

An assessment of the applicability of ambient NH₃ instrumentation under field conditions

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Abstract

Ammonia (NH₃) is an important atmospheric base which can contribute to eutrophication, acidification of ecosystems and the formation of secondary aerosols. In order to monitor potential policy driven reductions and provide information on NH₃ emissions, transport and deposition, active sampling is required. There are, however, many challenges in measuring NH₃ as it is a 'sticky' reactive molecule which is readily soluble and rapidly interacts with other trace gases to form secondary inorganic aerosols. When undertaking ambient NH₃ measurements, inlet set up, use of filters, reliable calibration standards and potential chemical interferences in the analytical technique thus need particular attention. Due to these complexities of NH₃ active measurements, a metrology-centred project on "Metrology for Ammonia in Ambient Air" (MetNH₃) funded by the European Metrological Research Programme (EMRP), was started in 2014, with the aim of developing traceable NH₃ monitoring methods and NH₃ certified reference material, which will be applicable under field conditions. In this project a commercial cavity ring down instrument is being characterised and further developed to be the traceable method of choice, alongside the development of an open path absorption spectrometer.

The following study presents the first results of a field intercomparison of different NH₃ instrumentation verified against traceable methods developed and characterised as part of the MetNH₃ project, held in South East Scotland. In addition, the applicability of dynamic calibration systems, under field conditions which have developed within the project is assessed. The overall objective of this study will be to establish recommendations for ambient NH₃ measurements.

Key Words

Ammonia, ambient, techniques, concentration, metrology

Introduction

It is estimated that 94% of the total NH₃ emissions in Europe (2011 data) originate from agriculture (<http://www.eea.europa.eu/data-and-maps/indicators/eea-32-ammonia-nh3-emissions-1/assessment-4>). The emissions of NH₃ can have direct and indirect impacts on the environment, including eutrophication and acidification of ecosystems. In addition NH₃ can indirectly impact climate and health, through formation of secondary aerosols (Sutton et al, 2009). The potential mitigation of NH₃ as an aerosol precursor has been demonstrated with a reduction of NH₃ resulting in a reduction in PM_{2.5} (particulate matter with <2.5µm in diameter) based on present day conditions (Vieno *et al.* 2016). It is currently estimated that there will be an increase in NH₃ emissions from 65 Tg N yr⁻¹ to 135 Tg N yr⁻¹ between 2008 and 2100, when assuming a global temperature change of 5°C and increased demand in animal products (Fowler *et al.* 2015). Given the uncertain future both in climate and anthropogenic emissions it is essential to monitor ambient NH₃ concentration and measure changes in atmospheric composition to quantify current and future impacts on the environment and human health.

Until recently the primary NH₃ sampling was done through acid coated denuders (most typically citric acid), which sampled at a 2 -12 hour resolution with offline analysis. This is still referred to as the reference method both within the European Measurement and Evaluation Program (EMEP, 1996) and by the United States Environmental Protection Agency (US EPA, 1997). The disadvantages of this method are that it is labour intensive for long term measurements and susceptible to artefacts during the handling and storage of the samplers. Later in the 1990s, online wet chemistry methods were developed, including annular rotating wet denuders, such as the Ammonia Measurement by ANnular Denuder with online Analysis (AMANDA, NL,

Wyers et al. 1993) which used online flow injection analysis (FIA). This method however is still labour intensive. A commercial unit was developed in 2000s called the AirrMonia (Mechatronics, NL), which appears to have addressed some of the challenges encountered with the wet chemistry systems including a reduction in labour and consumables (Otjes and Erisman, 1999). Besides wet chemistry systems, mass spectrometry (Norman *et al.* 2009) has been used periodically in the field to measure NH₃, it is still rather labour intensive and thus tend to be used merely for only research purposes.

Absorption spectrometry is an ideal method for NH₃ analysis, which is molecule specific and can ensure according to the Beer-Lambert law, an absolute “calibration free” measurement. In the Netherlands, there has been a recent change from using an online wet chemistry method to using differential optical absorption spectroscopy (DOAS) for long term monitoring of NH₃ (Volten *et al.* 2012) which uses the UV spectrum. In addition, over the last 20 years, major advances were achieved in infrared (IR) laser sources. Lead salt diode lasers, which required cryogenic cooling and frequently were multimodal have been replaced by stable and monochromatic quantum cascade lasers (QCL). The development of reliable IR sources has resulted in the development of a number of commercial instruments in the last 10 years, which utilise cavity ring down (CRD), multi pass, open path, Fourier Transform InfraRed (FTIR) and photoacoustic methods.

In the 8 years following the most recent NH₃ intercomparison study (Bobrutzki et al. 2010), there have been significant advances in the commercial technologies available to measure NH₃. Commercial instruments became more affordable and now, no longer require specialist operators, have reduced labour costs and quantitative measurements down in to the ppt range. However, their capabilities under field conditions still have to be evaluated. In addition there are no standard operating protocols for field calibration of these instruments and a lack of a traceable NH₃ standard for routine quality assurance and quality control.

In 2014 the MetNH₃ project (Pogány et al. 2015), which is part of the European Metrology Research Programme, was started. The primary goal of MetNH₃ is to improve comparability and reliability of ambient air NH₃ measurements by achieving metrological traceability for NH₃ measurements in the fraction range 0.5-500 nmol/mol from primary certified reference material (CRM), and instrumental standards to the field level. The consortium consists of 10 partners (6 national metrology and 2 designated institutes as well as 2 researcher excellent grant holders) from Europe, as well as 19 global collaborators from both academia and industry. This study presents the design and first results of a field intercomparison study being held over summer 2016 in South East Scotland. Active measurement techniques are compared to metrological traceable methods developed within the project and the applicability of a mobile calibration system is assessed. The objective of this study is intended to set a series of recommendations for the measurement of ambient NH₃ under field conditions.

Methods

Field site

The NH₃ intercomparison will deploy instrumentation for one month (15th August – 16th September 2016) at an intensively managed grassland in South East Scotland, approximately 12 km south of Edinburgh. The grassland is dominated by *Lolium perenne* (perennial ryegrass) over approximately 5 ha, which are split into two fields, the sampling enclosure sits along the boundary fence between the two fields (Figure 1). The fields are normally intensively grazed by sheep, but for the period in the run up to the campaign the field with the dominant wind direction will be used for silage. For this site, typical, ambient NH₃ concentration of up to 10 ppbv are reported (Bobrutzki et al. 2010). The field is typically dominated by winds from the SW direction annually. The average August wind rose for the years 2010-2013, is shown in figure 1. Rainfall is typically lower in August, with an average total rainfall at this site of 98 mm in August (based on 2005 – 2014 data), and an average T of 14.1 °C with data ranging from 3.5°C to 35 °C for the same period.

During the campaign to test instrumentation at both ambient and elevated conditions, approximately 35 kg N ha⁻¹ of urea will be applied, which have historically resulted in conditions of up to 120ppbv of NH₃ at the site (Bobrutzki et al. 2010). However this depends on local meteorological conditions.

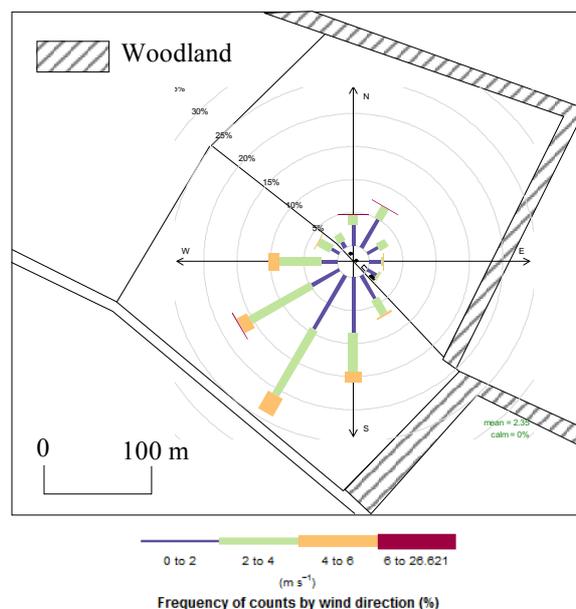


Figure 1. Average wind rose for August based on measurements from 2010 to 2013 on schematic of the field site

Instrumentation

At least 10 participants with a range of technologies will take part in the intercomparison with a range of technologies including infrared laser absorption spectrometry, DOAS and wet chemistry methods. Details of instruments and samplers participating are currently being finalised. For all instruments, a measurement height of ~2m is intended to be used with a combination of individual inlets and a universal manifold for some instrumentation. Within MetNH₃, a commercial CRD instrument, combined with a modified data evaluation algorithm was identified as a potentially traceable method. Raw spectra measured by the CRD instrument are evaluated with a spectral line fitting algorithm developed within the MetNH₃ project using spectral line parameters measured by the project partners to obtain traceable and absolute ammonia concentrations. The instrument has been characterised in the laboratory and will take part in the intercomparison as the reference instrument. In addition, an open path absorption spectrometer is being developed as part of the MetNH₃ project and will be deployed during this study. The study presented will be the first application of the open path QCL in the field, as it has only been tested under controlled conditions in the laboratory to date.

Portable dynamic calibration sources

Two partners within MetNH₃ have been developing portable reference gas generators in order to produce traceable CRM under field conditions. The calibration systems will be used to calibrate as many of the instruments during the intercomparison as possible. A protocol for future application of a calibration system under field conditions will be presented based on challenges with inlets, ambient conditions and practical logistics. It is intended that instruments will be calibrated at the beginning and end of the experiment to assess stability and drift within the instrument ensemble.

Results and Conclusions

This study will be the most recent investigation to determine the applicability of both commercial and research instrumentation in the measurement of ambient NH₃. It is hoped that from the results of this study conclusions can be drawn on future recommendations in the measurement of ambient NH₃ by active sampling methods, which can be used to further understand NH₃ and the impacts of mitigation strategies. Analysis of the measurement data will draw on the methodologies developed in Bobruztski et al. (2010), in order to understand the relative performance of the instrumentation including response time and the influence of relative humidity/precipitation. The applicability of the instrumentation to specific science and policy related studies will be discussed in the paper being presented along with a first assessment of the challenges which still remain to be addressed.

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