**Biogeosciences
Discussions**

Interactive comment on "Estimation of isoprenoid emission factors from enclosure studies: measurements, data processing, quality and standardized measurement protocols" by Ü. Niinemets et al.

Ü. Niinemets et al.

ylo@emu.ee

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We thank both anonymous reviewers for the insightful and very useful comments on the MS and are pleased to see that both the reviewers value this work. We intend to include all their suggestions in the MS and modify the MS in pertinent places to change the accent in places where needed. Detailed point by point responses are provided below.

Rev. 1.These detailed experimental guidelines for generating quantitative VOC emis-

sion data and the associated measurement/data processing errors are excellent and much needed. In my opinion, the description of, "standardized experimental and calculation protocols for generating quantitative biogenic VOC emission data" should be the focus of the article.

We suggest to include following changes 1) in the title change estimation to "estimations" to emphasize the point that there are so far multiple approaches 2) as explained below, we intend to emphasize throughout the MS that we are dealing with experimental protocols and measurements of emission rate rather than with the dynamic concept of ES that has been explored in BG 2010 paper.

Rev. 1: many of the same coauthors recently published a paper which is not well discussed in the current manuscript entitled, "The emission factor of volatile isoprenoids: stress, acclimation, and developmental responses" By Niinemets et al. Biogeosciences Discuss., 7, 1529-1574, 2010. The main point of this paper is that Es is not a constant but rather a dynamic variable that changes on timescale of seconds to decades, "overall indicating that the constancy of values used from study to study is illusion."/ES concept has limited value within an Earth System modeling framework/variable ES approach

We agree that ES is a dynamic concept as demonstrated in the BG 2010 paper. On the other hand, there is an emission capacity at any time moment that can be assessed experimentally. In BG 2010 paper we have contended that the implication of variable ES is that novel algorithms need to be developed that capture the dynamics in ES, but at any rate, even in the case of such dynamic models, the key predictive variable will be the emission capacity at any moment of time, and the basis for any model parameterization is precise and accurate assessment of this variability. In BG paper, it was demonstrated that the variation in ES occurs mainly over several days, weeks and months, and we advocate against the use of ES as a constant over such relatively long time periods or as a species-specific constant. We did not explicitly state that ES can change as fast as within seconds to hours. Thus, we do not feel that there is an inherent contradictory in the dynamic nature of ES and relatively rapid (within minutes

to hours) assessments of emission capacity that is needed for model parameterization (either static or dynamic models). Clearly ES dynamically varies, but any experimental assessment of ES is associated with a number of potential problems that can lead to very large errors or even complete loss of detection of given BVOCs, assignment of given BVOC emission rate to a wrong species etc. These aspects are the focus of this study. Thus, we do acknowledge that ES is dynamic, but also that its estimation at any moment of time carries a number of experimental problems.

We do agree that these aspects need to be made more clear and the confusion over the message in the two papers need to be avoided.

We suggest to include the following changes: 1) in the title, change "emission factor" to "emission capacity" to avoid the confusion with the BG 2010 paper, and highlight the circumstance that we are talking of a quantity that can be experimentally assessed

2) add "at a certain time" in the first sentence of the abstract and a sentence "However, there is large variation in published ES estimates for any given species partly driven by dynamic modifications in emission rates due to acclimation and stress responses" to highlight that ES is a dynamic concept

3) insert "over days, weeks and months" into the sentence "In addition to the naturally dynamic nature of ES over days, weeks and months and " in the Intro

4) add the following sentence at the end of the Intro "We argue that in addition to the dynamic nature of ES, (Niinemets et al., 2010a; Niinemets et al., 2010b) that requires modification of emission algorithms, there are a number of potential experimental and processing sources of errors that can affect the precision and accuracy of emission data. "

5) reword the first sentence of the Conclusions as "This analysis demonstrates that in addition to inherently dynamic nature of the BVOC emission factor, ES, important uncertainties in the experimental estimation of the emission capacity at any given moment

of time can be associated with analytical shortcomings as well as with data processing following emission measurements"

We believe that with these changes, we have solved the confusion.

Rev 1: I believe the authors mistakenly consider vegetation as only sources of isoprenoids without considering their further metabolism.

Actually, we do consider that vegetation can also be a sink of BVOC (para starting on L17, P4666) and we also state that there can be a BVOC compensation point (P4664). So, we believe that this aspect is adequately covered.

Rev 1: Introduction: When referencing text here, please include only the most relevant references. Including 10 or more references reduces the readability.

We agree, and intend to keep only the most relevant references

Rev 1: When using statements like accuracy with respect to Es, the authors are treating Es as if it is a constant.

We intend to make clear that this statement must be understood that ES is stable over a certain time period. Surely, ES varies over days/months and seasons. In most cases, we intend to solve this problem by changing ES to "emission rate" that is the quantity measured.

Rev 1: Static vs. Dynamic enclosures; What about very large mesocosm and whole enclosed biome ecosystems which contain both autotrophs and heterotrophs?

So far, there is a limited number of measurements with such big systems, e.g. Pegoraro et al. 2006 in Global Change Biol (12: 456-469) report measurements in Biosphere 2 tropical rain forest using a closed system approach. Clearly these systems can provide insight into physiological controls of the emissions, but we denote that determination of flux rates using a closed system approach is difficult, and these mesocosm systems cannot be readily replicated. Thus, derivation of ecosystem-level

ES estimates from mesocosm studies is complicated. In this regard, flux measurements using eddy covariance techniques may better serve the modeling community needs for ecosystem-level estimates. We suggest to briefly touch the flux measurements in the current study, but as we primarily focus on emission measurements at the leaf/shoot and branch levels, we feel that mesocosm studies, and detailed description of processes at atmosphere/soil interface are beyond the scope of this analysis.

Rev 1: Why is condensation a problem for isoprenoids? They are generally very poorly water soluble and are not expected to be lost in condensed liquid water.

This statement referred primarily to water-soluble isoprenoids. To clarify the point, we suggest to add "such as methylbutenol and oxygenated monoterpenes (e.g., linalool and 1,8-cineole)"

Rev 1: What about artifacts in measuring volatile isoprenoids by PTR-MS? Several biogenic compounds fragment or share the protonated parent molecular mass ions. E.g. MBO and isoprene.

We agree that this is an important point and suggest to add the following statement "Gas-chromatographic analysis is also recommended to avoid artifacts in isoprenoid emission measurements by PTR-MS due to protonated parent ions or fragment ions with the same m/z as the isoprenoid studied. For example, methylbutenol and several other alcohols and aldehydes can form fragment ions with m/z of 69+, i.e. with the same m/z as the protonated parent ion for isoprene (Fall et al., 2001; Karl et al., 2001), and several C6 aldehydes and monoterpenes can form fragments with m/z 81+ (Fall et al., 2001; Ishizuka et al., 2010)."

Rev 1: Do you mean inïňẠnitely precise? Or inïňẠnitely accurate?

We suggest to reword as infinitely precise and accurate

Rev. 2. "there could be a table listing the error sources discussed in the text and indication how important different error sources are."

We think that this is a great idea and intend to provide the table.

Rev. 2. - Page 4642, Eq. (1): sink/source term.

Yes, the equation is for empty chamber to provide insight into the effects of chamber size on the responsiveness of the gas-exchange system. As in Eq. 4, these terms are already included, we believe that it is best to clarify the situation in the way that we clearly mention in the text that the equation is for an empty chamber, and also add the following sentence "When a plant sample is included in the chamber or when there is compound adsorption on the surface or desorption from the surface of the gas-exchange system, full mass balance equation needs to include source and/or sink terms (s. Eq. 4)."

Rev. 2. - Page 4644 line 28 – page 4645, line 3: high air flow rates/diffusion problems/ quantification of diffusion effects

Yes, as it was written, it was a bit confusing. In fact, there are two partly interdependent problems. Clearly, the diffusion effect is the more problematic the larger is the concentration gradient, i.e., when the flow rate is small, while the detection limit becomes more an issue when the flow rate is high. To our knowledge, the BVOC diffusion problems have not been quantified so far, but enormous effects have been shown for CO2 and H2O. Given that the molecular mass of several BVOCs is quite low, such as isoprene, methanol etc., clearly we cannot neglect the diffusion problems for BVOCs. We suggest to reword the section in the following way "First, when the chambers are operated at high air flow rates, the BVOC detection limit will be poor, limiting measurement of low emissions. However, when the flow rate is kept low to result in higher BVOC concentration differences, chambers with small cross-sectional area and large chamber inner surface exposed gasket area for diffusion can generate errors in flux estimations due to diffusion of gases from the chamber air space with relatively high BVOC concentration into the ambient air with lower BVOC concentration (Flexas et al., 2007; Rodeghiero et al., 2007), especially for compounds with relatively small diffusion volume and high dif-

fusion coefficient such as isoprene (Niinemets and Reichstein, 2003 for a comparison of diffusion coefficients for various BVOCs)"

Rev. 2. Page 4645, lines 21-22: recommended chamber size is arbitrary.

We agree that this statement was somewhat arbitrary. We suggest to reword this section as "To reduce the errors due to diffusion, chambers with relatively large enclosed leaf area (AL) to exposed gasket surface area (AG) are recommended. For instance, large diffusion problems have been denoted for Li-Cor 6400 2 cm2 chamber (AL/AG ïĆż 0.67 cm cm-2), while the errors are considerably less for Li-Cor 6400 6 cm2 standard chamber (AL/AG ïĆż 1.0 cm cm-2), or for Walz GFS-3000 8 cm2 standard chamber (AL/AG ïĆż 1.11 cm cm-2) (Rodeghiero et al., 2007)."

Rev. 2. Page 4647, line 27: certain Viton families/properties of materials.

We suggest to change the text as "certain Viton$^®$ families (e.g., higher flexibility B and F types)" and also add statement that "The important points to consider for gaskets and O-rings in BVOC studies are gas-permeability, adsorption capacity and flexibility (hardness)". As the material physico-chemical properties have been compared in several recent studies, we suggest to point this out in the reference as " (for an overview of physico-chemical characteristics of various polymers see Rodeghiero et al., 2007; Sturm et al., 2004)" rather than adding a repetitive table here.

Rev. 2. Chapter 2.3: Use of adhesive tapes

We agree with this point and suggest to add the following statement "Apart from tubing and chamber wall materials, adhesive tapes are often used to attach films or tubes to support structures or to attach heating wires to tubing. This can constitute a further problem as adhesives of the tapes can further contribute to the background VOC level. This release of VOCs, together with re-emission of previously adsorbed plant BVOCs on tubing and chamber materials," and "As to the adhesive tapes in BVOC studies, they are best avoided, but whenever they need to be used, low VOC emission tapes

C2292

are recommended."

Rev. 2. Page 4650, lines 22-23: "n is a function of the difference of the compound concentrations at the tube and chamber surface, CS, and Cout."

We agree that it was somewhat inexplicit. We suggest to reword it as "difference between compound concentrations in the chamber or tube air (approximated by Cout in the leaf chamber and downstream the chamber) and at chamber or tube surface (CS)"

Rev. 2. Page 4653, lines 25-28: "Here we highlight some of the issues specific to BVOC emission measurements (BVOC air concentrations) and some that are not commonly considered (changes in water vapor concentrations) in calculations of BVOC emission rates." This sentence is poorly constructed. While I understand what the sentence without the parts in parentheses means the whole sentences with them is obscure at least to me.

We agree that it is somewhat cumbersome and intend to reword it as "Here we highlight the effects of BVOC ambient air concentrations, BVOC buildup in the measurement enclosure and the influences of changes in water vapor concentration on BVOC flux calculations."

Rev. 2. Page 4659, line 18 – page 4660, line 4: Ozone removal effects on emission capacity

We agree that chronic ozone exposure itself can affect the emission rates, but such effects are mainly significant over longer term, and would not be of much concern for the measurement periods typically used for BVOC screening exercises. Nevertheless, we suggest to add the following statement "From a cautionary perspective, chronic ozone exposure itself can affect the leaf's capacity for isoprene and monoterpene emissions (Velikova et al., 2005a; Velikova et al., 2005b), and removal of ozone would abolish such effects. However, modification of foliage capacity for isoprene and monoterpene emissions by ozone is typically time-consuming, taking from several hours (for excep-

C2293

tionally high ozone concentrations) to days (Loreto and Schnitzler, 2010), and thus, the effects of ozone removal on the emission capacity are of concern only for longer term measurements."

Rev. 2. Page 4663, lines 13-17: problems with high background concentrations/scrubbers/synthetic air

We agree that scrubbers typically result in a certain background of impurities and also that synthetic air can contain impurities. We suggest to reword the paragraph as "To remedy the problems with high background concentrations, incoming air can be scrubbed of BVOC along with ozone using scrubbers, e.g., charcoal filters (Geron et al., 2006; Manes et al., 1999; Okumura et al., 2008) or catalytic converters (pure air generator), or alternatively, synthetic air can be used. Nevertheless, it is important to be aware that most methods for gas cleaning provide zero air with certain background of impurities. In some cases, the hydrocarbon background can be moderately high such as for the synthetic air prepared from technical grade N2, O2 and CO2 (common in photosynthesis measurements) relative to the synthetic air prepared using GC-grade component gases."

Rev. 2. Page 4664, Equation (7): Assumption that the emission of VOCs is transported through stoma.

We believe that this is a valid assumption. There is a certain cuticular permeability of BVOCs, but even for relatively small molecules such as isoprene, the cuticular permeability is very small as demonstrated by Fall and Monson 1992 (Plant Physiol. 100, 987-992) – even when stomata were closed, the bulk of the emitted isoprene was only emitted from the leaf surface harboring stomata. Analogous observations were made for monoterpenes in monoterpene-non-storing species Quercus ilex by Loreto et al 1996 (Plant Physiol. 110, 267-275). As for the evidence provided by Guenther et al. 1991 for monoterpene emission from the leaf side lacking stomata, then these observations were made with monoterpene-storing Eucalyptus species. In their

C2294

study, monoterpene emissions declined in time-dependent manner, and we currently believe that these monoterpene emissions from leaf adaxial side reflect emissions due to breakage of oil glands rather than emissions through the cuticle (i.e. the rough handling problem discussed in section 2.5). In most cases, we believe that the transport pathway will be lipid phase/aqueous-phase/gas-phase/stomata. Under exceptional circumstances such as a severe water stress resulting in desiccation of cell walls, the direct lipid-phase/gas-phase pathway can be plausible, but such stress effects typically strongly modify the emission capacity as well such that the simplified model is no longer valid.

We agree that an explanation of the possibility of compound transfer through cuticle is pertinent and suggest to include the following statement "Implicit in this equation is that the diffusion flux of BVOC occurs through stomata. This assumption has been experimentally verified for isoprene and monoterpenes, where bulk of the emission flux occurred through the leaf lower side harboring the stomata (Fall and Monson, 1992; Loreto et al., 1996). In addition, very low cuticular monoterpene permeabilities have been demonstrated (Schmid, 1991)."

Rev. 2. Page 4665, Equation (9) valid when chamber concentration of the studied compound is far from saturation.

We agree and suggest to add the following statement "This equation is valid only when the compound concentration is far from saturating concentration. In fact, for most common plant BVOCs, the saturating concentrations are relatively large. For instance, at 25 ïĆřC, the saturating concentration is 0.727 mol mol-1 for isoprene and 5840 ïA∎mol mol-1 (ppm) for ïĄą-pinene (Copolovici and Niinemets, 2005 for a review of vapor pressures of key plant VOCs)." So, this equation will be valid almost always for plant BVOC studies.

Rev. 2. Page 4665, lines 24-26: Estimation of BVOC emission suppression by monitoring the non-linearity of the VOC concentration increase either by on-line monitor (e.g.

C2295

FIS or PTR-MS)

We agree that this can be an option and suggest to add the following statement "Even if the BVOC concentration inside the chamber is far from saturation, such an inhibition of BVOC emission by product buildup would lead to non-linearity of BVOC concentration increase in the chamber. Such effects can be detected by on-line analyzers such as PTR-MS."

Rev. 2. Page 4668, lines 20-21: "The rate of transpiration scales exponentially with temperature…"nearly correct in conditions far from saturation

We agree and suggest to modify the text as "The rate of transpiration scales positively with temperature due to temperature effects on ïĄőïĂăïĂĺnearly exponentially when vapor pressure is far from saturation), "

Rev. 2. Chapter 4.1. algorithms used for normalization of measurements/ the same symbol (f(TL)) for emissions from storage and synthesis.

We agree that it may arise confusion and suggest to use the subscripts fs and fe as suggested.

Rev. 2. Chapter 4.1. presentation of formal emission equations

We agree that this would be useful for less experienced readers and intend to add these equations in the revision

Rev. 2. Chapter 4.1. wrong response functions used in the literature for birch/ a significant part of monoterpene emission from conifers can originate from synthesis

We agree that this specific case with birch illustrates an important point and also that a mixed algorithm is needed for conifers. We suggest to add the following statements "Moreover, it is even not always known whether the emissions come directly from synthesis, indicating that Eq. 17 is appropriate for standardization, or rely on storage, suggesting that Eq. 19 should be used for standardization. For instance, due to lack

C2296

of knowledge of the emission controls in broad-leaved temperate deciduous Betula pendula, the emissions were standardized based on terpene evaporation (Eq. 19) in Hakola et al. (1998). However, now it has been established that the temperature response of monoterpene emissions in this species can be described by temperature effects on terpene synthesis (Eq. 17) (Ghirardo et al., 2010)."

"However, a significant part of monoterpene emission from conifers can originate from synthesis (Ghirardo et al., 2010; Shao et al., 2001), and in such cases hybrid algorithms based on both temperature effects on synthesis and emission may need to be used for data standardization (Niinemets et al., 2010b)."

Rev. 2. Page 4671, line 26: "…as high as 2-6…" does this refer to monoterpene synthesis or emission?

This refers to emission. Suggest to change as "but for terpene emissions, the range can be as high as 2-6"

Rev. 2. Page 4672, lines 21-28: "Analogously, for light dependence... …low light can have a large impact". This chapter is somewhat vague. Some quantitative information would make it stronger.

We agree that it needs to be substantiated and suggest to add the following statements " The value of the initial quantum yield for isoprene emission (ïĄą in Eq. 16) of 0.0027 mol mol-1 has been recommend to simulate isoprene emission across species (Guenther et al., 1993), but ïĄą varies in dependence on long-term light availability and can differ among the species (Harley et al., 1996, 1997). For instance, in broad-leaved temperate deciduous species Liquidambar styraciflua a value of ïĄą of 0.0017 mol mol-1 has been observed for upper canopy leaves and a value of 0.0040 mol mol-1 for lower canopy leaves. For measurements conducted at a quantum flux density of 300 ïA■mol m-2 s-1, the use of the general shape of the response curve with ïĄą fixed at 0.0027 mol mol-1 will result in 30% underestimation of ES for upper canopy leaves and 31% overestimation for lower canopy leaves. These extrapolation errors are ca. 20% if the

C2297

measurements are conducted at a light intensity of 500 ïA■mol m-2 s-1.”

“In addition, any error in the measurement of quantum flux density at relatively low light can have a significant impact on estimation of ES. For example, for this range of ïĄą values, a 10% error in quantum flux density measurement will result in ca. 5-40% error in ES estimations.”

Rev. 2. Page 4673, line 25 and 26: “...linear averaging...” are the authors referring to linear averaging of temperature and light or emission?

We suggest to specify as “linear averaging of emission rates and values of environmental drivers “

Rev. 2. Page 4674, lines 16: “The conventional approach to cope with this variability is to find average light, eQ, and temperature, e T... This will necessarily introduce integration errors” However, is one would calculate first the response functions f(Q) and f(T) and average these one would not introduce this error.

Yes, this could be possible in some cases when real-time sensor are used as stated below, but the other problem commonly is that both light and temperature vary simultaneously and so it is complicated to derive separate light and temperature response functions from measurements under non-controlled conditions.

Rev. 2. Page 4674, lines 26W29: “In the case of multiple estimates of E... ...then calculating the average”. One could also derive the Es by fitting E against f(Q)fs(T) or Fe(T).

We agree and we suggest to add the following statement “Correct ES values can also be obtained by fitting E against the product f(Q) fS(TL) (Eq. 15) or fS(TL) (Eq. 18).”

Rev. 2. Eq. (20): This equation is not correct if Q and T are measured with non-equal time steps.

Yes, we agree with this and suggest to add this equation and also the statement that

“When the measurements or E, Q and TL are conducted with equal time steps, Eq. 22 simplifies to” the equation reported in the previous draft.

Rev. 2. Page 4683, lines 7-9: “Although significant errors can result from the taxonomic approach/canopy scale emission factors derived from flux measurements.

At this point, we suggest to add the following sentence “In such species-rich floras, canopy-scale emission factors derived from flux measurements could be more practical for predictive purposes (Guenther et al., 2006) than trying to measure every single species.”

Rev. 2. Page 4683, lines 16-19: Taxonomy/allocation of resources for emission measurements: Whether one wants to do a few highly sophisticated emission measurements or a larger number of cruder measurements, which better covers the variability of the emissions.

We agree and suggest to add the following statement “This inherent variability raises the question of how best allocate the resources to describe the emission potential of a certain flora. In the case of complete lack of information of species emission capacity, a stepwise procedure is recommended, conducting first crude measurements to gain insight into the overall variability in emission potentials among the species, and then focusing on the emission controls in species identified as key emitters in the area.”

Rev. 2. Page 4643, lines 2-4: “...(Pape et al., 2009 for an example of a quantitative description of the modification of turbulent transport in an enclosure as compared to undisturbed ambient conditions).”

We suggest to reword it as “As an example of a quantitative description of the modification of turbulent transport in an enclosure as compared to undisturbed ambient conditions we refer to Pape et al. (2009)”

Rev. 2. Page 4656, line 29: “...sampling in field atmospheres with high humidity...” Poor use of language, needs revision.

We suggest to reword it as "sampling in the field where atmospheric humidity is often high can be particularly problematic"

Copolovici, L. O., and Niinemets, Ü.: Temperature dependencies of Henry's law constants and octanol/water partition coefficients for key plant volatile monoterpenoids, Chemosphere, 61, 1390-1400 doi:10.1016/j.chemosphere.2005.05.003 2005. Fall, R., and Monson, R. K.: Isoprene emission rate and intercellular isoprene concentration as influenced by stomatal distribution and conductance, Plant Physiol., 100, 987-992, 1992. Fall, R., Karl, T., Jordan, A., and Lindinger, W.: Biogenic C5 VOCs: release from leaves after freeze-thaw wounding and occurrence in air at a high mountain observatory, Atmos. Environ., 35, 3905-3916, 2001. Flexas, J., Díaz-Espejo, A., Berry, J. A., Cifre, J., Galmés, J., Kaldenhoff, R., Medrano, H., and Ribas-Carbó, M.: Analysis of leakage in IRGA's leaf chambers of open gas exchange systems: quantification and its effects in photosynthesis parameterization, J. Exp. Bot., 58, 1533-1543, 2007. Geron, C., Owen, S., Guenther, A., Greenberg, J., Karl, T., Rasmussen, R., Bai, J. H., Li, Q.-J., and Baker, B.: Volatile organic compounds from vegetation in southern Yunnan Province, China: emission rates and some potential regional implications, Atmos. Environ., 40, 1759-1773, 2006. Ghirardo, A., Koch, K., Taipale, R., Zimmer, I., Schnitzler, J. P., and Rinne, J.: Determination of de novo and pool emissions of terpenes from four common boreal/alpine trees by 13CO2 labelling and PTR-MS analysis, Plant Cell Environ., 33, 781-792, 2010. Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). Atmospheric Chemistry and Physics, 6, 3181-3210, 2006. Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses, J. Geophys. Res., 98, 12609-12617, 1993. Hakola, H., Rinne, J., and Laurila, T.: The hydrocarbon emission rates of tea-leafed willow (Salix phylicifolia), silver birch (Betula pendula) and European aspen (Populus tremula), Atmos. Environ., 32, 1825-1833, 1998. Harley, P., Guenther, A., and Zimmerman, P.: Effects of light, temperature and canopy position on net pho-

C2300

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C2301

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C2302