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Interactive comment on "From emissions to ambient mixing ratios: on-line seasonal field measurements of volatile organic compounds over a Norway spruce dominated forest in central Germany" *by* E. Bourtsoukidis et al.

Anonymous Referee #1

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General Comments

The manuscript aim to relate BVOC emissions to ambient mixing ratios thereof. That is to my opinion a valuable and needed topic to address because many models yet explain bare emissions and it has to be further estimated what ambient mixing ratio or concentration that will be. However, that ambient values are more crucial for a proper air chemistry and to assess the emission impact on the atmosphere as well as immediate feedbacks to the within the atmosphere-biosphere system. One very positive topic in this manuscript is therefore the "feedback" possibility by applying ozone, deposition and dilution losses to the emission algorithm.

The major problem of the manuscript is, to my opinion, that the authors get lost in a large set of possibilities the data allows to discuss. That lead to a broad but in many places speculative arguing. An example is the diel variation in emissions, without physiological parameters like photosynthesis, evapotranspiration, light, temperature and humidity given on a sub daily scale the special shape of such emissions can't be discussed. Also, the correlation analysis between oxygenated and terpenoid compounds (representing rather different biophysical and biochemical processes) would need further information and qualify a separate publication. Here, that disturbs a clear statement how the "translation" from emitted VOC to their ambient mixing ratios is conducted as given by the title.

The measurement system used is an open chamber approach that would need a proper set mass balance (and by that box model) equation to assess the dynamics of the measurements and then apply that as corrections to the emission algorithm used. Currently, it remains a small miracle how the equations have been formulated.

I do not challenge the choice of the emission algorithm chosen, but everything should be discussed carefully taking into account that the temperature dependent equation has a rather small explanatory power (see r^2 in table 2). Especially if there are obvious other emission driving factors discussed.

I would skip the correlation analysis and take the diel variations as they are without discussing them as there are lacking informations on the physiological state of the branch.

A focus could be drawn on the change in the emission composition (Fig. 4) and it's possible consequence for the seasonality in emissions and further in context to Fig. 8 where the emissions are mapped to ambient mixing ratios. Here, the non-linearity should be discussed, at least for oxVOCs.

Specific Comments

Page 30189, line off: The sentences in the end of the abstract are very unclear. What do you want to tell here? Do you apply only temperature dependent emissions or as it should be light and temperature dependent emissions? Spruce emit both ways, see Ghirardo *et al.* 2010 Plant Cell & Environment doi:10.1111/j.1365-3040.2009.02104.x for a recent reference.

Page 30190, line 9: I guess, you want to tell northern hemisphere vegetation instead of "north hemisphere..." here.

Page 30191, line 1: "... they grow in" instead of "grow at".

Page 30193, line 9: What is "leak tight"? Given your reference to Ruuskanen, that mean the cuvette is open, not tight. It should be clear as you later need this fact in your equation to describe the situation when measuring.

Page 30195, line 14ff: I would not name equation 1 a "mass balance" equation, that is a source term for an emission. A mass balance should be $dy/dt = \sum k_1 y - \sum k_2 y$ with a set of rate parameters k_1 that represent source terms and a set of rate parameters k_2 that represent the sink terms operating on the vector of relevant state variables y. Equation 1 can be the solution of such a mass balance equation as a function of time.

I further assume you mean k_{VOC} [O$_3$] = k_{chem}. This should be written or defined here.

Page 30195, line 23: I guess you mean 3 minutes, not seconds here. At least the cited papers used that time interval for closing the chamber.

Page 30196, line 2: What are "nearby tree emissions"? Do you mean the tree itself you measure (i.e branches outside the cuvette) or the emissions from trees in the surrounding? That is very unclear. As you want to refer to ambient concentrations C_a, that need to be well defined. Given your sentence here, C_a is all outside your cuvette! This may vary for several places (inside or above) canopy or near to a forest edge etc but still would stay just a C_a for your situation. Otherwise you need to define some C_{a0} that is ambient concentration far away from sources or so.

What do you further mean with "steady state of the measured monoterpene signal"? Is that you have been waiting long enough to have constant chamber concentration reached? Or, a constant emission?

Equation 2 does not make real sense as it tells that C_a the ambient concentration equals some concentration C_2 minus kind a difference drawn away by a flow and kind a dilution because that is replaced by the ambient concentration with the same flow. To my opinion, here should be the chamber's concentration that equals these source/sink terms.

In general, I would recommend to present a real mass balance equation (this actually also defines a box model) with all it's sources and sinks relevant. From that, it is possible to derive all the solutions that describe the dynamics of the system presented here.

What is the unit of C_a if solved equation 3 replacing the variables by their appropriate units?

Another problem according to units, you state in the description of equation 1 that C_1 and C_2 are concentrations, therefore something given as mass/volume as usual in atmospheric sciences. Equation 3 seems to end up in pptv which is a mixing ratio. Here it is needed to clarify the units and possible conversions to explain the equations you used for estimating the ambient mixing ratios.

Page 30198, line 11ff: Are these ppb values (NOx) also ppbv?

Page 30199, line 5: The negative fluxes may also originate from the problem of formulating the proper place in space where the mass balance holds. Is the model located inside the chamber? That would make everything in relation to the C_a as measured before closure and negative values might occur for weak emission and stronger losses as example.

Page 30201, line 6: "... For the rest months" I would say here "For the later months...". In line 14, same page you may define the correlation coefficient as CC because you use that later on.

Page 30202, line 13ff: The sentence "In all cases..." I do not understand it’s message? That reads like a sentence missing some parts. To what was monoterpenes "highest", how does the acetone’s temperature dependency links here?

Line 18ff: What do you like to express here? That is not understandable. Your data say that E_{30} in summer is about 1/3 of the spring value and E_{30} in autumn is 1/3 of the summer value. Your relation here is kind of opposite expressed.

Line 24: Figure 1 shows monoterpenes according to the axes description! Not sesquiterpenes. You need to be precise here what is shown and described.

Page 30203, Line 1ff: It is bit puzzling as you employ only temperature dependent

algorithms but here you clearly tell that there has to be a light dependency as well for monoterpenes. If you look to your table 2, it is also clear that the temperature bound algorithm is only explaining a mere of 40% of your data’s variation in general and during night time that diminishes to just 10% in the case of monoterpenes. Well, given that, the algorithm just can’t explain the measurements. You may trust it a bit more in the case of sesquiterpenes, that rises once to mere 70%.

Page 30204, line 9: I would rather say the metabolic pathways are known (not "now known") because this was clear rather long time. Maybe the interplay and the dependencies between several relevant pathways get more and more known and will be ongoing studied I guess.

Line 18ff: What is LAh? That whole section remains a bit puzzling to me. As it is well known, that also conifers emit light and temperature dependent and the presented correlations support this finding. Why you try to avoid getting into that (already in the section 3.3 before) and why not apply a mixed algorithm in the case of monoterpenes. As light and temperature are not independent from each other the temperature related algorithm seems to work most times kind of well enough which does not mean it has to be true. It might not be of importance for the major topic here, the explanation of ambient mixing ratios, but try to avoid strange reasonings like that given in line 20, "Despite ...". The monoterpene emissions will originate from both, pools and recent fixed carbon additionally complicated by non-specific storages (see eg. Niinemets *et al.*, Trends in Plant Science Vol.9 No.4, 2004) that occur in plant leaves due to physico-chemical properties of the compounds.I am a bit in doubt about correlating such weak predicted emissions to each other and draw conclusions from that, especially as the emission algorithm used just covers temperature as dependent variable and you ave here any kind of other impacting factors (ozone, humidity, light).

Page 30207, line 2: Either "...and their importance should..." or "...and the importance of them should...".

Line 13: What is the "time maximum"? Do you mean the seasonal emissions here or the time of the daily maximum emission?

Line 22ff: The sentence "This might be linked..." needs revision. It is unclear what you want to state here.

Page 30208, until line 15: Generally, the whole section 4.1 would need some additional information from photosynthetic status and the evapotranspiration of the branch enclosed. Many things, like the time of maximal emission are bound to diel cycles and the state of the leaf/branch. Water soluble compounds (like methanol or acetone) will rely a lot on the capability of the tree to evaporate. High humidity impacts here a lot on the possible emission activity. As long as there is no information on photosynthesis or light and temperature given it can't be assessed why as example monoterpenes emit more in the afternoon. The cuvette was placed at the side of the tree, when the sunlight reached there? Was it all day? Any shading occurred? There can be many reasons for the actual shape of the diel variation in emission and without additional data/information all that argumentation here remains speculative.

Page 30209, line 1: What competition? Between the factors presented here or between the species, that is not clear at this point. Later, after line 5, you say that the storage pools run empty? Do you have a citation for that? Are you sure that this happens? As told before, here you would need kind of information on the physiological state of the branch.

Line 14: You argue about the humidity as a driving factor, well, yes as this controls the actual evapotranspiration and therefore how the plant is able to do photosynthesis. Further, it is one force that will draw out water soluble compounds. So, clearly it should "drive" emissions but do you have a citation of the water film protection?

At the end of that page, you come back to the light dependent monoterpene emissions. You do not use the light dependency, because equation 5 is not light dependent it is clear that such features will not be mapped adequately. To my opinion, it is anyway a benefit to include the possible ozone losses if the sample system is large and the time inside the chamber is long according to the typical atmospheric reaction rates. Furthermore, your system was open and there happens a replacement of the air drawn to the PTRMS including ozone in the ambient air. I would rather try to concentrate on that topic here and not discuss too much about processes you can not prove.

Page 30210, line 17: You refer to the daily maximum mixing ratios that occur at the middle of the day on figure 1, that can not be seen on the figure as it's not clear where the day of year tick mark is located (start, end or middle of the day?). Further, the finding that is opposite to other findings might be a bit more discussed. What is about that "constant homogenous mixing"? What about the forest edge? Referring to unpublished data is a bit weak reasoning to explain a controverse result.

Line 17: Is the time in "Independent of time..." the daily or seasonal time interval? Later the same line, I guess it's "European conditions" not "Europe conditions".

Page 30212, end and next page: I can not understand how you come to this conclusion. You speak here of the "induced" emissions? But your model can rather weakly describe the emission's temperature relation. You also stated before that all data that where very high after some injury etc have been excluded, to my understanding your data are more or less thought to cover the constitutive emissions?

Figure 7: What correlation coefficient you have been using (Pearson)? That is not noted in the text.

Figure 8: To my opinion, for the water soluble compounds, most prominently for methanol and acetaldehyde, a bit less clear for acetone, the linear relationship does not hold. Is there any reason to have it linear? They seem to follow some logarithmic or power law better. For isoprene and monoterpenes the situation is not as clear but may also qualify better a non-linear behavior. The only one that seem to qualify is the sesquiterpene emission to ambient mixing ratio. A sure way to assess if a model qualifies is a residual analysis, whenever the residuals are not normal distributed and random the model can not (fully) describe the data. What are the colors in the graph?

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 30187, 2013.