

# Isoprene emission potentials from European oak forests derived from canopy flux measurements: An assessment of uncertainties and inter-algorithm variability

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## Supplementary Information

### S1.1 Alice Holt – Measurement setup

10 Above canopy-isoprene flux measurements at the Alice Holt forest site were made by combining fast measurements of isoprene  
made using a proton transfer reaction mass spectrometer (PTR-MS, Ionicon Analytik GmbH, Innsbruck, Austria), with  
measurements of the vertical wind velocity, made using a Gill Solent (R1012A) ultrasonic anemometer mounted atop a 25 m  
tall lattice tower at a height of 28.5 m. The PTR-MS was housed in a small container at the base of the tower and subsampled  
air from a 30 m PTFE tube (1/2" OD, 3/8" ID) which drew air from directly below the anemometer at a rate of 60 L min<sup>-1</sup> to  
15 ensure turbulent flow was achieved.

The PTR-MS operating conditions were held constant throughout the measurement period to ensure the reduced electric field  
strength ( $E/N$ , where  $E$  is the electric field strength and  $N$  is the buffer gas density) was maintained at 127 Td. The drift tube  
pressure, temperature and voltage were set to 2.01 mbar, 45 °C and 550 V respectively. When operating in flux mode the PTR-  
MS sequentially measured eight mass to charge ratios including the isotope of the primary ion ( $m/z$  21) and first water cluster  
20 ( $m/z$  37) which were both sampled at a rate 20 ms and  $m/z$  33, 45, 47, 59, 61, 69 and 71 which were all sampled at 50 ms.  
These dwell times are much shorter than is typical when measuring VOC fluxes by PTR-MS. This is because this campaign  
represented the first deployment of our flux system and therefore the optimal settings had not yet been determined. Here we  
only focus on the measurements of  $m/z$  69 which we attribute entirely to isoprene. Typically the ion counts reported by the  
PTR-MS are converted to a meaningful concentration by first calculating the instrument sensitivity to a specific compound  
25 determined by sampling from a gas standard. During the Alice Holt campaign no gas standard was available. Consequently,  
the recorded ion counts of isoprene per second ( $I(RH^+)$ ) were converted to a measurement of isoprene concentration in units  
of parts per billion as follows

$$[R] = \frac{1}{k\Delta t} \frac{I(RH^+)}{T(RH^+)} \left( \frac{I(H_3O^+)}{T(H_3O^+)} \right)^{-1}, \quad (1)$$

where  $I(RH^+)$  and  $I(H_3O^+)$  are the isoprene and primary ion counts, respectively,  $k$  is the reaction rate constant taken from  
30 Zhao and Zhang (2004) and  $\Delta t$  is the reaction term which is dependent upon the length of the reaction chamber.  $T(RH^+)$  and  
 $T(H_3O^+)$  are the instrument specific transmission efficiencies for isoprene and the primary ions. The transmission efficiencies  
were determined experimentally at the end of the measurement campaign. According to Taipale et al., (2008) the use of  
transmission efficiencies rather than instrument sensitivities calculated using gas standards can result in uncertainties of ~25%.  
The instrument background was measured once per day by sampling ambient air through a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst heated to 200 °C  
35 and these values were subtracted from the ambient concentration measurements. Fluxes of isoprene were calculated following  
the procedures outlined by Langford et al. (2009). A cross-correlation between the vertical wind velocity and isoprene

concentration was calculated for each averaging period to determine the time-lag between the two datasets which arises due to the spatial separation between ultrasonic anemometer and PTR-MS. Following the recommendations of Langford et al. (2015) we calculated a prescribed time-lag which changed each day to reflect the average day-time (11:00 to 14:00) time-lag of that day.

## 5 S1.2 Ispra – Measurement setup

Isoprene flux measurements were made from June 11 to August 12, 2013 at the Ispra forest field station. The forest is further characterized with a different focus in Ferrea et al. (2012). More technical information on the general setup of the Ispra forest station can be found in Putaud et al. (2014).

10 For the turbulent flux measurements of isoprene, 10 Hz measurement data from a sonic anemometer (Gill, HS-100) were combined with 10 Hz concentration data from a fast isoprene sensor (FIS, Hills Scientific) mounted aloft a 37 m measurement tower. For the latter, air was drawn into a sampling line located 30 cm away from the sonic anemometer and carried at a flow rate of 25 slpm through a Teflon tube with 6 mm inner diameter to the FIS located inside an air conditioned container on the ground.

15 The FIS measurements are based on the detection of chemiluminescence occurring during the reaction of isoprene with ozone. Ambient air with a flow rate of 4-5 slpm and a 4 % mixture of ozone at 0.8 slpm in O<sub>2</sub> from an ozoniser (Hills Scientific) are mixed inside the reaction cell of the instrument. Following the reaction of isoprene with ozone, light is emitted at a characteristic wavelength and detected using single-photon counting at near-zero background. Instrument calibration to obtain isoprene concentrations was done using zero air from a gas cylinder and air with certified isoprene concentrations on a weekly basis confirming practically no drift of the zero signal and little variation in the span during the measurement campaign.

20 The covariances between the high frequency wind data and isoprene concentration data were calculated using the EdiRe software package (University of Edinburgh). The median time lag between vertical wind speed and concentration measurements was 4.7 s with little fluctuation during the measurement campaign. This value was used in the final data processing.

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## S2. Isoprene Emission Potentials

Ecosystem ( $E_{eco}$ ), oak canopy ( $E_{can}$ ) and leaf-level ( $E_{LL}$ ) equivalent isoprene emission potentials (IEPs) and uncertainties for each of the five measurement sites are listed below. The IEPs were calculated using the six different implementations of the Guenther algorithm described in the manuscript. In each case the final IEP was determined using the weighted average IEP method.

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### S2.1 Alice Holt

Emission factors derived for Alice Holt are summarised in Tables S1 to S3.

**Table S1 Ecosystem-Scale isoprene emission potentials at Alice Holt**

| Algorithm     | $E_{eco}$ | $E_{eco+Fd}$ | $E_{eco+Fd+chem}$ |
|---------------|-----------|--------------|-------------------|
| G93           | 5613      | 6045         | 6347±1552         |
| G06           | 6542      | 7046         | 7398±1802         |
| PCEEA         | 8368      | 9013         | 9464±2296         |
| MEGAN 2.1 (a) | 9333      | 10052        | 10555±2557        |
| MEGAN 2.1 (b) | 9686      | 10433        | 10955±2653        |
| MEGAN 2.1 (c) | 8781      | 9458         | 9931±2424         |

**Table S2 Oak canopy isoprene emission potentials at Alice Holt**

| Algorithm     | $E_{can}$ | $E_{can+Fd}$ | $E_{can+Fd+chem}$ |
|---------------|-----------|--------------|-------------------|
| G93           | 6237      | 6717         | 7053±2154         |
| G06           | 7269      | 7829         | 8220±2505         |
| PCEEA         | 9298      | 10014        | 10515±3196        |
| MEGAN 2.1 (a) | 10370     | 11169        | 11727±3562        |
| MEGAN 2.1 (b) | 10762     | 11592        | 12172±3695        |
| MEGAN 2.1 (c) | 9757      | 10509        | 11034±3352        |

**Table S3 Leaf-level equivalent isoprene emission potentials at Alice Holt**

| Algorithm     | $E_{LL}$ | $E_{LL+Fd}$ | $E_{LL+Fd+chem}$ |
|---------------|----------|-------------|------------------|
| G93           | 74       | 80          | 84±31            |
| G06           | 77       | 883         | 87±32            |
| PCEEA         | 98       | 106         | 111±41           |
| MEGAN 2.1 (a) | 110      | 118         | 124±46           |
| MEGAN 2.1 (b) | 114      | 123         | 129±47           |
| MEGAN 2.1 (c) | 103      | 111         | 117±43           |

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**S2.1 Bosco Fontana**

Emission factors derived for Bosco Fontana are summarised in Tables S4 to S6.

**Table S4 Ecosystem-Scale isoprene emission potentials at Bosco Fontana**

| Algorithm     | $E_{eco}$ | $E_{eco+Fd}$ | $E_{eco+Fd+chem}$ |
|---------------|-----------|--------------|-------------------|
| G93           | 1529      | 1722         | 1791±440          |
| G06           | 720       | 810          | 843±375           |
| PCEEA         | 1488      | 1675         | 1742±441          |
| MEGAN 2.1 (a) | 1376      | 1550         | 1612±428          |
| MEGAN 2.1 (b) | 1338      | 1507         | 1578±424          |
| MEGAN 2.1 (c) | 1980      | 2230         | 2319±493          |

**Table S5 Oak canopy isoprene emission potentials at Bosco Fontana**

| Algorithm     | $E_{can}$ | $E_{can+Fd}$ | $E_{can+Fd+chem}$ |
|---------------|-----------|--------------|-------------------|
| G93           | 5663      | 6378         | 6633±4002         |
| G06           | 2667      | 3000         | 3120±2212         |
| PCEEA         | 5511      | 6204         | 6452±3906         |
| MEGAN 2.1 (a) | 5096      | 5741         | 5970±3648         |
| MEGAN 2.1 (b) | 4956      | 5581         | 5805±3560         |
| MEGAN 2.1 (c) | 7333      | 8259         | 8590±5069         |

**Table S6 Leaf-level equivalent isoprene emission potentials at Bosco Fontana**

| Algorithm     | $E_{LL}$ | $E_{LL+Fd}$ | $E_{LL+Fd+chem}$ |
|---------------|----------|-------------|------------------|
| G93           | 66       | 74          | 77±49            |
| G06           | 28       | 31          | 32±25            |
| PCEEA         | 58       | 65          | 68±46            |
| MEGAN 2.1 (a) | 54       | 61          | 63±43            |
| MEGAN 2.1 (b) | 52       | 59          | 61±42            |
| MEGAN 2.1 (c) | 77       | 87          | 91±60            |

**S2.3 Castelporziano**

15 Emission factors derived for Bosco Fontana are summarised in Tables S7 to S9.

**Table S7 Ecosystem-Scale isoprene emission potentials at Castelporziano**

| Algorithm     | $E_{eco}$ | $E_{eco+Fd}$ | $E_{eco+Fd+chem}$ |
|---------------|-----------|--------------|-------------------|
| G93           | 91        | 98           | 103±14            |
| G06           | 26        | 28           | 29±9              |
| PCEEA         | 74        | 79           | 83±12             |
| MEGAN 2.1 (a) | 38        | 41           | 43±10             |
| MEGAN 2.1 (b) | 51        | 54           | 57±10             |
| MEGAN 2.1 (c) | 107       | 115          | 121±15            |

**Table S8 Oak canopy isoprene emission potentials at Castelporziano**

| Algorithm     | $E_{can}$ | $E_{can+Fd}$ | $E_{can+Fd+chem}$ |
|---------------|-----------|--------------|-------------------|
| G93           | 331       | 356          | 374±214           |
| G06           | 95        | 102          | 107±68            |
| PCEEA         | 269       | 287          | 302±175           |
| MEGAN 2.1 (a) | 138       | 149          | 157±94            |
| MEGAN 2.1 (b) | 185       | 196          | 206±122           |
| MEGAN 2.1 (c) | 389       | 418          | 439±251           |

**Table S9 Leaf-level equivalent isoprene emission potentials at Castelporziano**

| Algorithm     | $E_{LL}$ | $E_{LL+Fd}$ | $E_{LL+Fd+chem}$ |
|---------------|----------|-------------|------------------|
| G93           | 1.9      | 2.1         | 2.2±1.3          |
| G06           | 0.5      | 0.5         | 0.6±0.4          |
| PCEEA         | 1.4      | 1.5         | 1.5±1            |
| MEGAN 2.1 (a) | 0.7      | 0.8         | 0.8±0.6          |
| MEGAN 2.1 (b) | 0.9      | 1.0         | 1.0±0.7          |
| MEGAN 2.1 (c) | 2.0      | 2.1         | 2.2±1.5          |

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## S2.4 Ispra

Emission factors derived for Ispra are summarised in Tables S10 to S12.

**Table S10 Ecosystem-Scale isoprene emission potentials at Ispra**

| Algorithm     | $E_{eco}$ | $E_{eco+Fd}$ | $E_{eco+Fd+chem}$ |
|---------------|-----------|--------------|-------------------|
| G93           | 5824      | 6385         | 6704±983          |
| G06           | 3591      | 3937         | 4133±748          |
| PCEEA         | 6975      | 7646         | 8029±1120         |
| MEGAN 2.1 (a) | 6599      | 7234         | 7596±1074         |
| MEGAN 2.1 (b) | 6670      | 7312         | 7678±1082         |
| MEGAN 2.1 (c) | 8598      | 9426         | 9897±1321         |

10 **Table S11 Oak canopy isoprene emission potentials at Ispra**

| Algorithm     | $E_{can}$ | $E_{can+Fd}$ | $E_{can+Fd+chem}$ |
|---------------|-----------|--------------|-------------------|
| G93           | 7281      | 7981         | 8380±2073         |
| G06           | 4489      | 4921         | 5167±1391         |
| PCEEA         | 8719      | 9558         | 10036±2443        |
| MEGAN 2.1 (a) | 8249      | 9042         | 9495±2321         |
| MEGAN 2.1 (b) | 8338      | 9140         | 9597±2344         |
| MEGAN 2.1 (c) | 10748     | 11782        | 12371±2969        |

**Table S12 Leaf-level equivalent isoprene emission potentials at Ispra**

| Algorithm     | $E_{LL}$ | $E_{LL+Fd}$ | $E_{LL+Fd+chem}$ |
|---------------|----------|-------------|------------------|
| G93           | 74       | 81          | 85±27            |
| G06           | 40       | 44          | 46±16            |
| PCEEA         | 76       | 84          | 88±28            |
| MEGAN 2.1 (a) | 72       | 79          | 83±27            |

|               |    |     |        |
|---------------|----|-----|--------|
| MEGAN 2.1 (b) | 73 | 80  | 84±27  |
| MEGAN 2.1 (c) | 94 | 103 | 108±35 |

## S2.4 O3HP

Emission factors derived for O3HP are summarised in Tables S13 to S15.

**Table S13 Ecosystem-Scale isoprene emission potentials at O3HP**

| Algorithm     | $E_{eco}$ | $E_{eco+Fd}$ | $E_{eco+Fd+chem}$ |
|---------------|-----------|--------------|-------------------|
| G93           | 5135      | 5642         | 5924±771          |
| G06           | 3439      | 3779         | 3967±551          |
| PCEEA         | 7018      | 7710         | 8096±1026         |
| MEGAN 2.1 (a) | 6926      | 7610         | 7990±1014         |
| MEGAN 2.1 (b) | 7606      | 8357         | 8775±1107         |
| MEGAN 2.1 (c) | 8684      | 9541         | 10018±1255        |

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**Table S14 Oak canopy isoprene emission potentials at O3HP**

| Algorithm     | $E_{can}$ | $E_{can+Fd}$ | $E_{can+Fd+chem}$ |
|---------------|-----------|--------------|-------------------|
| G93           | 6847      | 7523         | 7899±1945         |
| G06           | 4586      | 5038         | 5290±1328         |
| PCEEA         | 9357      | 10280        | 10794±2639        |
| MEGAN 2.1 (a) | 9235      | 10146        | 10654±2605        |
| MEGAN 2.1 (b) | 10142     | 11142        | 11699±2857        |
| MEGAN 2.1 (c) | 11579     | 12721        | 13357±3256        |

**Table S15 Leaf-level equivalent isoprene emission potentials at O3HP**

| Algorithm     | $E_{LL}$ | $E_{LL+Fd}$ | $E_{LL+Fd+chem}$ |
|---------------|----------|-------------|------------------|
| G93           | 68       | 74          | 78±25            |
| G06           | 40       | 44          | 47±15            |
| PCEEA         | 58       | 64          | 67±24            |
| MEGAN 2.1 (a) | 57       | 63          | 66±24            |
| MEGAN 2.1 (b) | 63       | 69          | 73±26            |
| MEGAN 2.1 (c) | 72       | 79          | 83±29            |

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## S3 Comparison of isoprene emission potentials

Tables S16 to S25 show a comparison of IEPs calculated at each of the five measurement sites using seven different methods to derive the average isoprene emission potential. All emission potentials shown have been corrected for deposition and chemical losses. The data in these tables forms the basis of Fig. 3 in the main manuscript.

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### S3.1 Alice Holt, UK

**Table S16 Comparison of isoprene emission potentials calculated using the MEGAN 2.1 (a) emission algorithm for Alice Holt in conjunction with the least square regression, orthogonal distance regression, weighted average and several variations of the midday average methods.**

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|  | Fluxes | $\overline{IEP}$<br>(weighted) | $\overline{IEP}$<br>(all hours) | $\overline{IEP}$<br>(08 to 18) | $\overline{IEP}$<br>(10 to 15) | $\overline{IEP}$<br>(11 to 13) | LSR  | ODR   |
|--|--------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|------|-------|
| IEP<br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]      | -      | 10555                          | 13251                           | 11712                          | 12316                          | 12671                          | 9349 | 12217 |
| Mean<br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]     | 779    | 779                            | 978                             | 864                            | 909                            | 935                            | 690  | 902   |
| $\sigma$<br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ] | 1066   | 1097                           | 1378                            | 1218                           | 1281                           | 1317                           | 972  | 1270  |

|                   |   |          |      |      |      |      |      |             |
|-------------------|---|----------|------|------|------|------|------|-------------|
| r <sup>2</sup>    | - | 0.54     | 0.54 | 0.54 | 0.54 | 0.54 | 0.54 | 0.54        |
| M score           | - | 1.37     | 1.34 | 1.31 | 1.31 | 1.32 | 1.53 | <b>1.31</b> |
| Relative Bias [%] | - | <b>0</b> | 26   | 11   | 17   | 20   | -11  | 16          |

Table S17 Comparison of isoprene emission potentials calculated using the G93 emission algorithm for Alice Holt in conjunction with the least square regression, orthogonal distance regression, weighted average and several variations of the midday average methods.

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|   | Fluxes | $\overline{IEP}$<br>(weighted) | $\overline{IEP}$<br>(all hours) | $\overline{IEP}$<br>(08 to 18) | $\overline{IEP}$<br>(10 to 15) | $\overline{IEP}$<br>(11 to 13) | LSR   | ODR   |
|---|--------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|-------|-------|
| IEP [ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]      | -      | 6348                           | 6062                            | 6261                           | 7607                           | 8344                           | 6995  | 7538  |
| Mean [ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]     | 779    | 779                            | 744                             | 768                            | 933                            | 1024                           | 858   | 925   |
| $\sigma$ [ $\mu\text{g m}^{-2} \text{h}^{-1}$ ] | 1327   | 915                            | 874                             | 902                            | 1096                           | <b>1203</b>                    | 1008  | 1086  |
| r <sup>2</sup>                                  | 0.58   | 0.58                           | 0.58                            | 0.58                           | 0.58                           | 0.58                           | 0.58  | 0.58  |
| M score   | -      | 1.239                          | 1.315                           | 1.260                          | 1.065                          | <b>1.054</b>                   | 1.121 | 1.069 |
| Relative Bias [%]                               | -      | <b>0</b>                       | -4                              | -1                             | 20                             | 31                             | 10    | 19    |

### S3.2 Bosco Fontana, Italy

Table S18 Comparison of isoprene emission potentials calculated using the MEGAN 2.1 (a) emission algorithm for Bosco Fontana in conjunction with the least square regression, orthogonal distance regression, weighted average and several variations of the midday average methods.

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|   | Fluxes | $\overline{IEP}$<br>(weighted) | $\overline{IEP}$<br>(all hours) | $\overline{IEP}$<br>(08 to 18) | $\overline{IEP}$<br>(10 to 15) | $\overline{IEP}$<br>(11 to 13) | LSR         | ODR   |
|---|--------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|-------------|-------|
| IEP [ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]      | -      | 1550                           | 1493                            | 1647                           | 1509                           | 1527                           | 1489        | 1547  |
| Mean [ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]     | 862    | 862                            | 830                             | 916                            | 839                            | 849                            | 828         | 860   |
| $\sigma$ [ $\mu\text{g m}^{-2} \text{h}^{-1}$ ] | 1113   | 1053                           | 1015                            | 1119                           | 1026                           | 1038                           | <b>1012</b> | 1052  |
| r <sup>2</sup>                                  | -      | 0.79                           | 0.79                            | 0.79                           | 0.79                           | 0.79                           | 0.79        | 0.79  |
| M score   | -      | 0.347                          | 0.356                           | 0.347                          | 0.353                          | <b>0.350</b>                   | 0.357       | 0.347 |
| Relative Bias [%]                               | -      | <b>0</b>                       | -4                              | 6                              | -3                             | -1                             | -4          | 0     |

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Table S19 Comparison of isoprene emission potentials calculated using the G93 emission algorithm for Bosco Fontana in conjunction with the least square regression, orthogonal distance regression, weighted average and several variations of the midday average methods.

|   | Fluxes | $\overline{IEP}$<br>(weighted) | $\overline{IEP}$<br>(all hours) | $\overline{IEP}$<br>(08 to 18) | $\overline{IEP}$<br>(10 to 15) | $\overline{IEP}$<br>(11 to 13) | LSR  | ODR  |
|---|--------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|------|------|
| IEP [ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]      | -      | 1722                           | 1229                            | 1643                           | 1996                           | 2240                           | 1953 | 1495 |
| Mean [ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]     | 862    | 862                            | 615                             | 822                            | 999                            | 1121                           | 977  | 748  |
| $\sigma$ [ $\mu\text{g m}^{-2} \text{h}^{-1}$ ] | 1113   | 854                            | 609                             | 815                            | 990                            | <b>1111</b>                    | 968  | 741  |
| r <sup>2</sup>                                  | -      | 0.75                           | 0.75                            | 0.75                           | 0.75                           | 0.75                           | 0.75 | 0.75 |
| M score   | -      | 0.66                           | 1.17                            | 0.70                           | <b>0.59</b>                    | 0.61                           | 0.60 | 0.81 |
| Relative Bias [%]                               | -      | <b>0</b>                       | -29                             | -5                             | 16                             | 30                             | 13   | -13  |

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### S3.3 Castelporziano, Italy

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Table S20 Comparison of isoprene emission potentials calculated using the MEGAN 2.1 (a) emission algorithm for Castelporziano in conjunction with the least square regression, orthogonal distance regression, weighted average and several variations of the midday average methods.

|  | Fluxes | $\overline{IEP}$<br>(weighted) | $\overline{IEP}$<br>(all hours) | $\overline{IEP}$<br>(08 to 18) | $\overline{IEP}$<br>(10 to 15) | $\overline{IEP}$<br>(11 to 13) | LSR  | ODR  |
|--|--------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|------|------|
| IEP<br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]      | -      | 43                             | 49                              | 46                             | 39                             | 38                             | 39   | 47   |
| Mean<br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]     | 44     | 44                             | 50                              | 47                             | 40                             | 39                             | 40   | 49   |
| $\sigma$<br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ] | 70     | 61                             | 69                              | 65                             | 55                             | 54                             | 55   | 67   |
| $r^2$  | -      | 0.55                           | 0.55                            | 0.55                           | 0.55                           | 0.55                           | 0.55 | 0.55 |
| M score  | -      | 1.25                           | <b>1.19</b>                     | 1.20                           | 1.38                           | 1.42                           | 1.38 | 1.20 |
| Relative<br>Bias [%]                               | -      | <b>0</b>                       | 14                              | 7                              | -10                            | -12                            | -10  | 10   |

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Table S21 Comparison of isoprene emission potentials calculated using the G93 emission algorithm for Castelporziano in conjunction with the least square regression, orthogonal distance regression, weighted average and several variations of the midday average methods.

|  | Fluxes | $\overline{IEP}$<br>(weighted) | $\overline{IEP}$<br>(all hours) | $\overline{IEP}$<br>(08 to 18) | $\overline{IEP}$<br>(10 to 15) | $\overline{IEP}$<br>(11 to 13) | LSR  | ODR  |
|--|--------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|------|------|
| IEP<br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]      | -      | 103                            | 67                              | 92                             | 114                            | 127                            | 113  | 104  |
| Mean<br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]     | 44     | 44                             | 29                              | 40                             | 49                             | 56                             | 49   | 45   |
| $\sigma$<br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ] | 70     | 45                             | 29                              | 41                             | 50                             | 57                             | 50   | 46   |
| $r^2$  | -      | 0.47                           | 0.47                            | 0.47                           | 0.47                           | 0.47                           | 0.47 | 0.47 |
| M score  | -      | 1.48                           | 2.72                            | 1.69                           | 1.32                           | <b>1.24</b>                    | 1.33 | 1.45 |
| Relative<br>Bias [%]                               | -      | <b>0</b>                       | -34                             | -10                            | 12                             | 24                             | 11   | 2    |

### S3.4 Ispra, Italy

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Table S22 Comparison of isoprene emission potentials calculated using the MEGAN 2.1 (a) emission algorithm for Ispra in conjunction with the least square regression, orthogonal distance regression, weighted average and several variations of the midday average methods.

|  | Fluxes | $\overline{IEP}$<br>(weighted) | $\overline{IEP}$<br>(all hours) | $\overline{IEP}$<br>(08 to 18) | $\overline{IEP}$<br>(10 to 15) | $\overline{IEP}$<br>(11 to 13) | LSR  | ODR  |
|--|--------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|------|------|
| IEP<br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]      | -      | 7596                           | 7212                            | 7558                           | 7928                           | 8142                           | 7504 | 9174 |
| Mean<br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]     | 2108   | 2108                           | 2002                            | 2098                           | 2201                           | 2261                           | 2083 | 2546 |
| $\sigma$<br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ] | 3126   | 2940                           | 2792                            | 2925                           | 3069                           | 3152                           | 2905 | 3551 |
| $r^2$  | -      | 0.86                           | 0.86                            | 0.86                           | 0.86                           | 0.86                           | 0.86 | 0.86 |
| M score  | -      | 0.28                           | 0.32                            | 0.29                           | <b>0.27</b>                    | <b>0.27</b>                    | 0.29 | 0.31 |
| Relative<br>Bias [%]                               | -      | <b>0</b>                       | -5                              | 0                              | 4                              | 7                              | -1   | 21   |

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Table S23 Comparison of isoprene emission potentials calculated using the G93 emission algorithm for Ispra in conjunction with the least square regression, orthogonal distance regression, weighted average and several variations of the midday average methods.

| Fluxes | $\overline{IEP}$<br>(weighted) | $\overline{IEP}$<br>(all hours) | $\overline{IEP}$<br>(08 to 18) | $\overline{IEP}$<br>(10 to 15) | $\overline{IEP}$<br>(11 to 13) | LSR | ODR |
|--------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|-----|-----|
|--------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|-----|-----|

|  |      |          |      |      |             |      |      |      |
|--|------|----------|------|------|-------------|------|------|------|
| <b>IEP</b><br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]                 | -    | 6703     | 5969 | 7629 | 7733        | 8359 | 7512 | 6966 |
| <b>Mean</b><br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]                | 2108 | 2108     | 1877 | 2399 | 2432        | 2629 | 2363 | 2190 |
| <b><math>\sigma</math></b><br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ] | 3126 | 2401     | 2139 | 2733 | 2771        | 2995 | 2691 | 2496 |
| <b>r<sup>2</sup></b>   | -    | 0.78     | 0.78 | 0.78 | 0.78        | 0.78 | 0.78 | 0.78 |
| <b>M score</b>   | -    | 0.51     | 0.65 | 0.44 | <b>0.43</b> | 0.44 | 0.44 | 0.48 |
| <b>Relative Bias [%]</b>   | -    | <b>0</b> | -11  | 14   | 15          | 25   | 12   | 4    |

### S3.5 O3HP, France

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Table S24 Comparison of isoprene emission potentials calculated using the MEGAN 2.1 (a) emission algorithm for O3HP in conjunction with the least square regression, orthogonal distance regression, weighted average and several variations of the midday average methods.

|  | Fluxes | $\overline{IEP}$<br>(weighted) | $\overline{IEP}$<br>(all hours) | $\overline{IEP}$<br>(08 to 18) | $\overline{IEP}$<br>(10 to 15) | $\overline{IEP}$<br>(11 to 13) | LSR         | ODR  |
|--|--------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|-------------|------|
| <b>IEP</b><br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]                 |        | 7991                           | 6914                            | 7795                           | 7883                           | 7889                           | 8138        | 8018 |
| <b>Mean</b><br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]                | 899    | 899                            | 777                             | 877                            | 886                            | 887                            | 915         | 902  |
| <b><math>\sigma</math></b><br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ] | 1371   | 1279                           | 1107                            | 1247                           | 1262                           | 1262                           | <b>1302</b> | 1283 |
| <b>r<sup>2</sup></b>   | -      | 0.90                           | 0.90                            | 0.90                           | 0.90                           | 0.90                           | 0.90        | 0.90 |
| <b>M score</b>   | -      | 0.23                           | 0.34                            | 0.24                           | 0.23                           | 0.23                           | <b>0.22</b> | 0.23 |
| <b>Relative Bias [%]</b>   | -      | <b>0</b>                       | 0                               | -13                            | -2                             | -1                             | 0           | 2    |

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Table S25 Comparison of isoprene emission potentials calculated using the G93 emission algorithm for O3HP in conjunction with the least square regression, orthogonal distance regression, weighted average and several variations of the midday average methods.

|  | Fluxes | $\overline{IEP}$<br>(weighted) | $\overline{IEP}$<br>(all hours) | $\overline{IEP}$<br>(08 to 18) | $\overline{IEP}$<br>(10 to 15) | $\overline{IEP}$<br>(11 to 13) | LSR         | ODR  |
|--|--------|--------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|-------------|------|
| <b>IEP</b><br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]                 |        | 5924                           | 6894                            | 5607                           | 6576                           | 6902                           | 7225        | 5513 |
| <b>Mean</b><br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ]                | 899    | 899                            | 1046                            | 851                            | 998                            | 1047                           | 1096        | 836  |
| <b><math>\sigma</math></b><br>[ $\mu\text{g m}^{-2} \text{h}^{-1}$ ] | 1371   | 1031                           | 1200                            | 977                            | 1145                           | 1201                           | <b>1258</b> | 960  |
| <b>r<sup>2</sup></b>   | -      | 0.84                           | 0.84                            | 0.84                           | 0.84                           | 0.84                           | 0.84        | 0.84 |
| <b>M score</b>   | -      | 0.43                           | 0.34                            | 0.49                           | 0.36                           | 0.34                           | <b>0.34</b> | 0.52 |
| <b>Relative Bias [%]</b>   | -      | <b>0</b>                       | 16                              | -5                             | 11                             | 16                             | 22          | -7   |

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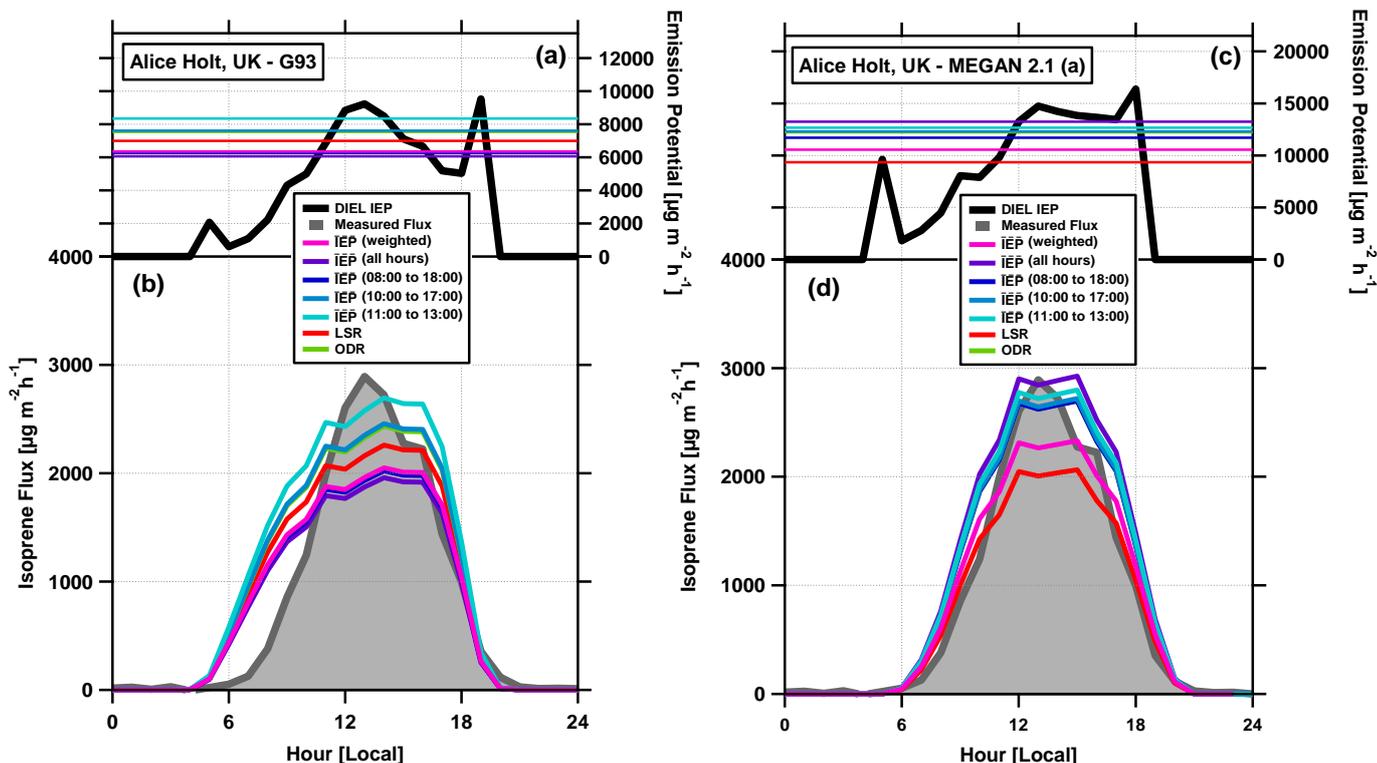
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Figures S1 to S4 show the average diurnal profile of the isoprene emission potential that have been calculated by inverting the G93 (Panel A) and MEGAN 2.1 (a) (Panel C) emission algorithms. Also shown are the average emission potential assigned to each site which were calculated using seven different methods (see main text for details).

S4.1 Alice Holt

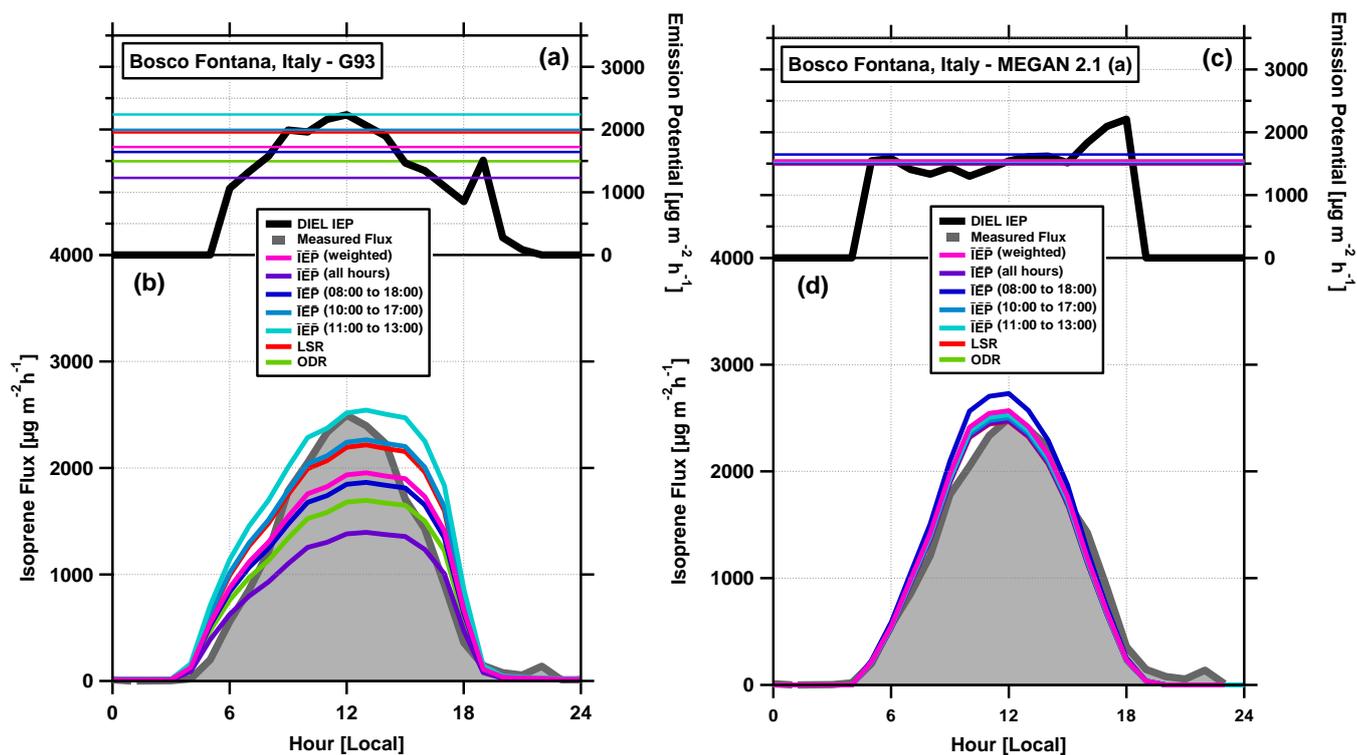


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Figure S1 Panels A and C show the average diurnal cycle in the isoprene emission potential (e.g.  $IEP = \left(\frac{F_{iso}}{\gamma}\right)$ ) calculated for the Alice Holt site, UK using the G93 (panel A) and MEGAN 2.1 (panel B) algorithms. Superimposed on top of these are the isoprene emission potentials calculated using the least square regression, orthogonal distance regression and average (with several averaging lengths) methods – see text for detailed description. Panels B and D show the average diurnal cycle of the measured fluxes and the average diurnal cycle of the fluxes modelled using the seven different isoprene emission potentials calculated for this data set.

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S4.2 Bosco Fontana

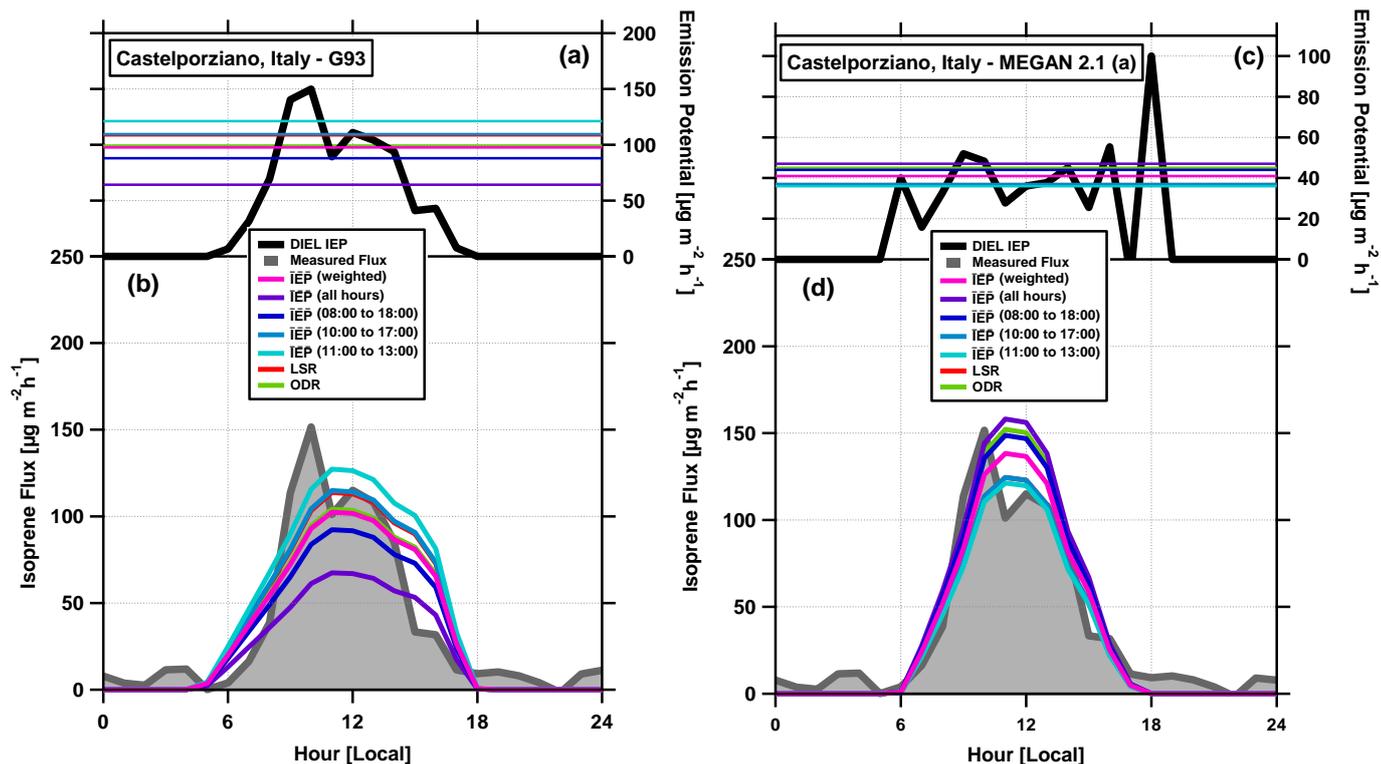


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Figure S2 Panels A and C show the average diurnal cycle in the isoprene emission potential (e.g.  $\text{IEP} = \left(\frac{F_{\text{iso}}}{\gamma}\right)$ ) calculated for the Bosco Fontana site, Italy using the G93 (panel A) and MEGAN 2.1 (panel B) algorithms. Superimposed on top of these are the isoprene emission potentials calculated using the least square regression, orthogonal distance regression and average (with several averaging lengths) methods – see text for detailed description. Panels B and D show the average diurnal cycle of the measured fluxes and the average diurnal cycle of the fluxes modelled using the seven different isoprene emission potentials calculated for this data set.

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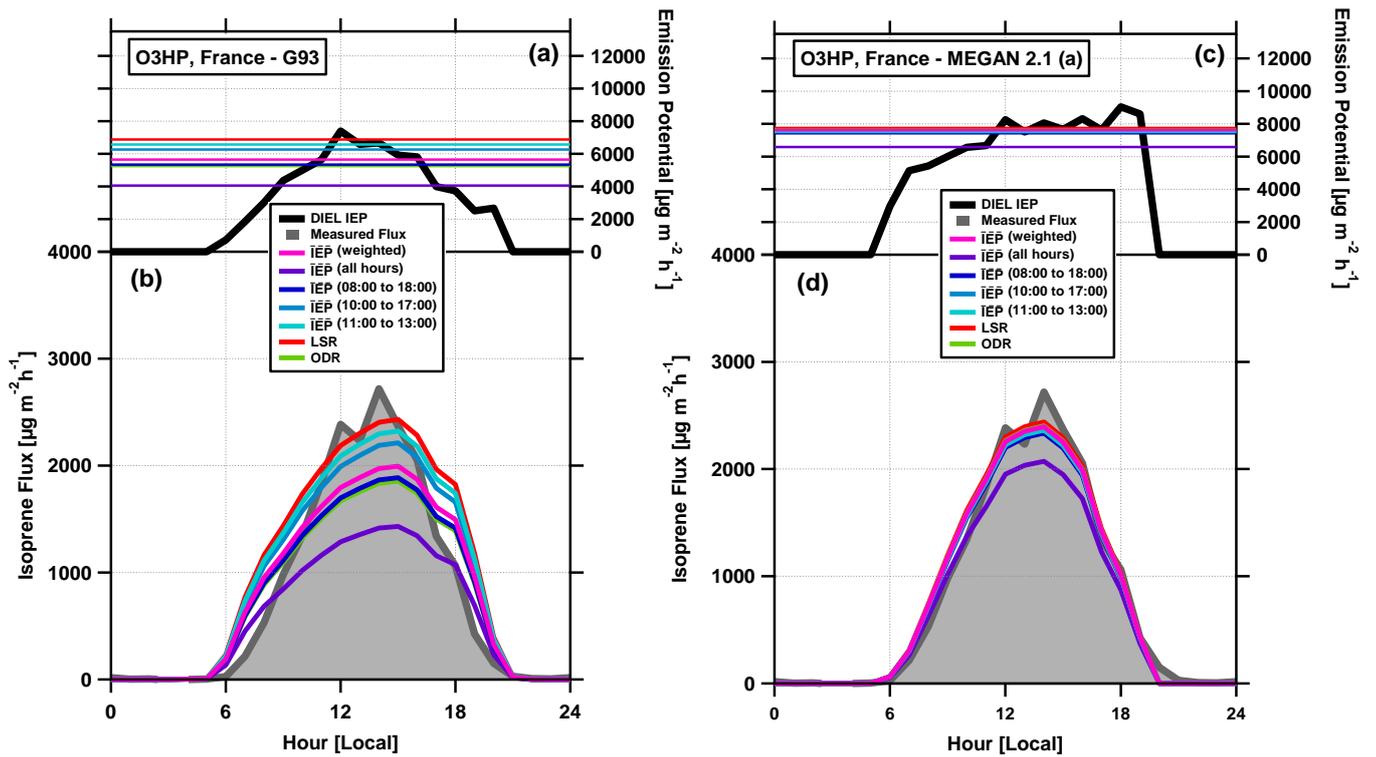
### S4.3 Castelporziano



5 Figure S3 Panels A and C show the average diurnal cycle in the isoprene emission potential (e.g.  $IEP = \left( \frac{F_{iso}}{\gamma} \right)$ ) calculated for the Castelporziano site, Italy using the G93 (panel A) and MEGAN 2.1 (panel B) algorithms. Superimposed on top of these are the isoprene emission potentials calculated using the least square regression, orthogonal distance regression and average (with several averaging lengths) methods – see text for detailed description. Panels B and D show the average diurnal cycle of the measured fluxes and the average diurnal cycle of the fluxes modelled using the seven different isoprene emission potentials calculated for this data set.

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S4.4 O3HP



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Figure S4 Panels A and C show the average diurnal cycle in the isoprene emission potential (e.g.  $IEP = \left(\frac{F_{iso}}{\gamma}\right)$ ) calculated for the Observatoire de Haute Provence site, France using the G93 (panel A) and MEGAN 2.1 (panel B) algorithms. Superimposed on top of these are the isoprene emission potentials calculated using the least square regression, orthogonal distance regression and average (with several averaging lengths) methods – see text for detailed description. Panels B and D show the average diurnal cycle of the measured fluxes and the average diurnal cycle of the fluxes modelled using the seven different isoprene emission potentials calculated for this data set.

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## S5 Influence of past light and temperature

The influence of past light and temperature on derived emission potentials using the MEGAN model. Figures S5 to S9 show the time series of the average 24 hour and 240 hour light and temperature for each of the five sites.

### 10 S5.1 Alice Holt

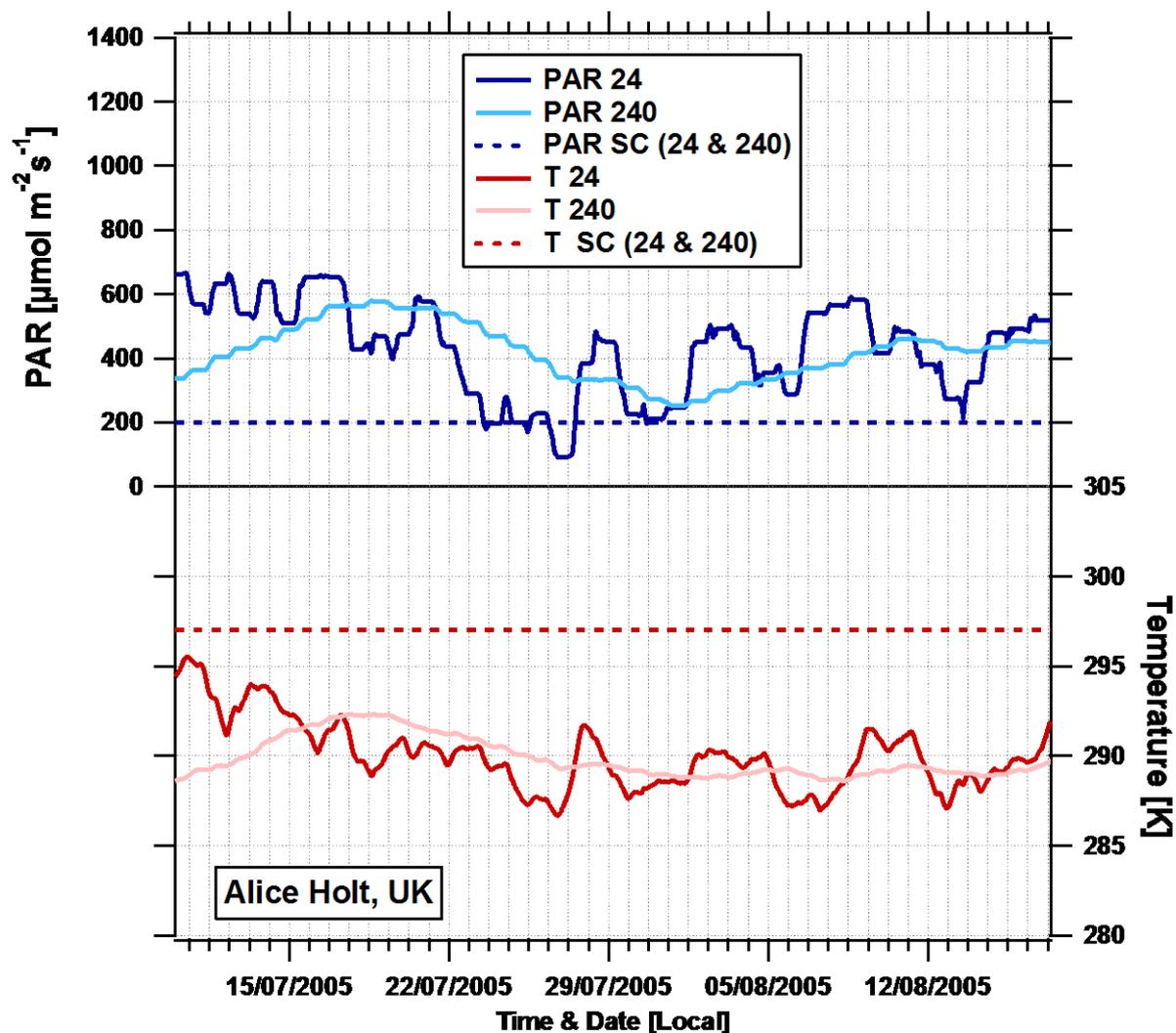


Figure S5. Time series of the previous (24 and 240 hours) light and temperature measurements made at the Alice Holt site relative to the standard conditions used in the Model of Emission of Gases and Aerosols from Nature (dashed lines).

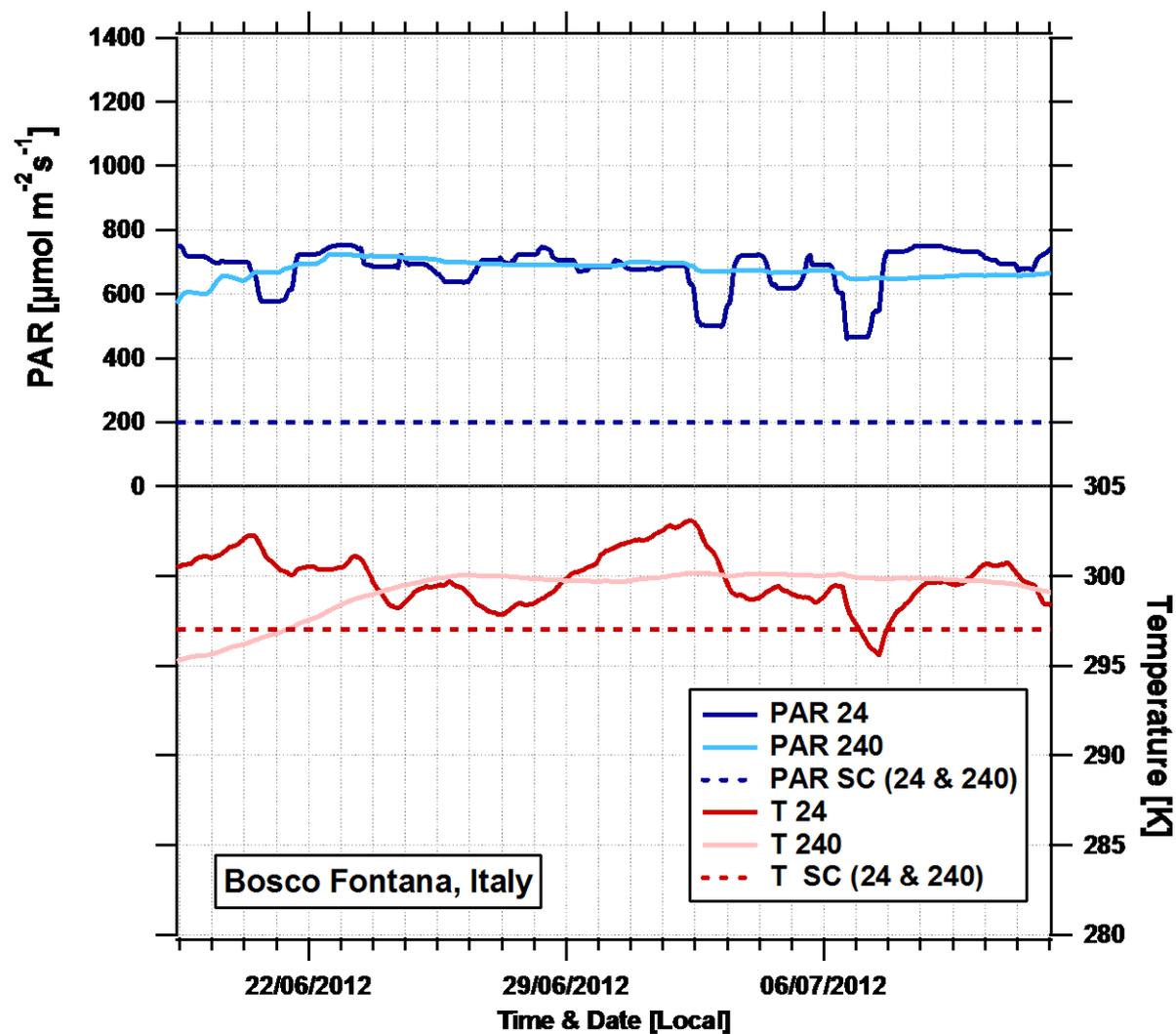
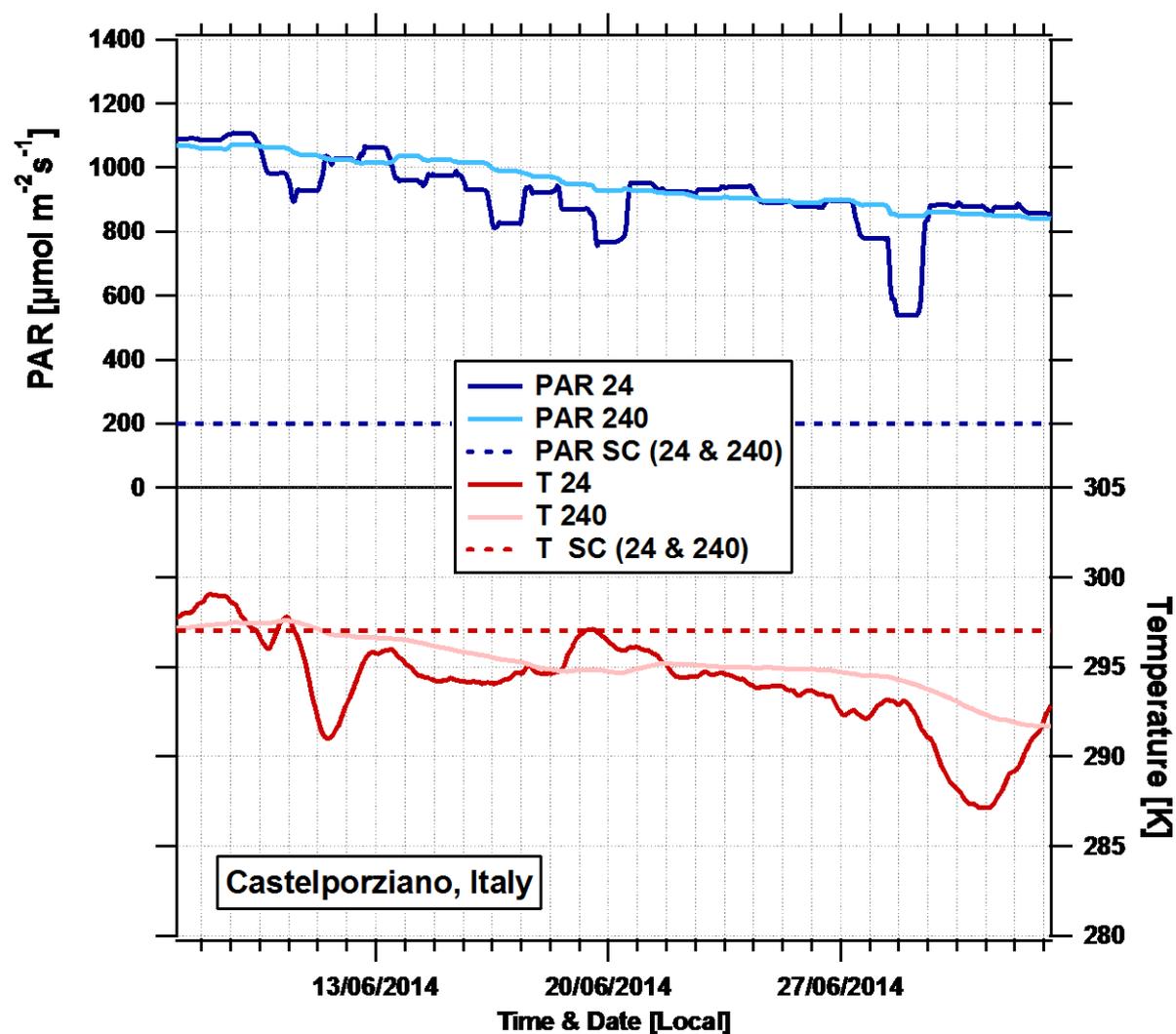
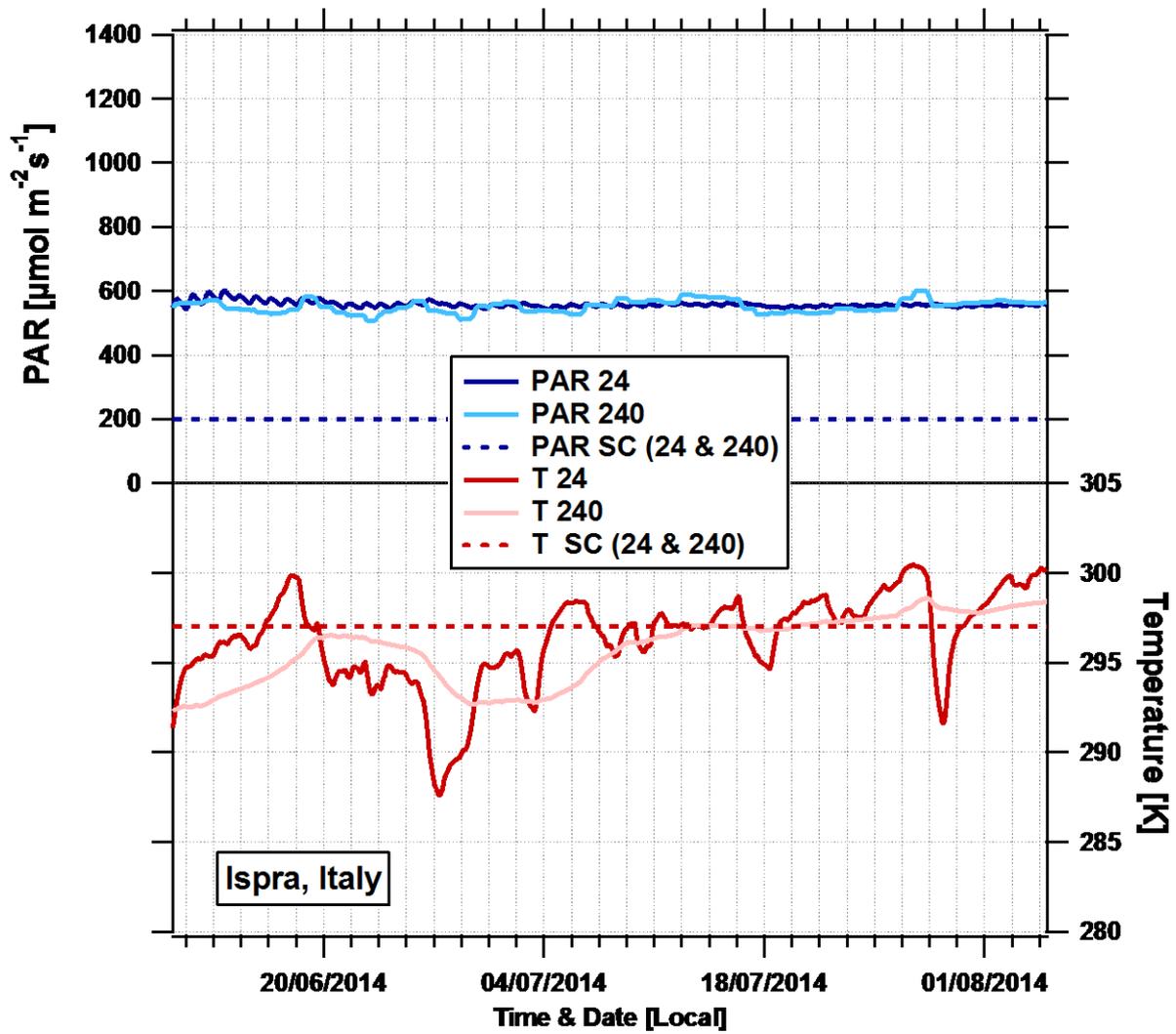


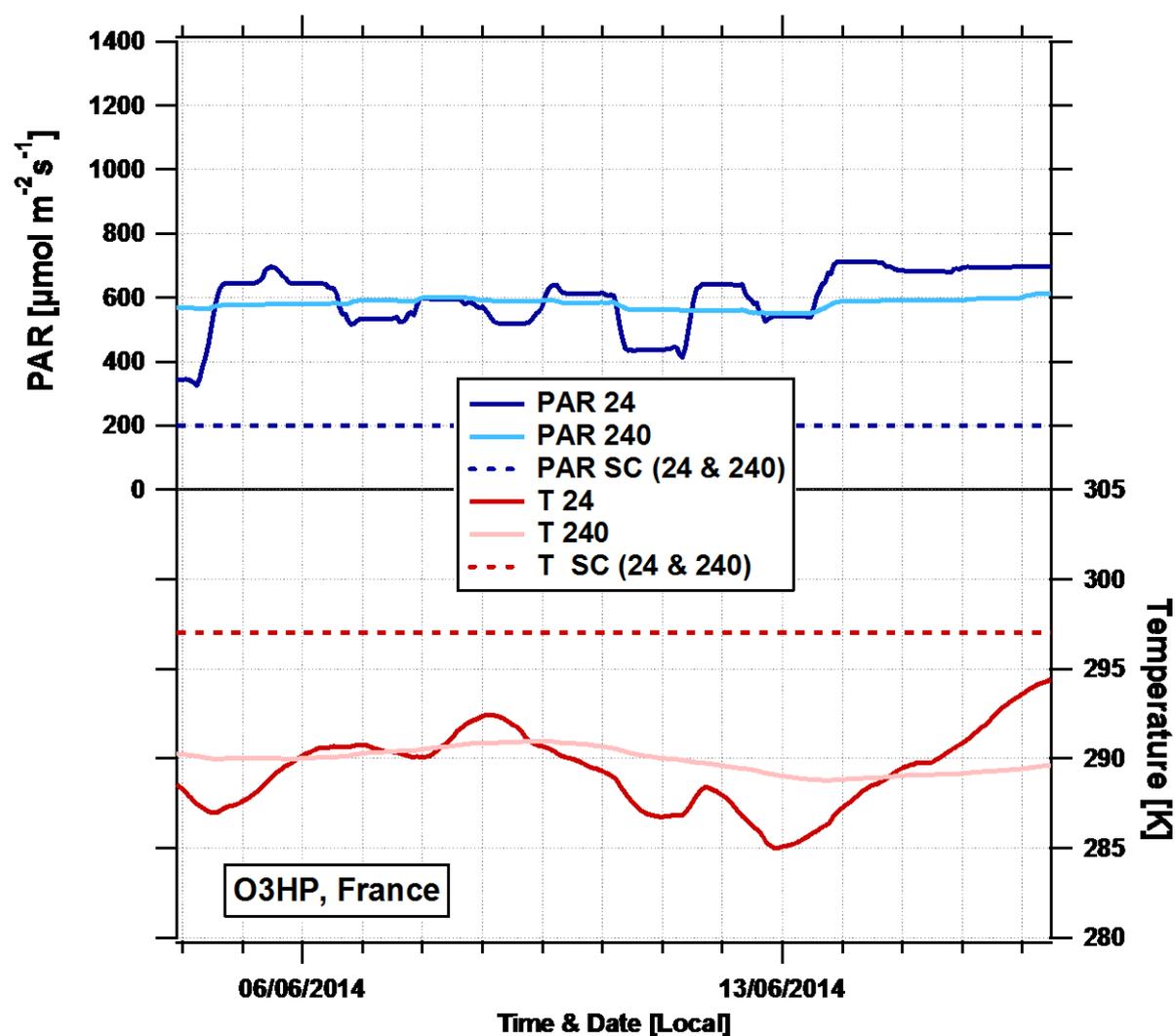
Figure S6. Time series of the previous (24 and 240 hours) light and temperature measurements made at the Bosco Fontana site relative to the standard conditions used in the Model of Emission of Gases and Aerosols from Nature (dashed lines).



5 Figure S7. Time series of the previous (24 and 240 hours) light and temperature measurements made at the Castelporziano site relative to the standard conditions used in the Model of Emission of Gases and Aerosols from Nature (dashed lines).



5 Figure S8. Time series of the previous (24 and 240 hours) light and temperature measurements made at the Ispra forest site relative to the standard conditions used in the Model of Emission of Gases and Aerosols from Nature (dashed lines).



5 Figure S9. Time series of the previous (24 and 240 hours) light and temperature measurements made at the Observatoire de Haute Provence site relative to the standard conditions used in the Model of Emission of Gases and Aerosols from Nature (dashed lines).

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