Reduced and Oxidised Nitrogen measurements in EMEP: Research and Monitoring Challenges

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With content from MM Twigg, YS Tang, E Nemitz, M A Sutton, NA Martin , NPL , MetNH_3 partners

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EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

MetNH3

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Pt 34 from EMEP strategy

- The EMEP monitoring network **must be dynamic and ready to adapt to new needs** and requirements identified by EMEP and the Convention. **At the same time, consistent long-term time series** should be maintained to monitor emission changes.

what makes an EMEP level 1,2,3?

Level 3 activities are research-oriented. The main objective of level 3 sites is to improve the scientific understanding of the relevant physico-chemical processes in relation to regional air pollution and its control. Level 3 activities will typically be undertaken by research groups and may also include campaign data. Level 3 sites are a **voluntary** component of the monitoring network. Level 3 sites are also nominated as "EMEP supersites"; this is intended to be an important motivation factor and to provide appropriate recognition of the data providers

Level 3: flux measurements...still valid, very important BUT expensive, research, unprotected

- do not see much emphasis on this within EMEP/TFMM

important for emission factor and deposition velocities capabilities

Level 1

The main objective of monitoring at level 1 sites is to provide long-term basic chemical and physical measurements of the traditional EMEP parameters.

Level 1 activities should be the first priority when extending the network to areas not adequately covered by measurements up to now in Eastern Europe, Caucasus and Central Asia (EECCA) and in South-Eastern Europe (SEE).

By undertaking a more demanding monitoring programme, a subset of the level 1 stations should gradually be upgraded to level 2 sites.

Level 2

- Level 2 sites provide
  - the additional physical/chemical speciation of relevant components that is necessary for assessing the air pollution including long-range transport of air pollutants, and thus represent an essential supplement to the level 1 sites.
  - The aim is to operate 20–30 level 2 sites throughout the EMEP domain.
  - Level 2 sites are defined according to a topic that Parties choose to focus on as the basis of their national priorities, and they do not have to cover all topics.
  - A level 1 site extending its programme to include the level 2 activities for any of the specific topics will be identified as a “supersite” for this topic.
  - Level 1 and level 2 sites will typically be operated by institutions nominated by the respective Parties for implementing their monitoring obligations.
  - Level 2 sites activities will typically involve long-term continuous monitoring.

EMEP Strategy 2010-2019

Measurements need to be fit for purpose(s):

- air quality (human health impacts),
- ecosystem impacts
- climate impacts
- (personal exposure)

➢ Evidence for an equable atmosphere;

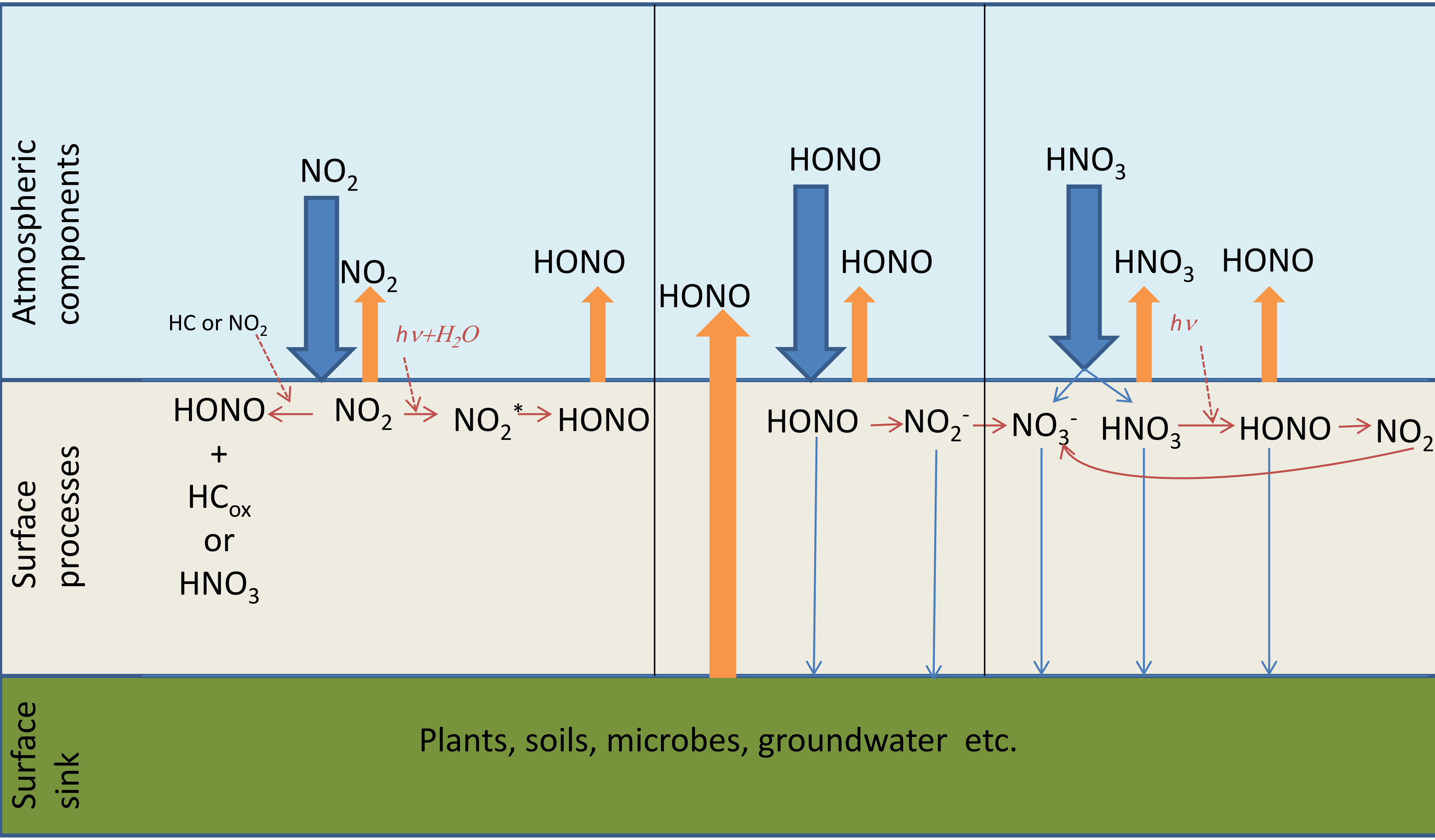
➢ measurement data good enough to be useful for verification purposes

➢ Good enough to provide evidence required to assess status for impact relevant to location and region

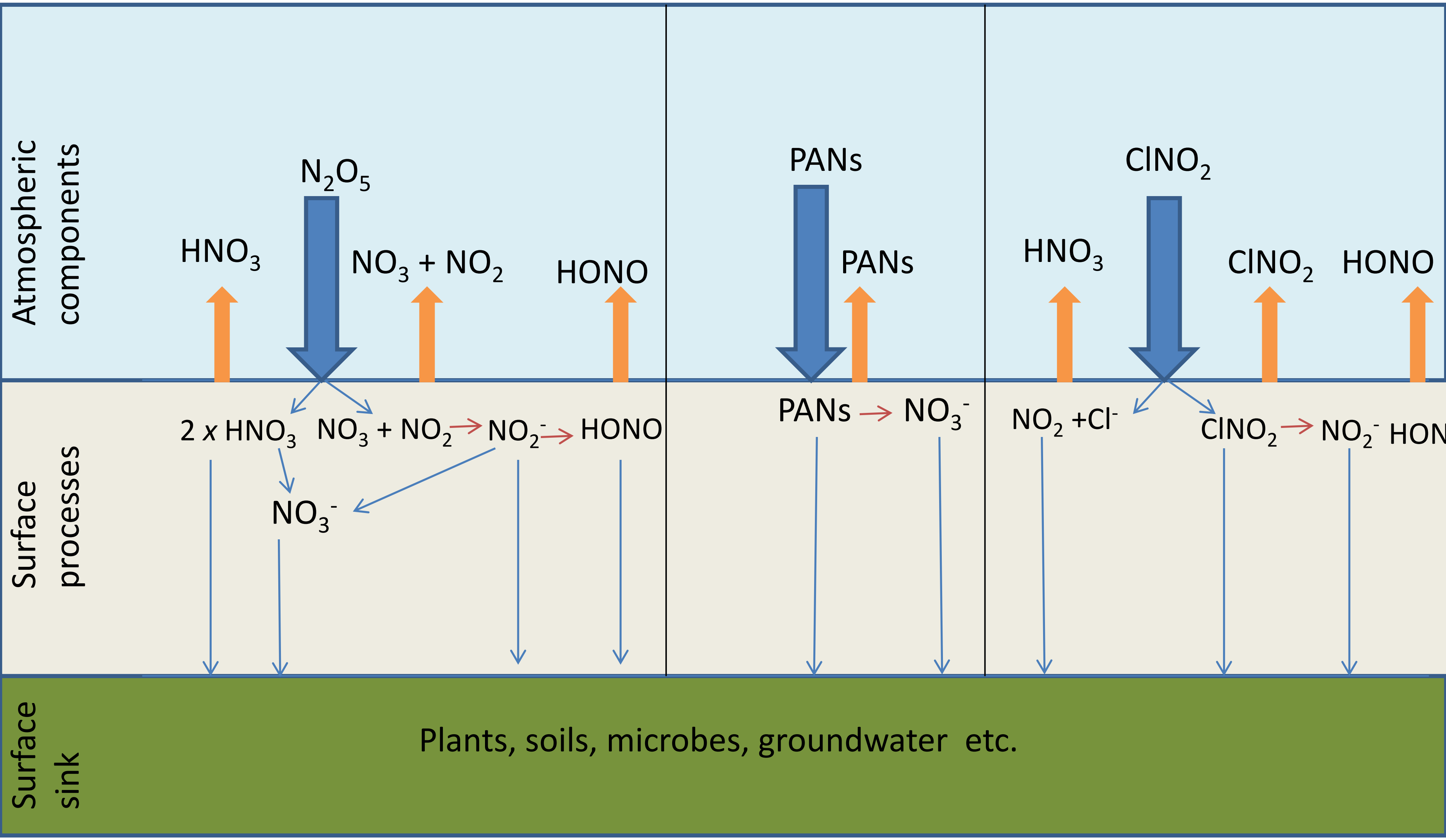
Current EMEP handbook

Components	Measurement period	Measurement frequency	Sampling methods	Methods in laboratory
Gas				
SO_2	24 hours	daily	KOH impregnated filters	IC / (Thorin)
NO_2	24 hours	daily	NaI impregnated glass frit	IC / Griess
O_3	hourly means stored	continuously	UV absorption	
HNO_3	24 hours	daily	denuder	IC / Griess after reduction
NH_3	**24 hours**	**daily**	**denuder**	**IC / Indophenol**
Light hydrocarbons C2-C7	10-15 mins	twice weekly	steel canisters	GC
Ketones and aldehydes (VOC)	8 hours	twice weekly	DNPH cartridge	HPLC
Hg	24 hours	weekly	Gold traps	CV-AFS
Particles				
SO_4^{2-}	24 hours	Daily	aerosol filter	IC / (Thorin)
NO_3^-	24 hours	Daily	aerosol filter after denuder	IC / Griess after reduction
NH_4^+	24 hours	Daily	aerosol filter after denuder	IC / Indophenol
Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-	24 hours	Daily	aerosol filter	IC / AAS / AES
PM_{10}	24 hours	Daily	EN 12341	micro balance
PMx	24 hours	Daily	To be decided	micro balance

Surface oxidised N budget: atmospheric deposition/emission possibilities



Surface oxidised N budget: atmospheric deposition/emission possibilities II



Measurement and QC Frameworks: e.g. NO_2

Global/WMO-GAW

↕

European research infrastructure

↓

European Long term monitoring

↓

European compliance monitoring

↓

National compliance monitoring (AURN)

↓

Local authority compliance monitoring (LAQN)

↓

Local authority and Agency AQ monitoring (other)

↓

Citizen science

<u>Photolytic analysers;</u>

- direct spectroscopic measurement
- Correction for inlet errors etc.
- Part of international calibration/round robins
- ACTRIS protocol daily calibration with traceable standard
- expensive/implementation variable

<u>On-line chemiluminescence analysers</u>

- Method defined by European compliance protocols
- Part of national calibration
- expensive

<u>Off-line diffusion tubes</u>

- Gas captured on coating, analysed in laboratory
- Methods defined by Working Groups
- Can be part of national intercomparison and bias correction
- Affordable but low resolutions (weeks)

<u>On-line electrochemical sensors</u>

- Gas-surface interactions = Voltage change
- Field testing underway
- New working group being established

ALPHASENSE: NO_2 sensor

PERFORMANCE			
	Sensitivity	nA/ppm at 2ppm NO_2	-160 to -320
	Response time	t_{90} (s) from zero to 2ppm NO_2	< 70
	Zero current	nA in zero air at 20°C	-25 to +50
	Noise*	±2 standard deviations (ppb equivalent)	12
	Range	ppm NO_2 limit of performance warranty	20
	Linearity	ppb error at full scale, linear at zero and 5ppm NO_2	< ±1
	Overgas limit	maximum ppm for stable response to gas pulse	50
	*** Tested with Alphasense ISB low noise circuit**		
LIFETIME	Zero drift	ppb equivalent change/year in lab air	0 to 20
	Sensitivity drift	% change/year in lab air, monthly test	-20 to -40
	Operating life	months until 50% original signal (24 month warranted)	> 24
ENVIRONMENTAL			
	Sensitivity @ -20°C	(% output @ -20°C/output @ 20°C) @ 2ppm NO_2	60 to 80
	Sensitivity @ 40°C	(% output @ 40°C/output @ 20°C) @ 2ppm NO_2	95 to 115
	Zero @ -20°C	nA	±10
	Zero @ 40°C	nA	70 to 200
CROSS SENSITIVITY	O_3	Filter capacity (ppm.hr) @ 2ppm O_3	> 500
	H_2S	sensitivity % measured gas @ 5ppm H_2S	< -80
	NO	sensitivity % measured gas @ 5ppm NO	< 5
	Cl_2	sensitivity % measured gas @ 5ppm Cl_2	< 80
	SO_2	sensitivity % measured gas @ 5ppm SO_2	< 5
	CO	sensitivity % measured gas @ 5ppm CO	< 3
	H_2	sensitivity % measured gas @ 100ppm H_2	< 0.1
	C_2H_4	sensitivity % measured gas @ 100ppm C_2H_4	< 0.5
	NH_3	sensitivity % measured gas @ 20ppm NH_3	< 0.2
	CO_2	sensitivity % measured gas @ 5% Vol CO_2	< 0.1
	Halothane	sensitivity % measured gas @ 100ppm Halothane	nd
KEY SPECIFICATIONS			
	Temperature range	°C	-30 to 40
	Pressure range	kPa	80 to 120
	Humidity range	% rh continuous	15 to 85
	Storage period	months @ 3 to 20°C (stored in sealed pot)	6
	Load resistor	Ω (ISB circuit is recommended)	33 to 100
	Weight	g	< 13

At the end of the product's life, do not dispose of any electronic sensor, component or instrument in the domestic waste, but contact the instrument manufacturer, Alphasense or its distributor for disposal instructions.

Note: "As applications of use are outside our control, the information provided is given without legal responsibility. Customers should test under their own conditions, to ensure that the sensors are suitable for their own requirements"

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AQ Mesh

NO2				
Version	v3.0	v3.5	v4.0	v4.1
Date	To December 2014	January 2015 – October 2015	Janaury 2015 – Q1 2016	Q2 2016 – present
NO2 sensor	Significant O3 cross-gas effect	O3-filtered	O3-filtered	O3-filtered
NO2 sensor characterisation	Manufacturer's data	Manufacturer's data	Manufacturer's data plus characterisation at factory	Quality check
Online processing	Correction for cross-gas effects and environmental factors	Correction for cross-gas effects and environmental factors	Correction for cross-gas effects and environmental factors	More sophisticated correction for cross-gas effects and environmental factors
Typical R2 against reference in co-location trials	0-0.3	0.1-0.7	0.5-0.8	0.7-0.95

R2 of >0.6 for NO2 is generally considered to be a strong enough performance for AQMesh to be suitable for most air quality monitoring applications.

http://www.aqmesh.com/performance/aqmesh-performance/

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	Current EMEP	**Flux**	**Concentrations**		
			Hourly (or better)	***Daily***	***Monthly***
NH3	Daily denuder	QCL; AMANDA	MARGA, wet chem, UV, IR instruments	Denuders	Denuders; passive samplers
Amines	n/a		PTR-MS; IMS-MS	Denuder	Denuder
HNO3	denuder	QCL? CIMS? Difficult	MARGA		
HNO2	denuder	paired LOPAP	LOPAP; MARGA	Denuder	Denuder
NO3	n/a				
N2O5	n/a		CIMS		
ClNO2	n/a		CIMS		
PANs	n/a		GC		
PM Ammonium	filter pack	AMS			
PM Nitrate	filter pack	AMS			
PM Organic N	n/a	AMS			
PM Total N	n/a				
Wet deposition	DWOC/offline		Metrohm 15 min/online.	DWOC	

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Protocols and standards

- CEN committee standards
- EMEP Handbook of methods
- ACTRIS/WMO-GAW protocol development

Best Practice delivered through the existing organisations however preparing draft documents to include important as process is slow

Due to continuous development of technologies and scientific understanding it is important to write inclusive, general protocols

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The ammonia measurement challenge

Aim: quantitative, molecule specific measurements fit to the purpose of the research or policy question

Gas-phase extraction followed by analytical chemical

On-line

Off-line

Direct gas phase measurement

Open path/remote

Closed path/gas sampling

Target data quality?
accuracy: ±5% reference traceable calibrations
Temporal resolution?

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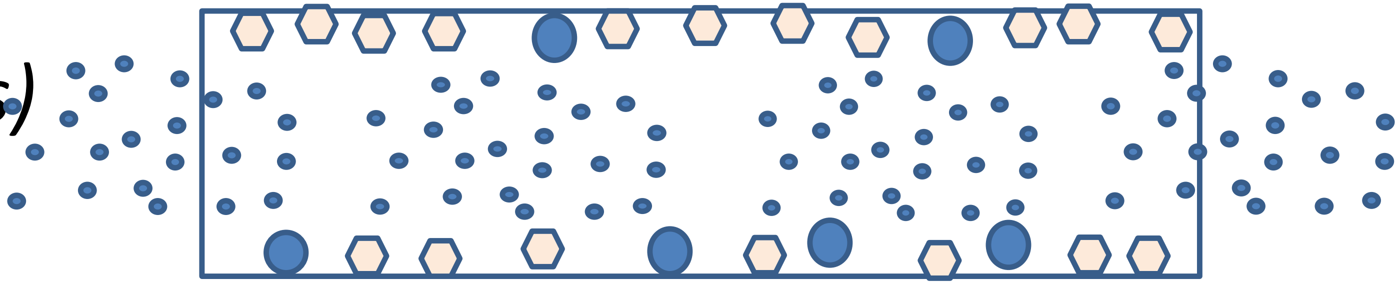
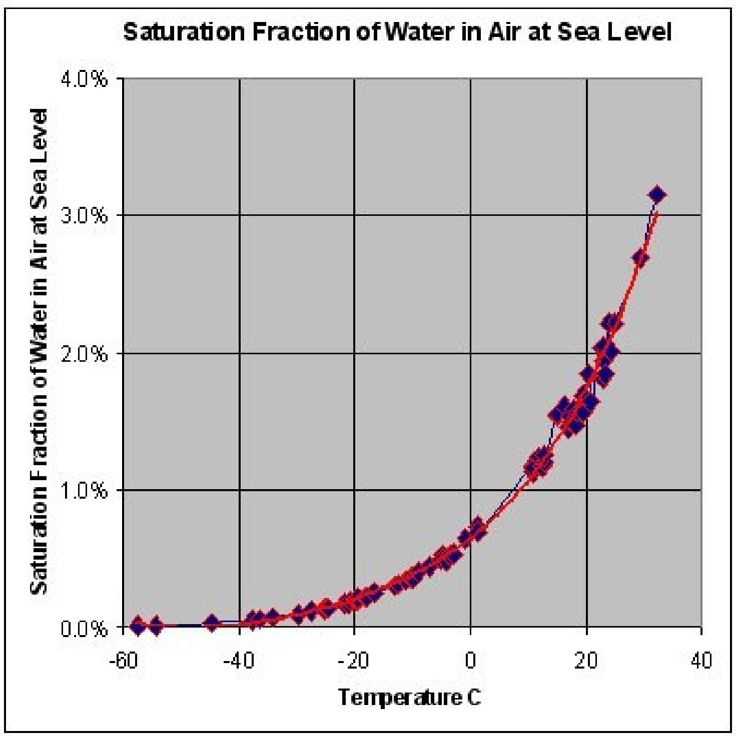
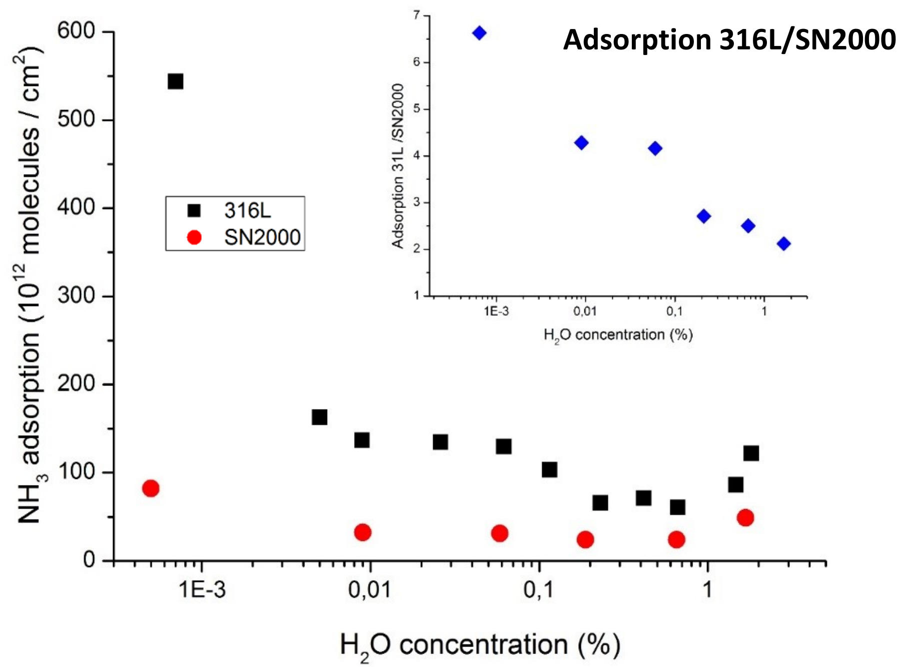
Instrument surfaces, inlets (and filters)

f (t)
f (T, RH)
f (air mass)







Policy: NH_3

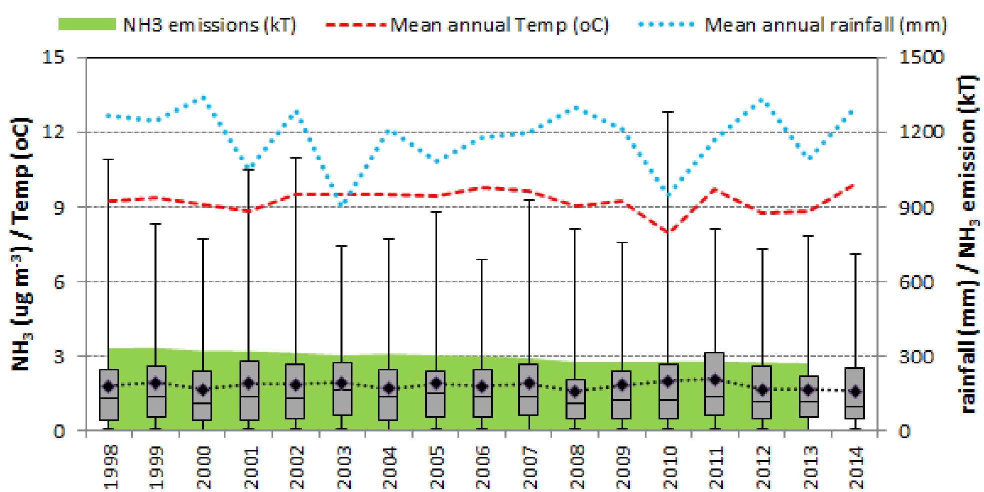
- The UN **CLRTAP** and related UN ECE **Gothenburg Protocol** to abate **Acidification, Eutrophication** and Ground-level Ozone: set limits and reduction goals for ammonia in signatory countries (Annex IX, revised 2012).
- In parallel the EU **NEC Directive** (2001/81/EC) applies even lower emission ceilings for NH_3. A revision as part of the Clean Air Policy Package shall ensure:applicability until 2020, new reduction commitments for ammonia from 2020 and 2030.
- national reports to use EMEP Emission Inventory Guidebook, **calculated** emission **data**.
- Real **effects should be underpinned by** AQ measurement data (as for SO_2, NO_x, CO, Benzene and PM)

NFR	SOURCE CATEGORY	SO2	NH3
1.A.1	Public power, cogeneration and district heating	A	
1.A.2	Industrial combustion	A	
1.A.3.b	Road transport	C	E
1.A.3.a 1.A.3.c 1.A.3.d 1.A.3.e	Other mobile sources and machinery	C	
1.A.4	Commercial, institutional and residential combustion	B	
1.B	Extraction and distribution of fossil fuels	C	
2	Industrial processes	B	E
3	Solvent use		
4	Agriculture activities		D
6	Waste treatment	B	
6	Disposal activities	C	E
-	Nature	D	E

D: 100 to 300 %
E: order of magnitude

(EMEP-EEA air pollutant emission inventory guidebook – 2013, Part A, Chapter 5, Table 3-3)

UK National Ammonia Monitoring Network

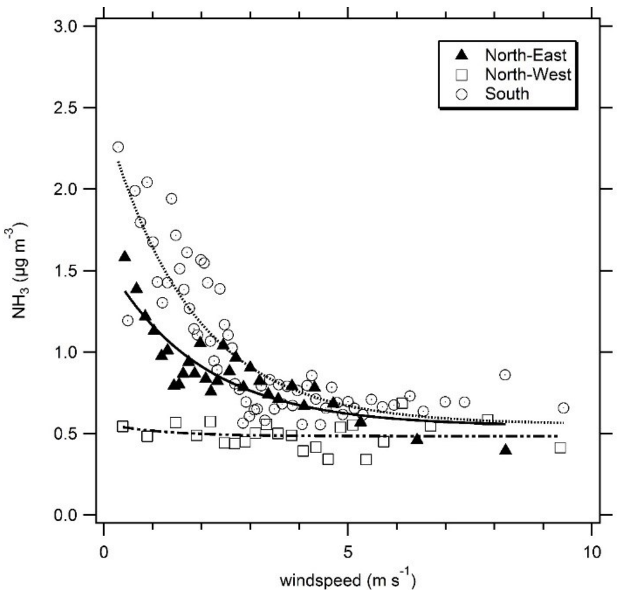


Ammonia Monitoring in UK: Monthly and hourly

- NH_3 measurements established 1996
  - Costs ~ €1k per site per annum
  - 12 triplicate measurement

Passive ALPHA samplers:
- *developed at CEH*
- *deployed around the world*

Active DELTA samplers:
- *Developed at CEH*
- *Wind-solar power options*



MARGA
2 sites

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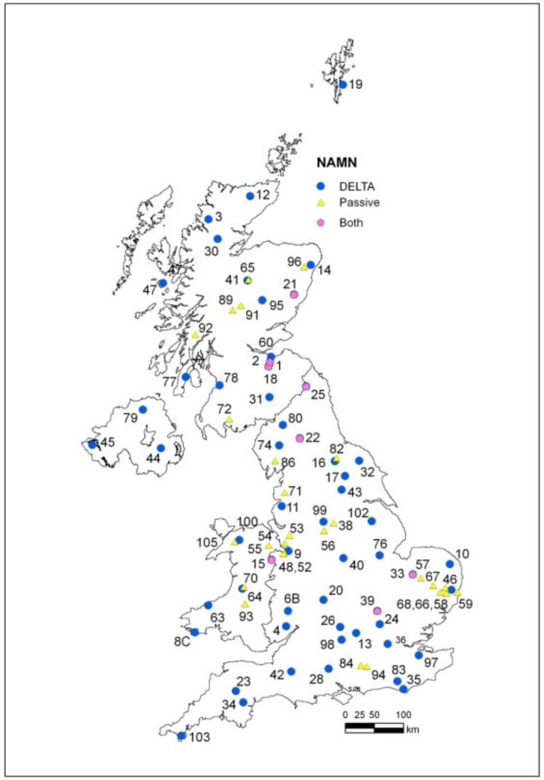
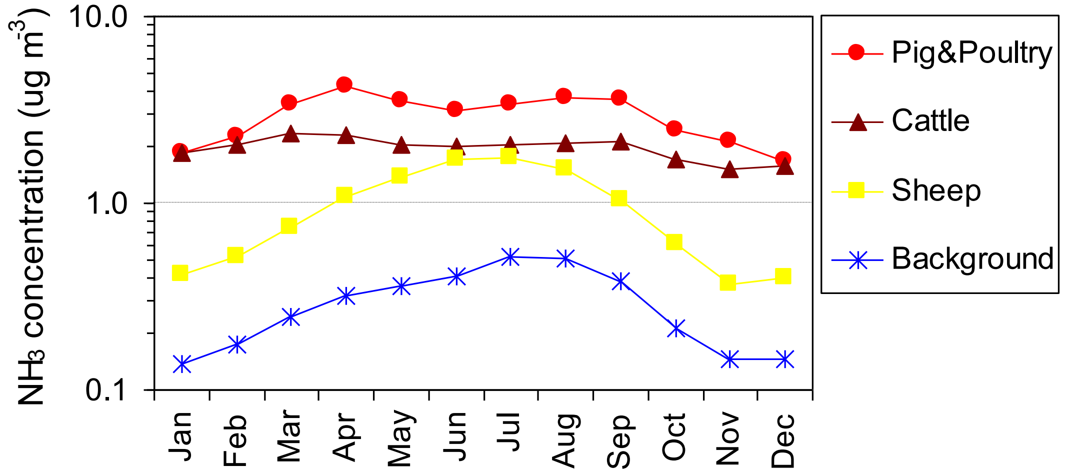
AEA

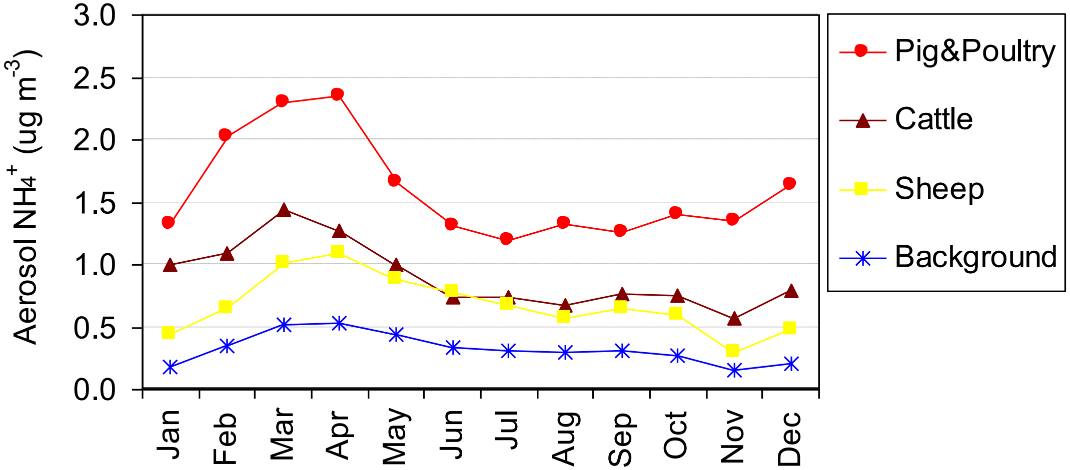
Ammonia temporal patterns… if you have a sufficient site density

NH3: strength of seasonal patterns vary according to emission source sectors

NH4+: peak in spring







Note: Agricultural sector assigned to activity which occurs in >45% of area of sampler. If none >45%, assigned "mixed"

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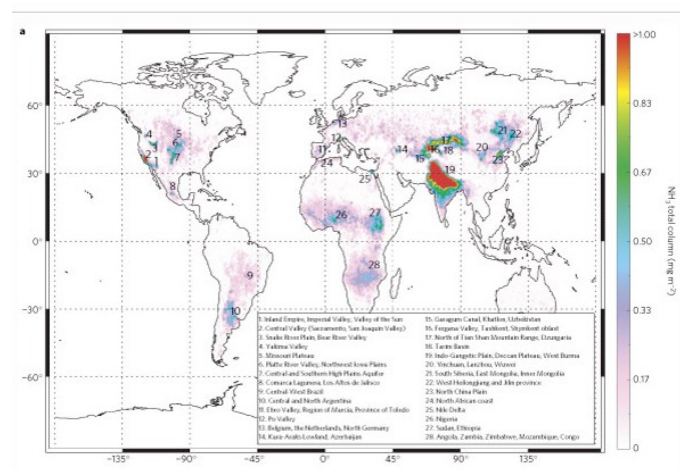
NH_3 technologies…

Multi-Gas Detectors

Fig. 3. Photograph of the RIVM DOAS instrument.



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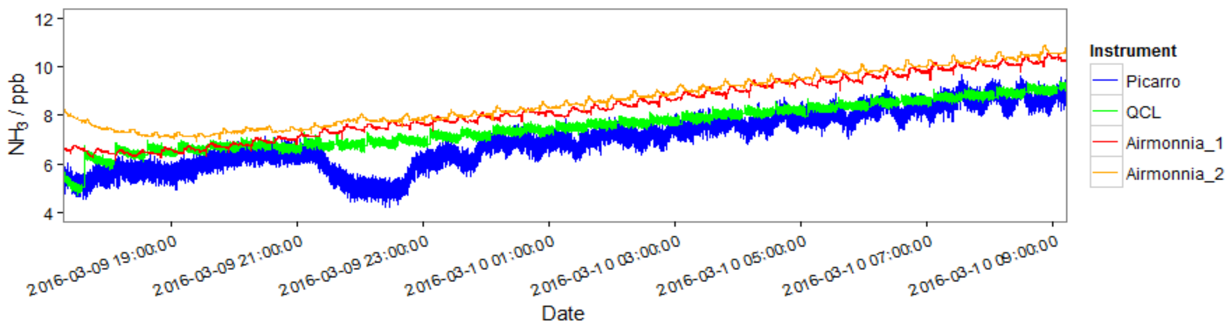
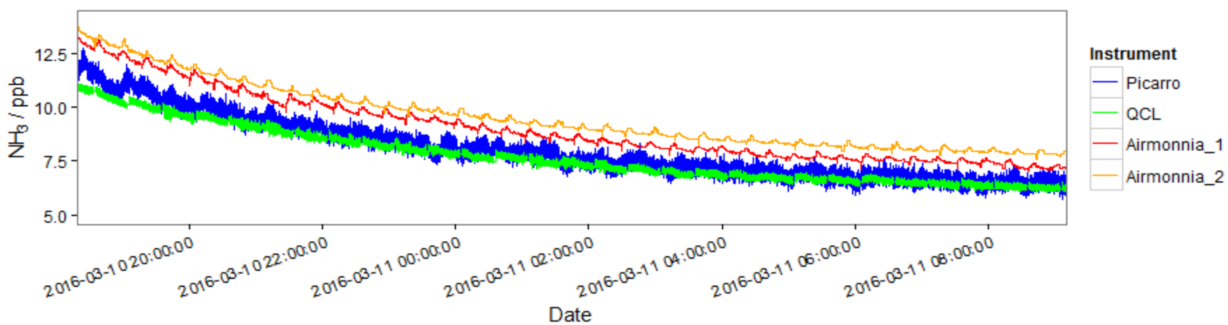
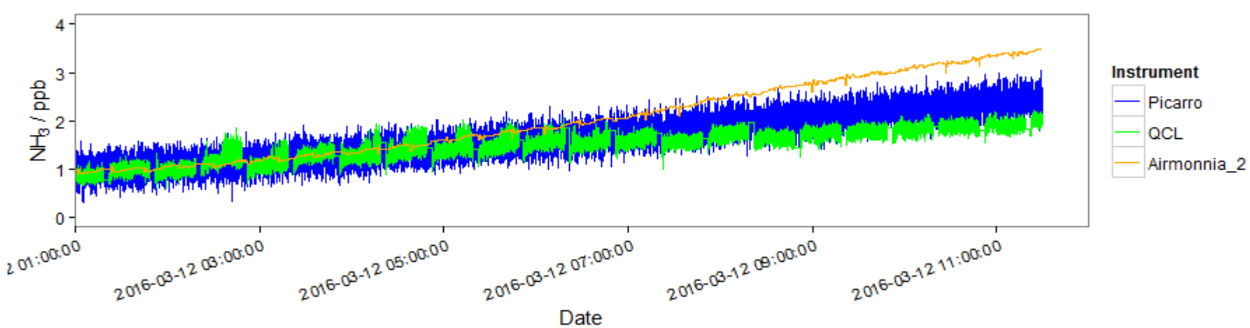
MetNH$_3$ chamber parallel measurements







- Leaving the instruments running overnight we can see how they compare with each other
- The instruments agreed fairly well with each other for the duration of the testing, although there appears to be an offset between the laser instruments and the wet chemistry instruments
- The NH_3 concentrations in the CATFAC chamber didn't remain stable enough to look at the stability of the instruments, although the slow change in concentrations allows us to see that the instruments all behave in a relatively similar way

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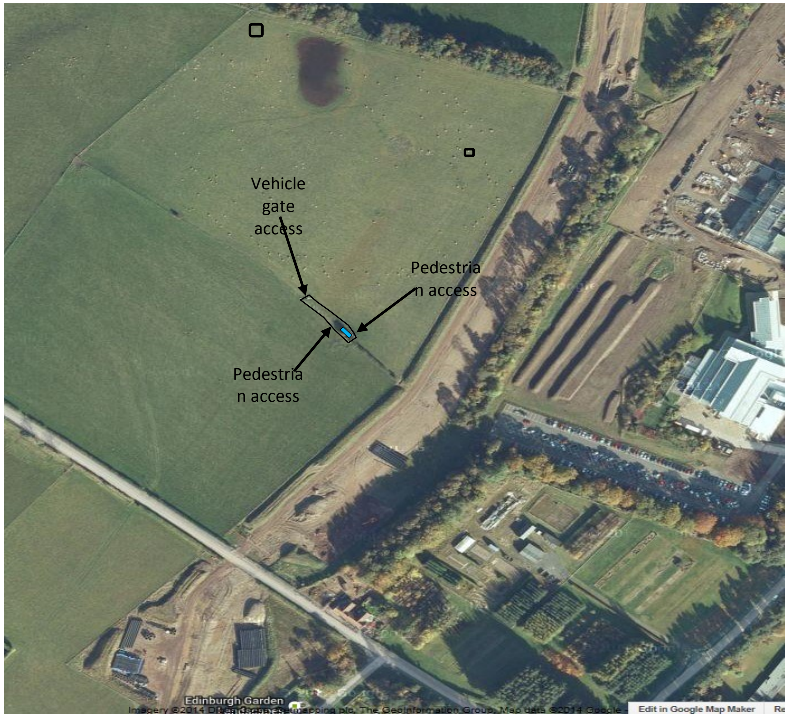
Confirmed parties for 2016 Easter Bush intercomparison

- 12 universities and institutes (both research and metrological) + 6 SMES
- Instruments include:
- Differential Optical Absorption Spectroscopy
- Infrared absorption Spectroscopy – quantum cascade lasers either using cavity ring down or multipass cell (both closed and open path methods)
- Photoacoustic spectrometer
- Chemiluminescence
- Rotating wet denuders with online IC
- Flow injection analysis



MISSING EMEP method DAILY DENUDERS…
….can anyone here help?

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PM Ammonium	filter pack	AMS	MARGA/ACSM	Filters	Filters (coated)
PM Nitrate	filter pack	AMS	MARGA/ACSM	Filters	Filters (coated)
PM Organic N	n/a	AMS	ACSM	Filters	Filters (coated)
PM Total N	n/a				
Wet deposition	DWOC		Metrohm 15 min.	DWOC	

make data provision and guidance wide and inclusive while maintaining standards; measurements according to capabiity and need

Use of calibration centres and test facilities

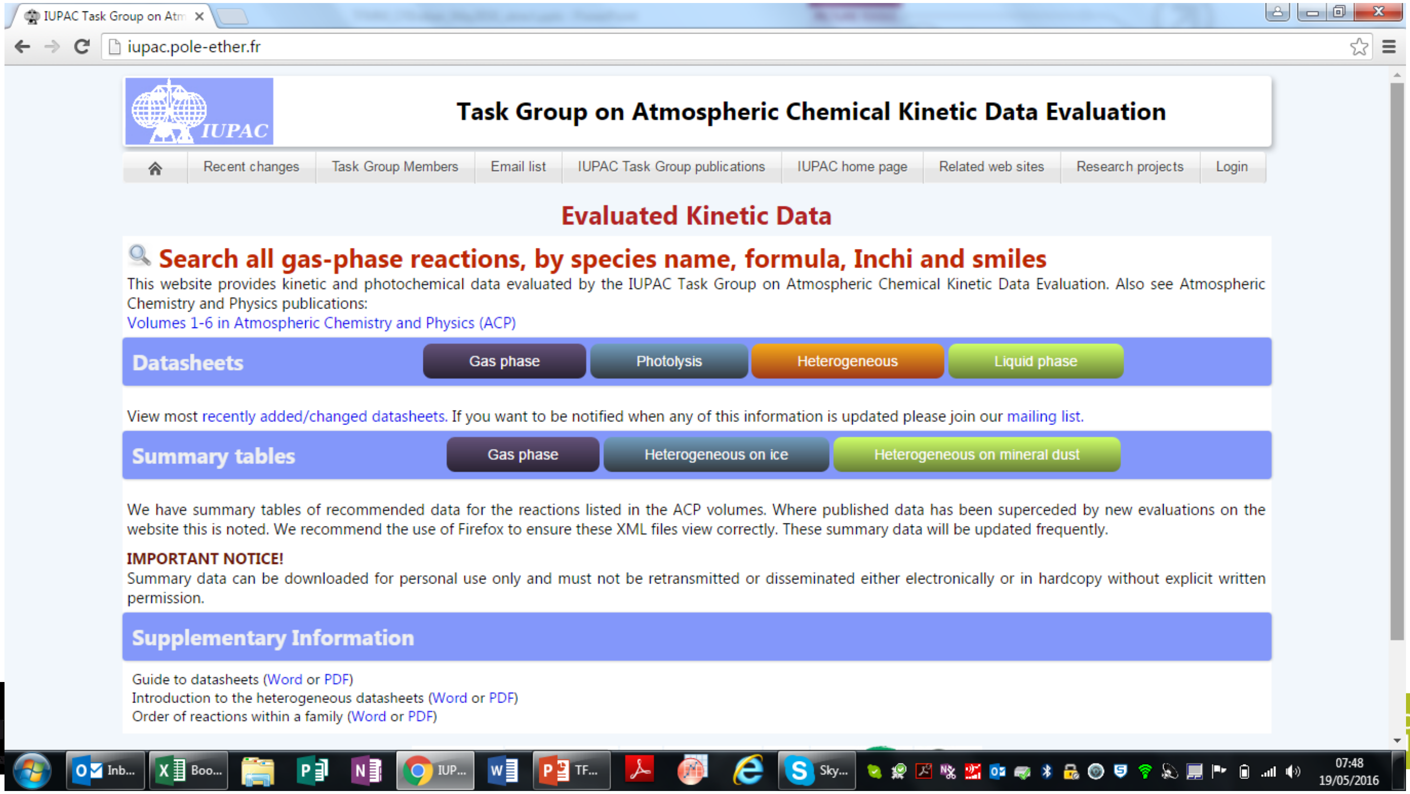
- Learn from the model of VOCs and NOx in ACTRIS.
  - Establish centres of excellence
  - On-going annual checks and improvement plans
  - Plan for access for SMEs, researchers to regularly check standards
  - Incorporate metrological standards (or close to them!)
- concentration and fluxes both important, but different requirements for each

Also learn from emission factors…?

Level	Description	Protocol	NO2	NH3
A	BEST PRACTICE	ACTRIS	Photolytic blue light with ACTRIS data label	QCL-TDLAS?; MARGA, annual denuder
B	Good practice	EMEP	photolytic not to ACTRIS standard; chemiluminscence in AQD network	CRD
C	Useable but know interferences	ISO standard/ Detailed QC protocol	Chemiluminscence not in compliance network;	Chemiluminescence NO conversion
D	Indicative (30-50%)	CEN standard	diffusion sampler	
E	Indicative with normal distribution of values about "real" value	Research paper/test documentation		
F	NOT RECOMMENDED EXCEPT FOR RESEARCH i.e. do not put in database!)		NO2 electrochemical sensor	
O	Campaign remote sensing		Citiscanner MAX DOAS	

Also learn from IUPAC

- Method sheets for each chemical with what is possible which ones are recommended with what level of uncertainty
- Group of volunteer experts to check ratings on regular basis



DELTA UPDATE:

Change in Protocol and data corrections

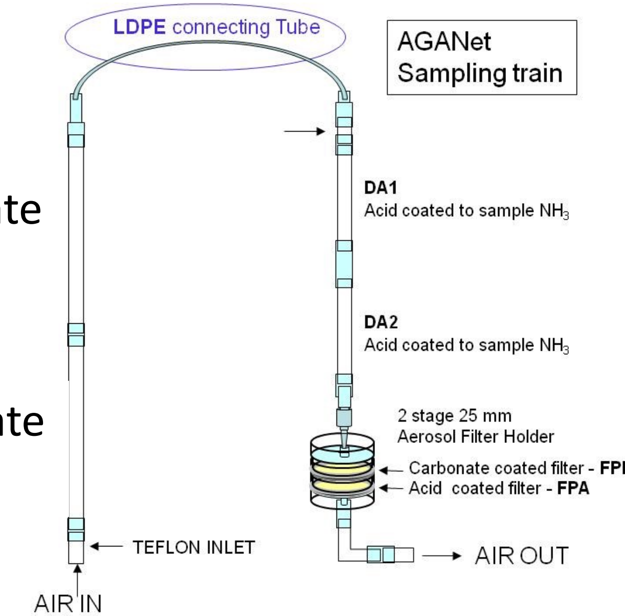
2. Denuders

carbonate

HNO_3 →	NO_3^-
HONO →	NO_2^- (-> NO_3^-)
PAN →	NO_2^- + NO_3^-
NO_2 →	NO_2^- + NO_3^-
SO_2 →	SO_4^{2-}
HCl →	Cl^-

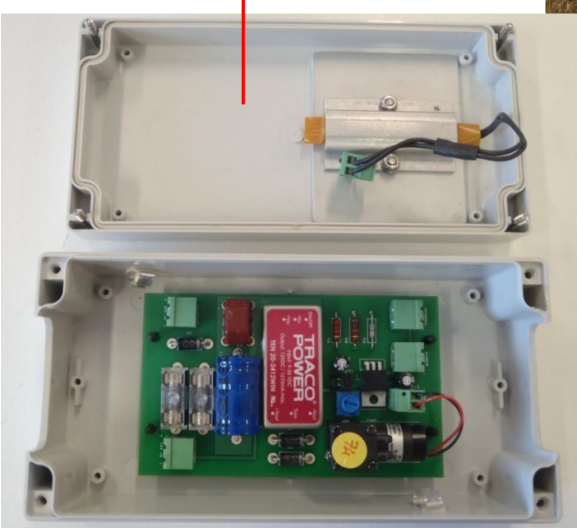
Potassium carbonate

Potassium carbonate

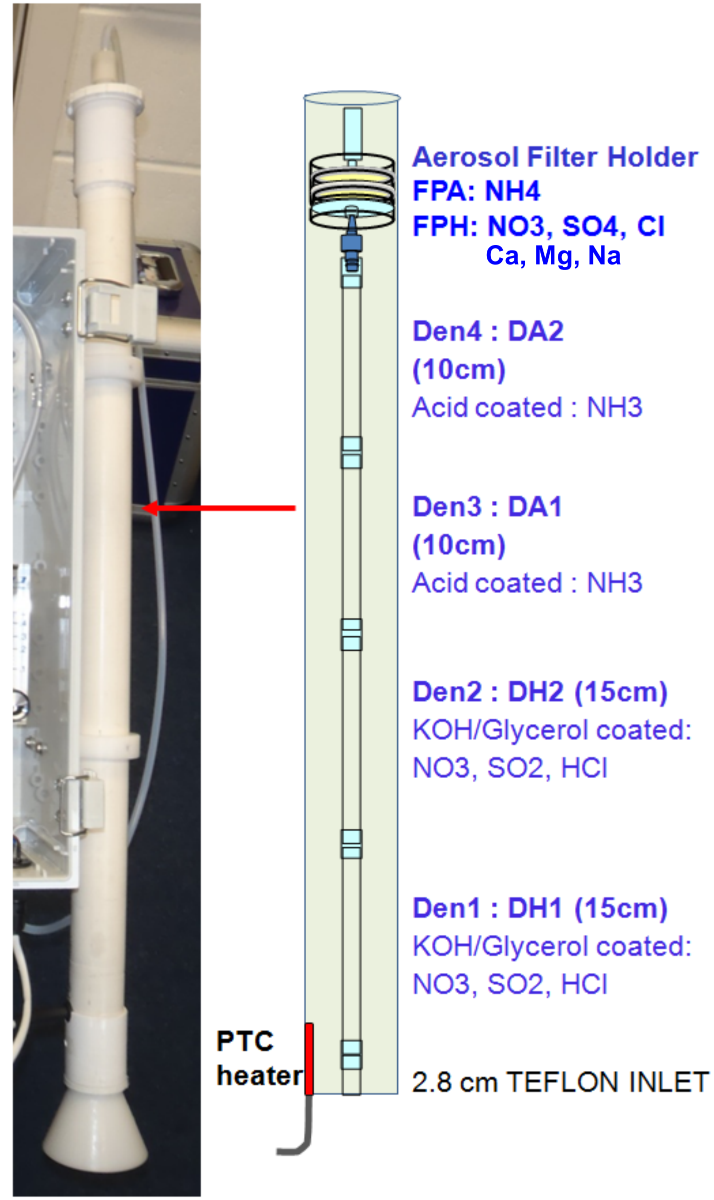


Issue: not completely HNO_3 specific.

DELTA II

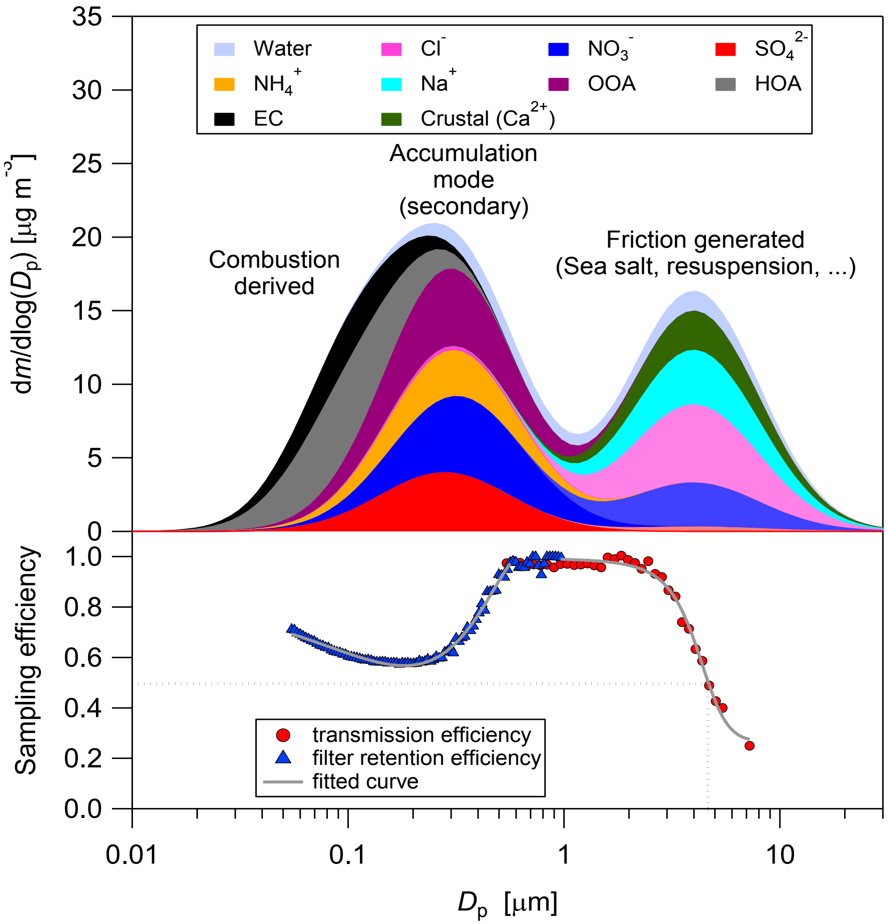


TRACO POWER



Aerosol Filter Holder
FPA: NH4
FPH: NO3, SO4, Cl
Ca, Mg, Na
Den4 : DA2
(10cm)
Acid coated : NH3
Den3 : DA1
(10cm)
Acid coated : NH3
Den2 : DH2 (15cm)
KOH/Glycerol coated:
NO3, SO2, HCl
Den1 : DH1 (15cm)
KOH/Glycerol coated:
NO3, SO2, HCl
PTC
heater
2.8 cm TEFLON INLET

Retention and transmission efficiency of the DELTA sampling train as used in the AGANET network (from AC0103 Final report).



Two approaches were adopted to investigate the processes occurring in the DELTA systems:

1) Analyse the acid coated filters (FPA) for NO_3^-, SO_4^{2-} and Cl^- at 5 DELTA sites, to check for breakthrough and analyse the K_2CO_3-glycerol coated filters for ammonium to check for retention.
2) 2)Addition of a Teflon filter (PTFE) between the K_2CO_3-glycerol (FPH) and acid (FPA) filters to capture any particles, which tests whether this is a particle or gaseous breakthrough effect (Figure 8).

Summary of findings

- intercomparison tests between the K_2CO_3-glycerol denuders and NaCl denuders show that the K_2CO_3-glycerol denuders do have significant interferences from other oxidised nitrogen species, with the interference dominating the measured concentration in the urban DELTA system.
- The UKEAP AGANet urban DELTA measurements (London and Edinburgh) are not used in the UK HNO_3 assessments (or the other atmospheric species) but the result has implications for the future use of DELTAs in urban environments and it would be a strong recommendation that this method is not generally useful for HNO_3 or NO_y measurements in urban areas.
- The DELTA method is however not problematic for NH_3, SO_2 and HCl.
- Potential NO_y interfering species are: NO_2, HONO, N_2O_5, PANs, $ClNO_2$ and other oxidised nitrogen species
- As previously noted, there are many unknowns for many of these chemical species, not least the ambient concentration variation, deposition velocities and possible bi-directionalities in fluxes (recently shown to be potentially important for HONO).

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