9th IWA Odour & VOC/Air Emission Conference

26-27 October 2021 Bilbao, Spain

FIRST DEVELOPMENT OF A GAS SENSOR ARRAY FOR MONITORING AMMONIA SURFACE EMISSION FLUX FROM GRASSLANDS

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Keywords: Fertilisation, grassland, ammonia, odours, MOS sensors

Abstract

Nitrogen is used in agriculture to fertilise croplands. During the spreading of fertilisers, a substantial part of Nitrogen is lost by volatilisation of ammonia (NH_3). These emissions are responsible for unpleasant odours but are also mainly precursors of particulate matters (PM). In Europe, agriculture is one of the main source of nitrogen-composed PM. There is a need to collect more emissions data to understand better this activity impact. Measurement techniques of NH_3, used for ambient air quality monitoring, are expensive and heavy to manage for the agricultural sector. Other techniques, less expensive, like passive sampling are also used to estimate ammonia flow but these are not adapted for a continuous monitoring. It's why we suggest to customise our usual e-nose devices to ammonia emissions from fertilised grasslands.

The sensor array is built using six commercial metal oxide semiconductor sensors. The sensors are inserted radially and evenly into a small size cylindrical PTFE chamber. Four of the selected sensors are sensitive to ammonia, one is sensitive to VOC and the last one is for combustible gas. The sensor resistance, the temperature and the humidity are recorded. A pump is used to suck air out of the sensor chamber, the flow being regulated at 200ml/min.

Ammonia concentration is measured with acid-soaked filters, this methodology is firstly developed in the lab. In order to determine the NH_3 concentration in the atmosphere, we perform experiments with known NH_3 concentration. Ammonia is fed into a system using mass flow controllers and commercial analytical air cylinder to dilute the gas down to the ppb level. Synthetic air is humidified at different values. Then, an organic fertilisation experiment was carried out on a grassland, with cattle slurry. The acid-soaked filters device and the sensor array were placed on the field at 30 cm over the vegetation. Odour samples are taken in addition to these two measurements for dynamic olfactometry analysis, also at 30 cm over the vegetation.

The results show that de acid-soaked filters device effectively traps NH_3 and can therefore be used to determine the NH_3 concentration in the air. This first experience of monitoring a nitrogen fertilisation with a metal oxide sensor array, shows that the instrument is able to clearly discriminate the change in air composition during the first 2 hours after the application of slurry. However, these results do not seem to be correlated with the odour concentration, which is stable during the first day after fertilisation.

Introduction

Agriculture is the main source of ammonia emissions. In Europe this corresponds to 93% of total emissions. These emissions come mainly from soil fertilisation and the storage of livestock manure (EEA 2020). This study focuses on ammonia emissions caused by nitrogen fertilisation of grassland. These emissions are influenced by many parameters (Behera et al. 2013; Sommer et Hutchings 2001; Gyldenkærne et al. 2005). They cause odour nuisance but can also have a negative impact on human health. Indeed, ammonia is a precursor of fine particles (Erisman et al. 2013). In addition, atmospheric deposition of NH_3 is phytotoxic, causing acidification and eutrophication of soils and surface waters (Erisman et al. 2013).

Numerous studies have been conducted on the techniques for measuring surface emissions of ammonia in agriculture. There are two types of methods, the micro-meteorological method and the chamber method. Micro-meteorological methods allow the measurement of ammonia volatilisation over a large area without altering the natural NH_3 emission. However, this technique generally requires expensive measuring instruments (Yang et al. 2018), although alternatives are being developed (Cohan et al. 2012). Chamber methods measure ammonia losses over a closed area, allowing multiple variations to be compared over a small area. However, these methods often do not reflect actual environmental conditions (Scotto di Perta et al. 2020). There are many chamber variants but three main principles are the wind tunnel, the static chamber and the dynamic chamber (Shigaki et Dell 2015; Smith et al. 2007).

Several methods of measuring ammonia concentrations exist. The wet chemistry techniques are the acid scrubbing, the annular denuder method or passive diffusion sensor (Phillips et al. 2001; Tang, Cape, et Sutton 2001). There are also different types of optical analyzers which have a higher temporal resolution but which are very expensive (Bobrutzki et al. 2010). Other technologies exist such as metal oxide sensors, catalytic ammonia sensors and conducting polymer gas detectors. However, the detection limit of these sensors is too high and they are non-specific which makes them difficult to use in environmental monitoring (Timmer, Olthuis, et Berg 2005).

Odour emissions after organic fertilisation have also already been studied by dynamic olfactometry, in order to define the olfactory nuisances (B. F. Pain et al. 1991; Zilio et al. 2021; Rzeźnik et Mielcarek-Bocheńska 2019; Pan et Yang 2007; Wilson 2013).

Electronic nose is generally used to measure odours (Misselbrook, Hobbs, et Persaud 1997a; Romain, Delva, et Nicolas 2008; Adam et al. 2013; Capelli, Sironi, et Del Rosso 2014; Jacek Gebicki, Tomasz Dymerski, et Jacek Namiesnik 2014). The low-cost sensors used in this kind of instrument do not allow to measure NH_3 concentrations of the order of ppb found during agricultural fertilisation. This study will try to find a correlation between the signature of a low-cost sensor network and the NH_3 concentration.

The goal of this research is to develop an instrument for measuring in real time ammonia concentrations and odour after fertilisation of grassland, with a temporal resolution of the order of a few minutes and which is inexpensive. The instrument is an array of nonspecific metal oxide sensors, similar to an electronic nose.

This article describes the development of the metal oxide sensor array and the initial stages of calibration. The two techniques used for calibration are acid-soaked filters for measuring NH_3 concentration and dynamic olfactometry for measuring odour.

Materials and methods

1. Study site

The outdoor experiments were conducted in Arlon in the campus park, it is a grassland. The experiment was conducted from June 08 to June 11. The fertiliser is spread on a surface of 50 m^2 with 100 nitrogen units of cattle slurry. The sample is taken at a height of 30 cm. Each type of measurement has its own sample tubing.

The filters are exposed for 60 minutes during 6 hours the day of application and the two following days. The sampling of odour bags is done every 3 hours during the first 6 hours and one time at 9:00 the second and third day.

The study site is equipped with a weather station.

2. **Acid soaked filters**

The filters are soaked with a 12% solution of citric acid in methanol. This solution is placed in the centre of the cellulose filter. The extraction of the ammonia captured on the filters is performed in ultra-pure water. The solution is analyzed by colorimetry with the modified Berthelot reaction. Ammonia is chlorinated to monochloramine which reacts with salicylate to form 5-aminosalycilate. An oxidation and an oxidizing coupling allows the formation of a green complex, whose intensity is measured at 660 nm to determine the ammonia concentration (mg N-NH4/l).

A soaked filter is placed in a custom-made Teflon sealed chamber.

The efficiency of the filters was first tested in the laboratory with a dilution unit consisting of mass flow controllers (MFC). Ammonia is taken from a 40 ppm NH_3 gas cylinders (Westfalen). The ammonia is diluted with synthetic air. Several humidity ranges are tested, for which the synthetic air is bubbled in ultra-pure water before being mixed with the ammonia. The dilution unit is set to output a constant flow of 1 l/min.

3. **Dynamic Olfactometry**

Odours are collected in 35l Nalophan bags. The bags are collected using the lung technique. The bag is placed in a rigid barrel with the air inlet of the bag attached to the barrel in order to collect outside air. The barrel is connected to a vacuum pump to draw air from the barrel and create a vacuum that will fill the Nalophan bag with outside air. The bag is then sealed and stored for a maximum of 2 hours in the dark before being analysed.

Dynamic olfactometry is performed in our lab according to the European standard EN 13725.

4. **Metal oxide sensor array**

The metal oxide sensor array is composed of 6 sensors. Four of these sensors were selected for their sensitivity to ammonia (see table 1).

Table 1: Metal oxide sensors present in the array.

Sensors	Compound	Concentration (ppm)
TGS 2602	NH_3, H_2S, COV	1-30
TGS826	NH_3	30-300
SB-53-01	NH_3	-
GGS4330	NH_3	-
TGS 2620	COV	50-5000
GGS 2330	CO, H_2, C_2H_5OH	1-1000

It should be kept in mind that these sensors are not specific. They will therefore not react only to ammonia but to all the compounds present in the ambient air, with a sensitivity that is higher for NH_3. In addition, these commercial sensors have different detection thresholds and concentration ranges in the ppmv range. The other two sensors were chosen to have very low sensitivity to ammonia.

The sensors are placed in a hermetic chamber with the temperature controlled at 50°C, to avoid condensation in the chamber. The chamber is made of PTFE to avoid any emission of organic compounds through it, as well as to reduce the absorption and chemical transformation of gaseous compounds Metal oxide sensors are very sensitive to temperature, humidity and atmospheric pressure variations, so temperature and humidity probes are placed in the chamber (Wang et al. 2010).

A pump, placed downstream of the chamber, sucks the ambient air through the chamber. The flow rate is fixed at 200 ml/min. The sensor signals are recorded on a computer. The time interval between each recording is 30 seconds.

5. **Data processing**

The data was processed with Rstudio software (version 1.4.1717). The ggplot2 package was used to perform the regression line for the calibration of the filters, the temporal graphical representation of the ammonia concentrations and the response of the MOS sensors. This package also makes it possible to carry out PCA (Principal Component Analysis) on the response of the metal oxide sensor array raw resistance data, taking a value every minute in order to reduce the number of points, making the graph more readable. The average weather data per hour is graphically represented using the openair package.

Results and discussion

1. Ammonia concentration measurement

Laboratory tests have shown that the filters soaked in citric acid are effective in capturing ammonia from the air (Fig.1). The linear coefficient of determination (R2) is 0.99.

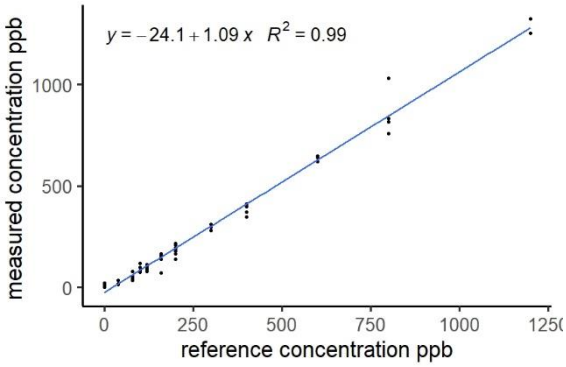

Fig.1: Linear regression of the reference concentrations obtained by dilution and the concentrations measured with the acid soaked filters.

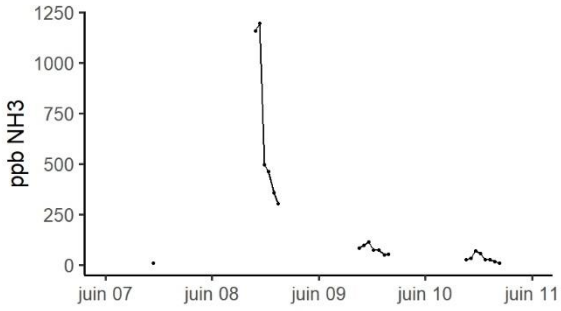

Fig.2: : Hourly evolution of the NH_3 concentration in ppb, measured with the acid soaked filters.

The perceived NH_3 concentrations by the filters before the application, performed on June 07 at 10:00, are close to 10 ppb and on June 08 at 09:00 after the application the concentration rise to about 1 ppm during the two first hours, then they drop sharply from the third hour (Fig.2). The following days the concentration decreased to below 100 ppb with a peak around 12 o'clock. Then, on the third day, the NH_3 concentration decreased to the concentration before application at the end of the day, with a peak again at 12 o'clock.

2. Odour monitoring

Odour concentrations on the first day were higher than on the following days with a slight increase at 12:00 probably explained by intense sunshine (Table 2).

Table 2: Dynamic olfactometry data.

date	Odour (uoE/m³)
08/06/2021 09:00	572
08/06/2021 12:00	641
08/06/2021 15:00	564
09/06/2021 09:00	212
10/06/2021 09:00	232

3. Metal oxide sensor array response

The temporal evolution of the individual sensors shows a sharp drop in the electrical resistance at the time of slurry application (Fig.3). The signal then rises gradually during the

day to reach the starting signal at sunset. The signal decreases again slightly the next morning. Compared to the data of a previous day (Fig.4), it seems that the sensors reacted again to the spreading on the morning of the second day but not on the third day.

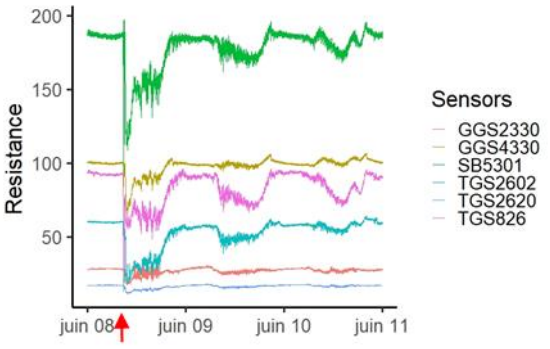

Fig.3: Real-time monitoring of the signal, in resistance, of the sensors present in metal oxide sensor array, after the slurry application. Red arrow = time of slurry application.

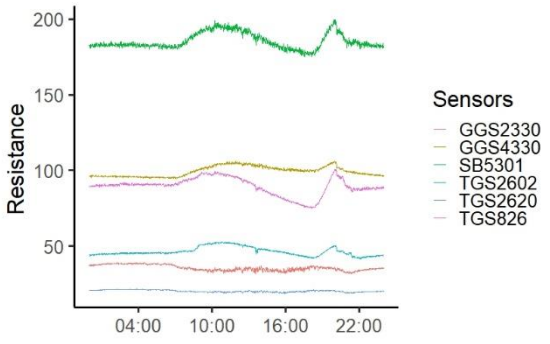

Fig.4: Real-time monitoring of the signal, in resistance, of the sensors present in metal oxide sensor array, after the slurry application, few days before the spreading.

The signal of the metal oxide sensor array was analysed with a PCA, one value every 5 minutes of the raw resistance data was used. During the first 6 hours after the application of slurry, the PCA shows a time evolution of the signal from left to right (Fig.5). A second PCA was performed with the sensor signal recorded before and 4 days after the application (Fig.6), the hourly median was used.

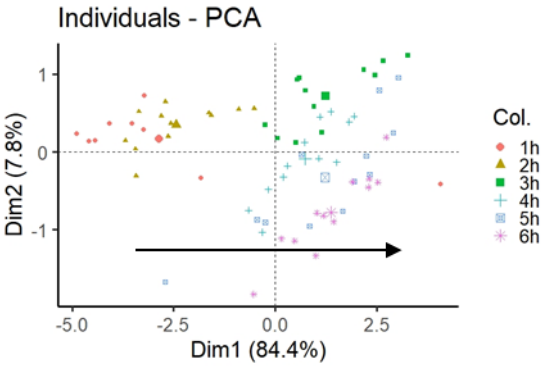

Fig.3: PCA representing the metal oxide sensor array signal during the first 6 hours after the slurry application. Black arrow = NH_3 concentration evolution.

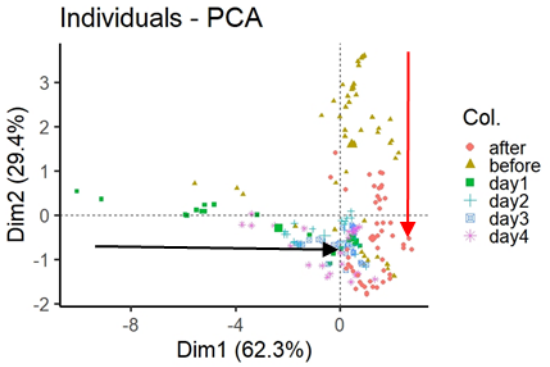

Fig.4: PCA representing the metal oxide sensor array signal before and after the slurry application. The hourly median was taken for the PCA. Black arrow = concentration evolution; Red arrow = humidity impact on the signal.

The principal component 1 (Dim1) describes the evolution of the signal on function of the air composition change after the application (black arrow Fig.6). The principal component 2 (Dim2) seems to show the impact of humidity on the signal (red arrow Fig.6 and Fig.7).

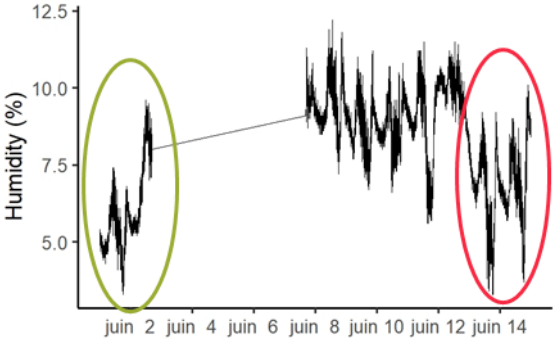

Fig.7: Evolution of humidity, in %, in the sensor chamber. Dark green circle = before spreading. Red circle = more than 4 days after spreading.

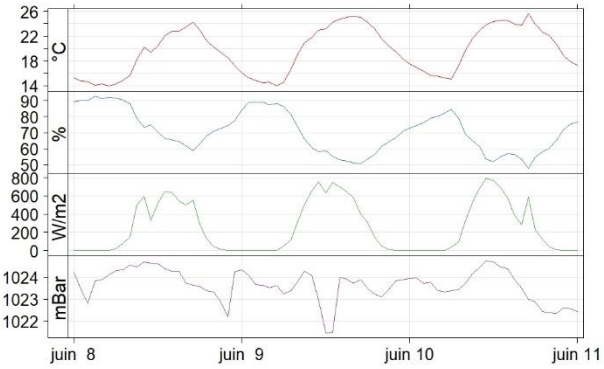

Fig.8: Weather data. Temperature in °C, relative humidity in %, sunshine in W/m2 and air pressure in mBar.

Discussion

In the literature, ammonia volatilization is usually highest in the first 12 to 24 hours after fertilization (Pain et al. 1989; Thompson, Pain, et Rees 1990; Huijsmans, Hol, et Hendriks 2001). Our results show that during the first two hours after slurry application, the NH3 concentration in air increased sharply to ~1ppm (Fig.2). The PCA results for the instrument show a different signal during these first two hours (Fig.5 and 6). Then the NH3 concentration decreases strongly, which is also visible with the PCA scores. From the second day, although the NH3 concentration is higher than before spreading, the instrument does not seem to be able to differentiate the polluted atmosphere anymore. Unlike other research where the odour decreases sharply after a few hours (Pain et al. 1991; Misselbrook, Hobbs, et Persaud 1997; Brandt et al. 2011), our results shows that the odour level did not change on the day of spreading. This results suggests that the instrument is more sensitive to ammonia than to the odour composition of the slurry. The sensors signal is influenced by the surrounding conditions. Indeed, the sensors response evolves according to the temperature, humidity and sunshine curves (Fig.8). As said before, a peak of NH3 concentration appears at about 12 o'clock on the second and third day after fertilisation. Beauchamp, Kidd, et Thurtell (1982) had observed the same diurnal phenomenon, which is influenced by temperature. This explanation is consistent with our observations, which show an increase in temperature and sunshine at this time.

Conclusions

This first experience of monitoring a nitrogen fertilisation with a metal oxide sensor array, shows that the instrument is able to clearly discriminate the change in air composition during the first 2 hours after the application of slurry. This correlates with the concentration of NH_3 raised in the ppm range. However, these results do not seem to be correlated with the odour concentration, which is stable during the first day after fertilisation. The next step is to repeat this experiment to have enough data to create a model to translate the signal from all the sensors into an ammonia concentration.

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