Supplement of

Eddy-covariance data with low signal-to-noise ratio: time-lag determination, uncertainties and limit of detection

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**Supplementary Information:** Eddy covariance data with low SNR ratio: time-lag determination, uncertainties and limit of detection.

1. **Sensible heat, isoprene, and acetone fluxes**

   1.1 Site description
   Canopy scale flux measurements of sensible heat and volatile organic compounds (VOCs) were recorded over the Bosco della Fontana nature reserve situated north of Mantova in the Po valley, Italy (45° 11' 51'' N, 10° 44' 31'' E) as a part of the ECLAIRE (Effects of Climate Change on Air Pollution and Response Strategies for European Ecosystems) EC FP7 project. The nature reserve is a 233 ha area of broadleaf woodland dominated by four species: *Carpinus betulus, Quercus robur, Quercus rubra* and *Quercus cerris*. The measurement tower was situated to the south-west of a cleared area in the centre of the forest.

   1.2 Instrument setup
   VOC fluxes and concentrations were recorded using a high sensitivity Proton Transfer Reaction-Mass Spectrometer (PTR-MS, Ionicon Analytik GmbH, Austria). The PTR-MS was located in an air-conditioned cabin at the base of a 42 m open lattice walk-up tower. Air was sub-sampled from a PFA (O.D. ½", I.D. 9 mm) inlet line which ran from just below a Gill HS sonic anemometer mounted at 32 m above ground level, 5 m above the canopy top, to the cabin below. Data were logged from the sonic anemometer and the PTR-MS onto a single laptop using a program written in LabVIEW (National Instruments, USA).

   The PTR-MS operating conditions were controlled so that the reduced electric field strength (the ratio of the electric field strength, $E$, to the buffer gas number density, $N$) was kept to 122 Td ($1.22 \times 10^{-19} \, \text{V m}^2$). The drift tube temperature, pressure and voltage were set to 0.21 KPa, 45 °C and 550 V respectively. Measurements followed an hourly cycle with the instrument measuring zero air for 5 minutes followed by 25 minutes of flux measurements, 5 minutes scanning the full mass spectrum and a final 25 minutes of flux measurements. While in flux mode 11 protonated masses were monitored at $m/z$ 21, 33, 39, 45, 59, 61, 69, 71, 73, 81 and 137. These masses were assigned to the hydronium ion isotope, methanol, the water cluster isotope, acetaldehyde, acetone, acetic acid, isoprene, methyl vinyl ketone (MVK) and methacrolein (MARC), methyl ethyl ketone (MEK), a monoterpene fragment and monoterpens respectively. An instrumental dwell time of 0.2 s was used for both $m/z$ 21 and 39 for the other masses a dwell time of 0.5 s was applied, resulting in a total measurement cycle of 4.9 seconds.

   Calibration of the PTR-MS was performed using a gas standard containing isoprene, acetone, and 15 other volatile organic compounds (VOCs) at a concentration of approximately 1 ppmv (Ionicon Analytic GmbH, Austria).
1.3 Time-lag calculation

A constant prescribed time-lag was chosen by plotting a histogram of the empirical time-lags for isoprene, which had the largest observed fluxes and thus the cleanest cross-covariance functions. Each individual isoprene time-lag was determined by searching for the absolute maximum in the cross-covariance between isoprene mixing ratios and vertical wind velocity measurements (MAX method). Figure S1 displays a clear peak at 7.5 s which was subsequently used as the constant prescribed time-lag in this study. Many of the other measured VOCs showed weaker fluxes and hence did not display such a consistent time-lag. Consequently, the time-lags of all remaining masses were calculated by adding or subtracting the instrument dwell time from the prescribed isoprene time-lag. For example the acetic acid prescribed time-lag would be 7.0 s (7.5 s minus the 0.5 s dwell time). These measurements are presented in full by Acton et al. (2015).

![Figure S1 Histogram of the isoprene time-lags calculated by searching for the absolute maximum in the cross-covariance function.](image)

2. Benzene fluxes

Here we present a brief description of the benzene flux measurements used in this manuscript. For a more complete detailed description please refer to Valach et al. (2015).

VOC flux measurements were taken from a mast on the roof of the King’s College Strand building (51°30'42.43"N/0° 7'0.07"W, 31 m.s.l) in Central London between 7th August and 19th December 2012 as part of the ClearfLo (Clean air for London) project. Surrounding roads supported a medium traffic volume (annual average of 30k-50k vehicles per day, DfT 2014) with the river Thames situated 200 m to the
south. The site is classed as an urban site category 2 (intensely developed high
density urban with 2–5 storey, attached or very close-set buildings made of brick or
stone, e.g. old city core) by criteria from Oke (2006).

The inlet and CSAT3 sonic anemometer (Campbell Scientific) were mounted on a
triangular tower (Aluma T45-H) at approx. 50 m (2.2 x mean building height, z_H)
above ground level (Kotthaus and Grimmond, 2012). A 20 m ½” OD (I.D. 10 mm)
PFA tube inlet line was sub-sampled using the same high sensitivity proton transfer
reaction – mass spectrometer (PTR-MS, Ionicon Analytik GmbH, Innsbruck, Austria)
described above (see Lindinger et al., 1998; De Gouw and Warneke, 2007 for more
detailed description of the instrument), which was used to measure VOC
concentrations. Data from the sonic anemometer were logged at a frequency of 10
Hz and flux calculations were averaged over 25 minute periods. The mean line flow
rate was 81 l min^{-1} of which the PTR-MS sub sampled air at 0.25-0.3 l min^{-1}.

Operating parameters were controlled to maintain an E/N ratio of 122 Td. The
instrument was operated in MID (Multiple Ion Detection) and SCAN modes in the
following duty cycle: 5 min zero air (ZA), 25 min MID followed by a further 5 min
SCAN and 25 min MID mode. During the ZA cycle air was pumped through a
custom-made gas calibration unit (GCU) fitted with a platinum catalyst heated to 200
°C to provide instrument background values. The SCAN mode measured the
concentrations of a wide range of masses (m/z 21 – 206 using 0.5 s per m/z). In
MID mode, the quadrupole scanned 11 predetermined protonated masses with a
dwell time of 0.5 s for all but m/z 21 which was sampled at 0.2 s. The duty cycle
used comprised of the following masses: m/z 21 (indirectly quantified m/z 19 primary
ion count [H3^{18}O^+]), m/z 33 (methanol), m/z 39 (indirectly quantified m/z 37 first
cluster [H3^{16}O^+ H2^{16}O^+]), m/z 42 (acetonitrile), m/z 45 (acetaldehyde) m/z 59
(acetone/propanal), m/z 69 (isoprene/furan), m/z 79 (benzene), m/z 93 (toluene), m/z
107 (C2-benzenes) and m/z 121 (C3-benzenes).

Measurements of turbulence and VOC concentrations were logged on separate
computers which meant the two data sets had to be carefully synchronised during
post processing. Data synchronisation was achieved by searching for the absolute
maximum in a cross-covariance function between the vertical wind velocity and the
VOC concentrations. As well as correcting for drift between the two PC clocks, the
cross-covariance also accounted for the time-lag between sonic and PTR-MS
measurements associated with the long inlet line used. Acetone showed the clearest
cross-covariances which are shown in Fig. S2. A prescribed time-lag for acetone
was calculated based on the clustering of time-lags seen in Fig S2. Time-lags for all
other species were derived from this prescribed time-lag ensuring to take into
account the sequential nature of the PTR-MS duty cycle e.g. adding or subtracting
time depending on the m/z position relative to acetone in the PTR-MS duty cycle.
Figure S2. Time series of time-lags derived for acetone fluxes by searching for the maximum in the cross-covariance between the vertical wind velocity and acetone concentrations. The red line shows the prescribed time-lag which was fit to the data.

3. \(\text{N}_2\text{O}\) fluxes

Fluxes of \(\text{N}_2\text{O}\) were measured above two intensively managed grassland fields at the Easter Bush field site, Penicuik, Scotland in 2003. Concentrations of \(\text{N}_2\text{O}\) were measured using a tunable diode laser (TDL) absorption spectrometer (Aerodyne Research Inc., Billerica, MA, USA) at a rate of between 5 and 7 Hz. Further details of the instrument setup, site description and results can be found in Jones et al. (2011).

4. Particle number fluxes

Eddy covariance particle number fluxes were made in 2009 above Speulder Bos forest (52°22’N, 05°32’W, 20 m asl), a mature Douglas fir forest located in the Netherlands. Measurements were made 8 m above the top of the 28 m tree canopy from a 45 m tall walk-up tower. Particle number concentrations were measured at 10 Hz using an ultra-high sensitivity aerosol spectrometer (UHSAS, Droplet Measurement Technologies, Boulder, CO, USA) and combined with vertical wind velocity measurements from a sonic anemometer (R3, Gill Instruments, Lymington, U.K.) to give size segregated particle number fluxes (0.08 and 0.8 µm).

5. Bias effects of different time-lag determination methods

Figure S3 relates to Fig. 6 in the main manuscript and shows the average relative bias between unmodified and noisy sensible heat fluxes when calculated using a disjunct sampling interval of 5 s.
Figure S3. Average relative bias of a half-hourly flux as a function of the analyser signal-to-noise ratio for 31 days of sensible heat flux data. Fluxes were calculated using the disjunct eddy covariance method with a 5 s sampling interval. The signal-to-noise ratio of the temperature data was deteriorated to match pre-defined limits. The errors shown are relative to the sensible heat flux calculated using the unmodified temperature data and a constant (0 s) time-lag.

References


