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Atmospheric
Chemistry
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Discussions

Interactive comment on "Emissions of isoprenoids and oxygenated biogenic volatile organic compounds from a New England mixed forest" *by* K. A. McKinney et al.

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We thank the reviewer for the valuable comments, which have helped to improve the manuscript. Our response to the individual comments is below.

Comment: It is important to note that when comparing Harvard forest with coniferous ecosystems one would certainly expect distinct differences in the exchange of VOC emissions (e.g. methanol and acetone). The composition of terpene fluxes can also vary considerably between different ecoregions.

Response: We agree with the reviewer. To emphasize this point, we have added the following sentences on p. 28585, l. 20:

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VOCs emissions from a deciduous-dominated ecosystem such as Harvard Forest may differ significantly from those from the coniferous ecosystems cited above. The comparisons here and elsewhere in the paper to BVOC emissions at forest sites with larger fractions of coniferous species are provided with this caveat in mind but are included because of the relatively small number of published studies at comparable midlatitude deciduous-dominated forests.

Comment: When interpreting OVOC fluxes it is important to point out that ecosystem scale flux measurements infer a net flux; many OVOC could exhibit a compensation point and a flux dependence on ambient concentrations.

Response: We concur. We have addressed this point in conjunction with the following:

Comment: P 28584, line 20 ff: The HLC's of compounds addressed here (e.g. ketones) are quite small, such that solubility can not explain their uptake. The bidirectional change of these compounds therefore has to be governed by chemistry (e.g. enzymatic and nonenzymatic reactions in the mesophyll).

Response: We agree that mesophyllic processes are an important contributing factor to the uptake of these compounds and did not intend to imply that solubility alone is responsible. We have addressed this and the previous point by clarifying the language used in the paragraph on p. 28584, l. 20-30 as follows:

Negative fluxes of oxygenated VOCs above forest canopies have been observed in other studies (Karl et al., 2005;Seco et al., 2007) and are consistent with bidirectional exchange. Compounds such as methanol, acetone, and MEK are somewhat soluble in water within the leaf and on its surfaces (Henry's Law constants at 298 K of 0.46, 4.1, and 6.8 Pa m3 mol-1, respectively (Sander, 1999)). Gas-phase mixing ratios of these compounds will respond to changes in aqueous-phase concentrations from production or consumption in the mesophyll and to changes in water volume on canopy surfaces. Thus, they will exhibit either positive or negative fluxes depending on whether ambient concentrations are above or below the partial pressure in equi-

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librium with aqueous concentrations in the mesophyll (compensation point). Because canopy-scale flux measurements detect the net ecosystem exchange, they reflect the sum (either positive or negative) of these production and removal processes.

We have also revised the paragraph in Section 4.2 (p. 28595, l. 16-19) that discusses the effect of the stomatal opening on the emission of soluble compounds:

Short-chain alcohols and ketones, which are slightly soluble, exist partially in the aqueous phase inside the foliage. Because their vapor pressure is buffered by the aqueous-phase concentration, emissions of these compounds are more sensitive to stomatal conductance than the highly volatile isoprenoids and terpenoids, which accumulate high internal partial pressures that compensate for reduced stomatal conductance (Niinemets and Reichstein, 2003a).

Comment: m/z 153: another candidate for m/z 152 is methylsalicylate. Many oxygenated terpenes (e.g. camphor) are typically associated with coniferous species. Since MeSA is a plant hormone signaling stress it would be an interesting to identify the species using GC-MS or PTR-TOF-MS.

Response: The fraction of coniferous species at Harvard Forest is not insignificant (21% hemlock, white pine, and spruce), so it is possible that camphor or other oxygenated terpenes from these species could be detected. Nonetheless, it is also possible that the compound detected at m/z=153 is not a terpene derivative. We thank you for suggesting methyl salicylate. We have added this possibility to the abstract and to p. 28587, l. 16 and the following sentences to p. 28603, l. 8:

Another possible candidate with protonated m/z = 153 is methyl salicylate ($C8H8O3$), a plant hormone signaling stress (Loreto and Schnitzler, 2010). Further studies using a method that provides additional structural information, such as GC-MS or PTR-TOF-MS, are needed to identify this species.

We have also added the following sentences to the end of p. 28603, l. 27:

Karl et al., (2008) report ecosystem-scale fluxes of methyl salicylate from a walnut orchard in California. Emission rates as high as 0.25 mg m-2 h-1 were observed when the plants were under stress. These results suggest that methyl salicylate can have a significant canopy-scale flux and is also a viable candidate for detection by PTR-MS at this mass-to-charge ratio.

Comment: P 28587, line 10 ff: if no considerable flux of MVK+MAC has been observed the flux detection limit of the current setup is probably too high to detect deposition fluxes. The flux detection limit should be calculated (e.g. according to Lenschowand Kristensen, 1985) and compared to the typical magnitude of expected for deposition fluxes.

Response: We have estimated the uncertainty in the fluxes by calculating the standard deviation of the covariances obtained at lag times far away from the true lag, as described in the last paragraph of Section 2.3 of the discussion manuscript (p. 28581, l. 13). This method is similar to that of Lenschow and Kristensen, 1985 in that it is also a means of estimating the contribution of random variations in the signals to the flux. This quantity also represents a reasonable estimate of the flux detection limit. To show how the detection limit compares to the reported fluxes for each species, we have added a line indicating the flux detection limit for an individual 30-minute integration period to Figure 5, which presents the diurnally binned flux data. Points which fall below the line are not statistically significant fluxes. The results show that the majority of the measured fluxes for m/z = 71 (both positive and negative) are below the detection limit. Hence we conclude that no net flux of m/z = 71 was detected. It is certainly possible that fluxes below than the detection limit were present but not detected. However, it is difficult to predict expected deposition fluxes for the site based on other studies (which vary considerably) because the differing ecosystem types and local conditions would be expected to affect the observed fluxes. We have added the following sentence to the end of the paragraph on p. 28587, l. 10: The mixing ratios of MVK + MAC above the canopy were relatively low (0.1 – 0.6 ppbv), thus it is possible that no flux was observed because the ambient concentrations were close to the compensation point (Karl et al., 2010).

Comment: P 28589: It is not clear whether the effect of past temperature history has been considered when modeling isoprene emissions using MEGAN.

Response: The effect of past temperature and PAR history (1- and 10-day effects) is included in the model. To clarify this point, we have modified the sentence starting on p. 28588, l. 20 as follows: Among other changes, the MEGAN algorithm used here includes terms to account for the effect of temperature and PPFD over the 1- and 10-day periods prior to the measurement.

Technical corrections: Reformat references given in the Introduction (e.g. p 28567, line21) P 28591, l11: change to Müller

Response: The corrections have been made. Thank you for pointing out these errors.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 28565, 2010.

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