Advances in sensing ammonia from agricultural sources

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Abstract

Reducing ammonia emissions is one of the most difficult challenges for environmental regulators around the world. About 90% of ammonia in the atmosphere comes from agricultural sources, so that improving farm practices in order to reduce these emissions is a priority. Airborne ammonia is the key precursor for particulate matter (PM2.5) that impairs human health, and ammonia can contribute to excess nitrogen that causes eutrophication in water and biodiversity loss in plant ecosystems. Reductions in excess nitrogen (N) from ammonia are needed so that farms use N resources more efficiently and avoid unnecessary costs. To support the adoption of ammonia emission mitigation practices, new sensor developments are required to identify sources, individual contributions, to evaluate the effectiveness of controls, to monitor progress towards emission-reduction targets, and to develop incentives for behavioural change. There is specifically a need for sensitive, selective, robust and user-friendly sensors to monitor ammonia from livestock production and fertiliser application. Most currently-available sensors need specialists to set up, calibrate and maintain them, which creates issues with staffing and costs when monitoring large areas or when there is a need for high frequency sampling. This paper reports advances in monitoring airborne ammonia in agricultural areas. Selecting the right method of monitoring for each agricultural activity will provide critical data to identify and implement appropriate ammonia controls. Recent developments in chemo-resistive materials allow electrochemical sensing at room temperature, and new spectroscopic methods are sensitive enough to determine low concentrations in the order of parts per billion. However, these new methods still compromise selectivity and sensitivity due to the presence of ambient dust and other interferences, and are not yet suitable to be applied in agricultural monitoring. This review considers how ammonia measurements are made and applied, including the need for sensors that are suitable for routine monitoring by non-specialists. The review evaluates how monitoring information can be used for policies and regulations to mitigate ammonia emissions. The increasing concerns about ammonia emissions and the particular needs

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from the agriculture sector are addressed, giving an overview of the state-of-the-art and an outlook on future developments.

Keywords: Ammonia, Sensors, Nitrogen losses, Livestock production, Fertiliser Application.

1. Introduction

In most developed countries, the dominant source of ammonia (NH_3) emissions is the agro-industry . Efforts to mitigate these emissions must therefore focus on improving those agricultural activities that are important contributors - such as livestock feeding and housing, excreta management, and fertilisation practices. To develop better agricultural practices it is critical to know which sources contribute to these emissions, when, and by how much. Ammonia measurements are primarily needed to understand emission rates, the effectiveness of control measures, the impact of atmospheric processes and the outcomes of exposure. Many types of sensors and devices for measuring NH_3 are commercially available, and some promising new developments will be discussed in this paper. However, most of the current devices are relatively specialised, costly or difficult to apply in "real world" farming situations, so they are not readily used for day-to-day monitoring by non-specialist practitioners. Also, there are only a few sensors that have enough sensitivity to measure NH_3 emissions from fertilised soils, such as those using mid-ultraviolet absorption spectroscopy , photoacoustic spectroscopy or the recent artificial nose with fluorescence detection . NH_3 measurements are needed to improve agricultural efficiency, and to contribute to a better quality of life – because excess concentrations of NH_3 lead to adverse impacts on human health and on the health and diversity of ecosystems. Reductions in NH_3 emissions would support more efficient food production that uses fewer resources, and so would reduce the environmental impacts of food supply chains. Availability of simple, reliable and low cost measurements and procedures will help developing an improved understanding of NH_3 emissions which is important for:

i) Agricultural producers: reduced NH_3 emission will generate savings in nitrogen fertilisers . More efficient use of crude protein in animal feed reduces N excretion,

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and these emission reductions could attract farm payments if they are linked to environmental improvements.

ii) Researchers: to develop new and more suitable technologies to reduce emissions and solve problems for the agroindustry and society.

iii) Wider society and the economy: to decrease the combined cost for human health and biodiversity from excess NH_3, which is estimated to be 4-30 euros per kg N pollution in 2011 .

iv) Regulators: to target control measures effectively onto culpable sources, and to evaluate source performance and the effectiveness of controls.

v) Policymakers and government: monitoring NH_3 emissions is required to meet international emission reduction targets .

2. Ammonia in the environment

The distinct smell of ammonia is often noticed in rural parts of developed countries with high-density livestock farming, especially near intensive pig, poultry or cattle facilities or after liquid manure has been spread on the land. NH_3 is a colourless with a very perceptible odour, even at very low concentrations. It is a common gas that is released in the natural environment from decomposing organic material and animal waste. In the agricultural industry, NH_3 can be used as a fertiliser in the pure gas form of anhydrous NH_3, but it is also widely used to make nitrogen-based fertilisers such as urea, urea-ammonium nitrate, ammonium sulfate, ammonium nitrate and diammonium phosphate. NH_3 is also used as a refrigerant, and in the manufacture of plastics, explosives, textiles, pesticides, dyes and other chemicals. Although NH_3 is commonly present in nature and widely used in industry, it is classified as an extremely hazardous substance because it is both caustic and flammable . The United States Environmental Protection Agency has classified NH_3 as a hazardous substance because of its toxicity to humans, and has set a maximum safe level of 25 ppm for long term exposure (8 hours) and of 35 ppm for short term exposure (15 min) . For livestock, exposure to 25 ppm of NH_3 can adversely affect weight gain, feed conversion and mortality rates . Several institutions regulate exposure and peak instantaneous

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concentrations, but there are no regulations for NH_3 emission rates. The ‘Environmental Permitting Regulations’ relate to ammonia emissions , which set a limit for large livestock facilities on the number of animals that can be kept near a sensitive habitat. Critical level of ammonia concentration cannot be exceeded, and these concentrations are calculated based on accepted emission factors for livestock for different production systems. Another relevant piece of legislation is the National Emission Ceilings Directive (NECD), which sets targets for maximum annual emissions from individual European countries . There is also the Gothenburg Protocol of The United Nations Economic Commission for Europe (UNECE) which is an international agreement to abate acidification, eutrophication and ground-level ozone, that aims to reduce emissions of several pollutants including NH_3 .

Livestock excreta and fertilisers are major sources of ammonia. Large amounts of NH_3 are released from excreta immediately after deposition and during decomposition. Livestock are often fed high-protein feeds containing N to ensure that their nutritional requirements are met, but the N that is not converted to animal protein is excreted in the urine and the faeces. Once the N compounds are in the faeces or urine, enzyme reactions or microbial activity quickly release NH_3 to the atmosphere . This is because the urea produced and excreted by mammals is rapidly converted to NH_3 gas by the urease enzyme. In the case of poultry, it is uric acid that is excreted and mostly converted to urea, and then to NH_3. There are several technologies that can be implemented to reduce NH_3 emissions by reducing the availability of both precursors (urea and the urease enzyme) such as controlling the contents of livestock diets or using urease inhibitors such as is N-(n-Butyl)-thiophosphoric triamide (NBPT) . Another control option is to reduce urea hydrolysis by separating the urea and faeces . Key methods to control ammonia emissions from animal excreta are to keep it as dry as possible (i.e. by using indirect heating or heat exchangers); to keep it covered (e.g. floating covers for slurry stores and lagoons); to acidify it; and to avoid adverse weather conditions such as high temperatures, high humidity and adverse wind direction when manure is injected into the soil. The other large source of NH_3 gas is the application of N

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fertilisers, which represents a significant fraction (23%) of NH_3 emissions (Figure 1, data from the UK Code COGAP). All fertilisers containing ammonium (NH_4^+) are subject to volatile losses and the NH_3 emissions is largely controlled by pH . Precision agriculture can help adjusting fertiliser rates to reduce excess N application and hence losses by volatilization or run-off.

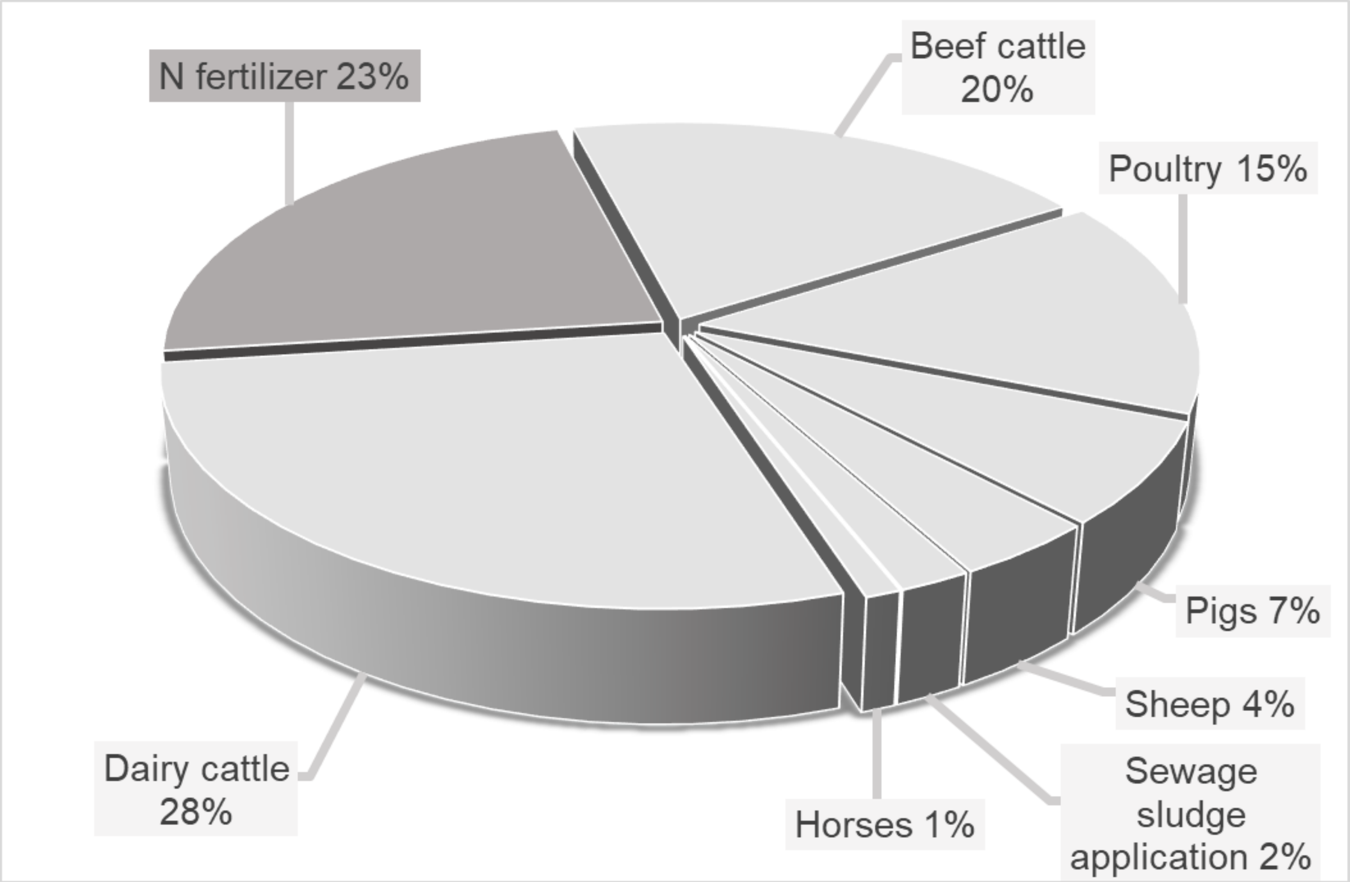

Figure 1: Agricultural NH_3 emissions in the UK by livestock (light grey) and fertiliser category .

Presently, NH_3 stands out as the air pollutant whose ambient concentrations are not decreasing rapidly, and occasionally increase slightly. Similarly, emissions of NH_3 during the last 3 decades have reduced much more slowly than those of other major air pollutants such as NO_x, SO_2 and non-methane volatile organic compounds . A recent study shows that there are numerous NH_3 hotspots and unknown sources unidentified around the world . Areas with high beef cattle density are reported to produce an average of 50 μg N m^{-2} s^{-1} (85 g $animal^{-1}$

day^{-1}) . The Po Valley in northern Italy is considered the region in Europe with the highest intensity of NH_3 emissions, which can reach maximum values close to 250 µg m^{-2} s^{-1} during the season of manure application . After urea application to soils, NH_3 emissions can reach an peak of about 5 µg m^{-2} s^{-1} around midday if there is no rain . In order to address the environmental burden of NH_3 emissions and to design management strategies, it is necessary to distinguish the main sources of agricultural NH_3, because 88-94% of NH_3 in the troposphere comes from farming practices , of which 65-71% is from livestock and 16-23% from fertiliser application. There are several options to mitigate NH_3 emissions and increased efforts are needed to lower concentrations to safer levels. To support the implementation of policies and changes to farming practices are effective, there is a need to monitor emissions and ambient levels of NH_3. For that purpose, a transformative improvement in monitoring technology is required to get real-world data from multiple sites and activities.

3. Impacts of ammonia emissions

Ammonia in the atmosphere has become a concern for environmental and health agencies for two main reasons: because of excess N deposition and because NH_3 is a precursor of fine particulate matter, both of which can impair human health. NH_3 is an alkaline compound, and when released into the air it is rapidly adsorbed to surfaces and significant deposition (up to 20%) may occur over distances ranging from a few hundreds of meters of the source to hundreds of miles . The remaining atmospheric NH_3 can rapidly react with acid gas compounds (such as SO_2 and NO_x from vehicular and industrial combustion processes) to form very small secondary aerosol particles . This fine particulate matter has an aerodynamic equivalent diameter of <2.5 microns (referred to as PM2.5), having a lifespan of up to 2 weeks and contributing to atmospheric haze and low visibility . NH_3 is transported by wind and deposited not far away from the source where it can promote plant growth in areas where N was previously a limiting factor . An example of this phenomenon is the eutrophication in catchments, including algal blooms that impair water quality and can harm

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ecosystems and people . Dry N deposition is a continuous process where the gases and aerosols from the atmosphere are transferred to the surface by atmospheric turbulence and diffusion, whereas wet deposition is the intermittent removal of chemical species from the atmosphere by precipitation. Airborne NH_3 concentrations reflect and approach a dynamic equilibrium between deposition and re-emission, an ongoing exchange between the surface and the atmosphere. Changes in plant species composition have been observed in natural ecosystems where high N deposition occurs . There is a loss of biodiversity because N-intolerant plants become depleted and N-tolerant plants become dominant . An example of this effect is the direct damage to sensitive vegetation such as lichens and bryophytes that occur even at very low NH_3 concentrations of around 1 μg NH_3 m^{-3} . Moreover, the deposition of N onto soils with a low buffering capacity can result in soil acidification and consequently basic cation depletion . Harm to human beings is caused by the fine particles that are inhaled deeply into the lungs and impair respiratory function and cardiovascular health . In addition, high concentrations (25 ppm) of atmospheric NH_3, as it is an irritant compound, have a negative effect on animal production in confined buildings and farm workers should avoid prolonged exposure .

4. Detection and quantification of ammonia

We review here the methods currently available to measure NH_3 and discuss some of the previous and significant developments in the field. The instant value of NH_3 concentration in the air, a measure that the currently available sensors usually provide, is only useful to meet the requirements of regulations in different activities. For some farming activities, regulators require instantaneous measurements of NH_3 concentrations, but these measurements have to be used in modelling platforms with other data to estimate wider emissions and impacts of airborne ammonia. To be able to manage emissions from agriculture there is a need for sensors to identify and quantify different sources, including point, area and volume sources, and to identify major contributors. Monitoring programmes should provide data on NH_3 concentrations across a range of different scales and environments linking sources and

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receptors. At present a major challenge is to detect the low concentrations occurring in the troposphere (0.3–6 ppb) . Moreover, when the aim is to provide meso-scale and regional patterns, in traditional monitoring schemes, low-frequency (weekly, monthly) sampling is usually selected, which presents the challenge of delivering data over long periods. Most of the available sensors require a qualified operator to set up, calibrate, maintain and de-commission the measurements, which creates issues with staffing and costs when monitoring large areas or when there is a need for high frequency sampling. One of the biggest challenges is to design monitoring that can be used successfully by non-specialists e.g. farmers. A range of monitoring techniques is required that covers different levels of complexity and detail e.g. cheap and easy-to-deploy methods that non-specialists can use for basic reconnaissance and scoping of sources, and more sophisticated methods can be used to identify individual source contributions and performance in complex or specialised studies. Quantifying NH_3 gas emissions needs devices that measure concentrations but also modelling methods to scale concentrations and to calculate emission rates . Also, important critical information is needed to achieve accurate estimations of emission rates, like information on livestock housing facilities, feeds, temperature, wind speed, ventilation rates, among others. Several modelling approaches have been used to estimate NH_3 emission rates, and in order to obtain robust estimates they must take account of variables like wind speed, humidity and air temperature at different heights – which may be measured or derived from numerical weather prediction models. There are particular challenges when measuring NH_3 at low concentrations, because the polarity and geometry of the molecule make it highly soluble in water so it tends to adsorb onto surfaces such as air sampling tubes, which can result in significant errors when concentrations are low .

For review purposes, the range of sensors available can be classified by different aspects, such as cost, temporal resolution, and level of automation. In this review, sensors were classified by the analytical technique used to detect NH_3 molecules. The sensors covered are only those considered suitable for agricultural applications. These sensors need to be

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portable, and be selective for NH_3 so that measurements are not compromised by interference from other ambient chemicals. They also need to have a wide range of operation to measure concentrations found in farming and sensitive ecosystem situations, including the low concentrations that occur in some environments. Some sensors are suitable for measurements in livestock housing and manure storage situations, whereas others are suitable for measuring lower concentrations of NH_3 from fields (Figure 2 and Table 1). As shown in Table 2, only high-cost equipment (e.g. chemiluminescent or photoacoustic, cost >$25.000) is suitable for directly measuring low concentrationsof NH_3 (<0.1ppm). Lower-cost sensors (electrochemical types, cost $500-$2000) are generally designed for higher-concentration situations e.g. for NH_3 leak detection (>1 ppm) . An alternative to high-cost sensors is the use of passive and active samplers that can accumulate NH_3 over long periods (usually between 1 week and 1 month), which enables them to detect low time-averaged concentrations . Moreover, an interesting new device can provide information about the location of a source without needing a power supply. This is a directional passive air sampler which resolves concentrations into 12 x 30^o sectors, and combines a static carousel containing passive samplers with a rotatable inlet that aligns with the wind . Passive samplers tend to be cheaper and easier to deploy than active (powered) samplers, but they provide lower temporal resolution and still need laboratory analysis to obtain an average value of NH_3 concentration.

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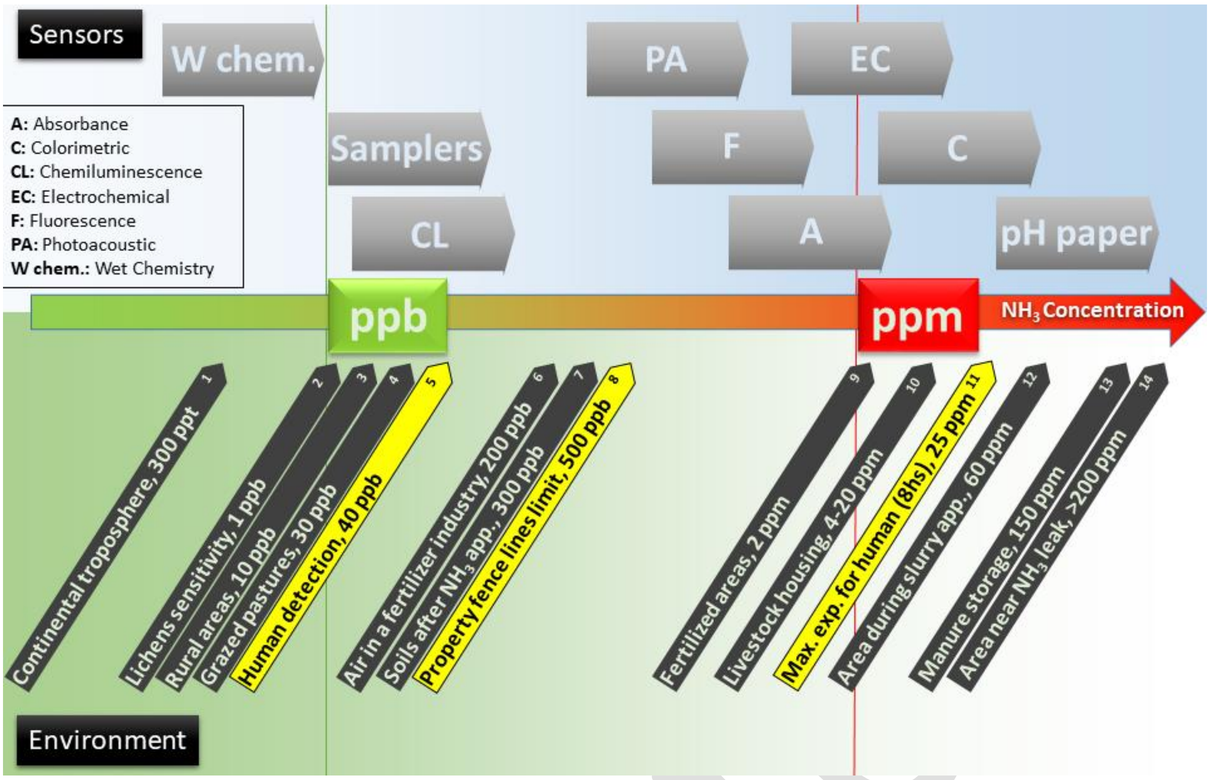

Figure 2. Reported NH_3 concentrations in different environments and sensor techniques for different concentration; see Table 1 for details. The yellow arrows indicate established limits for NH_3 in air. 1) , 2) , 3), 4) , 5) , 6) , 7) , 8) , 9) , 10) , 11) , 12) , 13) , 14) .

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Table 1. Concentrations and limits for airborne ammonia

Typical concentrations are shown for different source and receptor situations, ranging from remote background locations to near-source storage and leakage situations

Source/Environment	Reported concentrations*				Reference
Continental Troposphere	0.1-1.5	ppb	0.13-1.9	µg NH$_3$ m^{-3}	
Lichens sensitivity	1	ppb	1.3	µg NH$_3$ m^{-3}	
Rural areas	10	ppb	13	µg NH$_3$ m^{-3}	
Urban areas	10.9-15.3	ppb	1.4-2.0x10^{1}	µg NH$_3$ m^{-3}	
Industrial areas	20	ppb	2.6x10^{1}	µg NH$_3$ m^{-3}	
Grazed pastures	40	ppb	5.2x10^{1}	µg NH$_3$ m^{-3}	
Odour threshold for human detection	40	ppb	5.2x10^{1}	µg NH$_3$ m^{-3}	
Near-road	41.3	ppb	5.4x10^{1}	µg NH$_3$ m^{-3}	
Air in fertiliser industry	30-380	ppb	0.39-4.9x10^{2}	µg NH$_3$ m^{-3}	
Soils after anhydrous ammonia applied	400	ppb	5.2x10^{2}	µg NH$_3$ m^{-3}	
Property fence lines limit	500	ppb	6.5x10^{2}	µg NH$_3$ m^{-3}	
Dairy wastewater lagoons	0.4-1.6	ppm	0.52-2.1x10^{3}	µg NH$_3$ m^{-3}	

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Areas after manure or synthetic fertilise application	0.01-5	ppm	$0.01\text{-}6.5x10^3$	µg NH_3 m^{-3}
Beef cattle housing	4	ppm	$5.2x10^3$	µg NH_3 m^{-3}
Dairy Housing	0.8-10	ppm	$0.1\text{-}1.3x10^4$	µg NH_3 m^{-3}
Hog housing	5-28	ppm	$0.7\text{-}3.6x10^4$	µg NH_3 m^{-3}
Poultry houses	20	ppm	$2.6x10^4$	µg NH_3 m^{-3}
Maximum exposure for humans (8hs)	25	ppm	$3.3x10^4$	µg NH_3 m^{-3}
Area during slurry application	60	ppm	$7.8x10^4$	µg NH_3 m^{-3}
Manure storage	150	ppm	$2.0x10^5$	µg NH_3 m^{-3}
Area near an ammonia leak	100-600	ppm	$1.3\text{-}7.8x10^5$	µg NH_3 m^{-3}

*Transformation rate of NH_3 concentrations: 1 µg m^{-3} ≅ 0.774 ppb.

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Table 2. Reported ammonia sensors and their measured concentrations. The table is separated in commonly reported concentration for each class and outstanding sensors.

Technique or method based	Usual concentration		Sample rate	Concentration of selected sensors		Sample rate	Use	Reference
	LOD	Range		LOD	Range			
Wet chemistry	0.1 ppb	0.1 ppb – 1000 ppm	> min.	0.58 ppt	5.5-30 ppt	-	NH_3 concentrations below ppb levels and reference methods.	
Chemiluminescence	0.2 1 ppm	0.25-100 ppm	> min.	60 ppb	0.31-59.6 ppm	-	Field instrumentation for low ppb NH_3 concentrations	
Passive Collectors	0.2 ppb	0.2 -100 ppb	> hours – months.	-	>0.2 ppb	-	NH_3 diffusion tubes are useful for providing long-term estimates.	
Photoacoustic	0.3 ppm	0.3-10 ppm	> sec.	0.1 ppb	0.1 ppb - 3 ppm	5 L/min	Laboratory instrumentation for NH_3 concentrations below ppm levels	
Fluorescence	0.5	0.5-50	> min.	30	30-380	15	Laboratory instrumentation for NH_3	

	ppm	ppm		ppb	ppb	L/min	concentrations of low ppm levels	
Absorbance	0.5 ppm	0.1-10 ppm	> sec.	3 ppb	3 ppb-10 ppm	~6 /min	Field sensors for NH_3 concentrations of low ppm levels	
Electrochemical	1 ppm	1-50 ppm	> min.	0.5 ppm	0.5-5 ppm	6 /min	Field sensors for NH_3 concentrations of low ppm levels	
Colorimetric	10 ppm	10-300 ppm	> min.	10 ppm	10-200 ppm	4 /min	Field sensors for NH_3 concentrations of low ppm levels	
pH papers	50 ppm	50 - 1000 ppm	> min.	50 ppm	50-300 ppm	30 /min	Field sensors for NH_3 concentrations above 50 ppm levels	

- LOD: Limit of detection.

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4.1. **Types of Sensors**

Based on the main system used to detect ammonia, there are two broad types of sensors: electrochemical and spectrometric. There are also two main strategies for obtaining an analytical signal from the NH_3 molecule: direct measurement of NH_3 itself, or indirect measurement of a compound that derives from a reaction with NH_3. Most methods described here rely on collecting gaseous NH_3 in an acidic medium and then measuring the concentration. There is a need to distinguish between gaseous and particulate ammonia. The volume of air passed through a sampler is recorded and the NH_3 concentration in the air is calculated.

4.1.1. **Electrochemical sensors**

The principle of electrochemical sensors involves detecting the change in an electrical signal (resistance, potential, current) caused by adsorption of NH_3 into different materials. Voltametric or potentiometric determinations were developed typically to measure NH_3 in aqueous samples, for which the detection limits (~1-100 ppm) are much higher than for air samples . Although amperometric NH_3 sensors offer high sensitivity, they are characterised by low selectivity because the NH_3 signal cannot be readily distinguished from interfering signals due to other compounds that are present . Because of this interference, these types of sensors are not suitable for agricultural applications and so are not discussed further. Generally, those studies that present new developments in electrochemical sensing are conducted by material scientists, which could explain why their application in agriculture is rarely discussed. In addition, the concentrations investigated in these studies (1-10,000 ppm) tend to be higher than the concentrations applicable to agricultural NH_3 situations (0.01-100 ppm). Nevertheless, the chemical alarm systems used to signal potentially unsafe levels of NH_3 in housing facilities do not require very sensitive sensors, so that small and low-power electronic devices are feasible in these situations. Overall, semiconductor and metal-oxide gas sensors seem best-suited for these chemical alarm applications .

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Several new materials have been developed which can change their electrical conductivity as a function of the NH_3 concentration in air. Chemi-resistive materials have been used to detect a number of oxidizing or reducing gases such as NH_3, based on the charge transfer that can occur between the sensing element and the redox gas . Typically these detectors incorporate semiconductors that can be categorized as metal oxide, conductive polymers, or combinations of metal nanoparticles and conductive polymers that result in promising composite materials . Metal oxides-based NH_3 sensors have shown good performance compared to carbon materials, and are competitive in analytical performance in relation to conductive polymers . The main disadvantage of metal-oxide-based technologies is the requirement for activation energy to convert the low conductivity of the materials into semiconductors . In metal-oxide-based sensors, the activation energy is usually supplied by using temperatures above 200°C, while conductive polymers are activated through a “doping” synthesis that generates delocalized charges in the sensing element .

In recent decades, polyaniline-based materials have emerged as the preferred choice among polymer-based sensor materials, because of their cost-effectiveness, ease-of-preparation, and superior sensing performance . Most up-to-date developments have improved stability and repeatability by combining polyaniline with other NH_3-sensing materials, including combinations of polyaniline nanocomposites with metal oxides, graphene, carbon nanotubes, and other carbon nanomaterials . These developments allow polymer-based sensing materials to readily transduce the sorption of NH_3 into an electrical signal at room temperature . Nevertheless, the mechanistic understanding of the mix of this polymer with carbon nanomaterials or metal oxides remains elusive, representing a challenge for the next generation of these sensors. The disadvantages of the conductive material-based sensors are that they require regular maintenance and lack sensitivity and selectivity. For example, conducting polymers need regular regeneration to prevent loss of sensitivity . Most of these developments are not suitable for the agricultural environment where other redox gases are present (N_2O, NO_2, H_2S and CH_4) . Moreover, most of these

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sensors provide only first order data, reading only one signal value per sample, so no multivariate calibration could be applied to resolve interferences . In addition, there is a need to use non-linear regression models, which adds an extra layer of complexity to these electrochemical determinations. A few minutes per sample is needed to achieve measurements in the order of several ppm which is a high concentration for most agricultural purposes, except for alarm systems in livestock housing facilities . More complex methodologies could be used to address the problem of sensitivity. For example, Timmer et al. (2004) used miniaturization and pre-concentration by membranes and an acid trap to reach the required concentration levels (ppb). Another approach that addresses selectivity is the use of indirect measurements of electrolyte conductivity detection . However, these methods seem to be unsuitable for long term sensing in dusty environments such as agricultural facilities, because their membranes and filters get clogged easily.

4.1.2. **Spectrometry based-sensors**

Optical devices based on spectrometry can meet stringent requirements for sensing, such as strong resistance to electromagnetic noise, high stability, low power consumption, and compatibility with explosive environments.

4.1.2.1. Absorbance-based and colorimetric sensors

The most common absorbance-based and colorimetric sensors involve direct measurements using long-path instruments and NH_3-derived compounds, and indirect measurements of changes in pH. The methods have a broad range of applications, and sensor selection depends mainly on the NH_3 concentrations to be measured. The various methods cover a calibration range between 1 and 18,000 ppm of NH_3, and one study reports a limit of detection of 1 ppb_v NH_3 . Continuous monitoring over large areas or long paths can require low detection limits, and absorbance-based sensors seem to be the best option for these situations (See Table 2). Direct measurements can be done with open-path sensors at infrared (IR) or ultra-violet (UV) wavelengths. The methods can be used to integrate NH_3

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concentrations over several metres of air path up to 120 meters . Another method involving a long optical path is cavity-ringdown spectroscopy which has been used successfully to identify NH_3 emission sources, and when used with real-time data it can explain the correlation between concentrations of NH_3 and other precursor gases for $PM_{2.5}$ in urban air . The main disadvantages of the methods are that the initial costs for equipment and set up are high, that qualified personnel are needed to deploy and maintain the sensors, and that interferences from dust, water vapour and other gases (e.g. NO_x, CO_2, O_2, etc.) commonly occur in agricultural environments . Invalid data from long-path instruments due to dust or laser reflector alignment issues could be avoided using the latest chemometrics approaches that can predict values with uncalibrated interferences . Moreover, miniaturized systems could solve the problem of needing large sample volumes for absorption spectroscopy, or they could enhance the absorption signal by using specific and very sensitive colour reactions that are already available .

Chemicals for deriving NH_3 concentrations can be held on a variety of surfaces. The most commonly used methods for deriving NH_3 are the Berthelot, Nessler and pyridine-pyrazole reactions, or their modifications . There are two commonly used arrangements that use colour changes to infer a sample gas concentration. One arrangement uses gas tube samplers that are coated inside with colour-change reagent, and are attached to a hand pump that sucks a pre-defined volume of air per stroke . Tubes are available with different measurement ranges e.g. a range of 0.25-30 ppm is suitable for NH_3 in livestock buildings . However, the sensitivity of the tubes is generally too low (>2 ppm) for measuring outdoor NH_3 concentrations. The second arrangement uses a chemcassette system where a coil of paper embedded with chemicals is coupled to a measuring device . The paper acts as both a sampling medium, and as an analysis facility for detecting and measuring nanogram amounts of the target gas. These devices use a small length of paper tape per sample, allowing scheduled automatic measurements. On exposure to the target gas, the tape changes colour in direct proportion to the sample gas concentration, and a photo-optical

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system measures the colour intensity change from which the sampled gas concentration is determined .

Other thin-films samplers are reported in the literature but they are still not widely used. An example is the change in optical absorption of a thin dye-doped nanostructure polypyrrole film . Another sensor uses polyaniline deposited on the surface of a polyethylene tube . Also, there are non-specific sensors available like pH papers that measure indirectly the presence of NH_3 in air . This method provides inexpensive *in situ* records for estimating NH_3 concentrations by matching the colour change against a calibrated chart. Other sensors use patterns of different dyes to obtain values of NH_3 and to discriminate different interferences like SO_2, Cl_2, CO_2 or volatile amines . Chemometrics analysis is used for multivariate calibration when several dyes are used at the same time . Because these indirect methods have low sensitivity and precision, they could be suitable for preliminary and rapid analysis in high concentration environments like slurry lagoons and housing facilities.

4.1.2.2. Fluorescence-based sensors

Fluorescence is not frequently used to measure air quality in agricultural situations because few relevant compounds fluoresce, compared to those that absorb radiation . However, there is a growing interest in replacing conventional organic dyes with stable semiconductor or carbon-based photo-luminescent nanomaterials for fluorescence-based sensing. Fluorescence sensors offer relatively high sensitivity (~50 ppb), easier design strategies, lower cost, and higher portability. Photo-luminescent carbon dots (CDs) are better than semiconductor nanomaterials in terms of their high biocompatibility, low toxicity and lower cost . To date, fluorescent CDs have been successfully exploited in a wide range of applications and a recent study uses fluorescent determination in solid and liquid samples from agriculture, based on simultaneous extraction and fluorimetric labelling of NH_3, followed by fluorescence measurement. The fluorimetric labelling reagent is the o-phthalaldehyde (OPA), and the reaction is based on the deprotonation of a pH indicator .

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As the NH_3 molecule is not fluorescent by itself, quantifications are done using derivatization reactions like that used for the sensor in section 4.1.2.1. The signal recorded is the emission of photons after irradiation of the derivatization reagent. A trapping solution or new porous matrices like sol-gel or latexes have been developed to obtain a fluorescent signal from the non-fluorescent NH_3 molecule . Thin films involve the reversible absorption and desorption of NH_3 over periods of about one minute, that change the fluorescent signal of the polymer . Future developments could use such fluorescence sensitivity to measure NH_3, and current applications of fluorescence-based sensors often measure NH_3 concentrations down to about 5-50 ppm.

Another fluorescent sensor uses an array of seven chemical materials with fluorescent properties as the sensing elements . These kinds of materials can identify interactions between molecules such as p-p molecular complex action, bond formation, acid-base interactions, physical adsorption, and Van der Waal forces. The sensor elements interact with specific gases that can change their fluorescent and photochemical properties, so that the change in their fluorescence can be detected. This approach has been successfully used in detecting NH_3 once is dissolved in water, but could also be a good starting point to obtain rapid and inexpensive sensors for NH_3 in air. Also, chemometrics could be used to calibrate or to discriminate contributions from other gases present in media, as it has been done with colour dye arrays .

4.1.2.3. Photoacoustic based-sensors

This optical technique involves the absorption of modulated laser radiation with a specific wavelength of ~1530 nm for the NH_3 molecule. The deactivation of the excited molecule via collisions is converted into a modulation frequency that induces acoustic waves that can be monitored with a low-noise microphone. The instrument layout consists of a laser source, a resonant photoacoustic (PA) cell, a microphone to monitor the sound waves and an

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electronic control module for laser modulation and signal processing . The PA spectroscopic gas detection technique has numerous advantages, making it a very promising candidate for NH_3 detection in agriculture . PA provides continuous, selective and automatic measurements with outstanding long-term stability . Carbon dioxide (CO_2) and water vapour are the major potential interferences, but these can be addressed by using an isotopic $^{13}CO_2$ laser with a different wavelength to suppress the signals . Although PA is a very sensitive technique, it still lacks the robustness needed for use in agricultural environments because the sensors have a significant cross-sensitivity to nitrous oxide (N_2O) and methane (CH_4) . Moreover, electronic developments are needed to reduce the cost of the equipment (> $10,000) in order to allow large-scale use of PA cells in commercial sensors. Most developments using this technique measure in the range of 0.1 ppm to 100 ppm , so it could be used for monitoring NH_3 in poultry houses, dairy wastewater lagoons and at property fence lines where the regulations mandate a maximum concentration of 0.5 ppm .

4.2. Use of monitoring to support emission estimates

4.2.1. Emission factors

Several approaches have been developed with different complexity levels to estimate NH_3 emissions over large areas. The simplest method is collecting field data through surveys and multiplying each identified source by an emission factor (EF) . For example, official estimates in several countries have been done using livestock numbers and amount of N fertilisers sold per year, multiplying these values by an average EF for each type of livestock and fertiliser . To achieve more accurate results, further developments added more variables to the models because the NH_3 emission rate is affected by temperature, wind speed, air humidity, soil type, slurry pH, among others . Specific EF have been developed for each individual emission source with information such as manure management system, housing facilities and season . The official NH_3 emission estimates in China include sources like livestock excreta, fertiliser application, type of agricultural soil, nitrogen-fixing plants, crop residue compost, biomass burning, urine from rural populations, chemical industry, waste

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disposal and traffic . The EFs are disaggregated both spatially and temporally according to the climatic conditions and local practices across the country. The next step increasing complexity and accuracy is inferring NH_3 emissions combining survey data with atmospheric dispersion models. This type of approach has demonstrated that is possible to estimate, with reasonable low bias, NH_3 emissions from different sources across large areas with high resolution .

4.2.2. Emission inventories

Collecting data through farm surveys make the information independent from (subjective) expert judgment. The use of farm surveys to collect field data is an affordable method to populate NH_3 inventories that are critical to evaluate policy changes in the agricultural sector and to verify compliance to international agreements . However, these inventories suffer from a number of inadequacies: i) poor spatial resolution, few measurements for large areas, leading generally to overestimations for non-agricultural zones and underestimations for emissions from farms; ii) poor temporal resolution, long term values underestimating the fertiliser application season; and iii) EFs are not specific for each source, average default values are used and several factors are left out of calculations .

4.2.3. Monitoring networks and alternative approaches

Higher spatial and temporal resolution and more reliable data are obtained adding measurements collected by sensors that are used to feed dispersion models. Large-area measurements are performed with commercial passive samplers , calibrated monthly against NH_3 active sampling devices . An example using a combination of the dispersion model Fine Resolution NH_3 Exchange (FRAME) and a network of passive diffusion samplers is the NH_3 emission monitoring in the UK . FRAME describes the main atmospheric processes (emission, diffusion, chemistry and deposition) taking place in a column of air moving along straight-line trajectories following specified wind directions, taking into account also the transboundary chemical composition imported from other areas of Europe . Adding

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more variables to the calculations like the size and shape of the source, the locations of targets, the dynamics and magnitude of each source, the meteorological conditions, the background concentration and a set of passive diffusion sensors which integrate over a few hours to weekly periods helped improving the accuracy of the estimates of NH_3 emissions from multiple small fields located near each other . Several passive and active samplers have been placed across countries to establish NH_3 monitoring networks including: the UK (NAMN, National Ammonia Monitoring Network) , the Netherlands (MAN, Measuring Ammonia in Nature) , Switzerland , the United States (AMoN, Ammonia Monitoring Network) and Ireland . The main aim of the networks is to monitor national trends, to assess regional variability and to validate model calculations.

Traditional monitoring networks can be expensive, thus, a solution to poor temporal and spatial resolution can be crowdsourced information involving citizens in monitoring . Citizen science projects have become important data sources to scientists, and an attempt to estimate NH_3 concentration from butterflies abundance has been published in a recent study . Others biomonitors can be used to provide valuable spatial information, like biodiversity measures such as lichen surveys .

4.2.4. Communication technologies and monitoring

The national inventories of NH_3 emissions can be improved with further developments in low-cost portable devices based on the techniques mentioned in the previous Section 4.1. Nowadays, there is a class of wireless network technologies that enable low power consumption and wide area coverage (LPWANs - Low Power Wide Area Networks) such as Sigfox or LoRa technologies that fit the need of large-area deployments of NH_3 sensors. Usually, these technologies have low-rate sporadic communications under unlicensed frequency bands, obtaining long distance links, normally 5 km in urban or over 25 km in rural or suburban areas . The use of these communication technologies together with sensitive sensors could be next upgrade to national inventories and NH_3 monitoring giving a better temporal resolution.

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5. Future NH_3 sensing requirements

There is great potential for NH_3 sensing technology to contribute to both improving inventories and to the design of emission mitigation strategies. The next generation of sensors has to specifically monitor sources to avoid the harmful effects of NH_3 and to help improve the efficiency in N use in the agroindustry. The deployment of appropriate sensors can support data collection to be used for:

i) Improving the formulation of livestock diets. Urea excretion and subsequent NH_3 emissions increase with increased dietary crude protein concentration.

ii) Developing urea hydrolysis inhibitors, and investigating the effects of other mitigation strategies for NH_3 emissions like soil pH control or irrigation after fertilising.

iii) Improving fertilising practices to maximize the N fertiliser value and improving manure management. The magnitude of NH_3 losses depends on both weather and management practices so, improving the knowledge of the factors affecting NH_3 emissions will help to develop better practices.

iv) Prompt decision making using real-time data, which is important for corrective actions such as switching on automatic water sprays or ventilation fans when a maximum threshold is reached in livestock housing.

v) Monitoring and detecting emission sources. NH_3 emitted could impair soil, air and water quality by contributing to over-fertilisation, acidity and formation of particulate matter (PM). Monitoring networks can generate long-term emission trends, which are critical for environmental policies . Regulations could be designed for minimum distances between precursor sources. Data from NH_3 monitoring networks are transforming the way that we understand and model the natural environment.

Ammonia emissions are indeed an important problem for society, where the dominant source is agriculture, creating not only an environmental problem but also nutrient losses

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that affect the efficiency of the agroindustry. Developments in NH_3 monitoring can contribute in several ways to mitigate these emissions by improving inventories to set international targets and by forecasting future trajectories of the contribution from the agroindustry to improve farm efficiency. Future monitoring systems built by simple and easy-to-deploy sensors that sample and accumulate ammonia signals over representative periods (e.g. 1-4 weeks) can be used to scope farm ammonia performance in sensitive environments. These systems do not need to be highly accurate but they do need to resolve individual farms or significant sources e.g. passive directional samplers located up- and down- wind of intensive livestock buildings. These systems should be deployable by non-specialists, who can send samples to central laboratories for analysis and interpretation.

The current recommendations in the livestock industry are to avoid alkaline environments for ammonium (pH >9.25), maintaining low temperature and avoiding air exchange in the superficial layer of manure (NH_3 vapour equilibrium). Nevertheless, every farm has its own characteristics in terms of climate, soil condition, type of manure, fertiliser applied, farm facilities and equipment, etc. So, weather data acquisition is essential for interpreting air-quality data, and can be either measured or extracted from numerical weather prediction models. Tailored advice on manure and fertiliser management, and on livestock diets will have an important impact on nutrient balances in order to avoid unnecessary costs. There is also a need for activity data to be collected and reported alongside air quality data, so the data can be interpreted and attributed to specific activities.

Currently and despite advances in monitoring devices, direct measurements at each farmyard and plot are impractical due to the cost and labour involved. Additional research is needed to extend cost-effective monitoring to large areas. An important contribution could be the use of wireless technology to connect sensors to make large deployments without human intervention during long periods of time. In addition, the air produced in agriculture environments is a mixture of a large number of gases plus relatively high moisture content.

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Some of the currently available sensors are prone to have severe interferences since they are sensitive to water vapour and other gases than NH_3. Therefore there is a need for new measurement methods customized for agriculture environments, where interferences are correctly calibrated. Future sensors should provide multivariate signals about the target compounds and interferences, for the application of statistical modelling.

6. Conclusions

Agricultural emissions of NH_3 are primarily associated with livestock production where the losses are notably high and there is a pressing need for new developments so that farmers monitor and control NH_3 emissions from fertiliser use. New user-friendly sensors are needed with enough sensitivity for monitoring low concentration (ppb). For this purpose, spectroscopic sensors can provide appropriately selective and sensitive measurements because the spectra from these sensors usually include information that allows interferences to be removed or reduced. Also, spectroscopic sensors can be automated and miniaturized to create low-cost sensors that offer real-time data for day-to-day decisions on ammonia control. The key improvements required in electrochemical sensors are better sensitivity and the development of sensing materials that work at room temperature. Photoacoustic sensors require new advances in electronics to lower their cost. It can be concluded that there is an immediate need of sensors that are more sensitive, selective, low-cost and user-friendly. Sensors must be capable of dealing with the high interferences arising in agricultural environments. Above all, there is an urgent need for new sensors to support the optimal use of N in agriculture so that nutrient pollution in the troposphere is minimised.

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Conflict of interest

None.

Disclaimer

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