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Sources of uncertainty in eddy covariance ozone flux measurements made by dry chemiluminescence fast response analysers

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Eddy covariance ozone flux measurements are the most direct way to estimate ozone removal near the surface. Over vegetated surfaces, high quality ozone fluxes are required to probe the underlying processes for which it is necessary to separate the flux into the components of stomatal and non-stomatal deposition. Detailed knowledge of the processes that control non-stomatal deposition is limited and more accurate ozone flux measurements are needed to quantify this component of the deposited flux. We present a systematic intercomparison study of eddy covariance ozone flux measurements made using two fast response dry chemiluminescence analysers. Ozone deposition was measured over a well characterised managed grassland near Edinburgh, Scotland, during August 2007. A data quality control procedure specific to these analysers is introduced. Absolute ozone fluxes were calculated based on the relative signals of the dry chemiluminescence analysers using three different calibration methods and the results are compared for both analysers. It is shown that the error in the fitted parameters required for the flux calculations provides a substantial source of uncertainty in the fluxes. The choice of the calculation method itself can also constitute an uncertainty in the flux as the calculated fluxes by the three methods do not agree within error at all times. This finding highlights the need for a consistent and rigorous approach for comparable data-sets, such as e.g. in flux networks. Ozone fluxes calculated by one of the methods were then used to compare the two analysers in more detail. This systematic analyser comparison reveals half-hourly flux values differing by up to a factor of two at times with the difference in mean hourly flux ranging from 0 to 23% with an error in the mean daily flux of $\pm 12\%$. The comparison of analysers shows that the agreement in fluxes is excellent for some days but that there is an underlying uncertainty as a result of variable analyser performance and/or non-linear behaviour of disc sensitivity.

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1 Introduction

Tropospheric ozone (O_3) is an important greenhouse gas and thus influences climate, but it is also a secondary air pollutant relevant to air quality, with effects both on human health and vegetation. It is produced through photochemical reactions with precursor species such as nitrogen oxides and volatile organic compounds (VOCs). Emission control measures in Western Europe, particularly of VOCs, have resulted in a decrease of peak ozone concentrations over the last few decades (de Leeuw, 2000; NEG-TAP, 2001; Jenkin, 2008). At the same time precursor emissions have increased globally, resulting in a rise in ozone background concentrations in Europe over the same time period (e.g. Derwent et al., 2007), due to increases in hemispheric background concentrations. Thus, because ozone is long-lived, non-European precursor emissions have the potential to impact on Europe's ozone levels, making emission controls a global issue when air quality targets are to be met in Europe (Royal Society, 2008) and the same applies to other regions in the world. These increased ground-level ozone background concentrations are of particular concern as ozone can cause adverse health effects in humans and vegetation (Ashmore, 2005). All types of vegetation can be affected, including semi-natural grasslands, forests and agricultural systems. Negative effects on crops such as reduction in yield can contribute to issues of food security, and in natural/semi-natural ecosystems ozone might potentially affect biodiversity (Fuhrer, 2009).

To assess impacts on plants a UNECE critical level approach has been used and the exceedance of the critical level corresponds to a potential negative response in plants. For ozone, an accumulated exposure concept was originally conceived, which was based on exposure-response relationships obtained in chamber studies. AOT40, (Accumulated Ozone concentration above the Threshold of 40 ppb) for daytime conditions during the growing season, was used to set a critical level for different vegetation. One limitation of the AOT40 concept is that it is not based on a mechanistic model of ozone uptake which can potentially lead to overestimating damage to the plant. Thus,

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assessed if it is to be incorporated into the latest vegetation risk assessment models. Assessing current and especially future risks can be difficult as climate, ozone and other trace gases interact in a complex manner to influence the actual risk to the plant (Fuhrer, 2009). Both deposition pathways are important and are not independent as the ozone flux into the plant is also influenced by surface destruction of ozone (Fuhrer, 2009).

High quality ozone flux measurements are the only way to quantify fluxes directly and to probe the stomatal/non-stomatal partitioning and help understand destruction processes and relationships with other variables. The most direct method to measure fluxes is by eddy covariance. The eddy covariance technique typically requires analysers that are fast response and highly sensitive, although an alternative method of measuring ozone fluxes with a slower-response analyser has recently been suggested (Wohlfahrt et al., 2009), requiring large flux loss corrections which add uncertainty. A variety of suitable analysers exist for ozone, all of which are based on chemiluminescence. The reagents can be either in liquid, solid or gaseous form and hence the type of chemiluminescence is called wet, dry and gas-phase chemiluminescence respectively.

The use of the wet chemiluminescence method is not uncommon and it has advantages over the dry method (e.g. regarding signal drift and water vapour influence), but the operation can be hampered by liquid flow problems (e.g. Keronen et al., 2003) and the sensitivity can be lower than for the dry method. Gas phase chemiluminescence (GPC) is generally based on the homogeneous reaction with NO (Pearson, 1990) and used least frequently for surface flux measurements. This method is highly sensitive and reaction kinetics are better known than for any of the other chemiluminescence techniques. One of the main practical disadvantages of GPC is that NO is a toxic compound and is required as compressed gas during operation.

The dry chemiluminescence (DC) method has been used most regularly and successfully in a variety of environments and settings (e.g. Tuovinen et al., 1998, Bauer et al., 2000; Gallagher et al., 2001; Bassin, et al., 2004; Rummel et al., 2007). In DC

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air passes over a silica gel disc (0.026 m in diameter) coated with the reagents gallic acid and coumarin 47 which produce photon emissions in the blue spectral range. The response time and sensitivity is flow rate dependent and high flow rates are used to operate in the flow-independent regime and achieve the fast response times required for eddy covariance measurements (Guesten et al., 1992). The chemiluminescence reaction with ozone consumes the reagent over time and discs need to be replaced periodically. Guesten et al. (1992) point out that the sensitivity of the discs depend on humidity and that sensitivity does not decrease linearly with time. Signal drift as caused by the consumption of the reactive compounds on the target disc can occur, which is one of the reasons why each disc has a limited lifetime and careful and frequent calibrations are required (Weinheimer, 2006). Knowledge about the relationship between sensitivity, temperature and humidity and its variability over time with increased accumulated ozone exposure is lacking and fundamental understanding about the reaction mechanism of chemiluminescence is also missing. In comparison with other reactive trace gases which require more sophisticated detection techniques and compared to the wet and gas-phase chemiluminescence techniques, this dry method is relatively low cost, low power and low weight and has become quite popular as operation of these systems is straightforward and simple.

Ozone fluxes have been measured by dry chemiluminescence for over 15 years using an analyser originally developed as an ozone sonde by GFAS (“Gesellschaft Für Angewandte Systemtechnik”, Guesten et al., 1992), which has since then been reproduced by other groups (e.g. by NOAA-ATDD as detailed in Bauer et al., 2000). Fluctuations of ozone are detected optically via the fast heterogeneous chemiluminescence reaction of coumarin/gallic acid with ozone. The chemiluminescence target discs are made in a manner described by Speuser et al. (1989) and can be purchased from Bagus Consulting (Speyer, Germany). There is some variability in sensitivity as a result of the production process, storage and/or handling. Speuser et al. (1989) reported a variation in sensitivity of $\pm 5\%$ of the pre-ozonised discs. The detection limit for ozone was found to be better than 50 ppt of ozone (Guesten et al., 1992). Interferences in

the chemiluminescence reaction have been tested by Guesten et al. (1992 & 1995) who identified interference from water vapour and sulphur dioxide above 100 ppb, with response times of 2 s & 30 min respectively. No interference from NO_x, PAN or H₂O₂ was observed.

5 In terms of the luminescence mechanism, the currently available literature contains a variety of ideas for the reactions of ozone with the reagents, but comprehensive laboratory studies would be required to provide more definitive answers. Hodgeson et al. (1970) suggested (for compound rhodamine B) the mechanism for chemiluminescence is based on a resonance energy transfer where the initial ozone during activation
10 reacts with the dye to produce a dye molecule in an excited singlet state which then emits upon second exposure to ozone. This would be consistent with the reported loss of sensitivity from water vapour where the water vapour could quench the excited specie that is responsible for luminescence. Schurath et al. (1991) studied the dye coumarin 47 for chemiluminescence and found a response to ozone which showed
15 great sensitivity when the disc was conditioned with ozonised air. They do not however provide a definitive answer to the question of the sensitizing mechanism. This conditioning or activation with ozonised air before use of the chemiluminescence discs has become standard practice and activation lengths in the range of 100 to 225 ppb h of ozone have been reported (McKendry et al., 1998; Schurath et al., 1991). Guesten et
20 al. (1992) suggest that discs be replaced after 50 hours of operation.

To fully understand ozone destruction processes occurring at plant surfaces high quality ozone flux data are required. However, the quality of the flux data provided by the fast response DC instruments is currently poorly determined since the dry chemiluminescence reaction mechanisms remain somewhat unclear and the effect on ozone
25 fluxes from this source of uncertainty has not been investigated. In this paper, ozone flux measurements by two effectively identical dry chemiluminescence instruments are presented and uncertainties in the fluxes examined with the help of the direct comparison of the analysers.

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2 Experimental

2.1 Measurement set up

Continuous eddy covariance ozone flux measurements were made at a managed grassland site in Southern Scotland, UK, from 2 August to 3 September 2007. The Easter Bush site is located in the foothills of the Pentland Hills at 190 m above sea level and is surrounded by agricultural fields and farms (Milford et al., 2001). The fields surrounding the site are predominantly perennial rye-grass (*Lolium perenne*) and were grazed by sheep during August 2007. The canopy height reached about 0.1 m. For the eddy covariance measurements a Metek USA-1 sonic anemometer (Meteorologische Messtechnik GmbH, Germany) was used for 3-D wind speed measurements at 2.5 m height. Fast ozone measurements were made using a GFAS ozone sonde OS-G-2 (Guesten et al., 1994) and a Rapid Ozone Flux Instrument (ROFI) which is in effect a clone of the GFAS ozone sonde built by CEH (Coyle, 2005). Both instruments were mounted on the eddy covariance mast and the sampling inlets placed alongside each other. Relative concentrations as mV analogue signals from both analysers were sampled through the same anemometer interface box. A LabVIEW programme (National Instruments™) was used for data acquisition at a sampling frequency of 20 Hz, online flux analysis and post-sampling flux reanalysis. Absolute ozone concentration measurements from the Bush EMEP monitoring site situated about 400 m S of the Easter Bush flux site were used for the flux calculations. These concentration measurements were made using a TECO 49C UV ozone instrument (Thermo Electron Corp) which is regularly calibrated to comply with the required monitoring network standards. Ozone concentrations were also measured at the Easter Bush site, but due to instrument failure data coverage for August 2007 was unsatisfactory for the eddy covariance flux calculations. The Bush ozone data were deemed acceptable as the regression between the Bush Monitoring site and the Easter Bush flux site for available ozone concentrations yielded a correlation coefficient (R^2) of 0.95 with a slope of 1.05 and an intercept of -3.23 ppb.

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The chemiluminescence target discs for the GFAS and ROFI analysers were obtained from Bagus Consulting (Speyer, Germany) and changed in both instruments on 2, 6, 10, 14, 20, 24 and 28 August 2007. The disc surfaces were primed by pre-ozonisation at a nominal concentration of 100 ppb using a GFAS ozoniser unit for 90 min immediately before exchanging the disc in the analysers.

2.2 Analysis

As the dry chemiluminescence method provides a relative measure of ozone, absolute ozone concentrations, measured generally by a UV absorption instrument, are needed to calibrate the relative ozone signal. There are different approaches to obtaining absolute ozone fluxes from the relative signal and most authors do not clearly report what method is used. Since there has been no systematic investigation into the calculation methods, three different approaches have been used and compared here.

2.2.1 Eddy covariance data processing

The high frequency eddy covariance data series were de-spiked, but not de-trended and wind vectors were rotated according to a best plane of fit correction. The raw ozone time series was shifted according to the inlet lag time, based on the maximum correlation of vertical velocity w' and raw ozone signal X' . Fluxes were averaged over 30 min and filtered for stationarity according to Foken and Wichura (1996). Corrections for density fluctuations due to temperature and water vapour were applied (Lee et al., 2004). No further flux loss corrections were made. Data were also filtered for obstructed wind direction and for very low friction velocity, u_* , values below 0.03 m s^{-1} .

2.2.2 Absolute ozone fluxes by Ratio Method

The Ratio Method (RM) does not require the calculation of a calibration factor obtained by the relative ozone fluctuation measurements and absolute ozone concentrations. Instead, only average ozone concentrations at the frequency of the flux averaging period

are needed to obtain absolute fluxes.

The raw flux covariance of the vertical wind component with the raw O_3 signal in V ($\overline{w'X'}$, with units of $V \text{ m s}^{-1}$) is divided by the mean raw O_3 signal (X , units of V), to provide the deposition velocity v_d in m s^{-1} :

$$v_d = \frac{\overline{w'X'}}{X}. \quad (1)$$

To obtain the absolute flux of ozone (F_{O_3} in $\mu\text{g m}^{-2} \text{ s}^{-1}$), the deposition velocity is multiplied by ozone concentration (χ_{O_3} $\mu\text{g m}^{-3}$):

$$F_{O_3} = -v_d \times \chi_{O_3} \quad (2)$$

In this study, fluxes were calculated over 30 min periods, so the absolute flux can be described by:

$$F_{O_3(30)} = \frac{\overline{w'X'_{(30)}}}{X_{(30)}} \times \chi_{O_3(30)}. \quad (3)$$

One implied assumption in this method is that the analyser output is proportional to χ_{O_3} with a zero offset. If that is not the case, the absolute flux will be overestimated for negative offset values and underestimated for positive offset values.

2.2.3 Absolute ozone fluxes by Ratio Offset Method

The Ratio Offset Method (ROM) is based on the Ratio Method (Eq. 3) with the modification that accounts for the offset in the analyser. The offset value is effectively the mean output at zero ozone concentration, as obtained by a regression of the mean output, X , against absolute ozone concentrations, χ_{O_3} . As the offset might change on a disc by disc basis, an offset value is obtained for each disc period by a least squares

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fit using 15 min averaged data. (15 min averages resulted in higher regression coefficients than the use of 30 min data). For the number of values from $i = 1$ to N in each disc period, the offset (a) can be estimated as

$$a = \frac{\sum X_{(15)i} \times \sum \chi_{O_3(15)i} - \sum \chi_{O_3(15)i} \times X_{(15)i} \times \sum \chi_{O_3(15)i}}{N \times \sum \chi_{O_3(15)i}^2 - \left(\sum \chi_{O_3(15)i}\right)^2} \quad (4)$$

Subtracting the offset from the mean output, Eq. (3) is modified to obtain absolute half-hourly flux as follows

$$F_{O_3(30)} = \frac{\overline{w'X'}_{(30)}}{X_{(30)} - \frac{\sum X_{(15)i} \times \sum \chi_{O_3(15)i} - \sum \chi_{O_3(15)i} \times X_{(15)i} \times \sum \chi_{O_3(15)i}}{N \times \sum \chi_{O_3(15)i}^2 - \left(\sum \chi_{O_3(15)i}\right)^2}} \times \chi_{O_3(30)} \quad (5)$$

The Ratio Offset Method provides more accurate flux estimates than the Ratio Method when the offset is non-zero and changes from disc to disc period as is the case for the ROFI analyser, as illustrated for disc periods 1 and 4 in Fig. 1.

The error bars in F_{O_3} as calculated by ROM are estimated using two times the standard deviation, i.e. 2σ , in the offset value a obtained by the regression of raw ozone signal with absolute ozone concentrations (Eq. 4).

2.2.4 Absolute ozone fluxes by Disc Calibration Method

The Disc Calibration Method (DCM) applies a calibration factor to the raw flux ($V m s^{-1}$) for each disc period. The calibration factor is obtained by regressing the absolute ozone concentration measurements, χ_{O_3} , against the averaged analyser output (X). A linear fit using the least squares method is used assuming that the sensitivity is linear across the range of ozone concentrations and linear with time. The calibration factor and associated error depend on how well the voltage output correlates with absolute ozone concentration, and the choice of averaging time can make a difference. As for

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the offset (see above), calibration factors have been calculated using 15 min averaged data, as better correlations were achieved with 15 than 30 min data. The least square method allows estimation of the slope of the fit (c), for each disc period with data (X , χ_{O_3}) values ranging from $i = 1$ to N , viz

$$c = \frac{N \times \sum X_{(15)i} \chi_{O_3(15)i} - \sum X_{(15)i} \times \sum \chi_{O_3(15)i}}{N \times \sum X_{(15)i} - (\sum X_{(15)i})^2} \quad (6)$$

The slope of the fit or calibration factor c ($\mu\text{g m}^{-3} \text{V}^{-1}$) is multiplied with the raw flux ($w'X'$, with units of V m s^{-1}) to obtain absolute ozone fluxes:

$$F_{O_3(30)} = c \times \overline{w'X'}_{(30)} \quad (7)$$

The absolute flux can thus be described for each disc period separately as

$$F_{O_3(30)} = \overline{w'X'}_{(30)} \times \frac{N \times \sum X_{(15)i} \chi_{O_3(15)i} - \sum X_{(15)i} \times \sum \chi_{O_3(15)i}}{N \times \sum X_{(15)i} - (\sum X_{(15)i})^2} \quad (8)$$

Error bars for the flux values from DCM are calculated by using two times the standard deviation in the estimated calibration factor c .

The Disc Calibration Method has an implicit assumption that there is no degradation of sensitivity over the time period considered. This should be a reasonable assumption provided that the discs are changed before such degradation occurs. Here, only the slope of the regression (i.e. the calibration factor c) and not an intercept is used, as in this approach the constant intercept would not correlate with w' (which is zero on average) and thus the intercept would not contribute to the flux.

2.3 Data Quality Control procedure

To ensure that the data quality from the chemiluminescence analysers is satisfactory, the following quality control (QC) procedure has been implemented to identify and discard erroneous or low quality data points:

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1. Discard data points during logged downtime, power cuts etc.
2. As the first few hours of a disc period can contain spurious values, all data up to 2 h immediately after renewing the chemiluminescence target disc are deleted.
3. By visual inspection, compare time series (15 min) of the average ozone signal (V) and χ_{O_3} to find and remove outliers or periods of erroneous data points.
4. Plot 15 min (or other higher resolution than flux average period) χ_{O_3} vs. average output (voltage) on a disc by disc basis, colour coding with disc hours. Discard outliers and potentially clusters/periods of questionable data, especially occurring towards the end of a disc period, when disc sensitivity might be reduced. When a reduction in sensitivity occurs, the ratio between the relative voltage output and absolute ozone concentration is decreased. Figure 2 shows data from a period where a clear loss in sensitivity of the chemiluminescence target disc occurred with time (Disc Period 6 – closed symbols, Disc Period 7 – open symbols) and more variability occurred towards the end of the disc period. The step change in the ratio from Disc Period 6 to 7 also illustrates that the sensitivity can change from one disc to another.
5. Obtain calibration factors, i.e. slopes of a linear fit between χ_{O_3} and voltage output, and R^2 of the fit. If the R^2 value is above 0.5, the data quality is acceptable and the calibration factor can be applied to the raw voltage flux. If the R^2 value is below 0.5, it might be possible to remove further outliers/data values at the end of the disc period to improve the correlation. If this is not successful, the whole period has to be identified as not reliable and data points need to be discarded. Use the same dataset for obtaining the offset for ROM.
6. A final visual inspection for outliers is recommended on the absolute flux data as not all erroneous flux values correspond to erroneous average voltage output and are thus removed by the above steps.

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This procedure is recommended even when the RM and ROM are used because questionable discs and periods as well as individual outliers are removed with this protocol.

3 Results and discussion

3.1 Meteorological conditions and analyser performance

The UK national weather report (Weather, 2007) described August 2007 as a “quiet, rather cool month” and Scotland was mainly under the influence of low pressure systems, including fronts passing over the experimental site during the first three weeks. During the last two weeks of August, high pressure systems and anticyclonic circulation produced somewhat warmer temperatures and light winds. Overall, conditions were typical for the site with an average windspeed (at 2.5 m) of 3.35 m s^{-1} (range from 0.06 to 8.1 m s^{-1}), an average temperature of 10.9°C (range from 5.1 to 21.4°C) and an average relative humidity of 80.8% (range from 42.1 to 100%). The mean ozone concentration of 24.2 ppb, ranging from 4.0 to 57.8 ppb of ozone, is typical for the site and time of the year.

Data capture for absolute ozone concentrations from the UV absorption instrument was good with only 6% data loss as a result of a daily calibration routine and additional short downtime. For the eddy covariance measurements, the dry chemiluminescence analysers were running for 1506 half-hourly periods. After full quality control of the flux data, the final data capture was 75% for the GFAS and 62% for the ROFI analyser. The loss of data is attributed to the following effects: 2% of the data was discarded because of the removal of two hours at the beginning of each disc period, 2% as a result of the wind direction filter, 2% because of the low u_* filter, 7 and 8% for GFAS and ROFI respectively for conditions of non-stationarity and 12 and 25% for GFAS and ROFI respectively for downtime/outliers/end-of-disc period sensitivity loss (details see quality control procedure above).

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3.2 Comparison of the calculation methods and resulting uncertainties

The three different methods (RM, ROM and DCM) were used to calculate absolute ozone fluxes and Fig. 3 shows the time series for the ROFI and GFAS analyser for each method.

5 The comparison of the calculation methods for the whole dataset shows that the DCM produces smaller mean and median deposition fluxes than the RM and ROM (Table 1), with a smaller range of 30-min values. There is no obvious systematic difference between the RM and ROM for both analysers. The overall statistics can only reveal limited information about the data and it is evident from the time series (Fig. 3)
10 that there are some periods when the agreement of the different methods is better (e.g. 15 August 2007) than at other times (e.g. 10 August 2007).

Table 2 shows the basic statistics for each method and each analyser for each disc period. The median and mean deposition fluxes in each disc period are smallest for the DCM. In case of the GFAS, the ROM generally gives values that are in closer
15 agreement with the DCM than the RM. This is not the case for the ROFI where there is no such systematic difference between the RM and ROM. This would imply that the offsets on the GFAS are larger than on the ROFI which is indeed the case: Based on the absolute values of the offsets, the mean offset for the GFAS is 2.0 V and 1.1 V for the ROFI. For the GFAS 6 out of 7 offsets were negative whereas for the ROFI 2 out of
20 5 were negative.

The comparison of methods shows there can be differences in absolute ozone fluxes depending on the choice of calibration or calculation method. All three methods presented here are in principle viable options to calculate ozone fluxes, although it could be argued that the offsets in this study are large enough to preferably choose the
25 DCM or ROM over the RM. The observed differences between the methods add to the uncertainty of the calculated flux and for a substantial part, the difference cannot be explained by the error associated with the calibration fit as illustrated in Fig. 3. This naturally raises the question as to which method gives values closest to the true flux

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was 0.5 and for most discs this is an achievable value. However there are cases when the scatter can be considerable and a R^2 value of 0.5 is not achieved before removing data points at the end of the disc periods on the grounds of reduction in sensitivity. This shows that there can be periods when the assumption of linearity fails. If RM is used without the proposed data filter, these periods of non-linearity are not identified and in the absence of a non-linearity test for every flux averaging period, the approach used here gives confidence in the accuracy of the flux data from this method. Another inherent problem with RM is that it assumes that there is no voltage offset. In fact the offset values (as used in ROM) in this study were non-zero, both positive and negative, ranging from -4.2 to 3.2 V. To investigate whether the offset affects calculated fluxes more when the output voltage is low, the absolute difference in flux between the methods was regressed against the mean voltage output. The largest R^2 value was 0.1 which indicates that no correlation between the spread of values and mean output voltage exists and that the offset is somehow dependent on voltage output.

In this study, ROM could be considered preferable to the RM as the offsets in the analysers were non-zero and varied from disc to disc. Although accounting for the offset mostly improves the match with the DCM, the flux values are still not generally within the error as obtained by the variability in the parameter fits (Fig. 3).

To establish which calculation method is preferable, an empirical approach was used comparing the two analysers for each method and each disc period, checking which method provides the best match. Comparing the inter-quartile ranges (IQR) i.e. 50% of the data, GFAS and ROFI fluxes by RM do not agree for disc periods 4, 6 and 7. The ROM fluxes give a good agreement for all periods. The DCM data also agree well for all periods. Comparing DCM with ROM, the quality of agreement of the IQR and median and mean flux values varies with the disc periods, but the DCM does slightly better overall. As DCM produces the closest agreement between the GFAS and ROFI for most of the time, DCM is used in the following section “Comparison of analysers”.

The comparison of methods shows that the choice of calibration or calculation method can be a substantial source of uncertainty in the absolute ozone fluxes. Ex-

act data quality control and calibration procedures are often not described sufficiently when ozone fluxes from fast-response dry chemiluminescence analysers are reported. If results are to be compared, a clear description of the calibration method is essential for interpretation. If these analysers are to be used in a network of flux sites, a tested protocol on how the ozone data are to be treated needs to be implemented to minimise the source of uncertainty in fluxes from the choice of calibration method.

3.3 Comparison of analysers and uncertainties associated with the detection method

The comparison of the GFAS and ROFI analysers is made using fluxes calculated by the Disc Calibration Method. Focussing on the performance of the two analysers compared to each other, Fig. 4 shows the time series of ozone fluxes for the GFAS and ROFI instruments.

There are some days when the two analysers agree well, e.g. on 7, 10, 12 and 21 August 2007. However there are also days when the ROFI measures smaller fluxes than the GFAS, as on 13, 15, 16, 17, 22, 25 and 26 August 2007. The measurements can differ up to about a factor of two. This is starkly illustrated by fluxes on 21 and 22 August in Fig. 5, where one day with very good agreement is followed by a day with poor agreement.

To understand the differences in fluxes that occurred for the some periods and not others, it is important to exclude a change in instrument performance as the reason for the observed difference. Figure 6 shows the frequency-weighted, “log-binned” power spectra (top panels) and co-spectra (bottom panels) for a selected time during 12, 17, 21 and 26 August 2007. These are representative of periods when the analysers agree (12 and 21 August) and when they do not agree (17 and 26 August). It is evident that both analysers performed and compare relatively well for all the selected periods. The power spectra follow the $f^{-2/3}$ slope reasonably well as expected for turbulence dissipation within the inertial sublayer (Stull, 1988). For the period when fluxes do not agree the power in the GFAS is larger than in the ROFI (for $n = 0.1$ to 1) which could

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0.25 s, indicating a possible high frequency lag between the time series. The fans are designed to produce flow rates around 100 L min^{-1} and variability of about 10% should not impact on the sensitivity and response time (Guesten et al., 1992). The mean lag times of the ROFI were generally larger than those of the GFAS (mean ROFI 0.75 s and mean GFAS 0.50 s), and values close to the mean were found for all periods shown in Fig. 6, which implies that the analysers operated normally. The larger lag-times for the ROFI can be explained by the slightly larger internal volume of the inlet tube. The length of both inlets is the same with 1.2 m, but the inlet diameter of the ROFI inlet is larger by 0.007 m.

It is generally assumed that all factors but the target discs remain the same for both analysers. The difference in cross-correlation functions could potentially be due to the change in fan performance but it could also be a result of other factors: for instance there could be differences as a result of the different thermal properties of the analysers themselves or changes in the characteristics of the target discs are also possible.

If these ozone flux measurements had been made with only one of the analysers, each dataset would have been accepted as a good estimate of the flux. These measurements however show that, although absolute flux values might be reasonable in terms of expected ranges and the data have been deemed of sufficient quality by the adopted QC protocols, ozone fluxes still might potentially include a considerable uncertainty. Based on this study, the true half-hourly flux value might differ from the measurement by up to a factor of two (Fig. 5) under some circumstances.

The mean diurnal cycle in fluxes for both analysers shows that the fluxes on average agree during night time when fluxes are smaller, but larger discrepancies are evident during daytime, 9 a.m. to 6 p.m. (Fig. 8). This difference effectively constitutes the true error in the measurements and the mean error, as estimated from the mean GFAS and ROFI flux, can range from 0–23%. The overall daily mean error is 12%. The median diurnal cycles do not differ greatly from the mean cycles and differences in fluxes from the two instruments are equally evident in the median statistic. It might be argued based on the averaged diurnal profile that there must be a systematic difference

between the two analysers, but it is important to consider that the absolute differences can change dramatically from one day to the next (Fig. 5). This highlights the variability and uncertainty that is associated with these analysers.

3.4 The implications of uncertainties in ozone fluxes on deposition velocity and canopy resistance estimates

Ozone fluxes are often used to estimate the rate at which ozone is deposited to a surface as described by the deposition velocity v_d . To estimate the impact of the flux error on the deposition velocity, both GFAS and ROFI fluxes were averaged for every half hourly period. These data were then used to estimate a deposition velocity time series which is summarised as an average diurnal cycle in Fig. 9. The mean hourly deposition velocities range from 1 to 4 mm s⁻¹ and errors are largest during the daytime hours (Fig. 9), reflecting the same pattern in errors as for the deposition fluxes (Fig. 8). The mean daily deposition velocity is 2.3±0.3 mm s⁻¹, i.e. with an average error of about 13%.

Many surface-atmosphere exchange models are based on an electrical resistance analogy where the total resistance to deposition or uptake is the inverse of the measured deposition velocity. In its simplest form the total resistance (R_t) can be described as the sum of aerodynamic (R_a), laminar boundary layer (R_b) and canopy resistances (R_c). Based on total wind speed u and friction velocity u_* , a simple parameterisation for R_a is used, valid for neutral conditions,

$$R_a(z - d) = \frac{u(z - d)}{u_*^2}, \quad (9)$$

where z is height and d is the zero plane displacement height. Using the parameterisation from Seinfeld and Pandis (1998), estimates for R_b are calculated from the

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molecular diffusivity of ozone (D) and the kinematic viscosity of air (ν) as well as u_* :

$$R_b = \frac{5 (\nu/D)^{2/3}}{u_*}. \quad (10)$$

Values for ν of 1.42×10^{-4} and D of $1.37 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ (mean value from Massman, 1998) were used.

R_c was then estimated from the difference between R_t ($R_t = 1/\nu_d$) and ($R_a + R_b$) (Seinfeld & Pandis, 1998).

Figure 8 shows the median diurnal cycles of R_c based on deposition velocities of GFAS and ROFI. Differences in daytime resistances from the two analysers can be up to about 100 s m^{-1} . Whilst a comprehensive resistance error analysis is beyond the scope of this paper, Fig. 9 illustrates that whilst the relative diurnal trend in R_c from both analysers is generally the same, differences in absolute values do occur. Total or bulk canopy resistance R_c can be partitioned into a stomatal and non-stomatal component, by using the water vapour measurements to estimate the stomatal resistance. The non-stomatal resistance is then the difference between the total canopy resistance (R_c) and stomatal resistance. Estimates of the non-stomatal component are thus directly dependent on the absolute ozone flux. Investigations into the factors that control non-stomatal resistance require high quality ozone fluxes (Coyle, 2005) and uncertainties in the flux measurements propagate into the errors in the component fluxes and might contribute to the difficulty with which these factors can be identified clearly and quantified with confidence.

4 Conclusions and recommendations

Two dry chemiluminescence fast response ozone analysers have been run side by side for eddy covariance ozone flux measurements at a grassland site near Edinburgh, Scotland during August 2007. A detailed quality control procedure for the data obtained

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by the GFAS/ROFI type dry chemiluminescence ozone analysers has been produced. Uncertainties associated with this measurement method have been investigated and implications for surface-atmosphere exchange modelling considered.

Errors or uncertainties by the eddy covariance method have not been discussed in detail here and a full treatment of errors from eddy covariance in general can be found for instance by Businger (1986) and Finkelstein and Sims (2001). In this study the same sonic anemometer, logging and analysis software was used for both fast response ozone analysers, so some sources of error could be eliminated or can be at least considered the same for the ozone fluxes obtained by the two instruments. One potential source of error arises from the way the lag-time between the vertical velocity and fast ozone signals are determined. The underlying reason for this to be a source of error during some periods and not others could not be identified unambiguously. It is speculated that reported differences are likely to be due to the detection technique.

Three main sources of uncertainty have been identified with the use of fast response dry chemiluminescence analysers for eddy covariance ozone flux measurements:

(1) Uncertainty in the regression parameters is dependent on how well the fast ozone analyser's mean output correlates with the absolute ozone concentrations. Based on all disc periods, analysers and calculation methods, the 2σ error in the mean flux value can range from 8–34%. Overall for the whole dataset and both analysers and calculation methods, the mean 2σ error in the mean flux is 16%.

(2) Uncertainty as result of the chosen method to calculate absolute ozone fluxes arises from the different approach to “calibrate” the relative analyser output. Comparing the Ratio Method (RM) and Ratio Offset Method (ROM) on a disc by disc basis, 50% of the time the two methods agreed within the 2σ error associated with the regression parameters (see point 1). For the remaining half of the time, the flux values differed on average by 13%. Comparing the ROM and Disc Calibration Method (DCM) for each disc period, the methods agreed within error about 20% of the time. For the remaining time period, the flux values differed between the methods on average by 8%.

(3) Uncertainty as result of disc variability or analyser performance can cause the

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single most sizeable error. The analyser comparison for DCM revealed that there can be periods when the flux can be different by a factor of 2. The mean diurnal cycle reveals that true mean error can be up to 23%, with the largest errors on average occurring around midday. If measurements are made only with one analyser and no additional validation option is available, the error in the mean daily flux values from the variability in discs or analyser performance should be assumed to about $\pm 12\%$.

Uncertainties from point (1) can potentially be minimised by using a stricter quality control threshold for the regressions, i.e. a higher regression coefficient R^2 . This might result in a greater loss of data points that are not deemed of sufficient quality and there might be a trade off between final % data capture and % error in the regression parameters. Uncertainties from (2) are especially important to consider when ozone fluxes from different datasets are to be compared. Unless the exact procedure and calculation method is reported, differences in fluxes could be due to the choice of calculation method. It is recommended that a common data quality control and flux calculation method procedure is applied when these analysers are used in ozone flux networks. Minimising uncertainties from (3) could be reduced by increasing the knowledge of what causes the variability. For instance, laboratory studies testing how the high frequency response varies with an increased accumulated ozone exposure and whether the relationship with the mean output remains linear could be useful. There are other open questions such as what the exact surface activation mechanism during the pre-ozonisation stage is, and the influence of a range of humidities and temperatures on the disc sensitivity with an increased accumulated ozone exposure.

The GFAS/ROFI type dry chemiluminescence (DC) analysers have clear advantages over other fast response ozone instruments: they are simple in their operation, they have low power requirements and they are relatively lightweight, small and robust which makes them ideal for use in a variety of environments. The comparison of the two analysers in this study shows that on average the diurnal trend of ozone deposition is captured well. On some days there is an excellent agreement between the analysers and confidence in the accuracy of the ozone flux can be gained from that agreement.

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If for instance the ozone flux measurement overestimates the total deposition to the surface, the non-stomatal contribution will also be overestimated as a consequence. Non-stomatal sinks are generally understood to be surface removal processes and/or fast chemical reactions, e.g. with NO or fast VOCs such as sesquiterpenes, and the understanding of their relative importance will be improved by better quantification of the overall non-stomatal sink. To determine the sink by chemical reactions, additional measurements or modelling of the relevant species would be required in addition to the ozone flux measurements, but it is clear that better, more accurate ozone flux measurements are one important step to improving understanding of ozone sinks and destruction rates near the surface.

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Table 1. Statistics based on whole GFAS and ROFI flux datasets for all calculation methods, using paired samples only. All values are in units of $\text{ng m}^{-2} \text{s}^{-1}$.

		Min.	Lower Quart.	Median	Upper Quart.	Max.	Mean	2σ mean error
RM	GFAS	-914	-303	-195	-129	159	-218	-
	ROFI	-753	-220	-138	-87	105	-161	-
ROM	GFAS	-928	-250	-158	-104	45	-180	± 26
	ROFI	-632	-230	-147	-95	114	-170	± 33
DCM	GFAS	-420	-175	-108	-69	49	-125	± 17
	ROFI	-453	-147	-101	-68	45	-112	± 16

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Table 2. Basic statistics for each disc period for all methods RM, ROM, DCM for both GFAS and ROFI analysers, using paired samples only. Median values in bold and mean values in italic. 2σ error is the mean error for that disc period based on the standard deviation in the regression parameter fit. All values are in units of $\text{ng m}^{-2} \text{s}^{-1}$

	<i>Disc Period 1</i>		<i>Disc Period 2</i>		<i>Disc Period 3</i>		<i>Disc Period 4</i>		<i>Disc Period 5</i>		<i>Disc Period 6</i>		<i>Disc Period 7</i>	
	GFAS	ROFI												
RATIO METHOD (RM)														
Minimum	-914	-753	-486	-440	-582	-593	-553	-500	-516	-390	-624	-349	-417	-258
Lower Quart.	-337	-297	-314	-287	-335	-293	-273	-155	-248	-178	-343	-166	-206	-138
Median	-232	-225	-233	-209	-213	-204	-172	-115	-143	-101	-247	-108	-148	-97
Upper Quart.	-140	-130	-135	-139	-124	-116	-135	-80	-85	-57	-165	-77	-99	-69
Maximum	-39	-58	159	105	15	14	-31	-21	67	56	-87	-35	35	40
<i>Mean</i>	<i>-264</i>	<i>-234</i>	<i>-225</i>	<i>-210</i>	<i>-237</i>	<i>-212</i>	<i>-202</i>	<i>-120</i>	<i>-167</i>	<i>-118</i>	<i>-256</i>	<i>-122</i>	<i>-165</i>	<i>-108</i>
2σ error	n/a	n/a												
RATIO OFFSET METHOD (ROM)														
Minimum	-928	-632	-362	-482	-415	-604	-486	-510	-427	-357	-492	-516	-425	-289
Lower Quart.	-341	-254	-238	-309	-251	-299	-244	-157	-182	-161	-269	-259	-213	-162
Median	-235	-194	-175	-228	-213	-204	-151	-117	-114	-89	-185	-178	-153	-118
Upper Quart.	-144	-112	-102	-148	-84	-119	-118	-82	-49	-42	-123	-132	-104	-83
Maximum	-39	-46	61	114	9	15	-18	-22	45	48	-57	-80	38	55
<i>Mean</i>	<i>-268</i>	<i>-198</i>	<i>-170</i>	<i>-229</i>	<i>-170</i>	<i>-212</i>	<i>-177</i>	<i>-123</i>	<i>-124</i>	<i>-106</i>	<i>-198</i>	<i>-204</i>	<i>-171</i>	<i>-130</i>
2σ error	± 57	± 26	± 31	± 77	± 14	± 26	± 22	± 10	± 10	± 16	± 26	± 60	± 33	± 31
DISC CALIBRATION METHOD (DCM)														
Minimum	-420	-453	-307	-458	-347	-447	-292	-368	-360	-258	-365	-337	-399	-227
Lower Quart.	-209	-199	-156	-154	-220	-217	-166	-128	-153	-100	-197	-129	-149	-129
Median	-130	-143	-100	-114	-126	-149	-99	-96	-102	-67	-142	-99	-113	-90
Upper Quart.	-68	-93	-63	-82	-71	-90	-73	-68	-38	-27	-94	-70	-65	-62
Maximum	-24	-31	46	45	7	9	-10	-13	49	33	-42	-33	27	43
<i>Mean</i>	<i>-150</i>	<i>-153</i>	<i>-107</i>	<i>-121</i>	<i>-147</i>	<i>-153</i>	<i>-119</i>	<i>-100</i>	<i>-106</i>	<i>-69</i>	<i>-149</i>	<i>-103</i>	<i>-127</i>	<i>-98</i>
2σ error	± 31	± 19	± 18	± 23	± 13	± 16	± 15	± 8	± 9	± 9	± 22	± 26	± 21	± 23

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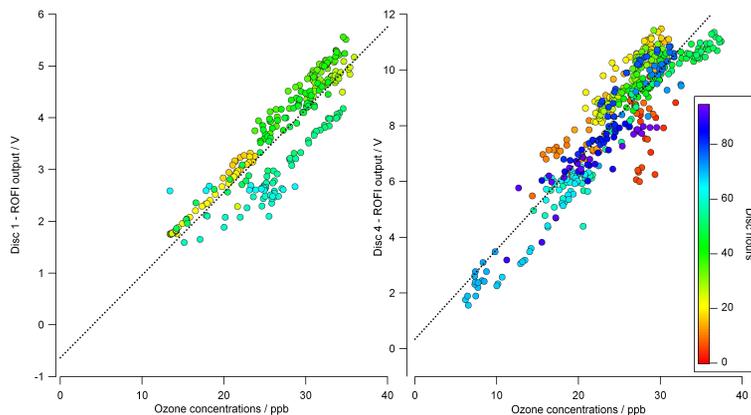


Fig. 1. Offsets in analyser output vary from disc to disc. Negative offset of -0.65 V for disc period 1 (left panel) and positive offset of 0.35 V for disc period 4 (right panel). The colour of the symbols is based on the number of hours the disc has been exposed to the atmosphere.

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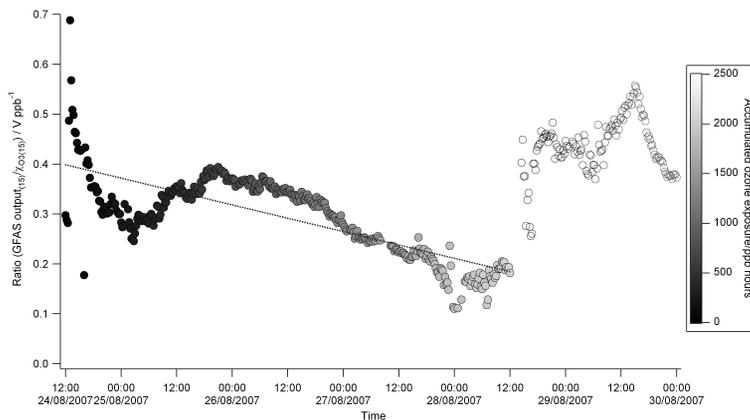


Fig. 2. Ratio of 15 min relative ozone concentration (GFAS mean output) and absolute ozone concentration for Disc Period 6 (closed symbols) and Disc Period 7 (open symbols). Fitted slope, i.e. trend in ratio is $-6.21 \times 10^{-7} V \text{ ppb}^{-1}$.

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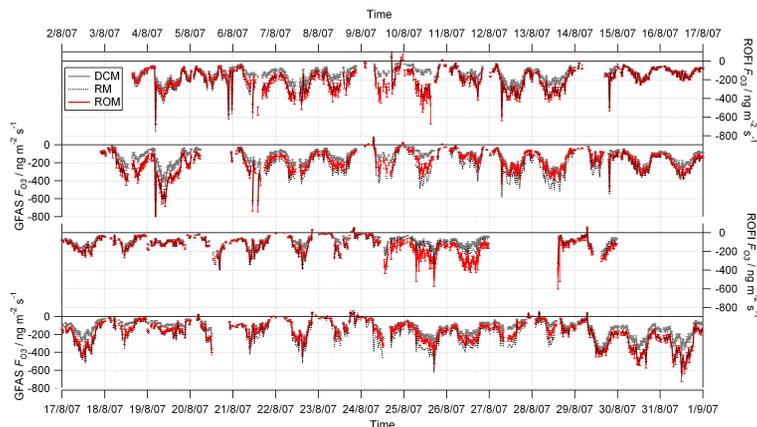


Fig. 3. Time series of ROFI and GFAS fluxes for each calculation method, with error bars based on $2\times$ standard deviation in the parameter fit of the calculation method. Disc Calibration (DCM, grey) and Ratio Offset Method (ROM, red). The Ratio method (RM) is the black dotted line. Top two panels cover the period 2 August 2007 to 17 August 2007 and bottom two panels show period 17/8/07 to 1 September 2007.

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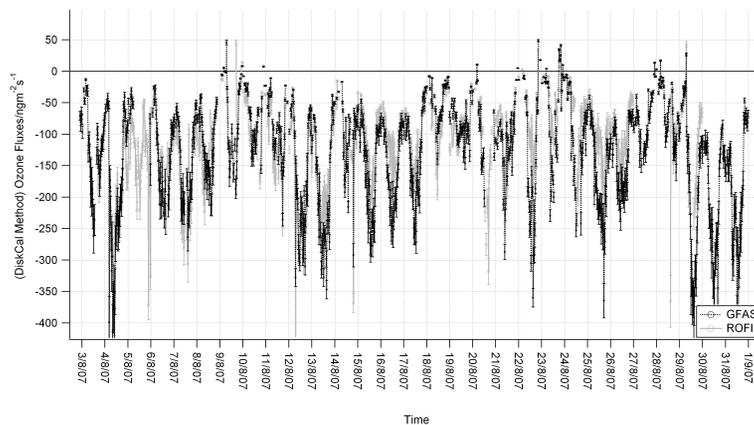


Fig. 4. Time series of fluxes by DCM for the GFAS (black dotted line) and ROFI (grey solid line) with error bars for the calculation method DCM.

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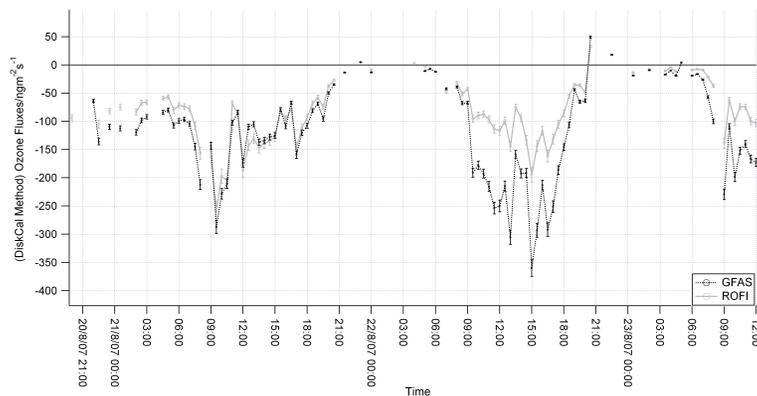


Fig. 5. GFAS and ROFI ozone fluxes for 21 and 22 August 2007. GFAS is the black dotted line and ROFI the grey solid line with error bars for the calculation method DCM.

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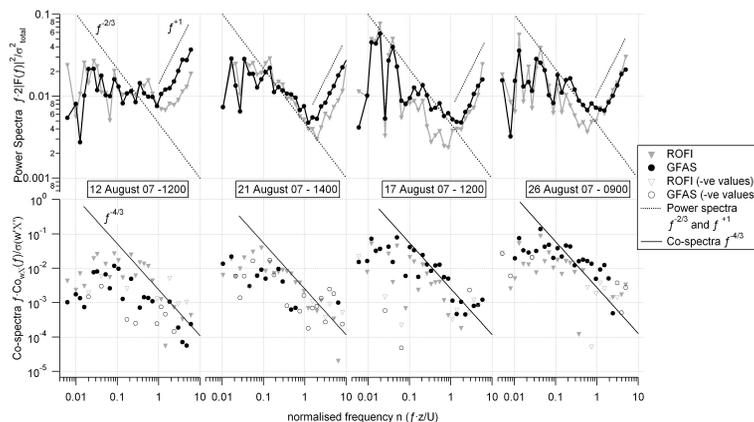


Fig. 6. Frequency weighted power spectra (top panels) for GFAS and ROFI analysers for the 12 and 21 August (when absolute fluxes agree) and 17 and 26 August (when absolute fluxes do not agree) and corresponding co-spectra (bottom panels) showing that high frequency noise in analyser (f^{+1} slope) is not correlated with w' and co-spectra follow $f^{-4/3}$ slope. ROFI – grey triangle and GFAS – black circle.

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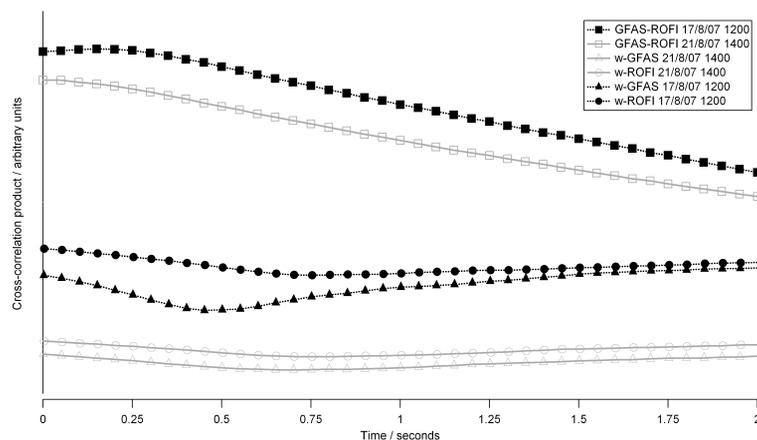


Fig. 7. Cross correlations between GFAS and ROFI output (top) and cross correlations of vertical windspeed w with both GFAS and ROFI (bottom). Black lines with solid symbols are for periods when fluxes do not agree (17 August 2007) and grey lines with open symbols for periods when fluxes agree (21 August 2007). Triangle symbols for GFAS, circle symbols for ROFI.

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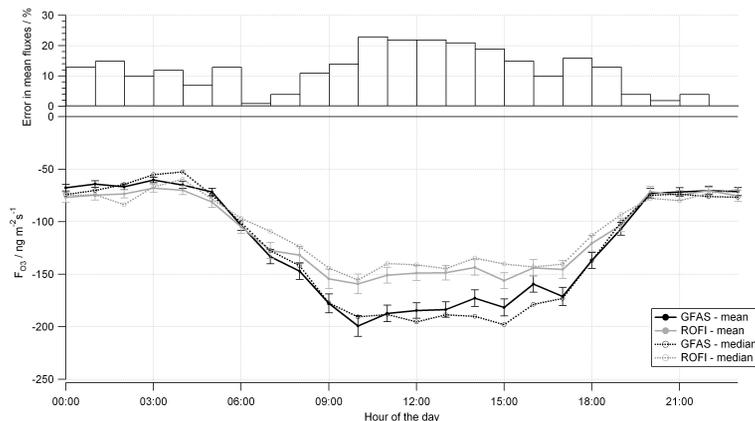


Fig. 8. Mean diurnal cycle of GFAS and ROFI fluxes with error bars from calculation method (bottom panel – GFAS in black, ROFI in grey, solid lines for mean, dotted lines for median) and mean error based on the discrepancy between mean GFAS and mean ROFI fluxes (top panel).

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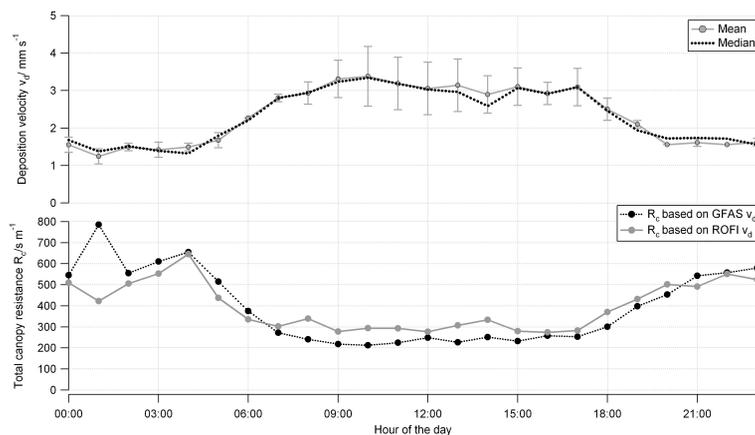


Fig. 9. Mean and median diurnal cycle of deposition velocity based on both GFAS and ROFI fluxes with error bars representing true error in the mean (top panel – mean values in grey symbols and solid line, median in black dotted line) and median diurnal cycle of total canopy resistance R_c based on median GFAS and ROFI v_d (bottom panel – R_c based on GFAS v_d in black, R_c based on ROFI v_d in grey).

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