Atmos. Chem. Phys. Discuss., 14, 4505–4535, 2014
www.atmos-chem-phys-discuss.net/14/4505/2014/
doi:10.5194/acpd-14-4505-2014
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Atmospheric Chemistry and Physics Discussions
Open Access

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Uptake and emission of VOCs near ground level below a mixed forest at Borden, Ontario

M. Gordon[1], A. Vlasenko[1,*], R. M. Staebler[1], C. Stroud[1], P. A. Makar[1], J. Liggio[1], S.-M. Li[1], and S. Brown[2]

[1]Atmospheric Science and Technology Directorate, Science and Technology Branch, Environment Canada, Toronto, Canada
[2]Agriculture and Forest Meteorology, Guelph University, Guelph, Canada
[*]now at: Airzone One Ltd., Mississauga, ON, Canada

Received: 30 January 2014 – Accepted: 6 February 2014 – Published: 20 February 2014

Correspondence to: M. Gordon (mark.gordon@ec.gc.ca)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Understanding of the atmosphere/forest canopy exchange of volatile organic compounds (VOCs) requires insight into deposition, emission, and chemical reactions of VOCs below the canopy. Currently, uncertainties in canopy processes, such as stomatal uptake, deposition, and sub-canopy chemistry, make it difficult to derive biogenic VOC emission inventories from canopy VOC concentration gradients. Between 18 July and 9 August 2009, VOCs were measured with proton-transfer-reaction mass spectrometry (PTR-MS) at 6 heights between 1 and 6 m beneath a 23 m high mixed-forest canopy. Measured VOCs included methanol, isoprene, acetone, methacrolein + methyl vinyl ketone (MACR+MVK), monoterpenes and sesquiterpenes. There are pronounced differences in the behaviour of isoprene and its by-products and that of the terpenes. Non-terpene fluxes are predominantly downward. In contrast, the terpene fluxes are significantly upward. A 1-dimensional canopy model was used to compare results to measurements with and without surface deposition of isoprene and MACR+MVK and emissions of monoterpenes and sesquiterpenes. Results suggest deposition velocities of 27 $mm\,s^{-1}$ for isoprene and 12 $mm\,s^{-1}$ for MACR+MVK and daytime surface emission rates of 63 $\mu g\,m^{-2}\,h^{-1}$ for monoterpenes. The modelled isoprene surface deposition is approximately 2 % of the canopy top isoprene emissions and the modelled emissions of monoterpenes comprise approximately 15 to 27 % of the canopy-top monoterpene emissions to the atmosphere. These results suggest that surface monoterpene emissions are significant for forest canopy/atmosphere exchange for this mixed forest location and surface uptake is relatively small for all the species measured in this study.

1 Introduction

Biogenic volatile organic compounds (BVOCs) can play a significant role in atmospheric chemistry (Schade et al., 2011) and forests are a significant source of BVOC emissions (Lappalainen et al., 2009). The emission of BVOCs is the largest terrestrial

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Uptake and emission of VOCs inside a forest

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source of reactive carbon to the atmosphere and isoprene is the largest contributor (Guenther et al., 1995). BVOCs are involved in the formation and growth of atmospheric aerosol particles (Tunved et al., 2006). Holzinger et al. (2005) found a large number of higher molecular weight compounds (> 100 amu) in the air within and above a ponderosa pine plantation. Most compounds are from reactions between ozone and terpenoids emitted from the forest (Calogirou et al., 1999) while some are from the reaction of ozone with leaf surfaces (Fruekilde et al., 1998; Wildt et al., 2003). Methanol is produced in plants and is attributed to plant cell wall growth and repair (Kreuzwieser et al., 2000). Isoprene, monoterpene, and methanol emissions are controlled by air temperature (Tingey et al., 1980) and light intensity (Guenther et al., 1991; Folkers et al., 2008). However, direct correlations are difficult to measure, as plants acclimate to the environment following cues from previous hours, days, or even seasons (Oquist and Huner, 2003; Mäkelä et al., 2004).

The loss of BVOCs to reactions within the canopy is a poorly understood process. Makar et al. (1999) found a 40 % loss of isoprene due to in-canopy chemistry using a one-dimensional canopy model, while the isoprene loss modelled by Karl and Gunther (2005) was between 2 and 5 %. It is unknown how production and loss of VOCs are connected to reactions at the forest surface. Leaf litter and forage have been identified as potentially significant sources of VOCs to the atmosphere (Kirstine et al., 1998; Warneke et al., 1999, de Gouw et al., 1999; Schade et al., 1999). Leaf litter may be a strong source of methanol, possibly accounting for $40 \times 10^{12}\,\mathrm{g\,yr^{-1}}$ of global emissions (Warneke et al., 1999). Trace gas uptake in soils is generally microbially mediated (Schade et al., 2011), while compounds such as methanol, acetaldehyde, and acetone can be released from decaying plant material (Warneke et al., 1999).

In a recent study by Stroud et al. (2005), a one-dimensional model was compared to VOC measurements made at a pine plantation in order to determine escape efficiencies for terpenoid emissions. The model output was compared to sub-canopy measurements of isoprene, pinene, and methyl vinyl ketone and methacrolein (MVK+MACR). To improve model accuracy near the forest floor, surface deposition of isoprene and

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MVK+MACR (both 2 $mm\,s^{-1}$) and emission of α,β-pinene (69 $\mu g\,m^{-2}\,h^{-1}$) were added to the model. Although the surface deposition of isoprene and MVK+MACR is a negligibly small fraction of the canopy-top fluxes, the surface emission of α,β-pinene, which is attributed to decaying pine needles, is 10 % of the canopy-top flux.

Measurements to verify these deposition and emission rates are limited. In the same pine forest of the Stroud et al. (2005) study, Karl et al. (2005) used an inverse-Lagrangian model with VOC profile measurements to demonstrate a surface uptake of methanol, acetone and MVK+MARC, and emission of C3/C4 carbonyls, which verified the Stroud et al. approximations. A previous report of the same study (Karl and Guenther, 2005) also shows a surface uptake of isoprene and emission of monoterpenes. In a tropical rainforest, Karl et al. (2004) used an inverse-Lagrangian model with VOC profile measurements to demonstrate a surface uptake of methanol, acetone, and isoprene. Aaltonen et al. (2011) used sample chambers in a boreal pine forest and measured surface emissions of isoprene, monoterpenes, and sesquiterpenes (0.05, 5.04, and 0.04 $\mu g\,m^{-2}\,h^{-1}$ respectively). Hence there is a large amount of variation in both the direction and magnitude of surface flux measurements.

The goal of this study was to measure and quantify the uptake and emissions of VOCs by a surface beneath a mixed-deciduous forest canopy. We deployed a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) at the Borden Forest Research Station to measure VOC profiles near the forest floor in July and August 2009. An eddy-covariance system was used to estimate VOC fluxes near the surface. Based on these flux estimates, the one-dimensional canopy model of Makar et al. (1999) and Stroud et al. (2005) was modified to include deposition and emissions of VOCs, allowing for the investigation of the relative importance of VOC uptake and emissions at this sub-canopy surface.

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2 Methods

2.1 Site description

This study took place at the Borden Forest Research Station (44°19′ N 79°56′ W) in Ontario, Canada. The study was part of a larger study investigating aerosol fluxes (Gordon et al., 2011), isotopes (Santos et al., 2012), and sub-canopy transport (Brown et al., 2013). A 2006 stem count (Teklemariam et al., 2009) gave a forest composition of 52 % red maple (*Acer rubum* L.), 14 % eastern white pine (*Pinus strobus* L.), 8 % large-tooth aspen (*Populus grandidentata* Michx), 7 % white ash (*Fraxinus americana* L.), 6 % American beech (*Fagus grandifolia*), with the remainder composed of a mixture of aspen, ash, cherry, pine, elm, and maple. The forest is regrowth on abandoned farm land, with an age of approximately 100 yr (Lee et al., 1999). During the 2009 summer, the average canopy height was approximately 21 m with an understory height of approximately 9 m. The forest soil is loamy sand (Barr et al., 2002) composed of 91 % sand, 6 % silt, and 3 % clay (Chang, 2011). The surrounding area is generally flat within a radius of about 4 km. The available forest fetch is about 4.3 km to the south, and 3 km to the SSW. Outside of this range was predominantly grass and cropland, with the town of Angus, Ontario less than 4 km to the ENE and the Canadian Forces Base Borden 5 km to the SE.

2.2 Instrumentation

The Borden Forest Research Station includes a 44 m tower, which supports an array of instruments for routine measurements of temperature, wind speed, humidity, and fluxes of energy, water vapour, NO, O_3, SO_2, and CO_2. Details of the measurement setup can be found in Lee et al. (1999), Staebler et al. (2000), Barr et al. (2002), and Teklemariam et al. (2009). Incoming shortwave radiation (SW) was measured (PSP, Eppley Laboratory Inc) above the canopy, and photo-synthetically active radiation (PAR) was measured (LI-191, Licor Inc.) at the forest floor. Temperature was measured at 12 heights

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between 1.7 and 41.5 m. A 3-D sonic anemometer (K-Type, Applied Technologies Inc.) was mounted on the tower at 33 m and measured turbulence at 10 Hz. O_3 was measured (49*i*, Thermo Scientific Inc.) at six heights between 1 and 41.5 m. NO was also measured (42*s*, Thermo Scientific Inc.) between 16 July and 12 August 2006 at the same 6 heights as O_3; however, NO measurements at the tower were not available during the 2009 study. To estimate the NO values during the 2009 study measurements at a station 15 km south of the Borden forest (Egbert, ON) were used. The Egbert station is an open area above the surrounding canopy. During the 2006 measurements the median hourly values of NO at Borden (at the 41.5 m height) and at Egbert correlated well ($r^2 = 0.68$) with an average of 0.26 ppb at Egbert and 0.27 ppb at Borden. This suggests that the Egbert NO measurements are a suitable proxy for above-canopy Borden NO values. To estimate the sub-canopy NO profiles, hourly average profiles were generated from the 27 days of 2006 Borden tower measurements. These hourly profile shapes were normalized with the 41.5 m height value. The normalized profile shapes were then scaled to the above canopy values estimated from the 2009 Egbert station measurements. Sensitivity of the model to NO approximation is discussed in Sect. 4.2.

A proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS, Ionicon Inc.), installed at ground level, was operational from 18 July to 9 August 2009. The PTR-ToF-MS sampled from 6 levels (heights of 1, 2, 3, 4, 5, and 6 m) on a 6 m tower. A schematic of the set-up is shown in Fig. 1. Samples were drawn though 12 m of 6.35 mm (0.25 inch) outside diameter Teflon tubing at each level. The residence time was measured at ~ 2 s by introducing benzene pulses to each line and timing the response. An automated valve system switched between each line once per minute. Each one minute average was background subtracted and normalized by the m/z 21 reagent ion signal and subsequently converted to mixing ratio using gravimetrically prepared calibration standards. Due to a lack of calibration standards, the sesquiterpene concentrations were estimated using the monoterpene standard. Since the sesquiterpene calibration ratio is known to be linear (Kim et al., 2009), the mixing ratios are presented

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as relative values only without units. Uncertainty in all the PTR-ToF-MS measurements is estimated at 20 %. The 1 min concentration measurements at the 6 levels were averaged in 30 min intervals. Due to instrument malfunction, 6.5 % of the 30 min profiles from 22 days could not be used. To ensure adequate fetch and horizontal homogeneity, measurements were filtered to use only wind direction in the range 20° to 285° following Teklemariam et al. (2009) and Froelich (personal communication, 2013). This resulted in a removal of 17.8 % of the remaining data.

Water mixing ratio was sampled from the 6 m tower at a height of 2.0 m with a CO_2/H_2O analyser (LI-6262, Licor Inc). The analyser was calibrated on-site with a dew-point generator ($r^2 = 0.97$). A 3-D sonic anemometer was mounted on the tower at 1.8 m (CSAT3, Campbell Scientific Inc.) and recorded wind speeds at 10 Hz. Cross-correlation of the vertical wind speed, w, and the H_2O mixing ratio, ρ_w, identified a residence time of 4.4 s for the H_2O measurement system.

2.3 Canopy modelling

The canopy model is described in detail in Makar et al. (1999) and Stroud et al. (2005). It is a one-dimensional model which solves the equations

$$\frac{\partial C_{i,j}}{\mathrm{d}t} = E_{i,j} + f_{i,j} + \frac{\partial}{\mathrm{d}z}\left(K(z_j)\frac{\partial C_{i,j}}{\mathrm{d}z}\right), \quad (1)$$

where $C_{i,j}$, $E_{i,j}$, and $f_{i,j}$ are the concentration, emissions rate, and rate of change due to chemical reactions, respectively, of the ith chemical species in the jth model layer, $K(z_j)$ is the eddy diffusivity, t is time, and z is height. The model domain is 1001 m with a 1 m vertical resolution and a 1 min time resolution. Operator splitting was used in the model such that diffusion is performed in two 30 s sub-steps before and after chemical reactions and emissions, which are included in the same operator. Environmental inputs to the model are at a 30 min time resolution and include temperature (T), relative humidity (Rh), pressure, PAR, cloud fraction, O_3 and NO concentrations, and

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vertical wind variance (σ_w). Median diurnal variations of temperature, relative humidity, and incoming solar radiation are shown in Fig. 2. Leaf Area Index (LAI) profiles were updated for the Borden forest based on 2009 measurements at a 2 m resolution. Eddy diffusivity (K) was output from the Global Environmental Multiscale (GEM) Model (Côté et al., 1998) for the Borden location concurrent with the time period of the study.

The atmospheric transport within the canopy model is based on a modified K-theory of vertical turbulent diffusion from Raupach (1989),

$$\frac{\partial C}{\mathrm{d}t} = -\frac{\partial}{\mathrm{d}z}\left(R(\tau/T_\mathrm{L})K\frac{\partial C}{\mathrm{d}z}\right), \tag{2}$$

where the eddy diffusivity (K) is modified by the factor R, which accounts for canopy effects on turbulence (so-called "near-field" effects). The variable R is dependent on the ratio of τ/T_L as

$$R = \frac{[1-\exp(-\tau/T_\mathrm{L})](\tau/T_\mathrm{L}-1)^{3/2}}{[\tau/T_\mathrm{L}-1+\exp(-\tau/T_\mathrm{L})]^{3/2}}, \quad \tau/T_\mathrm{L} > 1, \tag{3}$$

where τ is a transport lifetime and T_L is the Lagrangian timescale. Makar et al. (1999) found the modelled isoprene measurements above the canopy agreed well with measurement at the Borden forest location using a transport lifetime of $\tau = 1.17T_\mathrm{L}$, while Stroud et al. (2005) found that a value of $\tau = 4.0T_\mathrm{L}$ improved results at the Duke forest location. The model version used in the Stroud et al. (2005) study was modified to use a diffusion scheme which allowed for the inclusion of deposition and emissions at the surface. Stroud et al. (2005) hypothesized that the difference in transport lifetime could be due to either the change in the diffusion scheme, or a difference in the canopy structure between the two forests. Initial tests of the model with the new diffusion scheme at the Borden forest location demonstrated that a transport lifetime of $\tau = 4.0T_\mathrm{L}$ gave the best measurement/model comparison, which implies that the change in mixing timescale is due to the change in the diffusion scheme and not the canopy structure.

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This model version uses the Makar et al. (1999) isoprene basal emission rate of 17.5 µg g^{-1} h^{-1} and the α-pinene basal emission rate of 3.4 µg g^{-1} h^{-1}. Stroud et al. (2005) added sesquiterpenes to the model, represented by β-caryophyllene. In the Stroud et al. (2005) model, the basal emission rate of sesquiterpenes was set to 1/3 the monoterpene emission rate. They estimated the dry deposition velocities of O_3 as 4 mm s^{-1}, HNO_3 as 40 mm s^{-1}, NO_2 as 1 mm s^{-1}, isoprene as 2 mm s^{-1}, MACR+MVK as 2 mm s^{-1}, and surface emission of monoterpenes as 69 µg m^{-2} h^{-1}. No sesquiterpene surface emissions were included in the Stroud et al. (2005) model.

2.4 Flux calculation

The wind speed measurements were rotated following Wilczak et al. (2001) using 30 min averages, with the first rotation around the z-axis to give $< v >= 0$ and the second rotation around the y-axis to give $< w >= 0$, where v and w are the cross-wind and vertical velocities respectively (angular parentheses <> denote an average value). It was found that the second rotation resulted in unrealistic rotation angles due to low wind speeds in the understory. For this reason a fixed anemometer tilt of 2.0° was determined based on the distribution of the second rotation angles as a function of the first rotation angle. VOC fluxes were calculated from the 1 to 6 m gradients using the diffusion equation,

$$< w'\rho' >= -K\frac{d\rho}{dz}, \tag{4}$$

where ρ is the gas concentration, z is the height and K is the vertical diffusion coefficient, which is given (Garratt, 1994) as

$$K = \kappa u_* z/\varphi. \tag{5}$$

Here $\kappa = 0.4$ is the von Karman constant, u_* is the friction velocity calculated from the $z = 1.8$ m anemometer, and φ is the stability function, which is a function the Monin–

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Obukhov length, L, (Garratt, 1994) as,

$$\varphi = \begin{cases} (1-16z/L)^{-1/4}, & z/L < 0 \\ 1+5z/L, & z/L > 0 \end{cases} \tag{6}$$

Integrating between a reference height z_r and z gives

$$\rho(z) = \rho(z_r) - \frac{< w'\rho' >}{\kappa u_*/\varphi} \ln\left(\frac{z}{z_r}\right). \tag{7}$$

Each 30 min concentration profile was least-squares fit to

$$\rho(z_i) = a + b\ln\left(\frac{z_i}{z_r}\right), \tag{8}$$

where a and b are the parameters of a least-squares fit, $z_r = 1$ m, and $z_i = \{1,2,3,4,5,6\}$ m. A comparison of Eqs. (7) and (8) gives the concentration flux as $< w'\rho' >= -\kappa u_* b/\varphi$. This method of analysis is referred to herein as the profile method.

To compare the profile method with the Eddy Covariance (EC) for an inert species, water-vapour (latent heat) fluxes were calculated from the PTR-ToF-MS profiles following the method described above. The PT-ToF-RMS signals at m/z 55 were converted to water vapour concentrations by comparing the 1 min average m/z 55 values at 2 m to coincident 1 min averages of water-vapour measurements from the CO_2/H_2O analyser at the same height. The coefficient of correlation of the resulting exponential least-squares fit equation is $r^2 = 0.93$. Concurrent water-vapour fluxes were calculated in 30 min intervals from the CO_2/H_2O analyser and the anemometer measurements using the EC method. Figure 3 compares the average hourly fluxes determined by both methods. The profile method shows a negative (downward) flux throughout the night, while the EC method shows a weak, consistent upward flux. During the daytime

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hours (14:00 to 01:00), the fluxes predicted with the profile method are on average 2.8 time higher than the fluxes predicted with the EC method.

Other studies (Karl et al., 2004; Karl and Guenther, 2005) have estimated VOC fluxes within the canopy using Inverse Lagrangian Modelling (ILM). Here, latent heat fluxes were also calculated from profile measurements with ILM, as described in Brown et al. (2013), with further details in Raupach (1989) and Warland and Thurtell (2000). This process solved for a source/sink distribution using a parameterized dispersion matrix with the 6 concentration levels and 3 source/sink layers (1, 3, and 6 m). The hourly averages of the modelled fluxes are compared to the other methods in Fig. 3. Due to a large amount of variability in the hourly fluxes at each height level, each hourly flux presented is an average of the 3 source/sink layers. The ILM method predicts negative fluxes at night, similar to the profile method. In the early morning (near 12:00 UTC) the ILM predicts a strong negative flux. It is likely that ILM fails here during very stable conditions, due to a small sampling height range (1–6 m) relative to the overall canopy height (23 m). In the first half of the day, the ILM method predicts average fluxes similar to the EC method, while during the latter half of the day, the predicted fluxes are similar to the profile method. There is a significant amount of uncertainty in the ILM method, as demonstrated by the 67 % confidence intervals (one standard error). For much of the day, both the EC and profile hourly averages are within the 67 % confidence intervals of the ILM hourly averages.

There are difficulties with all three methods. EC inside the canopy fails to account for turbulence due to the proximity of flow-disturbing canopy structures. EC is also unreliable during very low wind speeds, as occurs during the night beneath the canopy. Canopy structures may also contribute to errors in the parameterization of the diffusion coefficient, K, in the profile method. ILM is a more realistic model than the profile K parameterization, as it accounts for sources and sinks from canopy elements at different height levels. However, there is a large amount of uncertainty in the results and it is difficult to parameterize the matrix solution (see Brown et al., 2013). Hence it is difficult to estimate the uncertainty in the fluxes derived from the profile method and

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it would be presumptuous to assume that the derived fluxes are equal to the emissions or deposition fluxes to or from the surface. For this reason, the fluxes derived from the profile method are referred to as “apparent fluxes”. The one-dimensional model described in Sect. 2.3 is then used to approximate the surface fluxes by comparing the measured apparent fluxes to the apparent fluxes derived by the model.

3 Results

3.1 Mixing ratio and flux measurements

Diurnal mixing ratios in the study time period are shown in Fig. 4a–f. Although sesquiterpenes are not calibrated, the relative measurement provides insight into their behaviour. All of the measured VOCs increase in mixing ratio at sunrise, peak between 18:00 and 20:00 UTC, and decrease into the night, with the exception of monoterpenes and sesquiterpenes. Monoterpenes and sesquiterpenes decrease at sunrise to a minimum near 17:00 UCT, and then increase through the rest of the day and night. Generally speaking, the majority of the VOCs follow the diurnal temperature trend shown in Fig. 2a, while the terpenes follow a diurnal trend similar to relative humidity (Fig. 2b). The temperature dependence is supported by the coefficients of correlation, which are generally good between mixing ratio and temperature ($0.35 < r^2 < 0.51$) for non-terpene VOCs (for all 30 min averages throughout the study).

The range of the median VOC mixing ratios at $z = 4$ m are compared to measurements of two other studies in Table 1. In the Karl et al. (2005) study, various VOCs were measured beneath a sweetgum and pine plantation using a sampling inlet which was continuously moving between the ground and a height of 24 m. The range of measured values are estimated from the Karl et al., 2005 study (their Fig. 7) for a height of $z = 4$ m. The mixing ratios of methanol and acetone are nearly a factor of 3 higher during the day in the Karl et al. study compared to our measurements and the mixing ratios of MACR+MVK are more than a factor of 12 higher. In the Holzinger et al. (2005)

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study, monoterpene mixing ratios were measured at 5 heights in a pine plantation. The range of measured values are estimated from Holzinger et al. (2005) study (their Fig. 2) for a height of $z = 4$ m. This measured range is similar to the diurnal range of mixing ratio seen in this study at the same height.

Diurnal variation of apparent VOC fluxes calculated using the profile method are shown in Fig. 4g–l. As with the mixing ratios, the measured VOCs follow similar patterns, with the exception of the terpenes. Fluxes at night are generally near-zero, although some negative acetone fluxes and positive sesquiterpene fluxes are seen. The daytime fluxes suggest an uptake of non-terpene VOCs and an emission of monoterpenes and sesquiterpenes by the soil and/or forest litter during the day. However, since these are chemically reactive species which may not be conserved with height, further investigation is necessary to demonstrate that these apparent fluxes represent surface deposition or emissions.

The peak daytime median fluxes are compared to similar measurements from previous studies in Table 1. There have been few studies which have measured VOC fluxes below the canopy and only a small number of VOCs have been measured. Measurements in a pine plantation (Schade and Goldstein, 2001) and a sweetgum and pine plantation (Karl and Guenther, 2005) give varied results, with observations of both emission and uptake of methanol, and emission of acetone, isoprene, and monoterpenes. Although the emission of monoterpenes is also seen in the Borden forest measurements, methanol, acetone and isoprene fluxes are predominantly downward. The measurements of our study are similar to the measurements of Karl et al. (2004) beneath a tropical forest, where uptake of methanol, acetone, and isoprene are seen at similar magnitudes. The Karl et al. (2004) and Karl and Guenther (2005) fluxes were calculated between 0 and 5 m (compared to 1–6 m for this study), while the heights of the Schade and Goldstein (2001) measurements are not specified.

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3.2 Model comparison

In order to investigate whether or not the apparent fluxes seen in Sect. 3.1 are due to surface emissions and deposition, the 1-dimensional canopy model was run with and without surface deposition and fluxes. To best match measurements, the basal emission rates were modified to give 21.2 $\mu g\,g^{-1}\,h^{-1}$ for isoprene, 2.3 $\mu g\,g^{-1}\,h^{-1}$ for monoterpenes, and 0.33 $\mu g\,g^{-1}\,h^{-1}$ for sesquiterpenes (although this is only an estimate based on uncalibrated sesquiterpene measurements). This represents an increase of 20 % and a decrease of 11.5 % from the Makar et al. (1999) isoprene and monoterpene basal emission rates, respectively, and a factor of 3.5 decrease from the Stroud et al. (2005) sesquiterpene basal emission rate. In the case of the Stroud et al. (2005) study, these differences are likely due to the different forest environments, while differences between the Makar et al. (1999) study and this one (which takes place in the same location) could be due to a changing forest composition or different temperature and moisture histories.

The model was run with two scenarios: a base case with no surface emissions or deposition, and an active surface case which included deposition of isoprene and MACR+MVK, and emissions of monoterpenes and sesquiterpenes. Based on initial test runs, day-time surface deposition velocities were modified to 2.7 $mm\,s^{-1}$ for isoprene and 1.2 $mm\,s^{-1}$ for MACR+MVK. Surface emission rates were modified to 63 $\mu g\,m^{-2}\,h^{-1}$ for monoterpenes and 0.86 $\mu g\,m^{-2}\,h^{-1}$ for sesquiterpenes. This represents a 35 % increase for isoprene, a 40 % decrease of MACR+MVK, a 7 % decrease for monoterpenes, and 19 % decrease for sesquiterpenes from the Stroud et al. (2005) deposition velocities and emission rates at a pine plantation.

The resulting modelled mixing ratios at a height of 6 m are compared to the measurements in Fig. 5a–d. The active surface has a negligible effect on the mixing ratios compared to the base case scenario. Generally, the model output of isoprene and monoterpene mixing ratios are with the quartiles of measured values. MACR+MVK are over-predicted by the model in the late afternoon. Both monoterpenes and sesquiter-

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penes decrease to background levels in the model between 10:00 and 12:00 UTC (sunrise), while the measurements reduce more slowly, between 10:00 and 15:00. Model statistics for the base case are compared in Table 2. The model demonstrates relatively good agreement for isoprene ($r^2 = 0.5$ and 65 % of modelled values between 50 % and 150 % of the observations), moderate agreement for MACR+MVK and monoterpenes ($r^2 \sim 0.3$), and poor agreement for sesquiterpenes ($r^2 = 0.1$).

The apparent fluxes were calculated from model results between 1 and 6 m using the profile method (Eqs. 6–8). The apparent fluxes for the daytime hours are compared in Fig. 5e–h. In the base model case, the apparent isoprene fluxes are upward, compared to the downward apparent fluxes seen in the measurements, and the modelled apparent fluxes of MACR+MVK, monoterpenes, and sesquiterpenes are negligible relative to the measurements. Inclusion of isoprene deposition in the model gives similar apparent fluxes to the observed values. Deposition of MACR+MVK gives apparent modelled fluxes which underestimate the apparent observed fluxes in the morning and overestimate the apparent observed fluxes in the afternoon. Emission of monoterpene and sesquiterpenes from the surface by the model produces apparent fluxes which are similar to the observed values, although there is some overestimation of apparent monoterpene fluxes between 15:00 and 19:00 UTC.

There is good agreement between the measured and modelled apparent fluxes for isoprene and MACR+MVK at night between 00:00 and 12:00 UTC (not shown). During this time period the mixing ratios and apparent fluxes of isoprene and MACR+MVK are near zero, as shown in Fig. 4b, d, h and j. Because the ground fluxes in the active surface model case are input as deposition velocities for isoprene and MACR+MVK, the near-zero concentrations at night result in low deposition fluxes (from the definition of deposition velocity as the ratio of flux to concentration). For monoterpenes and sesquiterpenes, which are input as surface fluxes in the active surface model case, the modelled apparent fluxes are non-zero at night, which is in disagreement with the observed apparent fluxes, as shown in Fig. 4k and l. Due to the difficulty in determining fluxes at night and the disagreement between measured and modelled apparent fluxes

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during this period, the actual behaviour of terpene emissions during the night remains unclear.

4 Discussion

4.1 Canopy-top fluxes

Based on these model results, the average fluxes from the surface due to deposition of isoprene ($2.7\,\mathrm{mm\,s^{-1}}$) and MACR+MVK ($1.2\,\mathrm{mm\,s^{-1}}$) and emissions of monoterpenes and sesquiterpenes are calculated for the 22 day period (after filtering for wind direction). These are compared to the average modelled fluxes out the canopy top (upward positive) in Table 3 for the active surface case model run. Due to the uncertainty in the night-time emissions of terpenes, as discussed in Sect. 3.2, the monoterpene and sesquiterpene surface emissions are presented as a range between zero emissions at night and constant emissions for the full 24 h period. The average emissions seen here are much larger than those measured by Aaltonen et al. (2011) in a boreal Scots pine forest in southern Finland. Aaltonen et al. measured yearly average emissions of $0.05\,\mu\mathrm{g\,m^{-2}\,h^{-1}}$ for isoprene, $5\,\mu\mathrm{g\,m^{-2}\,h^{-1}}$ for monoterpenes, and $0.04\,\mu\mathrm{g\,m^{-2}\,h^{-1}}$ for sesquiterpenes. These large differences are likely due differences in the climates, tree compositions and densities, and seasons. For example, in the Aaltonen et al. (2011) study, α,β-pinene emissions increased by a factor between 3 and 5 in June and October. Similar seasonal difference could change results at this mixed forest location for different time periods.

As shown in Table 3, the model suggests that the amount of isoprene that is emitted from the forest to the atmosphere is reduced by approximately 2 % due to surface uptake. Although this is a relatively small fraction of the total, on a regional scale this could have a significant effect on the total isoprene released from forests. With the inclusion of MACR+MVK deposition, there is negligible release of MACR+MVK to the atmosphere from the canopy over the period of the study and any MACR+MVK that is

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created as a by-product of chemical reactions is, on average, absorbed at the forest surface. This is consistent with the small canopy-top fluxes for MACR+MVK seen in other studies (Karl et al., 2004; Spirig et al., 2005).

According to model results, the emission of monoterpenes from the surface represents a significant amount (15 to 27 %) of what is released from the canopy-top to the atmosphere. This is a much larger fraction than the 10 % which was modelled by Stroud et al. (2005) for a pine plantation using the same canopy model. This is an important result for the interpretation of measured canopy top emissions relating to basal tree emission rates. Although a large fraction of monoterpene emissions may relate to leaf respiration, a significant amount may also be due to leaf litter or other unknown surface emissions. Hence, basal tree emission rates based on canopy top emission measurements may be overestimated.

Although sesquiterpene measurements in this study were uncalibrated, the model output provides some insight into the relative surface flux of sesquiterpenes. According to the model estimates, approximately 2 to 5 % of sesquiterpenes emitted from canopy top are due to surface emissions. Although we are not able to confirm the basal tree and surface emission rates used in the model, sesquiterpene emissions from canopies are typically more than an order of magnitude lower than they are for primary VOCs such as isoprene, suggesting that the emissions of sesquiterpenes from the sub-canopy surface is not significant.

4.2 Model sensitivity to NO

To estimate the error in the model due to the estimation of model input NO from nearby measurements, two 2 day model runs were done with modified NO levels. The base case was used with a 50 % reduction in NO levels (the low NO case) and a 50 % increase in NO levels (the high NO case). For the 2 day period the 50 % reduction in NO resulted in a reduction of average mixing ratios of 17, 14, 13, and 31 % of isoprene, MACR+MVK, monoterpenes, and sesquiterpenes, respectively. The 50 % increase in NO resulted in an increase in the average mixing ratio of 14, 8, 8, and 26 % for isoprene,

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MACR+MVK, monoterpenes, and sesquiterpenes, respectively. These changes in mixing ratios occurred in daylight hours (12:00 to 24:00) for isoprene and MACR+MVK and at night (0:00 to 12:00) for monoterpenes and sesquiterpenes, corresponding to the higher mixing ratios in all four cases (see Figs. 4 and 5).

As discussed in Sect. 2.2, the Egbert NO measurements used as a proxy for the Borden measurements correlate well ($r^2 = 0.68$) with an average of 0.26 ppb at Egbert and 0.27 ppb at Borden. However, there is a high root-mean-square error ($E_{rms} = 0.66$ ppb) over the same period, primarily due to high NO values seen at only one site during non-aligned wind directions. In the model sensitivity runs, the average VOC mixing ratio changes due to modified NO levels are much smaller than the 50 % increase and decrease in NO. Hence, it would be expected that over the 22 days of the study, the average error due to the use of proxy NO levels should be smaller than the 6 % average difference in NO between Egbert and Borden; however hourly errors may be much higher, as suggested by the relatively high root-mean-square error.

5 Conclusions

Direct measurements of VOC mixing ratios between 1 and 6 m demonstrate a trend of increasing methanol, isoprene, acetone, and MACR+MVK during the day, and increasing monoterpenes and sesquiterpenes during the night for this forest location. Mixing ratios of methanol, acetone, and monoterpenes compare well to other near-surface measurements made at pine plantations and plantations with both sweetgum and pine.

The apparent fluxes, calculated using a profile method which assumes a constant diffusion constant and an inert species, demonstrate a downward flux of methanol, isoprene, acetone, and MACR+MVK during the day, and an upward flux of monoterpenes and sesquiterpenes during the day. Apparent fluxes through the night are near zero, as is consistent with reduced mixing at night. A comparison of flux calculation methods with water vapour using the profile method, EC, and ILM demonstrates substantial variation between the three techniques. Hence, the apparent fluxes calculated with the

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profile method may not be an accurate representation of surface fluxes. There is also a large amount of variation in observed fluxes of VOCs near the surface in previous studies; however directional consistency is seen between measurements at the Borden forest and the deposition of methanol, isoprene, and acetone in a tropical forest (Karl et al., 2004). There is also directional consistency with the emission of monoterpenes from a Scots pine forest (Aaltonen et al., 2011).

A 1-dimensional canopy model was used to determine if the apparent fluxes were due to deposition and emissions of VOCs to the sub-canopy surface. Model results suggest a deposition of 27 $mm\,s^{-1}$ for isoprene which results in average downward (negative) surface flux of 4.9 $\mu g\,m^{-2}\,h^{-1}$ for the duration of the study. This represents 2 % of the magnitude of the canopy top emissions of isoprene to the atmosphere. Model results suggest a deposition of 12 $mm\,s^{-1}$ for MACR+MVK which result in an average downward (negative) surface flux of 1.4 $\mu g\,m^{-2}\,h^{-1}$. This compensates for the formation of MACR+MVK in the canopy resulting in negligible emissions of MACR+MVK from the canopy top into the atmosphere. Results suggest a surface emission of 63 $\mu g\,m^{-2}\,h^{-1}$ for monoterpenes, which comprises 15 to 27 % of the total emissions from the canopy-top into the atmosphere. This represents a significant fraction of the emitted monoterpenes, suggesting that forest surface emissions at this location, possibly due to the decay of pine-needles and surface litter, is comparable in scale to the emissions from tree foliage and should be taken into account in canopy modelling. Results were less conclusive for sesquiterpenes, owing in part to a lack of calibration standard. However, it appears that the emissions of sesquiterpenes from the sub-canopy surface are generally not significant.

This study represents initial, explorative research into VOC deposition and emissions from the sub-canopy surface of a mixed forest location. Further study is necessary in order to study the variation of surface emissions seasonally and the behaviour of terpene emissions during the night, and to quantify VOC concentrations for the entire forest height, which would allow verification of model results for the full height of the canopy.

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Acknowledgements. This work was supported by the Natural Science and Engineering Research Council of Canada and was funded by the Science and Technology Branch, Environment Canada. The authors thank the Canadian Forces Base Borden for hosting the Flux Tower site.

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Table 1. A comparison of understory minimum and maximum median mixing ratios and peak fluxes. Karl et al. (2005) (K05) and Karl and Guenther (2005) (KG05) were in a sweetgum and pine plantation. Holzinger et al. (2005) (H05) and Schade and Goldstein (2001) (SG01) were in a pine plantation. Karl et al. (2004) (K04) was in a tropical forest.

VOC	Min–max MR at 4 m [ppb]			Peak fluxes near surface [$\mu g\,m^{-2}\,h^{-1}$]			
	This study	K05	H05	This study	KG05	K04	SG01
Methanol	0.5–2.4	0.5–7.0		−18	−30	−70	250
Isoprene	0.1–0.6			−19	30	−100	
Acetone	0.7–1.6	1.0–4.0		−20		−10	50
MACR+MVK	0.02–0.2	∼ 0–2.5		−5			
Monoterpenes	0.4–1.9		0.5–2	100	50		

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Table 2. A comparison of mean mixing ratios from observation (μ_O) and model output (μ_M) for the 22 day period. Coefficient of correlation (r^2), root-mean-square error (E_{rms}) and the fraction of modelled 30 min averages between 50 % and 150 % of the observed 30 min averages are listed.

	μ_O ppb	μ_M ppb	r^2	E_{rms} ppb	±50 % %
Isoprene	0.30	0.32	0.51	0.25	64.6
MACR+MVK	0.16	0.10	0.26	0.19	39.6
Monoterpenes	0.94	1.27	0.27	1.09	42.0
Sesquiterpenes	0.01	0.01	0.11	0.01	37.4

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Table 3. The average modelled fluxes (positive upward) from the surface (F_S) and at the canopy top (F_C) in units of $\mu g\, m^{-2}\, h^{-1}$. A range is given for terpenes with emissions from 12:00–24:00 only (no night-time emissions) and emissions from 00:00–24:00 (the full day).

	F_S		F_C	F_S/F_C	
Isoprene	−5.2		243.5	−2.1 %	
MACR+MVK	−1.5		−0.01		
	12–24 h	0–24 h		12–24 h	0–24 h
Monoterpenes	31.4	62.9	234.7	15.4 %	26.8 %
Sesquiterpenes	0.4	0.9	18.7	2.3 %	4.7 %

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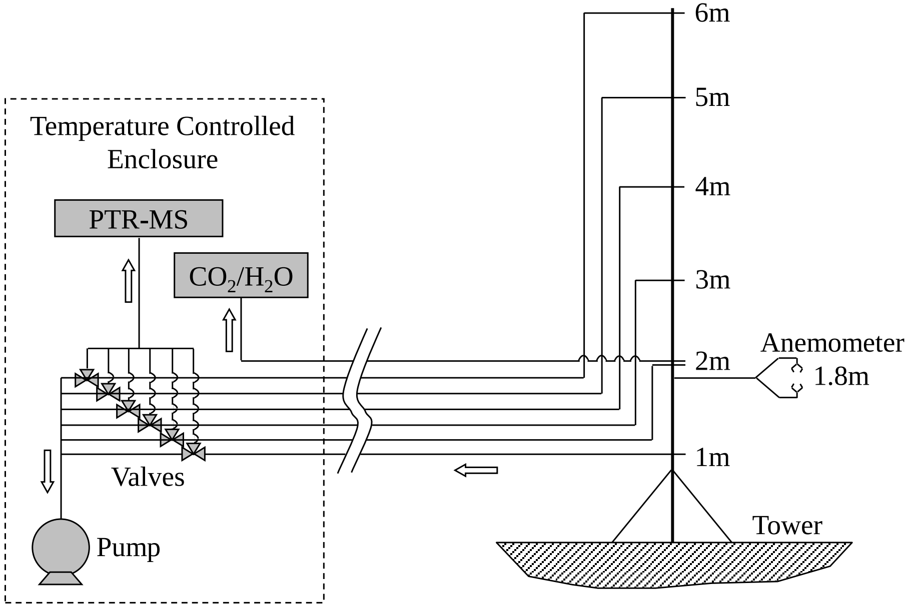

Fig. 1. Schematic of tower and sampling arrangement. All PTR-MS lines are equidistant (12 m) from inlet to instrument.

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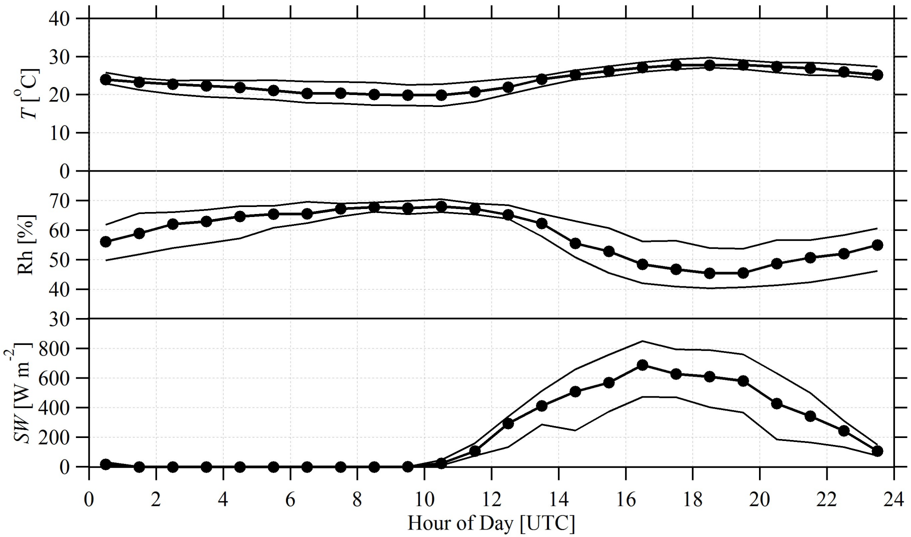

Fig. 2. Hourly median and quartiles of **(a)** temperature, T, **(b)** relative humidity, Rh, and **(c)** incoming solar radiation, SW, all at a height of 33 m, for the 22 days of the study.

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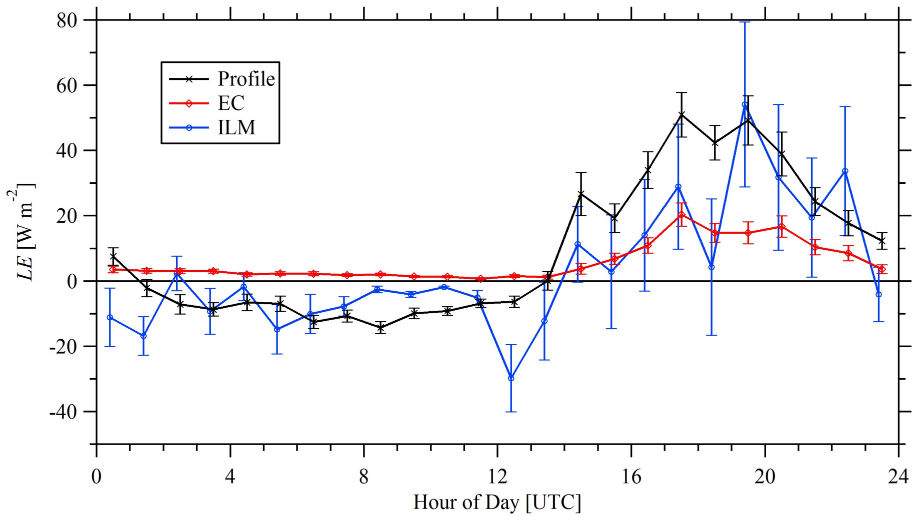

Fig. 3. Hourly averages of Latent Heat flux (LE) determined by three methods discussed in the text. Error bars show 67 % confidence intervals. The ILM plot (blue line) is offset by −0.1 h for clarity.

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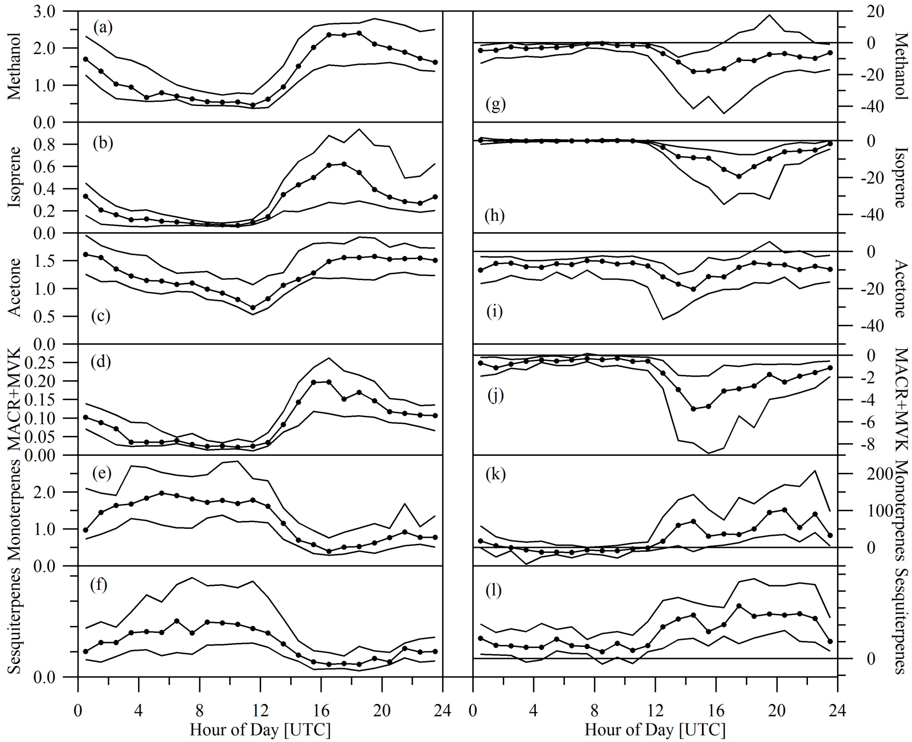

Fig. 4. Hourly medians and quartiles of VOC mixing ratios **(a–f)** and apparent fluxes **(g–l)** over the 22 day measurement period (after filtering for wind direction). Mixing ratios are at the 2 m level in units of ppb. Fluxes are in units of $\mu g\, m^{-2}\, h^{-1}$. Sesquiterpene mixing ratios and fluxes **(f, l)** are not calibrated and are presented as relative units only.

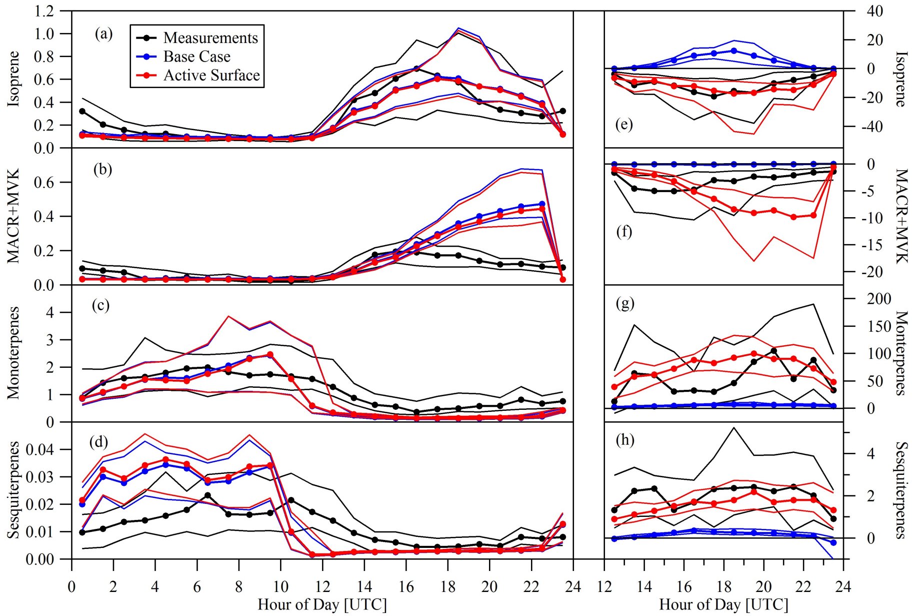

Fig. 5. Hourly medians and quartiles of measured and modelled mixing ratios **(a–d)** and daytime apparent fluxes **(e–h)**. Mixing ratios are at the 6 m level in units of ppb. Fluxes are in units of $\mu g\, m^{-2}\, h^{-1}$. Measurements (black lines), the base model case (blue lines), and the active surface case (red lines) are compared. Sesquiterpene measured mixing ratios and fluxes **(d, h)** are not calibrated and are presented with units in order to compare to model output.

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