

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.

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General comments:

The authors present very interesting results from lab and field studies. They attempt to elucidate complex exchange mechanisms of trace gases between atmosphere and biosphere. Such research is extremely important in order to better understand origin and fate of reactive trace gases in the air. Biogenic emission is acknowledged to be by far the largest source of reactive hydrocarbons into the atmosphere; despite this fact source strength and exchange mechanisms are poorly understood yet. Research of the

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type presented here will lead to a better understanding of processes occurring at the biosphere-atmosphere interface and thus help to improve initialization of air chemistry models on local, regional, and even global scales. The paper is of general interest to atmospheric scientists and therefore certainly worth publication in ACP. However, some matters need to be addressed and worked on - mostly minor and issues of presentation of the results.

Specific comments:

My major point is the interpretation of the production of oxygenated volatile organic compounds (OVOCs) from reactions of ozone on the leaf-surface or with airborne compounds. I am not convinced that the presented data show a dominance of ozone/leaf-surface reactions over reactions with biogenic emissions for following reasons:

a) Figure 2 shows that many compounds are produced when ozone is directly put into the leaf chamber but not when it is added to the effluent of the leaf chamber. The authors argue that this suggests ozone/leaf-surface reactions. However, many of these compounds are seemingly lost when ozone is added to the effluent! How can this happen?

I speculate that the experiment was set up as follows (unfortunately the manuscript does not provide details): (i) OVOCs in the leaf chamber were measured without O₃; (ii) OVOCs in the leaf chamber were measured with O₃; (iii) while measuring the leaf chamber the effluent was flowing through the downstream chamber, which was thus contaminated with sticky oxidation products; (iv) OVOCs in the downstream chamber were measured without O₃ - high concentrations of oxidation products were measured in the contaminated chamber; (ii) OVOCs in the downstream chamber were measured with O₃ - lower concentrations of oxidation products were measured because more time elapsed since the contamination. So, if a significant fraction of a primary emission is lost while being transported to the downstream chamber, gas phase reactions in this chamber may be completely masked by the previous contamination.

b) There is indication that some primary emissions were significantly lost while being transported to the downstream chamber, e.g. m145: the ppb-difference was lower in the downstream chamber and from the relative difference (upper panel in Fig 2) one can conclude that the absolute concentrations were significantly lower too.

c) There are masses (m101, m119, m125) that were produced in the downstream chamber despite the fact of its contamination.

Arguments a-c are in favor of a larger role of gas phase reactions with ozone. No matter how the actual setup was and if my speculations are right the authors' should discuss why the concentrations in the downstream chamber were higher for many compounds and how compounds can be produced in the leaf chamber while they are lost in the downstream chamber.

Other/minor issues in order:

ABSTRACT

The statement that methanol and acetone are “primarily” emitted from loblolly pine is misleading. Considering numbers given in Tables 1 and 3, and specific leaf weights for Duke forest, the contribution of sweetgum should be of order 30% of the total emission, which I think is quite significant!

2.1 LABORATORY LEAF LEVEL MEASUREMENTS

When were lab experiments performed? How was the second (downstream) chamber connected to the leaf chamber (tube length, ID, material)? What was a typical measurement cycle (this is especially important for interpreting the O₃ fumigation experiments)?

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?

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p5879,line 25: 'plastic fan' is somewhat imprecise. What kind of plastic was the fan made of?

p5880, lines 13-15: following sequence is confusing and needs clarification: "During ozone fumigation the background concentration of some oxygenated compounds (e.g. acetaldehyde, acetone) increased in the Teflon lines." BUT "The background in the glass cuvette was not impacted significantly." How is this possible?

2.2 FIELD SITE DESCRIPTION

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

p5880, line 28: What is a "control ring (6)"?

2.3 PTRMS

Since the authors report concentrations of unidentified m/z ratios more information is needed here. How have concentrations of unknowns been derived? 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?

3.1 LEAF LEVEL MEASUREMENTS

5883, 16: please specify young and old needles. Does "young" refer to present year needles? Needle age in months would be appreciated in this case. How old were "old" needles?

5884, 14, and also Figure 1: I guess the authors refer to the concentration of incoming air.

5885, 6-8, clarify following statement: While the slope of the compensation point measurement of acetaldehyde did not change significantly AS A FUNCTION OF TEMPERATURE, the compensation point itself followed an exponential temperature de-

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pendence (Table 2).

5885, 27: What plant species was measured and when?

5886, 14: m127 probably is not a product from ozonolysis on a leaf surface because it was also produced at similar amounts when ozone was entered after the plant chamber.

5886, 26-28: Caution with this statement! I think besides leaf-surface reactions it also has to be considered that primary emissions can be lost on walls and in tubing. Maybe the stickier of primary emissions never made it to the downstream chamber. Moreover, Figure 2 shows that besides the listed masses also m113, 159, 173, 177 and 191 are chemically produced in the second chamber.

3.2 CANOPY SCALE MEASUREMENTS

5887, 7 and 5888, 9: what does variability mean in this context? Uncertainty or accuracy would make more sense.

5888, 18/19: It should be motivated why the comparison with Wesely (1989) was done.

5888, 19-21: I do not see where the chamber data would justify this statement.

DISCUSION, CONCLUSION

Much of the arguing and reasoning in the 'Discussion' section is repeated in the 'Conclusion' section. I suggest that these 2 sections will be merged, shortened and focused.

TABLES

All tables need to be worked over. It is very unusual and confusing that the number of columns changes somewhere in the table and also that the column label is not consistent within an individual column. I also suggest exchanging Tables 2 and 3 because Table 3 is referred to earlier in the text.

Table1: The term "DEC" is nowhere defined in the manuscript. The terms "emission

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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 $\mu\text{mol}/\text{m}^2/\text{s}$; 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.

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.

FIGURES

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; ...)

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.

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

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