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***Interactive comment on “Seasonal variation in vertical volatile compounds air concentrations within a remote hemiboreal mixed forest” by S. M. Noe et al.***

**S. M. Noe et al.**

steffen.noe@emu.ee

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Reviewer # 3 expressed it's main concerns on the interferences of BVOCs and ozone during the sampling procedure as we expressed not to remove ozone from the air stream. The first issue covers our explanation "we did not remove ozone from the sample air stream as that would be a change in the chemical composition of air during the sampling". There, he or she (we use male form hereafter) states that he does not understand this explanation. We think it is, however, obvious. If assumed the atmosphere as is including, say 25 ppbv ozone, the removal or reduction of 25 ppbv ozone will for sure change the state of the sample air stream. In terms of the

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chemical composition of the ambient air we now sample that air minus ozone. We also acknowledge, that such a change might play not a big role for measuring ambient air (see also explanations later).

The reviewer next states: *"As a matter of fact, one of the articles cited by these authors right after their statement (Calogirou et al., 1996) very nicely demonstrates this effect, showing that BVOC loss rates depend on multiple variables..."*.

The publication by Calogirou *et al.* exclusively handles sampling on Tenax or mixtures including Tenax! Therefore, that can not be used as a comparison to our sample method using carbon adsorbents only. Moreover, Calogirou *et al.* state by citing Ciccioli *et al.*, 1992 and Steinbrecher *et al.*, 1994 that they found recoveries near 100% for carbon adsorbents.

There are good reasons to use ozone scrubbers, especially under laboratory conditions and when the adsorbent material contains Tenax or the sampling procedure uses cuvettes or container enclosures with comparatively long residence times. Typically in studies focused on that topic, there is either used scrubbed compressed air or even clean air. The mixing happens just before sampling (Helmig *et al.* 2003, 2004; Pollmann *et al.*, 2005), or some use BVOC preloaded cartridges and let clean air plus ozone pass over. The systems measured in such studies consist only of the wanted components, that is rather different to ambient air. Other experimental sets compared scrubber materials (eg. Fick *et al.* 2001) and compare their recoveries to clean air. That is, however, again another (chemical) system as measuring ambient air with all present compounds.

We do not deny the validity of the results of such studies and grade them as useful and important checkmarks to grade the accuracy of sampling methods. But, such checkmarks should enable us as well to grade if it make sense to change a system under investigation. In short, does it make sense to change the properties of the object

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of interest? There is always a trade-off and that question has to be answered from case to case.

The system we investigated during our measurements is a slab of 6 L ambient air over a time of 30 minutes. It is important to understand that the system measured has a space and time element. Supposed we could determine the state of that slab of air over the time period given with infinite accuracy, the outcome of that ideal measurement would be the time and space integral on the state of the compounds of interest. That is done by our sampling method, unfortunately with a finite accuracy and all we can expect is a value  $\mu(X) \pm \epsilon$  where  $\mu(X)$  denote the mean value over the time interval and  $\epsilon$  the measurement uncertainty. As it is not possible to remove instantaneously the ozone of the 6 L slab of ambient air, the only place and time where the removal of ozone will influence the measurement is the passing of the tube. Given the dimensions of our sampling tubes the maximal possible volume to sample on is  $0.74 \times 10^{-3} \text{ m}^3$ . The volume sucked per second is  $3.3 \times 10^{-3} \text{ m}^3$ , thus the tube volume is exchanged in 0.2 seconds. Given that these tubes are filled with adsorbents, the available volume is even smaller. If we further assume that ozone resides only in the free air space of the tube and that is about 10% of the total tube volume (included the adsorbent free parts) then we can estimate with 60 ppbv ozone, which is a maximal value for the forest in Järvselja, a total of about  $10^5$  molecules ozone inside the tube each 0.2 seconds. By sucking 6 L ambient air the total amount of ozone molecules sucked through will reach  $10^8$  molecules  $\text{m}^{-3}$  during the 30 minutes sampling. Given small amounts of monoterpenes ranging from 0.5 to 1 ppbv, we should reach up to  $10^{11}$  molecules  $\text{m}^{-3}$  accumulated on the absorber surfaces. Assuming that all ozone molecules will react in each 0.2 seconds volume exchange (what is quite unrealistic as we neglect the reaction rate etc.) that would lead to a mean loss in the range of 0.014% as the monoterpenes accumulate and their molecule numbers in the exchange volume reach fast (within minutes) concentrations of  $10^9$  molecules  $\text{m}^{-3}$ .

We had conducted laboratory experiments with ozone scrubbers in the past. Also,

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we conducted a small test during the current campaign at 21. July under comparable conditions (cloudless, air temperature 28 °C) at the same tower location on 2m height one samples with and one without ozone scrubber in the same time. We measured the ozone removal by a ozone analyser (Thermo, Model 49i), from ambient 28 ppbv to below 1 ppbv after the scrubber. The sample inlets have been placed at 5 cm distance, facing to the same direction. A simple subtraction of the chromatograms will not help out here as the procedure of analysis is usually to integrate the compounds under investigation. Therefore, the raw chromatogram was tripled and given for analysis of isoprene,  $\alpha$ -thujene,  $\alpha$ -pinene, camphene,  $\beta$ -pinene, 3-carene, limonene and if possible sesquiterpenes. The analyses were performed by three independent persons, skilled by their everyday work conducting GCMS chromatogram analysis. We calculated the mean of the integrated areas per BVOC and compared each single analysis to that. We found by, summing up all differences that this procedure yielded in an average deviation of  $\pm 2\%$  per chromatogram analysis. Therefore, given our theoretical estimate above, the difference in error by conducting the normal analysis procedure exceeded the theoretical error by a factor of  $10^3$  indicating the error source was the differences in conducting the integration as each person was free to decide what chromatogram integration method to use. Given the use of different sampling tubes, that error might grow even larger. Beside that, the procedure of thermodesorption, might lead as well to errors and any natural action of the ecosystem during the sampling and the difference in sampling times (we sampled 4 x 30 minutes for each height per sampling event) will lead to larger errors than the removal of ozone from the sample air stream.

*There is no information on how many days of sampling were performed and how many samples in total were collected. Without having insight into this information the reader can not evaluate the statistical significance and robustness of the data.*

The autumn and winter measurements were conducted at one day, that met the

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requirements, we negotiated by ourselves, cloudless and pressure above 1000 hPa. During spring and summer, we have extended measurement campaigns in the forest and there have been done several days of measures per month. We chose again always one day that met the requirements. Per height, we conducted 4 samples, each 30 minutes which covers the time from 11:00 to 13:30 EST including change of sample tubes and climbing. This information will be included into the revised manuscript.

*It would be valuable to provide the distance from the site to major populated areas.*

The distance to the next larger city Tartu (about 100 000 inhabitants) is 55 km in north-east direction of the tower site. We will include information on that in a revised version.

*14613/17: Explain what is meant by 'LOX' when first mentioned here.*

Yes, indeed, the explanation is in the next section and will be moved here.

*14615/5: More explanation why there is decreased mixing during the summer month should be provided. Typically one would expect larger mixing from convective transport due to higher surface heating and sensible heat flux during the summer. Larger CO<sub>2</sub> gradients during summer are likely a result of larger respiration activity under the warmer summer conditions.*

The forest canopy in Järvelja is rather dense, especially the top layer where the deciduous trees have the leaves from May to October. Venting and mixing in the lower canopy is hindered by that situation. Yes, the larger respiration activity is a part of that gradient. Above the canopy the situation is another one, there the mixing is larger due to the factors mentioned by the reviewer. That part will be revised to set it

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more clear.

*14616/2: The reported 140 microgram m-3 (equaling ~25 ppbv) are very high ambient concentrations (see also the overview of ambient levels cited at 14617/13). Such findings need to be supported with some robust quality control experiments, including sampling of gas phase standards under simulated ambient conditions within this concentration range.*

Well, our analysis system is quality controlled as we have to use it in everyday work and also offer analysis to state agencies. About using simulated ambient conditions, there is no way to simulate such conditions properly. Atmosphere consist of more than just some major and trace gases. There is already a possible choice of about 30 000 monoterpenes in certain concentrations, not to speak about other compounds. Such simulated ambient conditions will represent just a rudimentary sub-system of the ambient situation and one has again to clear if the result obtained can be applied to real atmospheric measurements. Again, as said above, we do not deny such approaches. They make perfectly sense if one uses artificial gas mixtures and directed experiments in chambers to simulate some mechanisms of atmospheric chemistry but there will be always a deviation between the simulation and the process under ambient conditions.

One explanation for the, indeed, very high concentrations is the heat and drought stress applied to the trees under the extreme hot temperatures in summer 2010. Many BVOC emitting plants can easily increase emissions 30fold under stress occurrence.

*14616/18: Given the high seasonal variability a display of the seasonal evolution of compound ratios is more meaningful than total annual means.*

We have in Figure 3 the seasonal evolution per height. Figure 4, do not represent annual means, the box plot represent annual median concentrations, the box

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boundaries show the 25 and 75 quantiles covering 50% of the data and the whiskers show the standard deviation. In that sense, to show the shape of the concentration profile over most time of the year and give access to the variability one can expect for these concentrations Figure 4 make sense.

*14621/6: It is mentioned that logging took place in winter. BVOC in ambient air are expected to be much enhanced during logging operations (Goldstein et al., 2004). Samples that may have been influenced by emissions from logging can not be deemed representative of natural forest emissions.*

We never stated that the emission pattern we present is pure natural in the manuscript. Even though the forest is according to air quality criteria graded as "remote" that does not mean it is a primeval unmanaged forest. There was no logging conducted in the vicinity of the tower but as the Järvselja Experimental Forestry Station covers about 11 000 ha, there is some logging conducted in that area. Also, we stated in the conclusions that during winter the anthropogenic emissions play a role.

We will revise that part as the sentence may imply logging took place near to the measurement site which was not the case.

*Overall, the data discussion, interpretation, and conclusions do not go much in depth and report few findings beyond what has already been shown in other previous studies.*

However, there are no other previous studies on that forest ecosystem type in terms of seasonal and spatial BVOCs as far we know.

*Figure 5: Axis titles are too small to be legible. - English writing needs some improvement throughout the manuscript.*

Will be changed in a revised version, the axis titles have been scaled automati-

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cally by the procedure of setting the manuscript into the ACPD online format, in a print optimized version the figure will be larger and the titles should be scaled normally.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 14607, 2011.

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