Ammonia in the 21st Century: Challenges for Measurements and Mitigation



Dr Christine Braban and CEH colleagues Centre for Ecology & Hydrology, RMetSoc July 2019



With content from colleagues at CEH including MM Twigg, YS Tang, MR Jones, S Leeson, U Dragosits-Harding, S. Riddick, C. Steadman, E Nemitz, M A Sutton Work in collaborations with NPL, METAS, Ricardo and many others!





Knowledge gaps in all areas



Global nitrogen flows around year 2000 (million tonnes N / year)



Past change – future risks Global fertilizer use







Sutton and Bleeker Nature 2013 based on FAO projections

Global ammonia in a future climate



Sutton et al. Phil Trans. Roy. Soc., 2013





Controlled cuvette experiments

[NH3](%)



NH₃ emission from different substrates



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NH₃ emission from different nesting habits



NH₃ emission from different substrates (%)



Perez-Alcon E. (project student, ERASMUS programme)

Knowledge gaps in all areas







Emission inventories: e.g. UK National













A simplified inorganic picture of chemical processing in the atmosphere







Measurement of ammonia in context



NH₃



- Reaction
- Precipitation
- consumption

Re-emission





Ammonia measurement challenges

Environmental Pollution 251 (2019) 668–680





More obvious air pollution impacts on variations in bacteria than fungi and their co-occurrences with ammonia-oxidizing microorganisms in $PM_{2.5}^{\ddagger}$



Atmospheric

and Physics

Chemistry

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SCIENTIFIC REPORTS

OPEN

Diversity, abundance and activity of ammonia-oxidizing microorganisms in fine particula

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matter

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Modeling reactive ammonia uptake by secondary organic aerosol in CMAQ: application to the continental US

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Measurement of ammonia in context



Knowledge gaps in all areas







Current Instrumentation







Wet chemistry



Conductivity detector block





Instrumentation







Non-extractive sampling



Most commercial spectrometers are based on infrared spectroscopy, though UV instruments also developing





Ammonia Sensors



Alphasense NH₃ Sensor: NH3-A1 Range: 0 – 50 ppm



Alphasense NH₃ Sensor: NH3-B1 Range: 0 – 100 ppm



http://www.indsci.com/products/ammonia/#

Personal single-gas detector GasBadge® Pro

Multi-gas detectors: Ventis™ Pro Series MX6 iBrid™ Radius™ BZ1 Area Monitor

Range = detect low ppm ammonia





Atmospheric Composition Change

National Ammonia Monitoring Network



Local Environmental Impact information







Calibration



V = DAt/L

t = time of exposure (s)A = area of absorbent filter (m²) L = diffusion path length (m) $D = 2.09 \text{ x } 10^{-5} \text{ m}^2 \text{ s}^{-1} \text{ at } 10^{\circ}\text{C} (\text{NH}_3)$

	parameters	unit
Int diameter	0.021	m
Cross Area	0.000346361	m ²
Diffusion coefficient (@10°C)	0.0000209	m ² s ⁻¹
length(z)	0.00804	Μ
Sampling Rate	9.00365E-07	m ³ s ⁻¹
	3.24131472	L hr-1
	0.003241315	m ³ hr ⁻¹

 $D(T,1) = D(0,1)(T/To)^{1.81}$

 $D = 2.226 \text{ x } 10^{-5} \text{ m}^2 \text{ s}^{-1} \text{ at } 20^{\circ}\text{C} (\text{NH}_3)$

Calibrated Uptake Rate @ 20° C = 3.45 x 10^{-3} m³ hr⁻¹

cf 3.49 x 10⁻³ m³ hr⁻¹ (chamber exposure validation)

Martin N. et al. (2018) Validation of ammonia diffusive and pumped samplers in a controlled atmosphere test facility using traceable Primary Standard Gas Mixtures. Atm. Env. Submitted





Contamination artefacts



Inlet	μg NH ₄ +	µg NH ₃ m ⁻³
Covered with Solid Cap	0.07 ± 0.01 (n = 18)	0.36 ± 0.07 (n = 18)
Not covered	0.37 ± 0.09 (n = 12)	1.85 ± 0.45 (n = 12)
Covered with parafilm	0.16 ± 0.04 (n = 12)	0.81 ± 0.19 (n = 12)





Diffusive and pumped samplers tested in NPL CATFAC







2016 Ammonia Intercomparison



Note: Not to scale North field



Passive NH₃ samplers





NH₃ (ppb)

Instruments vs Ensemble median (23/08 - 29/08)





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CIEI

Twigg et al. *in prep*

Relative deviation from the mean









Knowledge gaps in all areas







Field calibrations

- 1 dynamic and 1 static calibration systems present
- METAS traceable reference gas generator (REGaS) used to check concentrations before and after intercomparison for low flow instruments (Picarro, LGR, LSE, Tiger Optics)
- NPL static calibrator used for high flow instruments and mini DOAS











Provisional field calibration results





REference GaS generator (ReGaS1) – dynamic gas generator developed and characterised by WP1 of MeNH3 project.



Twigg et al. in prep



Conclusions from state of the art instruments

SET UP IS MAJOR FACTOR IN GETTING HIGH QUALITY MEASUREMENTS OF NH_3

- Users still need some understanding in order to choose the right instrument for their application
- Instruments either need minimal inlet or a high-flow inlet with subsampling off for operation
- Dynamic calibration should work but instrument response time make calibration challenging
- Quantitative measurement at "background" to close to emissions challenging







Knowledge gaps in all areas







How to improve the situation in the 21st century?

- Emitting less directly
 - Process change
 - Efficiency of use
 - Fewer "leaks" in the system
- Recapturing emissions
 - Green removal e.g. Agroforestry or "sacrificial" vegetation
 - Barriers (green or otherwise) between emissions and impacts





Mitigation Measures for Reducing Ammonia

Spreading - Injecting manure



Housing – ammonia scrubbing









Increased grazing and woodland effect





Multiple wins?

Tree belts for ammonia mitigation offers

improved animal welfare under silvopastoral systems

reducing critical load exceedance on protected sites

carbon sequestration

visibility screening around housing units



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multi win wins for the famer and society

supporting policy and regulators in emission reduction

supporting national afforestation policies.

price advantage of 'woodland chicken/pig' products



Dis-benefits?

where NH₃ concentrations are high the rate of dry deposition is less

> young trees may 'suffer' with increased NH₃ concentrations – careful species selection





adding nitrogen into the system can cause nutrient imbalances availability of base cations

trees may encourage wild birds and bird-flu infection

opportunity cost – changing arable to woodland



Planting Designs

Planting design for capturing ammonia emissions from housing systems

The backstop trees should be of a conifer type or evergreen or something which can make a thick barrier. Spacing should be 2m or less (if appropriate) to acheive a good barrier.



Farmtreestoair: New tool based on current knowledge



http://www.farmtreestoair.ceh.ac.uk/





Conclusions

- Atmospheric chemistry of ammonia is in its infancy
- Ecosystem, climate and human health impacts beginning to be well documented
- There is a need for laboratory process studies, further development of instrumentation
- On-line long term monitoring of ammonia beginning in the UK, and across the world
- Review paper on measurement protocols and knowledge gap in preparation
- Global emissions in most scenarios get bigger throughout the 21st century, so emission reduction and/or mitigation actions need to be prioritised





Thank you very much for your attention. ③

Any questions.

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