

Response to Reviewers

The authors wish to thank the reviewers for their comments and suggestions. We believe some valid shortcomings of the analysis are raised.

As Reviewer 2 points out, there are issues with using the profile method beneath a canopy, where the conditions invalidate many of the underlying assumptions. We originally tried to work around these issues by using the following method:

- Use the measured VOC profiles to calculate fluxes
- Label these as “apparent fluxes” so as not to imply that they directly represent surface exchange.
- Run the model with specified surface exchange values (emissions and deposition at the surface).
- Use the modeled VOC profiles to calculate modelled “apparent fluxes”.
- Compare the modelled “apparent fluxes” with the measured “apparent fluxes” to validate the modelled surface exchange values.

We believe that this method is too convoluted and confusing. We have modified the method as follows:

- Determine the change in mixing ratio with height (slope) from the measurements.
- Run the model with specified surface exchange values (emissions and deposition at the surface).
- Determine the change in mixing ratio with height (slope) from the modelled values.
- Compare the modelled and measured slopes to validate the modelled surface exchange values.

The assumption behind this approach is that if the model (which includes chemistry, emissions, and diffusion) can reproduce the measured change in mixing ratio with height, then the surface exchange specified in the model are likely to be a good estimate of actual conditions.

Further specific points are addressed in the comments below and in the revised manuscript

Reviewer 1

The reviewer points out that “[the experimental design is somewhat limited, since soil surface fluxes were not measured](#)”. While direct measurements of soil surface fluxes (with enclosures or transport of soil samples to a lab) are important, they represent only a small spatial sample of the complete sub-canopy surface. The measurement of VOC concentration profiles provides a larger footprint and effectively samples a larger and more representative area.

The section in which we state that trace uptake in soils is generally microbially mediated has been modified (Section 1 / Paragraph 2). We have attempted to reflect the reviewer’s comments with respect to methane and methanol and have included reference to the

Stacheter et al. (2013) study. The current lack of direct experimental evidence and the need for future research in this area are now emphasized (Sect5/Para4) and we are grateful to the reviewer for placing our results in this context.

The revised manuscript now refers to the studies of Faiola et al. (2014) and Leff and Fierer (2008), in which significant emissions of terpenes were measured in forest-floor soil and litter samples. These studies support the results of our study with direct soil measurements (Sect4.1/Para4 and Sect5/Para3).

The revised manuscript also points out the potential importance of uptake of methanol and acetone, but (as noted above) quantitative flux values for methanol and acetone are not possible, because they are not supported by the model (as with isoprene and monoterpenes). The modified manuscript avoids this confusion by talking about the change in mixing ratio with height only.

We agree that the style of writing can be overly technical and descriptive. We have attempted to eliminate any excessive wording throughout the manuscript. For example, unnecessary sentences are removed from the Abstract, Sect2.3/Para1, Sect3.1/Para1, and Sect3.2/Para4. The sections detailing the flux derivation and the comparison of flux derivation for latent heat flux have been removed, which streamlines the manuscript and makes it more readable.

Reviewer 2

The reviewer has three issues with the manuscript and believes these issues render the results and conclusions unsound: 1) The flux-profile relationships in a forest are not valid. 2) The model is constrained by measurements at a 6-m height within the canopy and not to measurements above the canopy. 3) There is no sensitivity analysis of below canopy chemistry and it is assumed that the compounds are inert. These points are discussed below.

1) The first point has been addressed as described above. There is no more use of the flux-profile relationship, except as a comparison at the end of the manuscript (Section 4.3).

2) The revised manuscript now explains that the basal emission rates used by Makar et al. (1999) were derived (for the same Borden forest) to match measurements of isoprene at 30 and 42 m. Monoterpene basal emission rates were based on a parameterization and were not constrained. (Sect2.3/Para3) For the model run of this study, basal emission rates were modified to match measurements at a height of 6 m, resulting in an increase of 20% for isoprene and a decrease of 11.5% for monoterpenes. Given the uncertainties in basal emission rate parameterizations for isoprene and monoterpenes (e.g. Guenther et al., ACP, 6, 3181-3210, 2006), this is a relatively small change from the Makar et al. rates.

The reviewer's suggestion that this difference could be due to below-canopy constraints (due to "turbulent transport within canopy, chemistry, light penetration into the canopy affecting the vertical distribution of emissions") has been incorporated into the revised manuscript (Sect3.2/Para1). However, the difference could also be due to "changing

forest composition or different temperature and moisture histories”, as stated in the manuscript. We have also added an uncertainty estimate (Section 4.2) for both the surface and canopy-top fluxes of approximately 40% for isoprene and less for monoterpenes, due to the below-canopy constraint.

3) We have added a section to the revised manuscript (Section 4.2) to discuss sensitivity of the fluxes to chemistry. The model is rerun for a 2-day time period with modified (+/- 50%) transport lifetime (from Eq. 3) and O₃ mixing ratio. The reviewer also suggests the modification of OH, and NO₃. However, these mixing ratios are controlled by the model’s internal chemistry routines. Instead, the input solar flux intensity is modified to test the model’s sensitivity to photochemical processes. NO was done in the original manuscript and is again included here. The effects of these changes on the average mixing ratios and slopes are listed in Table 4.

With respect to the assumption of compound inertness, this is a misunderstanding that should be cleared up with the presentation of slopes (change in mixing ratio with height) instead of “apparent fluxes”, as described above. The model employs more than 250 chemical reactions and more than 80 species, so this is not an issue.

Responses to the minor and technical points are listed below:

- The paper mentions (page 4508) sub-canopy EC system for VOCs. Why no data is shown and used in the analysis?

This is a typo and the authors apologize for the confusion. This has been changed in the revised manuscript. It is noted that eddy covariance was briefly attempted with the PTRMS, but the results (not presented) were inconsistent due to instrument noise and time response.

- Some of the figures could be presented without color, now it is impossible to distinguish different lines in black and white copy in e.g. fig 3. Some of us are still printing in black and white so unnecessary use of colors in simple graphs should be eliminated.

Distinct symbols and line types are now used in Figs. 3 and 4.

- Use of UTC time is confusing, please use rather the local time.

All graphs are converted to EDT (UTC – 4 hours).

- The deposition velocity depends not only on deposition flux but also on the height at which the concentration is measured. The height used here is not stated.

The model calculates deposition based on concentration at the lowest height level (1 m). This explanation is added at Sect 2.3/Para 3.