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Biogeosciences Discussions

Interactive comment on "The emission factor of volatile isoprenoids: caveats, model algorithms, response shapes and scaling" *by* Ü. Niinemets et al.

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We have conducted a through revision to incorporate all the suggestions and corrections in the MS. In our previous responses (S. Noe, R. Monson, Ü. Niinemets) we have clarified some of the aspects of top-down vs. bottom-up modeling raised by T. Karl, P. Harley and A. Guenther. In this response, we will not repeat our main unanimous response, i.e. that we do believe that both approaches are valid and needed. Here we will answer in detail to all the general and specific suggestions and explain how the MS was modified to incorporate these. As the discussion chain ended up being relatively complex, in the following, we refer to the page numbers in the interactive discussion.

T. Karl (C86-C88, C166-C167, C527-C528)

Here the key suggestion was that we need to focus more on top-down approaches to derive large-scale emission factors. In fact, we have intentionally focused at leaf-level approaches as this is where the emission factors and associated algorithms were initially defined and where mechanistic information of emission responses to environment is obtained. To make this entirely clear, we have now included in the title “leaf-level”. This should avoid the feeling that we have deliberately chosen to ignore a large body of important research. We agree that consideration of canopy-level emission factor estimates is needed and we have expanded the section 2.5.2. Canopy-level emission potentials in integration schemes. We have included most of the suggested references, and we have considered the inverse modeling approaches in this section. However, we also want to emphasize that so far, there is no standardized protocol for inverse modeling of BVOC emissions and most these studies recommended do not provide a value of inverse modeled Ecan based on flux measurements. As S. Noe (C92-C94) and R. Monson (C529-C530) mention, due to bijection, inverse modeling is associated with a number of problems that need to be addressed. Importance of standardization of inverse modeling approaches are becoming acknowledged by CO2 flux community (e.g., Carvalhais et al. 2008 paper cited in the MS), and we believe that BVOC community would benefit from an analogous effort.

The second key point raised was that the most error-prone part of the bottom-up emission models is the scaling from leaf to canopy. Well, in fact, we are not sure that this is an entirely valid statement. It is certainly true that the finer we want to become with our canopy description and modeling of environmental drivers, the more parameters we need. In very detailed models, such as Monte Carlo based ray-tracing approaches, the number of parameters approaches infinity. There have been recently virtual plant stands constructed closely adhering to real plant stands, and effective computational approaches developed, but clearly, for modeling BVOC source strength, a ray-tracing model would be impractical. In reality, in relatively homogeneous stands, even a 1D

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canopy model with a few layers will do a relatively good job. Comparisons of various canopy models and scaling-up routines demonstrate that the scaling-up errors are on the order of 30

C527-C528. Top-down approaches to get the “ground truth” estimates and constrain the range of estimates. As also R. Monson says (C529-C530), we fully agree with this. On the other hand, we will never be able to put flux towers everywhere and fly frequently enough. Bijection problems hinder us generalizing from large-scale measurements to other areas of interest, unless we correctly do the inversion and then put things correctly together again, i.e. rely on models such as MEGAN, where ultimately the emission mechanisms are based on fundamental principles we addressed in this MS.

R. Grote (C108-C112)

Main concerns were the lack of reported effect sizes in some cases (as specified in the pertinent comments below) and modifications needed in the Intro and conclusions. We have improved the MS in all these respects, i.e., conducted the relevant sensitivity analyses and reduced and modified Intro and Conclusions.

- Intro. As requested, we have reduced the single references and also removed the block of the text concerning the importance of BVOC flux modeling for atmospheric chemistry. CO2 is considered at the level of one sentence. As for scaling, this issue arose a lot of response from other reviewers and T. Karl and therefore, we have decided to keep this part, and clarified the text in several places. We removed the aggregations implications part from here.

- variation in the quantum yield (alpha) of isoprene emission. We can confirm that within-canopy variation in alpha is reported only in the cited Harley et al. papers. Funk et al. (2006) use a constant value of alpha within the canopy. However, their measured value was 0.0015 for Eucalyptus saligna. Interspecific variation in alpha is also demonstrated in Lerdau and Thorp (2000) and these studies are included now in the current version of the MS. As requested, we now demonstrated the effect of this

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variation and state “Using the value of a of 0.0027 to simulate the emissions in this species would overestimate isoprene emission by 34

- Effects of temperature function parameters on emissions. We have now conducted the pertinent sensitivity analysis and state in the MS “We conducted a simple sensitivity analysis by either reducing or increasing the optimum temperature by 5 °C relative to the default parameterization (Guenther, 1997), while adjusting the other parameters such that the condition f(TL) = 1.0 at 30 °C was still satisfied. This sensitivity analysis demonstrated that if the “true” optimum temperature was 5 °C less than the default value, the default parameterization underestimated f(TL) by 7

- Lack of reported range in beta. We have now stated this as “In the original parameterization of the Guenther et al. (1993) algorithms, a value of betaïĂă0.09 K-1 (Q10 = 2.46) was taken as a median of 28 published estimates of betaïĂă for different plant species based on individual monoterpene species. Although beta varied more than 2.5-fold (0.057-0.144 K-1) among...” and also “In Pinus sylvestris, beta for total monoterpenes varied between 0.076-0.18 K-1 over the season, whereas the range of variation was occasionally more than 4-fold for given monoterpene species, e.g., between 0.036-0.15 K-1 for alpha-pinene (Tarvainen et al. 2005). Analogously, in Pinus ponderosa, the seasonal variation in beta for total monoterpenes was 0.11-0.27 K-1 (Holzinger et al. 2006)”. We further say that “As whole canopy measurements demonstrate, use of a constant beta value determined from summer measurements can result in ca. 50

- Effects of mixed models on temperature responsiveness. We say now that “Simulation analyses demonstrate that temperature sensitivity of emissions relying on both de novo synthesis and storage can be significantly different from the emissions dominated by storage only, with 5 °C temperature change corresponding to 25-30

- Product concentration effects on emission dynamics. Yes, we agree that the intermediate pool dynamics also affects the labeling experiments, and this is also reported in Noe et al. 2010. We acknowledge this in the MS and included also the Grote et al.

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2009 paper, but we also mention that the dynamics of these pools is relatively fast and therefore the overall response is dominated by the non-specific storage.

- canopy stratification in 2.5.1. In fact, we do not have double discussion here, as earlier we discussed the variation in the response curve shapes, while here we discuss the effect of variation in emission factor on the integration of fluxes. As we put the response curve shape discussion into broader scale in the modified MS by including interspecific variation, we believe that this issue has now been straightened up. We agree that we are currently not in a position to define the optimality criterion and therefore, big-leaf models cannot yet defined on mechanistic grounds for BVOC.

- Conclusions. Yes, we have intentionally avoided in this section repetition of what we had already said in the Abstract. On the other hand, given the large number of comments, we feel that a section providing insight into the philosophy of writing this paper and providing future directions is needed. So, we reworded the title of this section as “Outlook”. In addition, this part was thoroughly modified to agree with the comments of all the Referees.

- induced emissions summary. We have attempted to make such a table, but feel that it cannot be currently done, because induced emissions demonstrated in many laboratory studies are not quantitative and what can be mainly reported in the table is just a list of induced compounds that we have already reported in the text. On the other hand, induced emissions in field studies typically lack an estimate of stress and it might be even unclear what was the stress, e.g. the data in Fig. 7 highlighting the variation in the emission factor in Pinus pinea. This is also why we feel that induced emissions cannot currently included in the emission models on the basis of mechanistic stress dose vs. emission relationships. As for the storage damages, this point has been included in the MS.

- MEGAN time-resolution vs. flux measurements. The point was that sometimes flux data are reported with higher resolution, but yes, conventionally not, and we have taken

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out this point from the MS.

- Problems with references have been fixed.

P. Harley (C479-C487)

The main critical points refer to the circumstance that the paper is a mixture of a review and an opinion. In particular, use of qualifying adjectives is highlighted. First of all, let me say that this MS was not intended to be a critique of BVOC emission modeling and in particular, of the previous work. We say in the MS that "Of course, every model is incomplete in its representation of true biochemical and physico-chemical processes, and ES is differently defined depending on the assumptions carried in each model. This recognition should compel us to continually assess missing processes and their importance to the uncertainties contained in model predictions, as well as to identify strategies for model improvement. It is within this spirit that we have undertaken the current analysis as a means to evaluate the current state-of-affairs of isoprenoid emission models and definitions of ES." Although some BVOC modelers consider including enzyme kinetics as somehow superior to using Guenther et al. algorithms we try to reconcile these different approaches and say in the MS that "A similar logic, defining the emission capacity and modifying this by environmental drivers is used in all upcoming emission models, even if including more detailed process-based descriptions of various biochemical steps and resulting environmental dependencies". So, this paper is a tribute to previous work. All previous and existing models define some sort of emission factor that can have any value between 0 and xx, and contrasting opinions and definitions about ES do demonstrate that the concept is opaque. On the other hand, we agree that the main message in the MS has nothing to do with the qualifying adjectives. We are sorry to see that this has become an irritating issue and so we have removed all these, "opaque, simple..." from the MS.

- modeler's vs. experimentalist's responsibility. We agree that it is modeler's responsibility to correctly parameterize the model. However, the thing is that the line between

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an observer and a modelers is not always straightforward. If someone measures the emission rates under arbitrary set of conditions in the field, and then fits an empirical curve over these data and calculates a ES value for “standard conditions”, this is already modeling. Now this value ends up in the emission databases and will be subsequently used by “real” modelers. When the primary data used to derive ES are not reported, a “real” modeler cannot be blamed for using a problematic value. Or let us approach the issue from another end. Modelers take the emission factors from the emission factor databases which contain the “best known average values”, and calculate the emission. When the modeled and measured fluxes agree, the model has got it “right”. When not, at the current state of the affairs, one commonly starts looking for problems in the model structure not in the emission factor that is by definition the best known estimate. We believe that this is the reason why models based on various assumptions, but using the same emission factor databases, converge worldwide in the isoprene emission estimates (Arneth et al. 2008 ACP paper). Also, are the emission factor databases reporting average values? Average is a representative value of the population mean (as the USEPA definition referred by Alex also tells). The number of measurements needed to get a standing value of average depends on the degree of variation. We have learned that there is huge variation in the standardized emission rates. Thus, we advocate in describing this variation in the models instead of assuming a single representative value. This is clearly modelers’ responsibility to include necessary equations in the models, but it is also experimentalists’ responsibility not to average out these variations and to tell “stop” to the modeler if the modeler asks “give me one value”.

- obligatory nod about the importance of BVOC. We have removed this.

- practical advice of this has to be done. We are not sure that it is practical to test, one by one every factor, whether it is worth to include this specific factor in large-scale models, but it cannot be said that we have not done any work to address these issues at larger scales of resolution. For instance, we have demonstrated that Europe-wide

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consideration of seasonality in the emission factor can reduce predicted emissions by as much as 65

- inclusion of solubility effects. Well, we have done this modeling exercise as well, but unfortunately could not publish this as the validation information on the order of 1 h was too crude and also because the night emissions predicted by the model with storage cannot be verified by current flux techniques. Yet, we know that OH radicals accumulate in the canopy during the night, so night emissions seem to be important to consider. From the perspective of the current paper, the idea is to provide enough information for modelers to make an educated guess of which response shape to use. This analysis demonstrates that the short-term response curves, e.g., sigmoidal light response curve sometimes measured in the lab is not necessarily the response shape that can be used with 1 h resolution in simulating the emissions. We have clarified this in the text of the MS now. "Especially in large-scale simulation where relatively crude time resolutions on the order of 1 h are used, and vegetation can be assumed to be close to a steady-state, use of sigmoidal shape is expected to introduce even a larger bias in the predicted emissions than use of the standard steady-state light response curve developed for isoprene (Eq. 2)." Also, we never call for inclusion of detailed dynamic model into a large-scale model running with higher than 1 h time resolution. This would be indeed naive and impractical. We explicitly say that this can be summarized at the level of a simple lag factor that should be applied together with the light and temperature responses that provide the synthesis rate.

- improvement of large-scale models by the emission factor and emission algorithms. Well, as stated above, we have incorporated many of these things into larger scale models and do believe that this has resulted in improved predictions. We have now revised the section "Outlook" significantly and tell that "On the basis of this knowledge, the accuracy of source modeling can be improved. Of course, inclusion of further details necessarily carries larger parameterization burden, but making this effort might be worthwhile when the accuracy of emission source estimates is critical to improve,

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e.g., in extrapolating to future environments".

- bias in leaf-level. Yes, as stated above, we have changed the title to make this more clear.

- detailed comments. Corrections introduced in all cases as suggested. Issues needing more clarification are outlined below.

- instantaneous vs. 1 h. Yes, this part was removed as said above.

- Es as "steady-state..." Done

- Es as constant. We have made this statement more neutral. In fact, I do not see that we ever suggested that early formulations considered it constant. We have made clear that after formulation, it has been considered invariant in many model exercises. In several of the references recommended by T. Karl, we see this, i.e., ES value coming from early set of measurements hinders the modeled estimate of emissions to match the flux data. Just because ES is considered invariant. We think that when applied in such a manner, such model applications do not do justice to Guenther et al. algorithms when saying that Guenther et al. algorithms over/underestimated the emission by xx

- opaque. Removed.

- ES should correspond to the structure, time step... As we say above, we do not say that early definitions did not attempt to do this. We have made this more clear.

- alpha value. We have made clear that the value corresponds to an average of 4 species. We also have now made the sensitivity analysis and shown other reported values as well. For instance, in Eucalyptus saligna (Funk et al. 2006), the values of alpha is outside the range of the measurements for these four species, and using a constant value will overestimate the emissions by 20-100

- default temperature response function. We have revised the text here as "In initial temperature response function parameterization based on measurements in Eucalyp-

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tus globulus (Guenther et al. 1991), the values used were CT1 = 95100 J mol-1, CT2 = 231000 J mol-1, Tm = 311.8 K and the temperature for standardization was taken as 301 K (27.8 °C). Later, based on further measurements in three additional species, Tm was taken as 314 K and the temperature for standardization as 303.16 K (30 °C) (Guenther et al. 1993). In addition, a non-dimensional empirical parameter CT3 was included (Guenther, 1997)."

- reflect. Yes, corrected.

- H units. Provided (the same units as in Table 1)

- stress in models. To our knowledge, T. Karl et al 2008 in Biogeosciences provide an encouraging example for including stress at the ecosystem level. We have also discussed more the ways of stress inclusion into models, but clearly it is more than a scalar to include effects such as insect outbreaks, where we need to get hold of insect population dynamics. This is unlikely possible in short-term simulations, although in predictive scenario analyses we can project the possible effects of such outbreaks.

- inclusion of mono- and sesquiterpene compositions. We are glad that we in agreement here.

- deposition. Included. This is partly where physico-chemical factors start play a role at large scale.

- micrometeorological techniques. Modified.

- tedium. This has been modified as "can skip the tedious step of leaf to canopy integration that can be error-prone and uncertainty-inducing if numerous assumptions need to be made due to practical reasons."

- integration of fluxes. This point was deleted as said above.

- simple. Deleted and the whole section was significantly revised. However, we feel that in these statements, there is some contradictory with the statements specified above.

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When light and temperature algorithms were developed for 4 species and generally accepted, then what is the problem with the CO2 response that has been proposed by Wilkinson et al. also on the basis of measurements in 4 species. As R. Monson (C524-C525) also emphasizes, general mechanisms can be recovered by even single species measurements as was the case with Farquhar et al. photosynthesis model. Of course, the parameter values attached to the model developed to mathematically describe the mechanism can be, and normally are, variable among and within the species, and it is our task to parameterize large-scale models effectively enough to include the mechanism and most of the variation.

A. Guenther (C493-C497)

Main critique refers to conceptual issues and bottom-up vs. top-down approaches partly overlapping with the issues raised by T. Karl and P. Harley and responded to above. We now have addressed all these concerns and modified the MS accordingly.

- modeling concept. We have made this more clear in the MS that we have different emission factors around. As initially defined, the emission factor was standardized emission rate under specified condition (or see P. Harley definition in C479-C487). The USEPA definition also says “of all available data”, i.e. the emission factor is based on measured emissions (data) in agreement with how the leaf-level emission factor was originally defined. Now, we have also emission factors that are not based on measurements, but are derived from response curves (i.e., standardization of field measurements) and emission factors that are outcomes of models. This is what we meant with “modeling concept” (vs. average data). Hope that this is now clear in the MS.

- Emission factor constant. This has been answered by R. Monson (C524-C525). We have also made it clear that as originally defined, the variability was fully acknowledged.

- Inclusion of CO2 effects. Yes, in particular, predictive scenario analyses need this as Arneth et al. 2007 ACP paper. But then CO2 concentration inside the leaf also varies during the day and during the season. We have now made this clear in the Abstract

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and in the pertinent section in the MS.

- leaf-level vs. canopy-level emission factor. We do not make the statement that leaf-level is preferable. In fact, the MS was based on leaf-level emission factor where the emission mechanisms can be studied. On the other hand, we thought that it is important to put the things also somewhat into the context of MEGAN. In fact, I can recall that this was the recommendation of P. Harley who commented on an early version of the draft. We have revised the section about canopy level emission factor a lot and do say that it is straightforward to derive it directly from flux measurements.

- Derivation of canopy-level emission factor. In ACP 2006 paper introducing MEGAN, most canopy level emission factors were likely derived by integrating from leaf to canopy. AT least this is the feeling, I got from reading the MS. It is great to see that the flux data are used increasingly more. Unfortunately, to our knowledge, there is no standardized protocol for derivation of canopy-level emission factors from flux measurements. At least there are some difficulties we highlight in the MS.

- Flux vs. Megan resolution. As explained above, we have removed this section.

- aircraft measurements. Yes, these are very good emission measurements, and there is no model needed, but then how can we generalize?

- canopy-scale emission factor always represents the entire canopy. We are not sure this is always the case. Canopy-level emission factor combines emission potential and canopy structure and leaf area. This means that no general environmental dependencies can be developed. For instance, canopy as a whole will respond differently to diffuse and direct irradiance, i.e. has different quantum yields for diffuse and direct light. This is the inherent property of aggregated structures averaging non-linear functions nicely demonstrated by Gu et al. (Science, 2003, 299:2035-) for carbon fluxes. We have clarified this in the MS.

- accompanying MS. We do not agree. Here we look at modeling concepts, while in

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the accompanying paper, we look at biological dependencies. Both papers are independent.

- simple, past... We have removed this. As stated above, we have done work to include seasonality, improved emission factors and CO2 into Europe-wide or world-scale models. We also revised the whole section, making it clear that "when the accuracy is critical to improve..."

A. Guenther (C531-C533)

- variability in the early emission algorithm papers. We did not say that the pioneering papers considered it constant. As R. Monson (C524-C526) points out, these are the studies coming after. We have made this more clear in the MS in several places. We also say that "Once estimated, ES values were often not modified in subsequent modeling exercises and the variation associated with any ES determination was not considered with only very few exceptions (e.g., Guenther et al. 1994; Hanna et al. 2005).

- emission factor variability and modeling. We are in full agreement here.

G. Wohlfahrt (C616-C617).

We have conducted a major revision trying to incorporate all the comments, and eliminate the conflict in opinions. So, we hope that the final version of this MS remedies all the issues raised.

Let me once again thank all who contributed to the discussion with many insightful suggestions and hope that the final version of the MS with the attached discussion contributes towards progress in BVOC emission and modeling community.

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