Nitrogen Oxides and nitrate radical flux and concentration measurements in the Auchencorth moss Supersite (NOMAS)

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- **Introduction and motivation**

Auchencorth Moss has been an EMEP supersite since June 2006, where currently routinely speciated N measurements are: HNO3, NO2, NO,, HONO, NH3 in gas phase and particulate NH4+ and NO3-. It is understood that the full speciated N-budget is currently unknown and recent studies have shown the importance of chemical species such as PANs, peroxy nitrates (RO2NO2, PNs), alkyl nitrate (RONO2, ANs), ClNO2 and N2O5 at background sites. In order to better understand the chemical climate at Auchencorth Moss and in particular quantify the N-speciation in the atmosphere over time and the co-variation of non-routinely measured species against the routine measurements, CEH are hosting an intensive experiment to monitor nitrogen chemical speciation over the Spring 2014 season. The spring has been chosen as the data records show that the site frequently experiences pollution events from agricultural activities and long range transport from continental Europe during this period.

- **Scientific objectives**

The aim of the N intensive is to build an atmospheric N budget for the spring period (which usually includes periods where agricultural and European mainland air masses are seen). The concept is to augment the routine measurements made as part of the UK monitoring networks with research instruments measuring species either not monitored or monitoring species currently measured but with higher time resolution/specificity. Therefore, in addition to the routine measurements, the deployment of the TD-LIF of the University of L'Aquila allows to measure the concentration and the flux of NO2, PNs, ANs and HNO3. The first objective is to speciate the NOy budget using the TD-LIF observationas. Since the TD-LIF measure NO2 directly, another objective is to validate the NO2 routinely measured at Auchencorth Moss, which uses to convert NO2 into NO and detect the latter with chemiluminescence technique. This indirect method is reported to suffer of interferences at low level of NO2 (Steinbacher et al., 2007) so the intercomparison of the two NO2 measurements technique is really worth. Another objective is to quantify the flux of the main NOy species: NO2, PNs and ANs using the high frequency (10Hz) measurements of the TD-LIF to understand if vegetation in this site is a source or a sink for NO2, PNs and ANs. The last objective is to evaluate the impact of ANs on the global oxidation capacity of the lower troposhere.

- **Reason for choosing station**

The Auchencorth Moss site was select because is a site with routinely measurements of some speciated NOy, therefore is excellent for the deployment of the TD-LIF that measures some other NOy species: together the TD-LIF and routine observations in this site allow to have a complete picture of the NOy budget in a background site impacted mainly by agricultural emissions. Moreover, the very low level of NO2 allows to test for a possible interference in the indirect measurements of NO2 using as reference the TD-LIF that measures NO2 directly. Finally the flux measurements of PNs and ANs, in a site dominated by vegetation and agriculture emissions, is of primary importance since to date the flux of these compounds in this kind of sites is not quantified.

- **Method and experimental set-up**

The Thermal Dissociation Laser Induced Fluorescence (TD-LIF) instrument is an integrate system for simultaneous measurements of NO2, total peroxy nitrates (RO2NO2, PNs), total alkyl nitrates (RONO2, ANs) and HNO3 using 4 distinct detection cells. All these species are detected with high frequency (10 Hz) and low detection limit: 3.6 pptv, 11.2 pptv, 13.1 pptv and 26.3 for NO2, PNs, ANs and HNO3, respectively (Di Carlo et al., 2013; Aruffo et al., 2014). The TD-LIF measures atmospheric NO2 directly, detecting the fluorescence of NO2 molecules excited by a Yag laser that emits at 532 nm, whereas PNs, ANs and HNO3 are thermal converted into NO2 followed by NO2 detection using the LIF technique. The high frequency of the TD-LIF observations, simultaneously with wind components measurements, can be functional to determine the flux of NO2 and of ΣPNs and ΣANs using the eddy covariance technique. Finally, due to the relatively long atmospheric lifetime of ANs, their concentrations can be used also to evaluate the air masses aging reaching the observation site.

- **Preliminary results and conclusions**

The TD-LIF was deployed for more than 2 months at Auchencorth Moss site and it worked fine with no interruptions, therefore we collected a quite unique and complete dataset that allow to address all the objectives of the project. The preliminary analysis of the data showed, as expected, a very low level of NO2, PNs and ANs (tens of ppt) with some sporadic increase of the concentrations due to transport of more polluted air masses. The analysis of the fluxes of the measured species as well as the intercomparison between the TD-LIF and those routinely used at the Auchencorth Moss are still in progress but at first look the quality of the collected data allow to better understand the budget of NOy in this site as well as the role of the vegetation in the flux of NO2, PNs and ANs.

- **Outcome and future studies**

From the results of this project we expect to better understand the role of PNs and ANs in the budget of the NOy in a background site. Moreover, we expect to give an answer to the question regarding the potential interference in the chemiluminescence measurements of NO2. A possible follow-up of this project is to organize a campaign in a similar background site to confirm the results that will come out from this project.

- **References**

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