According to the sensor measurement range (0-10,000 ppm) and the expected emission rate (0.060 $m^3 \cdot h^{-1}$, CIGR, 2002), the estimated ventilation flow range appropriate for this sensor, calculated using Equation 5, was on the order of 0.18 to 3.60 $m^3 \cdot h^{-1}$.

The temperature inside the chamber was similar to the one registered in the building and ranged between 23ºC and 31ºC. Relative humidity was significantly higher inside the chamber than outside, reaching air saturation during the coldest hours. This indicates that previous estimations of air flux were not enough to prevent condensation, although the ventilation rate used in this experiment (0.423 $m^3 \cdot h^{-1}$) was clearly higher than the one estimated according to environmental requirements (0.078 $m^3 \cdot h^{-1}$).

Finally, it was observed that rabbits needed about one hour to become accustomed to the chamber; the exploratory activity resulting in higher emissions during this time. According to the results obtained in this research, values from this first hour should be disregarded.

4.3.2. Experimental test 2 (manure emissions)

Measured gas concentrations of ammonia and carbon dioxide ranged between 0.25 and 7 $mg \cdot m^{-3}$ and 737 and 1,238 $mg \cdot m^{-3}$, respectively. In these terms, the ventilation flow selected for this study was appropriate for the measuring range of the gas analyser (0-50 $mg \cdot m^{-3}$ NH_3 and 0-10,000 $mg \cdot m^{-3}$ CO_2).

Calculated emission values for the three trials were 3.26±0.01, 2.95±0.15 and 3.07±0.01 mg $NH_3 \cdot h^{-1}$ and 216.9±0.3, 219.2±2.8 and 272.4±0.2 mg $CO_2 \cdot h^{-1}$, respectively. The evolution of measured ammonia and carbon dioxide emissions is depicted in ***Fig. 6***.

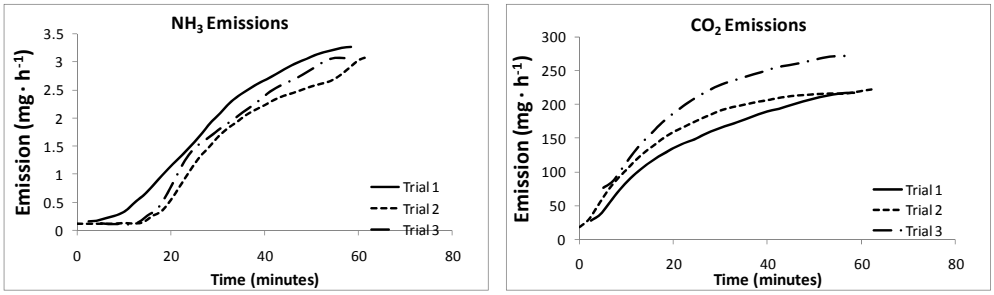

Fig. 6. NH_3 and CO_2 emissions from rabbit manure.

Emissions increased continuously during the first minutes, due to the transitory regime in the chamber. Fifty-five minutes were needed to achieve the stationary regime in the chamber, calculated using Eq. 8. In practice, it was observed that stationary regime was not completely reached after 55 minutes, and therefore, a longer measuring period would be necessary when using the same chamber set up. As an alternative solution, increasing the ventilation rate would reduce this period of transitory regime.

The performance of the chamber was appropriate, particularly to characterise emissions from rabbits. If the objective were to measure emissions from manure, a smaller chamber would be preferable for two reasons: firstly, reduced dimensions would facilitate the chamber's operation; secondly, the time to reach the stationary regime would be shorter according to Eq. 6.

4.3.3. Chamber design and operation

Considering the results obtained in these trials, several advantages should be noted regarding the chamber design and operation.

The material (PMMA) used is resistant (suitable for farm conditions), light enough to be handled easily and transparent so animals can see through it. Furthermore, as it is used indoors, the temperature is not affected by solar radiation (Shah et al., 2006b). For these reasons, a chamber with these characteristics may be deemed appropriate to measure emissions from animals and manure.

Regarding to the cost of the chamber, it is widely spread that dynamic chambers are one of the cheapest methods to measure emissions from point-sources like animals or small manure surfaces (Farrell, 1972; Shah et al., 2006a). However, the chamber cost can vary considerably depending on the accessories used, especially the air pump or fan and the gas analyzers. The cost of constructing the experimental chamber was approximately € 400, not including gas sensors, air pumps and other material (such as the cage, the drinker and the feeder).

The chamber described herein was appropriate to measure animal emissions, according to the morphology and size, and it was similar to the one used with poultry by Wang and Huang (2005). The surface area available for each animal inside the chamber (2,400 cm^2) is larger than those usual in commercial farms, which range between 400 and 700 cm^2 (Trocino and Xiccato, 2006). The cage height (40cm) is similar to common commercial cages, which vary between 30 and 40 cm (Trocino and Xiccato, 2006). Likewise, the chamber design was appropriate to determine manure emissions, since the surface area is similar to other chambers used before (Blanes-Vidal et al., 2007; Boriack, C. K., 2005; Skiba et al., 2006). However, as for the shape of the chamber and manure emissions, there is no clear recommendation in the literature, so it can be considered that it is not a highly determining factor.

4.4. Conclusions

Dynamic chambers are extremely useful to measure greenhouse gas and ammonia emissions from animal production.

When using the chamber to measure rabbit emissions (e.g. CO_2, CH_4), a 24-hour period is recommended to consider the daily variation in gas emissions from animals. To avoid excessive emissions from this source, longer measuring periods are not recommended unless faeces and urine are extracted from the chamber. It is also necessary to consider the period of animal adaptation to the chamber, in which emissions are not representative. According to the findings, an adaptation period of approximately 1 hour should be established. A ventilation flux of 0.423 $m^3 \cdot h^{-1}$ fulfils most animal needs, although high relative humidity levels are reached. Higher ventilation flows are therefore recommended to avoid condensation of water vapour. This is a crucial issue if ammonia

concentrations are also being measured, due to the ability of this gas to mix with water and condensate, which would cause a decrease in ammonia concentration.

To measure manure emissions (NH_3 and CO_2), the chamber used in this research performed properly. However, the use of a smaller chamber would reduce the measuring time and make the operation easier. The chamber airflow rate, however, cannot be previously established for all experiments; it depends on the emitting potential of the manure and must be determined for each experiment.

4.5. Acknowledgements

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Chapter 5

Daily carbon dioxide emission and activity of rabbits during the fattening period

An adapted version of this chapter has been published as:

Estellés, F., Rodríguez-Latorre, A.R., Calvet, S., Villagrá, A., and Torres, A.G. (2010). Daily carbon dioxide emission and activity of rabbits during the fattening period**.** ***Biosystems Engineering, 106(4), 338-343.***

Daily carbon dioxide emission and activity of rabbits during the fattening period

Abstract

Carbon dioxide balance is a powerful tool for determining ventilation rates in animal buildings. Accurate values for carbon dioxide emissions from animals and the daily variation of these emissions are required to work with these balances. Traditionally, the daily variation of carbon dioxide has been related to daily patterns of animal activity. Little information is available about carbon dioxide emissions from fattening rabbits. Carbon dioxide emissions from 21 fattening rabbits were measure throughout the fattening period. Emissions from each single animal were monitored during 24 h, using a flux chamber. Ten of these rabbits were monitored by video and their activity was assessed for the 24-hour periods. Results showed an average carbon dioxide emission rate per rabbit of 1.98±0.72 l h^{-1}, for an average weight of 1,240±412 g. An exponential relationship between animal weight and carbon dioxide emission was observed. Sinusoidal daily patterns of carbon dioxide emission and relative animal activity were determined and described using equations. A positive relationship between carbon dioxide emission and relative animal activity was observed, although differences in the amplitude of the curves were found: 16% of the average value for carbon dioxide emission and 41% for relative activity.

Keywords: fattening rabbits, carbon dioxide, emissions, metabolic rate, activity, daily pattern.

5.1. Introduction

The intensive rearing of rabbits for meat production is a specialised farming activity in certain countries, most of them located in the Mediterranean area. Several studies have been carried out in order to study rabbit management, nutrition and genetics but the impact on environmental pollution of this activity is not well known. In particular, few research papers can be found related to airborne emissions from rabbit (Hol et al., 2004; Michl and Hoy, 1996)

Airborne emissions from livestock facilities are usually estimated by means of mass balances. In these balances the difference between incoming and outgoing fluxes in a building is defined as the emission rate.

To determine these incoming and outgoing matter fluxes, two factors are needed: mass concentrations and airflow rates. The measurement of gas, dust and odour concentrations can be achieved, with adequate accuracy, by using a variety of techniques (Chen et al., 1999; Ni and Heber, 2001). However, measuring the ventilation rate in an animal house is one of the main challenges in estimating these emissions. Airflow rates can be determined using several methods. According to Phillips et al. (2001) they can be classified in two main groups regarding to their nature; indirect and direct measurement methods. The first one consists of using a tracer, which allows us to determine the ventilation flux both in mechanically and naturally ventilated houses. Direct measurement methods consist of determining the airflow rates through all openings in a building. This latter group of techniques is generally more accurate, but they can be used only in mechanically-ventilated houses and when all openings can be assessed.

When measuring airborne emissions from commercial livestock buildings, direct airflow measurements are difficult to apply in practice. Even in mechanically-ventilated buildings sometimes this technique cannot be applied because of technical difficulties associated with calibrating the fans, e.g. this is not usually possible without disturbing the normal operating procedures. Also, even if it is possible it is time-consuming (Pedersen et al., 1998).

Indirect methods are therefore a useful alternative for determining airflow rates in most situations. The principle of the indirect method is to monitor the inlet and outlet concentrations of a tracer gas with a known release rate. The airflow can then be calculated by applying a mass balance. The ideal characteristics of a tracer include a low and stable background level, safety, acceptability, ease of measurement, stability and low cost (Phillips et al., 2001). Carbon dioxide, which is emitted naturally from farms, fulfils all

these characteristics. Consequently, CO_2 balances have been commonly used in Europe to determine the ventilation rates in livestock buildings (Pedersen et al., 1998).

To develop these CO_2 balances it is necessary to know the amount of CO_2that is being released in the building. After a comprehensive literature review (CIGR, 2002), CO_2 emission rates have been provided for most livestock species and categories, such as poultry, cattle and pigs. Little information is available for rabbits. Some general values are provided in the same CIGR document and other authors provide experimental results in which carbon dioxide emissions from rabbits were measured (e.g. Estellés et al., 2009; Kiwull-Schöne et al., 2001; 2005), but no information is available about its daily pattern of CO_2 emission or its relationship with rabbit body weight.

If a 24-hour average value for CO_2 production is used to estimate the airflow, an error may occur due to the diurnal variation of emissions from the animals (Pedersen and Jorgensen, 2004). It is known that CO_2 emissions are related to the activity rate of the animals (van Ouwerkerk and Pedersen, 1994), and it is also known that this activity rate can vary during the day following a circadian rhythm (Kennedy et al., 1994). For this reason, when determining airflow rates using a CO_2 balance, knowledge about the daily variation in CO_2 production rate is required.

Animal activity has been traditionally used as a tool to determine the daily variation in heat production, mainly using sinusoidal variation patterns (Blanes and Pedersen, 2005; CIGR, 2002). Some authors, however, have found differences between the daily patterns of activity and respiration variables both in terms of phase (the time gap between variables) and amplitude (Seifert et al., 2000; Seifert and Mortola, 2002).

The aim of the research reported here was to determine the CO_2 emission rate from fattening rabbits and observe the effect of animal weight, hour and animal activity on these emissions.

5.2. Materials and Methods

5.2.1. Experimental layout

A flux chamber (600 mm long x 400 mm wide x400 mm high) built in Poly(methyl methacrylate) (see complete description in Estellés et al., 2009), was placed in one of the fattening rabbit rooms (with around 1,800 rabbits) in a farm located at the Universidad Politécnica de Valencia, Valencia, Spain. The experiment was conducted during August and September, 2008. The lighting in the rabbit house followed the natural rhythm of day light without use of artificial lights, with approximately 13 hours of light (07.00h to 20.00h). Inside the chamber the following devices were installed; two air pumps for ventilation

(Resun® Silent-Pump AC-9002, Guangdong Risheng Group Co., Ltd., Shenzhen, China), a small fan to circulate the air inside the chamber (Power Logic PL80S12M, Power Logic, Taipei Hsien, Taiwan), a water dispenser and a feeder.

Twenty-one hybrid rabbits (New Zealand White x Californian) were selected for the study. During the five week fattening period, five animals in their first week after weaning and four animals from each week of age were measured. Each rabbit was placed in the flux chamber for a 24-hour period. The rabbits were weighed at the beginning and at the end of each experiment. Animals were fed *ad libitum*, and the feeder and the water dispenser were weighed before and after the experiment to assess feed and water consumption.

5.2.2. Carbon dioxide emissions

For the measurement of gas emissions, two CO_2 sensors (Vaisala GMT-222, 0-10,000 ppm, Vaisala Oyj., Helsinki, Finland) were placed to measure internal and external gas concentrations. Carbon dioxide concentrations were recorded every five minutes with a data logger (HOBO H8 RH/Temp/Out, Onset Computer Corp., Pocasset, MA, USA.). Temperature and relative humidity were also measured with the same frequency as CO_2 concentrations, using two data loggers (HOBO H8 RH/Temp, Onset Computer Corp., Pocasset, MA, USA.), one of them inside the chamber and the other one outside. Pump flux was measured daily by means a rotameter (Yokogawa RAGH, Yokogawa Electric Corportation, Tokyo, Japan).

Emissions were calculated on a five-minute basis, using the general mass balance equation (Eq. 1);

$$E = \left(C_{outlet} - C_{inlet}\right) Flux\ 10^{-3} \qquad \text{Eq. 1}$$

where E is gaseous emission (l h^{-1}), C_{outlet} is the outlet air gas concentration (ppm), C_{inlet} is inlet gas concentration (ppm), and *Flux* is air exchange flux (m^3 h^{-1}).

The average CO_2 emissions were related to the animal weight in order to find a relationship between both terms.

To study the daily emissions pattern, the daily relative values of CO_2 emissions were calculated in order to homogenise the data for all animals, using

$$E_{i\_REL} = 100\ E_i / E_{AVG} \qquad \text{Eq. 2}$$

where $E_{i\ REL}$ is the relative emission (% of the daily mean) for each hour *i*, E_i is the emission value (l h^{-1}) for each hour *I*, and E_{AVG} is the daily average emission (l h^{-1}).

5.2.3. Activity assessment

A video camera (SONY® DCR-HC17E, Sony Corp., Tokyo, Japan), equipped with an infrared emitter (SONY® NightShot Plus, Sony Corp., Tokyo, Japan) was installed over the chamber. Video recordings of all tested rabbits were recorded during the experiment. Ten of the videos were selected according to the age of the rabbit. From each week, the videos corresponding to two animals were selected at random. These videos were assessed in order to determine the behaviour of the animals. The observed activities were recorded as lying, sleeping, sitting, eating, drinking, walking, standing and others. The start and end time of each activity was registered so the duration of each activity during the 24-h period could be defined.

The time during which the animal was lying, sleeping and sitting was considered as being an inactive period, while when the animal was performing other activities it was considered as an active period. An hourly relative activity index (AI) was calculated using Eq. 3

$$A_{i\_REL} = 100 \sum \left(Ea_i + D_i + W_i + S_i + O_i \right) / 3{,}600 \qquad \text{Eq. 3}$$

where AI_{i_REL} is the relative activity index (%) for each hour *i*, Ea_i is the time (s) spent by the animal eating during hour *i*, D_i is the time (s) spent by the animal drinking during hour *i*, W_i is the time (s) spent by the animal walking during hour *i*, S_i is the time (s) spent by the animal standing during hour *I*, and O_i is the time (s) spent by the animal performing other non-categorised activities during hour *i*.

5.2.4. Data analysis

A non linear regression was developed to determine the relationship between live animal weight and average CO_2 emissions. NLIN procedure of SAS Software (SAS, 2001) was used to this end. The regression equation is presented below.

$$E_A = \alpha \; LW^{\beta} \qquad \text{Eq. 4}$$

where E_A is the average daily CO_2 emission (l h^{-1}), α is a constant, *LW* is animal live weight (kg), and β is an allometric constant.

To analyse the circadian rhythm which describes the daily pattern of CO_2 emissions and animal activity, a non linear regression was also developed. Hourly average values for both terms were calculated for each animal. In addition, in order to homogenise the data for all animals, daily relative values were calculated using the following equation:

$$X_{i\_REL} = 100 \; X_i / X_{AVG} \qquad \text{Eq. 5}$$

where X_{i_REL} is the relative value for hour *i* (i.e. % of the daily mean), X_i is the measured value for hour *i*, and X_{AVG} is the daily average value.

It is known that circadian rhythms are periodic oscillations, therefore a Fourier transformed series was modelled. Considering the daily basis of the data, the length of the period was established in 24 h. The NLIN procedure of SAS was used again (SAS, 2001). The regression equation modelled was

$$X_{i\_REL} = 100 - A\cos\left(\frac{t2\pi}{24} - \frac{t_{\min}2\pi}{24}\right) \quad \text{Eq. 6}$$

where *A* is the modelled amplitude (% over daily average), t_i is the hour of the day (h), and t_{min} is the time at which the minimum value is achieved (h).

5.3. Results and discussion

5.3.1. Carbon dioxide emission

The results were similar to those obtained at the same experimental farm by Calvet et al (2008) and Estellés et al (2009), with an average feed consumption of 72.7±18.9 g per kg LW and water consumption of 189.8±105.2 ml per kg LW. The average daily gain was 48.1±26.0 g day^{-1}. Average results per week of age of the animals are presented in ***Table 1***.

Table 1. Number of animals, average weight, daily gain, feed and water consumption during the experiment for each week of age

Age (weeks after weaning)	*n*	*Average weight (g)*	*Daily gain (g day^{-1})*	*Feed consumption (g day^{-1})*	*Water consumption (ml day^{-1})*
1	5	721±173	66±21	63±21	138±55
2	4	1,038±63	42±31	75±19	220±118
3	4	1,217±153	55±6	93±10	348±154
4	4	1,626±171	38±42	85±17	175±78
5	4	1,715±184	35±13	120±14	233±26

The average carbon dioxide emission rate was 1.98±0.72 l h^{-1}, for an average weight of 1,240 g, which is higher than reported by Estellés et al (2009) where 1.26±0.12 l h^{-1} was obtained for an average weight of 853 g. By contrast Kiwul-Schone et al (2001; 2005) found higher emission values, ranging between 2.12 and 2.27 l h^{-1} for older animals with a live weight ranging between 3,260 and 3,520 g.

The relationship between emission rates and animal weight determined for this experiment was

$$E_A = 1.66\ LW^{0.85} \qquad \text{Eq. 7}$$

The power of this equation (β=0.85, s.e. 0.12, p<0.05) is directly related to the metabolic activity of the animal. Traditionally, this value has been established as 0.75 (White and Seymour, 2003), and heat production equations have been obtained using this relationship (van Ouwerkerk and Pedersen, 1994). In fact, CIGR (2002) report this value for most of the animals (cows, fattening pigs, sows, sheep, goats, horses and poultry). By contrast, for some species such as turkeys and some animal categories such as calves, heifers and piglets this value is slightly different, varying from 0.66 to 0.77 (CIGR, 2002). Lee (Lee, 1939) also found a value of 0.81 for a similar equation relating basal heat production rate and body weight for adult rabbits.

If the value β = 0.75 (metabolic weight) is forced into in the regression then Eq. 8 is obtained.

$$E_{A'} = 1.72\ LW^{0.75} \qquad \text{Eq. 8}$$

The scale factor of the equation (α=1.72, s.e. 0.06, p<0.05) represents the average emission value per unit of metabolic weight. This value is higher than those provided by the CIGR (2002) for cows (1.036) and fattening pigs (0.942), but slightly lower than that for broilers (1.965). This variation among species may be caused by the inverse relationship between metabolic rate and animal size.

Average daily CO_2 emissions for each single animal according to their body weight are shown in ***Fig. 1***. Regression lines between CO_2 production and LW (for β = 0.85 and β = 0.75) are also drawn on the same figure.

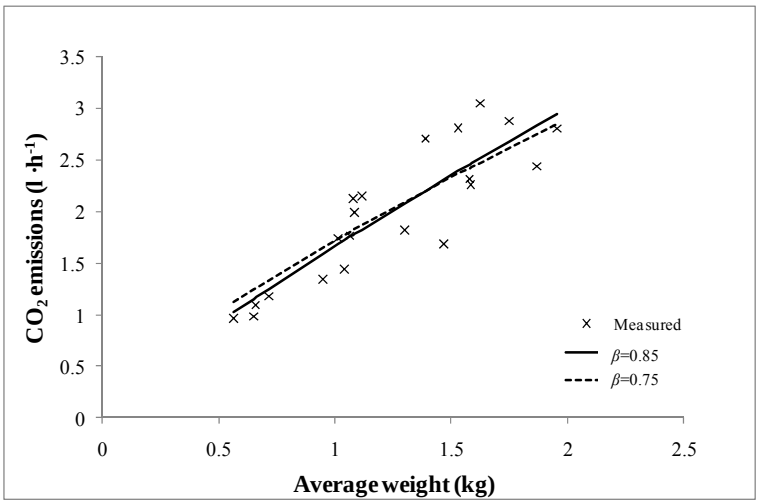

Fig. 1. Measured carbon dioxide emissions (l h^{-1}) and regression lines according to the average weight of the animals.

The daily emission pattern was identified in which a circadian rhythm can be observed (Anders, 1982). This pattern can be modelled by means of Eq. 9.

$$E_{REL} = 100 - 16.14\cos\left(\frac{t2\pi}{24} - \frac{14.87\ 2\pi}{24}\right) \quad \text{Eq. 9}$$

The amplitude of the wave indicates the absolute difference between extreme (maximum or minimum) and average daily values was 16.14% (s.e. 0.83, $p<0.05$). This value is lower than those proposed by CIGR (2002), for fattening pigs fed *ad libitum* and for daylight which ranged from 25 to almost 100% depending on their weight. According Eq. 9, the minimum emission is produced at 14:52 (14.87, s.e. 0.20, $p<0.05$).

5.3.2. Activity pattern

A daily pattern on animal activity was identified and fitted using Eq. 10.

$$AI_R = 100 - 40.65\cos\left(\frac{t2\pi}{24} - \frac{13.79\ 2\pi}{24}\right) \quad \text{Eq. 10}$$

A higher value for the amplitude was found in this case (40.65%, s.e. 5.76, $p<0.05$). This value is in the range proposed by CIGR (2002) for other animal types such as fattening pigs (43-53%), heifers (38%) and lactating sows (35%), but much higher than for broilers housed with permanent light conditions and *ad libitum* feeding (8%).

Regarding the daily variation, lower activity was generally observed during the daytime. The hour when the minimum activity is expected was established at 13:47 (13.79 s.e. 0.54, $p<0.05$). This pattern does not agree with the general one found by CIGR (2002) for most of the farm animals studied where higher activity rates occur during daytime, mainly related to feeding operations. In this sense, the rabbit is considered as being a nocturnal animal (Jilge, 1991) and its active period has been established previously as being between 23:00 and 5:00 (Princz et al., 2008).

With regard to the relationship between CO_2 production and activity index daily patterns, a direct relationship can be found (***Fig. 2***).

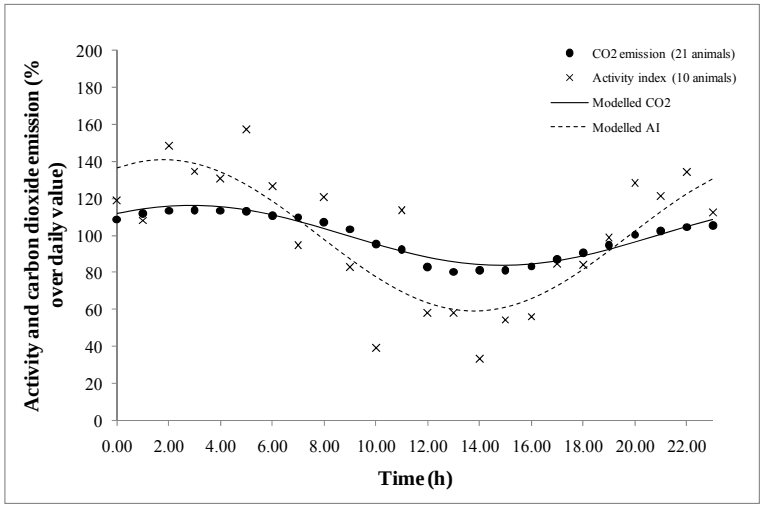

Fig. 2. Average carbon dioxide emissions (n=21) and activity (n=10) daily patterns.

However, despite that relationship a difference in the phase of approximately 1 h was observed. This difference may arise from the measurement method used, as the time that takes to homogenise the air in the chamber when an emission source is present is approximately 1 h (Estellés et al., 2009). A significant difference in the amplitude of both curves was detected (16% and 41% for CO_2 production and activity respectively). This difference agrees with previous experiments carried out with rodents (Seifert et al., 2000; Seifert and Mortola, 2002). In fact, it is well known that animals have a basal metabolic activity independent of their behaviour, leading to a basal CO_2 production independent of their activity as defined by the tranquil CO_2 exhalation rate (TCER) (Ni et al., 1999). This has several implications when relating CO_2 and animal activity daily variations, since the relationship between both terms is not direct. Therefore, the absolute activity daily

variation cannot be considered as being a good estimator to determine the absolute daily pattern of CO_2 emissions, and a scale factor should be used.

5.4. Conclusions

Average CO_2 emission factor for fattening rabbits in these experiments was established at 1.98±0.72 (l h^{-1}). A positive relationship between this emission rate and the live weight of the animals was also demonstrated and two regression models were developed.

A clear sinusoidal daily pattern was found for CO_2 emissions as well as for the activity of the animals. Those patterns confirmed a higher metabolic rate during night-time. Both patterns were modelled, providing a prediction line to determine carbon dioxide emissions and activity rate daily patterns. The amplitude of the sinusoidal function was established at 16% of the average value for CO_2 production and 41% for the activity index.

This daily CO_2 emission pattern is a powerful tool for the determination of airflow rates, through the development of CO_2 balances in rabbit fattening facilities, thereby avoiding the error that can occur when using daily average emission values.

Using the activity index pattern as an estimator to determine the carbon dioxide production variation can lead to errors, due to the observed amplitude differences between activity and emission curves.

5.5. Acknowledgements

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Chapter 6

Use of CO_2 balances to determine ventilation rates in a fattening rabbit house

Use of CO_2 balances to determine ventilation rates in a fattening rabbit house

Abstract

Determining accurately the ventilation rates from rabbits houses, using non-expensive and non-invasive methods, is needed. The main aim of this work was to test the carbon dioxide balance as a method to determine the ventilation rate in fattening rabbit farms. In addition, the CO_2 release rate from rabbit manure was determined, and the effect of CO_2 concentrations gradient between the inlet and outlet of the building, on the method accuracy was characterized. To these aims, a fattening rabbit farm was evaluated during two periods. CO_2 concentrations were simultaneously determined in the inlet and outlet air by using a photoacoustic monitor. Ventilation rates were also directly determined by calibration of the exhaust fans and monitoring their operation times. CO_2 emissions from manure were determined during a whole fattening period. Emissions were measured using a flux chamber and a photoacoustic monitor. The effect of CO_2 concentrations gradient between the inlet and outlet of the farm on the accuracy of the balance was studied through statistical regressions. The CO_2 emission from manure resulted in 13% of total CO_2 emissions (considering both manure and animals). No statistically significant differences were found between measured and calculated ventilation rates. The effect of the CO_2 gradient on the balance accuracy was statistically significant only in one of the trials. According to these results, the CO_2 balance can be recommended for the determination of ventilation rates in fattening rabbit buildings.

Keywords: fattening rabbits, carbon dioxide, ventilation rate, CO_2 balance.

6.1. Introduction

The intensive rearing of rabbits for meat production is a specialised farming activity in certain countries, most of them located in the Mediterranean area. Several studies have been carried out in order to study rabbit management, nutrition and genetics but the environmental pollution impact of this activity is not well known. In this sense, few publications can be found related to airborne emissions from rabbit farms (Hol et al., 2004; Michl and Hoy, 1996).

Airborne emissions from livestock facilities are usually estimated by means of mass balances. In these balances the difference between incoming and outgoing matter fluxes for the building measured is defined as the emission rate.

To determine these incoming and outgoing matter fluxes, two factors are needed: mass concentrations and airflow rates. The measurement of gas, dust and odour concentrations can be achieved, with adequate accuracy, by using a variety of techniques (Chen et al., 1999; Ni and Heber, 2008). On the contrary, measuring the airflow in an animal house is one of the main challenges that can be found to estimate these emissions. Airflow rates can be determined using several methods. According to Phillips et al. (2001) they can be classified in two main groups regarding to their nature: indirect and direct measurement methods. The first one consists of using a tracer, which allows us to determine the ventilation flux both in mechanically and naturally ventilated houses. Direct measurement methods consist of determining the airflow rates through all openings in a building. This second group of techniques is generally more accurate, but they can be used only in mechanically-ventilated houses and when all openings of the farm can be assessed.

When measuring airborne emissions from commercial livestock buildings, direct airflow measurements are difficult to apply in practice. As explained before, these methods can not be applied in naturally-ventilated buildings but even in mechanically-ventilated ones it may be a challenging task, due to the technical difficulties associated (e.g. calibrating the fans may disturb their normal operation procedure). Even if it is possible, this task is time-consuming (Pedersen et al., 1998).

Indirect methods arise then as a useful alternative, which allow us to determine airflow rates in most situations. The principle of the method is to monitor the inlet and outlet concentrations of a tracer gas with a known release rate. The airflow can then be calculated by applying a mass balance. The ideal characteristics of a tracer include low and stable background level, no hazard, acceptability, ease of measurement, stability and low cost (Phillips et al., 2001). Carbon dioxide, which is emitted naturally on the farm, fulfils all these characteristics, and consequently, carbon dioxide balances have been commonly

used in Europe to determine the ventilation rates in livestock buildings (Pedersen et al., 1998).

6.1.1. Carbon dioxide balances

Considering mass conservation under steady state conditions in the building, the general equation for the carbon dioxide balance can be expressed as follows (Eq. 1):

$$V_{CO_2} = \frac{CO_{2rel}}{\left(CO_{2outlet} - CO_{2inlet}\right)} \qquad \text{Eq. 1}$$

where, V_{CO2} is the ventilation flux estimated using the CO_2 balance ($m^3\ h^{-1}\ animal^{-1}$), CO_{2rel} is the CO_2 release rate ($mg\ h^{-1}\ animal^{-1}$), $CO_{2outlet}$ and CO_{2inlet} are the CO_2 concentrations ($mg\ m^{-3}$) in the outlet and inlet of the building respectively.

Therefore, to develop these CO_2 balances it is necessary to know the amount of carbon dioxide that is being released in the building (CO_{2rel}).

6.1.2. Carbon dioxide production

There are two sources of CO_2 in an animal house: animals and manure. Most of the CO_2 released in the building is originated by the animals during respiration processes while the rest is originated from the decomposition of manure (van Ouwerkerk and Pedersen, 1994) After a comprehensive literature review (CIGR, 2002), carbon dioxide emission rates have been provided for most animal species and categories, such as poultry, cattle and pigs. For rabbits, some general values are provided in the same CIGR document and other authors provide experimental results in which CO_2 emissions were measured (e.g. Kiwull-Schöne et al., 2001; 2005; Estellés et al., 2009).

It is known that the metabolism of the animals is not constant during the day, thus the production of CO_2 cannot be considered constant during the day for most animal species CIGR (2002). A relationship between the amount of CO_2 released by the animals and their daily activity pattern has been described in the literature (Blanes and Pedersen, 2005; Pedersen et al., 1998). The CIGR (2002) proposes sinusoidal curves to model this daily variation on animal activity and CO_2 production for most livestock species but for rabbits. Estellés et al (2010) proposed a cosine model to predict daily variations in CO_2 production from fattening rabbits.

Regarding to the amount of carbon dioxide that is emitted by the manure in the building, van Ouwerkerk and Pedersen (1994) proposed a relationship of 4% over the CO_2 production from animals. Other authors used a constant emission rate independently of the emissions from animals (Xin et al., 2009), or even neglect this factor (Li et al., 2005).

Therefore, if considering the effect of manure in carbon dioxide emission, as well as both factors affecting carbon dioxide release rates from the animals, Eq. 1 can be expanded to Eq. 2:

$$V_{CO_2} = \frac{CO_{2rel\_anim} D + CO_{2rel\_manure}}{\left(CO_{2outlet} - CO_{2inlet}\right)} \quad \text{Eq. 2}$$

where, CO_{2rel_anim} is the CO_2 produced by the animals (mg h^{-1} $animal^{-1}$), D is the correction factor for daily variation of animal activity (dimensionless) and CO_{2rel_manure} is the CO_2 produced by the manure (mg h^{-1} $animal^{-1}$)

The accuracy of carbon dioxide balance methods when determining ventilation rates has been demonstrated for most of farm species, such as poultry (Li et al., 2005; Xin et al., 2009) and pigs (Blanes and Pedersen, 2005), but not for rabbits.

Therefore, the aim of this work was to test the accuracy of carbon dioxide balances to estimate ventilation rates in fattening rabbit houses, by comparing ventilation rates measured and calculated through the CO_2 balance in two fattening rabbit houses at different measuring integration times. In addition, the CO_2 emission rate from manure was determined, and the effect of CO_2 concentrations difference between the inlet and outlet of the farm, on the accuracy of the balances, was studied.

6.2. Materials and Methods

Two experiments were developed in order to test the reliability of CO_2 balances to determine ventilation rates in fattening rabbit buildings. The experimental fattening rabbit farm (1,560 places) located in the Universidad Politécnica de Valencia (Valencia, Spain) was monitored to characterize CO_2 emissions, by simultaneous measurements of ventilation rates and CO_2 concentrations.

Fattening rabbits (*Oryctolagus cuniculus*) were used, resulting from the New Zealand x Californian cross (Khalil and Baselga, 2002). The farm had a conventional management for fattening rabbits in the Spanish Mediterranean area. Animals were reared in collective cages (80x50 cm and 9 animals per cage on average) above a manure pit.

Two periods were selected for the measurements in order to obtain representative data of different environmental conditions. The first experiment (Trial 1) was performed at the beginning of summer while the second one (Trial 2) took place at the end of autumn. The first experiment took 14 consecutive days in which the average weight of animals was 1.33 kg. During the second experiment 19 complete measurement days were taken in two

batches. The first one lasted for 10 days and the second one took place one week later. In this case, the average weight of the animals in the building was 1.63 kg.

6.2.1. Ventilation rate measurement

The house was equipped with constant flow wall fans. Ventilation rates were calculated considering the operation time of each fan and the corresponding fan performance at the nominal pressure drop in the farm. The percentage of time each fan was operational was registered by means of an electrical circuit connected to the auxiliary contacts of the fan relays (Calvet et al., 2010). Fan status was recorded every minute by means of a voltage data logger (HOBO H08-004-02, Onset Computer Corp., USA). Each fan was calibrated for airflow before and after each experiment, multiplying the free flow area by the average air speed in the fan. Air velocity was measured at 24 points of the cross section of the fan by means of a hot wire anemometer (Testo® 425; with measurement range 0 to 20 m s^{-1}) following the general recommended procedure (ASHRAE, 2001). Ventilation rates were then integrated and determined for period of two hours.

6.2.2. Gas concentrations and environmental conditions measurement

CO_2 concentrations were measured using a photoacoustic gas monitor (Innova-1412, Air Tech Instruments, Denmark). Air samples were conducted through Teflon tubes to a multiplexing system which allowed consecutive measurements at eight points every two hours. Six sampling points were placed inside building, which were located at the air exhaust to determine $CO_{2outlet}$. Two sampling points were used to determine background concentrations (CO_{2inlet}) by placing them outside the building. Temperature sensors (HOBO H8-004-002, Onset Computer Corp.) were also located outside the building.

6.2.3. Carbon dioxide release rate

Carbon dioxide production from fattening rabbits can be determined according to their live weight following the regression equation (Eq. 3) found in an experimental work by Estellés et al (2010):

$$CO_{2rel\_animal} = 2{,}660\ LW^{0.85} \qquad \text{Eq. 3}$$

where, LW is the live weight of the animal (kg)

Regarding the daily variation, the circadian rhythm for CO_2 production described by Estellés et al (2010) can be expressed by Equation 4 related to the hour of the day (0-24 hours)

$$D = 1 - 0.16\ \cos\left(h\ 2\ \pi\ 24^{-1} - 14.87\ 2\ \pi\ 24^{-1}\right) \qquad \text{Eq. 4}$$

where, *h* is the hour of the day.

Carbon dioxide released from manure was determined by direct measurement of emissions from representative manure samples in a dynamic chamber (Estellés et al., 2009), during two complete fattening cycles (five weeks each).

During each cycle, manure samples were taken by placing three 20x13 polymethyl methacrylate (PMMA) boxes in the manure pit below the cages (one box per cage). Cages were installed five days before the measurement and the manure produced by the rabbits in these days was accumulated.

A polymethyl methacrylate (PMMA) chamber was used to determine the emissions. The chamber had a 29x49 cm base and 29 cm height, with 4 mm thick walls. One extraction pump (Silent-pump AC-9902) was used to vent the chamber with a ventilation flow of 3 L/min, which was tested, before and after each measurement, using a flow meter (Yokogawa RAGH, Yokogawa Electric Corporation, Japan). A small fan was used to homogenise the air inside the chamber. CO_2 concentrations were measured every two minutes using a photo acoustic gas monitor (INNOVA 1412, Air Tech Instruments, Denmark). According to Estellés et al. (2009) and considering chamber dimensions and the ventilation flow, it was estimated that the equilibrium of gas concentrations was reached after approximately 45 minutes. The gas emission rate was estimated during 20 minutes after equilibrium was reached.

6.2.4. Data analysis

The absolute value of relative difference (*Diff*) between estimated and measured ventilation rate was used as an indicator of the accuracy of carbon dioxide balances. This relative difference was calculated for each bihourly period following Eq. 5:

$$Diff = Abs\left(\frac{V - V'_{CO_2}}{V}\right) \qquad \text{Eq. 5}$$

where, *V* is the directly measured ventilation rate ($m^3\ h^{-1}\ animal^{-1}$)

In order to assess the effect of carbon dioxide concentrations difference between the inlet and the outlet, on the accuracy of the method, a regression analysis was performed. PROC REG of SAS (SAS, 2001) was used to this aim. The following model equation was used (Equation 6):

$$Diff = \alpha + \beta \times \ln\left(\Delta CO_2\right) + \varepsilon \quad (6)$$

where, ΔCO_2 is the difference of CO_2 concentrations (in mg m^{-3}) between the inlet and outlet of the building

6.3. Results

6.3.1. CO_2 emission from manure

The results on CO_2 emissions from manure during the 5 measured weeks are presented in ***Table 1***.

Table 1. Average (±s.e.) CO_2 emission rates from manure measured during five weeks

Period	*Week 1*	*Week 2*	*Week 3*	*Week 4*	*Week 5*	*Average*
CO_2 emissions (mg h^{-1} $animal^{-1}$)*	42 ± 14	124 ± 66	590 ± 88	563 ± 140	1,125 ± 187	489 ± 87

*The average surface occupied by each animal was 0.044 m^2

The average CO_2 emission rate during the whole cycle was 489 ± 87 mg h^{-1} $animal^{-1}$, following an upward trend as animals grew up. Considering than the average CO_2 emission rate from animals during the whole fattening cycle is 3,221 ± 1,171 mg h^{-1} $animal^{-1}$ Estellés et al (2010), emissions from manure represent 13.18% of total CO_2 emissions in fattening rabbits farms.

6.3.2. Carbon dioxide concentrations

CO_2 concentrations measured in both farms are shown in ***Fig. 1***.

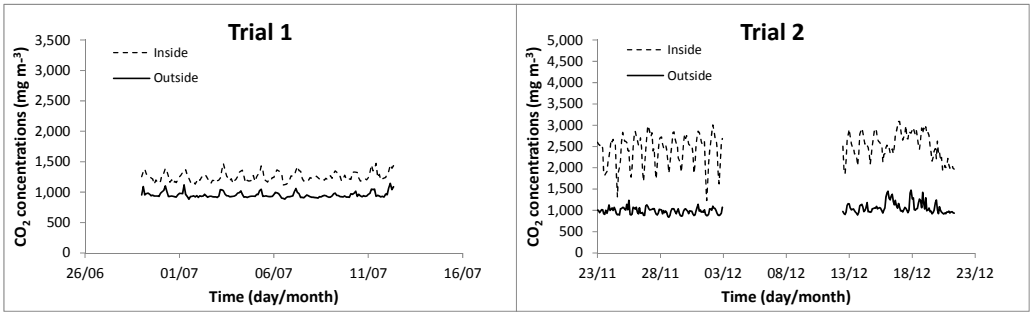

Fig. 1. CO_2 concentrations registered in both experiments.

Average CO_2 concentrations in the outside were similar in both experiments (954 ± 46 mg m^{-3} for Trial 1 and 1,024 ± 114 mg m^{-3} for Trial 2). CO_2 concentrations inside the building were on average 1,253 ± 77 mg m^{-3} for Trial 1 and 2,464 ± 347 mg m^{-3} for Trial 2.

Regarding to the daily variation of concentrations, ***Fig. 2*** includes the average concentrations for each hour registered in both experiments.

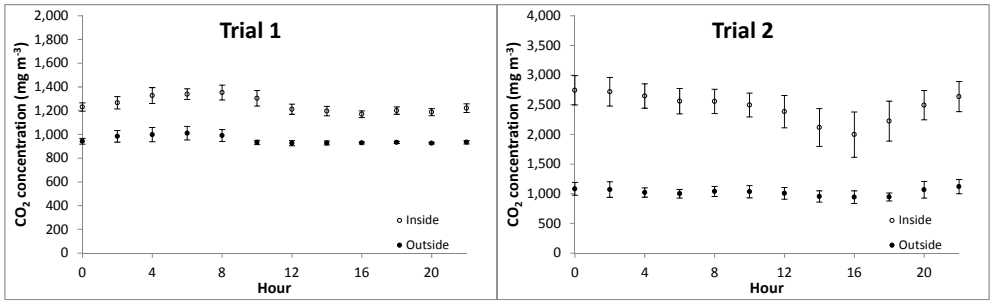

Fig. 2. Average (± s.d.) hourly CO_2 concentrations observed in both experiments.

Little effect of time of the day is observed on outside concentrations while this is higher for inside concentrations. Also this effect is higher in autumn measurements in which a higher variability is observed.

Concentrations differences between the inlet and outlet air ranged from 194 to 536 mg m^{-3} in Trial 1 and 357 to 2,013 mg m^{-3} in Trial 2.

6.3.3. Comparison between measured and calculated ventilation flows

Results of measured and calculated ventilation rates for both experiments, as well as outside temperatures are presented in ***Fig. 3***.

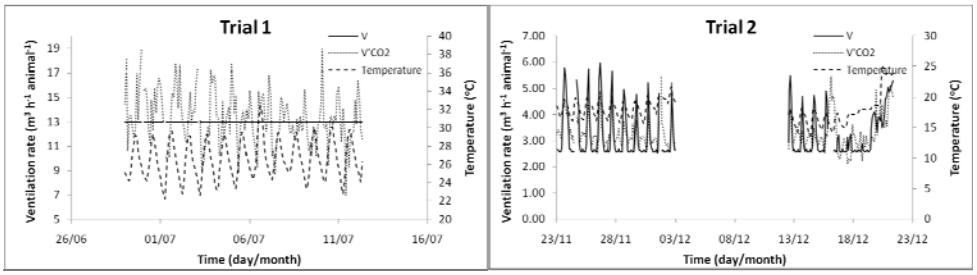

Fig. 3. Measured and calculated ventilation rates and outside temperatures for both experiments.

Regarding the direct measurements, as expected, higher ventilation rates were observed for summer conditions (constant at 12.99 m^3 h^{-1} $animal^{-1}$), than for autumn (3.24 ± 0.92 m^3 h^{-1} $animal^{-1}$).

Despite during Trial 1 no daily variation for ventilation rates is observed, in Trial 2 a clear daily pattern on ventilation rates can be noticed. The average ventilation rate determined using the CO_2 balances was 13.3 ± 2.2 m^3 h^{-1} $animal^{-1}$ in summer and 3.3 ± 0.6 m^3 h^{-1} $animal^{-1}$ in autumn conditions. Attending to these results of the t-test, differences were not significant for Trial 1 ($p>0.07$, $n=158$), neither for Trial 2 ($p>0.92$, $n=218$).

6.3.4. Effect of CO_2 concentrations difference on balance accuracy

There was no effect of CO_2 concentrations difference on the accuracy in Trial 1 since the slope (β) of the regression was not significant (p>0.5). This may be caused by the low variability of CO_2 concentrations differences, the small values of these differences, and the fixed ventilation rate measured in this case.

On the contrary, for Trial 2 the calculated slope (β=-0.27±0.04) resulted highly significant (p<0.001). Attending to the result of this regression, considering α=2.14±0.32 (p<0.001, R^2=0.14), the absolute error of the balance method achieves values below 10% when CO_2 differences become higher than 2,000 mg m^{-3}, and below 5% for differences higher than 2,325 mg m^{-3}.

6.4. Discussion

6.4.1. CO_2 emission from manure

The value obtained in this work for the CO_2 emissions from manure, in relation to the total CO_2 emissions in the farm, is over the range reported by van Ouwerkerk and Pedersen (1994), that varied between 0 to 8.5%, and is also higher than the values used by Pedersen et al (1998) in previous studies (4%). These higher rates may be caused by the management system of rabbits' manure in the studied farm, which is accumulated in deep pits during at least a whole cycle (5 weeks).

6.4.2. Carbon dioxide concentrations

Average CO_2 concentrations outside the buildings were higher than expected for fresh air (which is around 550 mg m^{-3}), due to the presence of other livestock buildings in the surroundings. Inside CO_2 concentrations followed similar patterns to these previously described by Estellés et al (2010). As expected, inside CO_2 concentrations were higher in autumn due to the lower ventilation rates registered (12.99 m^3 h^{-1} $animal^{-1}$ in summer and 3.3 m^3 h^{-1} $animal^{-1}$ in winter).

Regarding the concentrations gradient, according to van Ouwerkerk and Pedersen (1994), when carbon dioxide is being continuously recorded, the difference between inlet and outlet concentrations should be at least 240 mg m^{-3} (150 ppm). In this case, most of the data (94.5%) accomplished this requirement. However, part of the random variability expected could be caused by this reduced difference in CO_2 concentrations. The rest of this variability should arise from imperfect mixing processes and other error sources such as the measuring devices and not representative sampling (Van Buggenhout et al., 2009).

6.4.3. Ventilation rates

The fact that ventilation rates were much higher in summer than in autumn is explained by the high temperature difference registered (26.53 ± 2.12 ºC in summer and 17.88 ± 2.16 ºC in autumn), since the ventilation system in the farm was controlled by temperature sensors.

Regarding to the variation patterns, during Trial 1 it can be observed a constant ventilation rate during the whole period. This fact may be caused by the poor environmental control in the studied farm which was not able to achieve target temperatures inside the building.

The pattern observed in Trial 2 is directly related to temperature daily variations. It can be also observed a lower limit for the ventilation rate in the building (about 2.6 m^3 h^{-1} $animal^{-1}$). This limit is controlled by the ventilation control system of the farm, which is programmed to keep a minimum ventilation rate independently of the temperature.

6.4.4. Effect of CO_2 concentrations difference on balance accuracy

According to the prediction equation obtained in this work, for the minimum recommended difference on CO_2 concentrations of 240 mg m^{-3} (van Ouwerkerk and Pedersen, 1994), the expected error is 66% when determining the airflow rate for 2 hours periods. Despite the interesting information obtained, those results must be considered carefully, due to the low R^2 obtained. Further research is needed in this topic in order to obtain accurate prediction equations which may help to decide whether the CO_2 balance is an appropriate method to determine ventilation rates, according to the CO_2 gradient.

6.5. Conclusions

The CO_2 emission factor for fattening rabbits manure was established at 489 ± 87 mg h^{-1} $animal^{-1}$ during a whole fattening cycle. These emissions represent around 13% of total CO_2 emissions in fattening rabbit buildings.

The CO_2 balance demonstrated to be an accurate tool for the determination of ventilation rates in fattening rabbit houses, since no statistical differences were found among the airflow rates calculated using this method and the directly measured values.

The difference on CO_2 concentrations between the inlet and outlet of the building had an effect on the accuracy of the method for one of the experimental periods. According to these results, CO_2 concentrations differences below 2,000 mg m^{-3} lead to errors higher than 10% when using this methodology to determine ventilation rates.

6.6. Acknowledgements

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Chapter 7

Effects of diurnal emission patterns and sampling frequency on precision of measurement methods for daily ammonia emissions from animal houses

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Effects of diurnal emission patterns and sampling frequency on precision of measurement methods for daily ammonia emissions from animal houses

Abstract

Ammonia concentrations and airflow rates are the main parameters needed to determine ammonia emissions from animal houses. It is possible to classify their measurement methods into two main groups according to the sampling frequency: semi-continuous and daily average measurements. In the first method, ammonia concentrations and airflow rates are monitored during a certain period and instant emission rates are calculated. When using daily average methods, 24-hour average ammonia concentration and airflow rates are used to determine the average daily emission rate. As less information is used in the second method, an error may be expected. The aim of this work was to determine the nature and magnitude of this error. Three databases containing data from semi-continuous ammonia emissions measurements from different animal houses (pigs, poultry and rabbits) in three European countries (Denmark, The Netherlands and Spain) were used to characterize this error. An average systematic deviation between methods of 1.5% was found. The magnitude of this bias was directly related to the daily variation of ammonia concentration and airflow rate. The magnitude of this bias, and also the random component of the error were modelled. The developed model adequately described variation in bias in the studied dataset (R^2=0.85) and can be used as a tool to decide which type of measurement methods can be used.

Keywords: ammonia, emission, sampling frequency, error, airflow rate

7.1. Introduction

Livestock production is one of the major sources of ammonia emissions, contributing directly up to 62% of total European anthropogenic emissions (EEA, 2009). Deposition of emitted ammonia is responsible for damages to natural ecosystems related to acidification and eutrophication of soils and water (Krupa, 2003). Furthermore, its effect has a long-range dimension, since the volatilised ammonia binds with acid atmospheric species to form aerosols which are easily transportable over long distances (Asman et al., 1998).

In the livestock production chain the first stage of ammonia emission is the livestock housing, followed by emissions from manure storage systems and land application of manure. The characterization of emissions from animal houses is particularly important because it will determine the nitrogen available for volatilization in the following phases. Gas emissions from animal housings can be either estimated or measured by different methods (Phillips et al., 2000). If ventilation flow can be measured, the most widespread method to determine emissions from animal buildings is the mass balance in this air volume (e.g. Gates et al., 2006; Groot Koerkamp et al., 1998). To this aim, ammonia concentrations and airflows must be determined simultaneously following a pre-established sampling strategy which may affect the precision of the measurement.

To determine the daily emission in a livestock building two different sampling options can be considered. The first one corresponds to a continuous or semi-continuous measuring strategy, in which frequent measurements of gas concentrations and ventilation flows are performed, typically during short sampling intervals that can arrive up to 5 or 10 minutes. Ammonia concentrations can be measured in this case with chemiluminiscence analyzers, photoacoustic monitors, Fourier Transform InfraRed (FTIR) analyzers or electrochemical sensors. It is also necessary to measure the ventilation flow at least with the same sampling frequency. This task is relatively easy in mechanically ventilated compartments of animal houses, by using devices such as fan wheel anemometers. However, in naturally ventilated farms, and in large animal buildings with a high number of fans, the ventilation flow is more difficult to determine and, when possible, it implies higher costs.

The second option to determine daily emission is a simplified approach in which average daily values of gas concentrations and ventilation flows are measure. This approach allows the use of wet chemistry based methods (e.g. impingers) for determining ammonia concentration. In this system, a constant air flow is forced to pass through impingers with an acid solution during a fixed period (usually 24-h). The ammonia concentration of the sampled air can be calculated from the ammonia accumulated in the solution and the

total volume of sampled air. This system has advantages in comparison to (semi-)continuous gas measuring systems. Firstly, due to its high precision and accuracy, wet chemistry is considered as a reference method to determine ammonia concentrations in air. Secondly, their robustness and simplicity make ammonia impingers easier to install and less sensitive to malfunction than gas analyzers under farm conditions because of their simple and robust layout. And finally, the investment cost is lower than for continuous gas analyzer systems. However ammonia impingers only provide an average value for ammonia concentration over the sampling interval, while frequent measurements provide more accurate temporal resolution in the results.

If only estimates for average daily emissions are required, which is often the case when results are used for regulatory purposes, simplified measurement methods based on average daily values of gas concentration and air flow provide an attractive and cost effective option. However, considering the traditionally known (Oldenburg, 1989) daily variation of ammonia concentrations and ventilation flows, the product of 24-h average values for both terms may differ from the true daily emission, which is defined as the integration of concentration and flow over the day. Thus, the simplified method may lead to commit errors when determining ammonia emissions. Since the magnitude and nature of these errors in emission measurements are not known, it is necessary to characterize them in order to justify or reject the use of simplified measurement methods in emission research.

This paper focuses on the nature of the errors in estimates of daily emissions derived from average daily ammonia concentration and air flow measurements, in comparison to frequent measurement methods. The effect of a variety of animal categories from different regions will be explored. The errors will be characterized by separating the systematic error component (bias) from the random part (imprecision). Thus, the objectives of this paper are:

1. To investigate the magnitude of error committed when determining the mean daily ammonia emission from an animal houses, based on 24-hour averaged ammonia concentration and airflow, in relation to semi-continuous measurements.
2. To characterize this error and identify its systematic (bias) and random components.
3. To study the effect of different animal categories and climatic conditions on these errors.
4. To develop and evaluate a model to predict these errors.

7.2. Materials and Methods

7.2.1. General overview

To study the differences between average 24-hour measurements (hereafter called simplified method) and frequent measurements (reference method), different databases including high resolution semi-continuous measurements of ammonia emissions will be used to obtain the magnitude of individual daily errors of the simplified method against the reference method. Subsequently, the bias will be determined for different situations (including different animal categories and climatic conditions). The random error associated to the determined bias will be also determined. Finally, a model to predict the error will be developed and tested.

7.2.2. Ammonia emissions datasets

Ammonia concentrations and emission were obtained from previous research carried out during the last twenty years in three countries: Denmark (DK), The Netherlands (NL) and Spain (S) (Jørgensen, 2009; Mosquera et al., 2008; UPV, 2008 respectively). Ten datasets were used, containing semi-continuous measurements of the ventilation rate and ammonia concentration of exhaust air from animal houses of different species (pigs, poultry and rabbits). The datasets included different mechanically-ventilated housing systems. Data were also distributed among different seasons.

Measurement methods for airflow and ammonia concentrations differed among countries. Danish and Dutch measurements were conducted by means of fan-wheel anemometers measuring the flow continuously. Airflow values in Spain were calculated by means of a previous calibration of the fans using grid methods for different pressure drops (ASHRAE, 2001), and by continuous logging of the time of operation and pressure drop of each fan. Chemiluminescence methods were used to determine ammonia concentrations in The Netherlands, electrochemical monitors in Denmark and a photoacoustic gas monitor in Spain. The sampling frequencies for ammonia concentration measurements were 60 minutes in The Netherlands, 80 minutes in Denmark and 120 minutes in Spain.

Table 1 shows characteristics of the database with regard to animal categories, countries, number of farm locations and the number of measurement days per season.

7.2.3. Calculating individual daily errors

To calculate the relative error of each single daily measurement, emission rates were determined by using both methods: for the simplified method, daily average values were calculated for concentration and ventilation rates, while for the reference method, all

semi-continuous values for concentrations and ventilation rates were used. To obtain daily errors the following equation was used:

$$Error = \frac{100 \times \left[\left(F_{AVG} \times C_{AVG} \times n \right) - \sum_{i=1}^{n} \left(F_i \times C_i \right) \right]}{\sum_{i=1}^{n} \left(F_i \times C_i \right)} \quad \text{Eq. 1}$$

where, *Error* is the relative difference between both methods (%), F_i is the ventilation flow for time *i* ($m^3\ h^{-1}$), C_i is the ammonia concentration for time *i* ($mg\ m^{-3}$), F_{AVG} is ventilation flow daily average ($m^3\ h^{-1}$), C_{AVG} is the ammonia concentration daily average ($mg\ m^{-3}$) and and *n* is the number of daily measurements.

The error was calculated only for the days in which the measurement setting was complete along the day, resulting in 7,047 days of complete measurements. A statistical exploratory analysis of daily errors was performed in order to obtain the overall error value and also its frequency distribution. The bias will be defined as a systematic deviation of errors from zero and the random error was defined as the random variation of values around this defined bias.

7.2.4. Factors affecting the error

To study the effect of the factors defined before (animal category, country and season) on the bias and random error, the error for each single day in each combination was calculated using Eq. (1). The bias was the average value of these deviations while the random component of the error associated to each bias was its standard error.

7.2.5. Modelling of bias

In order to develop a model to predict the bias, a theoretical approach was conducted in which the nature of these errors was investigated. This allowed the identification of variables that affect bias.

Theoretical approach

According to the authors' experience and the evaluation of the databases available for this work, it can be assumed for most cases that, the daily variation of gas concentrations and ventilation flows follow sinusoidal patterns. These variables are determined by the daily average value, the amplitude (A_C and A_F) and the phase, characterized by the hour of the day at which the maximum values of gas concentrations and airflows are produced ($t_{C,max}$ and $t_{F,max}$, respectively). According to this, the daily pattern in gas concentrations and ventilation flows can be approximated for most of the cases as a function of the time (t):

$$C = C_{AVG} + A_C \cos\left[\frac{2\pi}{24}\left(t - t_{C,\max}\right)\right] \quad \text{Eq. 2}$$

$$F = F_{AVG}\ A_F\ \cos\left[\frac{2\pi}{24}\left(t\ - t_{F,\max}\right)\right] \quad \text{Eq. 3}$$

Given the sinusoidal model described above, the reference emission for one day (E_{day}) is calculated by integrating the product of the two curves over the day:

$$E_{day} = \int_0^{24}\left[\left(C_{AVG} + A_C\ \cos\left[\frac{2\pi}{24}\left(t - t_{C,\max}\right)\right]\right)\left(F_{avg} + A_F\ \cos\left[\frac{2\pi}{24}\left(t - t_{F,\max}\right)\right]\right)\right]dt \quad \text{Eq. 4}$$

Which results in the following expression:

$$E_{day} = 24\ C_{AVG}\ F_{AVG} + 12\ A_C\ A_F\ \cos\left[\frac{2\pi}{24}\left(t_{F,\max} - t_{C,\max}\right)\right] \quad \text{Eq. 5}$$

On the other hand, the emission calculated using the simplified method (E'_{day}) is derived from the following equation:

$$E'_{day} = 24\ C_{AVG}\ F_{AVG} \quad \text{Eq. 6}$$

Fig. 1 represents an example in which the emission rate is calculated using both methods, assuming that concentrations and ventilation flows follow a sinusoidal daily pattern with given values for amplitude and phase.

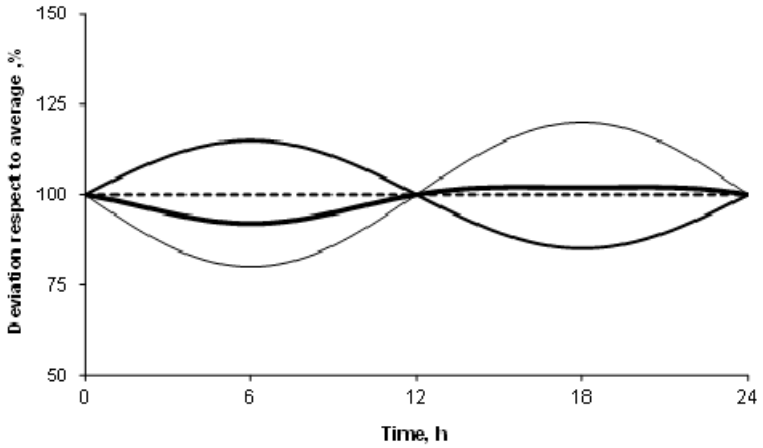

Fig. 1. Illustration of the relative variation of gas concentrations (amplitude = 15%) and ventilation flows (amplitude = 20%). For this example the maximum value of gas

concentration is supposed to occur at 6:00h, and for ventilation flow at 18:00h. The emission rate on a 24-hour average is compared to the continuous measurement

The relative deviation (*bias*) between the accumulated daily emission calculated using the simplified method and the reference method can be calculated as:

$$bias = \frac{E'_{day} - E_{day}}{E_{day}} = \frac{-A_C\ A_F\ \cos\left[\frac{2\pi}{24}\left(t_{F,\max} - t_{C,\max}\right)\right]}{2\ C_{AVG}\ F_{AVG} + A_C\ A_F\ \cos\left[\frac{2\pi}{24}\left(t_{F,\max} - t_{C,\max}\right)\right]} \qquad \text{Eq. 7}$$

If the variability (expressed as amplitude) of gas concentrations and ventilation flows are low in comparison to the corresponding average values (below 50%, see ***Fig. 2***), the second term in the denominator is negligible in comparison to $2\ C_{AVG}\ V_{AVG}$, thus resulting in the following approximation:

$$bias \approx -\frac{A_C\ A_F\ \cos\left[\frac{2\pi}{24}\ \left(t_{F,\max} - t_{C,\max}\right)\right]}{2\ C_{AVG}\ F_{AVG}} \qquad \text{Eq. 8}$$

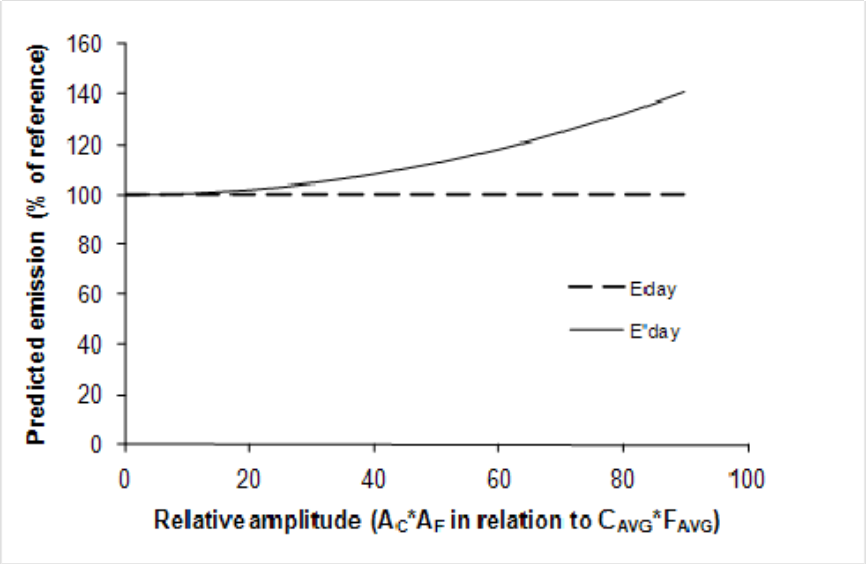

Fig. 2. Modelled percentual bias of average 24-hour measurements against high temporal resolution measurements (E_{day}) as a function of the daily amplitude of gas concentrations (A_C %) and ventilation flow (A_F %). The simplified approach for the bias (E'day) is also considered. A difference of 12 hours between maximum gas concentration and maximum ventilation flow is considered.

If we replace A_C/C_{AVG} and A_F/F_{AVG} by percentual amplitudes, and calculate the bias as a percentage of the reference, then from Eq. 7 it follows:

$$bias(\%) \approx -0.005 A_C(\%)\, A_F(\%)\, \cos\left[\frac{2\pi}{24}\left(t_{F,\max} - t_{C,\max}\right)\right] \qquad \text{Eq. 9}$$

Model development

Eq. 9 theoretically relates bias of the simplified method to parameters that characterize diurnal patterns of ammonia concentration and air flow. This relation can be utilized as a basis for a model to predict bias for a specified setting. In this study the model is developed to be applied to the different combinations of animal category, country and season in the available dataset, as specified in ***Table 1***.

Table 1. Animal categories, countries and number of farm locations and the distribution of measurement days over season.

Category	***Country***	***Locations***	***Season***			
			Spring	***Summer***	***Autumn***	***Winter***
Sows	NL	10	148	588	201	250
Farrowing sows	NL	5	291	259	131	133
Fattening pigs	NL	10	809	1265	923	850
	DK	2	-	-	142	144
Piglets	NL	6	75	156	34	367
Broilers	NL	4		233	157	33
	S	1	-	48	-	41
Laying hens	NL	8	22	392	398	158
Does	S	3	35	25	50	12
Fattening Rabbits	S	2	-	25	28	-

For the model development estimates of the required amplitude and time parameters for the different combinations have to be derived first. To this aim three steps were followed: firstly, “standardized days” (see below) in terms of daily variation of ammonia concentrations and ventilation fluxes were calculated for each case. The corresponding error (observed bias) was determined following Eq. 1. Secondly, using these “standardized days”, the diurnal parameters (amplitude and maximum hour) for concentrations and ventilation fluxes were determined. Thirdly, a statistical prediction model based on Eq. 9 was derived by fitting this model to the observed systematic errors of the different combinations in the dataset. The goodness of fit parameters were used to evaluate the performance of this model.

To calculate "standardized days" for each situation average hourly ammonia concentrations and airflows were determined for each animal category (*j*), country (*k*) and season (*l*). In order to homogenize the data for all situations, daily relative values of concentrations and airflows were calculated following Eq. 10.

$$X_{i\_REL} = 100\ X_i\ X_{AVG}^{-1} \qquad \text{Eq. 10}$$

where, X_{i_REL} is the hourly relative value of ammonia concentration and airflow rate (% of the daily mean), X_i is the measured value at hour *i* and X_{AVG} the calculated daily average value.

Sinusoidal daily patterns for concentration and ventilation fluxes were determined for each situation (j,k,l) using NLIN procedure of SAS (2001) by fitting parameters *A* and t_{max} of the following model:

$$X_{i\_MOD} = 100 + A(\%)\ \cos\left[\frac{2\pi}{24}\left(t - t_{\max}\right)\right] \qquad \text{Eq. 11}$$

where X_{i_MOD} is the relative hourly value for the modelled parameter (% of the daily mean), 100 is the average daily value for the modelled parameter (100% per definition), *t* is the time (h) and 24 is the period (hours).

Finally, a statistical prediction model (Eq. 12) including the estimated diurnal parameters was obtained by fitting its regression coefficient β to the observed systematic errors of the combinations j,k,l :

$$bias_{\ jkl} = -\beta\ A_{C\,jkl}(\%)\ A_{F\,jkl}(\%)\ \cos\left[\frac{2\pi}{24}\ \left(t_{F,\max\ jkl} - t_{C,\max\ jkl}\right)\right] + \varepsilon_{jkl} \qquad \text{Eq. 12}$$

7.3. Results

7.3.1. Individual daily errors

The distribution of errors for all datasets is represented in ***Fig. 3***, which shows a clear positive asymmetry. On average, the 24-hour measurement was 1.50% over the reference system. However, the most common value of error (mode) was 0. Also, an important variability in these errors was found, with an associated standard deviation of 3.36% of the reference emission, and extreme individual errors of -27% and +180%. The 0.025 and 0.975 percentiles, which contained the 95% of all error values, corresponded to -1.58% and +10.75%, respectively.

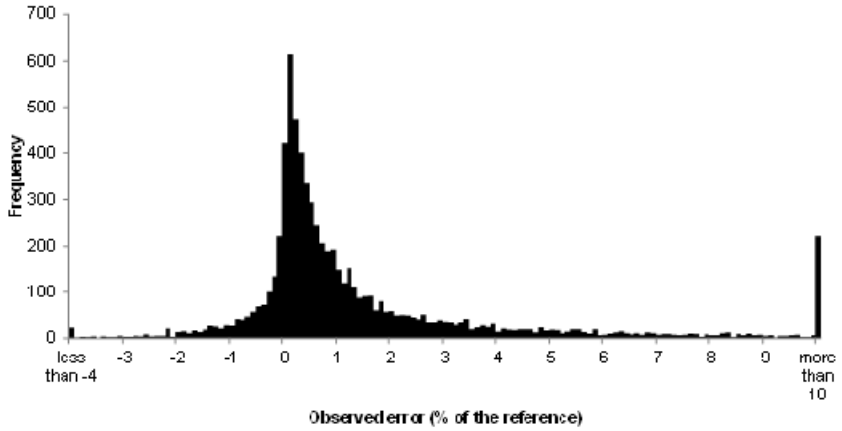

Fig. 3. Distribution of the relative errors between the simplified and reference approaches.

7.3.2. Factors affecting the error

The bias estimated for each season, animal category and country are presented in ***Table 2***.

Table 2. Seasonal distribution of observed bias (% over true value) for each database.

Category	*Country*	*Spring*	*Summer*	*Autumn*	*Winter*
Sows	NL	2.55±0.33	1.87±0.15	0.53±0.18	-0.35±0.08
Farrowing sows	NL	1.40±0.17	0.28±0.27	0.34±0.10	0.32±0.06
Fattening pigs	NL	1.68±0.11	2.70±0.14	1.05±0.08	0.55±0.05
	DK	-	-	1.31±0.16	0.36±0.04
Piglets	NL	1.78±0.39	1.11±0.15	0.15±0.15	0.16±0.03
Broilers	NL	1.86±1.00	0.10±0.69	0.44±0.28	1.79±0.64
	S	-	9.01±2.19	-	4.10±0.69
Laying hens	NL	4.81±1.39	2.01±0.23	0.65±0.14	-0.12±0.09
Does	S	3.73±0.76	3.54±1.13	1.57±0.47	7.53±2.70
Fattening Rabbits	S	-	5.61±1.99	5.53±0.86	-

In general, it can be observed that the systematic component of error varied from -0.35% to 9.01%. Most values were positive, which indicates than 24-hour average measurements overestimate the emission value. A seasonal effect can be also clearly observed from the data. In most cases, higher values for bias are found in spring and summer, while in winter and autumn observed bias was generally lower. Higher values for bias were also obtained for Spanish conditions comparing to Dutch and Danish conditions.

Regarding to the random component of the error, on average it is proportional to the bias, taking values around 0.26 times the calculated value for each case.

7.3.3. Modelling of bias

Standardized days

Results obtained for airflow (A_F) and ammonia concentration (A_C) amplitudes, and the hour of maximum value for both terms ($t_{max,F}$ and $t_{max,C}$), from daily pattern models for all animal categories considered and different seasons are presented in ***Tables 3*** and ***4*** respectively

Table 3. Modelled airflow and concentration amplitudes (% over average value) and their standard error, per animal category and country.

Category		***Fattening Rabbits***	***Does***	***Laying hens***	***Broilers***		***Piglets***	***Fattening pigs***		***Farrowing sows***	***Sows***
Country		***S***	***S***	***NL***	***S***	***NL***	***NL***	***DK***	***NL***	***NL***	***NL***
Airflow (A_F)	Spring	-	27.4±2.5	36.9±1.0	-	21.0±1.0	17.2±0.8	-	18.7±0.4	15.5±0.4	27.0±1.8
	Summer	12.0±2.2	12.9±1.2	24.1±0.8	34.9±1.9	24.0±0.8	11.0±0.5	-	17.6±0.5	8.7±0.4	21.3±0.5
	Autumn	24.8±5.4	6.2±0.6	15.8±1.0	-	7.2±0.6	2.8±0.3	14.4±1.4	13.7±1.0	4.6±0.5	5.0±0.9
	Winter	-	41.0±3.0	15.4±1.5	37.9±4.9	21.4±2.0	1.4±0.2	13.1±1.3	11.1±1.1	9.6±0.5	6.7±1.0
Concentration (A_C)	Spring	-	9.2±3.3	15.3±1.5	-	5.4±1.7	10.9±0.3	-	8.2±0.5	7.5±0.5	18.9±5.5
	Summer	68.7±12.1	18.9±2.2	7.7±1.2	33.9±4.8	14.5±1.0	6.1±0.9	-	16.5±1.3	3.9±0.6	13.0±3.5
	Autumn	27.2±4.3	21.8±1.1	8.1±0.7	-	5.8±0.9	4.5±0.8	6.7±1.2	5.8±0.5	6.1±1.3	12.0±3.4
	Winter	-	15.7±2.3	7.8±0.5	19.5±3.0	4.2±1.0	2.3±0.5	3.3±1.0	3.1±0.4	2.5±0.4	9.1±2.3

Table 4. Modelled hour of maximum value (24-hour basis) and their standard error, for airflow and concentration in each situation, category and country.

Category		***Fattening Rabbits***	***Does***	***Laying hens***	***Broilers***		***Piglets***	***Fattening pigs***		***Farrowing sows***	***Sows***
Country		***S***	***S***	***NL***	***S***	***NL***	***NL***	***DK***	***NL***	***NL***	***NL***
Airflow (A_F)	Spring	-	18.4±0.3	15.7±0.1	-	15.6±0.1	17.3±0.2	-	16.4±0.1	17.5±0.1	17.5±0.3
	Summer	18.2±0.7	18.2±0.3	15.5±0.1	17.7±0.2	15.3±0.2	17.8±0.2	-	16.3±0.1	18.1±0.2	16.3±0.1
	Autumn	16.4±0.8	18.7±0.3	14.6±0.2	-	15.4±0.3	15.3±0.4	14.5±0.3	15.7±0.3	16.5±0.4	14.0±0.7
	Winter	-	17.8±0.3	13.3±0.3	16.5±0.5	14.0±0.4	13.6±0.7	14.1±0.4	15.6±0.4	15.2±0.1	15.5±0.5
Concentration (A_C)	Spring	-	8.0±1.4	4.8±0.4	-	11.1±1.2	6.5±0.1	-	4.8±0.2	6.1±0.3	9.6±1.1
	Summer	8.1±0.7	8.1±0.5	5.7±0.6	7.0±0.5	4.6±0.3	7.9±0.6	-	5.0±0.3	8.6±0.6	6.5±1.0
	Autumn	6.7±0.6	6.4±0.2	13.0±0.3	-	4.0±0.6	16.6±0.7	4.6±0.7	5.1±0.3	17.7±0.8	12.0±1.1
	Winter	-	4.3±0.5	13.7±0.2	6.9±0.6	10.0±0.9	1.4±0.9	4.4±1.2	5.2±0.5	2.0±0.7	12.2±1.0

Higher airflow and ammonia concentration amplitudes were found for spring and summer seasons in both cases. Amplitudes calculated from Spanish data were also higher on average than those observed from Danish and Dutch data. Regarding to the time of the maximum value, no significant differences were found among seasons, animal categories neither countries. The difference between the hour when maximum airflow ($t_{max,F}$) and ammonia concentration ($t_{max,C}$) are reached, ranges between 0.39 and 10.48 hours, with an average value of 9.81 hours.

Prediction model

Following Eq. 12 a relationship between observed bias and modelled diurnal parameters was established. This relationship is shown in ***Fig. 4***. The value of the constant β was 0.0057±0.0001 ($p<0.001$) and the goodness of fit of the regression was r^2= 0.96.

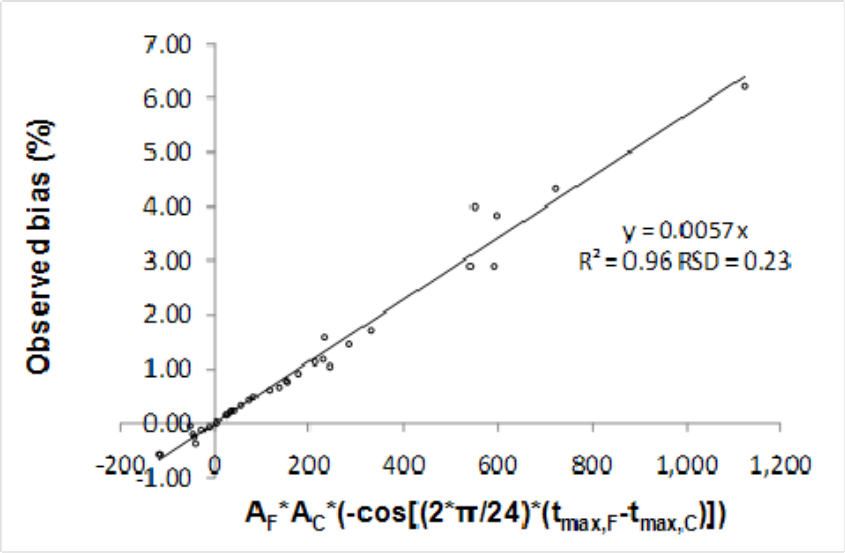

Fig. 4. Model to predict the relative bias. All amplitudes are expressed as percentage of the average daily values.

7.4. Discussion and Conclusions

7.4.1. Individual daily errors

Considering that 80% of the daily errors have an absolute error smaller than 3%, the error of the simplified 24-hours average method could be considered negligible for most of the cases compared with other sources of error in measuring ammonia emissions from animal houses. According to Leftcourt (2002), errors arising from choosing incorrect sampling

points when measuring ammonia emissions can rise to 400% of the measured value. The error associated to the calibration gases is typically 2% (Air Liquide America Speciality Gases LLC, 2009), although errors as high as 38% have been reported by Ni and Heber (2008). The reference method to measure the airflow of a fan is the fan wheel anemometer, which typically presents a 5% error after installation in livestock buildings (Demmers et al., 2000). Other methods show larger deviations against this reference method for the determination of ventilation flows. Using the tracer gas technique in comparison with the reference fan wheel anemometer, Demmers et al. (1999) obtained a deviation of 14 to 16%, and Demmers et al. (2000) obtained deviations of -7% to +19%. Pedersen et al. (1998) reported the measuring error for three indirect methods to determine the ventilation flow: the heat balance (6.9% to 18.9%), moisture balance (4.3% to 23.9%) and carbon dioxide balance (3.2% to 11.6%). On the other hand, this error contains a systematic component that cannot be compensated by repeating measurements as is the case for random errors.

Regarding the sign of the error, the observed overestimation of emissions calculated using simplified methods with respect to reference methods, is a consequence of the common situation of negative correlation between airflow and ammonia concentration, also observed by Melse et al. (2006) and Jeppsson (2002) for fattening pigs. However, the dataset studied in this work presented also situations of positive correlation between airflow and ammonia concentration, which led to negative errors.

Most of the values around zero for the observed bias were caused by a reduced daily variation in airflow or ammonia concentration. This situation was described by Zhu et al. (2000), who found homogeneous daily concentrations of ammonia in animal houses during 12-h measurements (from 7 a.m. to 7 p.m.).

7.4.2. Factors affecting the error

Within animal categories, regional differences were present, which may be attributable to the combined effect of climatic conditions and housing systems. Average bias calculated for Spanish measurements is higher than for Dutch and Danish ones. For example, the bias calculated for Spanish experiments in broiler production in summer and winter is 95 and 4 times higher, than bias calculated for the same species and season in experiments carried out in The Netherlands, respectively. Comparing the values obtained from Danish and Dutch measurements, for fattening pigs, differences were negligible. Regarding seasonal effects, average absolute bias was higher in spring and summer than in autumn and winter (2.54, 2.92, 1.29 and 1.59 respectively). When measurements were conducted during the four seasons for the same country and animal category, higher bias values correspond to

spring except for fattening pigs in The Netherlands (summer) and rabbit does in Spain (winter).

According to the theoretical approach, the variation of airflow and ammonia concentration affects the magnitude of bias, whereas the daily correlation between both parameters determines the sign of this systematic error. It is clearly observed than these amplitudes are larger in Spain than in The Netherlands and Denmark (***Table 3***), leading then to higher errors. A higher variation of both terms can be also generally observed in summer and spring opposite to autumn and winter, mainly when considering data from The Netherlands and Denmark. During cold seasons, the amount of air needed to control the temperature inside the barn is generally low, so ventilation rate is mainly based on CO_2 concentrations in the house (CIGR, 1992), and is therefore more stable during the day. In Spain however, winter temperatures are not that low on average, which means that during daytime, temperature control plays also an important role in controlling ventilation rate.

7.4.3. Modelling of bias

The model developed to predict the bias adequately describes the variation in bias between the studied combinations in the available dataset (***Fig. 4***). With this model, not only the bias absolute value, but also its sign can be determined accurately. In addition, the slope of the regression (0.0057) is close to the theoretical value (0.005) proposed in Eq. 9, which supports the assumptions made in the theoretical approach. Despite this robustness, it's important to remark than obtaining reliable data on airflow and ammonia concentration amplitudes, as well as the gap between maximum values for both terms cannot be derived from 24-hours average measurement methods but should be made available from other information sources.

7.4.4. Conclusions

The error arising from 24-hours average measurement methods for ammonia emissions has been characterised. A systematic error has been observed with an average value of 1.5% over the reference method (semi-continuous measurements of ammonia concentration and airflow rate). A positive asymmetry was found in the error distribution, and 95% of the error values were within the range from -1.58% to +10.75%. The magnitude of this error is directly related to the daily variation of ammonia concentration and airflow rate, while its sign is opposite to the correlation sign between both terms.

Differences were observed among errors calculated for different countries and seasons, while no differences were found for different production stages of fattening animals.

This systematic error can be predicted, and the measured value corrected by means of the model developed here, in which daily variation (amplitudes) of ammonia concentrations and airflow rate are involved.

The characterization of the error conducted in this work can be very useful when establishing a measurement protocol for ammonia emissions. In this sense, an estimation of the bias and random error may be available if an average 24-hour measurement is the choice to determine ammonia concentration or ventilation flow.

7.4.5. Practical considerations

Systematic error related to 24-hours average measurement methods for ammonia emissions can be corrected using Eq. 12. The random part of the error can be also determined (0.26 times the predicted bias).

A prediction of the bias can also be made before starting an experiment. If data on daily variability of airflow is available for a determined situation, a daily sinusoidal pattern can be modelled and the amplitude of this equation used to predict the bias (Eq. 12). This information can be useful to decide on the measurement method to be used to determine ammonia emissions, either semi-continuous or daily average measurements.

7.5. Acknowledgements

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Chapter 8

General conclusions and Future work

8.1. Introduction

As introduced in Chapter 1, this thesis is aimed to analyse tools and options designed for resource optimization in the measurement of emissions from livestock houses. This work has been developed throughout the six previous chapters (Chapters 2 to 7), in which these tools and options have been analysed in different practical scenarios. This final chapter is intended to provide an overall discussion of these tools and options. To this aim, this chapter is structured as follows: firstly, a brief summary of the previous chapters is presented; next, a discussion on each of the four main objectives of the thesis is developed; later, a general discussion integrating all objectives and results obtained is included, and finally the main conclusions of the thesis are listed.

8.2. Summary of previous chapters

In Chapter 2, an uncertainty model has been developed in a theoretical framework. This model allows evaluating the accuracy of results when determining N_2 and N_2O emissions from biological scrubbers using a N-balance. The final uncertainty of the results was high (over 130% of the average value) when using nitrogen balances for determining N_2 and N_2O formation in the system. The main contributors to this uncertainty were the airflow rate and water volume measurements. Chapter 3 must be considered a practical validation of the results obtained in Chapter 2. The NH_3 removal efficiency of a chemical scrubber installed in a pig facility was evaluated in Chapter 3. Two methods were used. One of them is the most spread method, based on the measurement of gas concentrations before and after the scrubbing process (air balance). The second method is based on a combined nitrogen balance in air and water (combined water-air balance). The results obtained using the air balance, were more accurate than those obtained with the combined water-air balance. Precipitation and deposition of ammonium salts in the packing material seemed to introduce errors in the combined water-air balance. The results of this work are representative for the type of scrubber analysed.

Chapter 4 describes the development and test of a flux chamber for the measurement of emissions from rabbits. The constructed chamber resulted in a useful tool for the determination of emissions from the animals and their manure. This chapter also includes practical recommendations for the use of the chamber.

In Chapter 5, the chamber developed previously was used to determine CO_2 emissions from fattening rabbits. The general activity of the animals was also studied. An average emission factor for these animals of 1.98±0.72 (l h^{-1}) was determined in this chapter. A sinusoidal daily pattern was identified for both, carbon dioxide emissions and animal

activity. The variability of the activity is much higher (41% over the daily average) than the variability of CO_2 emissions (16%).

Carbon dioxide balances was tested in Chapter 6 for the determination of ventilation rates in fattening rabbit buildings. The CO_2 emission factor determined in Chapter 5 was used. Ventilation rates determined using the CO_2 balance were compared to the results of direct measurements of ventilation. The results obtained in this chapter confirm that CO_2 balances are an accurate tool for the determination of ventilation rates in fattening rabbit buildings. According to these results, a CO_2 difference between the inside and outside of the building of at least 2,000 mg m^{-3} is needed to obtain accurate results.

Finally, Chapter 7 includes a study on the effect of reducing the sampling rate when determining ammonia emission. Ammonia emissions were calculated using semi-continuous high resolution measurements on NH_3 concentrations and airflow, and 24-hour average values for these parameters. Three databases containing data of measurements on different animal categories and countries were used. It was observed that the results obtained using 24-hour average measurements were on average 1.5% higher than when using the high resolution measurements. Nevertheless, this bias is low when compared with other error sources of ammonia emissions measurement.

8.3. General discussion

8.3.1. *Uncertainty analysis*

Comparison of different methods to measure the same variable have been made before in studies on emissions from livestock production (Reidy et al., 2006; Reidy et al., 2007; Teye and Hautala, 2009). Furthermore, uncertainty analysis have been successfully used before in environmental modelling for selecting models (Carrasco and Chang, 2005). Nevertheless their use is scarce for the comparison of livestock emissions methodologies or models (Gates et al., 2009). Therefore, the uncertainty model developed in this work (Chapter 2) can be considered the first comprehensive approach to develop this methodology in the field of livestock and environment. A big effort has been carried out in order to provide a straightforward methodology, easy to follow and understand, for its later use in other studies. A deep review has been conducted to characterize the individual uncertainties of the variables involved in the model. This information may be useful for other studies. Nonetheless, this model still lacks of some uncertainty sources such as the nitrogen accumulation in the packing material of scrubbers. Results evidence that this variable may significantly contribute to the final uncertainty when characterizing a scrubbing systems (see Chapter 3).

In the framework of uncertainty analysis, sensitivity analyses have been previously used in environmental sciences (Benke et al., 2008; Gates et al., 2009; Smith and Heber, 2001). These studies allow identifying the main contributors to the final uncertainty, turning into a powerful tool. For example, in a practical study (Gates et al., 2009), found than the main contributor to the final uncertainty was the measurement of the airflow rate when determining emissions from a livestock building. Calvet et al. (2010) studied deeply this effect, finding that the sampling error due to estimating the overall ventilation by measuring a sample of the fans was a main contributor to the ventilation rate uncertainty when measuring low airflow rates. However, for high airflow rates the main contributor to the final uncertainty was the fan's calibration process itself. Boriack et al. (2004) analysed the cost of reducing the uncertainty by influencing all parameters involved in the measurement of ammonia fluxes. They also found that the most reasonable way to reduce the final uncertainty (considering the cost increase and the accuracy improvement) was improving the ventilation rate measurement system. The results obtained in Chapter 2 of this thesis are consistent with these findings. The main contributors to the final uncertainty in this work were the airflow and water volumes. By the contrary, in Chapter 3 it was found that the variability of airflow rates and water volume measurements was low for this case study. In this case, it was concluded that the main contributors to the final uncertainty were ammonium salts accumulation and precipitation processes. These processes and their uncertainty are not well known, thus there is a need to characterize and include them in the developed uncertainty model.

In general terms, uncertainty analyses and the associated sensitivity analyses are powerful tools when selecting a measurement method. They may help to identify whether a measurement methodology or technology is able to fulfil the requirements of the measurement objective. Nevertheless, these uncertainty models must be accurate and all uncertainty sources must be quantified and included in the models. This may result in a difficult task due to the scarce prior knowledge about some of these variables.

8.3.2. *Downscaling measurements*

The measurement or airborne emissions using chambers is a widely used technique. It allows determining separately emissions from different sources, such as manure and animals. In this sense, gas emissions from animals have been traditionally determined using chamber methods (Beauchemin and McGinn, 2005; Blummel et al., 2005; Kurihara et al., 1999; Wang and Huang, 2005). Dynamic and static chambers have been also used to determine manure emissions inside livestock buildings (Blanes-Vidal et al., 2007; Boadi et al., 2004; Elwinger and Svensson, 1996).

The determination of emissions from individual origins presents three main advantages. Firstly, it allows identifying and characterizing every origin without disturbance of other variability sources. This is a crucial issue when developing and analysing techniques for the mitigation and control of these emissions. Secondly, it may reduce the cost of equipment and time needed to determine emissions from a global system like an animal facility. Finally, these methods can be used in naturally ventilated animal houses, where the implementation of whole source measuring methods can be very difficult or even impossible (e.g. very open houses). This method also present some inconveniences, such as the modification of environmental conditions around the emitting surface and the spatial resolution restriction. It is known that the use of static chambers alters the environment within the chamber, leading to underestimating the actual emission rate from surface sources (Rayment, 2000; Senevirathna et al., 2006), but these errors can be analytically corrected (Senevirathna et al., 2007; Venterea, 2010). When using flux chambers to determine emissions from manure in farms, it is also needed to consider the spatial emission variability at the surface of the farm (Miles et al., 2006), which increases the number of measurements to be made.

This method can be considered as an alternative to the determination of emissions from whole buildings, and the only available method in some cases. Nevertheless, it is important to consider the aim of the measurement before deciding to use it. It is a powerful tool when it is needed to determine the effect of animals and manure over the global emissions separately. Nevertheless it has not been proved in practice that the sum of emissions measured with chambers from animals and the manure, are equivalent to the emissions measured in whole buildings. For the moment It has been satisfactorily tested measuring ammonia emissions from facilities without the presence of animals (Blanes-Vidal et al 2007).

8.3.3. *Airflow rates estimation using tracers*

Tracer balances have demonstrated to be a robust tool to determine ventilation rates (Blanes and Pedersen, 2005; Pedersen et al., 1998; Xin et al., 2009). They arise as powerful tools in naturally ventilated houses, where direct measurements of ventilation rates cannot be performed. Nevertheless, their implementation in very open naturally ventilated buildings is extremely difficult. These methods can be also used in mechanically ventilated houses, when the accuracy required for the ventilation rates measurements is not too high, e.g. when determining emission factors in a large regional scale (Pedersen et al, 1998).

The deviation of the ventilation results obtained with these methods with respect to a direct measurement, can vary from 86% to less than 10% depending on the sampling

location for gas concentrations (Van Buggenhout et al., 2009). The use of these techniques at farm-scale has provided satisfactory results in terms of accuracy. Demmers et al. (1999) found a systematic error (between -6% and -12% over the reference) when comparing the ventilation rate calculated using a CO balance with mechanical measurements in poultry and pigs facilities. Demmers et al. (2000) found deviations from 1% to 9% when using a N_2O balance and the difference of concentration between the inlet and outlet of the building. Li et al. (2005) and Xin et al. (2009) found deviations below 10% (depending on the integration time of the measurements) for commercial poultry buildings using carbon dioxide balances. In this work (see Chapter 6) no statistical differences were found among the airflow rates calculated using CO_2 balances and the directly measured values, in a fattening rabbit house.

The main error sources when using these methods are related to the mixing process of the tracer with the air inside the building and the proper selection of the sampling positions (Van Buggenhout et al., 2009), as well as all parameters related to the emission rates from animals and their manure (e.g. average weight, number of animals, emission rates, activity effect, etc.) when using natural tracers (Xin et al., 2009). In this sense, little experimental information is available on the emission of tracer from the manure, in relationship with the emission rates from animals. The use of chamber for the determination of these emissions from manure or litter material may provide useful information to improve the accuracy of ventilation rates calculated using tracer balance.

8.3.4. *Sampling rate reduction*

The number of measurements needed to obtain a representative result is one of the main questions when defining a measuring protocol. This number of measurements and the sampling rate intensity may depend on the aim of the measurement since it directly affects the accuracy of the results. Consequently, it is crucial to identify and evaluate the main sources of variability.

Regarding the temporal variability of the emissions, seasonal patterns have been identified for gas and odour concentrations in animal houses. However, the effect of different climatic conditions on airborne emissions is not that clear (Sun et al., 2010). Attempts to reduce the number of sampling days when determining ammonia emissions from livestock houses have been successfully developed (Vranken et al., 2004). Intermittent measurements may reduce measurement and manpower cost up to 90%, by keeping the maximum measurement error below 10% (Dekock et al., 2009). Nevertheless, the information about the magnitude of the error committed when reducing the number of samples is scarce. In Chapter 7, the effect of using 24-hour average measurements for the measurement of ammonia emissions in livestock houses, instead of using semi-

continuous measurements was evaluated. As a result, an average overestimation of 1.5% of the measured value was found when using the 24-hours average values. This is a low error in comparison with other error sources described before such as ventilation rates. These results have several practical implications. For example, according to these results, when the measurement is aimed to monitor a system or to obtain an emission factor, it is not needed to use high time-resolution measurement devices. This fact may imply a reduction of the overall measurement costs. Although, when a measurement is aimed to characterize the emissions in a precise moment, high time-resolutions devices are more appropriated.

8.3.5. *Optimizing resources when measuring emissions*

The measurement of emissions from livestock facilities can be made using several techniques. The decision about the technique used in each case may be taken after reflecting on the aim of the measurement, the needs and the availability of resources.

Uncertainty analyses may help to decide whether a method is appropriate for an aim or not. In this way, information about the accuracy of a method is determined before it has been used, thus they are powerful tools for decision-makers. These analyses can be used in combination with all other options drawn in this document. Nevertheless, they need previous information about the uncertainty of variables involved in the measurements, which in some cases can be difficult to obtain.

Using chambers and/or tracer balances are good options when measuring emissions from naturally ventilated houses. They also can be used in mechanically ventilated houses when the required accuracy of the measurements allows it. These techniques can help to optimize the resources when measuring emissions.

Sampling frequency has a straightforward effect on the use of resources when determining emissions. A reduction on the sampling intensity affects the accuracy of the final results, but this error increase may be not significant when compared with other error sources. This decision will depend on the aim of the measurement.

The combination of all these tools and techniques, together with a deep reflection, may lead to obtain high quality results by optimizing the resources when determining emissions from animal houses.

8.4. General conclusions

The main conclusions of this thesis, extracted from the previous chapters are listed below:

1. Uncertainty analysis can provide useful information on the performance of measuring methods before they are tested in the field.
2. Combined water-air balances in scrubbers provide uncertain results of NH_3 removal and N_2O generation, due to the amount of parameters to be measured and their associated uncertainty.
3. A flux chamber for the measurement of gas emissions from rabbits was designed, built and tested satisfactorily.
4. CO_2 emissions from fattening rabbits and their manure, as well as the daily pattern of these emissions were characterized.
5. CO_2 balances are a robust tool for the determination of ventilation rates in fattening rabbit buildings in a daily basis.
6. The error committed when using 24-hours averaged values for NH_3 concentrations and ventilation rates instead of continuous measurements can be considered negligible, if compared with other common errors in emission measurements. In any case, this error can be predicted for a determined animal type, season and climate conditions.

8.5. Future work

This thesis should be considered as a single step in the search of more rational and optimized methods for the measurement of airborne emissions from livestock houses. There is a large volume of published studies on measurement methods of airborne emissions from livestock houses and manure, but nowadays, the need for accurate measurements rationalizing the use of resources is one of the main challenges of this topic. In this sense, this thesis has provided a framework for future research. One tool and four main options for the resource optimization of emissions measurements have been investigated in technical terms. Nevertheless, it is needed to define comparative studies between the defined techniques and the reference ones, in terms of both technical and economic aspects.

The use of uncertainty analysis in the research area of this thesis is not yet spread. The nature of the uncertainty itself makes it difficult to completely understand the processes underlying its calculation. It is needed to provide a simple and robust methodology for uncertainty calculation which makes it available for all researchers. In any case, it is crucial to more critically analyze errors in emission measurements. Uncertainty should not be taken as a defect of the measurement, but an intrinsic characteristic of it, which is extremely value to take decisions, as discussed previously.

Static and dynamic chambers have been widely used to measure airborne emissions. Several studies have been conducted with chambers in order to study metabolic processes in animals. Nevertheless, there are few practical handbooks which help to design experiments when using chambers for the measurement of airborne emissions from manure and animals. In addition, the effect of enclosing an emitting source on the measured emissions is still not completely characterized. These methods arise as candidate techniques for the determination of emissions from very open naturally ventilated animal buildings, in which traditional mass balances cannot be performed, but standardization and homogenization of techniques is still necessary, as well as a comparison with a reference measurement technique, when possible. In addition, it is recommendable to simplify and optimize chamber measurements when determining emissions from animals, e.g. by reducing the sampling time with prior knowledge about the daily patterns on emissions.

Carbon dioxide balances have been demonstrated to be a useful tool for the determination of ventilation rates from livestock buildings. However, accurately determining CO_2 emission rates from animals and their manure is still necessary. Since this is the crucial factor when developing these balances, it is recommendable to put the efforts on that issue. Despite these emissions have been studied in the past, an update of this factor is needed due to the changes in conditions such as genetics, management systems, etc. Thus, it is needed to investigate not only the average daily emission rates, but also the daily pattern of variation. This may result in an increase of the method accuracy. Furthermore, it is needed to evaluate the effect of other metabolic variables such as energy intake and weight gain on the carbon dioxide emission rates. Regarding the emissions from manure, they have traditionally been linked to animal emissions, paying little attention to other effects that may have more significant effects over those emissions, such as the temperature of the building and manure management systems. Since characterization of CO_2 emissions from manure is essential to accurately determine emissions from manure, the use of chamber can pay an important role at this point.

It is recommendable to carry out measurements in which different sampling periods can be compared. If so, a comprehensive study on the accuracy and cost implications of the sampling reduction will be possible. In addition, little is known about the effect of reducing sampling when measuring other airborne emissions than ammonia. The effect of this sampling reduction should be studied also for particulate matter and odour emissions, which are expected to follow different emission patterns according to their emission processes. If those works confirm the results obtained in this thesis, new measurement protocols should be developed including reduced sampling measurements, and thus optimizing the research efforts.

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