



CF Braban, A C M Stephens, YS Tang, MM Twigg, S R Leeson MR Jones, I Simmons, D Harvey, N van Dijk, K Yeung, E Nemitz, , D Leaver, C. Martin Hernandez C Andrews, R Smith, L Banin, D Sleep, HT Carter, S Thacker, M Patel, B Tanna, PO Keenan, G Pereira, A Lawlor, C Conolly, K Vincent, A Sanocka, S Richie, D Knight, D Knight, S Halser, B Donovan, E Osbourne, A Sampford and the UKEAP field team, H. Walker

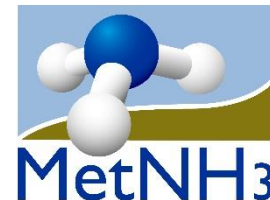
- human health, ecosystem health, pollution and atmospheric chemistry
 - Ammonia, reactive nitrogen, particulate matter
 - Ozone, emerging pollutants
- Environmental metrology
- Infrastructure and capacity building
- Chemical climate concept applications





Table 1 — Summary of upper limits of NH₃ concentrations for protection of ecosystems under field conditions

Concentration (µg/m ³)	Specification	Types of locality
1	UNECE Critical Level (annual mean) for lower plants (lichens, bryophytes)	Sensitive ecosystems in which the lichens and bryophytes are important components, e.g. designated sites for nature conservation and protection of sensitive species, e.g. Natura 2000 sites
3	UNECE Critical Level (annual mean) for higher plants	Sensitive ecosystems in which the higher plants are important components, e.g. designated sites for nature conservation and protection of sensitive species, e.g. Natura 2000 sites
10	German First General Administrative Regulation Pertaining the Federal Immission Control Act Maximum near installations where ecological monitoring undertaken.	Near installations
23	UNECE critical level (monthly mean) – for peak emission periods such as in months where slurry spreading takes place.	In close proximity to emission sources



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EUROPEAN STANDARD

EN 17346

NORME EUROPÉENNE

EUROPÄISCHE NORM

May 2020

ICS 13.040.20

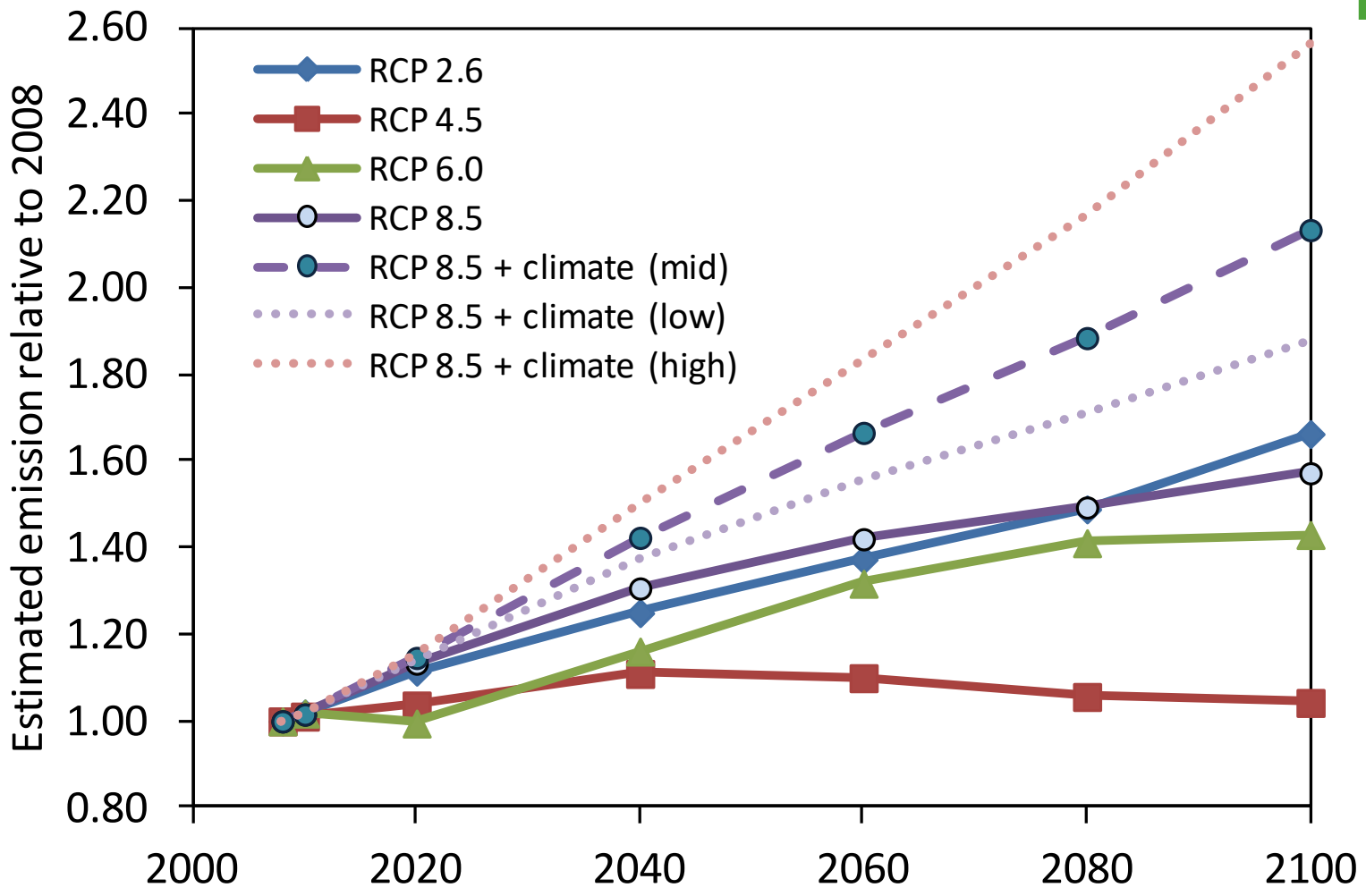
English Version

Ambient air - Standard method for the determination of the concentration of ammonia using diffusive samplers

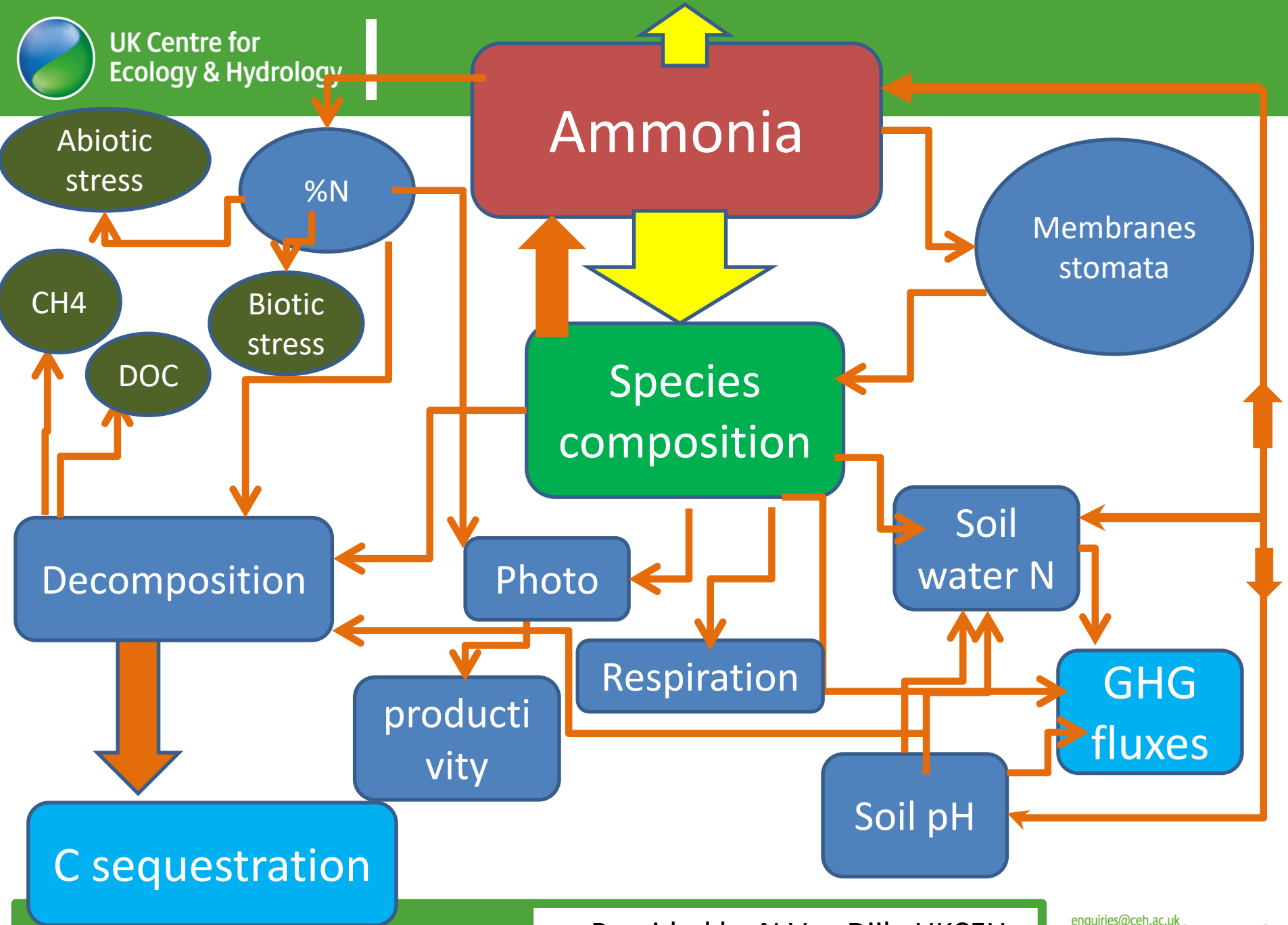
Air ambiant - Méthode normalisée pour la
détermination de la concentration en ammoniac au
moyen d'échantillonneurs par diffusion

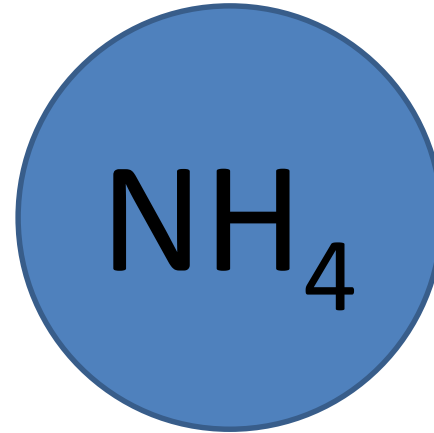
Außenluft - Messverfahren zur Bestimmung der
Konzentration von Ammoniak mit Passivsammlern

TFMM, 2021



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





- Amines
- Co-emitted organics

- Reaction
- Precipitation
- consumption
- Re-emission



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Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol



More obvious air pollution impacts on variations in bacteria than fungi and their co-occurrences with ammonia-oxidizing microorganisms in PM_{2.5}[☆]



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SCIENTIFIC REPORTS

OPEN

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

Received: 23 June 2016

Accepted: 14 November 2016

Published: 12 December 2016

Jing-Feng Gao, Xiao-Yan Fan, Kai-Ling Pan, Hong-Yu Li & Li-Xin Sun

Atmos. Chem. Phys., 18, 3641–3657, 2018

<https://doi.org/10.5194/acp-18-3641-2018>

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Atmospheric Chemistry and Physics
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EG

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

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Received: 12 October 2017 – Discussion started: 6 November 2017

Revised: 1 February 2018 – Accepted: 1 February 2018 – Published: 13 March 2018

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Auchencorth Moss

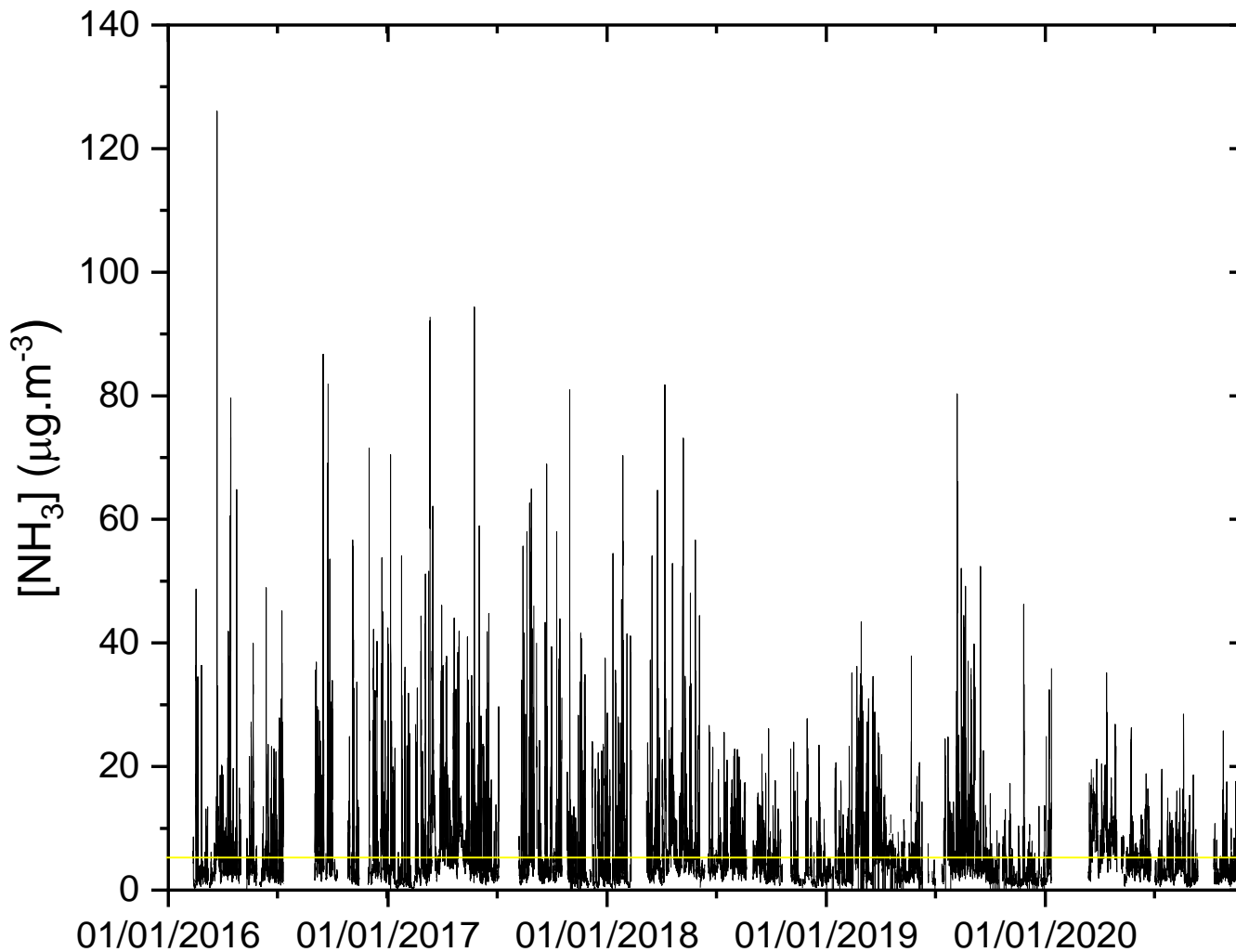


$[\text{NH}_3] = 1 \mu\text{g}\cdot\text{m}^{-3}$

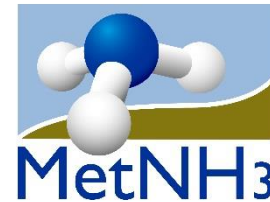
EMEP sites are “background” sites however background varies significantly



$[\text{NH}_3] = 5.5 \mu\text{g}\cdot\text{m}^{-3}$



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Außenluft - Messverfahren zur Bestimmung der
Konzentration von Ammoniak mit Passivsammlern

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4 Description of samplers

4.1 Principle

The diffusive sampler is exposed in air for a measured time period. NH_3 migrates through the sampler along a diffusion path of defined dimensions and is collected by reaction onto an acid sorbent.

Determining the sampling rate is essential when deploying diffusive NH_3 samplers in the field, either by:

- calculation based on Fick's first law of diffusion (see EN 13528-3 [35] and Annex E),
- calibration by exposure to standard atmospheres, or
- co-located calibration studies against another well characterized NH_3 measurement method in the field.

NOTE Denuders can be used as a cost effective surrogate reference method until there are improvements in the continuous optical methods.

Details of these approaches shall be documented.

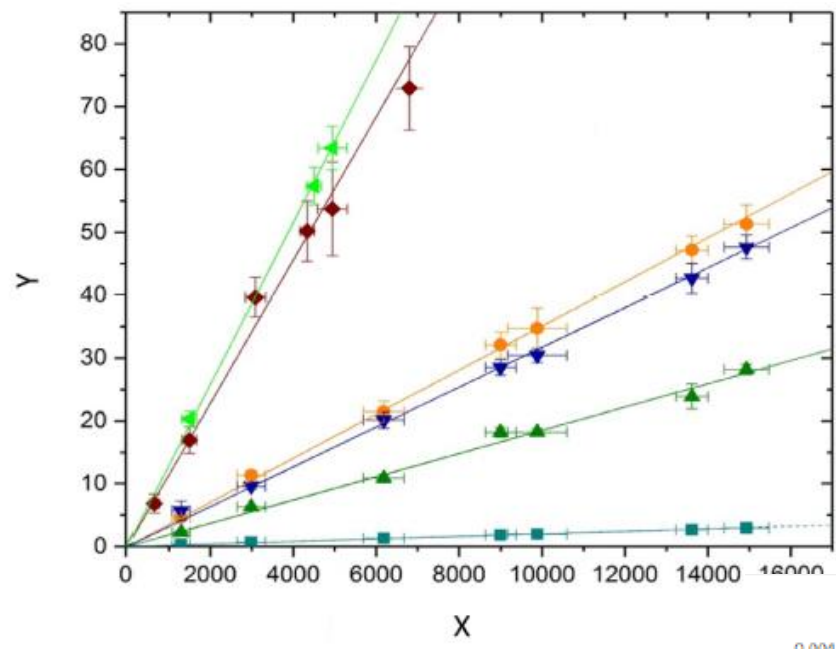
Samplers can be provided with manufacturer measured sampling rates. Samplers in networks often have on-going measurements of sampling rates. Users can calculate a locally derived sampling rate. Sampling rates are also documented in literature [see [36], and Annex D].

The sampling rate in the field is a function of local meteorology. Samplers can be deployed with protective shelters to minimize meteorological influences. When doing so, the user shall apply a suitable protocol to ensure a consistent approach for all samplers. Ideally, the effect of the shelter on the sampler performance should be characterized.



Uptake rate calibrations

Laboratory calibration to calculate



Field calibration to calculate

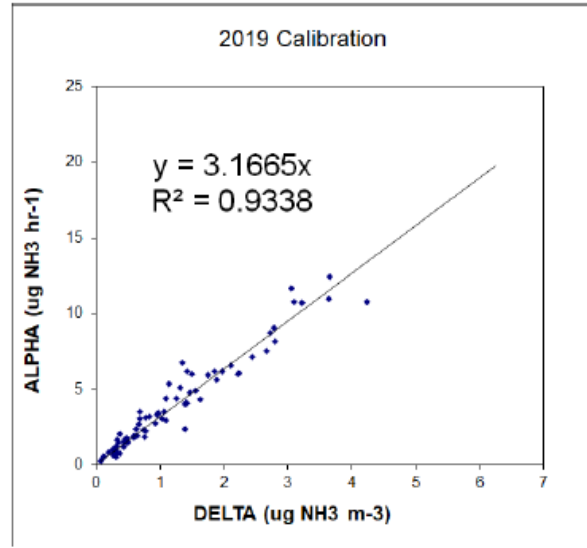
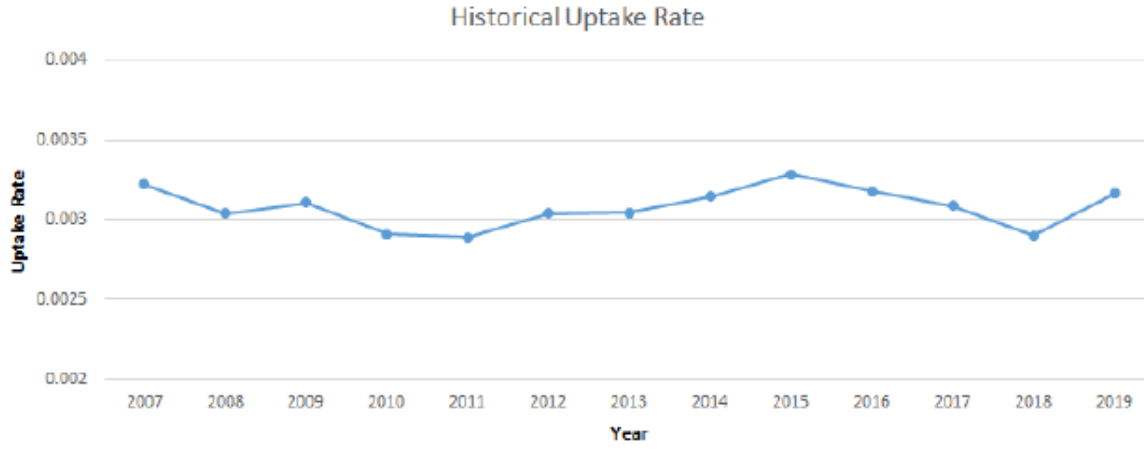


Figure 39 Historical UKEAP uptake rate for ALPHA samplers.

Data quality objective CV <15%





Syringe drives for liquid flow control

Mass flow controller



Fan

Air pump

Air inlet

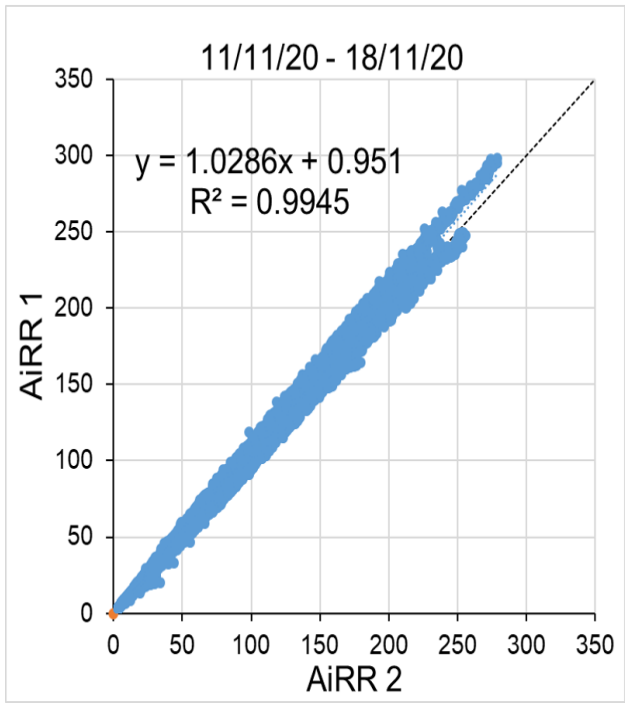
Sample Block

Conductivity detector block

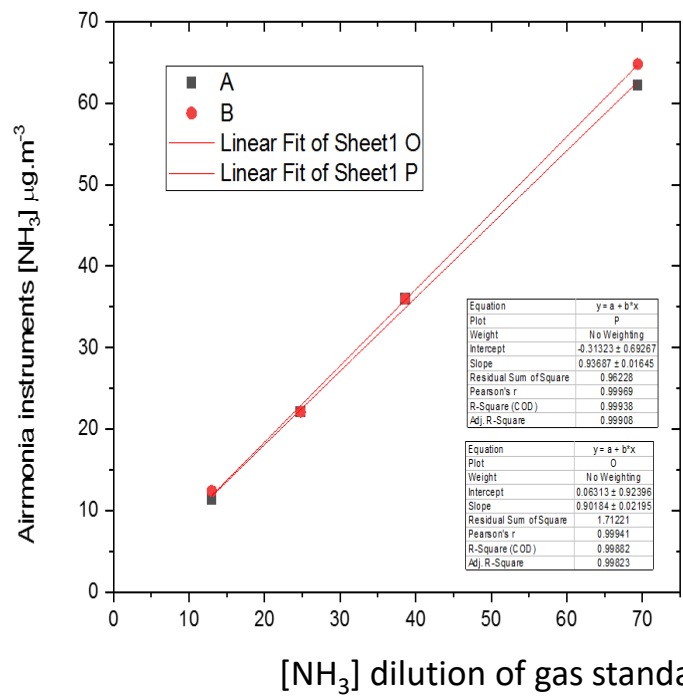




Calibration (Airrmonia)



Side by side calibration



Side by side calibration: Gas standard

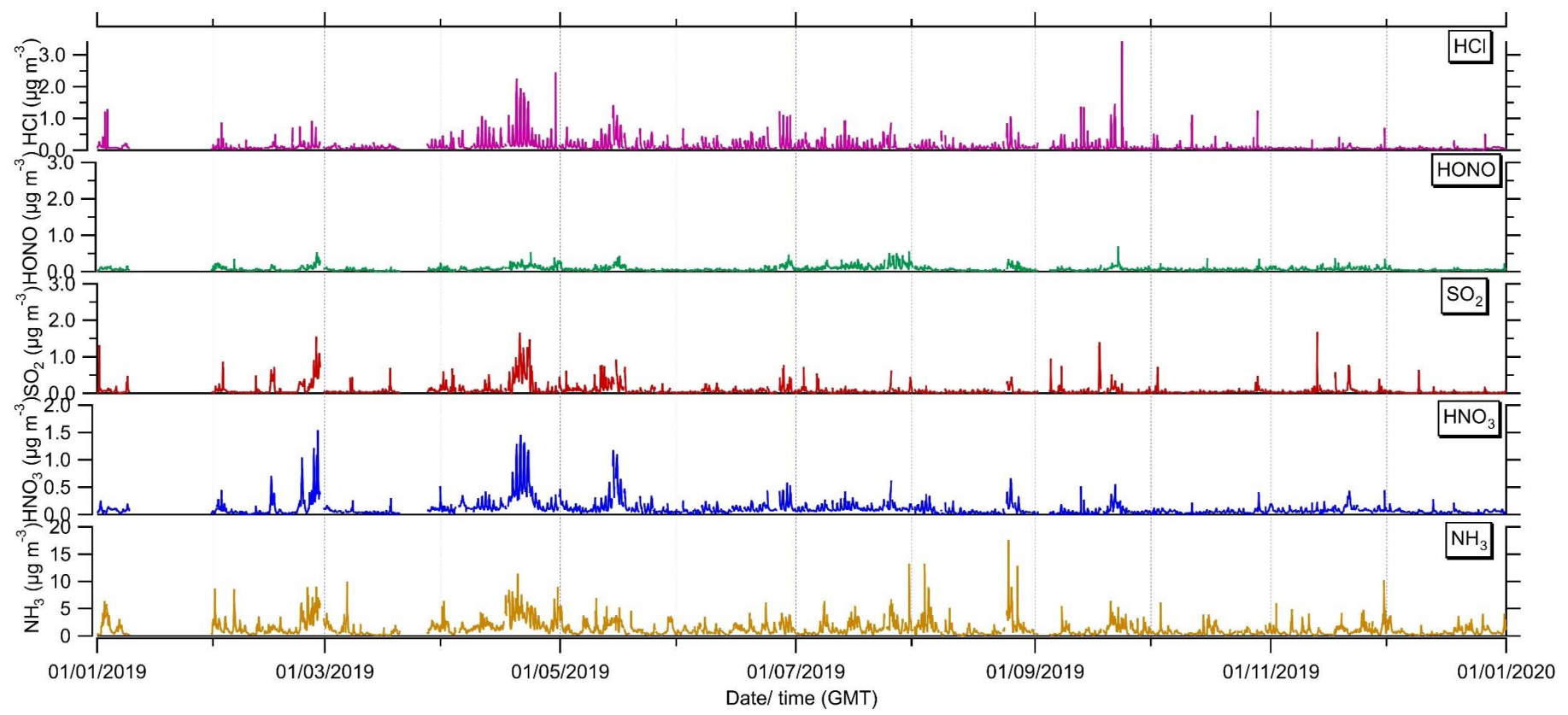
- No inlet
- Still needs T stabilisation



change every:	1	2	1	2	3	4	6	1	2
component	week	week	month	month	month	month	month	year	Years
Clean cyclone and PM ₁₀ head			x						
Replace air tubing					X	X			
Carry out a blank			x						
Take a subsample of internal standard for analysis					x				
2x absorbance liquid 20 Litre (with 1ml 30-35% H ₂ O ₂)	x								
2x eluent (anion and cation, both 8 Litre)	x								
Internal standard LiBr 4 (or 5) Litre				x					
Suppressor liquid 5 Litre 0.35M phosphoric acid (H ₃ PO ₄)		x							
2x empty waste container 30 Litre and add approximately 30 grams of NaHCO ₃	x								
2x sample filters behind SJAC		x							
2x sample filters behind WRD			x						
2x aspiration filters anion/cation			x						
2x inline eluent filter behind pump before pulsation dampener			x						
2x inline liquid filter behind suppressor pump			x						
2x suppressor pump tubing								x	
4x WRD seals located inside WRD heads								X	
4x WRD seals on outer tubing located against WRD heads								x	
2x IC pump seals								x	
2x IC pump check inlet valves								x	
2x IC pump check outlet valves								x	
2x membrane of gas sampling vacuum pump								x	
2x clean SJAC in 1% H ₂ O ₂ for 10 minute in an ultrasonic bath **							x		
2x clean WRD **							x		
clean or change all Teflon tubing 1/16" boxes**								x	
2x change guard column: 1 anion, 1 cation (+filters if dirty)			x						
1x change anion IC column if necessary ****				x		x			
1x change cation IC column if necessary ****						x			
1 x change cation pre-concentration column if necessary							x		
1 x change anion pre-concentration column if necessary						x			

(*) preventive replacement frequency based on local experience. Prevent filter blockage. Indicators of blocked filters: significant phosphate peak around 6 min; (**) Frequency depends on location of instrument, clean when visibly dirty; (***) Frequency depends on location of instrument, exchange when blocked/ together with 1/16" tubing. Exchange at least every 2 years (wear); (****) Frequency depends on local conditions (quality of solutions; for anion column: concentration of peroxide); (*****) Pump tubing including connectors

- PM removed for separate analysis
- High flow inlet (<1 s)
- Regular maintenance
- Internal standard
- Monthly blanks
- QA QC on quarterly and annual basis





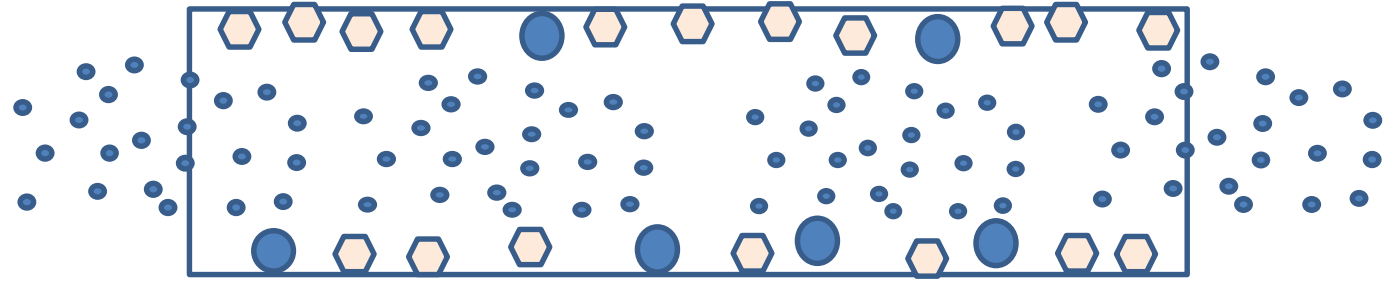
Instrumentation



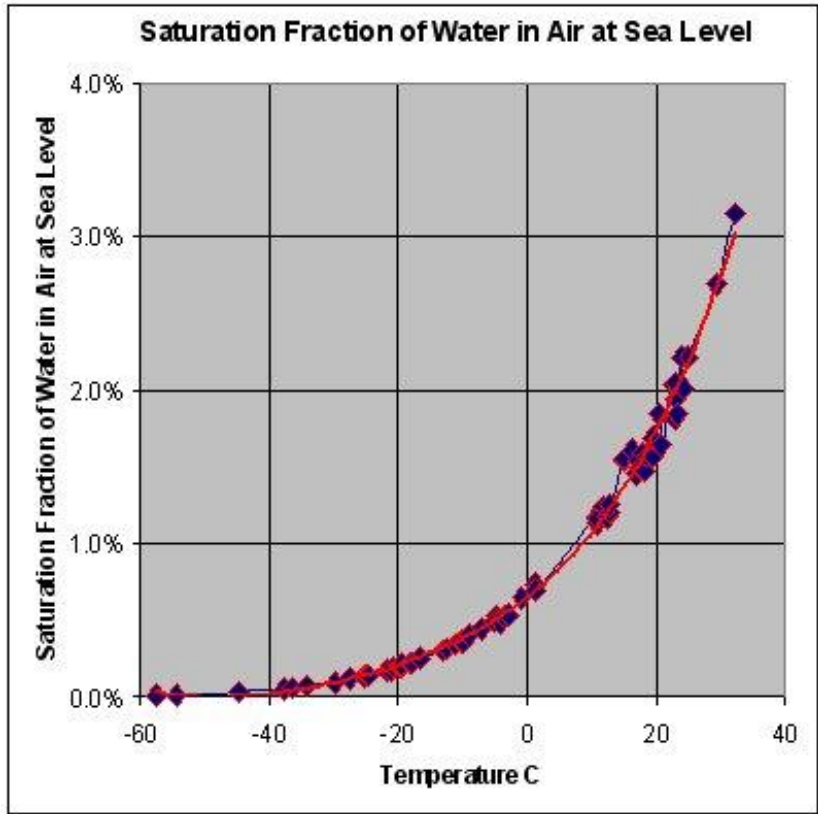
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Inlets (and filters)



$f(t)$
 $f(T, RH)$
 $f(\text{air mass})$





- 3 sites in the UK are using an LGR NH₃ analyser
- Much less maintenance
- Attention to data quality is required

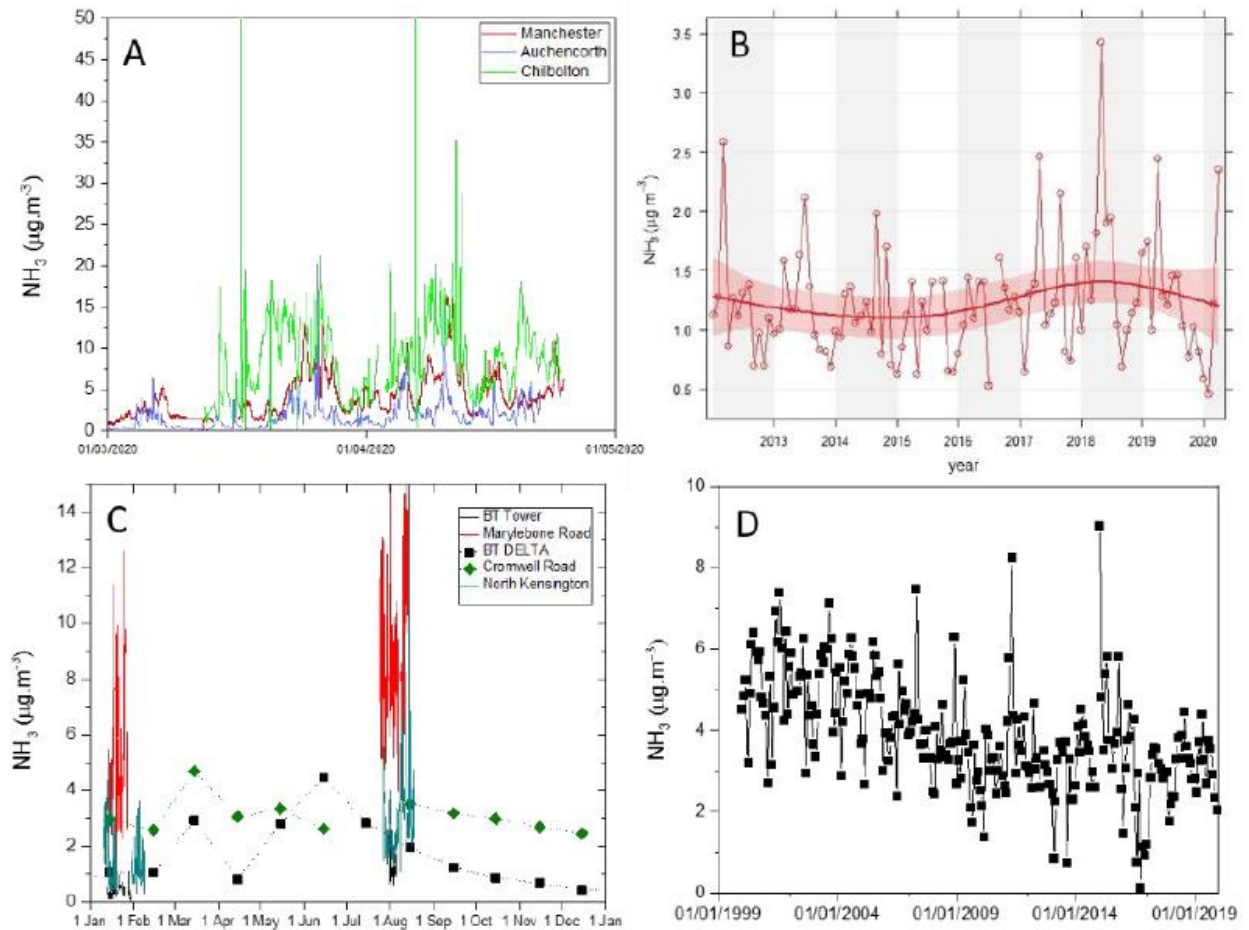
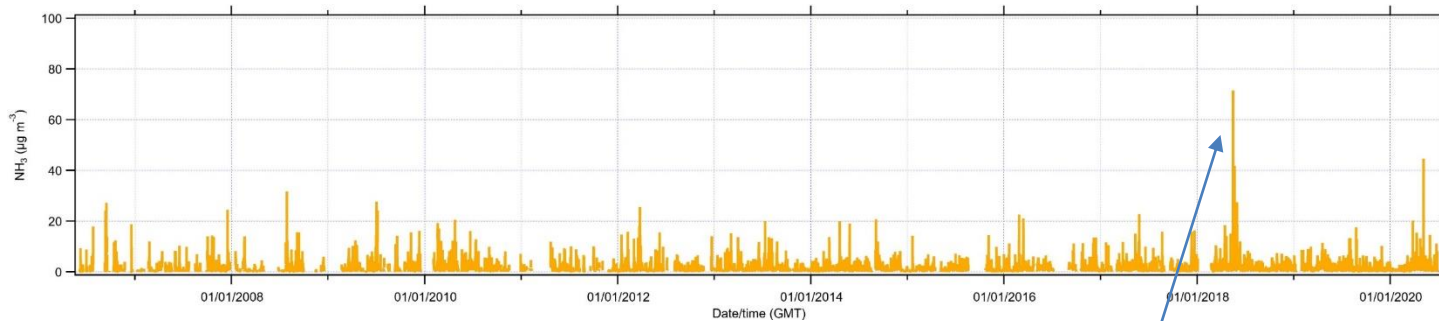
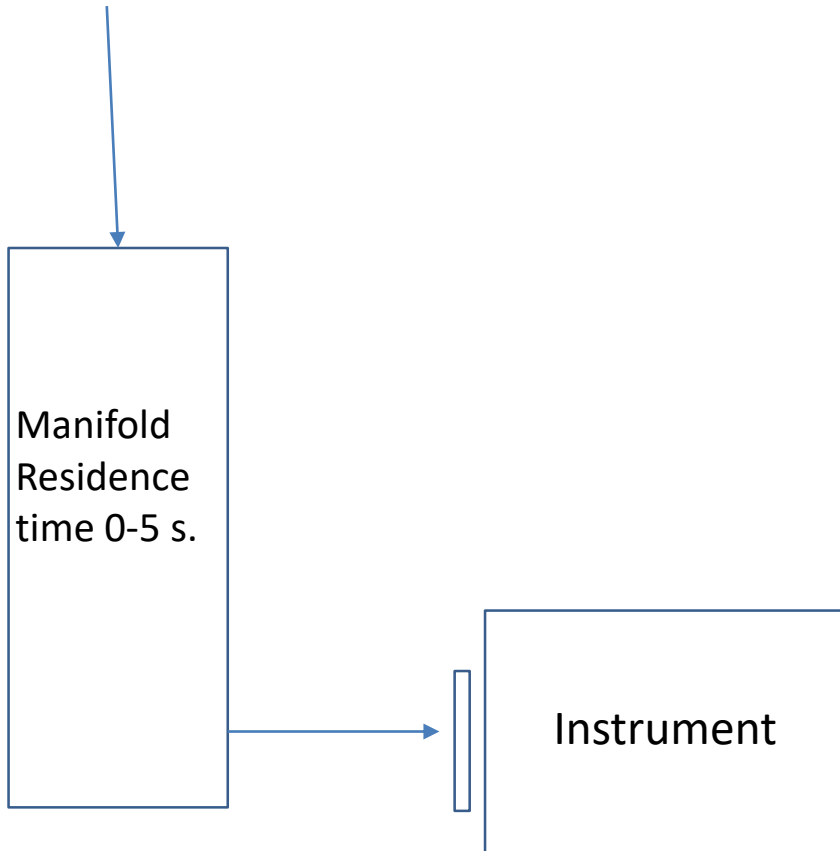


Figure 1 A: NH₃ concentrations over March and April 2020 for Chilbolton, Auchencorth Moss and Manchester OSCA Observatory (note all data provisional and unratified), B: Trend in ammonia concentration at Auchencorth Moss 2012-2020; C: 2012 NER Clearflo (BT Tower, Marylebone Road and N Kensington) and UKEAP NAMN London Cromwell Rd NH₃ data; D Defra/EA National Ammonia Monitoring Network site London Cromwell Road 1999-2019 monthly passive (ALPHA® sampler) data



Unexpected local manure heap!
(discussions were had)

- Significant evidence from UKCEH Met NH₃ field intercomparison that lots of automatic instruments on the market which have the potential to measure NH₃ accurately
- **However**, SOP for long term operation needed.
- Inlet, filter changing, internal mirror and surface cleaning protocols for easy and regular maintenance needed to make sure quantitative long term data available
- Similar protocols as the ACTRIS NO₂ SOP will be needed to ensure baseline and span drift is monitored and corrected in a timely way.
- UKCEH undertaking laboratory tests with both a permeation based calibration and a gas dilution- humidified gas stream calibration systems in order to begin to establish “gold standard” and “field” standard protocols
- Field tests to follow



Changeable filter?

Calibration

- Need accurate cylinder or permeation source
- Need to add in H₂O
- Need to have a blank with H₂O vapour present



Thankyou!

1. Site name	2. Country	3. Do you measure jNO2
Hohenpeißenberg	Germany	Yes with a filter radiometer
Mt. Cimone	Italy	No
PUY	France	No
Jungfrauoch	Switzerland	No
Beromuenster	Switzerland	No
Seoul	South Korea	No
All Norwegian sites..	Norway	No
Cape Verde Atmospheric Observatory (CVO)	Cape Verde	Yes with a spectroradiometer
Hohenpeissenberg Meteorological Observatory	Germany	Yes with a filter radiometer
Jungfrauoch	Switzerland	No
Rigi	Switzerland	No
Leba (PL0004R), Jarczew (PL0002R), Sniezka (PL0003R)	Poland	No
National Atmospheric Observatory Košetice	Czech Republic	No
Lampedusa	Italy	Yes with a spectroradiometer

Atmospheric chemistry is largely driven by solar radiation!

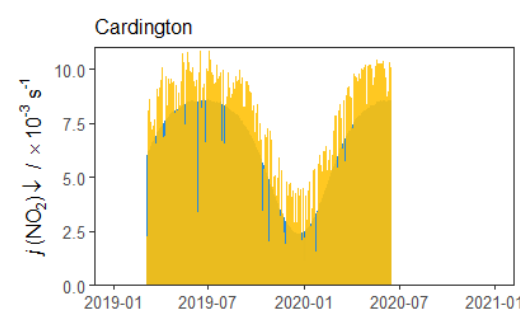
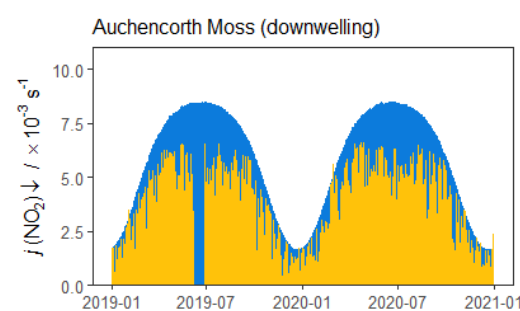
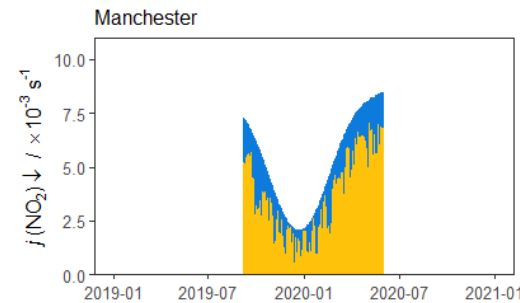
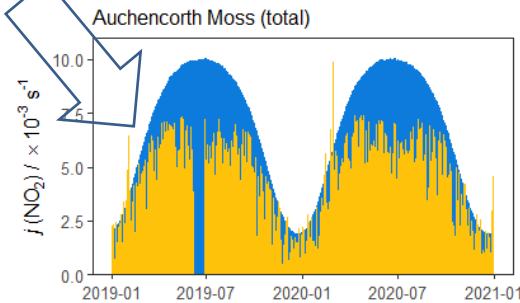


Can we do modelled photolysis better?

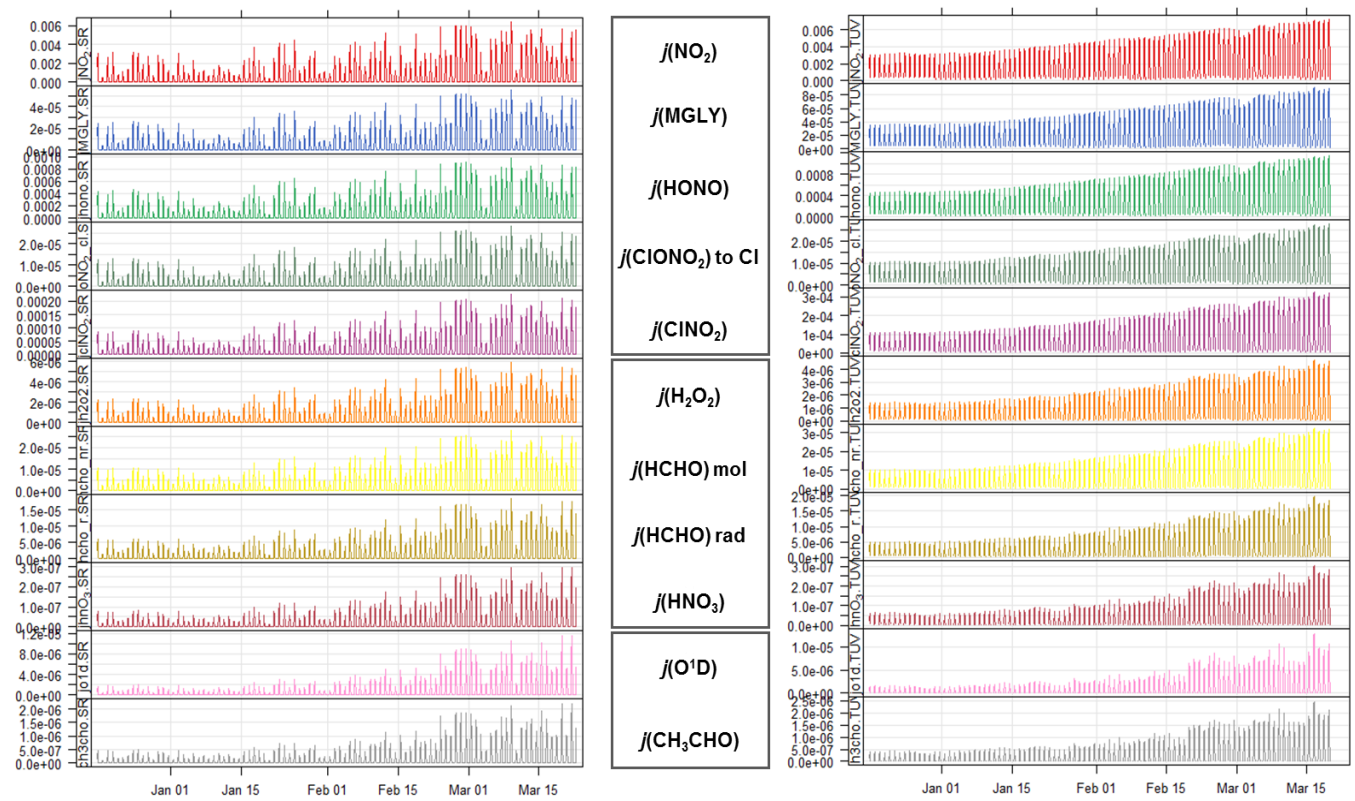
13th Feb



$$j(NO_2) = \int_{\lambda_1}^{\lambda_2} \sigma_{NO_2}(\lambda) \times \phi_{O(^3P)}(\lambda) \times F(\lambda) d\lambda$$



local conditions can mean that j is quite different at different locations for the same day (due to cloud cover, snow/frost on the ground, etc.)



Time series of hourly averaged photodissociation rate constants at Chilbolton Observatory, (left) measured by spectral radiometer with 2- π optic head and (right) modelled by TUV v5.3, for the full duration of measurements in this study.

- Research on-going however there is an opportunity and need to understand atmospheric chemistry better
- Long term improvement of model performance for air pollution needed