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Analysis of the reactive nitrogen (Nr) balance as a tool for assessing the performance of air scrubbers at livestock facilities

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Publisher
Wageningen UR Livestock Research
P.O. Box 65, 8200 AB Lelystad
Telephone +31 320 - 238238
Fax +31 320 - 238050
E-mail info.livestockresearch@wur.nl
Internet http://www.livestockresearch.wur.nl

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Abstract
The accuracy of the evaluation of air scrubber efficiency for ammonia removal using two types of mass balance calculations was assessed. In the first mass balance calculations only the gas phase ammonia concentration was used, whereas in the second calculations, the combined air-water mass balance was used.

It was shown that the gas based mass balance has a smaller uncertainty. In general, it was shown that due to the uncertainties when using mass balances, the formation of nitrous gases such as N_2O and NO_x can only be confirmed if these concentrations exceed 7-10% of the value of the ingoing ammonia concentration.

Keywords
Nitrogen balance, uncertainty, air scrubber, ammonia

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Authors
F. Estellés
R.W. Melse
D.A.J. Starmans
N.W.M. Ogink

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Preface

The work described in this report was commissioned by the Dutch Ministry of Economic Affairs, Agriculture and Innovation and the Dutch Ministry of Infrastructure and the Environment as part of the research program Programma Gecombineerde Luchtwassers (PGL). The study was carried out by Wageningen UR Livestock Research, Netherlands, in cooperation with the Institute of Animal Science and Technology of the Polytechnic University of Valencia, Spain.

The authors,

Fernando Estellés (Polytechnic University of Valencia)
Roland Melse (Wageningen UR Livestock Research)
Dick Starmans (Wageningen UR Livestock Research)
Nico Ogink (Wageningen UR Livestock Research)

Samenvatting

De veehouderijsector draagt bij aan emissies naar de atmosfeer van ammoniak (NH_3), geur, broeikasgassen (voornamelijk methaan (CH_4) en lachgas (N_2O)), en fijnstof (PM10 and PM2.5). Om deze emissies te verminderen is zowel nationale als internationale wet- en regelgeving van kracht. Er bestaan verscheidene methoden om emissies uit stallen tegen te gaan, zoals nageschakelde luchtbehandelingssystemen die de ventilatielucht behandelen. Dergelijke luchtwassers worden o.a. in Nederland op grote schaal toegepast.

In een luchtwasser wordt lucht door een poreus, meestal kunststof pakkingsmateriaal geleid dat continu bevochtigd wordt. Hoewel de luchtwassers binnen de veehouderij oorspronkelijk waren bedoeld voor de verwijdering van ammoniak uit de stallucht, wordt ook een deel van de geurcomponenten en stofdeeltjes verwijderd. In een chemische luchtwasser wordt ammoniak in de wasvloeistof gebonden met zuur en in een biologische luchtwasser wordt ammoniak door bacteriën omgezet in hoofdzakelijk nitriet en nitraat. In dit laatste type luchtwassers kunnen in principe ook andere gasvormige stikstofverbindingen worden gevormd, zoals lachgas (N_2O) of stikstofgas (N_2).

De ammoniakverwijderingsefficiëntie van een luchtwasser kan bepaald worden met behulp van een massabalans-methode, d.w.z. de hoeveelheid stikstof die de luchtwasser in gaat wordt vergeleken met de hoeveelheid stikstof die de luchtwasser vervolgens weer verlaat. Er kunnen twee typen massabalansen worden onderscheiden:

1. een massabalans gebaseerd op de luchtstroom (“luchtbalans”), waarbij de ammoniakconcentratie van de ingaande en uitgaande lucht van de luchtwasser wordt gemeten
2. een gecombineerde massabalans, waarbij behalve de lucht-balans ook een water-balans wordt opgesteld op basis van de opgeloste hoeveelheid ammonium, nitraat en nitriet in het was- en spuiwater.

De eerste methode is eenvoudig van opzet omdat het voldoende is om de ammoniakconcentratie van de ingaande en uitgaande lucht te bepalen zonder dat het nodig is het luchtdebiet door de wasser te bepalen. Er wordt echter geen rekening gehouden met de mogelijk productie van gasvormige stikstofcomponenten anders dan ammoniak. De tweede methode is mogelijk wél geschikt om een inschatting te maken van de hoeveelheid N_2 en N_2O die mogelijkerwijs wordt geproduceerd in een biologische luchtwasser (bij chemische luchtwassers wordt geen productie van gasvormige stikstofverbindingen verwacht).

Het doel van deze studie was om vanuit een theoretisch perspectief de meetonzekerheid van beide massabalans-methoden te evalueren en na te gaan of een gecombineerde water-lucht balans een geschikte manier is om de eventuele productie van N_2O en N_2 in biologische luchtwassers te kwantificeren.

Een onzekerheidsmodel werd opgezet dat het meest eenvoudige geval (d.w.z. zonder N_2O en N_2 productie) beschrijft, namelijk een chemische wasser op een vleesvarkensbedrijf. Het model werd ontwikkeld voor twee verschillende theoretische ammoniakverwijderingsrendementen (70% and 95%) en twee verschillende methoden voor het meten van de ammoniakconcentratie (respectievelijk nat-chemisch en m.b.v. een NO_x monitor).

Uit de modelberekeningen blijkt dat beide balansmethoden nauwkeurig zijn, dat wil zeggen dat de systematische fouten zeer klein zijn. De luchtbalans geeft echter een aanzienlijke hogere precisie (dat wil zeggen dat de toevallige fout klein is) dan de gecombineerde balans, waarbij het verschil in precisie afhankelijk is van het niveau van het verwijderingsrendement en de gekozen meetmethodes voor ammoniakconcentraties

Combinatie van beide massabalansen maakt het in principe mogelijk om de hoeveelheid N_2 en N_2O te berekenen die in de luchtwasser worden gevormd. Naar aanleiding van de berekende meetonzekerheden in beide methoden kan worden vastgesteld dat dit alleen mogelijk is als de hoeveelheid gemeten nieuw gevormde stikstof hoger is dan 7-10% van de totale hoeveelheid ingaande stikstof; lagere hoeveelheden worden gemaskeerd door de meetonzekerheid. De belangrijkste bijdrage aan de meetonzekerheid wordt geleverd door de meting van het luchtdebiet, gevolgd door de meting van de ammoniakconcentratie van de uitgaande lucht. Het verkleinen van de

onzekerheid van de luchtdebietmeting zal dan ook het sterkst bijdragen aan de verkleining van de overall meetonzekerheid.

Nader onderzoek is gewenst om het ontwikkelde model experimenteel te testen en te valideren. Daarnaast zou een complexer model gemaakt kunnen worden waarin ook de optredende biologische processen worden opgenomen. Verder is het zinvol om nader onderzoek uit te voeren naar de meetonzekerheid van elke parameter, waarbij vooral luchtdebietmetingen nader aandacht behoeven.

Summary

The environmental impact from livestock production is one of the main problems of this sector. Local and international regulations have been defined to reduce the environmental load of livestock farms. There are several techniques available aimed to the abatement of airborne emissions in farms. Among these techniques end-of-the-pipe approaches, such as air scrubbers, have turned into off-the-shelf techniques in Northern European countries such as The Netherlands.

An air scrubber usually is a packed-bed reactor filled with an inert, inorganic packing material. This material is intermittently sprayed with water to keep it wet. The exhaust air of the farm is driven through the scrubber. This process results in contact between air and water, and enables mass transfer from gas to liquid phase. Air scrubbers were originally aimed to reduce ammonia emissions but they also reduce particulate matter and odour emissions to the atmosphere. Ammonia scrubbers can operate under two principles: chemical and biological. Chemical scrubbers are based on the absorption of ammonia in an acid solution while biological scrubbers are based on the biological transformation of ammonium into nitrites and nitrates. This second type of scrubbers may produce other N-products such as nitrous oxide (N_2O) and molecular nitrogen (N_2) as a secondary reaction.

The ammonia removal efficiency of air scrubbers in livestock facilities may be determined using mass balance methods, *i.e.* a comparison of input and output nitrogen levels is made. There are two main techniques available:

1. air-based balances in which only ammonia concentrations are measured before and after the scrubber
2. combined balances, which combine the air-based ammonia balance with a water balance taking into account ammonium, nitrite, and nitrate amounts in the water.

The first method is straightforward because only ammonia concentrations need to be determined without the need for air flow measurement; however, the possible formation of gaseous nitrogen compounds other than ammonia is neglected. The second method might be appropriate to estimate the amounts of N_2 and N_2O that are possibly generated in biological scrubbers as the amount of nitrogen that can not be accounted for in the balance. For chemical scrubbers no formation of gaseous nitrogen compounds is to be expected.

At present, there is no internationally acknowledged standard procedure for the assessment of ammonia removal efficiency in scrubbers at livestock facilities. The main aim of this work was to evaluate, in a theoretical framework, the uncertainty of both methods available for the assessment of ammonia removal from scrubbers, *viz.* air-based balances and combined balances. In addition, it was assessed whether the combination of both massbalances is a reliable method for the quantification of N_2O and N_2 formation in biological scrubbers. Also the uncertainty introduced by all variables involved in the process was quantified in order to identify the main contributors to the uncertainty of the final results.

An uncertainty model was built considering the simplest case, *i.e.* without N_2O and N_2 formation, based on a chemical scrubber installed in a fattening pigs facility. The model was developed considering two different theoretical ammonia removal efficiencies (70% and 95%) and, for each one, two methods for the measurement of ammonia concentrations (impingers and NO_x monitors, respectively).

From the model calculations it follows that both balance methods are accurate, *i.e.* the systematic errors are very small. However, the air-based balance yields a considerably higher precision (*i.e.* the random error is small) than the combined balance. This difference in precision level depends on the removal efficiency and the applied ammonia measurement method.

Regarding to the uncertainties calculated, N_2 and N_2O formation can only be determined using the combined mass balances if they are higher than 7-10% of the input nitrogen flow, otherwise the error committed may mask the results. The main contributor to the final uncertainty was the airflow rate measurement, followed by the ammonia concentrations leaving the scrubber. Airflow rate measurement uncertainty was also the most sensitive parameter in the model, which means than reducing airflow uncertainty, would lead to a direct reduction of the final uncertainty of the model.

Further experimental work is necessary to practically validating the theoretical findings of this work. In addition, a more complex model that considered biological processes occurring in a biological scrubber could be developed and tested. Finally, additional investigations into parameter uncertainties would be beneficial, with special attention to the determination of uncertainties from airflow rate measurements.

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1 Introduction

1.1 Animal husbandry and atmospheric pollution

Intensive poultry and pig operations are main contributors to ammonia, odour and particulate matter emissions in agriculture. Furthermore, odour emissions from animal housing are being increasingly considered a nuisance, due to the close approximation of farming areas and rural residential development. During the last years, international commitments (*e.g.* Kyoto Protocol, European Ceilings Directive 2000/81 CE) are binding the countries to reduce the total emissions of atmospheric pollutants. As a result, techniques that reduce these emissions have received a more prominent role in livestock farming.
The past decade has seen the development of a large variety of low-emission livestock housing systems. These systems include end-of-pipe solutions for treatment of the exhaust air from pig and poultry houses, such as acid scrubbers and bioscrubbers (also called biotrickling filters). As development progressed, these systems have become off-the-shelf techniques for the reduction of NH_3 emissions in countries like The Netherlands, Germany and Denmark.

1.2 Working principle of scrubbers

An air scrubber is a reactor filled with an inert packing material. This material is intermittently sprayed with water to keep it wet. The exhaust air of the livestock facility is driven through the air scrubber, resulting in an intense contact between air and water, enabling ammonia mass transfer from the gas phase to the liquid phase. The majority of the trickling water is continuously recirculated, whereas part of it is discharged and replaced by fresh water. The main scheme of a scrubber is shown in Figure 1.

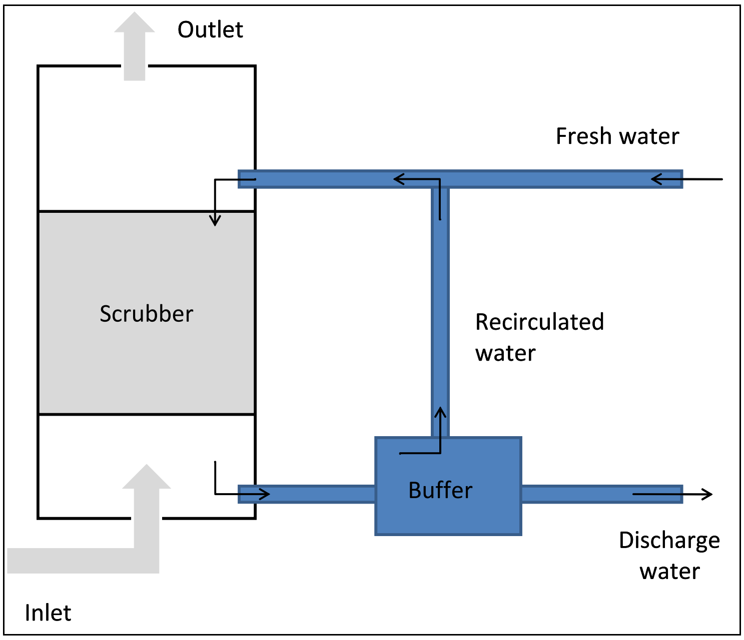


Figure 1 Scheme of a single stage scrubber
Source: Modified from (Melse and Ogink, 2005)

Based on operation principle scrubbers can be divided into three main groups: chemical scrubbers, bioscrubbers (or biotrickling filters) and multi-pollutant scrubbers.

Chemical scrubbers are based on the capture of ammonia in an acid solution that is being recirculated over the packing material. An ammonium salt is formed then, that is discharged at a pre-determined frequency. Sulphuric acid is often used as the acidic component to keep pH values between 2 and 4. Under these conditions, Melse and Ogink (2005) reported an average ammonia removal efficiency of 96% (ranging from 40 to 100%).

Bioscrubbers or ***Biotrickling filters*** are based on the capture of ammonia in a watery phase and subsequent breakdown by bacteria in a biofilm on the packing material. These bacteria convert the water soluble components of the treated air. Due to this bacterial activity, ammonia is converted into nitrites and nitrates. As these nitrogen compounds are toxic to the bacteria, the concentrations of these compounds are kept below inhibiting levels by regular discharge of the recirculation liquid. Average ammonia removal has been calculated to be 70% (ranging from 0 to 100%) by Melse and Ogink (2005).

Multi-pollutant scrubbers are in fact a combination of both previous systems. To improve the odour removal capacity of bioscrubbers, the ingoing air is a pre-cleaned using a cascade of a water scrubber and a chemical scrubber to remove dry matter and ammonia respectively. An average ammonia reduction of 83% (ranging from 63 to 98%), was reported by (Ogink *et al.*, 2008) for this system.

In bioscrubbers, and also during the biological step of multi-pollutant scrubbers, the nitrogen cycle is usually more complex that just forming nitrites and nitrates. First, part of the ammonia present in the air is converted into ammonium due to a natural equilibrium dependent of the pH (Equation 1).

Equation 1 Ammonia and ammonium equilibrium equation

$$\boxed{NH_3(g) + H_2O \leftrightarrow NH_3(aq) + H_2O \leftrightarrow NH_4^+ + OH^-}$$

Subsequent bacterial oxidation from ammonium to nitrite (NO_2^-) and from nitrite to nitrate (NO_3^-) is called nitrification which is mainly carried out by *Nitrosomonas* and *Nitrobacter* species respectively. Equation 2 and Equation 3 resume these processes.

Equation 2 Nitrification process I

$$\boxed{NH_4^+ + OH^- + 1.5O_2 \rightarrow NO_2^- + H^+ + 2H_2O}$$

Equation 3 Nitrification process II

$$\boxed{NO_2^- + H^+ + 2H_2O + 0.5O_2 \rightarrow NO_3^- + H^+ + 2H_2O}$$

If anaerobic conditions are achieved in the scrubber, denitrification processes also occur, converting nitrates into molecular nitrogen (Equation 4),

Equation 4 Denitrification process

$$\boxed{2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O}$$

But this reaction is more complex. Actually, the denitrification process consists in four steps (Equation 5). Depending on the conditions, mainly the amount of oxygen present, the process can be stopped in an intermediate point of the reaction, being produced nitrogen oxides such NO or N_2O.

Equation 5 Complete denitrification process

$$\boxed{NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2}$$

1.3 Problem definition

Measuring the efficiency of scrubbers in terms of ammonia removal is no standard procedure. Two main techniques can be found as described by (Shah *et al.*, 2008), both are based in mass balances.

The first technique is based on the reduction of ammonia concentration in the gaseous phase, using the ammonia concentration before and after the scrubbing process. This is the most widespread technique in The Netherlands (Melse and Moi, 2004; Ogink *et al.*, 2008).

The second technique consists in measuring the amount of nitrogen that has been recovered in the water, and relating it to the total amount of ammonia entering the system. This technique has been used in Germany (Hahne and Brandes, 2002).

The main advantage of the first technique defined is its simplicity; one only needs to measure ammonia concentrations, which means that measuring errors are drastically reduced. On the other hand, the second technique is much more robust, providing more information about the actual process inside the scrubber. Still, the latter calculation may result in higher errors due to the fact that nitrogen concentrations need to be analyzed in both watery and gaseous phase. Additionally, the water volume of the scrubber needs to be determined.

By finding the best way to estimate the efficiency of the system, a standard calculation procedure could be developed that could be used for in a certification program. To achieve this objective, both theoretical and experimental work must be evaluated. In the theoretical approach an analysis of the errors involved in both methods, as well as their propagation during the calculating process is the first step of this process is given.

In order to evaluate the experimental calculations, additional data is needed. Although the production of secondary nitrogen gases like N_2O during the process has been rarely investigated in scrubbers, Hahne and Brunswick (2004) reported a value of 3% in relation to the initial ammonia load (on a nitrogen basis), but no more information has been published in this respect. The amount of N_2O produced during the process, could be estimated through these mass balances, providing they are accurate enough. Therefore, the investigation about those balance errors can lead to decide if N_2O emissions from scrubbers can be determined using N balances instead direct nitrous oxide measurements.

This report will cover a review of basic information about the process to understand the need to know the error propagation in the mass balance calculations. In the upcoming chapters, a review is given on nitrogen balances in scrubbers, followed by a short summary of the main measurement techniques that can be used to gather the data needed in these mass balances. Finally, an overall explanation about the uncertainty and management of errors will be given.

1.4 Nitrogen mass balances

1.4.1 Primary considerations

When developing a nitrogen mass balance in which atmospheric air is involved, it is important to consider that most of the nitrogen present is in form of N_2, as this gas is the major component of the atmosphere (approximately 78%). In addition, N_2 is a very stable, inert molecule that can present a problem when its concentration is measured using a technique that requires a chemical reaction.

Failure to be able to measure N_2 leads to a hard-to-measure nitrogen-based mass balance. One possible solution to deal with this is to just consider the other N-containing molecules, know also as reactive nitrogen compounds (Nr).

According to the Woods Hole Research Centre (WHRC and UNEP, 2007), reactive nitrogen includes all biologically, chemically, and radio-active nitrogen compounds in the atmosphere and biosphere. It includes forms of nitrogen, such as ammonia (NH_3), and ammonium (NH_4^+), nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3), nitrous oxide (N_2O), nitrites (NO_2^-) and nitrates, and organic compounds such urea, amines, proteins and nucleic acids. This can be summarized as all the forms of nitrogen excluding molecular nitrogen (N_2).

1.4.2 General approach to balances

When considering ammonia removal in scrubbers, it is important to know about the reactive nitrogen cycle that takes place in it. Basically, Nr removed from the farm exhaust air, must be present in the discharge water of the scrubber, regardless if we are dealing with a single stage scrubber or a multi stage scrubber. Equation 6 resumes this simple balance:

Equation 6 Reactive nitrogen balance in an air and water exchange system in a steady state

$$\boxed{\Delta Nr_w = \Delta Nr_a}$$

Where:
ΔNr_W: Change of the reactive nitrogen content in the watery phase
ΔNr_a: Change of the reactive nitrogen content in the gaseous phase

As seen before it's known that nitrification-denitrification (NDN) processes can develop in the scrubber, mainly when a biotrickling filter is present, but also in acid scrubbers (see section 1.2, page 1). This means that some of the reactive nitrogen is removed from the inlet air and that it should either be found in the watery phase, or in the outlet gaseous phase as N_2O or N_2. If N_2O is produced, it can be measured as a part of the reactive nitrogen leaving the system, but not N_2. In that case it is needed to add a new term to the Equation 6 in which this produced non reactive nitrogen is considered. Equation 7 shows the reactive nitrogen balance when considering NDN processes.

Equation 7 Reactive nitrogen balance in an air and water exchange system with a NDN process

$$\boxed{\Delta Nr_w + N_{new} = \Delta Nr_a}$$

Where:
ΔNr_W: Change of reactive nitrogen content in water
ΔNr_a: Change of reactive nitrogen content in air
N_{new}: Newly-formed non-reactive nitrogen

Then, regarding to these questions, we can consider that the nitrogen balance in a scrubber it is composed of four components: one of them is the inlet air (reactive N), another two in the outlet air (reactive N and non-reactive N) and a last one in the watery phase (reactive N). Figure 2 resumes this process.

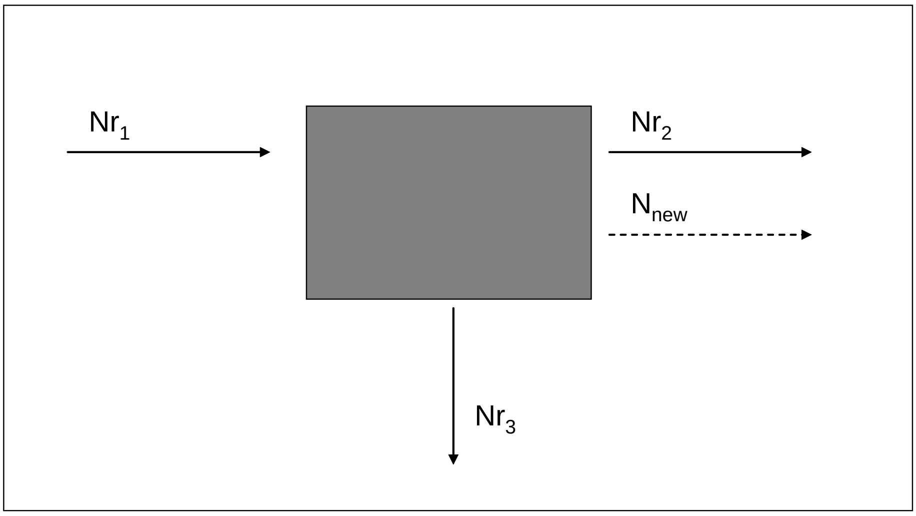


Figure 2 General scheme of a nitrogen balance in a scrubber
Source: Own elaboration

Therefore, considering the mass conservation law, the general equation that defines the nitrogen balance in a scrubber is (Equation 8):

Equation 8 General approach to reactive nitrogen balances

$$\boxed{Nr_1 = Nr_2 + Nr_3 + N_{new}}$$

Where:
Nr_1: Reactive nitrogen coming in the scrubber by air
Nr_2: Reactive nitrogen going out of the scrubber by air
Nr_3: Reactive nitrogen going out of the scrubber by the watery phase
N_{new}: New formed non-reactive nitrogen coming out by air

1.4.3 Types of mass balance

As seen before (see section 1.3, page 2) the reactive nitrogen balance in a scrubber can be generally dealt with in two ways. One of them is to calculate the difference between the reactive nitrogen content in the inlet and the outlet air (“***air balance***”). The second method consist in measuring, during a defined period, the amount of Nr coming in the system trough the inlet air and the recovery of Nr in the water (“***combined balance***”). The amount of reactive nitrogen removed from the air can be estimated using both systems. Figure 3 resumes both systems by showing the chosen system boundaries in both cases.

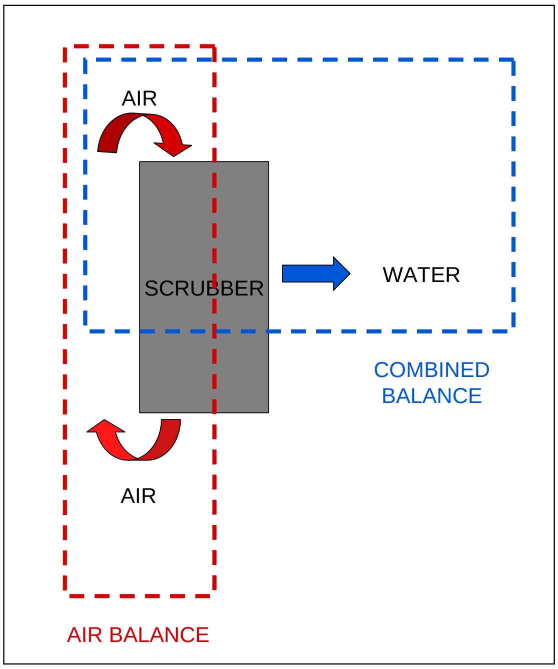


Figure 3 Types of reactive nitrogen balances in scrubbers
Source: Own elaboration

These two different approaches are used generally, to assess the scrubber efficiency (***ρ***). Scrubber efficiency calculated by means air balances ($\boldsymbol{\rho_a}$) is resumed in Equation 9, whereas Equation 10 resumes the process for combined balances ($\boldsymbol{\rho_c}$).

Equation 9 Calculated scrubbing efficiency in air balances

$$\boxed{\frac{Nr_1 - Nr_2}{Nr_1} = \rho_a}$$

Equation 10 Calculated scrubbing efficiency in combined balances

$$\boxed{\frac{Nr_3}{Nr_1} = \rho_c}$$

Considering that during the scrubbing period an unknown amount of N_2 is produced, the scrubbing efficiency calculated by the two mass balances may not be equal. That can be observed easily by developing Equation 8 (Equation 11 and Equation 12).

Equation 11 Development of Equation 8 (I)

$$\boxed{\frac{Nr_1 - Nr_2}{Nr_1} = \frac{Nr_3}{Nr_1} + \frac{N_{new}}{Nr_1}}$$

Equation 12 Development of Equation 8 (II)

$$\boxed{\frac{Nr_1 - Nr_2}{Nr_1} - \frac{Nr_3}{Nr_1} = \frac{N_{new}}{Nr_1}}$$

Combining Equation 12 with Equation 9 and Equation 10, we can obtain Equation 13 in which it can be observed that the differences observed between the efficiency calculated by means the two different approaches, they are equal to the difference between the immeasurable amount of nitrogen that comes in and out of the scrubber.

Equation 13 Relationship between calculated efficiencies

$$\boxed{(\rho_a - \rho_c) \times Nr_1 = N_{new}}$$

If we consider the errors (***ε***) that we made when measuring nitrogen fluxes (***Nr$_x$***), it leads us to Equation 14.

Equation 14 Relationship between calculated efficiencies considering errors

$$\boxed{(\rho_a - \rho_c) \times Nr_1 = N_{new} + \varepsilon}$$

Therefore, considering the value of these errors (***ε***) we could define with more or less accuracy the amount of non-reactive nitrogen that is being produced.

1.5 Reactive nitrogen fluxes in scrubbers

After defining the mass balance in terms of general fluxes, Nr fluxes described in Figure 2 were identified and developed. The amount of reactive nitrogen coming in the air inlet (Nr_1) is calculated by multiplying the volume of air moved through the scrubber during a period (***F***) by the concentration Nr. The Nr load present in the air is considered to be composed of gaseous nitrogen forms and solid nitrogen forms present in the dry matter that is carried by the air flow. These contributions to the reactive nitrogen flux are given in Equation 15.

Equation 15 Reactive nitrogen coming in the scrubber by the air (Nr_1)

$$\boxed{Nr_1 = F \times \left([N - NH_3]_1 + [N - N_2O]_1 + [N - NO_x]_1 + [N - DM]_1\right)}$$

Where:
Nr_1: Reactive nitrogen coming in the scrubber by the air (mg N)
F: Air volume through the scrubber (m^3)
$[N\text{-}NH_3]_1$: Concentration of N in ammonia form in the inlet air (mg/m^3)
$[N\text{-}N_2O]_1$: Concentration of N in nitrous oxide form in the inlet air (mg/m^3)
$[N\text{-}NO_x]_1$: Concentration of N in nitrogen oxides forms in the inlet air (mg/m^3)
$[N\text{-}DM]_1$: Concentration of N in dry matter in the inlet air (mg/m^3)

The flux calculation of the outgoing air is very similar to that of the inflowing air. Thus, the flux of Nr coming out the scrubber by the air (Nr_2), is given in Equation 16:

Equation 16 Reactive nitrogen coming out from the scrubber by the air (Nr_2)

$$\boxed{Nr_2 = F \times \left([N - NH_3]_2 + [N - N_2O]_2 + [N - NO_x]_2 + [N - DM]_2 \right)}$$

Where:

Nr_2: Reactive nitrogen going out of the scrubber by the air (mg N)
F: Air volume through the scrubber (m^3)
$[N\text{-}NH_3]_2$: Concentration of N in ammonia form in the outlet air (mg/m^3)
$[N\text{-}N_2O]_2$: Concentration of N in nitrous oxide form in the outlet air (mg/m^3)
$[N\text{-}NO_x]_2$: Concentration of N in nitrogen oxides forms in the outlet air (mg/m3)
$[N\text{-}DM]_2$: Concentration of N in dry matter in the outlet air (mg/m^3)

Finally, the reactive nitrogen flux going out the scrubber in the water phase (Nr_3), can be calculated as the sum of the amount of nitrogen recovered in the discharge water (Ndw) and the difference between the initial and final volume and Nr concentration in the bulk of the water phase during the measuring period, as given in Equation 17.

Equation 17 Reactive nitrogen coming out from the scrubber by the water (Nr_3)

$$\boxed{Nr_3 = Ndw + \Delta Nw}$$

Where:

Nr_3: Reactive nitrogen coming out the scrubber by the water (mg N)
Ndw: Nitrogen recovered in the discharge water (mg N)
ΔNw: Increase of nitrogen in the vessel (mg N)

The amount of nitrogen recovered in the discharge water must be assessed by multiplying nitrogen concentration by the volume of discharged water (Equation 18).

Equation 18 Determination of nitrogen recovered in discharge water

$$\boxed{Ndw = Vdw \times [Ndw]}$$

Where:

Ndw: Nitrogen recovered in the discharge water (mg N)
Vdw: Volume of discharge water recovered (m^3)
[Ndw]: Nitrogen content of discharge water (mg/m^3)

On the other hand, determination of the increase of nitrogen in the vessel requires knowledge of the N concentrations as well as the volume at the beginning and the end of the measuring period (Equation 19).

Equation 19 Determination of nitrogen content increase in the vessel

$$\boxed{\Delta Nw = V_f \times [Nw]_f - V_i \times [Nw]_i}$$

Where:

ΔNw: Increase of nitrogen in the vessel (mg N)
V_f: Final water volume in the vessel (m^3)
$[Nw]_f$: Final nitrogen content of water (mg/m^3)
V_i: Initial water volume in the vessel (m^3)
$[Nw]_i$: Initial nitrogen content of water (mg/m^3)

Finally, the concentration of Nr in the water is composed of different contributions, where both organic and inorganic forms are considered.
Equation 20 provides the correct nitrogen concentration in the water phase.

Equation 20 Nitrogen concentration in water ([Ndw]...[Nw]$_x$)

$$\boxed{[Ndw]\ldots[Nw]_x = [N-NO_2^-] + [N-NO_3^-] + [N-NH_4^+] + [N-DM]}$$

Where:

[N-NO$_2^-$]: Concentration of N in nitrite form in the water (mg/m^3)
[N-NO$_3^-$]: Concentration of N in nitrate form in the water (mg/m^3)
[N-NH$_4^+$]: Concentration of N in ammonium form in the water (mg/m^3)
[N-DM]: Concentration of N in dry matter in the water (mg/m^3)

1.6 Measurement of reactive nitrogen fluxes

As seen before, there are multiple contributions to consider when setting up a mass balance. Each contribution can be measured, but is subjected to specific errors related to the measurement methodology. To understand and quantify the individual errors related to the mass balance, a review and description of the main measurement methods for each contribution is necessary. Therefore, in the next sections, a review of the measurement methods to measure nitrogen concentrations and fluxes, both in air and water is given.

1.6.1 Airborne measurements

To measure the total amount of a gas dissolved in the air that is being released by a point source two data are needed. First of all the quantity of air (airflow) containing the gas that has been moved needs to be assessed, subsequently, the amount of gas present in the air (concentration) must be measured.

1.6.1.1 Airflow

There are two principal ways to measure the airflow. In the first method, the airflow is determined directly by the rate of rotation of a measuring fan. In the second method, the airflow is determined indirectly by using a tracer gas and calculating the ventilation rate from an overall mass balance. The second technique is mainly used in naturally ventilated livestock facilities, which means it is out of the scope of this work.

There have been a number of methods developed that directly determine fan ventilation rates. Three of them are discussed in this work: fan wheel anemometers, grid techniques, and finally, the use of manufacturer data regarding fan output.

a) Direct measurements

The most accurate way to assess ventilation rates in fans, it is to measure it directly by means an anemometer that covers the whole vane of the fan. That is generally achieved by using a fan-wheel anemometer installed upstream and in close proximity to the fan, to continuously measure the ventilation rate (Figure 4).

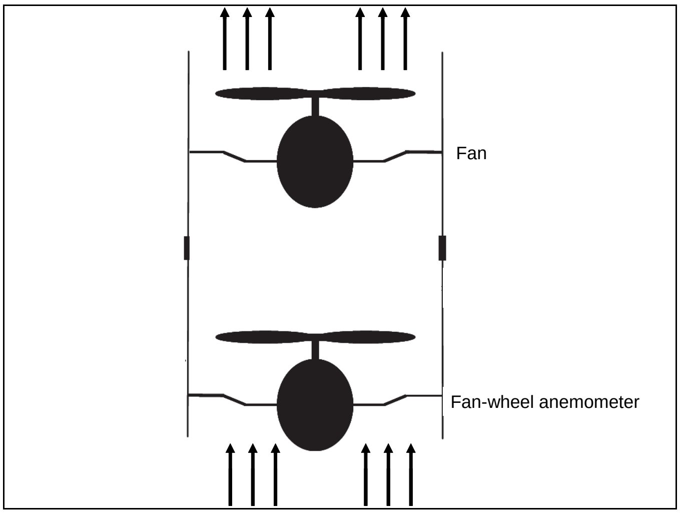


Figure 4 Scheme of direct ventilation measurement approach
Source: Adapted from (Mosquera et al., 2005)

The fan-wheel anemometer is calibrated in a wind tunnel at least once per year or before the start of the measurements (Mosquera *et al.*, 2005).

b) Grid techniques
In this technique, the anemometer used is smaller than the fan vane. Then, several measurements have to be done to obtain the average air speed. The amount of air moved is calculated then by multiplying the average air velocity and the fan surface Equation 21.

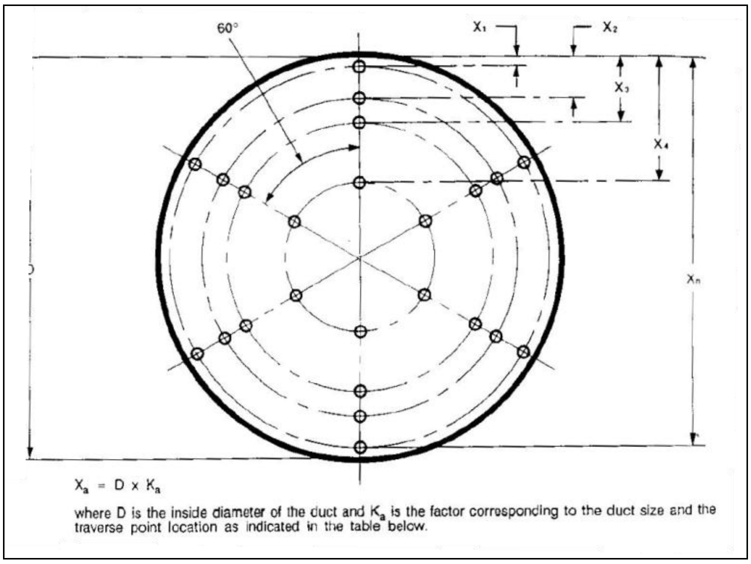
Equation 21 Ventilation rate determination in fans

$$\boxed{F = \bar{v} \times S}$$

Where:
F: Ventilation rate of the fan (m^3/h)
v: Average air velocity (m/h)
S: Fan surface (m^2)

Determination of fan surface it is not difficult and can be done with a high accuracy. On the other hand, the average air velocity in the fan it is not easy to determine due to the differences that can be found between different parts of the fan, and due to turbulences that introduce variable velocities at a fixed point. In such case, the local air velocity should be measured at each of a series of sampling points (traverse points) within the fan, forming a grid. The air flow is calculated using a numerical integration across the whole opening (Phillips *et al.*, 2001).

Air velocity measurements need to be carried out in a duct to avoid air turbulence. In order to obtain a representative average velocity it is necessary to locate each traverse point accurately. It is recommended that the number of traverse points increase with increasing duct size (ASHRAE, 2001). The distribution of traverse points for circular ducts can be seen in Figure 5.



$X_a = D \times K_a$

where D is the inside diameter of the duct and K_a is the factor corresponding to the duct size and the traverse point location as indicated in the table below.

Figure 5 Location of sampling points to determine average velocity in a circular fan
Source: ASHRAE (2001)

Usually, hot-wire anemometers are used to measure air velocities, despite the fact that small size fan-wheel anemometers can be used as well for this purpose.

It's also known that fans behave different at both varying pressure drop and rotational speeds (rpm). It is therefore necessary to determine the airflow for different pressure drops and different rotation speeds, providing calibration curves of the measuring fan prior to the actual measurement, for use during the experimental work.

c) Manufacturer calibration data
Finally, the less accurate, but cheaper and quicker method is to estimate the ventilation rate according to the data provided by the fan manufacturer. By measuring pressure and knowing the working regime of the fan, the ventilation rate can be assessed by checking manufacturer's tables or charts Figure 6).

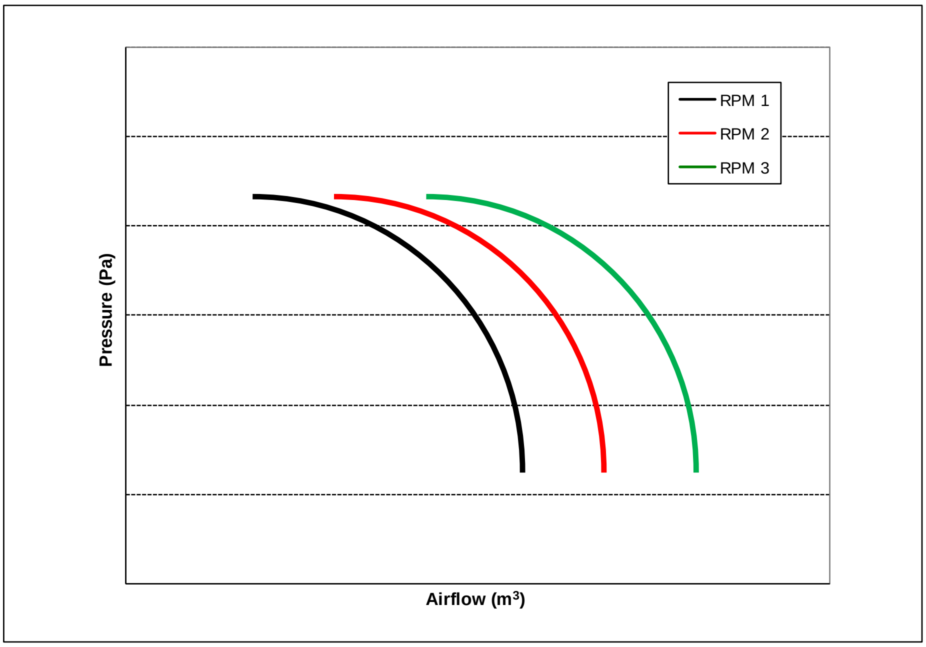


Figure 6 Fan curve for the determination of airflows
Source: Own elaboration

This methodology is considered less accurate because these tables or charts are calculated for whole models and not individual fans, and there is always a difference between the expected performance and the actual performance of fans, due to several reasons, including fouling and ageing.

1.6.1.2 Gas concentrations

There are several methods available to determine gas concentrations in the air. The most important ones regarding to their accuracy and use are:
a) Wet methods (impingers)
b) Chemiluminescence
c) Photo acoustic methods (PAS)
d) Fourier transformed infra red methods (FTIR)
e) Gas chromatography (GC)

a) Wet method (impinger)
In this method, a known airflow is taken through a liquid matrix containing an acid solution, the gas (mainly ammonia) is then captured in the matrix due to the chemical reaction produced Figure 7. Afterwards, the solution is analyzed in the laboratory and the amount of trapped nitrogen determined.

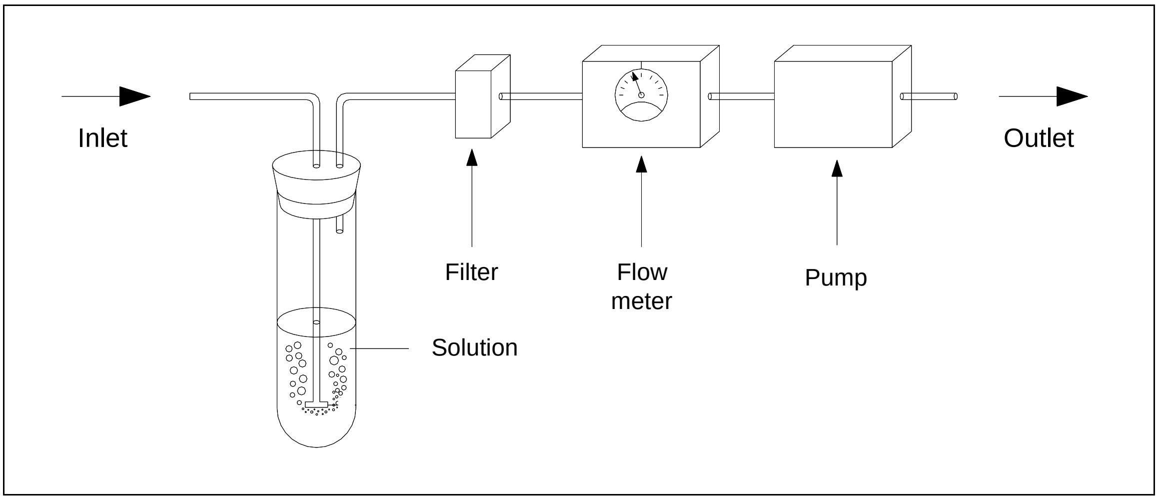


Figure 7 Wet methods components and working scheme
Source: Own elaboration

This methodology can be very sensible and useful to measure low gas concentrations. The accuracy depends directly on the measurement method used in the lab to determine the amount of ammonia trapped. The main problem of this method is that cannot be used for monitoring gas concentrations in real time, providing only mean values for a determined time basis.

b) Chemiluminescence (CL)
Chemiluminescence (CL) analyzers measure the amount of nitric oxide (NO) present in an air sample. The process is based in a reaction that involves NO and ozone (O_3) to produce nitrogen dioxide (NO_2) and a characteristic luminescence that can be measured by the analyzer Equation 22.

Equation 22 Reaction between NO and O_3 producing luminescence

$$\boxed{NO + O_3 \longrightarrow NO_2^* + O_2 \longrightarrow NO_2 + O_2 + h\nu_{1200\,nm}}$$

These devices are normally used to assess ammonia concentrations indirectly, by first converting NH_3 to nitric oxide, and then performing the NO analysis. The conversion of ammonia is achieved by means of a catalytic reaction (750-800^oC), using stainless steel as a catalytic active metal (Equation 23).

Equation 23 Conversion of NH_3 to NO

$$\boxed{NH_3 + 5O_2 + heat \xrightarrow{\substack{Fe_eO_3 \\ CrO_3}} 4NO + 6H_2O}$$

This is a very sensitive method that can be used for continuous gas concentrations monitoring.

c) Photo acoustic spectrophotometer (PAS)
In photo acoustic spectroscopy (PAS) the gas to be measured is intermittently irradiated by light of a pre-selected wavelength. The gas molecules absorb some of the light energy, which results in a repeating, momentary pressure increase similar to sound, that is detected using a microphone. The general principle of the PAS system and its constructive scheme is represented in Figure 8.

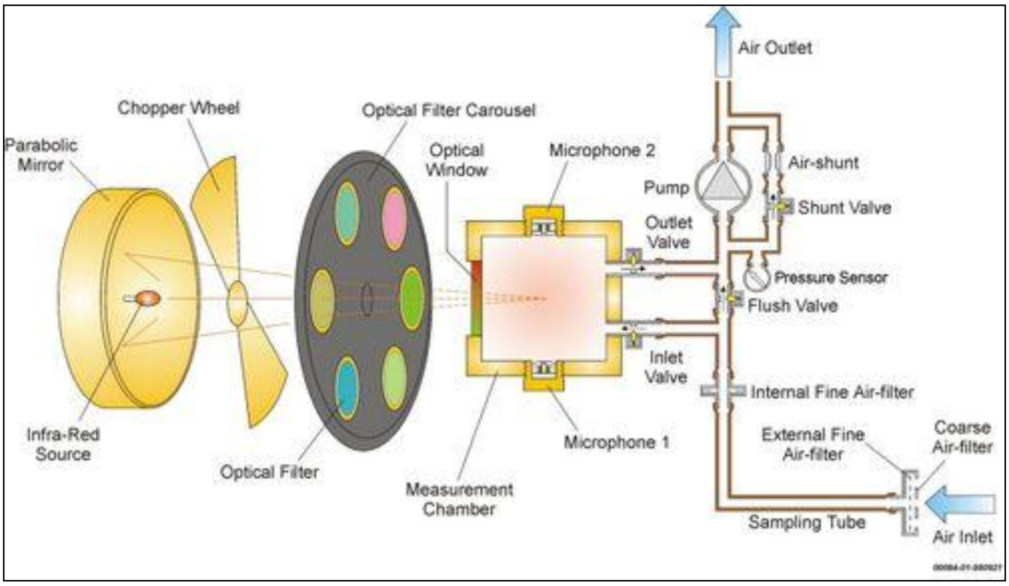


Figure 8 Schematic diagram of a PAS system
Source: LumaSense Technologies ®

This system can be used to measure multiple gases with the same instrument. It provides the measured value directly after the measurement. The sampling interval, and also the measurement interval, can be set by the user, being useful so to monitor gas concentrations.

d) Fourier transform infrared spectroscopy (FTIR)
This method consists of a measurement of the IR radiation absorption of a gaseous sample that is led through an interferometer (Smith, 1996). An interferometer is an instrument formed by two mirrors, one of them fixed and the other one mobile, and a light divisor. Depending on the mobile mirror movement, an interferogram is obtained. This information is mathematically transformed then into the Fourier domain, which turns the interferogram in a radiation absorption spectrum, depending on the wavelength.

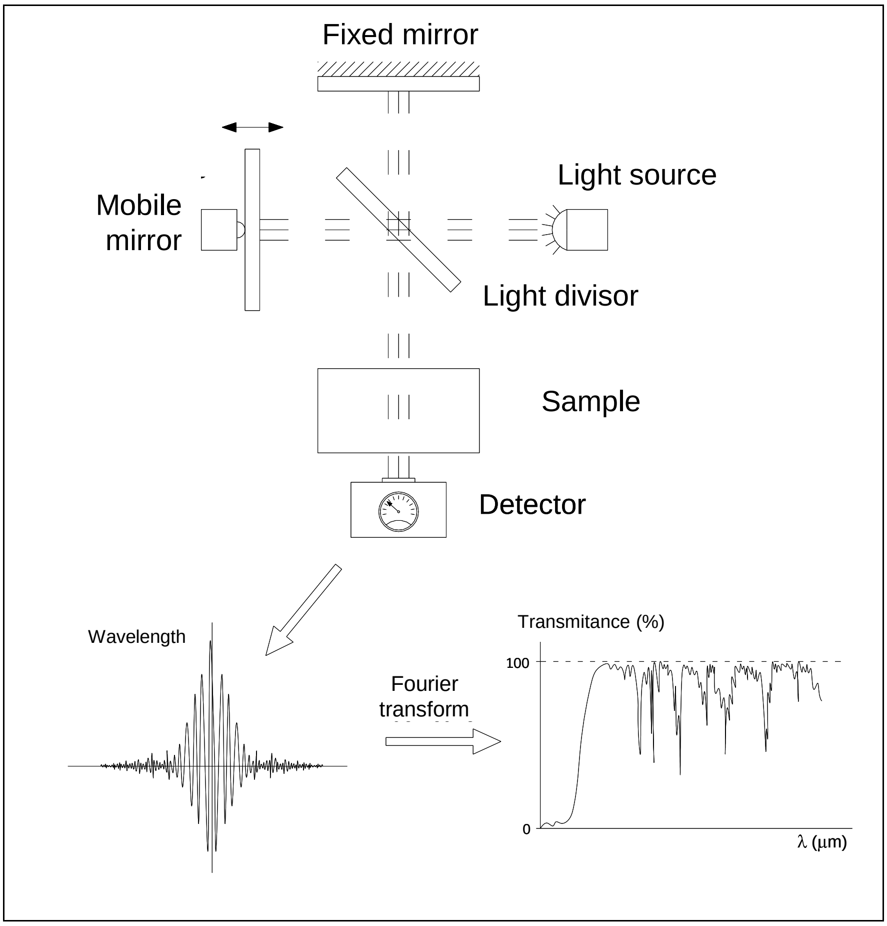


Figure 9 FTIR constructive scheme and data management
Source: Own elaboration

This absorption spectrum can be compared with absorption standards of known molecules, thus obtaining an accurate approach of the sample composition. The method sensitivity directly proportional to the distance over which the IR beam is changed by the sample, which means that for measuring low concentrations it is needed to project the beam through higher distances.
This system is very sensitive and accurate and can measure continuously in time, so it can be used for gas monitoring tasks. It can be used to measure different gases.

e) Gas chromatography (GC)
The most wide spread technique to measure gas concentrations is gas chromatography (GC). This methodology is based on the differences in distribution characteristics of molecules over a separation column with a stationary liquid phase that is perfused by a mobile gaseous phase containing the sample. As a result the individual components of the sample each have their own characteristic residence time on the column, allowing for each component to be identified and quantified consecutively by a detector.
This methodology can be used to measure almost all gases we can find in a livestock facility. The main problem is that concentration values cannot be obtained immediately in the field and must be determined in the laboratory, so it is not completely useful to monitor gas concentrations.

1.6.2 Liquid measurements

1.6.2.1 Volume

As mentioned before, the combined mass balance requires the determination of the amount of water that is discharged by the system, and the water volume difference in the vessel.

The ***volume of discharged water*** can be easily measured by using a flow meter, which should be calibrated before starting the experiment. This calibration can be done by comparing the values given by the flow meter with the direct measure of the volume discharged into a calibrated vessel.

The calculation of ***vessel volumes*** can be done in two ways: the simplest way would be based on measuring the differences in the water levels (Figure 10), at the beginning and at the end of the experiment. Knowing this level difference and the vessel surface, the volume increase can be calculated, assuming that the amount of water present in the scrubber packing material is the same at both moments.

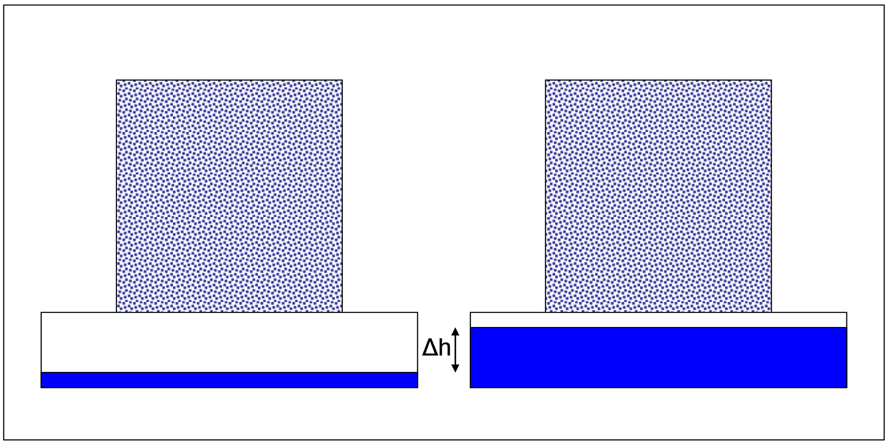


Figure 10 Water level differences in scrubbers vessels
Source: Own elaboration

Another possibility to measure the amount of water in the system, considering both water holding volumes (both packing material and the vessel), is by means of using a tracer. In this case, a known mass of an easily identifiable substance should be added to the vessel. Then, the recirculation pump must be run, without any discharge, until complete mixture of the tracer substance with the water has taken place. By analyzing the concentration of the tracer material, the total volume of water present in the system could be calculated. The same process must be carried out at the end of the period with a different tracer. The latter system can be much more exact than using the water level difference, provided that a complete mixture between water and tracer is achieved and no losses of the tracer component occur. Using this method, the water volume present in the whole system can be assessed, considering both, water in the vessel and water in the packing material.

1.6.2.2 Reactive nitrogen concentrations

a) Ammonium-N (N-NH_4^+) concentration
The determination of ammonium-N is done by ***spectrophotometry***. This technique is based on the ability of molecules to absorb light of a specific wavelength / energy. This phenomenon is used in a spectrophotometer, where normal light is refined to light of a specific wavelength by a grate, after which it is split over a reference beam and a beam that passes the sample. The molecules in the sample absorb part of the light, which is corrected for the reference beam intensity. The amount of light absorbed is proportional to the components that are present in the sample. The spectrogram is composed of multiple measurements using light of different wavelengths Figure 11.

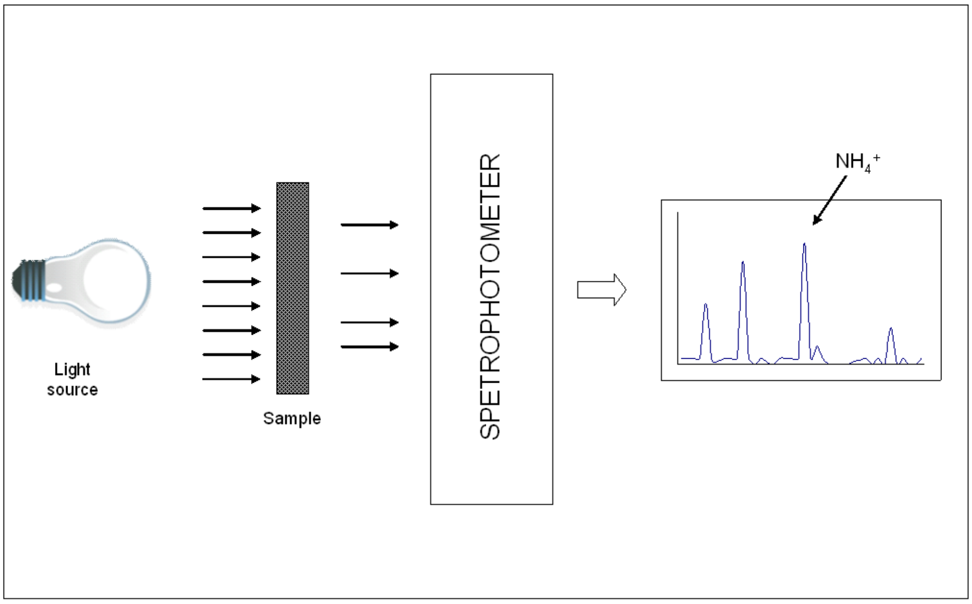


Figure 11 Basic scheme of spectrophotometry

In standardised measurements, only light of a wavelength that is absorbed best by a compound is used. This provides more accuracy. To determine ammonia-N, a wavelength of 655 nm was used as indicated in the standard norm NEN 6472.

b) Nitrite (NO_2^-) and Nitrate (NO_3^-) concentrations

To determine nitrite and nitrate concentrations, a type of chromatography named ***ion-exchange chromatography*** is used. This is a process that allows the separation of ions and polar molecules based on the charge properties of the molecules. It can be used for almost any kind of charged molecule including large proteins, small nucleotides and amino acids.

The principle of the technique is to measure concentrations of ionic species by separating them based on their interaction with a resin. Ionic species separate differently depending on species type and size. Sample solutions pass through a pressurized chromatographic column where ions are absorbed by column constituents. As an ion extraction liquid, known as eluent, runs through the column, the absorbed ions begin separating from the column. The retention time of different species determines the ionic concentrations in the sample Figure 12.

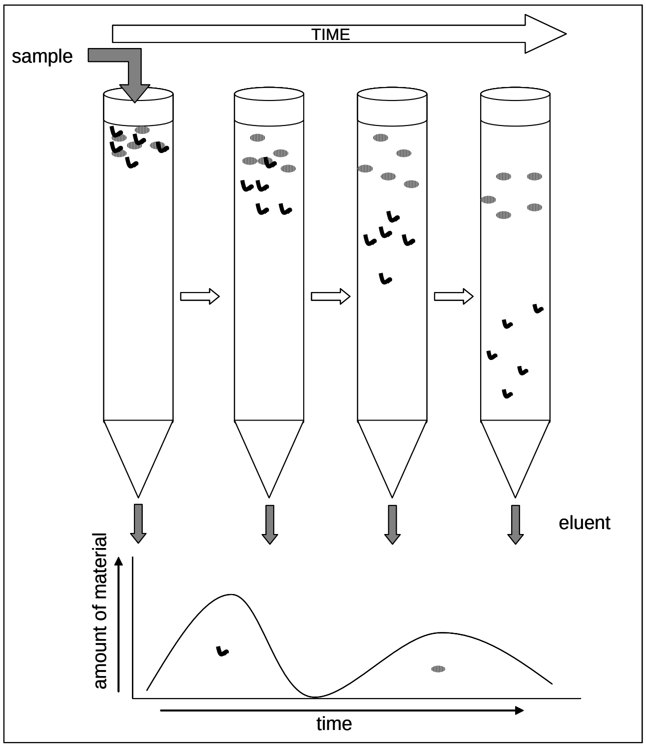


Figure 12 Basic scheme of ion-exchange chromatography

1.7 Uncertainty and error assessment

When reporting values from experimental data, an estimation of the reliability should be made. The reliability is constitutes of an error estimation and an uncertainty assessment. These concepts should not be confused. An error is defined as the difference between an individual result and the true value of the measured parameter.

Errors cannot be exactly known, and three types of errors exist (Ellison *et al.*, 2000). First, random errors arise from unpredictable variations of a quantity measured, and the statistical distribution of these errors results in the uncertainty value. Second, systematic errors are defined as the difference between the averages obtained from an infinite number of replicated measurements of a given measured parameter and its (unknown) true value (ISO, 2004). These errors must theoretically be corrected, as far as they are known and quantified. The third type includes spurious errors, which normally invalidate a measurement and typically arise through instrument malfunction or human failure. These errors should be easily identified.

Uncertainty is defined by ISO (1995) as a parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measured parameter. Uncertainty can be measured by statistical methods (Type A uncertainty) or by other means using prior knowledge (Type B uncertainty) which are not less accurate than Type A analysis, and can include expert judgement and calculated uncertainty by means of the law of propagation of uncertainty.

We can conclude that an error refers to a single measurement, whereas the uncertainty is related to a whole measuring system. Therefore, a measuring system may have a large uncertainty, yet a particular measurement with the system may have a small error due to a random choice.
The main causes of uncertainty in experimental processes, are mainly those related with the analysis of gaseous emissions. Further (and to a certain extent lesser) causes are the inherent variability of the process, the assumptions and models used to simplify some processes, the measurement methods and measurement instruments used and, finally, some random errors.

1.7.1 Sources of uncertainty

Contributions in the uncertainty of a reported value are best quantified by knowing their origin. According to the US EPA (1996), there are three main sources of uncertainty: variability of the data, parameter uncertainty and model uncertainty.

The ***variability of the data*** is something inherent to the parameter we are measuring, mainly when dealing with livestock systems we know there is a great variability due to biological influences on these measured parameters. We can consider two types of data variability depending on the scale, there are variations between different sources and within a source. In the case of air scrubbers we could consider variations between scrubbers due to the differences in their operation or performance, and variations within a scrubber that can be caused by the different amount and load of the inlet air, or the ageing of the packing material.

Parameter uncertainty is due to three kinds of errors: random measurement errors, sampling errors and systematic errors (or bias). Measurement errors are composed of two parts, random measurement errors and systematic errors. The former are mainly caused by the imprecision of the instruments used for measuring. Normally we can know the accuracy of the different methods and quantify this error. Sampling errors originate from having to draw a sample of a whole population, which can be more or less representative for this population. This sort of errors can be reduced by increasing the sample size and using adequate statistical procedures. Finally, systematic errors are the most important ones, because they are the most difficult to detect and reduce. They are caused by wrong assumptions when dealing with the data or inherent errors in the data abstraction process. They also can arise from a non random sample of a population, or even from incorrect calibrations of the measurement instruments (systematic measurement errors).

Finally, ***model uncertainty*** comes from the assumptions we make when working with models. Models allow us to simplify processes, ie by leaving out variables because these are considered negligible.

1.7.2 Uncertainty evaluation

Uncertainty evaluation is considered a process by which a function gives an output quantity (the uncertainty of the measured parameter) using certain input quantities (the uncertainties of the variables on which it depends). The three main steps of this process constitute formulation, propagation and summarizing (JCGM, 2006).

In the ***formulation*** step, first the parameter –to-be-measured must be defined clearly. After that, the variables on which this measured parameter depends must be determined. The next step is to define the model describing the relation between the defined variables and the measured parameter. Finally, the uncertainty or the probability density function (PDF) must be found for each of the variables.

In the ***propagation*** step, individual uncertainties are propagated through the model, to obtain the uncertainty of the measured parameter.

Finally, the ***summarizing*** stage consists of obtaining the value for the measured parameter with its standard deviation and a coverage interval that contains the value with a specified probability.

1.7.3 Propagation of the uncertainty

When an experimental result depends on one or more uncertain measurements, it is necessary to propagate the uncertainties of these measurements into a final result. There are many methods that can be used for the propagation of the uncertainties, including those under general descriptions of analytical methods, approximation methods and numerical methods. The two most used methods are the approximation method based on a first order Taylor series expansion, often referred to as the error propagation equation, and the propagation of distributions (IPCC, 2000).

The ***approximation method*** is based in the law of propagation of the uncertainty (Equation 24) that comes from a first-order Taylor series approximation of *y= f(*x_1*,* x_2*...)* and combines individual standard uncertainties and covariances between variables according to the given experimental equation relating the target measured parameter with the measured variables, to obtain the combined uncertainty (ISO, 1995).

Equation 24 Law of propagation of the uncertainty

$$u_c\left[y\;\; x_1, x_2 ...\;\right] = \sqrt{\sum_{i=1}^{n} c_i^2 \times u\;\; x_i\;\;^2 + 2\sum_{\substack{i,k=1,n\\ i\neq k}} c_i \times c_k \times u\;\; x_i, x_k}$$

Where:
u_c: Combined uncertainty
$y(x_1, x_2, \ldots)$: Function with several input variables x_i
c_i: Sensitivity coefficient, being $c_i = \delta y / \delta x_i$
$u(x_i)$: Uncertainty of the input variable x_i
$u(x_i, x_k)$: Covariance between xi and x_k; $u(x_i, x_k) = u(x_i) \cdot u(x_k) \cdot r_{ik}$
r_{ik}: Correlation coefficient between x_i and x_k

To use this equation all input uncertainties must be expressed as standard deviations and the correlations must be well known (Taylor and Kuyatt, 1994). Furthermore, if nonlinearity of *y= f(*x_1*,* x_2*...)* is significant, higher-order terms in the Taylor series expansion must be included in the expression for u_c.
There are five main requirements limiting the use the law of the propagation of the uncertainty (Cox and Harris, 2006). First, t

- The non-linearity of y must be insignificant, and otherwise higher order terms of the Taylor series must be added.
- y Can only be represented by a Gaussian distribution or a shifted and scaled t-distribution
- The standard uncertainties of the x_i must contribute in comparable amounts.
- The value of the uncertainty must be small in comparison to the value.
- The degrees of freedom of y must be calculated using the questioned Welch-Satterthwaite formula (Ballico, 2000).

The **propagation of distributions** can be made analytically or numerically. The analytical combination of distributions is the only exact method to propagate uncertainties (Cox and Harris, 2006), but it can be applied in relatively simple cases only (*e.g.* linear models with only Gaussian distributions), and therefore it is not used in practice.

The Monte Carlo methods (MCM) provide a general approach to obtain an approximate numerical representation of the PDF of the measured parameter (JCGM, 2006). MCM perform random sampling from given probability distributions of the parameters xi, and evaluate the result y in each case. When this process is repeated many times (*M* repetitions), a numerical approximation of the PDF of y is constructed, and any property such as expectation, variance and coverage intervals can be approximated from it.

MCM are much more versatile than the law of the propagation of the uncertainty because they have none of the requirements cited above. Even with relatively few iterations (*e.g.* $M = 10^3$) expectations and standard deviations can be obtained. To calculate coverage intervals more iterations are needed (*e.g.* $M = 10^6$) because the tails must be properly represented in the random sampling. Although MCM are computationally intensive, the calculation times taken are often only seconds or minutes on a PC, unless the model is very complicated (Cox and Harris, 2006).

In this work, propagation of distributions by using MCM will be developed to assess measured parameter uncertainty.

2 Objectives

The first objective of this work is to find out the best way to assess the efficiency of scrubbers when using nitrogen balances, that means to identify the most accurate way, in terms of uncertainty, to develop a nitrogen balance in a scrubber between the two common ways: a mass balance over the gaseous phase or a mass balance over the combined gaseous and liquid phases.

The second objective is to assess if it is possible to quantify the amount of nitrogen emitted to the atmosphere in terms of N_2 and N_2O during NDN processes in scrubbers, by using the information obtained when calculating nitrogen balances. And, if it is possible, determine the accuracy of this quantification.

3 Methodology

3.1 General approach

To achieve the objectives of the work, an uncertainty analysis will be carried out. Three main steps are involved in this process:

- ***Problem definition***. An uncertainty diagram in which all the variables involved in the process will be designed.
- ***Variables uncertainty characterization***. All variables in the system will be characterized attending to the nature of their uncertainty.
- ***Model building***. In order to obtain the uncertainty of the measured parameter, a model will be built in which individual uncertainties will be propagated.

3.2 Problem definition

The measured parameter in this case is the amount of N_{new} formed during the scrubbing process, calculated as the difference between the scrubber efficiency calculated by means of an mass balance over the gaseous phase (Equation 9) and a mass balance over the combined gaseous and liquid phases (Equation 10). The global calculation process has been schematically drawn in Figure 13. In this diagram all variables and uncertainty sources involved have been identified. Orange titles represent the input variables. The blue title is the target measured parameter. Green titles are intermediate variables.

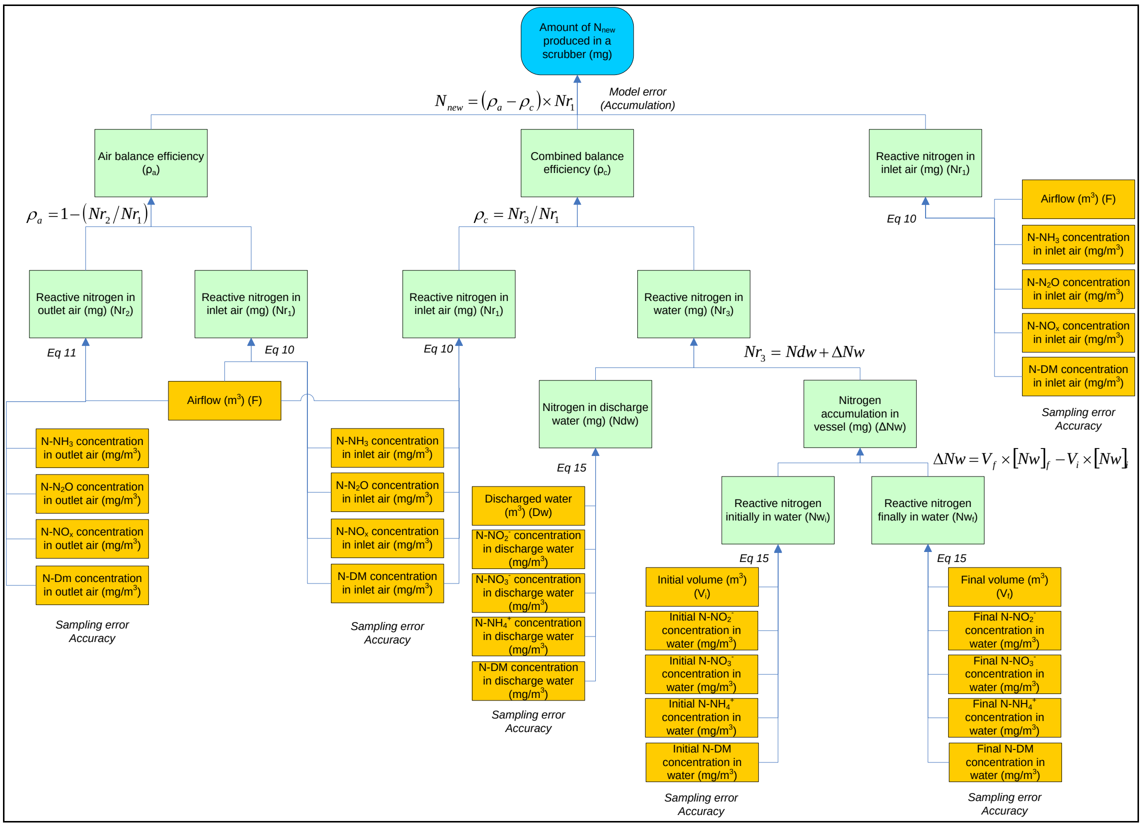


Figure 13 Uncertainty cause and effect diagram
Source: Own elaboration

As seen before, there are many parameters that can vary among scrubbers. Modelling the average scrubber is a hard task and out of the scope of this work. Thus, as a first approach, the simplest case is going to be analyzed. The results obtained from this first work will be very useful for more complicated models. The main characteristics of the studied case are defined in Table 1.

Table 1 Main characteristics of the modelled case

Parameter	Characteristics
Farm	Pig farm (1,000 fattening pigs)
Scrubber	Chemical scrubber
	Two performances: 70% and 95%
	No water discharge from liquid reservoir
Nitrogen sources	Only ammonia in air and ammonium in water
Start point	Initial nitrogen content in water is negligible
Gas concentration measurement	Two methods: impingers and NOx monitor
Time basis	24 hours

Source: Own elaboration

Therefore, the simplified model considering these conditions is summarized in Figure 14.

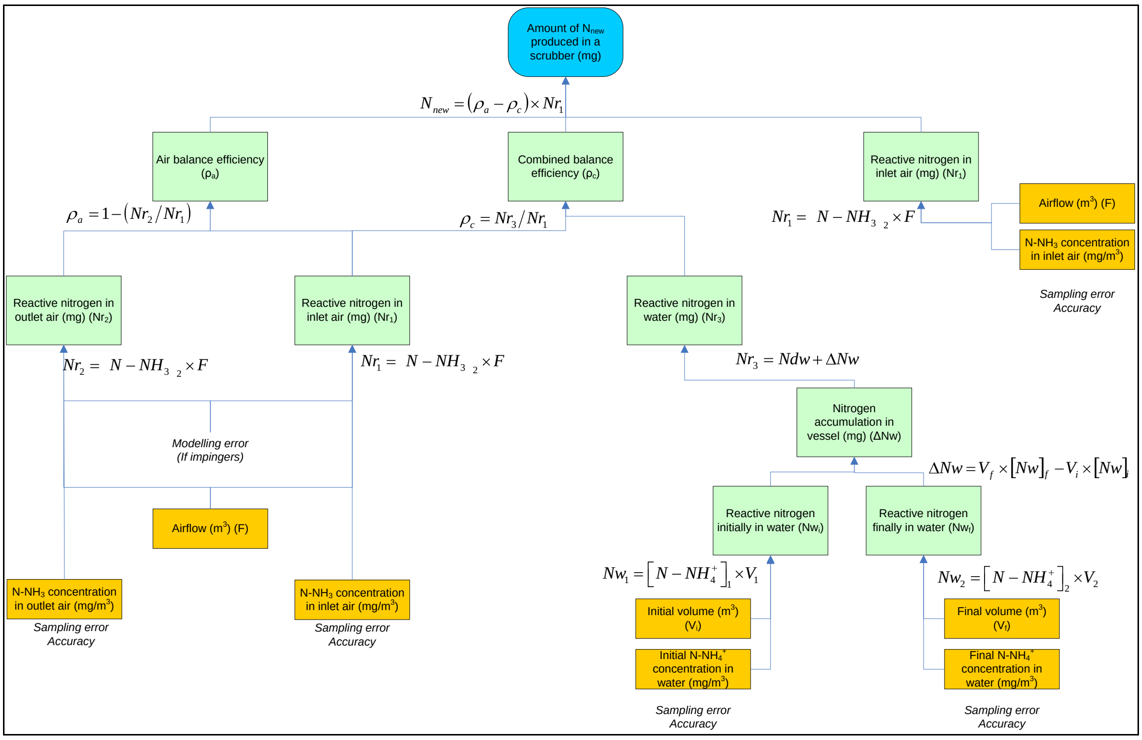


Figure 14 Simplified uncertainty cause and effect diagram for an acid scrubber
Source: Own elaboration

3.3 Variables uncertainty characterization

Classifying uncertainty sources is a needed previous step. Attending to the US EPA (1996) recommendations, uncertainties defined before are classified as shown in Table 2.

Table 2 Uncertainty sources in Nr balances in scrubbers

Category	Sub-category	Description / Source
Process variability uncertainty	Spatial uncertainty Temporal uncertainty	• Differences between scrubbers • Differences in ventilation fluxes • Differences in Nr concentrations in the air • Differences in Nr concentrations in the water
Parameter uncertainty	Measurement errors	• Gas concentrations • Nr concentrations in water • Airflow • Water volumes
	Sampling errors	• Representativeness of gas measuring point • Representativeness of gas measuring interval/time • Representativeness of water measuring point
	Systematic errors	• Unexpected
Modelling uncertainty	Modelling	• Assumption of no losses • Nr accumulation in the packing material • Average concentrations

Source: Own elaboration

If we focus on an experimental analysis, in which the aim of the work is not to evaluate the whole family of scrubbers, we can consider that the ***spatial uncertainty*** is negligible. Regarding to ***temporal uncertainty***, we should consider that the data obtained is fitted into an experimental period, which means that considering the uncertainty of this category is out of the scope for this work. Furthermore, ***process variability uncertainty*** can be, for the moment, considered negligible.

As a result, ***parameter uncertainty*** must be considered as the main source of uncertainty in this model. Both measurement errors and sampling errors have to be assessed in the uncertainty formulation stage.

Regarding to ***modelling uncertainty***, these sources can be described as new variables entering in the model, as system-perturbing quantities that must be modelled as well, by determining a PDF (Sommer and Siebert, 2006). Some assumptions must be done then:

- First of all, modelling errors related to non considered nitrogen losses can be assumed negligible. The general model assumes that there are not more nitrogen outputs that those related to nitrogen in air, water and accumulation in packing material.
- The amount of Nr that can be accumulated in the packing material during a short period are considered null.
- Using time averaged weighted values (TWA), to determine the amount of nitrogen during a determined period involves an error. This is due to the use of a different time basis for the measurement, in which gas concentration and airflow rate are determined as an average for a period, while during the real period implies a natural variation. This error is clearly bigger with the increase of the time basis for which TWA are calculated.

Uncertainty assessment for variables, classified regarding to their nature, are described in the next sections.

3.3.1 Ammonia concentrations

3.3.1.1 Chemiluminescence

Chemiluminescence analyses present two main error sources due to the two instruments that are used for the determination of ammonia. As explained before (section 1.6.1.2, page 11) the first step is to convert ammonia (NH_3) to nitric oxide (NO), and after that, NO is measured by the NO_x analyzer. For the instrument analyzed, the conversion efficiency in the first step rounds 95%, being represented by a Normal distribution N (0.949 , 0.007). Figure 15 shows the frequency distribution of observed converting efficiencies, measured during two years.

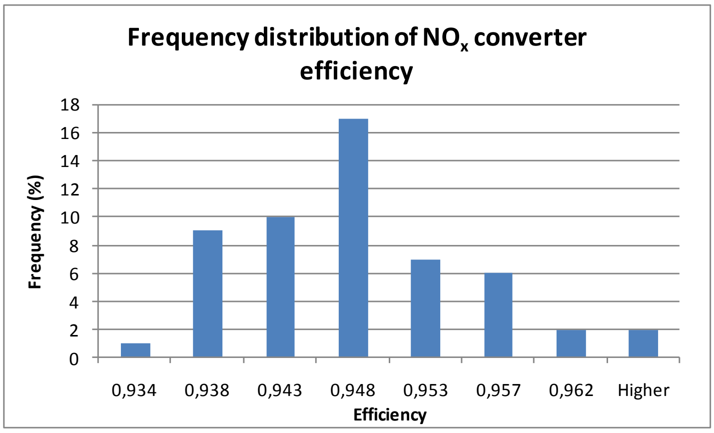


Figure 15 Frequency distribution of the analyzed NO_x converter efficiency

Regarding to the uncertainty of the analyzer, two error sources must be considered, the ***accuracy*** of the method, which can be assessed by means a stability test with a known stable concentration, and the other one related to the ***resolution*** of the instrument.
In order to obtain the ***accuracy*** of the system, 7 trials in which the stability of the instrument was assessed, at different gas concentrations, were analyzed. Figure 16 shows the distribution of the errors found. This error can be modeled then, as a Normal distribution N (-0.00024 , 0.00733).

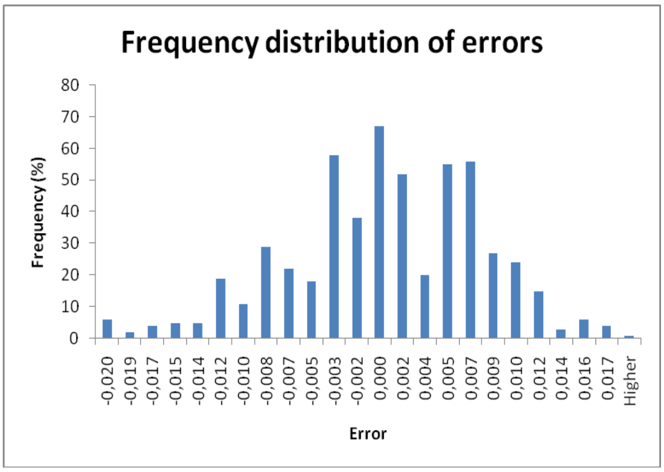


Figure 16 Frequency distribution of the NO_x analyzer errors

This is the random error estimated for a single measurement. In a practical situation however, the average value is taken when measuring for a defined intervals of 60 seconds when the device measures each 10 seconds. This means that each measurement provided by the device is the average value of six measurements. This is an important issue to consider because, due to the compensation of random errors, the absolute error is going to decrease with the number of measurements. Uncertainty of these average values must be recalculated then by means of Equation 25.

Equation 25 Uncertainty calculation for NO_x stability, regarding to the number of measurements integrated

$$\boxed{u_N = \frac{u_1}{\sqrt{N}}}$$

Where:
u_N: Uncertainty of the average value measure after N measures
u_1: Uncertainty of a single measurement
N: Number of measures averaged for each value

Considering then, that the uncertainty of a single measured value in a normal distribution is equal to its standard deviation (EURACHEM/CITAC, 2002), and that an usual procedure it is to obtain data from the measuring device each 60 seconds, when it measures each 10 seconds, the uncertainty of the measured value (u_1) can be calculated as resumed in Equation 26***.***

Equation 26 Uncertainty calculation in uniform distributions

$$\boxed{u_1 = \frac{0.00733}{\sqrt{6}} = 0.003\,mg\big/m^3}$$

This uncertainty, directly related to the accuracy of the system, is modeled by definition as a Uniform distribution.
The ***resolution*** of the analyzer was assessed too, obtaining a value of 0,0042 mg/m^3. This error can be modelled as a Uniform distribution U (-0.0042,0.0042).
Finally, to determine the value for NH_3 concentration and its uncertainty, mean values and standard deviation obtained from Equation 27 will be used respectively.

Equation 27 Determination of ammonia concentration with chemiluminescence analyzers

$$\boxed{NH_3 \;\; = \left(\frac{NH_{3\;\;m}}{N\;\;0.949,0.007} \right) + U\;\; -0.003,0.003\;\; + U\;\; -0.0042,0.0042}$$

Where:
$[NH_3]$: Ammonia concentration
$[NH_3]_c$: Measured ammonia concentration
$N(X,\sigma)$: Normal distributions with mean X and standard deviation σ
$U(a,b)$: Uniform distributions with extreme values *a* and *b*

3.3.1.2 Wet methods (Impingers)

When determining ammonia concentrations by means of impingers, two different errors directly related to the instruments have been identified and quantified. First of all we can find the error related to the method ***accuracy***, this error is assumed to have a rectangular distribution with upper and lower limits in accordance to the expected accuracy of 0,5% of the measured value (Patton and Crouch, 1977).
On the other hand, there is an error related to the ***sampling*** process that has been assessed by studying replicate ammonia measurements made in previous experiments. Statistical analysis proved that this error follows an exponential distribution E(0.07).
Therefore, to determine the value for NH_3 concentration and its uncertainty, mean values and standard deviation obtained from Equation 29 will be used respectively.

Equation 28 Determination of ammonia concentration with impingers

$$NH_3 = R \; -0.005\times \; NH_{3\;m} + \; NH_{3\;m}, 0.005\times \; NH_{3\;m} + \; NH_{3\;m} \; \pm E \; 0.07$$

Where:
[NH3]: Ammonia concentration
[NH3]c: Measured ammonia concentration
R(min,max): Rectangular distributions with minimum and maximum values
E(X): Exponential distribution with mean X

3.3.2 Water Nr concentrations

Aqueous ammonia concentrations can be determined by spectrophotometry, with a reported maximum accuracy of 0.005 mg/m^3 (Patton and Crouch, 1977). In routine laboratory practice, this means that values are measured with an accuracy of 5 mg/m^3, leading to a PDF that is an Uniform distribution U(X-5,X+5).

3.3.3 Airflow rate

Airflow rate error has been considered as a percentage of the measured value. When fan-wheel anemometers are used for the measurement of the airflow rate, the expected error has been established at 5% (Demmers *et al*, 1999; Mosquera *et al*, 2005), then, a Normal distribution N(X,0.05X) has been used to assess airflow rate measurements.

3.3.4 Volumes

The error related to volumes measurement depends directly on the methodology used. Then, if volumes are going to be measured by water height differences in the bulk, the error made when measuring is related to both:

- The ruler used to measure (resolution)
- The surface of the vessel

Together with the resolution of the ruler, the stability of the water level should be considered. In itself, the instability of the water level can produce a higher error than that caused by resolution. As a preliminary estimation, this accuracy has been established at 1mm. The surface of the vessel in combination with its height X will provide the volume. When a vessel with a surface area of 4,21 m^2 is considered as an example, the error related to the volume measurement can be defined as a Uniform distribution U(X-0.00421,X+0.00421), with values in m^3.

3.3.5 Modelling error

When calculating mass fluxes in air, by using measuring methods for gas concentrations in which time weighted averaged (TWA) values are obtained, it is needed to consider another source of error, arising from the assumption that daily emissions can be estimated by using average airflow and average concentrations, instead of short time measurements. To assess this error, a database with hourly values for ammonia concentrations and air fluxes has been analysed. Comparison between the emissions obtained by means of both methods is presented in Figure 17. It can be observed that there is a positive bias (around 1% of the measurement) when calculating on a 24 hours basis.

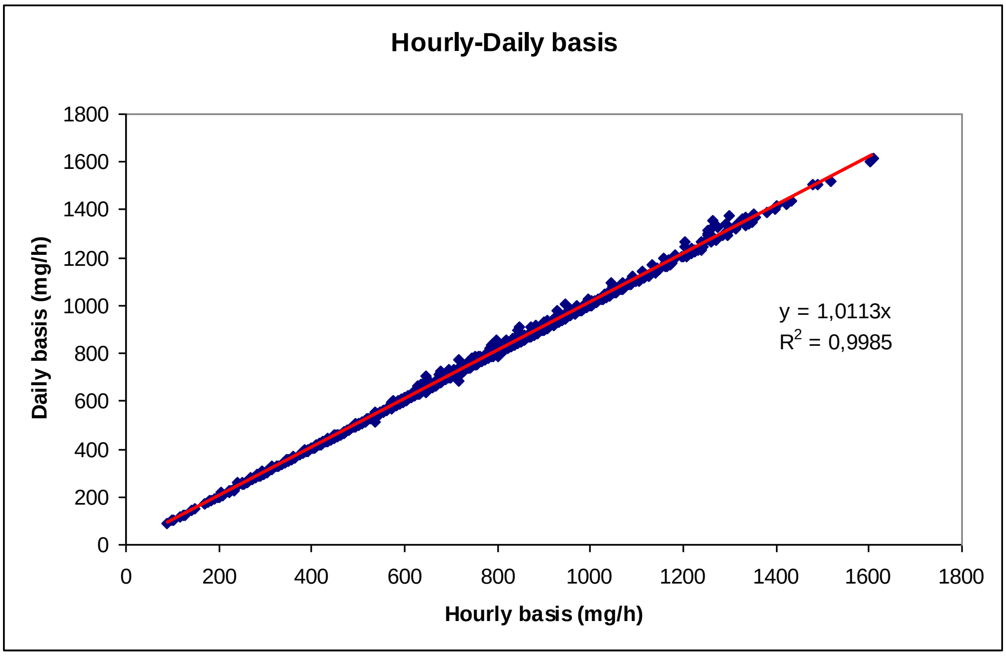


Figure 17 Ammonia emissions calculated in hourly and daily basis.
Source: Own elaboration

The absolute difference between values, can be modeled by means a Weibull distribution W(7.36,0.76). Therefore, to correct the error made when modeling emission using TWA for 24 hours periods Equation 29 must be used.

Equation 29 Correction of ammonia emission values when using TWA for 24 hours periods

$$\boxed{F_{NH_3} = F_{NH_3-24} - W \quad 7.36, 0.76}$$

Where:
F_{NH3}: Ammonia flux (mg/h)
F_{NH3-24}: Ammonia flux calculated using 24 hours average values (mg/h)
$W(\lambda,k)$: Weibull distribution with scale λ and shape k

3.4 Model building

A model has been developed with two main objectives, first of all, it has been developed as a useful tool to assess the uncertainty of the process, and on the other hand, it will be used to process the experimental results and find out the performance of the mass balances described earlier. This model has been built in a MS Excel book, in which all the equations developed previously which define the global nitrogen balances in scrubbers, are included. The general scheme described in Figure 14 has been followed.
In addition to the general characteristics of the studied scrubber defined in Table 1, some additional considerations were made:
The ventilation rate was established at 60 m^3/h per pig place which is in the normal range for Northern Europe countries (Seedorf *et al*, 1998). Ammonia concentration in the inlet air was fixed at 10 mg NH_3/m^3. Outlet air ammonia concentration was estimated according to the expected removal efficiency. Initial water volume in the aqueous bulk and the ammonium concentration were considered zero. Final ammonium-N concentration in the water was 45 g/L. Final water volume in the aqueous bulk was calculated considering nitrogen fluxes in air and assuming no nitrogen losses during the monitoring period.

3.4.1 Uncertainty propagation

As explained before, the propagation of PDFs based on numerical methods (MCM) is the methodology selected for this work. The software RiskAMP Monte Carlo Add-In Library version 2.70 was used (Structured Data, 2005). By using this software, random values from the given PDFs defining the input variables were used, and the results (mean, standard deviation and coverage interval) were obtained from the resulting PDF for *y*. The number of iterations used was $M=10^5$, that allow us to obtain accurately coverage intervals.

3.4.2 Individual uncertainties contributions

The relative contributions of the input variables to the combined uncertainty were numerically calculated according to Cox and Harris (2006). When uncertainty is calculated using numerical methods, to estimate the relative contribution of each variable uncertainty, for each variable x_k, the whole MC simulation was repeated holding all other input quantities at their central estimates. Then, for each run we obtain an uncertainty value of the measured parameter $u_k(y)$. The estimation of the relative contribution can be calculated afterwards by means of the Equation 30.

Equation 30 Relative contribution of variables to final uncertainty

$$\boxed{Contribution\left(x_k\right)=\left(\frac{u_k\left(y\right)}{u\left(y\right)}\right)^2}$$

Where:

Contribution (x_k): Contribution of the uncertainty of the variable x_k to the measured parameter uncertainty

$u_k(y)$: Measured parameter uncertainty calculated with the only uncertainty source of the variable x_k

$u(y)$: Measured parameter uncertainty

3.4.3 Sensitivity analysis

To assess the sensitivity of each variable uncertainty on the measured parameter uncertainty, a sensitivity analysis was carried out. To do that, all-but-one variable uncertainties were fixed to study the non-fixed variable uncertainty. Then, this uncertainty was changed (from 0 to 200% of the initial value) and the final measured parameter uncertainty changes were observed. Different curves were obtained which show this sensitivity.

4 Results

4.1 Measured parameter uncertainty

The efficiency calculated using the air balance (ρ_a) and the combined balance (ρ_c), and its associated uncertainty is presents in Table 3 for both ammonia measuring methods and scrubber types.

Table 3 Estimated scrubber efficiency and its uncertainty

Method	Efficiency	Parameter	Estimation	u	95% C.I.
Impinger	70%	$Efficiency_a$	0.700	0.012	[0.674 , 0.726]
		$Efficiency_c$	0.702	0.038	[0.633 , 0.780]
	95%	$Efficiency_a$	0.950	0.012	[0.925 , 0.975]
		$Efficiency_c$	0.952	0.050	[0.861 , 1.085]
NOx monitor	70%	$Efficiency_a$	0.700	0.003	[0.694 , 0.706]
		$Efficiency_c$	0.701	0.037	[0.634 , 0.779]
	95%	$Efficiency_a$	0.952	0.001	[0.951 , 0.954]
		$Efficiency_c$	0.951	0.049	[0.861 , 1.054]

Source: Own elaboration

As expected, the central estimation for all values is close to the expected value in each case (70% or 95%). The use of NOx monitors to determine ammonia concentrations reduces the uncertainty of the estimation. The most relevant finding drawn from this table is the lower uncertainty associated to the air balances when comparing them to the combined balances in all cases.

When impingers are chosen as the measurement method for NH_3 concentrations, the uncertainty of combined balances is between 3 and 4 times the uncertainty of the air balance. On the other hand, if NOx monitors are chosen, the difference is much higher (between 10 and 50 times higher for the combined balance). This is due to the involvement of more parameters (and consequently more uncertainty sources) in the case of the combined mass balance.

Regarding the value of the measured parameter (formation of new reactive nitrogen forms in the scrubber), its standard uncertainty, and the confidence interval for 95% of the data expressed as the percentage of the input nitrogen flux (Nr_1) are presented in Table 4.

Table 4 N_{new} formation in a simulated acid scrubber

Method	Efficiency	Parameter	Estimation	u	95% C.I.
Impinger	70 %	N_{new}	-0.19	4.01	[-8.50 , 7.19]
	95 %	N_{new}	-0.24	5.16	[-10.93 , 9.24]
NOx-monitor	70 %	N_{new}	-0.12	3.75	[- 7.97 , 6.70]
	95 %	N_{new}	0.14	4.93	[-10.16 , 9.13]

Source: Own elaboration

It can be observed that the estimated value in all cases is close to zero, which is in line with the theoretically assumed absence of N_{new} formation in chemical scrubbers. The 95% confidence interval however show considerable ranges, with an order of magnitude in both directions of 7-10% of the N inlet. Regarding to the uncertainty of this value, the range is similar for both measurement methods. Compared between both scrubber types the uncertainty value (u) is lower for the 70% scrubber. This is related to the higher absolute value for the term Nr_2, which reduces the relative weight of the uncertainty in this term.

The probability distribution functions of the measured parameter for different expected efficiencies are represented in Figure 18 and Figure 19 for impingers and NOx monitor respectively.

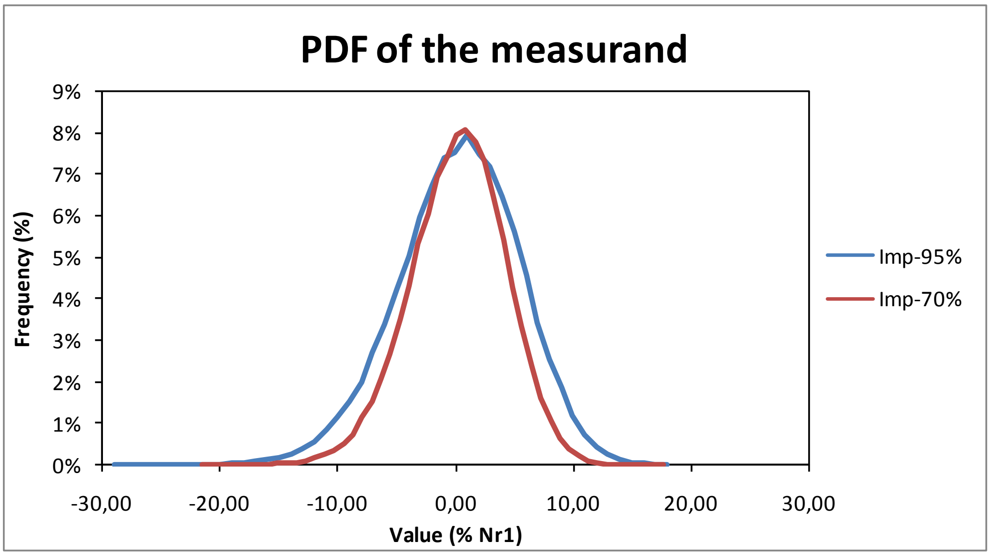


Figure 18 Measured parameter PDF in a simulated acid scrubber (Impingers)
Source: Own elaboration

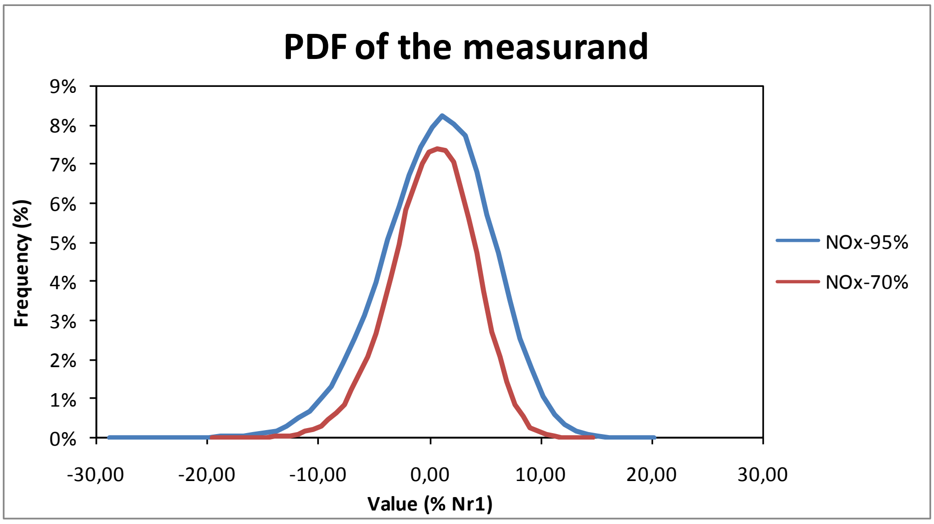


Figure 19 Measured parameter PDF in a simulated acid scrubber (NOx monitor)
Source: Own elaboration

The PDF of the measured parameter in all cases has a similar shape, grouped around zero. Some other data can be extracted from the model once run, as for example the uncertainty of both balance approaches, which is presented in Table 3.

4.2 Variables contribution

Individual uncertainties calculated for each variable, expressed as percentage on the simulated value are presented in Table 5.

Table 5 Variables estimated uncertainty (% of the measured value)

Method		Impinger		NOx monitor	
Efficiency		70%	95%	70%	95%
Parameter	Airflow	5.00	5.00	5.00	5.00
	NH_{3i}	1.18	1.19	0.74	0.74
	NH_{3o}	3.92	23.66	0.75	1.06
	$Volume_2$	1.32	0.97	1.32	0.97
	$[N\text{-}NH_4^+]_2$	0.00	0.00	0.00	0.00
	Modelling	0.00	0.00		

Source: Own elaboration

In general, the uncertainty of ammonia concentrations is lower when using NO_x converter for the measurement. It is also important to underline the increase of the relative uncertainty in the outlet concentration respect to the inlet concentration, due to lower absolute concentration values. For the same reason, it can also be observed a relative uncertainty increase for the outlet concentration, when the efficiency is higher.

The result of the parameter contribution analysis provided the data presented in Table 6.

Table 6 Contributions to measured parameter uncertainty

Method		Impinger		NOx monitor	
Efficiency		70%	95%	70%	95%
Parameter	Airflow	0,78	0,88	0,91	0,96
	NH_{3i}	0,09	0,05	0,04	0,02
	NH_{3o}	0,09	0,05	0,00	0,00
	$Volume_2$	0,05	0,03	0,06	0,03
	$[N\text{-}NH_4^+]_2$	0,00	0,00	0,00	0,00
	Modelling	0,00	0,00		

Source: Own elaboration

The main source of uncertainty in all cases lies in the calculation of the airflow. Both ammonia concentrations in the inlet and the outlet are the second main contributors to the final uncertainty value when measuring with impingers. On the contrary, when measuring with an NO_x monitor, the uncertainty in the ammonia concentration in the scrubber outlet is not significantly contributing to the final uncertainty. This is caused by the smaller error caused by the chemiluminescence method, which makes the uncertainty term for the Nr_2 smaller. Final volume of the vessel should be considered as a significant uncertainty contributor in all cases, leaving the ammonium concentration contribution close to negligible.

4.3 Sensitivity analysis

The results of sensitivity analysis are represented in Figure 20. In this figure, the uncertainty of the measured parameter $u(N_{new})$ is drawn for different uncertainty values of the main input variables (this is, airflow rate, Nr1, Nr2 and water volume measurement).

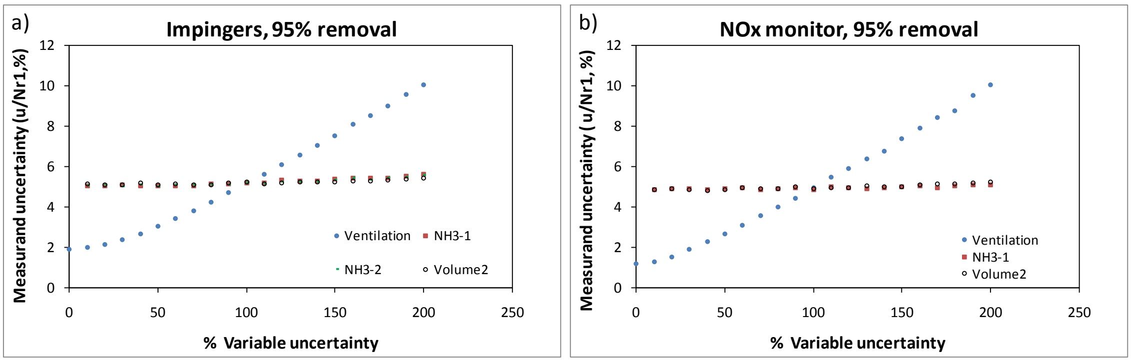


Figure 20 Parameters uncertainty sensitivity for 95% of efficiency scrubbers, using impingers (a) and NOx monitors (b) for the determination of ammonia concentrations
Source: Own elaboration

In both cases it can be observed than the uncertainty in the airflow rate is the most sensitive parameter. When modifying other variable's uncertainties, from 0 to 200% of their original values, only a slight variation of the measured parameter uncertainty is observed (below 0,5%). In contrast to this, the effect of the uncertainty in the airflow rate measurement strongly affects the measured parameter uncertainty.

In practical terms, this means that the improvement of the airflow rate measurement methods is the key factor to increase the accuracy of nitrogen balances estimation. In contrast, putting an effort to improve the measuring systems for ammonia concentrations or water volumes does not lead to a significant improvement on the final value's uncertainty.

4.4 Improvements needed

As observed in the previous sections and considering all assumptions made, a mass balance based on the gaseous inlet and outlet changes across an air scrubber results in a more accurate evaluation than using a mass balance based on inflow gas and ammonia found in the watery phase.

As this report only deals with the numerical aspect of the interpretation, however, it would be needed to compare both mass balance methods also in a more practical way. In addition, it would be also recommendable to check whether the assumptions that were made, were feasible. In this regard, the accumulation of nitrogen in the packing material and in other N forms such as organic N, should be checked.

Knowing than the main parameter introducing uncertainty in the model is the airflow rate, further studies should best be aimed towards determining the uncertainty associated with the measurement method more precisely. The development of uncertainty models aimed to determine the uncertainty associated to the measurement of ventilation rates in these conditions is needed.

The model used in this work is useful only for acid scrubbers, in which no Nnew (mainly N_2O or N_2) formation is expected. The adaptation of this model to a biotrickling scrubber is crucial in order to find the best method for the determination of the formation of Nnew during biological processes.

5 Conclusions

According to the results obtained in this work, the best way to assess the efficiency of a chemical scrubber, regarding to the uncertainty associated to the method, is the mass balance that uses the inlet and outlet ammonia concentrations in the gas phase.

The higher number of parameters involved in the calculation of the mass balance based on the combined inlet gas ammonia concentration and ammonia uptake in the watery phase, seems to be the cause of the uncertainty increase in this method.

According to the results of this investigation, both types of mass balances are able to demonstrate the formation of N_2O/N_2 only if this amounts exceeds 7-10% of the N inlet. It is therefore not recommended to use these mass balances to estimate the amount of nitrogen that is being released from a scrubber in form of N_2 or N_2O.

No significant differences on calculated uncertainties have been found between expected efficiencies of the scrubber (70 and 95%), neither between different measuring methods (impingers and chemiluminescence).

The main contributor to the uncertainty of the model is the airflow rate measurement. This fact has two main implications:

- methods which do not involve the measurement of airflow rates may be more accurate;
- the best way to reduce the uncertainty of the measured parameter (efficiency or Nnew formation) is reducing the uncertainty of airflow rate measurements.

Future work in this field is required, mainly testing the model assumptions in a practical experimental setup. Further research on input parameters uncertainty, such as the airflow rate uncertainty, must be carried out in order to optimize the balance. Finally, this model as well as practical validations must be implemented in biotrickling scrubbers for the determination of N_2O and N_2 formation.

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Wageningen UR Livestock Research

Edelhertweg 15, 8219 PH Lelystad T 0320 238238 F 0320 238050

E info.livestockresearch@wur.nl I www.livestockresearch.wur.nl