ACTRIS TNA Activity Report

Fast-ozone Intercomparison, FOSE

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Introduction and motivation

Quantifying ozone deposition to the surface is an important part of fully understanding the ozone budget, what controls its concentration in the atmosphere and its interaction with other trace-gases such as NO/NO_2 and VOCs. As part of the ECLAIRE and ACTRIS project a group of researchers interested in measuring ozone deposition has been brought together; most use dry chemiluminescent instruments to measure rapid fluctuations in ozone concentration and so the flux. These instruments are all based on a methodology originally described by Gusten et al. (1992) and use disks coated in an ozone sensitive laser-dye. It is evident from other measurement campaigns that these sensors do not always give the same results and although two instruments running in-situ maybe quite well-correlated the magnitude of the flux can be quite different ((Muller, Coyle et al. 2009; Muller, Percival et al. 2010). In order to obtain a dataset of collocated measurements and examine the differences between the instruments we ran a "short" experiment at Auchencorth Moss.

Scientific objectives

The focus of the measurements was to examine:

• Zero offsets in each instruments and its variation with time and ozone sensitive disk
• Noise levels in each instrument
• Co-spectra etc for each instrument
• Effects of humidity and temperature on the above

Reason for choosing station

A flux gradient system exists at the site which will provide a useful comparison to the eddy-covariance results and suitable infrastructure and other measurements are available.

Method and experimental set-up

The instruments are relatively easy to run and setup so we asked the group to send an instrument to Auchencorth Moss where they have been setup and operated by Mhairi Coyle, Angelo Finco and Giacomo Gerosa. These instruments are all based on a methodology originally described by Gusten et al 1992 for a small, lightweight (1.5 kg) and fast-response ozone sensor for direct eddy flux measurements. The basis for detection is the chemiluminescence of an organic dye adsorbed on dry

silica gel in the reaction with ozone. The chemiluminescence is monitored with a cheap and small blue- sensitive photomultiplier. At a flow rate of 100 l min^{-1} the ozone sensor has a 90 % response time of significantly better than 0.1 s with a detection limit lower than 50 ppt at S/N = 3. There are no interferences from other atmospheric trace gases like NO(x), H_2O_2 and PAN. Water vapour and SO_2 enhance the chemiluminescence efficiency of the ozone sensor. Since their response times are 22 seconds and 30 minutes, respectively, no correlation between rapid ozone fluctuations and those of these two trace gases is noticed by the ozone sensor when operating at a frequency of 10 Hz.

For the period 16/05/2014 to 11/07/2014 the following fast ozone sensors were installed on the small scaffolding tower at Auchencorth (Figure 1):
- CEH ROFI mk1 & mk2
- Sextant FOS from JRC-Ispra
- COFA from UNICATT

Alongside:
- HS sonic anemometer to measure the turbulence
- Li-7500 open path CO2/H2O to quantify the water-vapour flux and concentration.

All the instruments were logged via a laptop and Labview program. Other meteorological measurements were obtained from the nearby met station on the site. Three other instruments were submitted to the experiment but where not operable for this period.
- Enviscope from Szent István University
- NOAA original prototype from Szent István University
- GFAS from University of Manchester
- Sextant FOS from INRA-Grignon

Ozone sensitive disks were pre-exposed using the same ozone source for the same time period. Data were recorded from each instrument for a period of 3-4 days before the disks was changed. Where the instruments used the same sized disks during one period they were swapped between instruments to see if this affects their response.

Preliminary results and conclusions

Unfortunately issues with the logging system and power supplies limited the overall data capture achieved, Table 1 summarises the dataset obtained.

Table 1 FOSE Instruments 16/05/2014 to 10/07/2014

Sensor	Provided By	Status	Data Capture
ROFI mk1	CEH	Operable/ data comm. issue	43%
ROFI mk2	CEH	Fully operational	80%
Sextant FOS	JRC-Ispra	Operable/ data comm. issue	50%
COFA	UNICATT	Operable/ power supply issues	21%
Enviscope	Szent István University	Inoperable/ data comm. issue	
NOAA	Szent István University	Inoperable (unable to repair)	
GFAS	University of Manchester	Inoperable (repairable)	
Sextant FOS	INRA-Grignon	Fully operational	Not used as weather conditions prevented it's installation

Figure 2 plots the time series of voltage readings obtained from the four operational sensors and the main ozone sensitive disk changes can be clearly seen where the voltage suddenly increases. The COFA and ROFI sensors' output voltages saturate at 5V whereas the Sextant does so at 2.5V. On the

3rd of June all the sensors were zeroed after a disk change and on the 6th of June disks were swapped between COFA <> ROFI mk1 and Sextant <> ROFI mk2.

Outcome and future studies

This experiment provided a useful initial assessment of 4 types of chemiluminescent instrument (the ROFIs, COFA and Sextant) but due to faults with the other instruments we were unable to test them during this period. The experiment has continued in 2015 (19/03/2015 – 15/05/2015) and using the all the instruments except the old NOAA sensor. The data from both periods will be fully analysed using a Labview program that implements the same protocol agreed for the ECLAIRE project, as well as providing other useful statistics. These results will contribute to a paper discussing ozone flux measurements by the eddy-covariance technique.

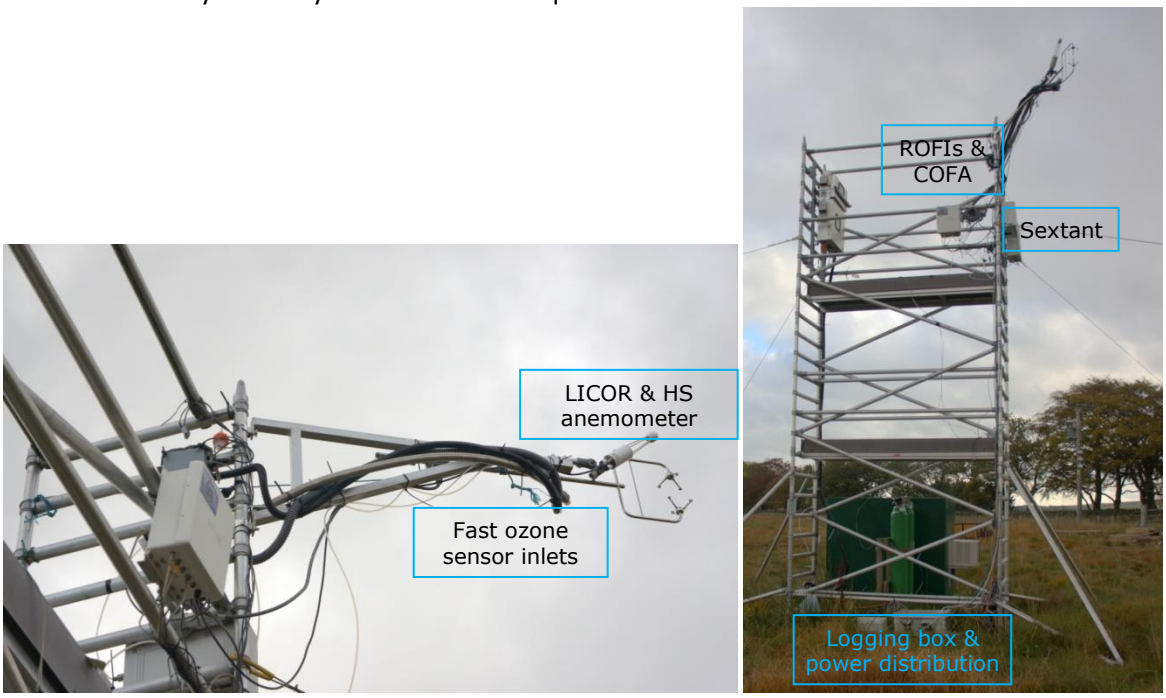

Figure 1: Equipment setup on Hg Tower at Auchencorth Moss, May 2014

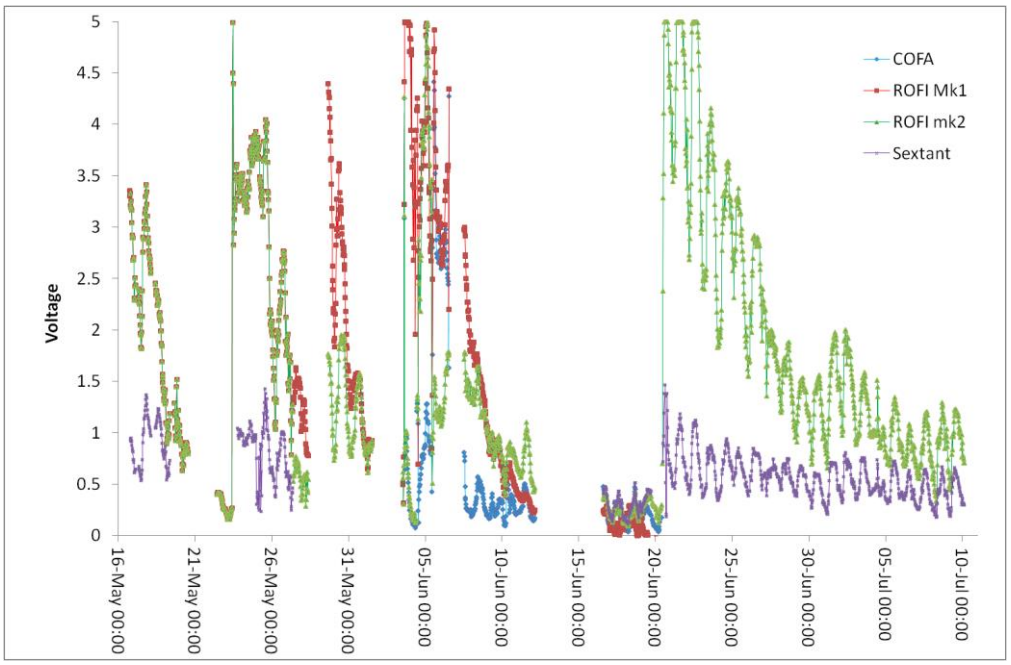

Figure 2: Time series of voltage readings obtained from each operational sensor.

References

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*Muller, J. B. A., C. J. Percival, et al. (2010). "Sources of uncertainty in eddy covariance ozone flux measurements made by dry chemiluminescence fast response analysers." Atmos. Meas. Tech. **3**(1): 163-176.*