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

Marie SCHEUREN; Anne-Claude ROMAIN

Sensing of Atmospheres and Monitoring (SAM-Lab), Department of Environmental Sciences and Management,

Research Unit SPHERES

University of Liege, - Avenue de Longwy 185, 6700 Arlon (Belgium). mscheuren@uliege.be

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Introduction

- **Agriculture is the main source of ammonia emissio**
  - 93% of total EU emissions
  - Due to soil fertilisation and livestock manure storage

This study focuses on ammonia emissions caused by nitrogen fertilisation of grassland

- **Objective**
  - Development of a metal oxide sensor array for real time amm
    and odour measurement

    - Dynamic olfactometry to measure odour
    - Acid-soaked filters to determine NH_3 concentration

Materials and methods

- **Acid soaked filters**

Material

- Filters are placed in a custom-made Teflon sealed chamber
- +12% solution of citric acid in methanol

Efficiency tests of the filters in the lab

- Several ammonia concentrations (gas cylinders)
- Various humidity values

(Dilution unit consisting of mass flow controllers (MFC))

The filters are exposed to ambient air 60 minutes during outdoor experiments

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Materials and methods

- **Odour sample**
  - Dynamic olfactometry according to the European standard EN 13725
  - Olfasense TO evolution olfactometer
  - 4 panelists
  - Max. 2 hours storage

Sampling every 3 hours
during the first 6 hours after fertilizer spreading and
at 9:00 the second and the third day

Materials and methods

- **Metal oxide sensor array**
  - Sensors selected for their sensitivity to ammonia
  - Placed in a hermetic PTFE chamber with temperature controlled at 50°C
  - Temperature and humidity monitoring
  - Ambient air sucks through the chamber at 200 ml/min

  (2 devices)

Sensors	Compound specified by the manufacturer	Concentration (ppm) specified by the manufacturer
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

Material and methods

- **Outdoor experiments**
  - 50 m^2 grassland
  - Fertilisation of 100 nitrogen units of cattle slurry
  - Air intake of all samples at a height of 30 cm

  - June 2021

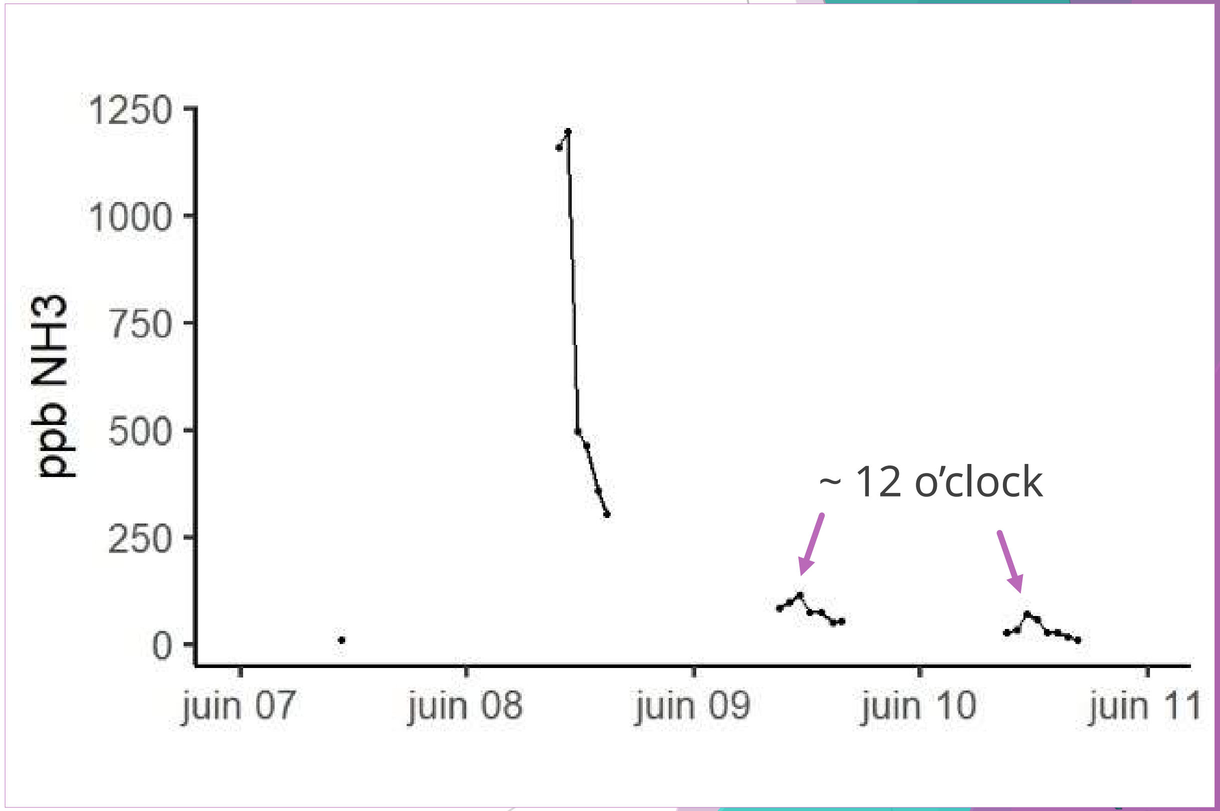
The study site is equipped with a weather station

Results
Ammonia concentration

- **Efficiency tests of the filters**
  - Efficient trapping of ammonia in the air (in the lab)

    $R2 = 0.99$

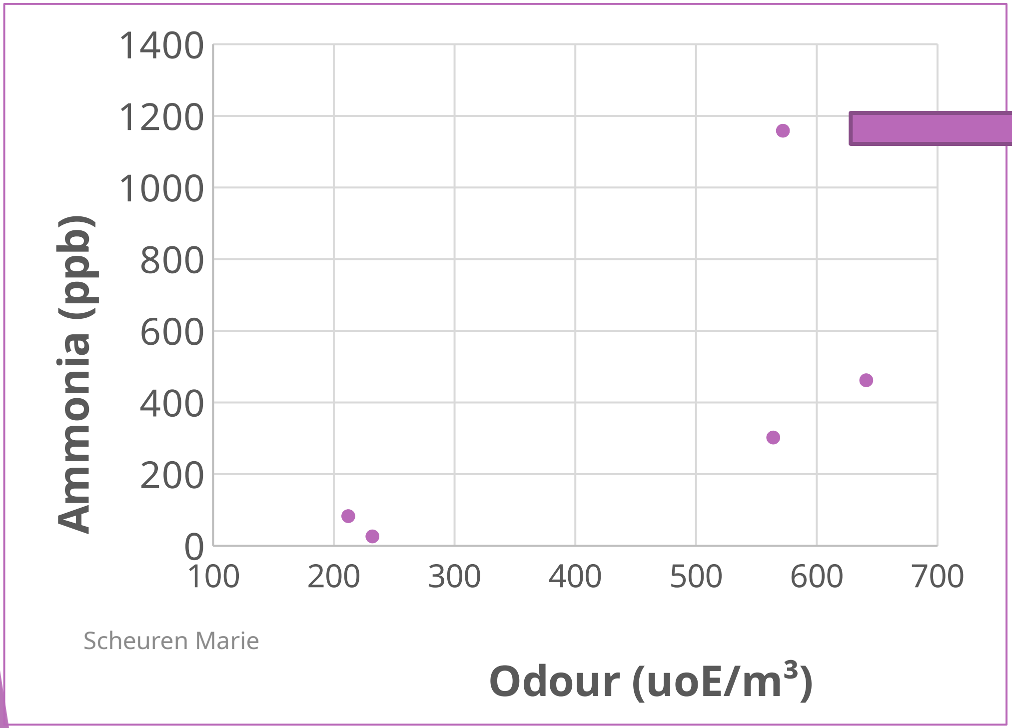
- **Filters: Outdoor experiment**
  - **Before** fertilisation ~10 ppb
  - **After** fertilisation
    - 2 first hours ~1 ppm
    - Succeeding days, the concentration decreased below 100 ppb with a peak around 12 o'clock



Results

Odour concentration

Sampling (and measurement) day	Odour (uo$_E$/m^3)	Standard deviation	Ammonia (ppb)	Time after fertilisation
08/06/2021 09:00	572	333	1158	Few minutes
08/06/2021 12:00	641	390	462	3 hours
08/06/2021 15:00	564	231	302	6 hours
09/06/2021 09:00	212	234	83	24 hours
10/06/2021 09:00	232	216	26	48 hours

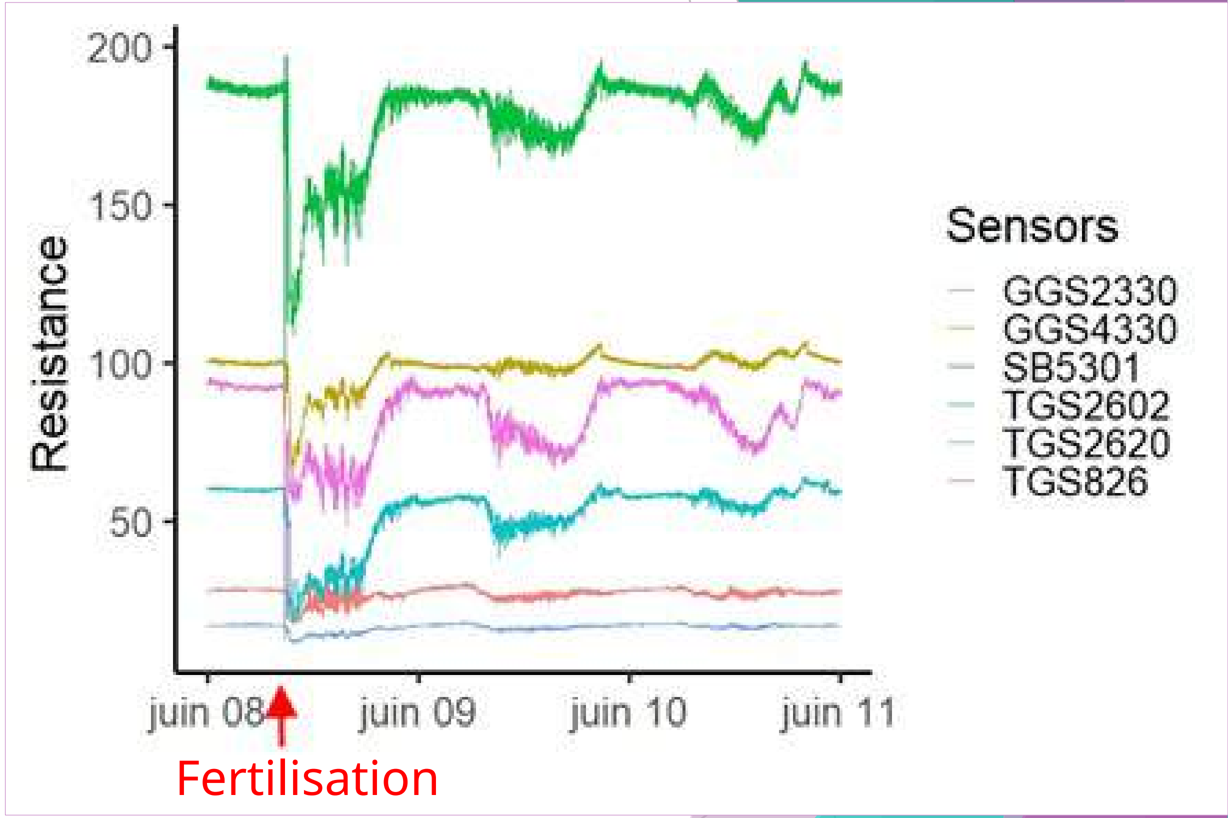


- First odour concentration (just after spreading) too low regarding the high NH_3 value (1158 ppbv);
- Except for very high value of NH_3, a trend between odour and NH_3 is observed

NH_3 is not the main contributor of odour but could be a good indicator of spreading odour when NH_3 is not too high

Results
Metal oxide sensor array response

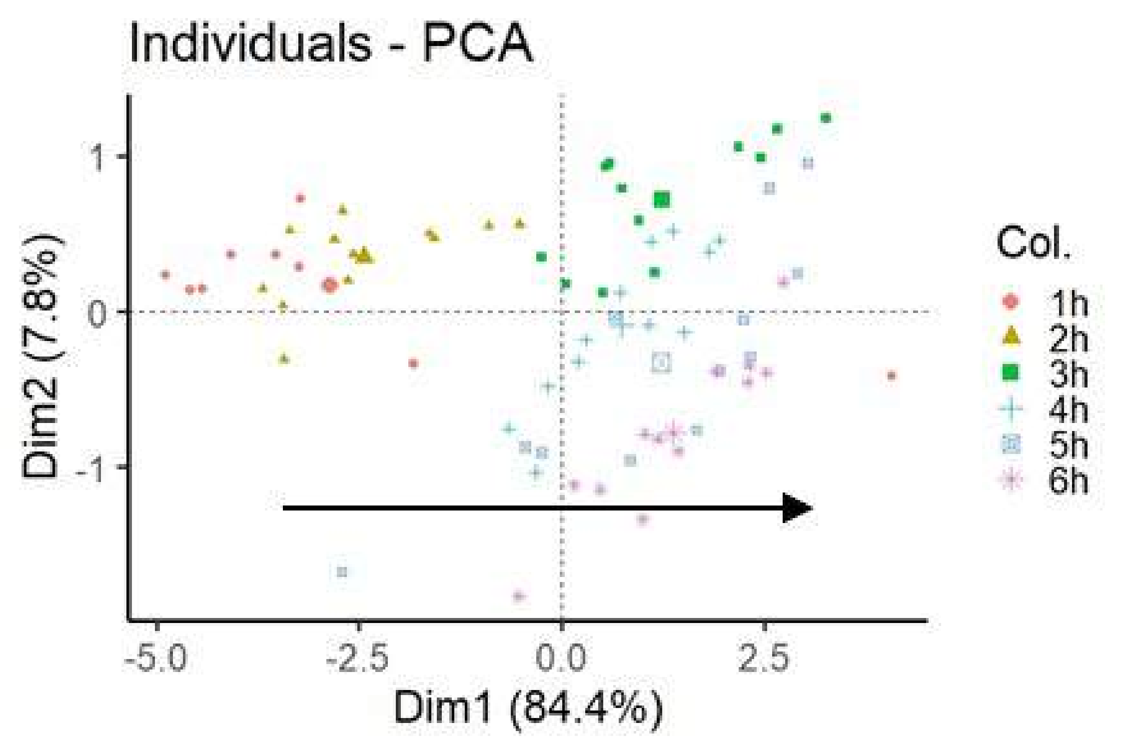
- **Outdoor experiment**
  - **Day 1**
    - Resistance (R) variation due to the fertilisation
    - R increase in accordance with the emission decrease
  - **Day 2**
    - Slightly signal decreases
  - **Day 3**
    - Signal seems similar to days before fertilisation

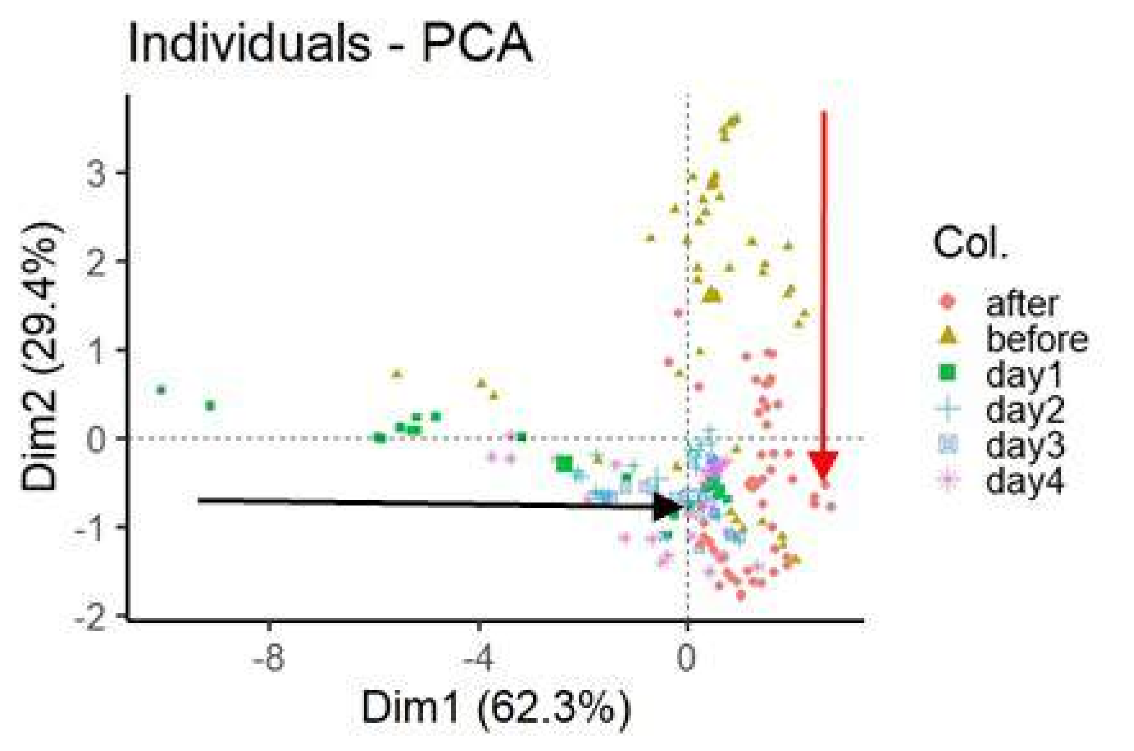


Results
Metal oxide sensor array response

PCA analysis (raw R values in kohms)

- Day 1: 69 obs. 6 variables (value every 5 minutes)
  - First 6 hours after fertilisation
- Campaign : 193 obs. 6 variables (hourly median)
  - 3 days before + 6 days after





- PC 1 (Dim1) = time evolution of the signal
- PC 1 (Dim1) = air composition
- PC 2 (Dim2) = impact of humidity

Conclusions

- **Ammonia concentration**
  - **Day 1:** first two hours, NH_3 increases to ~1 ppm, fast decrease to low level (<500 ppb)
  - **Day 2:** value of ~ 100 ppb
  - **Day 3:** level similar to background (<20 ppb)
  - Peak at about 12 o'clock on the second and third day after fertilisation **= temperature and sunshine**

- **Odour concentration**
  - **Day 1:** High concentration with low increase at 12 o'clock
  - **Day 2 and 3:** lower as day 1

- **Metal oxide sensor array**
  - Correlation with NH_3 concentration
  - No direct link with the odour concentration but with the chemical composition

Acid soaked filters = good tool for ammonia concentration validation
Metal oxide sensor array = promising tool for low cost ammonia real time monitoring

Next step
- Repeat the tests and increase the dataset
- Quantification algorithm development from sensors signals

Thank you
for your kind attention

Acknowledgements to

SPGE
Société Publique de Gestion de l'Eau

S.A.M.

AGRA OST

Intercomparison campaign with various analysers

Campagne de mesures IPSL

Analyse Multi-Instrumentale des Concentrations d'Ammoniac (AMICA)

L'ammoniac (NH_3) est un gaz réactif dont les émissions, principalement liées à l'agriculture, ont fortement augmenté depuis l'ère industrielle. Il est parmi les moins bien renseignés des précurseurs de particules en suspension qui sont particulièrement nocives pour la santé humaine. L'ammoniac participe donc aux évènements de pollution particulaire dans les mégacités, mais la compréhension de ces épisodes de pollution n'est pas complète et nécessite des observations de qualité des concentrations d'ammoniac pour caractériser finement les processus physico-chimiques de l'atmosphère. Il est cependant très difficile de mesurer la concentration ambiante d'ammoniac dans l'air étant donné la nature collante, volatile, et réactive de cette molécule.

Pour évaluer les différents types d'analyseurs de NH_3 dans l'atmosphère, un exercice d'inter-comparaison se déroulera en octobre 2021 sur le site de l'INRAE à Thiverval-Grignon (78), à proximité de la ferme AgroParisTech de Grignon. Cette campagne de mesures regroupe 8 instituts de recherche dont 3 laboratoires de l'IPSL : LISA, LATMOS, LSCE, INRAE Grignon, IMT Nord Europe, GSMA Reims, INRAE Rennes, et le Laboratoire Sensing of Atmospheres and Monitoring de l'Université de Liège. Les différents analyseurs sont comparés sur une large gamme de concentrations d'ammoniac allant de la concentration atmosphérique ambiante à des concentrations boostées par des peignes d'émissions d'ammoniac de $400m^2$ (Figure 1).

Figure 1 : Dispositif d'émission d'ammoniac avec des peignes

Cette campagne de mesures s'intègre étroitement dans le cadre du projet LEFE-CHAT NH3IDF 2019/2020 (PI : Pascale Chelin) et permettra notamment d'appréhender les performances des différents analyseurs de NH_3. Les mesures du site ICOS écosystème FR-Gri et de la station météorologique du réseau Agroclim d'INRAE, situées à proximité directe seront mises à disposition du projet pour interpréter les mesures.

Dates programmées : 4 au 30 octobre 2021

Personnes impliquées :

- **LISA** : Pascale CHELIN, Vincent MICHOUD, Antonin BERGE, Xavier LANDSHEERE
- **LATMOS** : Camille VIATTE, Cristelle CAILTEAU-FISCHBACH, Nadir GUENDOUZ
- **LSCE** : Jean-Eudes PETIT, Douglas ORSINI
- **INRAE Grignon** : Alain FORTINEAU, Pauline BUYSSE, Benjamin LOUBET, Baptiste ESNAULT, Sophie GENERMONT, Céline DECUQ, Erwan PERSONNE
- **IMT Nord Europe** : Sabine CRUNAIRE, Pablo ESPINA, Nathalie REDON
- **GSMA** : Lilian JOLY, Julien COUSIN, Florian PARENT, Sylvain CAVILLE
- **INRAE Rennes** : Chris FLECHARD, Yannick FAUVEL
- **Laboratoire Sensing of Atmospheres and Monitoring de l'Université de Liège** : Anne-Claude ROMAIN et Marie SCHEUREN