

1 Response to Co-Editor Decision:

2 I finally found the time to carefully check your response to the comments raised by the reviewers on  
3 your article on bi-directional exchange of methanol and acetaldehyde submitted for publication in  
4 ACP. The comments by reviewer #1 tackle a number of issues and going through your response as  
5 well as the suggested revisions, it seems that this helps in overall arriving at an improved version of  
6 the ms. Consequently, I decided to accept the ms for publication in ACP after you have tackled this  
7 last round of minor editor comments just coming up reading your response and revisions.

8 In the revised ms version I noticed this feature that should be corrected: Pp 4, lines, 17-19, “While  
9 firmly based in plant physiology and plant response to environmental conditions, this approach would  
10 allow modelslackingleaf-level processestoaccountforthechanges in fluxdirection”

11 Thanks for picking that up. We have inserted spaces between the words.

12 Furthermore add the units after the term 3000, “where  $R_{\text{stom}}$  ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ )-1) is the stomatal  
13 resistance, 3000 ( $\text{s m}^{-1}$ ) is the model default limiting night time value of  $R_{\text{stom}}$  and  $n$  is a scaling  
14 factor”

15 Done

16 I have to say that this discussion on the selection of the values of the nocturnal stomatal resistance is  
17 not a strong feature of the paper also since it apparently is also included to represent removal over  
18 night by the (wet/dry) cuticle. Generally, choice of this nocturnal (stomatal) resistance term, which  
19 should reflect a general complete stomatal closure is rather arbitrary also due to the lack of direct  
20 observations. But having a quite high LAI can then even with such a selected large nocturnal value  
21 still result in quite some nocturnal removal and impact on simulated concentration also due to the  
22 limited mixing volume. Why did you not simply include the  $R_{\text{cut}}$  and  $R_{\text{stom}}$  terms as parallel  
23 resistances as is commonly done in dry deposition calculations and where  $R_{\text{stom}}$  (e.g.,  $1\text{e}6$ ) is much  
24 higher than  $R_{\text{cut}}$  ( $3000 \text{ s m}^{-1}$ ) resulting in a nocturnal  $R_{\text{leaf}}$  of  $3000 \text{ s m}^{-1}$  and a daytime  $R_{\text{leaf}}$   
25 dominated by  $R_{\text{stom}}$ ?

26 This is exactly how the model deals with “stomatal” resistance. It is the effective leaf resistance  
27 calculated from the parallel cuticle and stomatal resistances; at night the overall value is 3000 as the  
28 stomata are assumed fully closed. As the editor points out the night-time stomatal resistance is  
29 arbitrary and our initial choice of scaling factor was selected to be consistent with the resistance to dry  
30 deposition. Our sensitivity tests (in which we altered  $n$ ) showed that this choice made no difference to  
31 our overall conclusion – that stomatal control of emissions at the leaf-level was not observable at the  
32 canopy-scale. We have re-phrased our explanation of the stomatal control factor in the text to read:

1 “The night-time “stomatal” resistance is in fact equal to the cuticular resistance and  $n$  was introduced  
2 to account for this. (During the day, the leaf resistance, the combination of the stomatal and cuticular  
3 resistances in parallel, is dominated by the stomatal resistance). The value of  $n$  was initially set to 3 for  
4 the S-storage and S-combo simulations, as Jarvis (1976) reported a limiting value of 1000 although  
5 this was species-dependent. The effect of the choice of value of  $n$  is explored in Section 3.5.”

6 In your response to the reviewers comment on the role of advection, I see your point about the  
7 potentially small impact of “anthropogenic” air masses with the winds generally coming from a  
8 direction with a small anthropogenic footprint. But what about having a footprint from a natural source  
9 region with also substantial biogenic sources of methanol and acetaldehyde? Would there be other  
10 ecosystems located more to the north that could also potentially have a large bVOC source?

11 While there could be large biogenic sources of methanol and acetaldehyde to the north of Harvard  
12 Forest, the inclusion of advected bVOCs did not improve the model-measurement fit. We conclude  
13 from this that there was little long-range transport from the north during the summer of 2012, i.e. that  
14 the winds were light and the site was impacted only by local sources of methanol and acetaldehyde  
15 with the same diel cycle as that emitted in-situ.

16 In your response to the reviewer on issues on the nocturnal decrease in methanol you mention that: “It  
17 is most likely due to the lack of an explicit treatment of wet deposition or wash-out within the model.  
18 We intend to develop FORCAST in the future to include a representation of loss of methanol and other  
19 water-soluble compounds to wet surfaces based on relative humidity within the canopy as  
20 observations suggest this may be an important sink for such compounds”. I agree with this point on the  
21 potential role of wet-canopy removal. This might be interpreted as a formality (also since you have not  
22 included a reference to this in the paper) but according to my long-term knowledge on the dry  
23 deposition process, removal of gases/aerosols by a wet canopy are also seen as a dry deposition  
24 process feature and not referred to a wet deposition or wash-out. This is really referring to the process  
25 of removal of gases and aerosols by scavenging and rain-out.

26 We acknowledge our choice of terminology was perhaps a little ambiguous; we were referring to  
27 removal of gases and aerosols by surface wetness within the canopy, a process that observations  
28 suggest may be important at some sites.

29

1 **Modelling bi-directional fluxes of methanol and**  
2 **acetaldehyde with the FORCAsT canopy exchange model**

3

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19 **Abstract**

20 The FORCAsT canopy exchange model was used to investigate the underlying mechanisms  
21 governing foliage emissions of methanol and acetaldehyde, two short chain oxygenated  
22 volatile organic compounds ubiquitous in the troposphere and known to have strong biogenic  
23 sources, at a northern mid-latitude forest site. The explicit representation of the vegetation  
24 canopy within the model allowed us to test the hypothesis that stomatal conductance regulates  
25 emissions of these compounds to an extent that its influence is observable at the ecosystem-  
26 scale, a process not currently considered in regional or global scale atmospheric chemistry  
27 models.

28 We found that FORCAsT could only reproduce the magnitude and diurnal profiles of  
29 methanol and acetaldehyde fluxes measured at the top of the forest canopy at Harvard Forest

1 if light-dependent emissions were introduced to the model. With the inclusion of such  
2 emissions FORCAST was able to successfully simulate the observed bi-directional exchange  
3 of methanol and acetaldehyde. Although we found evidence that stomatal conductance  
4 influences methanol fluxes and concentrations at scales beyond the leaf-level, particularly at  
5 dawn and dusk, we were able to adequately capture ecosystem exchange without the addition  
6 of stomatal control to the standard parameterisations of foliage emissions, suggesting that  
7 ecosystem fluxes can be well enough represented by the emissions models currently used.

8 **Key points:** Canopy exchange model used to probe mechanisms controlling fluxes of  
9 methanol and acetaldehyde; The effects of stomatal control of leaf-level emissions of  
10 methanol and acetaldehyde emissions are not evident at the ecosystem scale; Bi-directional  
11 exchange of oxygenated volatile organic compounds can be simulated by models that  
12 explicitly and holistically consider canopy processes

## 13 **1 Introduction**

14 The exchange of many oxygenated volatile organic compounds (oVOCs) from forest canopies  
15 has recently been observed to be bi-directional, with periods of strongly positive (i.e. up out  
16 of the canopy to the atmosphere above) and negative (i.e. downward) fluxes (Park et al.,  
17 2013;Karl et al., 2005;McKinney et al., 2011). Several of these compounds, e.g. acetone,  
18 acetaldehyde, and methanol, are present in the atmosphere in large quantities (Singh et al.,  
19 1995; Heikes et al., 2002; Millet et al., 2010; Jacob et al., 2002). They are also chemically  
20 active, with acetone and acetaldehyde leading to the formation of PAN (peroxyacetyl nitrate)  
21 and the transport of reactive nitrogen to remote regions (Fischer et al., 2014), and methanol  
22 contributing significantly to the production of ground-level ozone (Tie et al., 2003). These  
23 oVOCs have potentially important implications for regional air quality and climate modelling  
24 and for estimating global atmospheric burdens of many trace gases (e.g. Folberth et al., 2006;  
25 Fischer et al., 2014). However, many regional and global atmospheric chemistry and transport  
26 models (CTMs) do not explicitly include dynamic biogenic sources and sinks of oVOCs.  
27 While most now incorporate on-line calculations of biogenic emissions of isoprene and  
28 monoterpenes, based on the light and temperature-dependence algorithms developed by  
29 Guenther et al. (1995; 2006; 2012), methanol emissions have only been recently included in  
30 some CTMs (e.g. GEOS-Chem; Millet et al., 2010; Laboratoire de Météorologie Dynamique  
31 zoom (LMDz); Folberth et al., 2006) and most still rely on non-dynamic emissions  
32 inventories for methanol and acetaldehyde if primary biogenic emissions of these species are

1 included (e.g. UKCA: O'Connor et al., 2014). Furthermore, Ganzeveld et al. (2008)  
2 demonstrated the weaknesses of the algorithms currently used in 3-D chemistry transport  
3 models to calculate primary emissions of methanol on-line. Similarly, dry deposition schemes  
4 in CTMs are usually based on fixed deposition velocities (Wohlfahrt et al., 2015) or  
5 calculated from roughness lengths and leaf area index values assigned to generic landcover  
6 types (e.g. FRSGC-UCI: Wild et al., 2007; LMDz: Folberth et al., 2006). This simplistic  
7 approach to biogenic sources and sinks may be a critical omission limiting their capability of  
8 accurately simulating atmospheric composition in many world regions.

9 Here we focus on methanol and acetaldehyde, two oVOCs that are frequently observed in and  
10 above forests but whose sources, sinks and net budgets are not known with any certainty  
11 (Seco et al., 2007; Niinemets et al., 2004). While biogenic sources of both are strongly  
12 seasonal, fluxes and concentrations can remain high throughout the growing season  
13 (Stavrakou et al., 2011; Millet et al., 2011; Karl et al., 2003; Wohlfahrt et al., 2015). Methanol  
14 fluxes are on the same order of magnitude as isoprene at many sites in the US (Fall and  
15 Benson, 1996), suggesting their regional and global importance. The fundamental  
16 mechanisms leading to the synthesis and/or subsequent release of methanol and acetaldehyde  
17 are not currently fully understood (Karl et al., 2002; Seco et al., 2007).

18 Methanol is known to be produced from demethylation processes during cell wall expansion  
19 and leaf growth with emissions peaking during springtime leaf growth and declining with leaf  
20 age (Fall and Benson, 1996). The factors controlling its subsequent release to the atmosphere  
21 are harder to decipher (Huve et al., 2007; Niinemets et al., 2004). Measurements at all scales  
22 from leaf-level to branch enclosure and ground-based ecosystem-scale field measurements  
23 (e.g. Kesselmeier et al., 2001; Karl et al., 2003; Seco et al., 2015; Wohlfahrt et al., 2015), as  
24 well as satellite inversions (e.g. Stravakou et al., 2012) demonstrate a strong diurnal profile of  
25 methanol fluxes similar to that of isoprene (e.g. Fall and Benson, 1996). Methanol synthesis,  
26 unlike that of isoprene, is not specifically linked to photosynthesis and the light-dependence  
27 observed in leaf-level emissions have been shown to result from regulation by the stomata due  
28 to the high solubility of methanol in water (e.g. Nemecek-Marshall et al., 1995; Niinemets  
29 and Reichstein, 2003a,b; Huve et al., 2007).

30 The pathways leading to both the synthesis and emission of acetaldehyde are not clear (Karl  
31 et al., 2002; Jardine et al., 2008). Acetaldehyde has long been known to be an oxidation  
32 product of ethanol produced in leaves under anoxic conditions (Kreuzwieser et al., 2000) but

1 this cannot explain the strong emissions observed under normal environmental conditions at  
2 mid-latitude forests (e.g. Seco et al, 2007; Karl et al., 2003). Karl et al. (2003) observed that  
3 bursts of acetaldehyde were emitted during light-dark transitions and postulated that such  
4 emissions were associated with pyruvate decarboxylation. Leaf-level measurements of  
5 acetaldehyde emissions have also been found to be tightly coupled to stomatal aperture (e.g.  
6 Kreuzwieser et al., 2000; Karl et al., 2002; Niinemets et al., 2004) and it has been suggested  
7 that this may account for observed light-dependent ecosystem-scale emissions of  
8 acetaldehyde (Jardine et al., 2008).

9 Previous studies have suggested that the role of stomatal conductance in determining net flux  
10 of oVOCs could be incorporated in large-scale models by adopting a compensation point  
11 approach (see e.g. Harley et al., 2007; Ganzeveld et al., 2008; Jardine et al., 2008). The  
12 compensation point for a given compound is the atmospheric concentration of that compound  
13 at which the leaf, plant or canopy switches from acting as a net source to a net sink. While  
14 firmly based in plant physiology and plant response to environmental conditions, this  
15 approach would allow models\_lacking\_leaf-level processes\_to\_account\_for\_the\_changes in flux  
16 direction (Harley et al., 2007; Ganzeveld et al., 2008). Observational (Jardine et al., 2008) and  
17 modelling studies (Ganzeveld et al., 2008) have both shown the potential power of this  
18 approach, although Jardine et al. (2008) found that the compensation point was heavily  
19 dependent on light and temperature and may therefore not be straightforward to implement.

20 Here we use the FORCAsT (FORest Canopy-Atmosphere Transfer) canopy-atmosphere  
21 exchange model (Ashworth et al., 2015) to investigate the key processes driving fluxes of  
22 methanol and acetaldehyde, and explore possible underlying causes of their bi-directional  
23 exchange. The model represents all within-canopy processes: primary emissions, chemical  
24 and photolysis reactions, turbulent mixing and deposition. A particular strength of the  
25 FORCAsT model is the inclusion of plant processes relevant to photosynthesis and  
26 respiration; stomatal conductance is explicitly calculated by FORCAsT. We therefore focus  
27 on exploring the role of primary biogenic emissions of methanol and acetaldehyde on canopy-  
28 top fluxes. We assess the effectiveness of different representations of bVOC emissions  
29 mechanisms in capturing ecosystem-scale fluxes. For the first time in a canopy exchange  
30 model, we implement a mechanism by which stomatal conductance explicitly regulates  
31 primary emissions in order to assess its role in governing primary emissions and influencing  
32 ecosystem-scale bi-directional exchange of these key oVOCs. We compare modelled fluxes

1 using this mechanism with those from traditional empirical algorithms for direct and storage  
2 emissions and with fluxes measured just above the top of the canopy at Harvard Forest in July  
3 2012.

## 4 **2 Methods**

### 5 **2.1 Harvard Forest measurements**

6 Harvard Forest is situated in a rural area of Massachusetts, approximately 90 km from Boston  
7 and 130 km from Albany. It is classified as a mixed deciduous broadleaved forest, with red  
8 oak (36%) and red maple (22%) as the dominant species (Urbanski et al., 2007). Continuous  
9 measurements of micro-meteorological variables and air pollutants have been made from the  
10 Environmental Monitoring Station (EMS) Tower, part of the AmeriFlux network, for 25 years  
11 (Urbanski et al., 2007; Munger and Wofsy, 1999a; b). The tower, located at 42.5°N and  
12 72.2°W and an elevation of 340m, is 30m high and is surrounded by primary forest with an  
13 average height of around 23m. The long-term meteorological measurements include  
14 photosynthetically active radiation (PAR), relative humidity (RH) and air temperature at  
15 multiple heights on the tower, together with wind speed and direction recorded just below the  
16 top of the tower (at ~29m) (Urbanski et al., 2007; Munger and Wofsy, 1999a). In addition to  
17 exchanges of CO<sub>2</sub> collected to assess photosynthetic activity and productivity, concentrations  
18 of CO at the top of the tower and fluxes of O<sub>3</sub> (at multiple heights on the tower) are also  
19 routinely measured (Munger and Wofsy, 1999c). NO and NO<sub>2</sub> concentrations and fluxes have  
20 been recorded in the past (Munger et al., 1996; 1998), with the most recent measurements in  
21 2002 (Horii et al., 2004). In addition to these continuous atmospheric measurements, a suite  
22 of other data is gathered periodically to determine ecosystem health and functioning. Such  
23 data include leaf area index, tree girth, litter mass, leaf chemistry, and soil moisture and  
24 respiration (Barford et al., 2001; Urbanski et al., 2007; Munger and Wofsy, 1999b).

25 Concentrations and fluxes of bVOCs and their oxidation products have also been measured at  
26 the EMS Tower during several summer growing seasons (McKinney et al, 2011; Goldstein et  
27 al., 1999; 1995), augmenting the AmeriFlux suite of observations. Between 7th June and 24th  
28 September 2012, a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS  
29 8000, Ionicon Analytik GmbH, Austria) was used to measure the concentrations of volatile  
30 organic compounds at the site. The PTR-TOF-MS is capable of the rapid detection of  
31 hundreds of different VOCs at concentrations as low as a few pptv. PTR-TOF-MS has been

1 described previously by Jordan et al. (2009a; b) and Graus et al. (2010). The instrument  
2 utilizes a high-resolution TOF detector (Tofwerk AG, Switzerland) to analyze the reagent and  
3 product ions and allows for exact identification of the ion molecular formula (mass resolution  
4 >4000).

5 Ambient air was sampled from an inlet mounted at the top of the 30-m EMS tower at a total  
6 flow rate of 5 slpm using a configuration identical to that used by McKinney et al. (2011) in  
7 2007.  $\text{H}_3\text{O}^+$  reagent ions were used to selectively ionize organic molecules in the sample air.  
8 The instrument was operated with a drift tube temperature of 60°C and a drift tube pressure of  
9 2.20 mbar. The drift tube voltage was set to 550 V, resulting in an E/N of 126 Td (E, electric  
10 field strength; N, number density of air in the drift tube; unit, Townsend, Td; 1 Td =  $10^{-17}$  V  
11  $\text{cm}^2$ ). PTR-TOF-MS spectra were collected at a time resolution of 5 Hz. Mass calibration was  
12 performed every 2 min with data acquisition using the Tof-Daq v1.91 software (Tofwerk AG,  
13 Switzerland). A calibration system in which gas standards (Scott Specialty Gases) were added  
14 into a humidified zero air flow at controlled flow rates was used to establish the instrument  
15 sensitivities to VOCs. Every 3h the inlet flow was switched to pass through a catalytic  
16 converter (platinum on glass wool heated to 350°C) to remove VOCs and establish  
17 background intensities.

18 The PTR-TOF-MS captures the entire mass spectrum in each 5-Hz measurement, providing a  
19 continuous mixing ratio time series at each mass-to-charge ratio rather than the disjunct time  
20 series obtained in previous PTR-MS studies at this site (McKinney et al., 2011). As a result,  
21 direct, rather than virtual disjunct, eddy covariances were determined and are reported herein  
22 (Mueller et al., 2010). Wind speeds recorded at 8 Hz by a tri-dimensional sonic anemometer  
23 located at the same height and less than 1 m away from the gas inlet were averaged to a 5-Hz  
24 time base, synchronized with the mixing ratio data, and used in the eddy covariance  
25 calculations. Eddy covariance fluxes were calculated from the data for 30-minute intervals  
26 using methods described in McKinney et al. (2011). Ambient mixing ratios were averaged  
27 over the same 30-minute intervals for which fluxes were calculated. The 30-minute average  
28 mixing ratios and fluxes were then binned by time of day to calculate diurnal averages.

29 Eddy covariance is a powerful technique for the direct detection and estimation of ecosystem-  
30 scale fluxes of trace gases within and above vegetation canopies (see reviews by Baldocchi,  
31 2003; 2014). However, its reliability for measuring night-time fluxes can be low (Gu et al.,  
32 2005; Baldocchi, 2014; Goulden et al., 1996; Jarvis et al., 1997). Its successful application



1 relies on assumptions of steady-state conditions, conditions that do not always exist at night  
2 (see e.g. Baldocchi, 2003). The night-time formation of a stable atmospheric layer near the  
3 surface can result in stratification, trapping trace gases below the instrument detection height  
4 and altering the footprint of the flux measurement (Gu et al. 2005; Baldocchi, 2003) leading  
5 to high associated errors in flux estimation (Goulden et al., 1996). While we acknowledge that  
6 the magnitudes of the night-time fluxes recorded during summer 2012 may have large  
7 associated errors, we are confident that the direction of the exchange is well captured as the  
8 observed fluxes for different species were not correlated, suggesting no systematic bias in the  
9 application of eddy covariance at this site.

10 Isoprene, total combined monoterpenes, MVK and MACR (detected as a single combined  
11 species), methanol, acetaldehyde and acetone were all detected at concentrations well above  
12 the PTR-MS detection limit and determined to be free from interference from other  
13 compounds (McKinney et al., 2011). Here we confine our analysis to concentrations and  
14 fluxes of methanol and acetaldehyde. Table 1 summarises the relevant flux, concentration and  
15 meteorological measurements made at the EMS tower during the summer of 2012.

## 16 **2.2 FORCAsT1.0 canopy exchange model**

17 FORCAsT (version 1.0) is a single column (1-D) model that simulates the exchange of trace  
18 gases and aerosols between the forest canopy and atmosphere. A full description of  
19 FORCAsT is given in Ashworth et al. (2015). Here we provide a brief overview, summarise  
20 biogenic emissions and flux calculations in the model and describe the simulations performed.

21 FORCAsT1.0 has 40 vertical levels of varying thickness extending to a height of ~4km, with  
22 the highest resolution nearest the ground where the complexity is greatest, i.e. within the  
23 canopy space. Micro-meteorological conditions (temperature, PAR, RH) within the canopy  
24 are determined prognostically by energy balance, accounting for the physical structure of the  
25 canopy. The gas-phase chemistry scheme incorporated in FORCAsT1.0 is a modified version  
26 of the CalTech Chemical Mechanism (CACM; Griffin et al., 2002; 2005; Chen and Griffin,  
27 2005), which includes 300 species whose concentrations are solved at every chemistry  
28 timestep (currently 1 minute), plus O<sub>2</sub> and water vapour (Ashworth et al., 2015). Ninety-nine  
29 of the species are assumed to be condensable, and are lumped into 11 surrogate groups based  
30 on similar volatility and structure. Aerosol-phase concentrations of these surrogate groups are

1 also calculated at every timestep based on equilibrium partitioning (Ashworth et al., 2015;  
2 Chen and Griffin, 2005).

3 The CACM chemistry mechanism in FORCAsT treats methanol explicitly with no chemical  
4 sources (e.g., production from peroxy radicals) and a sink via oxidation by OH to produce  
5 formaldehyde. Acetaldehyde is not treated explicitly but is instead included in a lumped group  
6 of aldehydes (ALD1, with  $<C_3$ ). The oxidation reactions for this group are based on  
7 acetaldehyde and no other species is currently emitted into the ALD1 group. Acetaldehyde  
8 has a far greater number of chemical sources and sinks in the FORCAsT simulations of a  
9 forest environment than methanol. See Ashworth et al. (2015) for details of the reactions and  
10 reaction rates included in FORCAsT.

11 FORCAsT incorporates dry deposition of all species based on the resistance scheme of  
12 Wesely (1989) and modified by Gao et al. (1993). The scheme assumes that the rate of  
13 deposition of a compound to canopy surfaces is determined by atmospheric, boundary and  
14 surface resistances operating in series or parallel analogous to electrical resistances.  
15 Atmospheric and surface boundary layer resistances are common to all chemical species and  
16 are dependent on turbulence. As FORCAsT includes an explicit representation of the canopy,  
17 the surface resistance term includes cuticular, mesophylllic and stomatal resistances which are  
18 dependent on the physic-chemical properties of the depositing species as well as the light,  
19 temperature and water potential of the leaf. The deposition scheme described in Ashworth et  
20 al. (2015) and Bryan et al. (2012) has been updated to include methanol. The deposition  
21 velocity of acetaldehyde is calculated using parameters for the lumped ALD1 group, and the  
22 parameters for ALD1 and methanol deposition are shown in Table 3.

23 While a 1-D model cannot capture horizontal transport, FORCAsT does include a simple  
24 parameterisation to account for advection (Bryan et al., 2012; Ashworth et al., 2015). For the  
25 simulations here, only advection of  $NO_2$  is considered such that a  $NO_2$  mixing ratio of 1 ppbv  
26 is set just above the canopy based on average midday (defined as 10:00-17:00 EST)  $NO_x$  and  
27  $NO_y$  (total reactive nitrogen species) concentrations. While nitrogen species were not  
28 measured at Harvard Forest in 2012, concentrations reported from the site by Munger et al.  
29 (1996) are extrapolated to 2012 using July monthly average  $NO_x$  levels measured at the  
30 nearby US EPA monitoring station at Ware 42.3°N, 72.3°W, elevation 312m (roughly 30km  
31 southwest of the EMS Tower). This scaling accounts for the observed decrease in  $NO_x$  levels  
32 across the region as a result of emission reduction strategies (see e.g. EPA, 2015). All  $NO_x$  is

1 assumed to be advected as NO<sub>2</sub>. The initial concentration of N<sub>2</sub>O<sub>5</sub> at 29m was set to give an  
2 average NO<sub>x</sub>:NO<sub>y</sub> ratio of 0.4 (Munger et al., 1996), assuming all residual NO<sub>y</sub> to be N<sub>2</sub>O<sub>5</sub>  
3 initially. Lee et al. (2006) also reported that air masses reaching the Harvard Forest site from  
4 the north, northwest and west had consistently low levels of anthropogenic VOCs. Such  
5 conditions prevailed >60% of July 2012 and we found that including advection as an  
6 additional source of methanol and acetaldehyde did not improve model fit (results not shown).

### 7 **2.2.1 Flux calculations**

8 Fluxes of gases and particles are calculated to be proportional to both the concentration  
9 gradient and the efficiency of vertical mixing between adjacent model layers (Eq. 1). Upward  
10 fluxes are modelled as positive and occur when the concentration of a particular species is  
11 higher at a lower height. The flux,  $F_i$  (kg m<sup>-2</sup> s<sup>-1</sup>) of an individual species,  $i$ , between two  
12 model levels is given by:

$$13 \quad F_i = -K_H \frac{\Delta C_i}{\Delta z}, \quad (1)$$

14 where  $K_H$  is the eddy diffusivity (m<sup>2</sup> s<sup>-1</sup>),  $\Delta C_i$  the difference in mass concentrations (kg kg<sup>-1</sup>) at  
15 the mid-height of the levels, and  $\Delta z$  the difference in height (m) between the levels. Eddy  
16 diffusivity, concentrations of all gas-phase and aerosol species, and fluxes are calculated at 1-  
17 minute timesteps. The eddy diffusivity at the instrument height of 29m is constrained by  
18 observed windspeeds (Bryan et al., 2012).

19 Vertical mixing is calculated prognostically in the model following Blackadar (1979) and  
20 driven by observed top of canopy radiation and wind speed. The within-canopy wind profile  
21 is calculated following Baldocchi (1988). Turbulence and mixing in the canopy space is then  
22 modified according to Stroud et al. (2005) with wind speed and eddy diffusivity constrained  
23 to observations at the top of the canopy. A full description of the vertical mixing and its  
24 impact on concentration gradients is described in Bryan et al. (2012).

25 Modelled fluxes should be viewed as an instantaneous snapshot, both temporally and  
26 spatially, as the calculation relies heavily on the concentration gradient across an arbitrary  
27 boundary level, in this case the instrument height of 29 m. Actual concentration gradients  
28 display rapid fluctuations (see e.g. Steiner et al., 2011) due to heterogeneity in emissions (see  
29 e.g. Bryan et al., 2015) and chemistry (see e.g. Butler et al., 2008), as well as the occurrence

1 of coherent structures which can result in counter-gradient flow of matter (Steiner et al., 2011  
2 and references therein).

### 3 **2.2.2 Biogenic emissions**

4 Emissions of VOCs from vegetation can be described as following one of two possible routes  
5 (Grote and Niinemets, 2008). In the first, the compound is released to the atmosphere  
6 immediately on production (e.g. isoprene). Such emissions are tightly coupled to  
7 photosynthesis and are therefore dependent on both temperature and light, falling to zero at  
8 night. We refer to such emissions as “direct”. In the second pathway, VOCs are stored in  
9 specialist structures within the plant after their production (e.g. monoterpenes). Emissions  
10 from these storage pools occur by diffusion and are controlled by temperature alone. We term  
11 these “storage” emissions. It is thought that emissions of oVOCs are a combination of these  
12 (“combo”), with a proportion released directly on synthesis and the remaining fraction  
13 emitted from storage pools.

14 Emission rates are calculated in FORCAsT by modifying basal emission factors (rates at  
15 standard conditions, usually 30°C and 1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$  of PAR) according to empirical  
16 relationships describing their dependence on light and temperature. These modifications  
17 (referred to as activity factors) follow the standard parameterisations of Guenther et al. (1995;  
18 2012). For storage emissions, which are modelled as dependent on temperature only, the  
19 activity factor is a simple exponential relationship:

$$20 \gamma_T = e^{-\beta(T_L - T_s)}, \quad (2)$$

21 where  $\gamma_T$  is the temperature-dependent activity factor for storage emissions,  $\beta$  the temperature  
22 response factor ( $\text{K}^{-1}$ ),  $T_s$  is 293K,  $T_L$  (K) the leaf temperature (see Guenther et al., 2012). For  
23 further details of the activity factors for direct emissions included in FORCAsT the reader is  
24 referred to Ashworth et al. (2015) and references therein.

### 25 **2.2.3 Stomatal resistance**

26 FORCAsT includes a physical representation of a forest canopy, with the lowest eight model  
27 levels set as trunk space and the next ten as crown space. The ten crown space levels contain  
28 the foliage; the total leaf area estimated for 2012 based on litter fall is distributed among the  
29 levels according to balloon measurements made at the site by Parker (1999). Within each  
30 crown space level, the leaves are assigned to one of nine equally-spaced angle classes

1 assuming a spherical canopy based on leaf normal angle (Goel et al., 1989) and the fraction of  
 2 shaded leaf area calculated. Photosynthetic parameters, including stomatal resistance, are then  
 3 calculated for each leaf angle class at each level within the crown space. The stomatal  
 4 conductance (inverse of stomatal resistance) describes the aperture of the stomata and  
 5 determines evapo-transpiration (hence heat flux and energy balance) and deposition rates  
 6 within FORCAST. It is not currently used to control the rate of biogenic emissions.

7 Stomatal resistance is modelled according to leaf temperature, PAR, water potential and  
 8 vapour pressure deficit using the relationships developed by Jarvis (1976) as described by  
 9 Baldocchi et al. (1987). The overall stomatal resistance ( $r_s$ ) is the product of these individual  
 10 factors (Eq. 3) which are summarised below in Eqs. 4-8

$$11 \quad r_s = r_{s\min} \cdot r_s(\text{PAR}) \cdot r_s(T) \cdot r_s(D) \cdot r_s(p), \quad (3)$$

12 where  $r_s(\text{PAR})$  is the response of stomatal resistance to changes in PAR,  $r_{s\min}$  ( $\text{s m}^{-1}$ ) is the  
 13 minimum stomatal resistance and  $b_{rs}$  is an empirical coefficient:

$$14 \quad r_s(\text{PAR}) = r_{s\min} \left( 1 + \frac{b_{rs}}{\text{PAR}} \right), \quad (4)$$

15 and  $r_s(T)$  is the response of stomatal resistance to changes in leaf temperature ( $T_{lf}$ , °C),  $T_{\min}$ ,  
 16  $T_{\max}$ , and  $T_0$  are the minimum and maximum temperatures for stomatal opening and optimum  
 17 temperature respectively:

$$18 \quad r_s(T) = \left\{ \left( \frac{T_{lf} - T_{\min}}{T_0 - T_{\min}} \right) \left( \frac{T_{\max} - T_{lf}}{T_{\max} - T_0} \right)^{b_T} \right\}^{-1}, \quad (5)$$

$$19 \quad b_T = \left( \frac{T_{\max} - T_0}{T_{\max} - T_{\min}} \right), \quad (6)$$

20 and  $r_s(d)$  is the relationship between stomatal resistance and vapour pressure deficit ( $D$ ;  
 21 mbar), and  $b_v$  is an empirical coefficient:

$$22 \quad r_s(D) = \left( 1 + \frac{b_v}{D} \right)^{-1}, \quad (7)$$

23 Water potential is assumed to act only once a threshold value is reached. Above this value it is  
 24 modelled as:

$$25 \quad r_s(\varphi) = \left( \frac{1}{\alpha \cdot \varphi + b_w} \right), \quad (8)$$

1 where  $\phi$  is the water potential (bar), and  $a$  and  $b_w$  are constants. Below the water potential  
2 threshold  $r_s(\phi)$  is taken as unity. The values of the constants used in these calculations are  
3 shown in Table 4.

4 Stomatal resistance is only calculated in FORCAsT during the day (defined within FORCAsT  
5 as  $\text{PAR} \geq 0.01 \text{ W m}^{-2}$ ); at night stomatal resistance is assumed equal to the minimum cuticular  
6 resistance ( $3000 \text{ s m}^{-1}$ ).

### 7 **2.3 FORCAsT simulations**

8 All model simulations were performed for an average day in July 2012, the middle of the  
9 growing season, to ensure measurement data did not include either the spring burst of  
10 methanol nor elevated acetaldehyde emissions during senescence. FORCAsT was initiated  
11 with site-specific parameters and measurements of the physical structure of the canopy and  
12 environmental conditions (Table 2). Initial meteorological conditions and atmospheric  
13 concentrations of chemical species were taken from the 2012 EMS tower data (see Table 2).  
14 Initial air temperature above the canopy is calculated on-line using the average lapse rate  
15 observed by the radiosonde at Albany (the nearest sounding station, ~90km from Harvard  
16 Forest), and within the canopy by interpolation with the 2-m temperature reading.  
17 Concentrations of  $\text{O}_3$  within the canopy are based on observations from the EMS tower, and  
18 above the canopy follow a typical night-time profile as described in Forkel et al. (2006).  
19 Concentrations of other species are assumed to decay exponentially with height such that the  
20 e-folding height is 100m for short-lived species and 1000m for longer-lived compounds. All  
21 model simulations started at 00:00 EST and continued for 48 hours, with the same driving  
22 data used for each 24-hour period and analysis confined to the second day to account for  
23 model spin-up.

24 In addition to a baseline simulation, we perform a series of simulations that represent the  
25 potential bVOC emissions routes using the “traditional” algorithms based on the observed  
26 light and/or temperature dependence encapsulated in the MEGANv2.1 model of Guenther et  
27 al. (2012); see Section 2.2.2. We then introduce stomatal control to the temperature-only  
28 dependent emissions (i.e. those from storage pools) to determine whether the observed leaf-  
29 level regulation of the emissions of oVOCs by stomatal aperture affects ecosystem-scale  
30 fluxes (Section 2.3.3). A final series of sensitivity tests explores the extent to which stomatal

1 control governs canopy-top fluxes (Section 2.3.3). Table 5 summarises the simulations and  
2 sensitivity tests.

3 Model performance was evaluated against average fluxes and concentrations measured at 29m  
4 throughout July 2012 at Harvard Forest. The raw measurement data were grouped and  
5 averaged for each model output time for the duration of the campaign period to create  
6 “typical” diurnal profiles of methanol and acetaldehyde fluxes and concentrations. The flux  
7 data in particular exhibited large variability introducing high uncertainty to the assessment.  
8 Observations of both fluxes and concentrations of acetaldehyde were more variable than those  
9 of methanol, reflecting the greater number of chemical sources and sinks of acetaldehyde in  
10 conjunction with lower emission rates. The observations referred to throughout the main text  
11 and shown in Fig. 4, 6 and 7 are these averages of the campaign data.

### 12 **2.3.1 Baseline**

13 All simulations were driven using meteorology for an average July day with initial conditions  
14 set to July average values for all variables at 00:00 EST (shown in Table 2). For the baseline  
15 simulation, default FORCAsT settings for emissions, dry deposition and chemical production  
16 and loss (Ashworth et al., 2015) were used; the default FORCAsT settings do not consider  
17 primary emissions of methanol and acetaldehyde. Only primary emissions of isoprene and the  
18 monoterpenes  $\alpha$ -pinene,  $\beta$ -pinene and *d*-limonene are included in the base case, with emission  
19 factors (Table 6a) based on average rates for mixed deciduous woodland in N America  
20 (Geron et al., 2000; Helmig et al., 1999).

### 21 **2.3.2 Primary emissions sensitivity tests**

22 Simulations including primary emissions of methanol and acetaldehyde were conducted to  
23 understand the effect of adding primary emissions of oVOC. The specific changes from the  
24 baseline are described below and summarised in Table 5.

25 In the first three “emissions” (E-) simulations, primary emissions of methanol and  
26 acetaldehyde are included: firstly with all emissions assumed to be direct (E-direct), then all  
27 from storage pools (E-storage), and finally as a combination of the two with 80% taken to be  
28 direct and the remainder storage (E-combo). Emission rates for methanol and acetaldehyde  
29 (Table 5) were initially based on standard emission factors for methanol and bidirectional  
30 VOCs, respectively, for temperate deciduous broad-leaved trees given by Guenther et al.

1 (2012) and scaled for this site by isoprene emission factor. The emission factors were then  
2 modified to best reconcile modelled and observed concentrations and fluxes at 29 m whilst  
3 conserving the total canopy emissions for each species as far as possible. Twenty-four hour  
4 aggregate emissions for each simulation were within ~10% of each other. The proportion of  
5 80% direct and 20% storage emissions included in E-combo was also based on the “light-  
6 dependent fractions” assigned to methanol and bidirectional VOCs by Guenther et al. (2012).  
7 A sensitivity test with the combination of 90% direct and 10% storage (E-combo90) was also  
8 performed. For each simulation, emission factors and total emissions are listed in Table 6b,  
9 and diel profiles of total emissions, deposition and canopy chemical production and loss are  
10 shown in Fig. 1. While the general pattern of emissions is the same in all simulations (Figs.  
11 1a,b), the magnitude of the midday peak and overnight emission rate vary between the  
12 different emission pathways introduced. The greater the contribution from storage the higher  
13 the overnight fluxes and the smaller the diurnal amplitude with E-direct (green line; 0%  
14 storage emissions) and E-storage (blue line; 100% storage) representing the extreme cases.  
15 Changes in emission rates alter the concentrations of methanol or acetaldehyde within the  
16 crown space driving differences in both dry deposition (Figs. 1c,d) and chemical production  
17 and loss (Figs. 1e,f) rates. Fig. 1 further demonstrates the relatively small contribution of  
18 chemical production and loss to the canopy space budgets of methanol and acetaldehyde.

### 19 **2.3.3 Stomatal control sensitivity tests**

20 Previous theoretical and laboratory-based studies have demonstrated the importance of  
21 stomatal aperture in the regulation of emissions of oVOCs from storage structures (e.g.  
22 Niinemets and Reichstein, 2003a,b; Nemecek-Marshall et al., 1995; Huve et al., 2007; Karl et  
23 al., 2002). Controlled experiments and leaf-level measurements suggest that emissions of  
24 many VOCs are dependent on stomatal conductance, although the extent to which the stomata  
25 regulate emission rates is highly dependent on both the compound and the leaf structure  
26 (Niinemets and Reichstein, 2003a).

27 Further sensitivity tests were performed specifically to test the dependence of the emissions of  
28 methanol and acetaldehyde on stomatal conductance. Stomatal resistance (the reciprocal of  
29 conductance) is explicitly calculated for every canopy level at every model timestep based on  
30 incident PAR, leaf temperature and water potential (Eq. 3). In this series of tests, the  
31 calculated resistances were used to scale the temperature-dependence of storage emissions of



1 methanol and acetaldehyde (given in Eq. 2) for both the storage and combo emission  
2 pathways as shown in Eq. 9.

$$3 \gamma_{\text{TR}} = \gamma_{\text{T}} \cdot R_{\text{fct}} = e^{-\beta(T_{\text{L}} - T_{\text{S}})} \cdot R_{\text{fct}}, \quad (9)$$

4 where  $R_{\text{fct}}$  is a stomatal control factor.

5 In the first of the “stomatal control” (S-) sensitivity tests,  $R_{\text{fct}}$  increased proportionally with  
6 stomatal conductance (i.e. inversely with stomatal resistance) as shown in Eq. 10:

$$7 R_{\text{fct}} = \frac{3000}{n \cdot R_{\text{stom}}}, \quad (10)$$

8 where  $R_{\text{stom}}$  ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) is the stomatal resistance, 3000 ( $\text{s m}^{-1}$ ) is the model default  
9 limiting night-time value of  $R_{\text{stom}}$  and  $n$  is a scaling factor. The night-time “stomatal”  
10 resistance is in fact equal to the cuticular resistance and  $n$  was introduced to account for this.

11 (During the day, the leaf resistance, the combination of the stomatal and cuticular resistances  
12 in parallel, is dominated by the stomatal resistance). The value of  $n$  was initially set to 3 for  
13 the S-storage and S-combo simulations, as Jarvis (1976) reported a limiting value of 1000  
14 although this was species-dependent. The effect of the choice of value of  $n$  is explored in  
15 Section 3.5.

16 Fig. 2 shows the diel cycle of stomatal resistances calculated in FORCAsT for each model  
17 level within the crown space; an average canopy resistance is also indicated.  $R_{\text{stom}}$  is set to  
18 3000 overnight and falls to a minimum during the middle of the day when light levels are  
19 highest in the canopy.  $R_{\text{stom}}$  is lower at the top of the canopy and increases with increasing  
20 depth into the foliage layers. The profile of  $R_{\text{fct}}$  (Eq. 10) describes the inverse of  $R_{\text{stom}}$ ,  
21 reaching a peak at midday and having a greater value higher in the canopy. As shown in the  
22 middle panels  $R_{\text{fct}}$  reaches  $>1.0$  during the middle of the day for all but the very lowest canopy  
23 layers. Modelled stomatal control (S- simulations) therefore enhances emissions of methanol  
24 and acetaldehyde above those simulated by traditional emissions algorithms during this time.  
25 There is evidence that this may be biologically realistic with stomatal aperture limiting  
26 emissions from storage pools and leading to increased pool size and hence greater  
27 concentration gradients between plant tissue and the surrounding atmosphere (see e.g. Jardine  
28 et al., 2008). This in turn drives an increase in emissions above those predicted based on  
29 synthesis rates of oVOC. However, traditional emissions models were derived to fit observed  
30 emission rates (see e.g. Guenther et al., 1993) and could be assumed to account for this effect.

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1 Hence, a second set of “modified” stomatal control (R-) experiments was performed in which  
2 it was assumed that beyond a threshold stomatal aperture, stomatal conductance no longer  
3 controls emissions, which continue unhindered once the stomates are considered to be fully  
4 open. Beyond this point, emissions from storage pools are regulated by temperature alone  
5 according to the relationship in Eq. 2, i.e.  $R_{fct}$  in Eq. 9 takes a value of unity, thus assuming  
6 that “traditional” emissions algorithms correctly capture emission rates during the middle of  
7 the day. Within FORCAsT this was modelled using a threshold function:

$$8 \quad R_{fct} = \frac{3000}{n \cdot R_{stom}}, R_{fct} < 1.0 \quad (11a)$$

$$9 \quad R_{fct} = 1.0, \quad \text{at all other times} \quad (11b)$$

10 The use of the function shown in Eqs. 11a and 11b limits the temporal extent of stomatal  
11 control on methanol and acetaldehyde emissions for most canopy layers to the transition times  
12 of day (dawn and dusk) when the stomata are either opening or closing as light levels increase  
13 or decrease. This is consistent with results from controlled experiments and observations by  
14 Niinemets and Reichstein (2003a) that indicate that stomatal aperture has only a transient  
15 effect on the emissions of oVOC and is negligible under steady-state light conditions. It  
16 should be noted however that under the average July radiation conditions the lower canopy  
17 levels do not receive sufficient PAR to reach this threshold value within FORCAsT.

## 18 **3 Results**

### 19 **3.1 Summary of observations**

20 July was roughly the middle of the growing season in 2012 with emissions unaffected by  
21 springtime leaf flush or autumn senescence. As observed previously at many sites, fluxes of  
22 both methanol and acetaldehyde are highly variable with periods of net positive and net  
23 negative exchange (e.g. McKinney et al., 2011; Wohlfahrt et al., 2015; Karl et al., 2005). In  
24 prior years, concentrations of methanol at Harvard Forest remained high even outside of the  
25 spring emissions peak (McKinney et al., 2011).

26 Fig. 3 shows correlations of the observed daytime (05:00-19:00 EST) fluxes of methanol and  
27 acetaldehyde during July 2012 with air temperature, PAR, canopy stomatal conductance, and  
28 concentrations of methanol and acetaldehyde respectively. Canopy stomatal conductance for  
29 the tower footprint was estimated from energy fluxes measured at Harvard Forest following  
30 the methodology of Shuttleworth et al. (1984) to calculate surface resistances. The raw data

1 were highly scattered, and were therefore binned by the independent variable in each case  
2 with Fig. 3 showing only the mean values (with bars showing  $\pm 1$  standard deviation to give an  
3 indication of the variability of the data) for each of these bins for clarity. The weak  
4 relationships with each of the environmental variables evident in Fig. 3 illustrate the difficulty  
5 in identifying the key processes driving canopy-scale exchanges of oVOC under varying  
6 environmental conditions from observations alone.

7 Canopy-top fluxes of methanol appear to be positively correlated with temperature (Fig. 3a)  
8 and to a lesser extent with PAR (Fig. 3c). The correlation with temperature seems to be  
9 exponential as might be expected. The contribution of stomatal conductance to observed  
10 methanol fluxes is more difficult to interpret although the data appear to show a strong linear  
11 correlation at low conductance, suggesting that at small stomatal aperture the stomata exert  
12 control over fluxes of methanol to the extent that it is observable at the canopy scale.  
13 However, it is possible that this correlation instead reflects correlated responses of emissions  
14 and stomatal aperture to increasing light and temperature. The positive relationship between  
15 canopy-top methanol fluxes and concentrations at low concentration is likely due to the  
16 influence of increasing light and temperature increasing production of methanol at a greater  
17 rate than the loss processes (dry deposition to surfaces within the canopy and chemical loss).  
18 At higher concentrations, methanol loss rates increase sufficiently to balance production.

19 Fluxes of acetaldehyde are lower and more variable than those of methanol, and averages are  
20 clustered near zero. However, they do appear to be positively correlated with temperature  
21 (Fig. 3b) although the relationship is weaker and does not appear to be exponential. There is  
22 no discernible correlation between acetaldehyde fluxes and either PAR (Fig. 3d) or stomatal  
23 conductance (Fig. 3f). This might suggest that acetaldehyde emissions are not controlled by  
24 stomatal aperture but may rather indicate the influence of the greater number of sources and  
25 sinks for acetaldehyde at the spatial and temporal scale of the canopy. Jardine et al. (2008)  
26 describe a clear negative correlation between acetaldehyde fluxes and concentrations  
27 measured in the laboratory and Fig. 3h could be interpreted in a similar way although the  
28 correlation here (at the canopy scale) is far weaker.

29 The weakness of the observed correlations and variability of the observed fluxes are a  
30 reflection of the complexity of in-canopy processes and interactions, all of which (emissions,  
31 photo-chemical production and loss, and turbulent exchange) are strongly influenced by  
32 temperature while only photolysis and direct foliage emissions are directly dependent on light

1 levels (although the penetration of radiation into the canopy drives both leaf temperature and  
2 turbulence).

### 3 **3.2 Baseline**

4 When FORCAST is driven in default mode with average meteorology and initial conditions  
5 for July 2012 and primary emissions of only isoprene and monoterpenes, the model fails to  
6 capture either the magnitude or diurnal profile of the observed concentrations and fluxes of  
7 methanol and acetaldehyde at 29 m (Fig. 4(a)-(d); black lines). For both methanol and  
8 acetaldehyde FORCAST simulates negative fluxes at all times, with a pronounced decrease  
9 during daylight hours (Fig. 4(a) and (c)). Fluxes measured by eddy covariance by contrast  
10 show strongly positive (upward) exchange occurring during the day and fluxes near zero at  
11 night. Observed concentrations increase to 12.8 ppbv (methanol) and 0.72 ppbv  
12 (acetaldehyde) during daylight hours, dipping sharply after dusk and decreasing steadily to a  
13 minimum around dawn (Fig. 4(b) and (d)). By contrast the baseline modelled concentrations  
14 of both compounds decrease throughout the 24-hour period, (Fig. 4(b) and (d)), suggesting  
15 strong daytime sources of both methanol and acetaldehyde within the canopy, which  
16 FORCAST does not simulate with the default model settings.

### 17 **3.3 Biogenic emissions of methanol and acetaldehyde ('E-' simulations)**

18 Leaf-level measurements of methanol emissions have demonstrated that all C<sub>3</sub> vegetation  
19 types emit methanol at rates on a par with the major terpenoids (Fall and Benson, 1997).  
20 Given the lack of other in-situ sources of methanol, the diel cycle of fluxes and concentrations  
21 which is generally absent from anthropogenic and transported sources, and the magnitude of  
22 the underestimation of canopy-top fluxes (ranging from ~0.01 overnight to 0.7 mg m<sup>-2</sup> h<sup>-1</sup> in  
23 the early afternoon), it seems likely that there are substantial foliage emissions of methanol at  
24 Harvard Forest (see also McKinney et al., 2011). Furthermore the diurnal profile, strongly  
25 reminiscent of isoprene, suggests the emissions are both light and temperature dependent.

26 While the magnitude of the missing acetaldehyde fluxes is lower (between ~0.01 and 0.05 mg  
27 m<sup>-2</sup> h<sup>-1</sup>), the diel cycles of both fluxes and concentrations is similar to those of methanol. This  
28 again suggests relatively strong leaf-level emissions of acetaldehyde at this site. It is likely  
29 that the absolute concentrations and fluxes are lower as primary emissions of acetaldehyde

1 have generally been found to be a factor of 2-10 lower than those of methanol (Seco et al.,  
2 2007; Karl et al., 2003; Guenther et al., 2012).

3 Fig. 5 shows the relative contributions of the competing processes driving the evolution of  
4 methanol and acetaldehyde within and just above the canopy over the course of the day for  
5 the E-combo90 and E-combo simulations respectively. Concentrations of both oVOC (Fig. 5a  
6 and 3g) increase strongly at all levels from a minimum around dawn. In the case of methanol  
7 (Fig. 5a) there is a clear maximum just below the top of the canopy corresponding to the most  
8 densely foliated level where emissions also peak. This feature is less evident in the case of  
9 acetaldehyde (Fig. 5g) demonstrating its greater number of sources and sinks. Chemical  
10 production and loss is highest at the top of the canopy and the boundary layer just above due  
11 to the higher levels of radiation and temperature driving OH radical formation and reaction  
12 rates. For both oVOC it is emissions and deposition, both leaf-level processes governed by the  
13 stomata, that dominate production and loss; chemistry contributions are at least an order of  
14 magnitude lower. However, both chemistry and turbulent transport contribute to the  
15 complexity evident in the evolution of concentrations and fluxes and the high degree of  
16 variability seen in the observations (see e.g. Figs. 3 and 5).

17 Difficulties in simultaneously reconciling both fluxes and concentrations of methanol and  
18 acetaldehyde are also likely a result of the complexity of in-canopy processes. Fig. 5 shows  
19 that the top of the canopy is a region of abrupt transition for the sources and sinks of oVOC  
20 with emissions and deposition limited to the canopy and a sudden change in turbulent mixing  
21 above the foliage. The heterogeneity of concentrations, concentration gradients and fluxes of  
22 methanol and acetaldehyde in time and space are evident from Fig. 5, demonstrating that the  
23 level at which model and measurements are compared can also affect the measured-modeled  
24 bias.

### 25 **3.3.1 Methanol**

26 The effect of introducing the different mechanisms of methanol emissions (simulations E-  
27 direct, E-storage, E-combo; Table 5) on fluxes and concentrations of methanol are shown in  
28 Fig. 4(a) and (b). Storage emissions (dependent only on temperature) remain relatively high  
29 overnight. While modelled fluxes of methanol are positive when storage emissions are  
30 included and peak during the middle of the day, modelled midday fluxes are only around a  
31 third of measured fluxes (Fig. 6(a); E-storage) and modelled night-time fluxes are well above

1 (~0.15-0.20 mg m<sup>-2</sup> h<sup>-1</sup>) those observed which are close to but slightly below zero. The diurnal  
2 profile of E-storage modelled concentrations is the inverse of measured methanol mixing  
3 ratios: elevated at night and decreasing toward the middle of the day (Fig. 6(b); E-storage).  
4 This gives further credence to the light-dependence of methanol emissions, which has been  
5 identified at numerous other forest ecosystems (see e.g. Wohlfahrt et al., 2015; Seco et al.,  
6 2015; McKinney et al., 2011).

7 Direct emissions are intrinsically linked to photosynthesis and are therefore strongly  
8 dependent on light as well as temperature. Introducing purely direct emissions of methanol in  
9 FORCAsT (E-direct) reproduces the observed diurnal profile of both fluxes and  
10 concentrations and succeeds in capturing the pronounced daytime peak and sharp drop-off at  
11 night seen in both. Modelled mixing ratios, however, peak slightly in advance of the observed  
12 maximum (Fig. 6(b); E-direct) and do not drop sharply enough after dusk. Modelled fluxes  
13 remain negative at night (Fig. 4(a); E-direct) but are slightly below those observed during the  
14 dawn transition period, suggesting that while methanol emissions are light dependent they  
15 may not be purely direct emissions (which drop to zero at night), although the limitations of  
16 eddy covariance flux measurement techniques at night may introduce error into the  
17 observation-model comparison.

18 Combo emissions comprising 80% direct and 20% storage emissions (E-combo) do not  
19 reproduce the observed decrease in fluxes and concentrations at night. Modelled nighttime  
20 fluxes remain positive and ~0.05-0.1 mg m<sup>-2</sup> h<sup>-1</sup> above those observed (Fig. 6(a); E-combo),  
21 although as noted above, nighttime flux measurements usually have the greatest uncertainties  
22 due to the potential for stable boundary layers and changes in the flux footprint. Additionally,  
23 modelled concentrations do not rise sufficiently during the day (with a maximum discrepancy  
24 of ~1.5-2 ppbv or 15%) nor drop as steeply as observations after dusk (Fig. 4(b); E-combo).  
25 Increasing the proportion of direct emissions to 90% (Fig. 4(a) and (b)) improves the fit of  
26 both fluxes and concentrations at all times with maximum daytime differences reduced to 0.2  
27 mg m<sup>-2</sup> h<sup>-1</sup> (~30%) and 1.0 ppbv (~8%) respectively. Modelled concentrations still fail to  
28 capture the pronounced changes observed at dawn, although this may be the result of  
29 boundary layer dilution and canopy flushing.

30 The E-direct simulation gives the best overall model-measurement fit of the emissions  
31 sensitivity tests, emphasizing the strong light-dependence of methanol emissions previously  
32 noted. Including direct emissions in FORCAsT simulates the bi-directional fluxes and a diel

1 cycle of concentrations similar to those observed at this site. Such emissions do not fully  
2 capture all of the features of the field data, indicating that while methanol emissions are  
3 strongly light-dependent, traditional models of primary biogenic emissions (e.g. MEGAN;  
4 Guenther et al., 2012) may not fully account for the fundamental processes driving methanol  
5 exchange between the canopy and atmosphere even when a small contribution from storage  
6 pools (e.g. E-combo90) is included. However, it should be noted that the fluxes especially  
7 represent instantaneous assessments of a situation that rapidly fluctuates in both time and  
8 space, which may in part account for the discrepancies between model and measurements.

### 9 **3.3.2 Acetaldehyde**

10 Similar to methanol, introducing storage only emissions of acetaldehyde does not capture the  
11 peak in fluxes during the day (Fig. 4(c); E-storage), suggesting that acetaldehyde emissions  
12 are also light dependent. Modelled concentrations are close to those observed during daylight  
13 hours in both magnitude and profile with a maximum difference of  $\sim 0.2$  ppbv (15%), but do  
14 not reproduce the observed drop in concentration just after dusk nor the rapid increase after  
15 dawn (Fig. 4(d); E-storage). However, the greater complexity of acetaldehyde production and  
16 loss on the timescales involved in canopy-atmosphere exchange makes interpretation of the  
17 concentrations more difficult.

18 Introducing purely direct emissions of acetaldehyde (E-direct) has the same effect as for  
19 methanol. Fluxes are strongly negative at night in FORCAsT (around  $0.01$ - $0.015$   $\text{mg m}^{-2} \text{h}^{-1}$   
20 below observed fluxes – Fig. 4(c); E-direct) and concentrations rise too quickly during the  
21 day, peaking around 4 hours earlier and  $\sim 0.10$  ppbv ( $\sim 15\%$ ) higher than measured mixing  
22 ratios (Fig. 4(d); E-direct) with a maximum over-estimation of  $\sim 0.15$  ppbv ( $\sim 25\%$ ). The steep  
23 night-time drop in observed fluxes and concentrations is reflected (although over-estimated)  
24 in the model, but overall the simulations suggest acetaldehyde emissions are not purely direct.

25 In contrast to methanol, acetaldehyde fluxes are better represented by the inclusion of combo  
26 emissions comprising 80% direct emissions (Fig. 4(c); E-combo). This captures the diurnal  
27 profile of the observations, although not the midday peak, and does not exhibit the same  
28 variability in fluxes around dawn and dusk (which may be attributable to the previously  
29 described limitations of eddy covariance at these times). Modelled concentrations are within  
30  $\sim 0.01$  ppbv of those observed during daylight hours, and drop quickly after dusk (Fig. 4(d); E-  
31 combo). When the proportion of direct emissions is increased to 90%, concentrations peak in

1 the late afternoon when measured mixing ratios decline (Fig. 4(d); E-combo90). The  
2 maximum discrepancy is around half that of E-direct and the nighttime decrease in mixing  
3 ratios is well captured. Daytime fluxes are similar to those of the E-combo simulation but  
4 decrease more sharply in the afternoon and are lower overnight ( $\sim 0.05 \text{ mg m}^{-2} \text{ h}^{-1}$  below  
5 observations). None of the simulations captures the observed dip in concentration in the late  
6 afternoon. However, the results suggest that the canopy-atmosphere exchange of acetaldehyde  
7 may be best represented using the combination of emissions of traditional emissions models,  
8 with a “light-dependent” fraction of 80% as currently suggested (Guenther et al., 2012).

### 9 **3.4 Effect of stomatal conductance on modelled emissions (S- simulations)**

10 We now test the effects of stomatal control on the storage-based emissions mechanism by  
11 including stomatal regulation in the storage and combo emissions algorithms. These  
12 simulations effectively introduce a degree of light-dependence to releases of VOCs from  
13 storage pools, although it should be noted that the dependence on PAR introduced in this way  
14 is not as strong as for direct emissions. We first present and discuss the results of  
15 incorporating stomatal control throughout the day (i.e. the S- simulations using  $R_{\text{fct}}$  as shown  
16 in Eq. 10) for both methanol and acetaldehyde. The effects of modifying the control factor  
17 (i.e. the R- simulations using  $R_{\text{fct}}$  as shown in Eqs. 11a and 11b) are described in Section 3.5.

#### 18 **3.4.1 Methanol**

19 The inclusion of stomatal control of methanol emissions from storage structures into  
20 FORCAST improves the fit of modelled to observed fluxes of methanol for both simulations  
21 that include storage-type emissions, i.e. S-storage *vs.* E-storage and S-combo *vs.* E-combo  
22 (Fig. 6a). For 100% storage emissions (S-storage), daytime fluxes are enhanced and exhibit  
23 the pronounced midday peak of the measurements (generally  $< 0.2 \text{ mg m}^{-2} \text{ h}^{-1}$  below those  
24 observed). Night-time fluxes are reduced by  $\sim 0.1\text{-}0.15 \text{ mg m}^{-2} \text{ h}^{-1}$  bringing them much closer  
25 to observations but modelled fluxes are still positive at all times. Although modelled  
26 concentrations now show a rapid increase in the morning they plateau at around 11:00 EST  
27 and fail to match either observed late afternoon peak or subsequent nighttime drop, indicating  
28 a dependence on light that is not adequately represented by including stomatal control.

29 Modelled fluxes and concentrations for combo emissions (20% storage emissions) with  
30 stomatal control (Fig. 6a; S-combo) mirror those for S-storage although fluxes remain slightly  
31 higher during the middle of the day and drop a little closer to zero at night, and concentrations



1 continue to rise until around 16:00 EST. However, the diurnal profile of methanol  
2 concentrations simulated by E-combo90 emissions without stomatal control is closer to the  
3 observed than either of the simulations incorporating stomatal control, and 100% direct  
4 emissions still provides the best overall fit.

### 5 **3.4.2 Acetaldehyde**

6 The effects of including stomatal control of emissions of acetaldehyde from storage pools  
7 (Fig. 6c and d) are similar to those described above for methanol. For 100% storage (S-  
8 storage vs. E-storage) emissions the diurnal profile of modelled acetaldehyde fluxes is a good  
9 fit to observations (Fig. 6c) with a pronounced peak during the middle of the day ( $\sim 0.005$ -  
10  $0.01 \text{ mg m}^{-2} \text{ h}^{-1}$  (maximum 0.03) below measured fluxes) and dropping below zero overnight  
11 (again  $\sim 0.005$ - $0.01 \text{ mg m}^{-2} \text{ h}^{-1}$  below measurements). Modelled concentrations increase too  
12 rapidly during the day, peaking  $\sim 0.15 \text{ ppbv}$  ( $\sim 25\%$ ) above those observed and  $\sim 4$  hours earlier  
13 but do capture the night-time decrease in concentrations seen in the observations (Fig. 6d).

14 Model output for the S-combo simulation is almost identical to that for S-storage described  
15 above, with the two diverging only at night when the combo emissions are lower, reducing  
16 fluxes and, to a lesser extent, concentrations of acetaldehyde. Although introducing stomatal  
17 control of emissions from storage pools improves the magnitude and diurnal profile of  
18 modelled fluxes, acetaldehyde exchanges at Harvard Forest do not show a strong dependence  
19 on stomatal conductance at the canopy scale. Instead they are better represented by the use of  
20 traditional emissions models with a proportion of emissions from storage pools and the  
21 remainder via direct release (with the best fit given by 80% direct and 20% storage, i.e. E-  
22 combo). This is in agreement with the theoretical conclusions reached by Niinemets and  
23 Reichstein (2003b) and experimental and field results from Kesselmeier (2001) and  
24 Kesselmeier et al. (1997). Jardine et al. (2008) report strong evidence of stomatal control at  
25 the leaf and branch level and present field measurements that appear to demonstrate that  
26 stomatal regulation is relevant at the ecosystem scale for forests in the USA. While our results  
27 do not support this conclusion, the authors did report large differences in the effect of  
28 stomatal aperture between tree species (Jardine et al., 2008) which may help explain the  
29 apparent contradiction.

### 1 **3.5 Threshold stomatal control (R- simulations)**

2 In the R- simulations, the stomatal control function was modified to limit stomatal regulation  
3 of storage emissions to transition periods as outlined in Section 2.3.3. This is consistent with  
4 laboratory-based observations of transient emissions bursts associated with light-dark  
5 transitions assuming in effect that there is a point at which the stomatal aperture is sufficient  
6 to no longer be a limiting factor. After this point, we set the stomatal control factor to unity to  
7 ensure that emissions are no longer dependent on stomatal aperture, restricting differences  
8 between emissions, and therefore fluxes and concentrations, modelled in the R- and E-  
9 simulations to periods around dawn and dusk.

#### 10 **3.5.1 Methanol**

11 For both R-storage and R-combo simulations, methanol fluxes now show a dip just after dawn  
12 and again in the late afternoon, reflecting the period of time when the stomata are partially  
13 open (Fig. 7a), but do not otherwise diverge from E-storage or E-combo respectively.  
14 Concentrations still match neither the magnitude nor diurnal profile exhibited by the  
15 measurements, decreasing during the day but taking longer to recover in the late afternoon  
16 (Fig. 7b). The effect is more pronounced for 100% storage emissions, but methanol fluxes and  
17 concentrations measured above the canopy at Harvard Forest are still most closely matched  
18 with the E-direct emissions pathway (Fig. 7a, b).

#### 19 **3.5.2 Acetaldehyde**

20 By contrast, acetaldehyde fluxes for the R-storage simulation show very little change from E-  
21 storage until late morning (Fig. 7c), when R-storage fluxes are nearly double those modelled  
22 in E-storage but remain well below those observed. Following a steep decline in fluxes in the  
23 afternoon to a minimum just before dusk, the post-dusk spike in fluxes previously noted in the  
24 100% storage emissions simulations is enhanced. Acetaldehyde concentrations for R-storage  
25 differ little from E-storage during the day but remain elevated at night (Fig. 7d). Introducing  
26 stomatal regulation to combo emissions (Fig. 7c, d; R-combo vs. E-combo) has little effect on  
27 either fluxes or concentrations. Observed acetaldehyde fluxes and concentrations are still best  
28 reflected by E-combo “traditional” emissions algorithms without explicit parameterisation of  
29 stomatal regulation.

### 1 3.6 Scaling factor, $n$

2 The temporally limited effect of stomatal control in our model simulations is consistent with  
3 conclusions drawn from a theoretical study based on results from detailed laboratory  
4 experiments (Niinemets and Reichstein, 2003b; Niinemets and Reichstein, 2003a), showing  
5 that the stomatal control of biogenic VOC emission rates occur over short timescales and  
6 suggesting that regulation of emissions by stomata occurs over too brief a period to be of  
7 significance at an ecosystem scale for highly volatile VOCs. However, Niinemets and  
8 Reichstein (2003a; b) postulate that emission rates of highly water-soluble VOCs such as  
9 methanol are subject to stomatal regulation over longer timescales, potentially modifying  
10 emissions over scales relevant to canopy-atmosphere exchange. Niinemets and Reichstein  
11 (2003b) concluded that the strength and persistence of stomatal control on leaf-level  
12 emissions scaled with Henry's Law coefficient. Hence in the final stomatal control  
13 simulations (R-storageN15, R-storageN6, R-comboN15 and R-combo6) we scaled the  
14 "degree" of regulation by altering the scaling factor,  $n$ , in Eqs. 11a and 11b (see Table 5),  
15 altering both the magnitude and duration of stomatal control (i.e. the time taken for  $R_{fc}$  in Eq.  
16 10 to reach values over 1.0) as shown in Fig. 2.

17 Changing  $n$  makes little difference to modelled fluxes or concentrations of methanol or  
18 acetaldehyde (Fig. 7; R-storageN6 vs. R-storage and R-comboN6 vs. R-combo). Night-time  
19 fluxes were enhanced slightly ( $\sim 0.02 \text{ mg m}^{-2} \text{ h}^{-1}$  for 100% storage emissions and  $\sim 0.01 \text{ mg m}^{-2}$   
20  $\text{h}^{-1}$  for 80% storage emissions) when  $n$  was doubled. Concentrations of both were reduced in  
21 the late afternoon reflecting the extended duration of control of emission but the effect is  
22 short-lived and is not reflected in the observations. Changes at all times were negligible when  
23  $n$  was reduced to 1.5 (not shown).

24 These results are consistent with observations of canopy structure at Harvard Forest; foliage is  
25 densest in the upper canopy. Fig. 2 shows that changing  $n$  has the biggest impact on the lower  
26 canopy levels where light is limited, foliage biomass is low (over 50% of the biomass is found  
27 in the top 20% of the canopy at Harvard Forest; Parker (1998)) and emission rates small.

### 28 4 Conclusions

29 When light-dependent emissions of methanol and acetaldehyde were included, the FORCAsT  
30 canopy-atmosphere exchange model successfully simulated the bi-directional exchange of  
31 methanol and acetaldehyde at Harvard Forest, a northern mid-latitude mixed deciduous  
32 woodland. Overall, we find that the bi-directional exchange of methanol at Harvard Forest is

1 well captured with the algorithms currently used for modelling foliage emissions of oVOC  
2 (e.g. MEGAN; Guenther et al. 2012) assuming 100% light-dependent (direct) emissions. In  
3 the case of acetaldehyde, modelled concentrations prove robust with a relatively good fit to  
4 observations for all emissions scenarios employed here, likely due to the greater number of  
5 chemical sources and sinks of acetaldehyde in comparison to methanol, but we find that  
6 canopy-top acetaldehyde fluxes at this site are also best modelled with traditional emissions  
7 algorithms. In contrast to methanol, however, acetaldehyde emissions at Harvard Forest  
8 appear to be derived from both direct synthesis and storage pools, with 80% direct emissions  
9 giving the best overall fit.

10 The light-dependence of both methanol and acetaldehyde emissions at the leaf-level has been  
11 ascribed to the stomatal control of diffusion from storage pools, which would otherwise be  
12 expected to be dependent on temperature alone. We incorporated a simple parameterisation of  
13 the regulation of emissions according to stomatal aperture into FORCAsT to determine how  
14 stomatal control affects canopy-top fluxes and concentrations of methanol and acetaldehyde at  
15 this site. While we found that some simulations that included stomatal regulation of emissions  
16 showed a good fit to measured fluxes, none proved effective in reproducing both the observed  
17 concentrations and fluxes.

18 Instead, our simulations show that current emissions algorithms are capable of capturing  
19 fluxes and concentrations of both methanol and acetaldehyde near the top of the canopy and  
20 are therefore appropriate for use at the ecosystem-scale. Our results further demonstrate that  
21 canopy-top fluxes of methanol and acetaldehyde are determined primarily by the relative  
22 strengths of foliage emissions and dry deposition indicating that 3-D atmospheric chemistry  
23 and transport models must include a treatment of deposition that is not only dynamically  
24 intrinsically linked to land surface processes but is consistent with the emissions scheme.

25 Our results show that it is possible to model canopy top fluxes of methanol and acetaldehyde,  
26 and to capture bi-directional exchange without the need for including direct representations of  
27 stomatal control of emissions. This contrast to experimental evidence highlights the  
28 complexity of competing in-canopy processes which act to buffer the stomatal control of  
29 emissions observed at the leaf and branch level. Stomatal aperture affects emissions over too  
30 short a timescale to be observable at the canopy scale when other sources and sinks are fully  
31 accounted for. The times around dawn and dusk, when stomatal regulation has been  
32 demonstrated to occur, are also associated with rapid changes in chemistry and atmospheric

1 dynamics, which likely outweigh the small differences in emission rates. Our findings  
2 indicate that the inclusion of a “light-dependent fraction” in current emissions algorithms (e.g.  
3 Guenther et al., 2012) captures the changes in storage emissions due to changes in stomatal  
4 aperture sufficiently well to simulate exchanges at the canopy-scale.

5 Given that observed methanol fluxes appear strongly correlated with stomatal conductance at  
6 small stomatal apertures it is perhaps surprising that we found no evidence supporting the  
7 suggestion that stomatal control of methanol emissions is observable at the canopy scale. We  
8 ascribe this to use of empirically-derived emissions algorithms combined with the similar and  
9 competing strong dependence of methanol deposition on stomatal conductance.

10 Our results highlight the importance of the holistic treatment and coupling between land  
11 surface sources and sinks. The use of explicit and consistent dynamic representations of  
12 emissions and deposition, which dominate the in-canopy budgets for these longer-lived  
13 oVOC, are needed in atmospheric chemistry and transport models. Such an approach would  
14 adequately account for the role of the stomata in both processes and allow bi-directional  
15 exchange to be successfully simulated without the need for including either leaf-level process  
16 detail or a compensation point.

17 However, this study also demonstrates the need for a better understanding and representation  
18 of the complex relationship between turbulence, fluxes and concentration gradients within and  
19 above the forest canopy. Such understanding can only be achieved through further modelling  
20 studies at a range of scales in combination with robust measurements of concentrations and  
21 fluxes of VOCs, their primary oxidants and oxidation products at multiple heights within the  
22 forest canopy.

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28

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16

1 Table 1. Atmospheric and meteorological measurements relevant to this study made between  
 2 7<sup>th</sup> June and 24<sup>th</sup> September 2012 at the EMS Tower in Harvard Forest.

Type	Measurement	Height (m)	Instrument
<b>Chemical</b>			
Methanol, CH <sub>3</sub> OH <sup>a</sup>	Concentration, Flux	29	PTR-TOF-MS, IconiconAnalytik
Acetaldehyde, CH <sub>3</sub> CHO <sup>a</sup>	Concentration, Flux	29	PTR-TOF-MS, IconiconAnalytik
CO <sup>b</sup>	Concentration	29	Modified IR-absorption gas-filter correlation analyser
O <sub>3</sub> <sup>b</sup>	Concentration	29, 24.1, 18.3, 12.7, 7.5, 4.5, 0.8, 0.3	UV absorbance instrument
Water Vapour <sup>c</sup>	Concentration	29	Licor CO <sub>2</sub> -H <sub>2</sub> O sensor
<b>Meteorological</b>			
Air temperature <sup>c</sup>		29, 27.9, 22.6, 15.4, 7.6, 2.5	30kW precision thermistor in aspirated radiation shield
PAR <sup>c</sup>		29, 12.7	Quantum sensor
Windspeed <sup>c</sup>	Horizontal, vertical	29	AT1 sonic anemometer
Wind direction <sup>c</sup>		29	AT1 sonic anemometer
Relative humidity <sup>c</sup>		29, 22.6, 15.4, 7.6, 2.5	Thin film capacitor sensor in aspirated radiation shield

3 <sup>a</sup>data provided by McKinney and Liu; <sup>b</sup>Munger and Wofsy (1999b); <sup>c</sup>Munger and Wofsy (1999a)

4 Table 2. Boundary and initial conditions used for the FORCAsT simulations.

Model parameter or variable	Value
Total leaf area index (m <sup>2</sup> leaf area m <sup>-2</sup> ground area) <sup>a</sup>	3.67
Average canopy height (m) <sup>b</sup>	23.0

Average trunk height (m) <sup>b</sup>	6.0
<b>Meteorology (values measured at 29m)</b>	
Air temperature (°C) <sup>c</sup>	20.9
Wind speed (m s <sup>-1</sup> ) <sup>c</sup>	1.589
Friction velocity, u* (m s <sup>-1</sup> ) <sup>d</sup>	0.278
Standard deviation of vertical wind velocity, $\sigma_w$ (m s <sup>-1</sup> ) <sup>d</sup>	0.351
<b>Concentrations at 29m (ppbv)</b>	
Isoprene <sup>e</sup>	0.939
Total monoterpenes <sup>e</sup>	0.449
MVK-MCR <sup>e</sup>	0.786
Methanol <sup>e</sup>	10.11
Acetaldehyde <sup>e</sup>	0.620
Acetone <sup>e</sup>	2.608
Ozone <sup>f</sup>	33.54
CO <sup>f</sup>	164.8
Water vapour <sup>c</sup>	1.861%
<b>Miscellaneous</b>	
Ozone at ground-level (0.3m) <sup>f</sup>	20.35 ppbv
Temperature at ground-level (2.5m) <sup>c</sup>	18.1 °C
Soil Temperature at 15, 40, 50 and 90cm depth <sup>a</sup>	24.9, 25.9, 25.9, 21.4 °C
Soil Moisture at 15, 40, 50 and 90cm depth <sup>a</sup>	0.18, 0.15, 0.17, 0.18
NO <sub>2</sub> at 29m <sup>g</sup>	1.00 ppbv
N <sub>2</sub> O <sub>5</sub> at 29m <sup>g</sup>	1.50 ppbv



1 <sup>a</sup>Munger and Wofsy (1999c); <sup>b</sup>Parker (1998); <sup>c</sup>Munger and Wofsy (1999a); <sup>d</sup>data provided by Munger; <sup>e</sup>data  
 2 provided by McKinney and Liu; <sup>f</sup>Munger and Wofsy (1999b); <sup>g</sup>Munger et al. (1996)

3 Table 3. Deposition parameters for methanol and acetaldehyde.

Chemical	Henry's Law constant	Diffusivity	Reactivity factor
Methanol	2.2E02 <sup>a</sup>	1.33 <sup>b</sup>	1.0 <sup>c</sup>
ALD1 (acetaldehyde) <sup>d</sup>	11.4	1.6	1.0

4 <sup>a</sup>Sander (1999); <sup>b</sup>Wesely (1989); <sup>c</sup>Karl et al. (2010); <sup>d</sup>Ashworth et al. (2015)

5 Table 4. Values of stomatal resistance coefficients and parameters used in FORCAsT.

Coefficient	Value
$r_{smin}$	90.0
$b_{rs}$	200.0
$T_{min}$	-2.0
$T_{max}$	45.0
$T_0$	30.0
$b_v$	0.5
$a$	0.066667
$b_\phi$	1.666667

6 Table 5. Modifications to the base case for each of the sensitivity simulations.

Simulation	Changes from baseline simulation
Emissions (E) of methanol and acetaldehyde included as:	
<b>E-direct</b>	100% direct emissions
<b>E-storage</b>	100% storage emissions
<b>E-combo</b>	80% direct; 20% storage
<b>E-combo90</b>	90% direct; 10% storage
Stomatal control (S) of storage emissions included:	
<b>S-storage</b>	Activity factor, $\gamma_T$ , for storage emissions scaled by stomatal control factor,

	$R_{fct}$ (Eqs. 2 and 9, with $n=3$ )
<b>S-combo</b>	Activity factor, $\gamma_T$ , for storage emissions scaled by stomatal control factor, $R_{fct}$ (Eqs. 9 and 10, with $n=3$ ); 80% direct and 20% storage
Stomatal control of storage emissions using modified stomatal control factor, $R_{fct}$ (R):	
<b>R-storage</b>	Threshold stomatal control factor used (Eq. 11)
<b>R-storageP</b>	Threshold stomatal control factor used (Eq. 11) and daytime threshold for PAR increased to 10.0
<b>R-storageN15</b>	Threshold stomatal control factor used (Eq. 11) with scaling factor $n$ set to 1.5
<b>R-storageN6</b>	Threshold stomatal control factor used (Eq. 11) with scaling factor $n$ set to 6.0
<b>R-combo</b>	Threshold stomatal control factor used (Eq. 11); 80% direct and 20% storage
<b>R-comboP</b>	Threshold stomatal control factor used (Eq. 11) and daytime threshold for PAR increased to 10.0; 80% direct and 20% storage
<b>R-comboN15</b>	Threshold stomatal control factor used (Eq. 11) with scaling factor $n$ set to 1.5; 80% direct and 20% storage
<b>R-comboN6</b>	Threshold stomatal control factor used (Eq. 11) with scaling factor $n$ set to 6.0; 80% direct and 20% storage

1 Table 6a. Emission factors ( $\text{nmol m}^{-2}$  (projected leaf area)  $\text{s}^{-1}$ ) for VOCs included in  
2 FORCAsT baseline simulation.

VOC	Direct	Storage
Isoprene	4.83 <sup>a</sup>	0.000
$\alpha$ -pinene	0.000	0.071 <sup>b</sup>
$\beta$ -pinene	0.000	0.032 <sup>b</sup>
<i>d</i> -limonene	0.000	0.054 <sup>b</sup>
Methanol	0.000	0.000

Acetaldehyde 0.000 0.000

1 <sup>a</sup>Helmig et al. (1999); <sup>b</sup>Geron et al. (2000)

2 Table 6b. Emission factors,  $\epsilon$  (nmol m<sup>-2</sup> (projected leaf area) s<sup>-1</sup>) and total canopy emissions

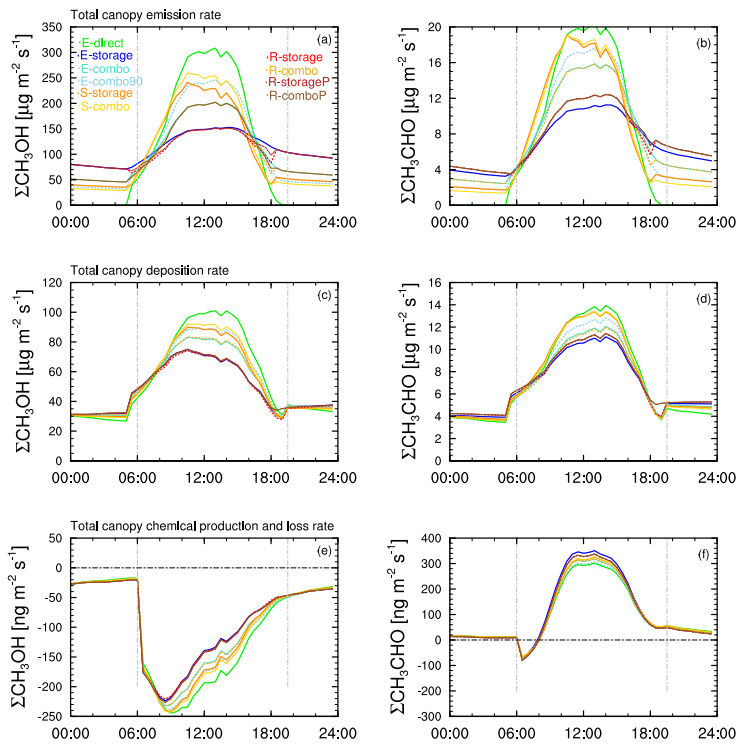
3 (mg m<sup>-2</sup> day<sup>-1</sup>) for methanol and acetaldehyde for the FORCAsT simulations in Table 5.

oVOC	Methanol			Acetaldehyde		
	Simulation	Direct $\epsilon$	Storage $\epsilon$	Total	Direct $\epsilon$	Storage $\epsilon$
<b>E-direct</b>	4.894	0.000	435.8	0.303	0.000	28.7
<b>E-storage</b>	0.000	0.653	457.0	0.000	0.036	28.5
<b>E-combo</b>	1.670	0.418	441.2	0.112	0.027	32.0
<b>E-combo90</b>	2.815	0.296	457.8	0.175	0.019	31.6
<b>S-storage</b>	0.000	0.326	441.0	0.000	0.019	32.1
<b>S-combo</b>	1.065	0.266	454.7	0.063	0.015	31.3
<b>R-storage</b>	0.000	0.653	438.6	0.000	0.040	30.5
<b>R-storageN15</b>	0.000	0.653	429.5	0.000	0.040	31.2
<b>R-storageN6</b>	0.000	0.751	445.6	0.000	0.046	30.9
<b>R-combo</b>	1.670	0.418	434.0	0.112	0.027	31.5
<b>R-comboN15</b>	1.670	0.418	435.8	0.112	0.027	28.7
<b>R-comboN6</b>	1.670	0.418	457.0	0.112	0.027	28.5
<b>S-storageP</b>	0.000	0.326	441.2	0.000	0.019	32.0
<b>S-comboP</b>	1.065	0.266	457.8	0.063	0.015	31.6
<b>R-storageP</b>	0.000	0.653	441.0	0.000	0.040	32.1
<b>R-comboP</b>	1.670	0.418	454.7	0.112	0.027	31.3

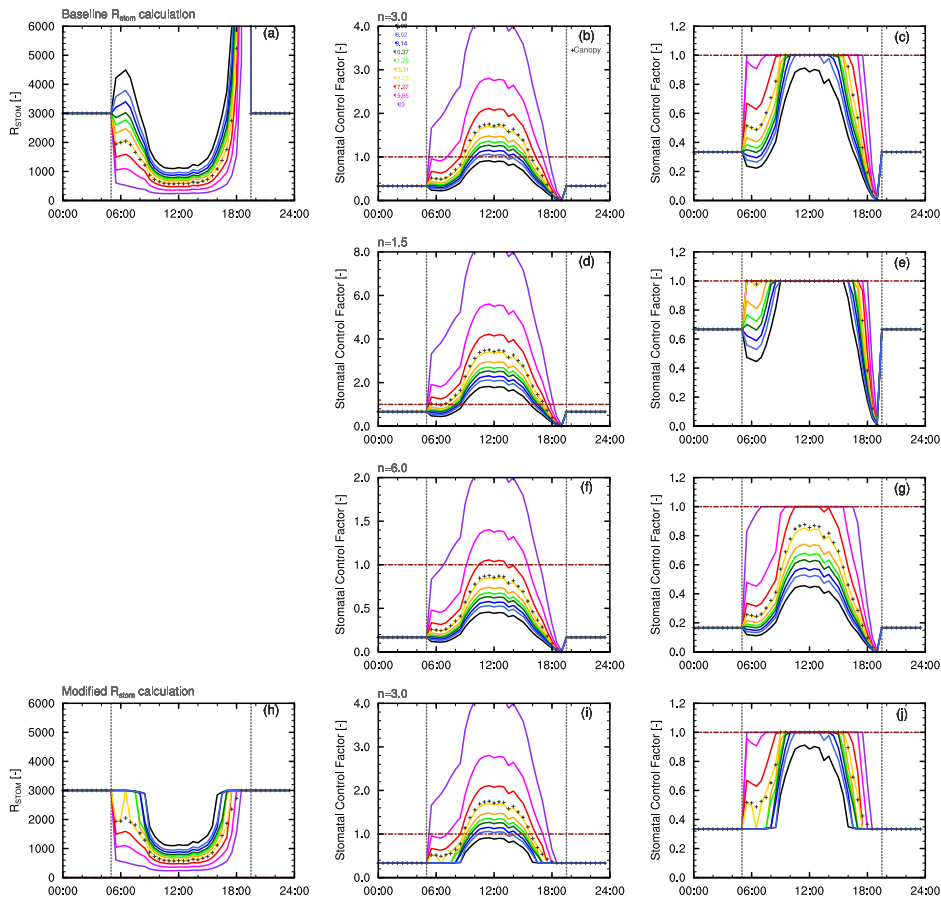
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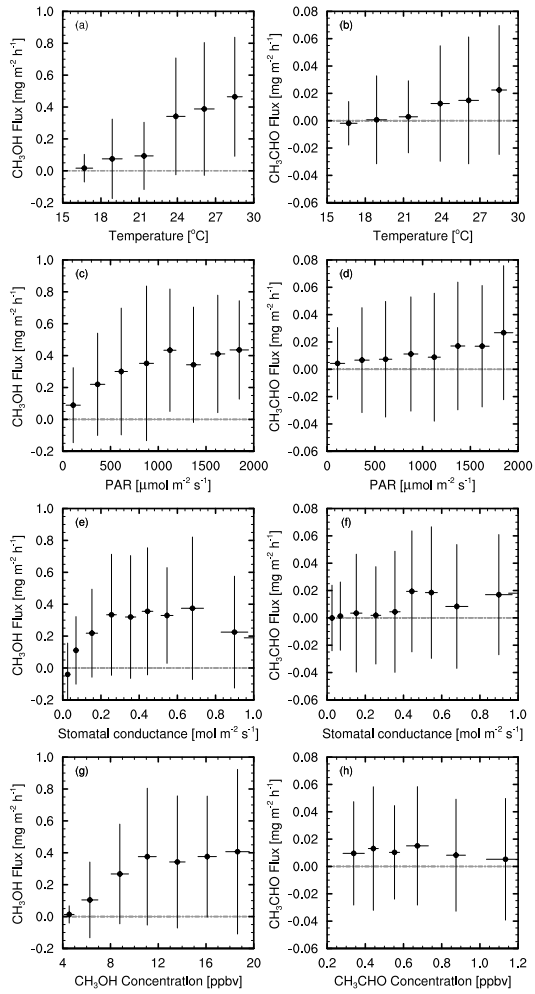


1 Figure 1. Total canopy production and loss rates per unit ground area for methanol (left) and  
 2 acetaldehyde (right) summed over the 10 crown space layers. Coloured lines show total  
 3 emissions (top), deposition (middle) and chemical production and loss (bottom) for each  
 4 simulation.



1 Figure 2. Stomatal control applied to storage emissions. The top row shows the baseline (a)  
 2 stomatal resistance, (b) stomatal control factor  $R_{fct}$  as calculated in Eq. 10, and (c) the  
 3 stomatal control factor as calculated in Eqs. 11a and 11b, i.e. with a limiting value of  
 4 1.0. Coloured lines show the resistances and control factors as a leaf area-weighted average for  
 5 each crown space model level across the 10 leaf angle classes. The crosses show the canopy  
 6 average weighted by foliage fraction in each level. The second and third rows show the effect  
 7 on  $R_{fct}$  of altering the scaling factor,  $n$ , in Eq. 10 ((d) and (f)) and Eqs. 11a and 11b ((e) and  
 8 (g)). The bottom row shows the same as the top for the modified stomatal resistance

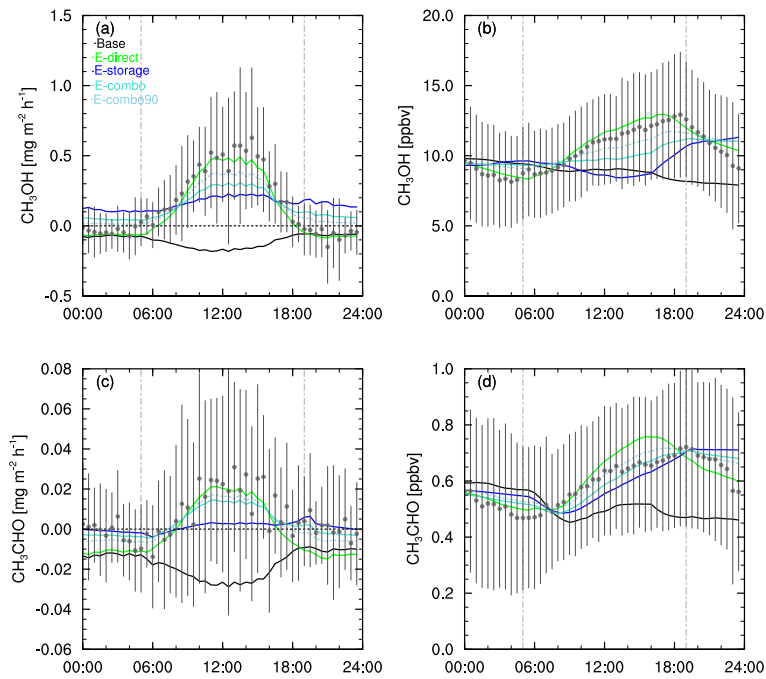
- 1 calculations in which “daylight” is assumed to start only when PAR exceeds a threshold of
- 2  $10.0 \mu\text{mol m}^{-2} \text{s}^{-1}$ .
- 3
- 4



1 Figure 3. Observed daytime (05:00-19:00 EST) fluxes of methanol (left) for July 2012 versus  
 2 (a) air temperature, (c) PAR, (e) canopy stomatal conductance, and (g) methanol  
 3 concentration (all measured at 29 m). The right hand column (panels b, d, f, h) shows the  
 4 same relationships for acetaldehyde. Temperatures were binned in 2.5 °C intervals, PAR in  
 5 250  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , stomatal conductance in  $\sim 0.1 \text{ mol m}^{-2} \text{s}^{-1}$  and concentrations in 2.5 ppbv  
 6 increments (methanol) and 0.2 ppbv (acetaldehyde). Average values for each bin are marked

1 with circles; vertical and horizontal bars indicate 1 standard deviation above and the  
2 mean in each case.

3

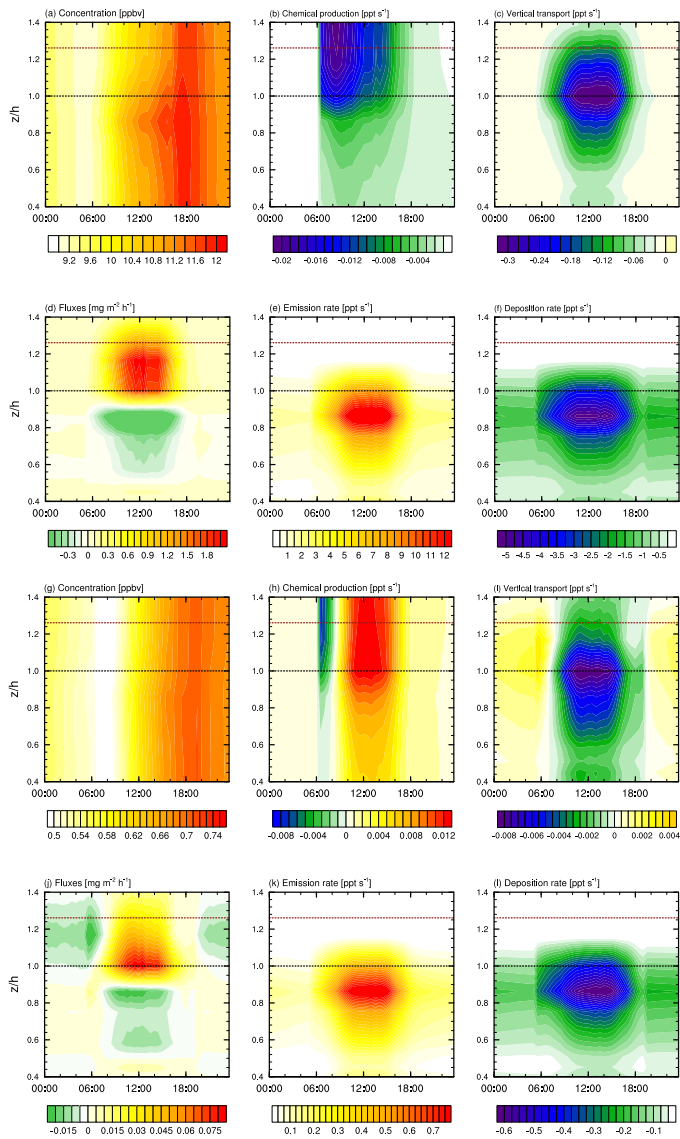


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5 Figure 4. Measured (grey circles with vertical bars indicating 1 standard deviation above and  
6 below the mean) and modelled (solid lines) fluxes (left) and concentrations (right) at 29 m for  
7 an average day in July 2012 for methanol (a) fluxes ( $\text{mg m}^{-2} \text{h}^{-1}$ ) and (b) concentrations  
8 (ppbv), and acetaldehyde (c) fluxes and (d) concentrations. The solid black line shows the  
9 baseline model simulation. Coloured lines denote E-direct (green), E-storage (blue) and E-  
10 combo (cyan) simulations in which direct, storage and combination emissions pathways  
11 respectively are included. The dashed turquoise line shows the E-combo90 (combo emissions  
12 with 90% direct and 10% storage emission pathways) sensitivity test. Dashed grey vertical  
13 lines show dawn and dusk. Times shown are Eastern Standard Time (EST).

14

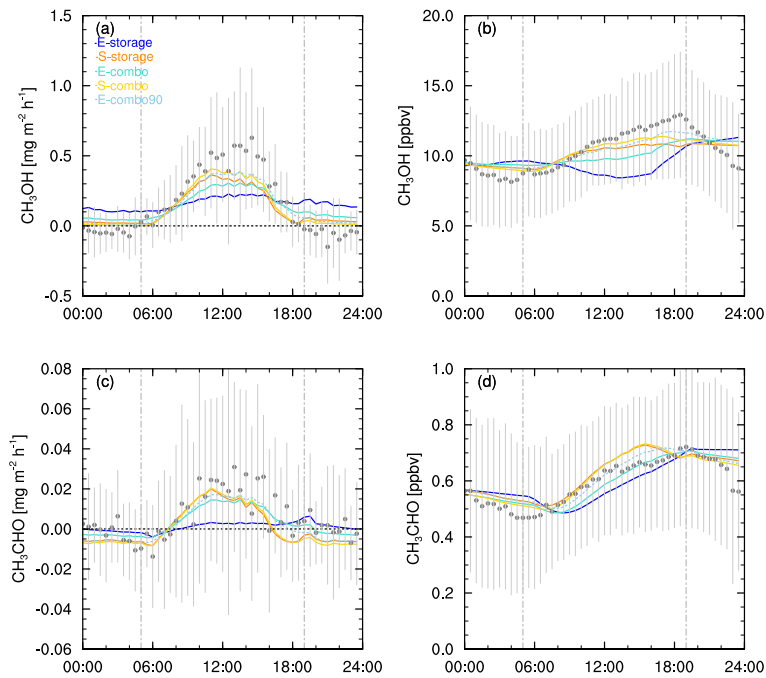




1 Figure 5. Production and loss within the canopy space for methanol: (a) concentration, (b)  
 2 chemical production rate (including photolysis), (c) changes in concentration due to vertical  
 3 mixing, (d) flux, (e) emission rates, and (f) deposition rates of methanol for the E-combo90

1 simulation. Rates are instantaneous in time and space. The vertical axis shows height relative  
2 to canopy top height; times on the horizontal axis are LT. Panels (g)-(l) show the same for  
3 acetaldehyde for the E-combo simulation. Dashed horizontal lines denote canopy top (black)  
4 and observation height (red).

5



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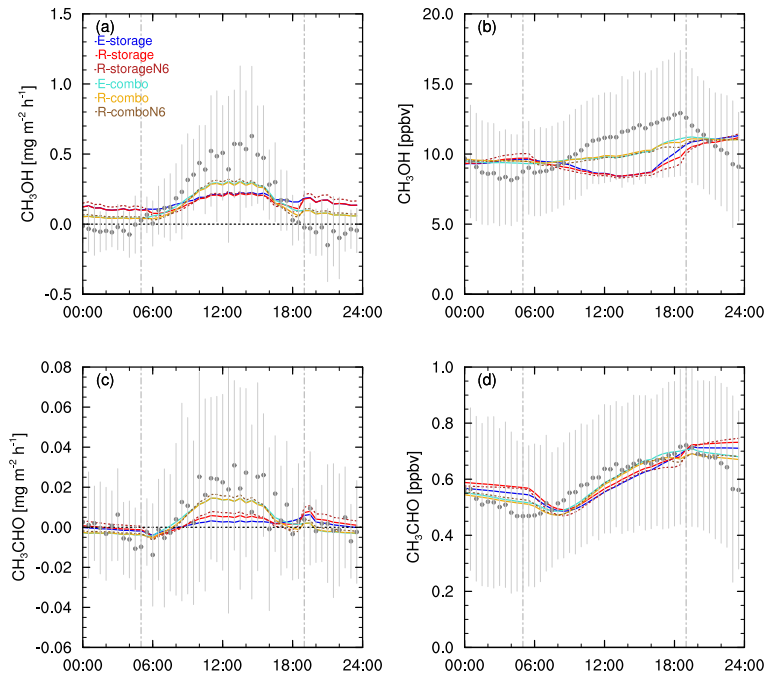
7 Figure 6. As Fig. 4 with blue lines showing E-storage and orange lines S-storage simulations,  
8 and turquoise and yellow lines showing E-combo and S-combo simulations respectively. The  
9 dashed turquoise line shows the E-combo90 sensitivity test. Panels show (a) methanol fluxes,  
10 (b) methanol concentrations, (c) acetaldehyde fluxes, and (d) acetaldehyde concentrations at  
11 29 m.

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2 Figure 7. Simulations of modified stomatal control of storage emissions (R-). Blue and  
 3 turquoise lines show E-storage and E-combo as Fig. 6. Red(R-storage) and dashed dark red  
 4 (R-storageN6) lines show the effects on 100% storage emissions for scaling factor n=3 and  
 5 n=6 respectively. Gold (R-combo) and dashed brown (R-comboN6) lines show the same for  
 6 combo emissions (20% storage). Panels show (a) methanol fluxes, (b) methanol  
 7 concentrations, (c) acetaldehyde fluxes, and (d) acetaldehyde concentrations at 29 m for an  
 8 average day in July 2012.

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