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Biogeosciences Discussions

Interactive comment on "Contribution of flowering trees to urban atmospheric biogenic volatile organic compound emissions" *by* R. Baghi et al.

R. Baghi et al.

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We appreciate the thorough reading and insightful comments from Reviewer 2. Below are our responses to these comments and corrections that will be applied to the manuscript.

Referee 2 Comment: For results presented as "averages", it would be good to also present SD or SE, otherwise, median and range. Ideally, some sensitivity studies would help give an estimate of uncertainties.

Author Response: We conducted a number of repeat enclosure experiments on the same tree species. We will report the standard deviation of the determined emission rates as statistical indicator for the repeatability of the measurement. This informa-

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tion will be added to the revised manuscript. This, however, should be considered a lower estimate. Our own work as well as studies by others have shown that branch to branch and tree to tree variability in emission rates typically exceed the experimental uncertainty of an enclosure experiment result by a large margin.

Referee 2 Comment: What exactly do you mean by "vegetative state"? Leaves on branches before flowering has occurred (if there are leaves at that time)? "Leaves only" during flower bud formation? Leaves on branches after flowering has occurred? etc. . . .? This is defined in the text, but a little more information would be useful in the abstract. Author Response: For clarification the term "vegetative" will be replaced by "post-blooming".

Referee 2 Comment: "The total normalized BVOC emission rate from crabapple" – Does this mean branches of crabapple with leaves and flowers? Or flowers only?

Author Response: In the text this statement is followed by "during the flowering period". In the case of the crabapple tree, flowers appeared before leaves. Consequently, this result is scaled to branches of crabapple with flowers only. This will be detailed in the abstract.

Referee 2 Comment: "The floral BVOC emitted during this three-month simulation constitute eleven percent of the cumulative monoterpene flux for the Boulder urban area" - What does "cumulative monoterpene flux" mean?

Author Response: "cumulative" here means accumulated, or integrated over the three-month period. We will further specify this by changing the wording of this sentence in the manuscript.

Referee 2 Comment: Page 3147, line 14: I question the use of the words "generic vegetation class" here, given that "generic" and "class" have very specific meanings in classification of living things. I suggest "this general vegetation group".

Author Response: This will be corrected in the revised manuscript as suggested by

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this reviewer.

Referee 2 Comment: Page 3148, line 14: Sampling was done at a nursery, and the sampled trees were in pots. Please include a discussion of stress – was CO2 exchange measured? Was there any way of assessing the stress status of the trees compared to what might be expected in their planted urban habitat?

Author Response: The degree of vegetation stress is difficult to assess. Trees had been growing in their pots for at least 6 months (over the previous winter) prior to the experiment and were well acclimated to their growing environment. All trees investigated were visually showing no indications of stress or damage. Flowers were developing and stayed on the tree for as long as other trees in the nursery. CO2 exchange was not measured during these particular experiments. We have conducted a large number of similar experiments with monitoring of photosynthesis rates by measuring CO2 in the in and out flowing air and have not seen reduced photosynthesis rates (i.e. indication of stress) under these chosen experimental conditions.

Referee 2 Comment: Page 3148, lines 24-26: Only large flowered species were sampled – do the authors think it possible that small flowers might be very strong VOC emitters, thus ignoring such a large % of species might result in high uncertainties in the subsequent work?

Author Response: As stated in the manuscript, sampling was performed on ∼65% of the insect-pollinated, non-catkin producing tree species in the City of Boulder tree inventory. Catkin-producing tree species, which generally are wind pollinated, are less likely to invest resources in the production of floral emissions to attract animal pollinators (Wragg and Johnson 2011). By "conspicuous, floral structures", we we did not mean to imply that we neglected to sample trees with small flowers, (i.e. only catkin-producing species as stated in the previous sentence).

Referee 2 Comment: Page 3148, lines 26-27: “The rationale for this sampling decision was that these tree species would be most likely to invest resources into floral BVOC

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production for the purpose of pollinator attraction." I think that it's quite possible for large showy flowers to have no VOC emissions at all, and that their size and colour alone attract insects. Conversely, some small insignificant flowers can have a very strong perfume – and hence large VOC emissions. A sensitivity study might help to give an idea of the uncertainties associated with these sampling issues.

Author Response: Since our emissions estimates are based on $\sim$ 65% of the insect-pollinated flowering tree species present in the tree inventory, and since catkin-producing species were not sampled, reported emissions should be considered lower-bounds of the likely actual emissions from urban trees within the study domain. We will add this statement to the manuscript to further clarify this point.

Referee 2 Comment: Page 3149, line 12: should this be "minimal contact of foliage and flowers with the bag"?

Author Response: Yes, we will correct this statement as suggested by the reviewer. Referee 2 Comment: Page 3149, line 16: please explain why the air had to be cooled before entering the bag enclosure, and what the difference in temperature was between bag air and ambient. Wouldn't the foliage and flowers emit less VOCs in cooled air, compared to ambient external conditions?

Author Response: The primary purpose of the cooled water trap was to scrub some water vapor out of the purge air flow for the purpose of keeping the water vapor concentrations inside the bag below saturation levels. Transpiration from the plant inside the enclosure is a significant source of water vapor leading potentially to saturated water vapor conditions and water droplets building up on the enclosure bag wall, which is an effect that we try to avoid as this high humidity can lead to interference in the sample collection and chemical analysis when using solid-adsorbent sampling techniques. A second goal was to counteract the greenhouse heating of the enclosure air during daytime, sunny conditions. However, this cooling effect is minimal, as air, by the time it enters the bag enclosure is not much colder than ambient air temperatures. In

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general, the air temperature inside the enclosure was very close to ambient air temperature during night-time, i.e. within 1-2oC. During daytime, despite the air flowing in being cooled, temperatures inside the enclosure typically exceeded ambient air temperatures, by approximately 1-6oC. These aspects of the experiment are discussed in further detail in (Ortega and Helmig 2008).

Referee 2 Comment: Page 3149, line 24: the internal standard mixture was introduced at 6.5 ml min-1 – so what was the concentration of this standard in the bag enclosure? Author Response: After dilution with the purge flow resulting concentration of the standard components inside the bag ranged ranged from 2.2 to 11.4 ppbv.

Referee 2 Comment: Page 3150, lines 1-2: how strong an adsorbant is Carboxen 1016 for the compounds of interest? In the event of breakthrough from the Tenax (which I assume was first in line in the multi-bed trap), VOCs would be adsorbed onto the Carboxen 1016. If this is the right assumption, would Carboxen 1016 release all the VOCs of interest for analyses, and would all the VOCs of interest be able to "breakthrough" Carboxen 1016?

Author Response: The samples were backflushed during thermal desorption such that analytes trapped on the Tenax adsorbent bed are not required to pass through the Carboxen 1016. This combination of adsorbents has been thoroughly tested in laboratory experiments and has been shown to be suitable for quantitatively trapping and releasing a wide range of BVOC spanning in volatility from isoprene to sesquiterpenes.

Referee 2 Comment: Page 3150, lines 5-6: it seems that emissions were sampled for 1 hour – please explain if there are issues/risks associated with such a long sampling time of these reactive compounds.

Author Response: The primary risk associated with sampling onto adsorbent cartridge is the loss of sample from reaction with of ozone. Precautions were taken to remove ozone from air being purged into the enclosure bag and again in the adsorbent cartridge sampling by placing ozone-scrubbing filters in line (Pollmann et al. 2005). The

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loading capacity of the adsorbent cartridge was tested regularly by placing a second cartridge (breakthrough) in line and by checking that no VOCs reached the breakthrough cartridge. No compound losses were found during extensive experiments with increasing sample volume that have been conducted in the past (Helmig et al. 2004). Please also refer to (Ortega and Helmig 2008) for more technical details.

Referee 2 Comment: Page 3150, lines 7-18: It's not clear how many different trees of each species were sampled; we are only told that "...for each tree, a single branch was chosen to be sampled repeatedly..."

Author Response: Only one tree of each species was sampled over the course of the study. This will be clarified in the revised manuscript. Referee 2 Comment: Page 3150, line 24: how were the samples stored prior to analysis? For how long were they stored?

Author Response: Samples were stored in a freezer for 1-2 days before being analysed. This information will be added to the revised manuscript.

Referee 2 Comment: Page 3151, lines 16-25: please describe how many sensors were deployed for each environmental variable, and where and how they were deployed, both inside and outside the chambers.

Author Response: One PAR sensor was mounted on a tripod, outside of the enclosures, and placed right next to the studied trees. One thermocouple was used to monitor ambient air temperature. A thermocouple was placed inside each bag to monitor the enclosure air temperature.

Referee 2 Comment: Page 3155 line 15: why no graphs for hawthorn? Author Response: Graphs showing the results for hawthorn will be added in the Supplementary Materials Section.

We will address all technical corrections suggested by the referee in the revision of the manuscript. (In the abstract please include the Latin names of the tree species studied. Page 3418 line 8: since no questions are posed here, I suggest using the

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word “issues” instead of “questions”. Page 3155 line 5: “and -terpineoldid show post-blooming increases” – delete “did” at the end of the word “terpineol”.)

Helmig, D., F. Bocquet, J. Pollmann and T. Revermann 2004. Analytical techniques for sesquiterpene emission rate studies in vegetation enclosure experiments. Atmospheric Environment. 38:557-572.

Ortega, J. and D. Helmig 2008. Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques - Part A. Chemosphere. 72:343-364.

Pollmann, J., J. Ortega and D. Helmig 2005. Analysis of atmospheric sesquiterpenes: Sampling losses and mitigation of ozone interferences. Environmental Science & Technology. 39:9620-9629.

Wragg, P.D. and S.D. Johnson 2011. Transition from wind pollination to insect pollination in sedges: experimental evidence and functional traits. New Phytologist. 191:1128-1140.

Interactive comment on Biogeosciences Discuss., 9, 3145, 2012.