Assessment of monitoring methods and modelling of atmospheric reactive oxidised nitrogen compounds in the UK by chemical ionisation spectrometry

(1) Dr Christine Braban – NERC Centre for Ecology & Hydrology (contact: chri2@ceh.ac.uk)
(2) Dr Mat Heal – School of Chemistry, University of Edinburgh (m.heal@ed.ac.uk)
(3) Dr Marsailidh Twigg – NERC Centre for Ecology and Hydrology

Project summary

Development of a chemical ionisation mass spectrometer to measure atmospheric nitrogen species HNO_3 and HONO. Results will assess current UK monitoring methods, N-deposition budgets and update biosphere-atmosphere exchange model parameterisations.

Project background

Major uncertainties in air quality and ecosystem impacts are in part due to the lack of understanding of many atmospheric oxidised nitrogen species. Currently nitric acid (HNO_3) is estimated to contribute 30% of the UK's nitrogen deposition and is the precursor of NH_4NO_3, (source of many UK particulate matter air quality exceedences). Nitrous acid (HONO) is a major sink of atmospheric OH that regulates the atmospheric oxidant budget. HONO and HNO_3 are measured with an on-line ion chromatography (IC) system (Rumsey *et al*. 2013) at the UK atmospheric measurement supersites, Auchencorth Moss, south of Edinburgh (http://pollutantdeposition.defra.gov.uk/emep (Figure 1) and Harwell, Oxfordshire. It is likely that these measurements are influenced by other nitrogen species (NO_y) such as $ClNO_2$, and N_2O_5, but the artefacts have not been quantified on a long-term basis (Phillips *et al*. 2013). Current modelling shows Auchencorth Moss as a net atmospheric HONO source and HNO_3 sink. Recent research suggests HNO_3 fluxes may be bi-directional.

Figure 1 The fieldsite, Auchencorth Moss, South East Scotland and the chemical ionisation mass spectrometer (CIMS).

This PhD project develops the state of the art CEH chemical ionisation mass spectrometer (CIMS, Huey, 2007) to measure concentrations and directional fluxes of HONO. The student will assess parameterisations in current surface-atmosphere exchange models for reactive N species.

In further developing the CEH CIMS for the direct measurement of fluxes of HNO_3 and HONO during this PhD project it will be possible to assess the current monitoring methods, scientifically suggest the future direction of routine measurements and understand the emission and deposition of HNO_3 and HONO at UK sites using process models. This study potentially reduces uncertainties in air quality- ecosystem impact understanding.

Key research questions

- Does the current routine online IC monitoring provide a quantitative measure of HNO_3 and HONO and does this modify understanding of atmospheric N-budgets?
- What are the driving forces of HONO and HNO_3 surface-atmosphere exchange at Auchencorth Moss and Harwell?

Methodology

The main components of the PhD are: (a) laboratory validation and field deployment of the

CEH CIMS for HONO and HNO_3 measurements (b) develop data analysis protocols (c) assess the performance of the IC monitoring technique (d) understand inferential models and develop parameterisations for surface interactions of HONO and HNO_3

Year	*Objective*
1	i) Review of HNO_3 and HONO metrology methods *(Introduction of thesis)* ii) Calibration and optimisation of the CIMS for HNO_3 and HONO measurements iii) Ambient air measurements at CEH Edinburgh Bush Estate site iv) Draft *Instrument development research paper based on Objective 1 (ii) and (iii)*
2	i) Deployment of CIMS to Auchencorth Moss for intercomparison with monitoring instruments and development of flux measurements ii) Assessment of current inferential models used to determine UK deposition *iii) Completion of 1(iv) and research paper based on results from Objective 2(i)*
3 – 3.5	i) Deployment of CIMS to the Harwell, Oxfordshire ii) Parameterisation of results to model HONO and HNO_3 surface processes *iii) Research paper based on Objective 3(i)* *iv) Synthesis research paper based on measurements and 2 (iii) and 3(ii) and thesis*

Training

A comprehensive training programme will be provided comprising both specialist scientific training and generic transferable and professional skills in both University of Edinburgh and in NERC CEH. Professional skills includes a programme focused on personal effectiveness, communication, and career management, as well as courses on safety assessment, project management, literature searching, presentations, and thesis writing. The student will also receive training in undergraduate laboratory demonstrating and project supervision. The student will attend relevant atmospheric science courses available in the UoE Schools of GeoSciences & Chemistry. They will gain skills in practical environmental science and relevant science policy and have opportunities to apply to NERC training courses (e.g. the NCAS Summer School on Atmospheric Measurements on Arran. The student will be trained on the CIMS operation and field deployment operations. The student will be trained in data acquisition, analysis routines and modelling using software packages (e.g. Igor & Origin)

Requirements

Essentials: A minimum 2:1 undergraduate or a Master's degree in chemistry (or a degree with major chemistry component), highly numerate, ability to work in a team and take the initiative. Aptitude for field work, driving licence, highly computer literate.

Desirable: Knowledge of mass spectrometry. Computer programming experience (e.g. R).

References

Huey, L. G. (2007), Measurement of trace atmospheric species by chemical ionization mass spectrometry: Speciation of reactive nitrogen and future directions. Mass Spectrom. Rev., 26: 166–184.

Phillips, G. J., Makkonen, U., Schuster, G., Sobanski, N., Hakola, H., and Crowley, J. N. (2013) The detection of nocturnal N_2O_5 as HNO_3 by alkali- and aqueous-denuder techniques, Atmos. Meas. Tech., 6, 231-237

Rumsey, I. C., Cowen, K. A., Walker, J. T., Kelly, T. J., Hanft, E. A., Mishoe, K., Rogers, C., Proost, R., Beachley, G. M., Lear, G., Frelink, T., and Otjes, R. P. (2013) An assessment of the performance of the Monitor for AeRosols and GAses in ambient air (MARGA): a semi-continuous method for soluble compounds, Atmos. Chem. Phys. Discuss. 13, 25067-25124,