review notes to

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Journal: ACP
Title: Canopy-scale flux measurements and bottom-up emission estimates of
volatile organic compounds from a mixed oak and hornbeam forest in northern
Italy
Author(s): W. J. F. Acton et al.
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General Comments

This manuscript presents data of a flux experiment over a mixed oak and hornbeam forest. It focuses on VOCs measured by vDEC / PTR-QMS and presents some comparisons to EC / PTR-TOF measurements, which are presented in a companion paper under review in ACPD (Schallhart et al). The VOC flux experiment at the Bosco Fontana field site is part of a work package of the EU FP7 project ECLAIRE (http://www.eclaire-fp7.eu/). The authors intend to compare the measured canopy scale fluxes (top-down) of isoprene (and MT) with MEGAN modelled emission rates that are partly based on enclosure measurements. Such a closure would be an important goal for a study of this scale but the experimental design of the cuvette measurements (as far as this can be inferred from the manuscript) does not allow to attribute the gap between measured fluxes and modelled emissions to certain aspects of the model or the measurement (see specific comments on basal emission factors). The introduction outlines that flux measurements of BVOCs in a polluted region were carried out to study the interaction of natural and anthropogenic emissions and their interactions regarding air quality. This aspect would be of great interest to the readers of ACP and the scientific community but the authors do not make this connection at all. In its current form this manuscript is a description of VOC flux measurement with primary focus on technical aspects and exploratory data analysis (correlations, statistics) that may be basis of very valuable scientific insights but this connection to atmospheric chemistry (or the intent how this may be done based on this dataset) is missing.

Specific Comments

Introduction

p29217 L10+: The Introduction relates average daily maximum concentrations measured in Modena. What does it mean if “the average daily maximum concentrations are peaking at 120µg m^{-3}” (the maximum is one data point with all other values of that day being lower. Over how many days were the maxima averaged and how can one value, i.e. the average, ‘peak’ at a certain value?) and how does that relate to the stated EU air quality legislation (how many exceedances where registered?). The authors mention the AQ standard ‘for comparison’ but the way in which the ozone situation is presented does not allow such a comparison.

Methods

The canopy height is stated as 28m in average. What is the range of tree heights in the vicinity of the tower? What is the roughness length and displacement height at the tower location? Why did the authors choose to measure at 32m on a 42m high tower, only 4m above the average canopy height? The authors need to demonstrate that the closeness to the canopy does not hamper the interpretation of the VOC fluxes (e.g. using turbulence data at the other tower levels).

The tower seems to be a substantial structure likely causing significant flow disturbance. The sonic/inlet setup was situated at 32m on the NW corner of the tower, sampling a significant portion of the fluxes with the tower obstructing the atmospheric flow. The authors do not mention a data QAQC criterion based on wind sectors. The authors either must demonstrate rigorously that the structural obstruction/setup does not affect the turbulence measurement or they must treat fluxes with a footprint from the disturbed sector with particular care (e.g. QAQC flag and exclusion from further analysis, compare turbulence parameters and VOC fluxes from disturbed vs undisturbed sector).

There is no data QAQC criterion on whether a significant portion of the flux foot print was within the forest. This should be a standard criterion.

To give the reader a better overview of the study site the authors should replace or extend Fig2 by an average flux foot print density overlaid on a map of the forest.

How long was the 1/8” Teflon line from the manifold to the PTR-QMS, what was the flow rate, pressure, residence time and Reynold’s number in that part of the inlet and how did this part contribute to the high frequency loss of the VOC measurements.

p29220 L3+ : The authors state the QMS dwell time for VOC masses was 0.5s. What is the response time (e.g. 95% rise time) of that particular instrument? Why did the authors choose relatively long dwell times when they could have increased the number of data points per 25min period by reducing the dwell time with the benefit of reducing the high frequency loss associated with 0.5s averaging? Also, in this paragraph the authors state there were ca 306 data points in each 25min period whereas on page 29223 L13 they say the typical number of measurement cycles, N, was 250 – which was it?

p29221 L12+: The authors assume the calibration error was below 5%. This seems a very strong or boldly casual assumption – please, substantiate this claim. Do the authors have a traceable certificate that their gas standard itself has an accuracy of better than 5%? Did the authors calibrate the PTR-QMS at 1ppm mixing ratios (in N2, dry) or may there be additional error associated with the dynamical dilution of the standard?

With further regards to calibrations, how many calibrations where performed on the PTR-QMS? With the primary ion count ranging between 1.33 and 9 MHz and the water running out during the measurements the performance is expected to have changed throughout the experiment. How well did individual calibrations compare with each other (accuracy, repeatability)?

p29222: Eq.2 suggests that normalized product ion count rates were calculated from individual count rates of hydronium and water cluster ions measured at their respective ^{18}O isotope masses, i.e. scaling factors of 500 and 250 respectively, for 0.2s (factor 5 to get to counting events). This might introduce unnecessary noise into the calculated mixing ratios. What is the measurement precision of the reported VOCs at typical mixing ratios (e.g. inferred from calibrations) based on the described method compared to calculating the concentrations based on averaged (e.g. running mean) primary ion counts?

p29224 L18+: Please, specify on which parameter(s) (c(t), w(t), <c’,w’>,…) the stationarity test is based on.

Regarding leaf level emission measurements (p29226+) it is a misconception that basal VOC emission factors should be measured at one set of basal conditions of PAR (1000 µmol photons m^{-2} s^{-1}) and leaf temperature (30C). This in fact renders the results of such efforts nearly useless with regards to upscaling as the parameter space is reduced from 2 dimensions to zero dimensions and the dependency of emissions on light intensity and temperature comes from the model rather than from the underlying measurements. A better strategy would be collecting emission rates at (near) ambient conditions for each leaf and calculating basal emission factors and PAR- and T-dependencies according to the parameterization of the used emission model. Also, the specific leaf area (leaf area per leaf mass for each species sampled) would be a valuable parameter to determine in such an effort. Sampling only leaves reachable from the ground is likely to result in a non-representative ensemble, as the authors state in the discussion (p29238, L10+). An experimental design that allows to put comprehensible error margins to the bottom-up and top-down approaches would further our scientific understanding, laborious speculation on the reasons for the discrepancies between the two less so. The concept of footprint and species dependent upscaling is innovative and interesting but the results are of limited substance. This reviewer, however, understands that the authors are using the data available and cannot go back in time to change the experimental design.

The discussion of monoterpene bottom-up vs top-down comparison (p29238, L17+) is strangely different from that of isoprene. Even though the upscaling of isoprene and MT emissions seem to have a similar skill, the discrepancy in the MTs is attributed to oxidation and deposition. The manuscript does not provide any evidence to which extent oxidation (what was the life time of the monoterpenes discussed) or deposition cause a discernable loss. The authors are encouraged to reconcile the two lines of argument and to replace speculations with tangible argumentation.

Results

p29230 L8+: The agreement of isoprene fluxes of the two PTR instruments is classified as very good even though the slope is 1.3. Please, clarify whether this is the PTR-QMS over PTR-TOF data or vice versa and specify how the regression was calculated (orthogonal distance regression as necessary for two datasets that have a measurement error). The authors might want to add a scatter plot in Fig4 that shows the regression results. Regarding Figure 4 this reviewer wonders why the MT flux data by PTR-QMS ends abruptly on June 25 whereas the isoprene fluxes from that same instrument continue after a one day gap. Please, clarify!

p29231 and p29233: regarding the description of Fig7 this reviewer does not see a bimodal relationship in the mixing ratio scatter plot but it appears that the temperature effect is gradual and the regression of pairs of VOC mixing ratios shifts. This is particularly obvious in the MEK vs acetone plot with regressions shifting from low acetone (x-axis) intercepts to higher acetone intercepts with increasing temperature but with very similar slopes. The consideration of concentration ratios rather than regression slopes leads to the misinterpretation of the relationship between MEK and acetone. The argument how Fig7 suggests two distinct sinks or sources is not comprehensible. Please, clarify and rephrase. Please, keep in mind that the receptor site receives a big mix of air masses.

p29234 and Fig8: What is the purpose of fitting an exponential curve into the scatter plot of isoprene mixing ratios vs temperature (bottom panel)? The authors have no hypothesis for such a relation nor does the figure suggest one. The isoprene flux vs temperature plot (top panel) demonstrates that an exponential fit with temperature alone is a poor model for isoprene emissions as all the low/no light data cling to the zero emission line. This reviewer doubts that R^2 in that exponential fit is 0.75 – please, clarify and consider skipping this exercise, substantiate it with scientifically sound reasons, or use a more comprehensive relationship.

p29236 L3+: "In order to assess the effect of light on monoterpene emission the residual values from the temperature only model were plotted against PAR". Where? This is not shown.

Supplement

Tab S1: The percentages of MeOH and acetaldehyde passing all tests is inconsistent with the failing of individual test aspects: MeOH failed the LOD criterion in 79% but is stated to pass all tests in 25% (>21%), which is logically impossible (acetaldehyde 18% > (100%-83%)). This reviewer agrees with the authors that VOC flux data should not be excluded per se from further analysis based on an LOD threshold (stated in the main text) since this may introduce a bias, but the authors must present their DAQC results in a consistent way (which portion of data went into which analysis and for what reasons where other portions excluded). Tab S1 and indeed the entire flux analysis is lacking either a criterion for undisturbed wind sectors or a rigorous demonstration that flow disturbances by the tower structure and the sonic do not impede the flux measurement.

Technical Comments

p29218 L6: The reservoir is to the north west of the tower location (45°11'51.0"N 10°44'31.0"E)

p29228 L10+: The temperature varies by some 10 degrees and remains certainly not 'more or less constant' – please, avoid vague terminology and rephrase the description of the field site's meteorology.

Figure 1: Use dots or small markers for presenting the wind direction data as this allows to discern relative frequencies of certain wind sectors whereas lines just overcrowd the graph.

p29230 L11: Add units to the intercept.