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A new method for estimating greenhouse gases and ammonia emissions from livestock buildings

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HIGHLIGHTS

- A new method for calculating emission rates from livestock buildings is proposed.
- The method is based on the measurement of temporal evolution of gases concentration.
- Gases concentration is measured by a remote sensing technique (Open-Path FTIR).
- This method has been tested in a cow shed in Tenerife Island (Spain).
- This is an alternative method to easily measure emission factors of livestock.

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ABSTRACT

It is widely known that carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are the main greenhouse gases contributing to global climate change. Emission factors for the aforementioned gases have been proposed in order to calculate the contribution of livestock farming to global climate change. However, these emission factors depend on many additional factors such as the housing system, environmental conditions, etc., which implies some uncertainties in their estimation. Therefore, works that aim at improving experimental calculation of these emissions are crucial to provide reliable estimates of the emissions produced by livestock. The purpose of this work was to apply a new methodology inspired by the accumulation chamber method to estimate emission rates from livestock buildings. The work was based on measuring the increase of gas emissions inside the livestock building by means of the remote sensing technique Open-Path FTIR (OP-FTIR). Previously to the measurements, livestock building cattle was confined outside of the building. Utilization of fan ventilation system favoured the homogenization of air inside the building. This experiment proved that evolution of CH_4 and CO_2 concentrations inside the livestock building behaved like an accumulation chamber unlike the N_2O which did not show such behaviour. Results showed CH_4, CO_2 and NH_3 emissions of 167 ± 54,700 ± 200 and 1.3 ± 0.2 kg head^{-1} year^{-1}, respectively. One of the main parameters affecting the estimated emission factors is the type of animal feeding. Therefore, it is essential to investigate the influence of food composition on CH_4 and CO_2 emission in a relative larger number of operating cattle buildings since the methodology herein proposed is an easy and cheap tool to study livestock emission factors and their variability.

1. Introduction

Farm work and animal breeding cause many gases to be emitted into the atmosphere: CH_4, CO_2, N_2O, NH_3, etc., especially during digestive processes (enteric fermentation) and the excreta decomposition. These emissions are very important as they contribute notably to global warming and climate change. Ruminant animals are one of the most significant sources of greenhouse gases because of the CH_4 and CO_2 excreted by the animals. About 25% of global methane emissions originate from animal husbandry, mainly from enteric fermentation (80%) and also from manure (20%) (European Environment Agency, 2007; Amon et al., 2001). The importance of NH_3 arises from its capability to form aerosol and smog (Aneja et al., 2006), its acidifying

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effect in soils, groundwater and surface waters and eutrophying power (Genfa et al., 1998; Bobbink et al., 1998). Approximately 80% of the total NH_3 emissions in Europe originate from agriculture practices, mainly from animal excreta, although this percentage depends on several factors (European Environment Agency, 2007).

Due to the global impact of these gas emissions, it is crucial to characterize the sources and their contributions to the total emissions in order to design specific environmental policies aimed at minimizing the effects of these pollutants. Typically, the emissions are calculated from emission factors and the methodology proposed in the EMEP/CORINAIR[1] Emission Inventory Guidebook provided by the European Environmental Agency (EEA) (European Environment Agency, 2007). However, emission factors are affected by uncertainties around 30% for CH_4 and NH_3 since livestock emissions depend on many other factors such as cattle feeding, housing system, climatic conditions, etc. For this reason, it is important to carry out studies aimed to improve estimates of the emission factors and their dependence on external causes.

There are several proposed techniques to calculate experimentally the emission factors of pollutants coming from enteric fermentation (Johnson and Johnson, 1995). Some of them are based on measurements of individual animal emissions that require a restrained and trained animal. There are also techniques based on prediction equations that calculate the methane emissions from the molar distribution of VFA (volatile fatty acids) (Wolin, 1960) or from the feed characteristics (Blaxter and Clapperton, 1965; Moe and Tyrrell, 1979). However the calculated emissions cannot be extrapolated accurately to all situations since it is well-known that emissions are influenced by many different factors such as environmental, housing conditions and animal feed. In fact, some works (Mosier, 1989; Schütz and Seiler, 1989) have proposed to conduct emission measurements continuously over 24-h periods and repeated over a year. Amon et al. (2001) suggested that emission measurements should be carried out under field conditions to consider and study the factors that influence emission rates, which could be very useful information to design efficient policies to reduce agricultural emissions.

Experiments involving groups of animals are performed to consider the effect of daily, seasonal and environmental variations and different housing systems. Several techniques can be applied such as gas-tracer methods (Lamb et al., 1986; Eklund, 1998) and mass balance techniques. The most appropriate technique to measure emissions from livestock buildings consists of measuring the difference between the concentration coming into and exiting the enclosure and the flux of air flowing through it; however it implies the use of many sensors for the concentration to be representative since pollutants could not be homogeneously distributed (Demmers et al., 1998). Moreover, the calculation of the ventilation rate for naturally ventilated buildings entails even more instrumentation (Demmers et al., 1998).

The objective of this work is to propose a new methodology to estimate experimentally the emission factor of CO_2, CH_4, N_2O and NH_3 associated to enteric fermentation and excreta decomposition in a dairy cattle building. This method is inspired by the accumulation chamber method used for CO_2 efflux measurements in soil respiration (Parkinson, 1981), and applied successfully during the last 20 years in surface-atmosphere trace gas exchange (Hutchinson and Mosier, 1981), volcanic areas (Baubron et al., 1991; Chiodini et al., 1996; Cioni et al., 1998), to estimate CH_4 flux in wetlands, aquatic ecosystems, sewage treatment plants (Nolasco et al., 2006), landfills (Nolasco et al., 2008; Cardellini et al., 2003) and to measure N_2O fluxes at the soil-atmosphere interface (Schäfer et al., 2012). A good review of methodologies applied to measure fluxes in environmental problems can be found in Denmead (2008).

The accumulation chamber method is based on the temporal evolution of gases concentrations. Even though the theory of molecular diffusion in a chamber causes concentration gradients decreasing with time (Hutchinson and Mosier, 1981; Livingston et al., 2006; Denmead, 2008), sometimes linear behaviour prevails (Forbrich et al., 2010). During recent years several non-linear models have been developed to study soil-atmosphere trace gas flux estimation with chambers (Livingston et al., 2006; Kroon et al., 2008; Pedersen et al., 2010). The most accepted models for these studies are non-linear HM (Hutchinson and Mosier, 1981) and the non-steady-state diffusive flux estimator NDFE (Livingston et al., 2006).

In this work, the accumulation chamber methodology has been applied to measure the CH_4, CO_2, N_2O and NH_3 emissions. A non-linear model has been used to estimate the fluxes of these gases. Since the methodology has been applied to a group of animals as a whole it can be used easily to monitor the variations due to the global factors affecting the emissions.

2. Materials and methods

The proposed methodology was applied to a naturally-ventilated cow shed in the surroundings of La Laguna, Tenerife Island, Spain, to measure emissions of CH_4, CO_2, N_2O, and NH_3, during a two-days measurement survey.

2.1. Accumulation chamber methodology

The accumulation chamber method (Hutchinson and Mosier, 1981; Parkinson, 1981; Baubron et al., 1991), is based on placing the opened side of a chamber on the emitting surface and measuring the increase of gas concentration during the filling time, i.e., until the concentration remains constant throughout. The concentration curve versus time in the first stage is closely related to the gas emission. However, some assumptions have to be made to apply this methodology. Following Baubron et al. (1991), if we make a mass balance equation in a "control volume" of interest, in this case the inverted chamber, the mass of the specie "*i*" within the inverted chamber at time $t + dt$ is equal to the mass of "*i*" present at time *t*, plus the mass of "*i*" entering the chamber in the interval of time *dt*, minus the mass of "*i*" leaving the chamber in the same interval of time. In mathematical terms:

$$V_c \cdot C_{i(t+dt)} = V_c \cdot C_{i(t)} + \Phi_e \cdot C_i^* \cdot dt - \Phi_l \cdot C_{i(t)} \cdot dt \quad (1)$$

where V_c represent the volume of the chamber, $C_{i(t+dt)}$ is the concentration of the component *i* at time $t + dt$, $C_{i(t)}$ is the concentration of the component *i* at time *t*, C_i^* is the concentration of the component *i* in the gaseous matrix released by the animals, Φ_e is the flux entering the chamber and Φ_l is the flux leaving the chamber. The C_i in the gas leaving the chamber during the considered interval of time is assumed to be equal to the C_i in the chamber at time *t*. This assumption is justified as the gas is well-mixed inside the chamber. The gas flow entering the chamber (Φ_e) is equal to the gas flow leaving it (Φ_l) below the wall, as no pressurization takes place (Fig. 1a). Equation (1) can be rearranged as follows for cylindrical and cubic chambers:

[1] EMEP: Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe CORINAIR: The Core Inventory of Air Emissions in Europe.

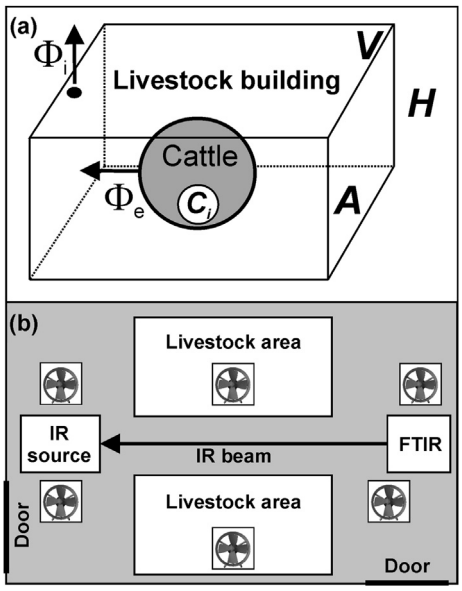

Fig. 1. a) Scheme of volume control inside of accumulation chamber, b) Scheme of the experiment inside the livestock complex. Fans are deployed at ground level and elevated to mix the air inside. The OP-FTIR system measures the path-integrated concentration between the IR source and the FTIR.

$$\frac{dC_i}{C_{i(t)} - C_i^*} = -\frac{\Phi_e}{H} \cdot dt \tag{2}$$

Equation (2) is a typical first-order linear inhomogeneous differential equation with constant coefficients and "H" is height of the chamber. Considering that at initial conditions C_i is the ambient concentration of the "*i*" component ($C_{i(air)}$), the integration of Equation (2) leads to the relation:

$$C_{i(t)} = C_i^* + \left(C_{i(air)} - C_i^*\right) \cdot e^{\frac{-\Phi_e}{H} \cdot t} \tag{3}$$

In this case, we consider the livestock building as a big accumulation chamber with the gases coming from the livestock instead of the soil. The imposed enrichment of "*i*" can be measured directly inside the building by different methods. The assumptions used to derive the technique were satisfied in practice since the air was mixed by means of several fans and the overpressure was avoided by not sealing the building hermetically. Also the CH_4, CO_2, N_2O, and NH_3 concentrations in air can be neglected since the concentrations produced by livestock emissions are much higher in ambient air as it will be shown in section 3. The fitting of C_i (in $\mu g\ L^{-1}$) versus time plot allows us to calculate the "entering flux" of "*i*" in the livestock building (coming from the animals). If we multiply C_i ($\mu g\ L^{-1}$) by the livestock building volume and divide by the number of animals, it is possible to estimate the amount of "*i*" produced by each animal per unit time. To measure the concentration of the target gases, the remote sensing technique Open-Path FTIR spectroscopy was applied. This technique will be briefly reviewed in next section.

2.2. OP-FTIR technique

The OP-FTIR technique uses an infrared (IR) source and a Michelson interferometer to analyze in wavelengths the energy coming from the IR source (spectra). Gases between the IR source and the interferometer absorb energy in their characteristic absorption lines. The concentration can be retrieved by measuring the amount of energy absorbed at each line. In this experiment, the IR source and the interferometer were installed at both sides of the building in order to measure representative path-integrated concentrations (see Fig. 1). Additional details about this technique can be found in Russwurm (1997) and Verein Deutscher Ingenieure (2000). This technique has been used to calculate emissions from experimental data by several different methods (Minnich et al., 2002; Griffith et al., 2002; Hashmonay et al., 1999; Eklund, 1998; Piccot et al., 1994). In particular, it has been applied previously to livestock emissions (Schäfer et al., 1997; Depta et al., 1997; Childers et al., 2001; Amon et al., 2001). In this work, this technique has been also applied to measured livestock emissions but using a completely new procedure.

The spectra analysis has been carried out using the AutoQuant Pro (AQPro) classical least squares (CLS) software package (MIDAC Corporation, Irvine, CA). This program provides an interface to design analysis methods to retrieve concentrations from experimental spectra. In order to define an analytical method it is necessary to provide a reference spectra library (spectra set of known concentrations).

Reference spectra have been generated by using the well-known HITRAN spectroscopic database (http://www.cfa.harvard.edu/hitran/). All spectra have been calculated in the 500–4500 cm^{-1} spectral region at a resolution of 0.5 cm^{-1}. This resolution corresponds to the best resolution of the FTIR spectroradiometer used for the experimental measurements. All spectra were generated in standard conditions (25 °C and 1 atm) and with a path length of 100 m.

There are several issues concerning the analysis methods that can affect the accuracy of the results. The most important are detector saturation, the non-linearity and interferences between absorption lines of different gases.

The first issue was checked by ensuring that any dip appeared in the detector cut-off region neither the baseline was elevated above zero as suggested by Russwurm and Childers (1997).

Concerning the non-linearity, although the range of concentrations is expected to be wide, AQPro is able to consider the non-linearity, if the range of experimental concentrations lies within the concentrations range of the reference spectra library for each component. AQPro can also calculate the effect of temperature variations if actual temperature information is included in the acquisition/analysis program.

In relation with the spectral interferences between gases, a previous spectral study has to be carried out to determine whether there is overlapping between the absorption lines of the different gases that are going to be used in the analysis. We have checked that only the H_2O absorption lines affect those of CO_2, CH_4 and NH_3. Several microwindows and their combinations were considered in the method design process to account for this interference. The microwindows selection is extremely important. A bad selection can introduce errors of 25%. In general, differences between methods are bigger as concentration increases. In the considered methods, differences are however lower than 9%. The studied methods were tested using with spectra of known concentration generated from the HITRAN database. All gases were considered when testing the spectra in order to evaluate whether the microwindows selection was able to solve the overlapping problem.

For CH_4 and NH_3, the best results were achieved when all the selected lines were used in the analysis. However, for H_2O, and CO_2 a single line (Table 1) gave better results. Although there is only one microwindow for N_2O, it includes three absorption lines. Some selected microwindows, the testing concentrations ranges and the errors obtained during the testing of the spectra are shown in Table 2. Experimental spectra were acquired by AQPro program in the 400–4500 cm^{-1} spectral region. Single beam spectra were transformed to absorbance using a synthetic background spectrum

Table 1
Main parameters used for OP-FTIR analysis. Also shown windows of spectral analysis selected for all components, concentration ranges and respective errors.

	CH_4	CO_2	H_2O	N_2O	NH_3
Microwindows (cm^{-1})	2881.5–2890.1 2894.3–2898.8 2904.0–2911.5 2913.4–2923.1 2923.2–2929.5 3154.0–3160.5	2076.4–2077.7	2113.5–2117	2203.2–2204.2	926.54–940.0 957.1–970.0 989.7–995.9 1138.8–1142.4 1157.5–1160.5
Concentration range (ppm)	1–400	500–3000	7000–19,000	0.1–0.6	0.75–11
Maximum error (%)	4.0	1.2	1.5	4.0	0.3

which was calculated for each spectrum. The ambient black body radiation was subtracted after having been transformed to single beam spectra. This correction is necessary because the NH_3 selected lines are between 760 and 1200 cm^{-1}, the spectral region that is most affected by the ambient emission.

2.3. Experimental set-up

In order to verify if the accumulation chamber technique can be applied to a livestock building to measure emissions of NH_3, N_2O, CO_2 and CH_4, a two-days measurements campaign was performed. The experiment was carried out in a naturally ventilated building of La Laguna (Tenerife Island, Spain). The dimensions of the shed were 30 (long) × 10 (wide) × 6 (high) yielding a volume of 1800 m^3.

After taking the cows out of the building, the first day was devoted to the preparation of the complex, building cleaning (mainly the soil surface), installation of scientific instruments, installation of six fans for mixing the indoor air, sealing the windows and holes in the barn to make “a closed chamber” and taking measurements with “clean air”. The second day was used to perform measurements after entering the livestock into the building again. After the start of the measurements, when clean-air concentrations were recorded, 20 cows entered in the building. Windows and gates were then closed in order to emulate an accumulation chamber. However, the building was not hermetically closed to avoid overpressure and satisfy one of the assumptions of the methodology. The measurements monitored the evolution of CH_4 and CO_2 concentrations until they remained constant, which meant that the plateau of the accumulation curve had been attained.

Gas measurements were obtained with OP-FTIR MIDAC system. The experimental scheme is shown in Fig. 1b (the scheme is not drawn to scale). The IR source and the interferometer were set-up at both sides of the building and between the two areas assigned to the livestock. The path length was 25 m at 1.5 m above the floor. The six fans were set-up to mix the air inside the building, four at floor level and two at elevated positions, ensuring a path length representative of the whole building.

A meteorological station registered the temperature, pressure and humidity inside the building. The pressure was stable during the experiment, bounded between 960 and 964 mb. The temperature varied between 18 and 25 °C. This information is necessary to convert the concentrations measured in ppm to μg L^{-1} units to calculate the emissions, as will be seen in Section 3. In addition, these meteorological parameters can be crucial when interpreting the results.

Table 2
Fluxes and emission factors per head cattle and year.

	CH_4	CO_2	NH_3
Flux (g $head^{-1}$ h^{-1})	19.1 ± 0.5	540 ± 30	0.15 ± 0.2
R^2	0.98	0.97	0.89
Emission factor (kg $head^{-1}$ $year^{-1}$)	167 ± 5	4743 ± 200	1.3 ± 0.2

3. Results

The OP-FTIR technique has been used to provide the concentrations needed to calculate the emissions. The spectra analysis requires a very careful design of the analysis method since it may easily lead to large errors in the concentrations retrieved from spectra. Absorbance spectra were analyzed with the tested method. The concentrations (ppm) obtained for CO_2, CH_4, NH_3 and N_2O are presented in Fig. 2.

The first measurements correspond to the empty building. The cows went into the building at 10:16 am and CO_2 and CH_4 concentrations started to increase. At 10:34 am the livestock was inside and the door was closed. From 10:34 am to 10:40 am, the detector was refilled with liquid nitrogen, which is reflected in Fig. 2 as a gap between the measurements. After this moment, the CO_2, CH_4, NH_3 concentrations increased although the level of N_2O remained nearly constant. The CO_2 and CH_4 concentrations reached a plateau approximately 2 h after the beginning of the measurements.

Although water vapour absorbs IR energy, it is not considered a greenhouse gas due to its high variability. However, it is interesting to study its evolution since it can be used to check the quality of the spectra and the analysis by comparing the concentrations with those calculated from the relative humidity and the temperature. The comparison can be used to reject any failed spectra. In this experiment, the H_2O concentrations calculated from OP-FTIR spectra also increase from the first measurements (almost linearly) when the cows went into the building, which agree with the water vapour emission from respiration and the temperature and relative humidity increase (from 18 to 25 °C for temperature and from 82 to 98% for relative humidity). Average differences between the H_2O concentration values calculated by both methods (OP-FTIR and relative humidity/temperature) are around 10%, which can be explained by the different measurement concept of both techniques: extractive methods vs. remote sensing methods (Bacsik and Komlósi, 2006). This agreement confirms the quality of the measurements.

The accumulation curve is a representation of the concentration (μg L^{-1}) versus time (h). The fluxes were calculated fitting the accumulation curve of each component by applying HMR model (http://cran.r-project.org/web/packages/HMR/index.html) (see Fig. 3). The period used to calculate the curve are those from 10:40 am (when all cows are inside the building) to 12:31 pm for CH_4 and CO_2, and from 10:40 am to 11:45 am for NH_3, since this range can be fitted to an exponential model (HM–HMR). All emissions factors have been obtained by HMR model and procedures proposed by Pedersen et al. (2010) and confirmed with accumulation curve (Equation (3)). The emission factors per animal, fluxes and errors values are depicted in Table 2.

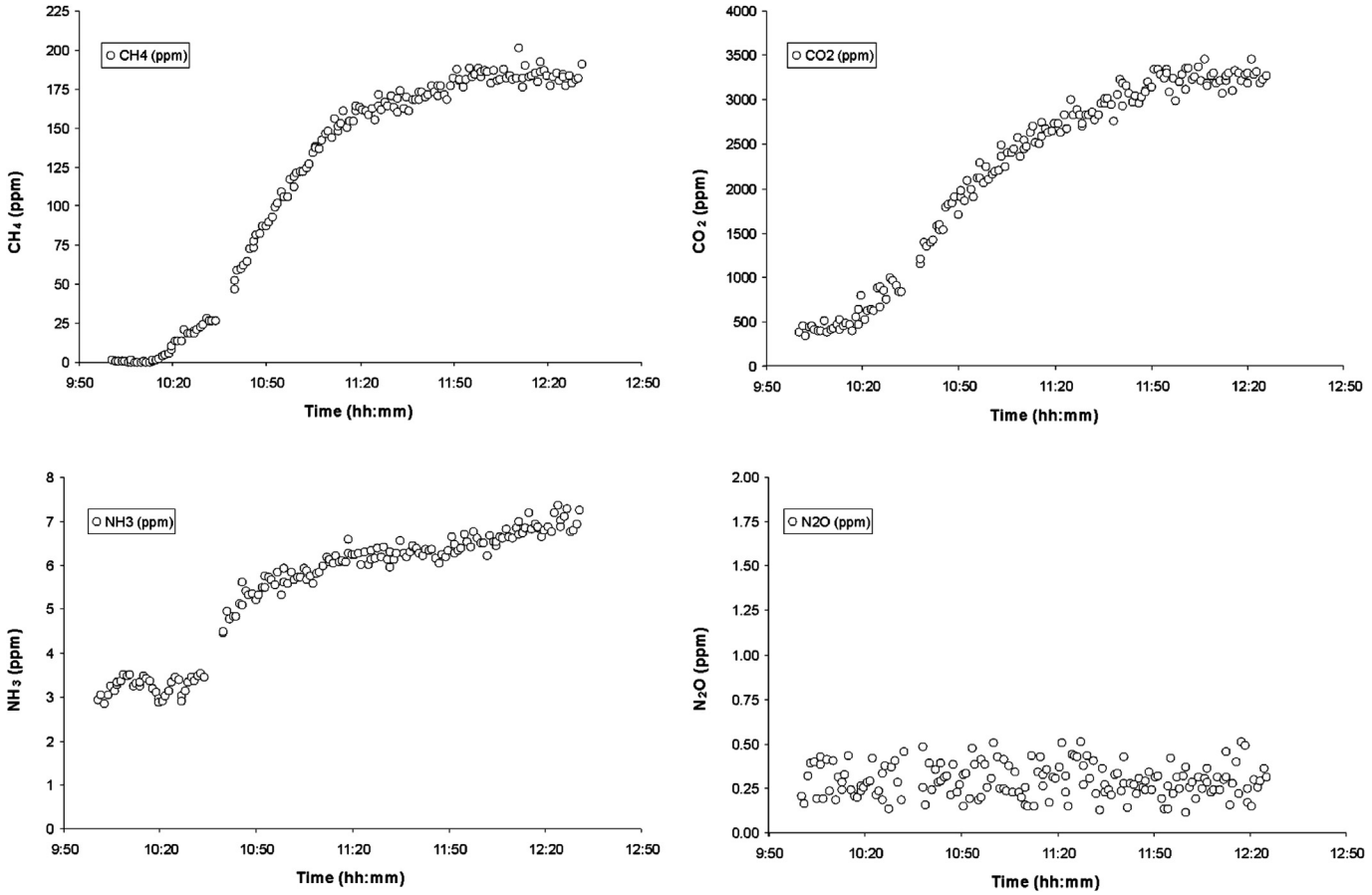

Fig. 2. Evolution of concentrations for each component. The concentrations begin to rise when animals are put into the building. The concentration increase of CO_2, NH_3, CH_4 and N_2O is associated to livestock emissions.

4. Discussion

4.1. Greenhouse gases

The temporal concentration evolution of target gases is shown in Fig. 2. The concentration ranges of CO_2 and CH_4 are in good agreement with those measured by Ngwabie et al. (2009) who also measured concentrations in a naturally-ventilated dairy cows building (see Table 3). The concentrations obtained by us are of the same order of magnitude although the lowest values are lower than those measured by Ngwabie et al. (2009). This is a reasonable result since the first measurements were made when the cows began to enter the building. In addition, the highest values obtained are very close to those of Ngwabie et al. (2009).

The N_2O concentration remains around a value of 0.3 ppm, which is also in good agreement with the indoor concentrations range measured by Ngwabie et al. (2009), from 0.16 to 0.75 ppm (see Table 3). The maximum concentration measured (0.6 ppm) is close to the one of (0.56 ppm) observed by Jungbluth et al. (2001).

The curves in Fig. 2 also show that the livestock building clearly behaves like an accumulation chamber for CH_4 and CO_2. That is, they exhibit a strong growth at the beginning of the experiment, after the building was closed. Then the increase slows down until a plateau zone is reached and the concentrations stay nearly constant.

The CH_4 emission calculated by the method here proposed (19.1 g head^{-1} h^{-1}) is higher than those obtained by Ngwabie et al. (2009), which are between 9 and 13 g LU^{-1} h^{-1} measured in May and January 2007 respectively (see Table 4). The CH_4 emission factor can be also compared with that provided by EMEP/CORINAIR data. The CH_4 emission factor calculated with the proposed methodology (167 kg head^{-1} year^{-1}) is higher than the EMEP/CORINAIR factor (100 kg animal^{-1} year^{-1}) considering only enteric fermentation and not including manure management. The higher emissions in this experiment can be attributed to the peculiarities of the livestock production system: cattle feeding, housing system etc.

In this work the CO_2 emission factor has been evaluated at 540 g head^{-1} h^{-1}, thirty times bigger than the CH_4 emission factor. However, it is difficult to compare this result with other data since CO_2 emissions are not taken into account in EMEP/CORINAIR guidebook and nor in other works because it is considered that its emission effect is balanced with photosynthesis.

No N_2O emission has been observed in this experiment. This was expected since N_2O is emitted in the degradation of the organic matter from manure, as a product of nitrification/denitrification processes during storage under condition of low oxygen availability, or manure spreading. However the building under study was cleaned just before the measurements. In fact, Ngwabie et al. (2009) refers to occasional outdoor N_2O concentrations higher than the indoor ones.

4.2. Ammonia

The temporal evolution of NH_3 concentration is shown in Fig. 2. The NH_3 concentration values also increase after livestock entered the building and the concentrations range (3–7 ppm) is in agreement with that of Ngwabie et al. (2009) (1.7–17.93 ppm) (see Table 3). However the increase took place around 20 min later than

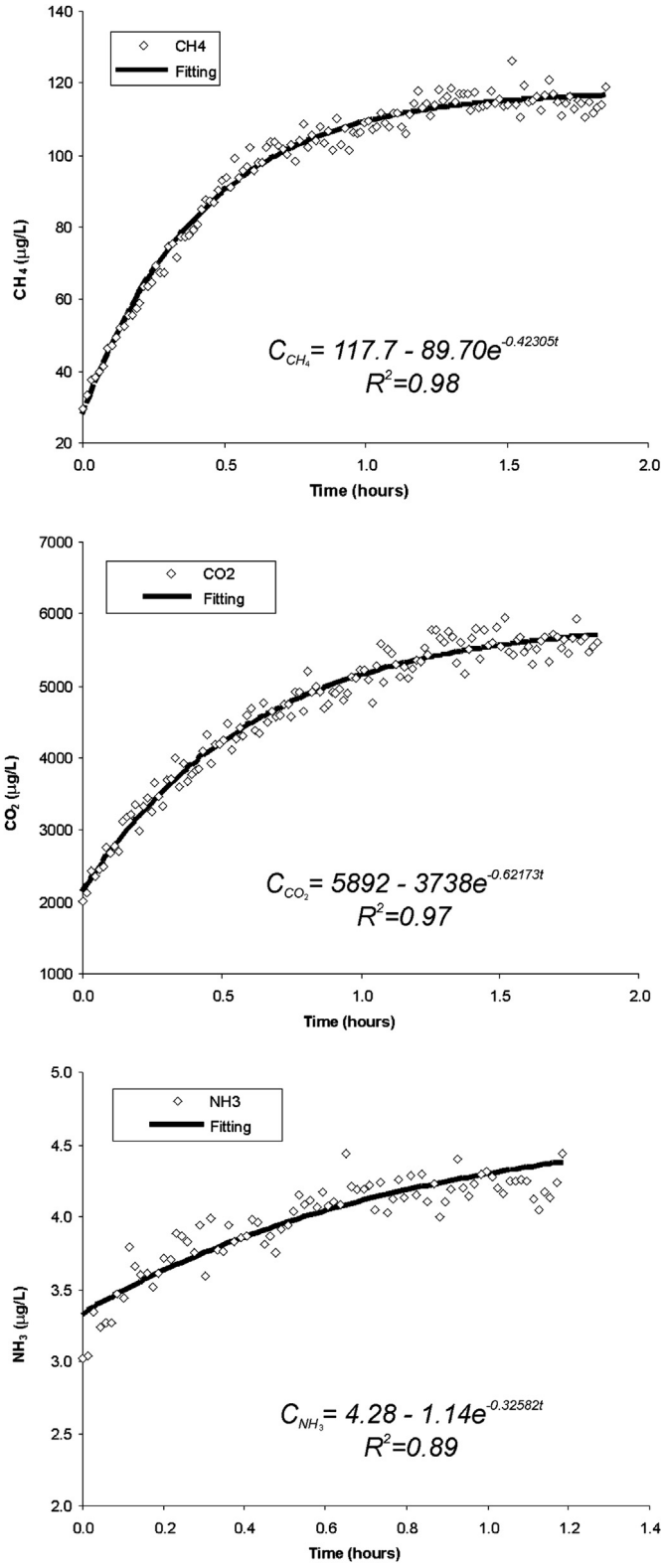

Fig. 3. Fitting and fluxes for each components (µg L^{-1}) with its equations and correlation coefficient.

for the rest of the gases, and, although a linear increase is observed, the NH_3 concentration does not fit exactly to an accumulation curve as well as can be seen in Fig. 2. Moreover, the typical zone of nearly constant concentration could not be observed, even at the end of the measurement time (15:00 pm).

Table 3
Comparison of concentrations ranges measured in this work and Ngwabie et al. (2009).

	CH_4	CO_2	N_2O	NH_3
Concentration range (this work) (ppm)	0.2–201.3	391–3457.0	BDL-0.6	3–7
Concentration range (Ngwabie et al., 2009) (ppm)	9–283	644–3530	0.16–0.75	1.70–17.93

There are several factors associated to NH_3 emissions that could explain this behaviour. To begin with, it is important to highlight that the building was cleaned before the measurements started. Therefore, there was no manure accumulated in it. The delay in NH_3 concentration increase reveals that it took a time for the manure to be emitted and NH_3 to be generated. This agrees with the fact that NH_3 is not a pollutant emitted directly from animals but generated instead from the urea and undigested proteins in the urine and faeces respectively. Moreover, the NH_3 emission involves chemical degradation reactions, liquid phase equilibrium between ammonium and ammonia and evaporation processes that depend on several factors such as pH and temperature (Elzing and Monteny, 1997). Nevertheless, the conversion rate NH_4^+–NH_3 is largely unknown (Aneja et al., 2001) since the reaction depends mostly on the acid concentration and air humidity and temperature (Seinfeld and Pandis, 1998). As mentioned before, these last two parameters evolved during the day. All these factors working together may contribute to explain the observations although it is difficult estimate the contribution of each one.

If we assume that the building can be considered an accumulation chamber, the NH_3 emissions can be inferred from the curve formed with the measurements. The NH_3 emission factor calculated from experimental measurements in the livestock building is 0.15 g $head^{-1}$ h^{-1} (1.3 kg $head^{-1}$ $year^{-1}$) (see Table 4), whilst the emission factor proposed by EMEP/CORINAIR is 0.993 g $head^{-1}$ h^{-1} (8.7 kg $head^{-1}$ $year^{-1}$). The difference is acceptable considering that the first value 0.15 g $head^{-1}$ h^{-1} take into account only the emissions due to the animal housing excreta and the second one 0.993 g $head^{-1}$ h^{-1} is a global emission factor. In Table 4 a comparison of the emissions obtained in this work with the values measured by other authors is shown. Our emission values obtained are similar to those reported as 0.158 g LU^{-1} h^{-1} (Oldenburg, 1989), 0.163 g LU^{-1} h^{-1} (Amon et al., 2001) and 0.157 g LU^{-1} h^{-1} (Bluteau et al., 2009) (see Table 3).

The differences in the emission factors cannot be accounted for by the inaccuracies of the method. On the contrary, they should be attributed to the dependence of emissions on multiple factors such as different species, age of the animals, manure storage (in this case only manure inside the building should be considered), climatic conditions, etc. This is further confirmed by the high variability of the

Table 4
Comparison of gas emission factors estimated in this work with other authors.

Emission	CH_4	CO_2	NH_3
This work (g cattle $head^{-1}$ h^{-1})	19.1	540	0.15
Ngwabie et al. (2009) (g LU^{-1} h^{-1})[a]	9–13		0.89–1.13
Amon et al., 2001 (g LU^{-1} h^{-1})			0.165–0.3
Oldenburg, 1989 (g LU^{-1} h^{-1})			0.158–0.45
Bluteau et al. (2009) (g cattle $head^{-1}$ h^{-1})			0.157–0.7583
Koerkamp et al. (1998) (g cattle $head^{-1}$ h^{-1})			0.314 (England litter)–2.001 (Netherlands cubicles)

[a] LU: live unit (500 kg animal weight).

emissions found in the revised bibliography from 0.157 g head^{-1} h^{-1} in Bluteau et al. (2009) to 23.38 g LU^{-1} h^{-1} in Koerkamp et al. (1998).

5. Conclusions

An experiment with dairy cows has been carried out in a naturally ventilated livestock building in Tenerife Island (Spain) in order to test a new methodology to calculate the emissions produced by cattle, based on the accumulation chamber technique. Livestock was put inside the shed and the CH_4, CO_2, NH_3 and H_2O concentration was measured by OP-FTIR technique.

The temporal evolution of CH_4 and CO_2 concentrations demonstrate that the closed building behaves like an accumulation chamber. This proves that the proposed methodology is applicable and makes it easier to calculate the emissions factors of gases produced by cattle and possibly by other kind of animals.

The emissions factors that were obtained experimentally in this work have been compared to those proposed by the EMEP/CORINAIR Guidebook and those measured by other authors. The calculated CH_4, CO_2 and NH_3 emissions in this work are of the same order of magnitude. The differences may be attributed mainly to the livestock feed and other relevant factors: different species, age of the animals, the manure storage, climatic conditions, etc. For this reason the emission factors cannot be applied to any livestock building. However the methodology can be applicable to natural ventilation buildings covered completely to simulate an accumulation chamber whenever the animals are in similar conditions.

Regarding the NH_3 concentrations, the results are not so easy to interpret since although the evolution increases in time in a similar way, NH_3 is not directly emitted by the livestock but generated from the urea and the undigested proteins in the urine and faeces. In fact, a delay of almost 20 min in the NH_3 emissions was measured. More work should be carried out in order to ensure that the NH_3 follows the same scheme at longer times. The method applied in this work offers many advantages. First of all it can be applied to groups of animals 'in situ', which provides more representative data of livestock in general and makes it possible to study the factors that influence the emissions in field conditions. It can also be applied to characterize the cattle facilities individually. This would prevent the need for extrapolation of the emission factors supplied by inventories or other authors.

The method is also advantageous when compared to other methods that are applied to naturally ventilated buildings (Demmers et al., 1998; Ngwabie et al., 2009) since these methods require accurate measurements of ventilation rates of the buildings and the concentration in the exit air. Ventilation rates can be obtained by monitoring the pressure differences over the ventilation openings or using a tracer gas mass balance, which entails measuring its concentration at the inlets and the outlets. The disadvantage of the tracer gas method lies in the non-homogeneous gas distribution that makes necessary the use of many sensors around the building in order to calculate a more representative concentration value. Since the method proposed is based on a fan system that mixes the air inside the building, the air homogeneity is ensured and the number of sensors can be reduce notably. Especially when OP-FTIR spectroscopy is used since it measures simultaneously all the target gases. In addition, the deleterious effects of the ambient conditions, such as temperature and humidity (Koerkamp et al., 1998), are reduced when the emission measurement is carried out with the openings (or windows) close.

Once it has been demonstrated that the building behaves as an accumulation chamber, the measurements can be repeated in cycles of ventilation/closing in longer periods of time to measure the emissions in different conditions. Besides, the instrumentation reduction makes possible the use of this method by non-specialized personnel.

In addition, this method could be a simple tool to calculate emissions factors associated to different activities provided that they take place in a closed building.

The methodology proposed could evolve in the future a simple tool to study the variability of emission factors with the characteristics of the animals and their breeding since the methodology errors are lower than EMEP/CORINAIR ones (30% for CH_4 and NH_3). This methodology also could be used to adapt the established emission factors to specific conditions of each building.

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References

Amon, B., Amon, Th., Boxberger, J., Alt, Ch, 2001. Emissions of NH_3, N_2O and CH_4 from dairy cows housed in a farmyard manure tying stall (housing, manure storage, manure spreading). Nutrient Cycling in Agroecosystems 60, 103–113.

Aneja, V.P., Bunton, B., Walker, J.T., Malik, B.P., 2001. Measurement and analysis of atmospheric ammonia emissions from anaerobic lagoons. Atmospheric Environment 35, 1949–1958.

Aneja, V., Wang, V., Tong, Q., Kimball, H., Steger, J., 2006. Characterization of major chemical components of fine particulate matter in North Carolina. Journal of the Air and Waste Management Association 56, 1099–1107.

Bacsik, Z., Komlósi, V., 2006. Comparison of Open Path and extractive Long-Path FTIR techniques in detection of air pollutants. Applied Spectroscopy Reviews 41, 77–97.

Baubron, J.C., Mathieu, R., y Miele, G., 1991. Measurement of Gas Flows from Soils in Volcanic Areas: The Accumulation Method. Napoli '91 International Conference on Active Volcanoes and Risk Mitigation. Napoli, Italy, 27 August–1 September, 1991.

Blaxter, K.L., Clapperton, J.L., 1965. Prediction of the amount of methane produced by ruminants. British Journal of Nutrition 19, 511–522.

Bluteau, C.V., Daniel, I., Massé, D.I., Leduc, R., 2009. Ammonia emission rates from dairy livestock buildings in Eastern Canada. Biosystems Engineering 103, 480–488.

Bobbink, R., Hornung, M., Roelofs, J., 1998. The effects of air-borne nitrogen pollutants on species diversity in natural and semi-natural European vegetation. Journal of Ecology 86 (5), 717–738.

Cardellini, C., Chiodini, G., Frondini, F., Granieri, D., Lewicki, J., Peruzzi, L., 2003. Accumulation chamber measurements of methane fluxes: application to volcanic-geothermal areas and landfills. Applied Geochemistry 18, 45–54.

Childers, J.W., Thomson, E.L., Harris, D.B., Kirchgessner, D.A., Clayton, M., Natschke, D.F., Phillips, W.J., 2001. Multi-pollutant concentration measurements around a concentrated swine production facility using open-path FTIR spectrometry. Atmospheric Environment 35 (11), 1923–1936.

Chiodini, G., Frondini, F., y Raco, B., 1996. Diffuse emission of CO_2 from the Fossa crater, Vulcano Island (Italy). Bulletin of Volcanology 58, 41–50.

Cioni, R., Guidi, M., Raco, B., 1998. Soil CO_2 flux measurements in volcanic and geothermal areas. Applied Geochemistry 13 (5), 543–552.

Demmers, T.G.M., Burgess, L.R., Short, J.L., Phillips, V.R., Clark, J.A., Wathes, C.M., 1998. First experiences with methods to measure ammonia emissions from naturally ventilated cattle buildings in the UK. Atmospheric Environment 32 (3), 285–293.

Denmead, O.T., 2008. Approaches to measuring fluxes of methane and nitrous oxide between landscapes and the atmosphere. Plant Soil 309, 5–24.

Depta, G., Neser, S., Becher, S., Gronauer, A., 1997. Distinction between different slurry application technics by their ammonia emission with FTIR-Open-Path measurements and dispersion modelling. In: Schäfer, K. (Ed.), Proceedings of SPIE 3106. Munich, Germany, pp. 145–152, 19–20 June (1997).

Eklund, B., 1998. Comparison of line-and-point-source releases of tracer gases. Atmospheric Environment 33, 1065–1071.

Elzing, A., Monteny, G.J., 1997. Modelling and experimental determination of ammonia emission rates from a scale model dairy-cow house. Transactions of American Society of Agricultural Engineers 40 (3), 721–726.

European Environment Agency, 2007. Joint EMEP/CORINAIR Atmospheric Emission Inventory Guidebook, third ed. European Environment Agency, Copenhagen.
Forbrich, I., Kutzbach, L., Hormann, A., Wilmking, M., 2010. A comparison of linear and exponential regression for estimating diffusive CH_4 fluxes by closed-chambers in peatlands. Soil Biology & Biochemistry 42, 507–515.
Genfa, A., Uehara, T., Dasgupta, P.K., Clarke, A.D., Winiwarter, W., 1998. Measurement of diffusive flux of ammonia from water. Analytical Chemistry 70 (17), 3656–3666.
Griffith, D.W.T., Leuning, R., Denmead, O.T., Jamie, I.M., 2002. Air-land exchanges of CO_2, CH_4 and N_2O measured by FTIR spectrometry and micrometereological techniques. Atmospheric Environment 36, 1833–1842.
Hashmonay, R.A., Yost, M.G., Mamane, Y., Benayahu, Y., 1999. Emission rate apportionment from fugitive sources using open-path FTIR and mathematical inversion. Atmospheric Environment 33, 735–743.
Hutchinson, G.L., Mosier, A.R., 1981. Improved soil cover method for field measurement of nitrous oxide fluxes. Soil Science Society of America Journal 45, 311–316.
Johnson, K.A., Johnson, D.E., 1995. Methane emissions from cattle. Journal of Animal Science 73, 2483–2492.
Jungbluth, T., Hartung, E., Brose, G., 2001. Greenhouse gas emissions from animal houses and manure stores. Nutrient Cycling in Agroecosystems 60 (1–3), 133–145.
Koerkamp, G., Metz, P.W.G., Uenk, J.H.M., Philips, V.R., Holden, M.R., Sneath, R.W., Short, J.L., White, R.P., Hartung, J., Seedorf, J., Schröeder, M., Linkert, K.H., Pedersen, S., Takai, H., Johnsen, J.O., Wathes, C.M., 1998. Concentrations and emissions of ammonia in livestock buildings in Northern Europe. Journal of Agricultural Engineering Research 70, 79–95.
Kroon, P.S., Hensen, A., van den Bulk, W.C.M., Jongejan, P.A.C., Vermeulen, A.T., 2008. The importance of reducing the systematic error due to non-linearity in N_2O flux measurements by static chambers. Nutrient Cycling in Agroecosystems 82, 175–186.
Lamb, B., Westberg, H., Allwine, G., 1986. Isoprene emission fluxes determined by an atmospheric tracer technique. Atmospheric Environment 20, l–8.
Livingston, G.P., Hutchinson, G.L., Spartalian, K., 2006. Trace gas emission in chambers: a non-steady-state diffusion model. Soil Science Society of America Journal 70, 1459–1469.
Minnich, T., Scotto, R.L., Brady, J.J., Kohlmann, H.J., O'Connor, P., Mallik, S., Parekh, K., 2002. Use of Open-Path FTIR Spectroscopy to support development of refined estimates of H2S emissions from a New York City municipal wastewater treatment plant. In: Air & Waste Management Association's 95th Annual Conference and Exhibition. Baltimore, Maryland, pp. 23–27. June.
Moe, P.W., Tyrrell, H.F., 1979. Methane production in dairy cows. Journal of Dairy Science 62, 1583–1586.
Mosier, A., 1989. Chamber and isotope techniques. In: Andreae, M.O., Schimel, D.S. (Eds.), Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere. Report of the Dahlem Workshop: 175–188, 19–24 Febr. 1989, Berlin, Germany.
Ngwabie, N.M., Jeppsson, K.-H., Nimmermark, S., Swensson, C., Gustafsson, G., 2009. Multi-location measurements of greenhouse gases and emission rates of methane and ammonia from a naturally-ventilated barn for dairy cows. Biosystems Engineering 103, 68–77.
Nolasco, D., Melián, G., Rancel, N., Hernández, P.A., Pérez, N.M., 2006. VOCs emission to the atmosphere from sewage treatment plant. In: 6° Congreso Internacional de Química de la ANQUE, 566, ISBN 84-690-2349-7.
Nolasco, D., Lima, R.N., Hernández, P.A., Pérez, N.M., 2008. Non-controlled emission of CO_2 and CH_4 to the atmosphere from Lazareto landfill, Tenerife, Canary Islands. Environmental Science and Pollution Research International 15 (1), 51–60.
Oldenburg, J., 1989. Geruchs- und Ammoniak-Emissionen aus der Tierhaltung. KTBL-Schrift 333. Kuratorium für Landtechnik und Bauwesen in der Landwirtschaft e.V., Darmstadt.
Parkinson, K.J., 1981. An improved method for measuring soil respiration in the field. Journal of Applied Ecology 18, 221–228.
Pedersen, A.R., Petersen, S.O., Schelde, K., 2010. A comprehensive approach to soil-atmosphere trace-das flux estimation with static chambers. European Journal of Soil Science 61, 888–902.
Piccot, S.D., Masemore, S.S., Ringler, E.S., Srinivasan, S., 1994. Validation of a method for estimating pollution emission rates from area sources using Open-Path FTIR spectroscopy and dispersion modeling techniques. Journal of the Air and Waste Management Association 44, 271–279.
Russwurm, G.M., Childers, J.W., 1997. Quality assurance/quality control issues in open-path FTIR monitoring. In: Cecchi, Giovanna, et al. (Eds.), SPIE Proceedings on Remote Sensing of Vegetation and Water, and Standardization of Remote Sensing Methods, 3107, pp. 86–92.
Russwurm, G.M., 1997. Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases, second ed.. In: Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Center for Environmental Research Information, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268, USA. Compendium Method TO-16.
Schäfer, K., Sussmann, R., Trickl, T., Reitebuch, O., HOechstetter, K., Emeis, S., Steinecke, I., Depta, G., Gronauer, A., Neser, S., Becher, S., Seedorf, J., Hartung, J., 1997. Measuring the emissions of trace compounds from a livestock building. In: Schäfer, K. (Ed.), Proceedings of SPIE 3106, pp. 137–144. Munich, Germany 19–20 June (1997).
Schäfer, K., Böttcher, J., Weymann, D., Von der Heide, C., Duijnisveld, W., 2012. Evaluation of a closed tunnel for field-scale measurements of N2O fluxes at the soil-atmosphere interface. Journal of Environmental Quality 41, 1383–1392.
Schütz, H., Seiler, W., 1989. Chamber and isotope techniques. In: Andreae, M.O., Schimel, D.S. (Eds.), Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere. Report of the Dahlem Workshop: 175–188, 19–24 Febr. 1989, Berlin, Germany.
Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics. Wiley Interscience, New York, p. 1326.
Verein Deutscher Ingenieure, 2000. Fernmessverfahren. Messungen in der bodennahen Atmosphäre nach dem FTIR-Prinzip Messen gasförmiger Emissionen und Immissionen. Grundlagen ((Remote sensing. Atmospheric measurements near ground with FTIR spectroscopy Measurement of gaseous emissions and immissions. Fundamentals)). Verein Deutscher Ingenieure. VDI4211, Blatt1/Part 1, Deczember 2000/December 2000.
Wolin, M.J., 1960. A theoretical rumen fermentation balance. Journal of Dairy Science 40, 1452–1459.