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Supplement of

Canopy-scale flux measurements and bottom-up emission estimates of volatile organic compounds from a mixed oak and hornbeam forest in northern Italy

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1 Virtual disjunct eddy covariance lag time determination

The lag time between the measurement of vertical wind speed and concentration measurements using PTR-MS were calculated by identifying the absolute maximum value of the covariance function within a 30 s time window (MAX method, Taipale et al. 2010). Points for which the noise to signal ratio was greater than one were substituted for a flux calculated using a fixed lag time to prevent an overestimation of the flux from the MAX method. A histogram of isoprene lag times calculated using the MAX method is displayed in Figure S1. This histogram shows a clear maximum at 7.5 s, hence 7.5 s was taken to be the fixed isoprene lag time and lag times of other masses measured were calculated from this value ± the instrumental dwell time.

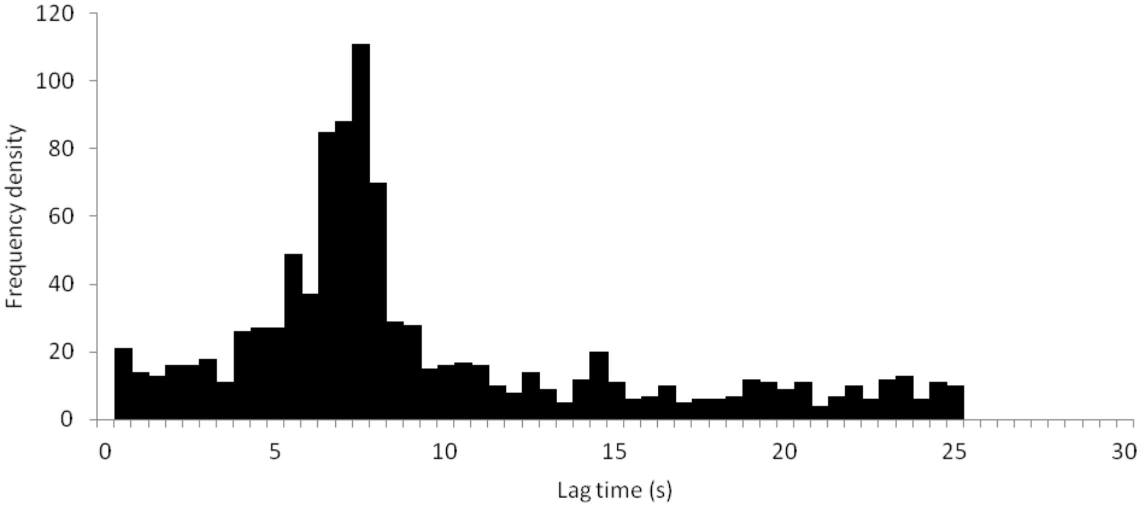


Figure S1. Histogram of isoprene lag times calculated using the MAX method

2 Assessment of the underestimation of total flux through the loss of low frequency fluxes

The loss of low frequency fluxes caused by the rotation of coordinates in order to set the mean vertical wind velocity to zero for each 25 minute averaging period is assessed in Figure S2. Sensible heat flux data were averaged over 50, 75, 100 and 125 minutes before coordinate rotation and plotted against the sum of two, three, four and five 25 minute coordinate rotated flux files respectively. The flux lost from the use of 25 minute averaging periods can be estimated from the gradient of the fitted line between the two fluxes. Eddies with a time period between 25 and 125 minutes were shown to carry an additional 2.8 % of the sensible heat flux. Therefore assuming that the frequency of VOC and sensible heat fluxes are comparable, 1.0-3.6 % of the VOC flux is lost by limiting the averaging period to 25 minutes.

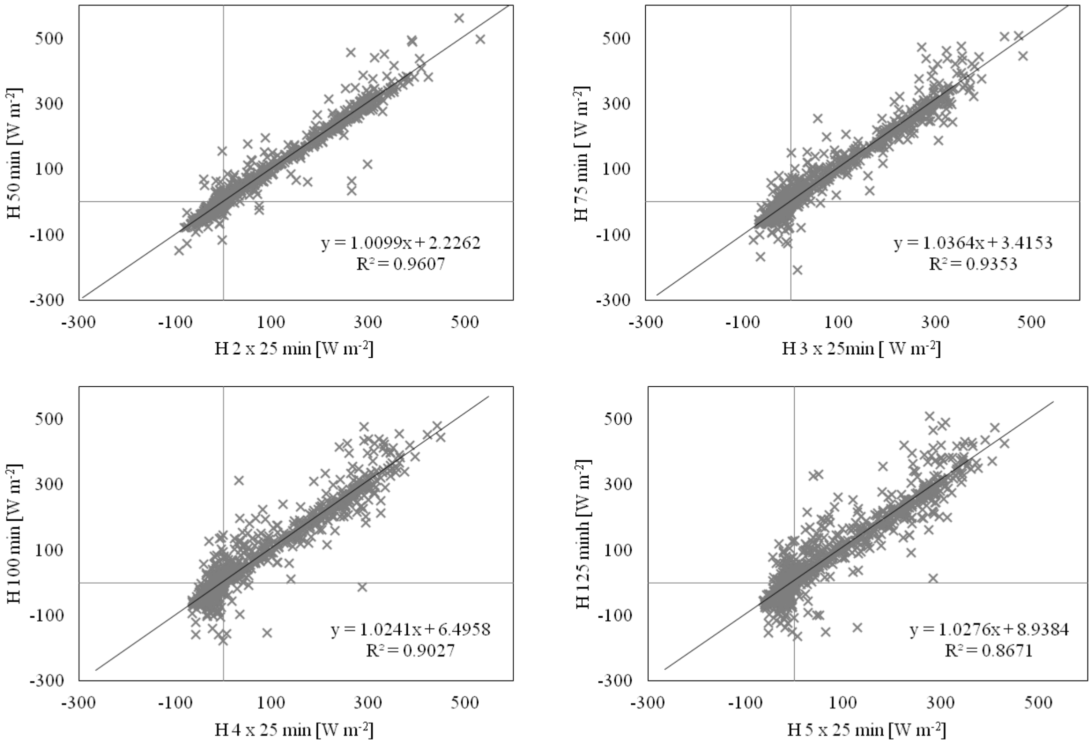


Figure S2. Plots of sensible heat flux (H) determined over differing averaging times during the intensive field campaign at Bosco Fontana. Solid line represents the best linear fit.

3 The uncertainty caused by disjunct eddy covariance

The uncertainty caused by disjunct eddy covariance was estimated by comparing the sensible heat flux (*H*) calculated using eddy covariance with *H* calculated using temperature measurements taken every 4.9 s. Figure S3 shows the correlation between H measured using eddy covariance and disjunct eddy covariance, as is shown the uncertainty introduced by disjunct sampling is 0.17 %.

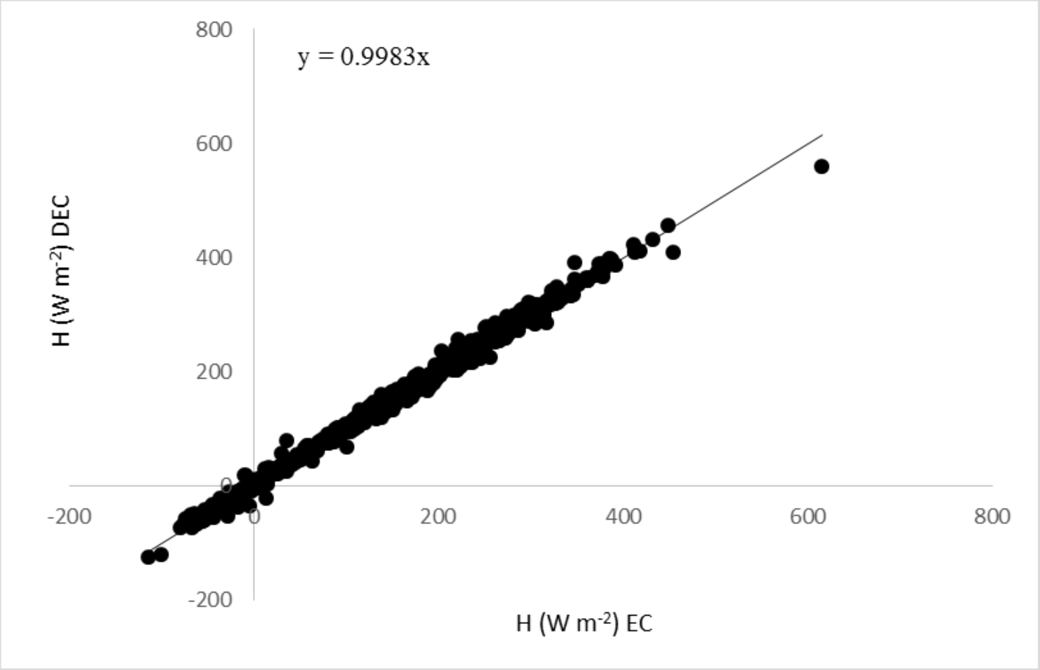


Figure S3. Sensible heat flux calculated (H) calculated using eddy covariance (EC) and disjunct eddy covariance (DEC).

4 Flux quality assessment

Each 25 min VOC flux file calculated from the PTR-MS data using the virtual disjunct eddy covariance (vDEC) method was subjected to three quality tests, each performed independently (Langford et al., 2010a). Flux files were flagged if they the mean frictional velocity over the 25 min averaging period dropped below 0.15 m s^{-1}, if they dropped below the limit of detection (Wienhold et al., 1994) or if they failed a stationarity test (Foken and Wichura, 1996). The percentage of flux files for each compound is displayed in Table S1.

Table S1. Summary of flux quality assessment test results

Compound	Turbulence test failed ($u_* < 0.15$ m s^{-1})	25 minute Limit of detection test failed (F < LOD)	Stationarity test fail ($\Delta s > 60\%$)	Passed all tests
Methanol (*m/z* 33)	29 %	79 %	6 %	25 %
Acetaldehyde (*m/z* 45)	29 %	83 %	3 %	18 %
Acetone (*m/z* 59)	29 %	88 %	3 %	11 %
Acetic acid (*m/z* 61)	29 %	81 %	7 %	14 %
Isoprene (*m/z* 69)	29 %	43 %	2 %	49 %
MVK + MACR (*m/z* 71)	29 %	85 %	3 %	15 %
MEK (*m/z* 73)	34 %	91 %	1 %	7 %
Monoterpenes (*m/z* 81)	34 %	81 %	0 %	19 %

5 Leaf surface temperature

The leaf surface temperature was estimated by extrapolation of ambient temperature using the resilience approach described by Nemitz *et al.* (2009). Figure S4 shows the diurnal patterns of average ambient and leaf surface temperature. At night average leaf surface temperature was found to be approximately 2 °C below the average ambient air temperature, during the day average leaf surface temperature peaked approximately 10 °C above the average ambient air temperature.

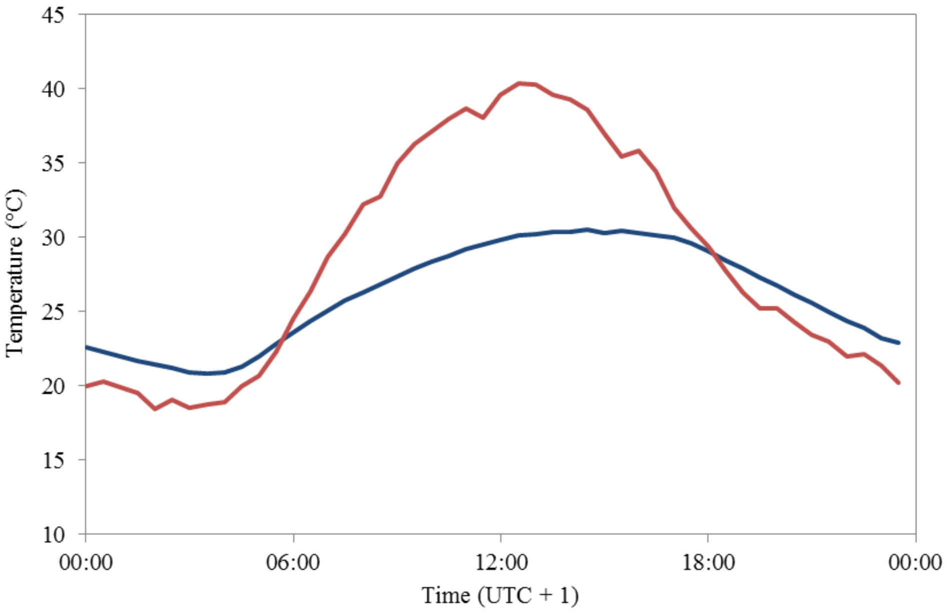


Figure S4. The diurnal pattern of average ambient temperature recorded 4 m above the canopy (blue) and leaf surface temperature (red).

6 Discussion of flux measurements

The fluxes and mixing ratios of the 8 masses monitored using the PTR-MS instrument during the field campaign at Bosco Fontana are discussed in more detail below.

6.1 Methanol (*m/z* 33)

The mass spectral peak at *m/z* 33 is commonly assigned to methanol (Misztal et al., 2011, Rinne et al., 2005) and published GC-PTR-MS measurements did not reveal any other significant contribution to this mass (de Gouw and Warneke, 2007). Here *m/z* 33 has been assigned to methanol, there may be some contribution to *m/z* 33 the O_2H^+ cluster ion but this should be removed in the background subtraction.

Methanol emission is of interest to atmospheric science and has been shown to have a significant effect on tropospheric oxidants (Tie et al., 2003). However, uncertainties in surface emission estimates result in significantly different model predictions of atmospheric oxidants (Jacob et al., 2005; Millet et al., 2008; Tie et al., 2003). Methanol fluxes have been recorded above temperate woodland (Karl et al., 2003; Park et al., 2013; Rinne et al., 2007; Spirig et al. 2005) and agricultural ecosystems (Custer and Schade 2007; Ruuskanen et al., 2011). The methanol mixing ratios recorded over the course of this study are displayed in

Figure S5. Methanol was the most abundant compound recorded during the campaign with a mean mixing ratio of 6.2 ppbv over the campaign which is comparable to the results obtained by Sprig et al. (2005) above a mixed European deciduous forest. The diurnal profile of the methanol mixing ratio is shown in Figure 6, it can be seen that mixing ratios are stable through the night at ca. 7 ppbv and drop to a low of ca. 5 ppbv in the mid-afternoon, most probably caused by expansion of the planetary boundary layer. The flux of methanol peaked at 0.49 mg m^{-2} h^{-1} with a mean day-time flux of 0.03 mg m^{-2} h^{-1} (Figure 5). Methanol deposition was observed in the mornings followed by a rapid increase in methanol emission in the late morning peaking in the early afternoon, a similar emission pattern of morning deposition followed by afternoon emission was observed by Langford et al. (2010a) and Misztal et al. (2011) above tropical rain forest and oil palms in South East Asia.

Biogenic methanol emission stems from a number of sources the largest of which is the demethylation of pectin in the primary cell walls (Galbally and Kirstine, 2002; Fall 2003). The strong temperature dependence of emissions reported previously (Hayward et al., 2004; Custer and Schade, 2007) indicates enzymatically driven emission or release from stored pools (inside the leaf or in water on the leaf surface). However, this was not observed in this study (data not shown suggesting that emission directly resulting from the enzymatically controlled demethylation of pectin is unlikely to be the sole source of methanol at this site. Other possible sources of methanol include emissions from decaying biomatter (Warneke et al., 1999; Grey et al., 2010) and as a result of herbivore feeding on the local vegetation and other wounding events (von Dahl et al., 2006; Arneth and Niinemets, 2010).

As a result of its low Henry’s law constant methanol can be lost from atmosphere through precipitation, wet deposition and dry deposition (Riemer et al., 1998; Seco et al., 2007). While the rain immediately preceding measurements and on the 6th of July corresponded with a period of lower methanol mixing ratios no drop was observed immediately following rainfall. This suggested that lower methanol mixing ratios were not caused by the rain event but by air mass change prior to the rain itself as shown by Schade and Goldstein (2006). There is also evidence (Asensio et al., 2007) that soil may act as a sink of bVOCs, this may therefore also be a contributing factor to the methanol deposition observed in the mornings but from our findings it is impossible to determine whether the sink driving the downwards flux was the soil, plant surfaces (wet or dry), the stomata or a combination of the above.

6.2 Acetaldehyde (*m/z* 45)

The signal measured at *m/z* 45 was attributed to acetaldehyde, while there may be a small contribution at this nominal mass from CO_2 this was corrected for by background subtraction. It has been reported that acetaldehyde may be formed as an artefact following the reaction of ozone with impurities in the inlet line (de Gouw and Warneke, 2007) but no correlation was observed between ozone and acetaldehyde so this is not thought to be a significant source of acetaldehyde in these measurements.

Together with formaldehyde, methanol and acetone, acetaldehyde is one of the major oxygenated volatile organic compounds in the atmosphere and plays a significant role in atmospheric chemistry (Andrews et al., 2012; Millet et al., 2010). Acetaldehyde emission has previously been reported from woodland (Karl et al., 2002; Karl et al., 2003) and grassland (Custer and Schade, 2007; Ruuskanen et al., 2011), and the close proximity of the forest at Bosco Fontana to urban areas means that a contribution from anthropogenic sources to the observed ambient concentrations is also likely (Langford et al., 2009; Langford et al., 2010b). Acetaldehyde mixing ratios above the Bosco Fontana nature reserve peaked at 3.4 ppbv from a mean value of 1.5 ppbv, a time series of acetaldehyde mixing ratios is displayed in Figure S5. The acetaldehyde daily profile, shown in Figure 3, shows a stable night time mixing ratio of ca. 1.5 ppbv dropping to ca. 1 ppbv in the mid-to-late afternoon. The daily mean acetaldehyde flux is displayed in Figure 5. While the peak acetaldehyde flux was recorded at 0.44 mg m^{-2} h^{-1} the daily maximum was usually ca 0.12 mg m^{-2} h^{-1}. The daily flux profile shows that emission fluxes increased until the early afternoon before stabilizing and then decreasing to zero in the evening. This represents a lower emission flux than reported previously from both a pine canopy (Rinne et al., 2007) and mixed forest (Karl et al., 2003). This may be related to the relatively small area of the forest at Bosco Fontana as the surrounding farmland is unlikely to contribute significantly to the acetaldehyde flux (Custer and Schade, 2007).

Millet et al. (2010) recently used the GEOS-Chem atmospheric chemistry model to identify acetaldehyde sources and sinks, identifying hydrocarbon oxidation as the largest acetaldehyde source. Both isoprene and monoterpenes have been identified as acetaldehyde precursors (Lee et al., 2006; Luecken el al., 2012), no correlation was seen between acetaldehyde and isoprene mixing ratios over the canopy at Bosco Fontana but a weak correlation (R^2 = 0.27) was observed between acetaldehyde and monoterpene mixing ratios. As well as formation from hydrocarbon oxidation, acetaldehyde is also directly emitted by plants in response to wounding (Brilli et al., 2011; Loreto et al., 2006) and via ethanolic fermentation in leaves and roots subject to anoxic conditions (Fall, 2003; Seco et al., 2007; Winters et al., 2009). In addition to emission from plants Schade and Goldstein (2001) also determined that soil and litter emission of acetaldehyde contributed significantly to the canopy-scale flux. As well as acting as a source of acetaldehyde into the atmosphere it has been shown that some tree species may act as an acetaldehyde sink at high ambient concentrations (Rottenberger et al., 2005; Seco et al., 2007). However, significant net deposition fluxes were not observed in this campaign.

The correlation between acetaldehyde and monoterpene mixing ratios indicates that there is likely to be a significant contribution from hydrocarbon oxidation to the acetaldehyde mixing ratio. However, the early afternoon peak in acetaldehyde flux coupled with no correlation with ozone suggests that the observed flux is predominantly of biogenic origin and most probably originates from ethanolic fermentation in leaves and soil.

6.3 Acetone (*m/z* 59)

The mass spectral peak observed at *m/z* 59 may be attributed to acetone or propanal. However, previous studies have indicated that contribution of propanal to this mass is low, 0-10 %, (de Gouw and Warneke, 2007) therefore *m/z* 59 is here attributed to acetone.

Acetone is one of the most abundant oxygenated VOCs in the atmosphere and fluxes of acetone have been recorded over both anthropogenic (Langford et al., 2009; Langford et al., 2010b) and woodland environments (Karl et al., 2002; Karl et al., 2003). Acetone may also play a significant role in tropospheric chemistry as it can act as a source of HOx radicals in the upper troposphere leading to increased ozone production (Singh et al., 1995).

At the Bosco Fontana site acetone was the second most abundant volatile recorded after methanol, the mixing ratio remained constant throughout the day (Figure 3) with a mean value of 3.2 ppbv. This value was higher than mixing ratios previously observed over hardwood forest where average mixing ratios have been reported in the range of 1.2-1.9 ppbv (Kalogridis et al., 2014; Karl et al., 2003) but comparable to mixing ratios recorded over ponderosa pine (Goldstein and Schade, 2000). No significant acetone flux was observed at night, the flux appeared to increase in the afternoon but remained below the LoD throughout the day (Figure 5). The mean day-time emission of 0.03 mg m^{-2} h^{-1} was significantly lower than that observed by Karl et al. (2003) above a mixed hardwood forest.

Acetone is produced in the atmosphere through the oxidation of VOC precursors (Jacob et al., 2002; Lee et al., 2006). It is also emitted directly by plants into the atmosphere via a number of pathways, for example acetone is produced as a by-product of cyanogenesis and is then released into the atmosphere (Fall, 2003). Acetone may also be produced by acetoacetate decarboxyation in the soil (Fall, 2003). While Jacob et al. (2002) found emission from plant decay inconsistent with the seasonal cycle observed at European sites, Karl et al. (2003) reported emission from decaying biomass based on the emission factors calculated by Warneke et al. (1999). Enhanced acetone emission is also commonly reported following plant wounding events (Davison et al., 2008; Ruuskanen et al., 2011).

6.4 Acetic acid (*m/z* 61)

The mass spectral peak observed at *m/z* 61was assigned to acetic acid, this is supported by de Gouw et al. (2003) who observed a correlation between *m/z* 61 and acetic acid. This mass spectral peak, assigned to acetic acid, has been detected previously over a Mediterranean oak forest (Kalogridis et al., 2014).

The dominant source of acetic acid in the troposphere is the photochemical oxidation of biogenically emitted hydrocarbons (Glasius et al., 2001; Lee et al., 2006, Paulot et al., 2011), and the direct emission of acetic acid into the atmosphere is comparatively low. However, acetic acid is emitted into the atmosphere by vegetation (Seco et al., 2007) with emission shown to be predominantly from tree species rather than crop plants (Kesselmeier et al., 1998). Emission is triggered by light (Kesselmeier et al., 1998; Staudt et al., 2000) and has been seen to correlate with transpiration (Kesselmeier et al., 1998; Seco et al., 2007). Acetic acid emission has also been recorded following stress events such as cutting (Ruuskanen et al., 2011) and herbivory (Bartolome et al., 2007; Llusià J. and Peñuelas, 2001; Scutareanu et al., 2002).

Field-scale emission of acetic acid from *Citrus sinensis* L. was observed by Staudt et al. (2000) in the noon and afternoon with deposition occurring in the early morning and night.

Sinks of acetic acid include wet deposition and dry deposition with wet deposition the most important sink (Paulot et al., 2011). Photochemical losses are low as acetic acid may be considered as the final product of the photo-oxidation of many BVOCs. Kuhn et al. (2002) hypothesised that the primary control on acetic acid uptake by plants was the ambient mixing ratio and that a mixing ratio compensation point exists. When acetic acid mixing ratios are above this compensation point acetic acid will be absorbed by plants and when ambient mixing ratios drop below this point acetic acid will be emitted. Soil may also act as an acetic acid sink with uptake of acetic acid by a Mediterranean forest soil observed by Asensio et al. (2007). Deposition of acetic acid has been reported both over tropical forests (Karl et al., 2004; Langford et al., 2010a) and pine woodland (Karl et al., 2005), but fluxes of acetic acid over temperate deciduous woodland have yet to be reported.

During the Bosco Fontana campaign the acetic acid mixing ratios dropped in the early morning and remained relatively stable at ca. 1.5 ppbv throughout the day before rising again to ca. 2.5 ppbv, in the evening (Figure 3). This likely corresponded to the changing height of the planetary boundary layer. In the latter half of the campaign a large increase in mixing ratio was observed at ca. 21:00 each day peaking at 14.9 ppbv on the 29th June (Figure S5), these spikes correspond to a northerly wind direction but no source could be identified. The acetic acid flux was low but appears to show a pattern similar to that observed by Staudt et al. (2000) with deposition observed in the morning followed by emission in the afternoon (see Figure 5). The change from acetic acid deposition to emission occurs when the ambient mixing ratio drops below ca.1.9 ppbv which is within the compensation point range calculated by Kuhn et al. (2002) for tropical tree species but no conclusions can be drawn with confidence from such a weak flux.

6.5 Isoprene (*m/z* 69)

Isoprene measurements using the PTR-MS mass spectral peak at *m/z* 69 have been shown to agree with GC-MS measurements (Kuster et al., 2004). Isoprene fluxes recorded using PTR-MS have been reported previously from temperate forest canopies (for example Karl et al., 2003) and given the clear diurnal cycle of *m/z* 69 fluxes and mixing ratios (Figures 3 and 5) coupled with the presence of two significant isoprene emitting species (*Quercus robur* and *Quercus rubra*). In the Bosco Fontana forest canopy *m/z* 69 was assigned to isoprene. Interferences from furan, associated with biomass burning, as well as a number of BVOCS, in particular 2-methyl-3-buten-2-ol (MBO) have previously been reported at *m/z* 69 (de

Gouw and Warneke, 2007). While large concentrations of MBO have been observed over coniferous forests in the USA (Goldan et al., 1993) emission has not been reported from European deciduous species and as biomass burning in the Italian summer is low a significant contribution from these species at *m/z* 69 was considered to be unlikely.

Four tree species: *Carpinus betulus, Quercus robur, Quercus rubra* and *Quercus cerris* (Dalponte et al., 2007) make up ca. 75 % of the Bosco Fontana canopy, and of these only *Quercus robur* and *Quercus rubra* are known to emit isoprene (Pérez-Rial et al., 2009; Pier, 1995). Owing to isoprene emission only occurring during the day time coupled with a short atmospheric lifetime both mixing ratios and fluxes peaked in the afternoon, with fluxes peaking ca. 2 h before mixing ratios and dropping to zero at night. At the Bosco Fontana field site large day-to-day variations in the daily maximum isoprene volume mixing ratios and fluxes were observed due to changing environmental conditions. Isoprene volume mixing ratios peaked in the late afternoon with maximum values ranging from 0.8 ppbv to 4.8 ppbv (Figure S5). The mean above canopy isoprene mixing ratio (1.1 ppbv) was comparable to that observed by Karl et al. (2003) above a North American hardwood forest but lower than the 1.2 ppbv observed by Kalogridis et al. (2014) above a French oak forest. This is to be expected given that 90 % of this canopy was made up of the isoprene emitting species *Quercus pubescens*. In addition, Bosco Fontana represents a relatively small area of isoprene emitting vegetation in mainly agricultural surroundings, with low isoprene emissions, possibly with the exception of some fields of poplar plantations. This implies that, as local isoprene emissions shut off at night, low-isoprene air is advected into the forest, giving rise to lower night-time concentration that found in extensive isoprene emitting areas.

The mean day-time isoprene flux, 1.91 mg m^{-2} h^{-1}, was higher than that observed by Laffineur et al. (2011) over a European temperate mixed forest but lower than the flux reported by Spirig et al. (2005) and Kalogridis et al. (2014) over European mixed broadleaf and oak forests, respectively.

6.6 MVK and MACR (*m/z* 71)

The structural isomers MVK and MACR are both detected at *m/z* 71 when analysed using PTR-MS. Analysis using PTR-MS only enables compound identification on the basis of nominal mass so it is not possible to separate these species, and for this reason together with their common chemical origin, they will be treated together here. Previous studies have shown good agreement between PTR-MS and GC-MS measurements of MVK+MACR (de

Gouw et al., 2003) although a significant contribution from crotonaldehyde at this mass has also been reported (Karl et al., 2007).

MVK and MACR are the main products formed following the first stage of isoprene oxidation in the atmosphere (Atkinson and Arey 2003a), accounting for 80 % of the carbon. Isoprene oxidation predominantly occurs via reaction with OH during the day and with NO_3 at night with a relatively small contribution from ozone (Monks et al., 2009). It has been proposed that isoprene oxidation to MVK and MACR may occur within the plant (Jardine et al., 2012; Llusià et al., 2011) as well and the atmosphere. MACR can also be directly produced within plants as a biproduct in the production of cyanogenic glycosides (Fall, 2003). Once formed MVK and MACR may undergo further atmospheric oxidation and photochemical reactions (Millet et al., 2010; Atkinson and Arey, 2003b) or be deposited onto the canopy (Karl et al., 2010).

Fluxes and mixing ratios of MVK and MACR have previously been reported over deciduous forests (Apel et al., 2002; Kalogridis et al., 2014; Spirig et al., 2005). Above the canopy of the Bosco Fontana natural reserve a positive flux of MVK + MACR (Figure 5) was observed peaking in the early afternoon with a day-time mean flux of 0.05 mg m^{-2} h^{-1}, suggesting significant within canopy oxidation of isoprene. This value is comparable to that observed by Spirig et al. (2005) over a European deciduous forest. The flux of MVK + MACR dropped below the limit of detection at night which was expected as isoprene mixing ratios fell to ca. 0 ppb overnight (Figure 3). As with previous campaigns over European deciduous forest no clear evidence for deposition was observed (Kalogridis et al., 2014; Spirig et al., 2005), this is in contrast to measurements over more remote tropical forests where deposition is usually reported (Karl et al., 2004; Langford et al., 2010a; Misztal et al., 2011). This suggests that deposition of these species to the forest canopy is low and that these species are lost through atmospheric transportation or undergo further reaction prior to being deposited. At the Bosco Fontana natural reserve, this is likely to be driven by the high oxidative capacity of the Po valley atmosphere. The mean MVK and MACR mixing ratio observed was 0.51 ppbv.

6.7 MEK (*m/z* 73)

The mass observed at *m/z* 73 was assigned here to methyl ethyl ketone (MEK), however the isomeric compound butanal could also contribute to this signal (Table 1). Previous studies have shown a quantitative agreement between PTR-MS and GC analysis of MEK at *m/z* 73

(Davison et al., 2008; de Gouw et al., 2006) but measurement is complicated by the humidity dependent background contribution from $H_3O^+(H_2O)_3$.

MEK can be emitted directly from some plant species as a by-product of hydrogen cyanide production from lotaustralin (Fall, 2003). MEK emission has predominantly been reported following plant wounding events such as grass cutting (Davison et al., 2008; Karl et al., 2001; Llusià et al., 2011) and insect herbivory (Peñuelas et al., 2005; Pinto et al., 2007). As well as direct emission MEK may also be formed photochemically (Luecken et al., 2012). MEK has been recorded over oak (Kalogridis et al., 2014) and coniferous forests (Müller et al., 2006), with mixing ratios peaking at 0.15-0.51 ppbv and 1.8 ppbv respectively. Above the canopy at Bosco Fontana MEK mixing ratios fell between these values peaking at 1.0 ppbv (Figure 3). MEK mixing ratios peaked at night before dropping to a low in the late afternoon, most likely caused by dilution in the expanding planetary boundary layer. Fluxes of MEK have not been reported in the literature and few of the flux files from this campaign passed the quality tests, the daily averaged flux (Figure 5), however, showed a low emission of MEK in the afternoon with a mean day-time flux of 0.02 mg m^{-2} h^{-1}.

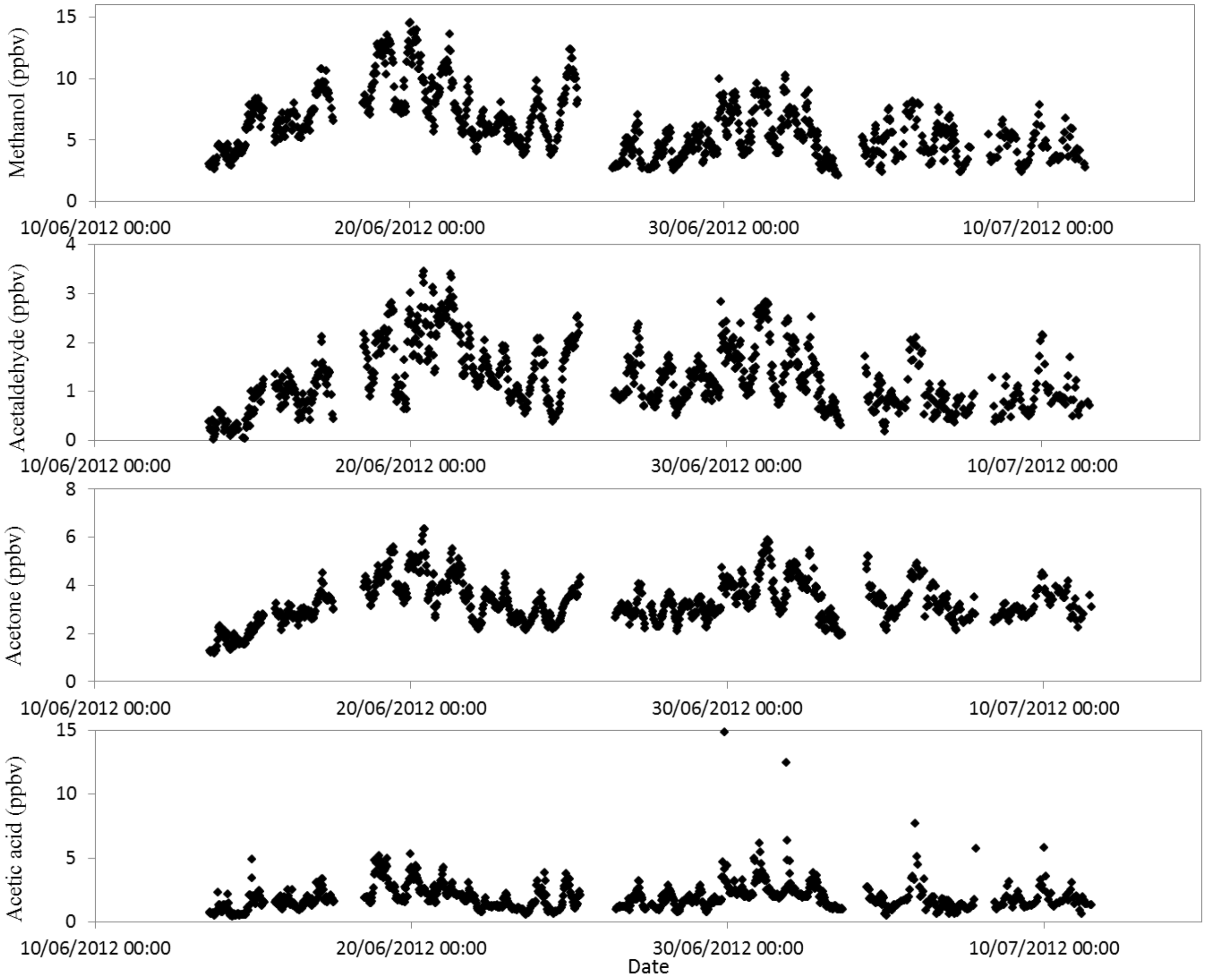
6.8 Monoterpenes (*m/z* 81)

Measurement of monoterpenes using PTR-MS is complicated by the differing fragmentation patterns of the numerous monoterpene species, however monoterpenes are commonly measured using PTR-MS at *m/z* 137 and 81 corresponding to the protonated parent ion and a principle fragment ion respectively (de Gouw and Warneke, 2007). Owing to poor instrumental sensitivity at higher atomic mass units (amus) the monoterpene fluxes and mixing ratios reported here are calculated from *m/z* 81. While there could be some contribution from sesquiterpene and hexenal fragment ions at this mass, previous studies have demonstrated that this signal can be assigned to monoterpenes (de Gouw et al., 2003; Rinne et al., 2005). Variability in the ratio between parent and fragment ions was limited by ensuring the *E/N* ratio was held constant throughout the measurements period.

Many plant species, including the four dominant species in the Bosco Fontana canopy, have been shown to emit monoterpenes (Isebrands et al., 1999; König et al., 1995; Owen et al., 2001; Pérez-Rial et al., 2009). Monoterpenes are emitted from plants both directly and from stored pools such as glandular trichomes and resin ducts (Maffei, 2010). Emission is driven by temperature (Tarvainen *et al.*, 2005) and also occurs as a response to both biotic

(Copolovici et al., 2011; Peñuelas et al., 2005) and abiotic (Kaser et al., 2013; Llusià et al., 2002) stress. As well as emission from plants, low levels of monoterpene emission have also been reported from litter and soil (Gray et al., 2010; Hayward et al., 2001; Leff and Fierer, 2008).

Above the Bosco Fontana forest canopy monoterpene fluxes peaked in the early afternoon with a mean day-time flux of 0.12 mg m^{-2} h^{-1} (Figures 4 and 5) which is comparable to the flux observed by Spirig et al. (2005) above a European mixed deciduous forest but much lower than those observed by Davison et al. (2009) over a macchia ecosystem in western Italy. As was observed by Spirig et al. (2005) the monoterpene flux dropped to ca. 0 mg m^{-2} h^{-1} at night. Laffineur et al. (2011) detected a weak temperature dependent monoterpene flux at night over a mixed European forest, this discrepancy may be due to larger emission from monoterpenes stored in pools from the coniferous species present in the mixed forest. While monoterpene deposition has previously been observed (Bamberger et al.2011) no net deposition was observed above the canopy at Bosco Fontana. The monoterpene mixing ratios followed a diurnal cycle with values peaking at ca. 0.2 ppbv at mid-day, dropping to ca. 0.18 ppbv at night (Figures 3 and 4). The mean monoterpene mixing ratio observed (0.2 ppbv) was much higher than the 0.06 ppbv observed by Kalogridis et al. (2014) over a Mediterranean oak forest but were within the 0.13-0.30 ppbv range of values recorded by Davison et al. (2009) and comparable to the mixing ratios observed by Spirig et al. (2005).


Methanol (ppbv)
15
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30/06/2012 00:00
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Acetaldehyde (ppbv)
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Acetone (ppbv)
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Acetic acid (ppbv)
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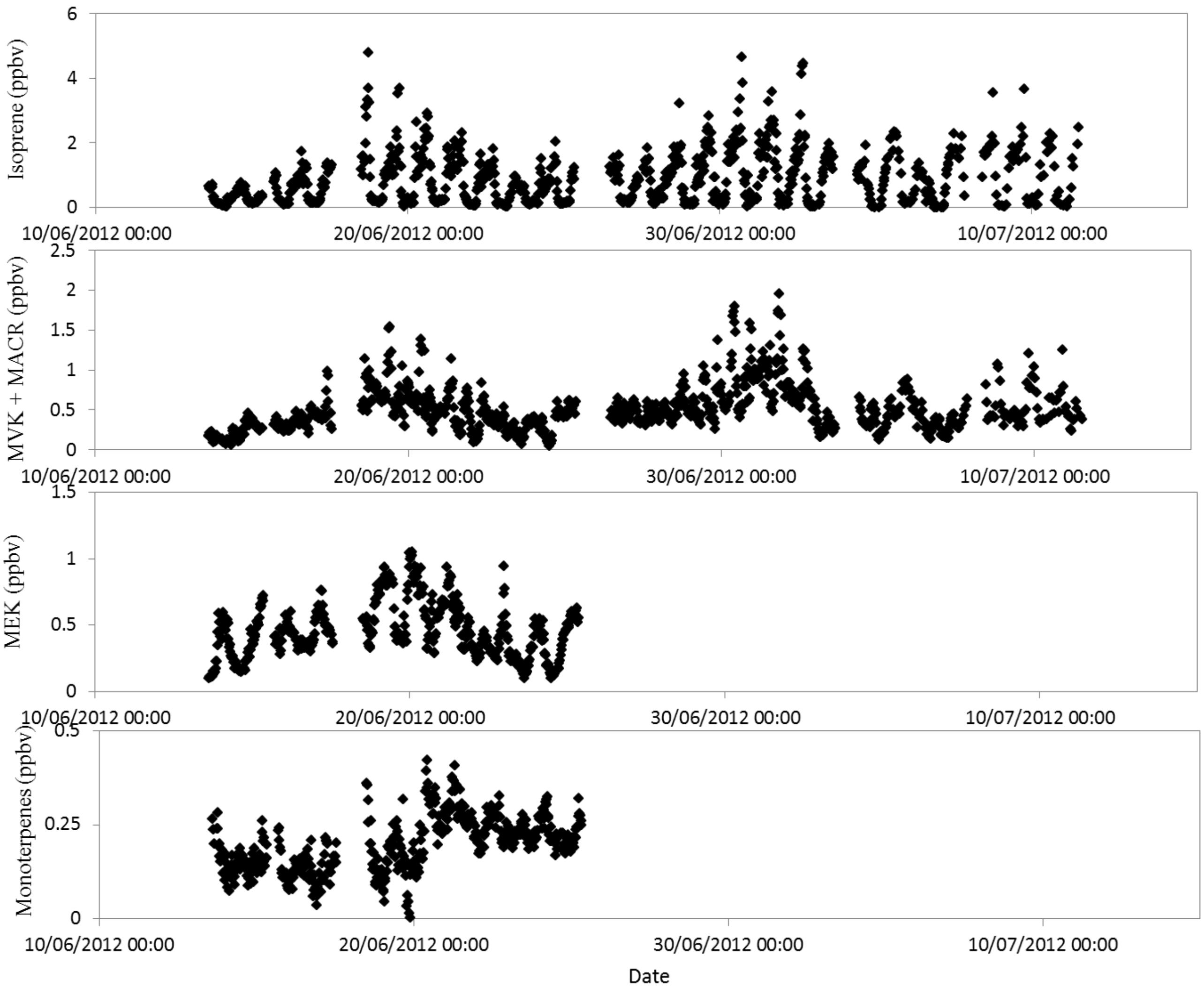

Figure S5. Time series of the volume mixing ratios of methanol, acetaldehyde, acetone, acetic acid, isoprene, MVK & MACR, MEK and monoterpene (calculated from fragment at *m/z* 81) measured at 4 m above the forest canopy

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