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 emissions
  - 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 ammonia 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))

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

<table>
<thead>
<tr>
<th>Sensors</th>
<th>Compound specified by the manufacturer</th>
<th>Concentration (ppm) specified by the manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGS 2602</td>
<td>NH₃, H₂S, COV</td>
<td>1-30</td>
</tr>
<tr>
<td>TGS826</td>
<td>NH₃</td>
<td>30-300</td>
</tr>
<tr>
<td>SB-53-01</td>
<td>NH₃</td>
<td>-</td>
</tr>
<tr>
<td>GGS4330</td>
<td>NH₃</td>
<td>-</td>
</tr>
<tr>
<td>TGS 2620</td>
<td>COV</td>
<td>50-5000</td>
</tr>
<tr>
<td>GGS 2330</td>
<td>CO, H₂, C₂H₅OH</td>
<td>1-1000</td>
</tr>
</tbody>
</table>
Material and methods

- **Outdoor experiments**
  - 50 m² 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)
    - $R^2 = 0.99$

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

Odour concentration

<table>
<thead>
<tr>
<th>Sampling (and measurement) day</th>
<th>Odour (uoE/m³)</th>
<th>Standard deviation</th>
<th>Ammonia (ppb)</th>
<th>Time after fertilisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>08/06/2021 09:00</td>
<td>572</td>
<td>333</td>
<td>1158</td>
<td>Few minutes</td>
</tr>
<tr>
<td>08/06/2021 12:00</td>
<td>641</td>
<td>390</td>
<td>462</td>
<td>3 hours</td>
</tr>
<tr>
<td>08/06/2021 15:00</td>
<td>564</td>
<td>231</td>
<td>302</td>
<td>6 hours</td>
</tr>
<tr>
<td>09/06/2021 09:00</td>
<td>212</td>
<td>234</td>
<td>83</td>
<td>24 hours</td>
</tr>
<tr>
<td>10/06/2021 09:00</td>
<td>232</td>
<td>216</td>
<td>26</td>
<td>48 hours</td>
</tr>
</tbody>
</table>

- First odour concentration (just after spreading) too low regarding the high NH₃ value (1158 ppbv);
- Except for very high value of NH₃, a trend between odour and NH₃ is observed

NH₃ is not the main contributor of odour but could be a good indicator of spreading odour when NH₃ 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

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 2 (Dim2) = impact of humidity

Scheuren Marie
Conclusions

Ammonia concentration
- **Day 1**: first two hours, $\text{NH}_3$ increases to $\sim 1$ ppm, fast decrease to low level ($< 500$ ppb)
- **Day 2**: value of $\sim 100$ 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 $\text{NH}_3$ 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 Scheuren Marie