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Interactive comment on "The bi-directional exchange of oxygenated VOCs between a loblolly pine (*Pinus taeda*) plantation and the atmosphere" *by* T. Karl et al.

T. Karl et al.

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General response to major comment:

In this manuscript we do not argue that oVOCs are only produced from leaf/surface reactions rather than gasphase reactions with ozone. For example many sesquiterpenes have lifetimes of minutes due to the reaction with ozone and their oxidation products likely contain oxygen. In fact for some species as pointed out on line 19 cf page 5893, gasphase reactions can be significant. Having this said, it is pointed out that much of the discussion on this topic is rather about the magnitude of reactive VOC emissions than their existence (which I would argue nobody would doubt), and the origin

of oxygenated species observed when ozone interacts with plant emissions and the plant itself. We do raise the possibility that other mechanisms of ozone reacting with and damaging plant material can generate substantial amounts of oVOCs. We clarify portions of the discussion and also include the possibility that ozone can trigger the production of oVOCs as the plant's response to damage. In addition we repeated experiments for loblolly and ponderosa plants and added ozone uptake measurements. These data are now included in the revised manuscript. We also added plant physiological data to the new figure and show time trends of a typical ozone fumigation experiment. In these laboratory experiments we observe that most of the ozone uptake can be explained by stomatal uptake. Gasphase losses of ozone are minor due to the short residence time in the enclosure. The experiment shows exponentially increasing emissions with respect to temperature and saturation of emissions at higher ozone dosage. Both suggest primary production of many oxygenated VOCs. In order to support the reviewer's views on substantial wall losses of reactive VOCs, the hypothesized large amounts of reactive VOCs would have to be lost in a 300 cm3 glass cuvette (˜20s residence time) attached to a 30 cm teflon line purged at 1 l/min (˜1 second residence time). This would imply that oxidation products of these hypothetical compounds, which are usually stickier due to the addition of oxygen, would be even less likely to make it through the sampling setup. It would also argue that these oVOCs would be likely lost through 10-50 m long Teflon lines in the field and that it would not be likely that oVOCs sampled in the field could origin from gasphase oxidation of sticky reactive terpenes as hypothesized by the reviewer.

Specific issues: comment on (a), (b) and (c)

(a)

Yes, this is correct. For example sesquiterpenes (m/z 205) are significantly reduced after adding ozone. Similarly we see a decrease of other reactive olfin compounds (e.g. monoterpenes m/z 137, linalool: 155) and sesquiteperne fragments (m/z 149) as expected due to their reactivity. It is well known that these reactive terpenes can react

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fast with respect to ozone. However it is also clear that many oxygenated compounds are higher when ozone is passed over the plant than when ozone is added after the plant chamber.

(a) and (b)

We added a better description of the ozone fumigation experiment in the experimental section. As described on line 14 cf on page 5885 we only used a second glass chamber when ozone was added to the effluent of the leaf cuvette; this was important to keep the total amount of time available for gasphase reactions approximately the same for both setups. Thus 'sticky compounds' could not contaminate the downstream chamber when adding ozone to the plant chamber since it was bypassed. We hope that this clarifies the main concern raised by the reviewer.

(c)

Again, we do not argue that gasphase reactions are completely unimportant as suggested by the reviewer. See comments above.

Minor issues:

We clarified the issue on methanol and acetone emissions. It is noted that quantitative extrapolations from laboratory measurements are subject to caution; they are usually more suitable to derive mechanisms for VOC emissions which subsequently have to be validated by field measurements. In fact we believe that the gradient measurements are more accurate for this purpose. Using source profiles obtained from Figure 3 we calculate that the understory (mostly sweetgum) actually acts as a sink for methanol (3 % of total emission is lost) and acetone (4% of total emission is lost). While there can be other loss processes in the canopy (e.g. dry deposition to surfaces and soil) we argue that even if there was some emission of methanol and acetone from sweetgum it could not have been very large. Low (or practically zero) emissions in the field can be explained by the fact that in addition to low biomass density (30% of total) and that

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transpiration rates in the understory (less light) are likely to be low. Age differences could also be a reason for higher methanol emission rates observed in the laboratory.

Response to individual reviewer comments (RC):

RC: "The authors tested for artifacts in the Teflon tubing. But what about artifacts of ozone reactions with chamber materials i.e. the glass tubes, plastic fan, and gasket? Have ozone fumigation experiments been performed in empty cuvettes?"

AC: Yes, we tested the blank cuvette by adding ozone through the empty glass cuvettes and did not observe significant contamination due to the fan + gaskets. We observed artifact formation for acetaldehyde and acetone in Teflon lines and added the following reference: Northway et al. (2004)

RC: "p5879,line 25:"

AC: PVC

RC: "p5880, lines 13-15:"

AC: Over time, Teflon material acts like a sponge. VOCs can diffuse in the Teflon wall and be subsequently released. Ozone probably enhances this process. In fact it is noted that most permeation tubes are made out of Teflon. For glass surfaces this is not an issue, which was tested in our blank runs.

2.2 Field description

RC: "I suppose sampling height was 24m but that's not clear from the text. Was the site impacted by transported pollution?"

AC: Yes, 24 m

RC: "p5880, line 28":

AC: "Control ring 6": This is flux tower number 6 surrounded by an air fumigation ring - however no canopy scale CO2 fumigation was performed at this ring. The CO2

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enrichment experiment uses it as control. We revised the sentence to: "flux tower 6 with no canopy CO2 fumigation"

2.3 PTRMS

RC: "How have concentrations of unknowns been derived?"

AC: The were calculated using the collisional reaction rate - now clarified in the experimental section

RC: "What was the detection limit? What reaction rate constants and transmission efficiencies (of the mass spectrometer) have been used? What were typical accuracies and precisions of reported data? Under what conditions was the PTRMS operated?"

AC: For a 10 s integration time assuming a reaction rate constant of 2 x 10-9 cm3/s and 1 counts per second background noise, it was on the order of 5 pptv. A collisional reaction rate of 2 x 10-9 cm3/s was used for compounds where no calibration standard was used. Transmission efficiencies were measured by spiking pure compounds in the mass spectrometer. Above 130 amus the transmission was 20% lower than in the 70-100 amu mass range. The instrument was operated at 119 Td at 2 mbar pressure in the drift tube. The experimental section on PTR-MS has been revised accordingly.

RC comment on "3.1 Leaf Level Measurements"

AC: Young needles were ˜2 month old and old needles were older than 6 months.

RC: "5884, 14, and also Figure 1. Exchange rates should be plotted vs ingoing air concentration".

AC: No, this is of course outgoing air! We refer to basic plant physiological literature on how to measure compensation points.

RC: "5885, 6-8: clarify following statement:

AC: Ok, this statement was clarified.

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RC: "5885, 27:"

AC: In total we performed 12 ozone addition experiments, 10 with loblolly pine (same tree different branch) and 2 with ponderosa pine (same tree different branch). Data shown in figure 2 are from one experiment performed with loblolly as stated in the text.

RC: "5886, 14:"

AC: Yes this is correct and we actually argue this way from lines 15 on. However contribution from compounds specifically produced from ozone/surface reactions remain a possibility when ozone flows over the plant surface.

RC: "5886, 26-28:"

AC: "Yes this is correct. We clarified this issue, but also refer to our earlier explanation related to (a), (b) and (c). In any case these ions are still produced in much larger quantities when ozone is in contact with the plant under approx. the same gasphase reaction time. We also point out again that we do not rule out gasphase chemistry. However the main point here is that the magnitude of gasphase chemistry for these m/z ratios can be smaller.

3. Canopy measurements:

RC: "5887, 7 and 5888, 9:"

AC: Natural variability associated with turbulent flux measurements.

RC: "5888, 18/19:"

AC: This is the parameterization that most air quality models use for deposition.

RC: "5888, 19-21:"

AC: The chamber data confirm the potential of acetone emissions from laboratory experiments; however the laboratory setup was not suitable to quantify deposition.

Results/Discussion/Conclusion:

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AC: As suggested by two reviewers we merged and clarified these sections. We deleted portions of the discussion section and merged the rest with the results section now called Results and Discussion.

RC: "Table3: What does negative emission mean? I suggest, that instead of reporting negative numbers, the authors should state that no acetaldehyde emission was observed from young sweetgum leafs."

AC: "Ok changed to exchange rates."

RC: "Table1: The term "DEC" is nowhere defined in the manuscript. The terms "emission rate at 30C" and "standard emission rate" need to be explained better. Usually the standard emission rate is defined as the emission at 30C and a PAR of 1000 umol/m2/s; since no light dependence is assumed for MeOH and acetone emission I don't understand why the figures are different. I am not sure that all numbers are correct."

AC: "Added DEC (=disjunct eddy covariance) to the table caption and simplified + clarified Table 1. We acknowledge that the table might be confusing, also because row numbers unfortunately shifted after the editing process. The emission rates listed in rows 4 and 5 (not 3 and 4 as stated in the figure caption) were fit to the equation shown in the footnote (E0 x exp (b x T (žC))). This explains the difference, since we did not normalize to 30C. We deleted the emission rates listed in rows 4 and 5 and show a fit to an exponential temperature dependence normalized to (E303 x exp (b x (T (žC)-303)).

RC: "Figure 1: Is the x-axis really outgoing acetaldehyde concentration? That does not make sense to me. I assume the plots are exchange rates vs acetaldehyde concentration in air entering the chamber. The symbols expressing statistics must be explained. Also, it would not hurt to better label the axes and plots (e.g. a: young, no O3; b: mature, no O3; ...)"

AC: Ok, we modified the figure according to the suggestions, but it should of course

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be the outgoing air concentration for the compensation point measurement! This is the concentration that the plant is exposed to. We refer to basic plant physiological literature on compensation point measurements.

RC: "Figure 2: More information I needed: Was the Figure compiled from one experiment? What plant species was measured? What were the respective times of measurement for the 2 sample locations and the 2 treatments? Figure 2 should also show absolute mixing ratios, I think the experiment can be much easier understood then."

AC: Ok, we added more explanation in the experimental section as suggested, however we think that plotting absolute mixing ratios in addition to an already complicated figure does not help to clarify it. The important information of this figure is contained in the difference plot.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 5875, 2005.