

The paper is well written and gives a good overview of the issue. Although it is a lengthy paper, the thoroughness of it justifies the length. I believe this will be a very useful paper for anyone conducting isoprenoid emission measurements. Thus I suggest publication after the authors have considered the following mostly minor comments.

#### General and scientific comments

In general there could be a table listing the error sources discussed in the text. The table could give an indication how important different error sources are.

Page 4642, Eq. (1): This equation describes the change of concentration in the chamber in the absence of any sources or sinks in the chamber. This should be explicitly stated. Also, the paper could be improved by presenting first the full mass balance equation of a chamber

$$V \frac{dc_{chamber}}{dt} = F(c_{in} - c_{out}) + S, \quad (R1)$$

where S is the source/sink term. This can be then be referred to when presenting e.g. equation (1) and special cases such as equations for dynamic and static chambers.

Page 4644 line 28 – page 4645, line 3: " First, at these high air flow rates, the BVOC detection limit will be poor, limiting measurement of low emissions. Second, 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, where the concentration is high, into the ambient air, with lower BVOC concentration..." The first and the second items seem a bit contradictory as in the first it is implicitly stated that the difference between ambient and atmospheric concentration is low whereas in the second it is required that the concentration difference is high. Also, has the effect mentioned in the second point been quantified? If so, some indication of the magnitude of this effect would be useful here.

Page 6445, lines 21-22: "To reduce the errors due to diffusion, chambers enclosing at least 6–8cm<sup>2</sup> leaf area are recommended". The recommendation seems somewhat arbitrary and not based on anything presented in the paper. Also, it would be better to give recommendations on chamber dimensions rather than how much leaf area can be fitted in the chamber.

Page 4647, line 27: "...certain Viton families..." Could you specify which ones. A table listing properties of materials could be useful here as it would make it easier for reader to get overall picture on the pros and cons of them.

Chapter 2.3: In this chapter the authors should comment on the use of adhesive tapes to attach films or tubes to supporting structures or to attach for example heating wires to tubes. The adhesives of the tapes can cause serious contamination as their volatile compounds can diffuse through the tube wall or film. This effect has been observed by many experimentalists, but they are rarely officially reported.

Page 4650, lines 22-23: “ $n$  is a function of the difference of the compound concentrations at the tube and chamber surface,  $C_s$ , and  $C_{out}$ .” This should probably read something like “difference between concentration in the chamber or tube air and chamber or tube surface”.

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.

Page 4659, line 18 – page 4660, line 4: Here the authors discuss the removal of ozone from chamber air. It should maybe be mentioned that there are mechanisms linking isoprenoid emission to ozone stress (Velikova et al., 2005), removal of ozone would cause changes in the isoprenoid emission of the enclosed branch.

Page 4663, lines 13-17: “To remedy the problems with high background concentrations... .. background air effect under particularly high ambient BVOC levels”. This paragraph is somewhat vague and problems of suggested methods are not discussed. E.g. charcoal filters do not necessarily remove all VOCs and synthetic air frequently has high concentrations of impurities.

Page 4664, Equation (1): Here the authors assume that the emission of VOCs is transported through stoma. However, it has been shown that for example the monoterpene emission from eucalyptus originates mostly from adaxial side with no stoma (Guenther et al., 1991). Also, in the paper by Niinemets et al., the insensitivity of isoprenoid emission to stomatal closure is explained by high volatility of these compounds. If I understand correctly the implicit idea behind equations (7) and (8) is that the transport route of isoprenoids would be lipid solution  $\rightarrow$  water solution  $\rightarrow$  intercellular air  $\rightarrow$  atmosphere. Has the transport route necessarily go through water or is it possible that the isoprenoids could evaporate directly from lipid solution to the intercellular air or even to the atmosphere not going through stoma?

Page 4665, Equation (9): It should be noted that this approximation is valid for relatively short closure times when chamber concentration of the studied compound is far from saturation. For longer closures and concentrations approaching saturation one should resolve the mass conservation equation leaving to exponential form.

Page 4665, lines 24-26: “A crude estimate of the suppression of emission rate due to BVOC buildup can be obtained by determining the within-leaf storage of the synthesized BVOC after enclosure of the foliage in the bag (Kirschbaum et al., 2007 for calculations)”. Another method is to monitor the non-linearity of the VOC concentration increase either by on-line monitor (e.g. FIS or PTR-MS) or by taking at least four air samples for off-line analysis.

Page 4668, lines 20-21: “The rate of transpiration scales exponentially with temperature...” While this statement is nearly correct in conditions far from saturation one should make clear that it is actually vapor pressure deficit that controls the evaporation. Thus the effect of evaporation of VOC emission calculation has a limit set by saturation vapor pressure in measurement conditions.

Chapter 4.1: Here the authors discuss the effect of algorithms used for normalization of measurements. Authors give the functional forms for isoprene and monoterpene emission originating directly from synthesis (Eqs. (15) and (16)) and monoterpene emission originating as evaporation from storage tissues (Eq. (17)). Here the temperature dependent response functions for synthesis and evaporative emission have same symbol ( $f(T_L)$ ) which may cause confusion. I would use e.g. subscripts to differentiate between the two functions (e.g.  $F_s$  and  $F_e$ ) A less experienced reader could benefit if formal emission equations were represented as well. I.e.

$$E = E_0 f(Q) f_s(T_L), \quad (R2)$$

for emission from synthesis and

$$E = E_0 f_e(T_L), \quad (R3)$$

for evaporative emission.

In this chapter the authors should also comment the usage of wrong response function for data normalization. E.g. Hakola et al. (1998) used temperature dependent algorithm describing evaporative emission (Eqs. (R3) and (17)) to normalize monoterpene emission from birch. It has since then been shown that monoterpene emission from birch originates from synthesis (Ghirardo et al., 2010) and one should use Eqs. (R2), (15) and (16). Beta values significantly higher than  $0.09 \text{ C}^{-1}$  for monoterpene emissions can be at least partly explained by the use of wrong response function.

Also a significant part of monoterpene emission from conifers can originate from synthesis (Shao et al., and Ghirardo et al. 2010). Thus one should maybe use hybrid algorithm for data normalization. The authors should comment on these issues in this chapter.

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

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.

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

Page 4674, lines 16: “The conventional approach to cope with this variability is to find average light,  $\bar{Q}$ , and temperature,  $\bar{T}$ ... 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.

Page 4674, lines 26-29: “In the case of multiple estimates of E... ..then calculating the average”. One could also derive the  $E_s$  by fitting E against  $f(Q)f_s(T)$  or  $F_e(T)$ .

Page 20, Eq. (20): This equation is not correct if Q and T are measured with non-equal time steps. Formally more correct would be

$$\bar{E} = \frac{E_s}{t_2 - t_1} \int_{t_1}^{t_2} f(Q)f_s(T)dt.$$

Page 4683, lines 7-9: “Although significant errors can result from the taxonomic approach, it is still used for species-rich floras such as Amazonian rainforests due to practical reasons (Harley et al., 2004)”. Even if it may be a bit outside the scope of this paper the authors could shortly comment here the possibility to use canopy scale emission factors derived from flux measurements.

Page 4683, lines 16-19: “Taxonomy is not a trivial point because different chemotypes have been observed even within a species (e.g., Niinemets et al., 2002a), and large variability in ES values can occur depending on species genetic origin (Staudt et al., 2004)”. This is very important point and it raises the question on the 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. The authors should comment on this.

#### Technical comments

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).” I personally find text placed in parentheses disturbing the flow of the text. If the sentence is really needed, why not formulate it in a way that it can be part of the text without parentheses. If it is not needed the sentence could be removed.

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

#### References

Ghirardo et al., 2010: Determination of de novo and pool emissions of terpenes from four common boreal/alpine trees by  $^{13}\text{C}$  labeling and PTR-MS analysis. *Plant, Cell & Environment*, 33, 781-792.

Guenther et al., 1991: Isoprene and monoterpene emission rate variability – observation with eucalyptus and emission rate algorithm development, *J. Geophys. Res.*, 96, 10799-10808.

Hakola et al., 1998: Hydrocarbon emission rates of tea-leaved willow (*Salix phylicifolia*), Silver birch (*Betula pendula*) and European aspen (*Populus tremula*). *Atmospheric Environment*, 32, 1825-1833.

Niinemets et al., 2004: Physiological and physicochemical controls on foliar volatile organic compound emissions. *Trends in Plant Science*, 9, 180-186.

Shao et al., 2001: Volatile organic compound emissions from Scots pine: Mechanisms and description by algorithms. *Journal of Geophysical Research*, 106, 20483-20491.

Velikova et al., 2005: Isoprene decreases the concentration of nitric oxide in leaves exposed to elevated ozone. *New Phytologist*, 166, 419-426.