Deriving a speciated atmospheric nitrogen budget at Auchencorth Moss, a background site in South East Scotland

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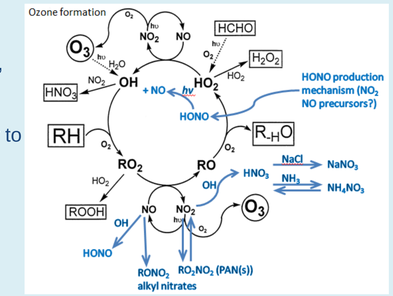
ACTRiS

INTRODUCTION

- Recent studies of $ClNO_2$, N_2O_5, PANs and trimethlyamines at background sites are important
- The background EMEP supersite 'Auchencorth Moss' in South East Scotland routinely measures NO_2, NO, NH_3 , HONO and HNO_3 in gas phase and particulate (PM_{10} and $PM_{2.5}$) NH_4^+ and NO_3^-.
- A study in spring 2014 aimed to:
  1. Develop a better understanding of the N speciated budget at Auchencorth Moss (refer to reactive N cycle).
  2. Identify potential artefacts in the routine N measurements

Location of Auchencorth Moss

Auchencorth Moss



Reactive N cycle in the troposphere (adapted from Jenkin and Clemitshaw (2000)).

METHODS

- The table lists N species measured and the instrumentation used
- Due to issues with baseline drift in the $ANNO_x$ the data hasn't been presented.
- PAN GC measured from 24 April 2014 to 06 May 2014
- All other instrumentation operated for the length of the campaign.

Routine and non-routine measurements during the campaign.

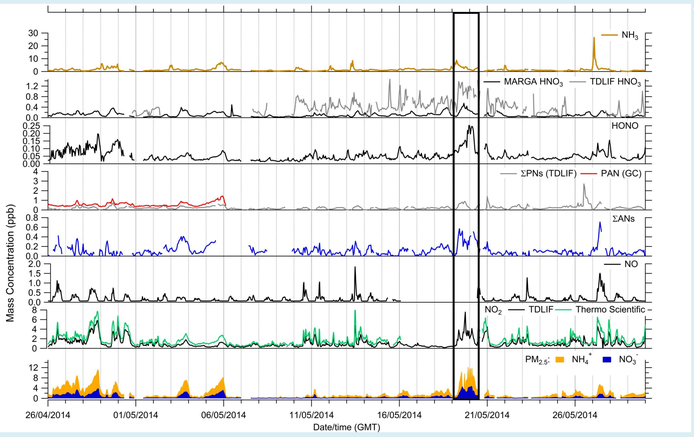
Species measured	Instrumentation	Measurement technique	Height (m)	Reference to method
PM_{10} and $PM_{2.5}$: Na^+ , NH_4^+, K^+, Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-} Gases: NH_3 , HNO_3 , HONO, HCl, SO_2	Montior for AeRosols and Gases in Ambient air (MARGA, Metrohm Applikon, NL.)	Wet rotating annular denuder and steam jet aerosol collectors with online IC analysis	3.60	Twigg, *et al.* (2015)
NO_2, total peroxy nitrate (ΣPNs), total alkyl nitrate (ΣANs), HNO_3	Thermal dissociation laser induced fluorescence (TDLIF)	Thermal dissociation with laser induced fluorescence detector	3.00	Di Carlo, *et al.* (2013)
NO/ NO_2	$ANNO_x$ analyser (CLD, 88 p, Eco Physics, AG. Switzerland)	Chemiluminesence analyser	3.00	
NO/ NO_2	Thermo Scientific Analyser (model 42CTL)	Chemiluminesence analyser (Molybdenum NO_2 to NO converter)	2.02	
PANs	GC-ECD	Online gas chromatography with electron capture detection	3.00	McFadyen and Cape (2005)

OVERVIEW OF MEASUREMENT PERIOD

- Changing air masses resulted in different N species composition.
- Periodic pollution events were observed during the study resulted in elevated N species
  - Example: 19 May 2014 where an observed increase in N species with the exception of NO as no data was available (highlighted on graph)
- The reported average HNO_3 from TDLIF is around four times that reported by the MARGA (refer to table).

Possible explanations:

1. MARGA suffers from loses at the inlet
2. TDLIF HNO_3 suffers artefacts from NO_3^- aerosol

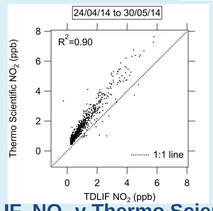


Time series from intensive campaign in spring 2014

Statistics for May 2014 using hourly averages from instrumentation

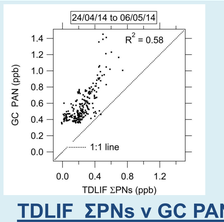
	Average (ppb)	σ (ppb)	Max (ppb)
TDLIF			
HNO_3	0.39	0.28	1.46
ΣANs	0.11	0.10	0.72
ΣPNs	0.24	0.22	2.71
NO_2	0.94	0.80	7.55
MARGA			
$PM_{2.5}$ NH_4^+	0.99	1.12	7.88
$PM_{2.5}$ NO_3^-	0.46	0.71	4.70
NH_3	1.38	1.64	26.51
HNO_3	0.09	0.08	0.55
HONO	0.04	0.03	0.25
Thermo Scientific analyser			
NO	0.15	0.17	1.64
NO_2	1.54	1.00	8.19

INTERCOMPARISON OF INSTRUMENTATION



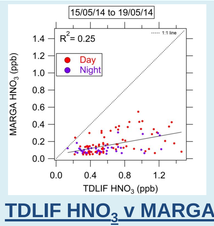
TDLIF NO_2 v Thermo Scientific NO_2

- Good correlation
- Thermo scientific analyser systematically report higher values than the TDLIF



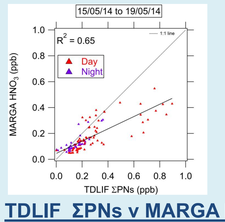
TDLIF ΣPNs v GC PANs

- Good correlation
- GC reports higher concentrations



TDLIF HNO_3 v MARGA HNO_3

- Poor correlation
- TDLIF reports higher concentrations



TDLIF ΣPNs v MARGA HNO_3

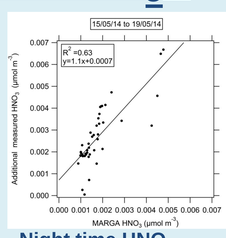
- MARGA HNO_3 correlates with the ΣPNs reported by the TDLIF

CHALLENGES OF DERIVING A SPECIATED N BUDGET: *WHAT IS HNO_3?*

- Di Carlo *et al.* (2013) demonstrated from flights over the UK that N_2O_5 dominated the ΣPNs at night measured by the TDLIF.
- Phillips *et al.* (2013) provided evidence to suggest night time HNO_3 reported by MARGA may include N_2O_5 , where:

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3 = \text{additional measured } HNO_3$$

- This work suggests a relationship between the MARGA HNO_3 and ΣPNs measured by the TDLIF
- 5 consecutive nights were plotted (see LHS graph) assuming ΣPNs = N_2O_5
- Molar N_2O_5 was used to calculate the molar HNO_3 , assuming a 100% capture efficiency and compared to the measured HNO_3 by the MARGA
- Night time HNO_3 measured by the MARGA correlates well with the additional measured HNO_3 derived from ΣPNs
- This suggests that the HNO_3 reported by the MARGA at Auchencorth Moss may additionally contain N_2O_5 , though further studies are required to confirm this



Night time HNO_3 measured by the MARGA compared to HNO_3 derived from ΣPNs

CONCLUSIONS:

INTERCOMPARISON STUDIES

- Poor correlation between the MARGA and TDLIF for HNO_3 measurements .
- The Thermo Scientific analyser reports higher NO_2 compared to the TDLIF most likely due to interferences at low NO_2 concentrations previously demonstrated by Steinbacher et al.(2007) .

NEXT STEPS OF STUDY:

- Determine if the GC overestimates PANs
- Assess the potential interference of particulate NO_3^- in the TDLIF measurements of HNO_3.

DERIVING A SPECIATED N BUDGET

- MARGA HNO_3 may have an N_2O_5 artefact in the measurement at night

NEXT STEPS OF THIS STUDY:

- Determine the N species to be used to derive a N budget
- Investigate the chemical transformations of N species at the site
- Examine the influence of long range transport of air masses on the speciated N composition at this background site

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