

## ***Interactive comment on “Laboratory and field measurements of enantiomeric monoterpene emissions as a function of chemotype, light and temperature” by W. Song et al.***

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Received and published: 21 January 2014

The authors wish to thank the reviewer for his/her time, comments and suggestions. We have considered each point carefully and responded as detailed below. The changes made have improved the manuscript.

First, a general comment regarding the analysis of atmospheric enantiomer ratios: The footprint of atmospheric concentrations is much larger than the footprint of fluxes (e.g. Kljun et al., 2002). Thus the concentrations and the enantiomer ratios are affected by the emission profiles of not only the nearest few hundred meters, but even several kilometers. Furthermore, the variation of enantiomer ratios, e.g. that mentioned in page

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16821, lines 25–28, could be due to the different contributions of different tree species to the landscape scale emission during the day and night. For example, the monoterpene emission from birch species is fully from de novo origin, and thus there is no contribution from these species during the night, whereas the monoterpene emissions from pine and spruce mix the de novo and pool in different degrees (e.g. Ghirardo et al., 2010). Thus these species contribute also to night time emission in different degrees. If there are differences in the enantiomer ratios of emitted monoterpenes especially between de novo emitters and pool emitters this could be seen as a signal in the enantiomer ratios of atmospheric concentrations.

We thank the reviewer for these insightful comments concerning diel variations of enantiomeric ratios. Certainly this would hold true for large scale heterogeneous forests.

Some specific comments: Page 16807, lines 13–14: “... which are often more than 90 % of the total plant VOCs emission. . .” I wonder how general this statement is as many plant species emit considerable amounts of methanol and some also acetone (citations here). Also “... VOCs emission. . .” should be “... VOC emission. . .”

The reviewer is correct, for some species isoprene or monoterpene may be of the dominant species. In order to be more general and accurate, it has been changed as follows: Among BVOCs, isoprene (C<sub>5</sub>), and monoterpenes (C<sub>10</sub>), which are often more than 50% of the total global biogenic VOC emission (Guenther et al., 1995), deserve special attention because of their high volatility, reactivity in the atmosphere and their large fractional contribution.

Page 16808, lines 11–12: “. . . for monoterpenes the situation is less clear. . .” I wouldn’t put it this way but maybe “. . .for monoterpenes the situation is more complex. . .” The first expression conveys a message that we would have less understanding on the monoterpene emission, but at least I feel that this is not the message here but the fact that emissions can originate either directly from synthesis, from storage pools, or from both.

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It has been corrected as suggested.

Page 16808, lines 26-27: "There is increasing evidence that both pools, de-novo synthesis and storage pools, can coexist: : ." It is awkward to me to use term "synthesis pool" as the general idea is that there is no pool (i.e. storage) involved in the de-novo emission but this emission originates directly from emission. I would rewrite with something like "there is increasing evidence that de-novo emission and emission from storages can occur within the same plant and simultaneously, each one significantly contributing to the total emission." The term "synthesis pool" appears also elsewhere in the text, at least on page 16811. I would rewrite all these parts.

It has been corrected.

Page 16808, line 29-page 16809, line 1: "In that case the emission should show an intermediate behavior with respect to light and temperature responses." I would rather write something like "In that case the temperature and light responses of the emission is a combination of the de-novo and pool emissions".

It has been changed.

Page 16811, line 26: "gown" should be "grown".

It has been corrected.

In chapter 3.2 and Figure 4 the analysis of the light dependence of the emission of (+)- and (-)-alpha-pinene is presented. It is somewhat confusing to write about temperature-normalized emission in the text and in the figure caption. For many readers familiar with isoprene and monoterpene emissions will associate this with emissions normalized using the isoprene and monoterpene emission algorithms by Guenther et al. (1993) and wonder how there can be light dependence in normalized emission. So I suggest writing "emission normalized by dividing with emission at 800 micromol m<sup>-2</sup> s<sup>-2</sup>" instead of "normalized emission" (In page 16816, lines 23-24 and in the caption of Figure 4). Similar analysis for temperature dependence is presented

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in chapter 3.3 and Figure 6. Also here I suggest replacing "normalized emission" with "emission normalized by dividing with emission at 30°C".

We thank the reviewer for this helpful point. It has been changed as suggested.

Page 16817, lines 14-15, and elsewhere: "enantiomeric enrichment" I am not comfortable with this term, as it sounds like an enantiomer would be enriched in relation to some standard level. As this is not the case I would use some other term, e.g. "enantiomer fraction", e.g. "(-)-alpha-pinene fraction".

It has been changed.

Page 16817, line 28: "enantiomeric discrimination" Also I do not like this term as it sounds like there were a process that discriminates one enantiomer over the other in the similar manner as in the case of isotopes. As these terms borrowed from the use of isotopes may confuse the reader I would replace also this.

This is changed now to "enantiomeric signature".

Page 16820, lines 8-10: "individuals that were more enriched with (-)-enantiomers were found to be much more sensitive to temperature." Can you give a quantitative figure on how much more sensitive they were, e.g. by giving the beta values?

This was changed to Regarding *Pinus halepensis* and *Rosmarinus officinalis*, the (-)-enantiomer fraction of those individuals that are predominant with (-)-enantiomer were found to be either increase or decrease with temperature, and those with a preference of (+)-enantiomer showed a relative stable (-)-enantiomer fraction with temperature.

In the beginning of the chapter 4, Summary and conclusions, there is unnecessary repetition of the measurement methods. The first paragraph could be removed.

It has been done.

Page, 16823, lines 9-10: "The screening experiments of *Quercus ilex* emissions under standard conditions together with the results from the light and temperature responses

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showed that the compositional profile of its emissions is mainly genetically controlled." This is quite strong statement and I am not sure if this is "show" rather than "indicate". If the aim is to "show" the genetic control, one should better indicate the hypothesis, the testable outcomes of the hypothesis, and the possible alternative hypotheses and their testable outcomes.

"showed" is changed to "indicated".

In Figures 3-9 the labels and numbers in the axis are too small. Also in the Figures 4 and 6 the dots are too small.

All figures have been improved according to this suggestion.

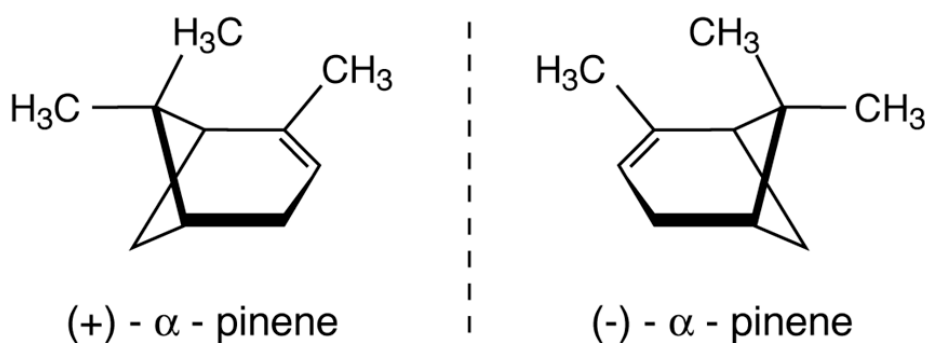
In Figure 8 the x-axis on the top panel should have the same range as is other two panels.

All panels are now in the same x-axis range.

References Kljun, N., Rotach, M.W., Schmid, H.P., 2002. A 3-D backward Lagrangian footprint model for a wide range of boundary layer stratifications. *Boundary-Layer Meteorology* 103, 205-226. Ghirardo, A., Koch, K., Taipale, R., Zimmer, I., Schnitzler, J.-P., Rinne, J., 2010. Determination of de novo and pool emissions of terpenes from four common boreal/alpine trees by  $^{13}\text{CO}_2$  labeling and PTR-MS analysis. *Plant, Cell & Environment*, 33, 781-792. doi: 10.1111/j.1365-3040.2009.02104.x

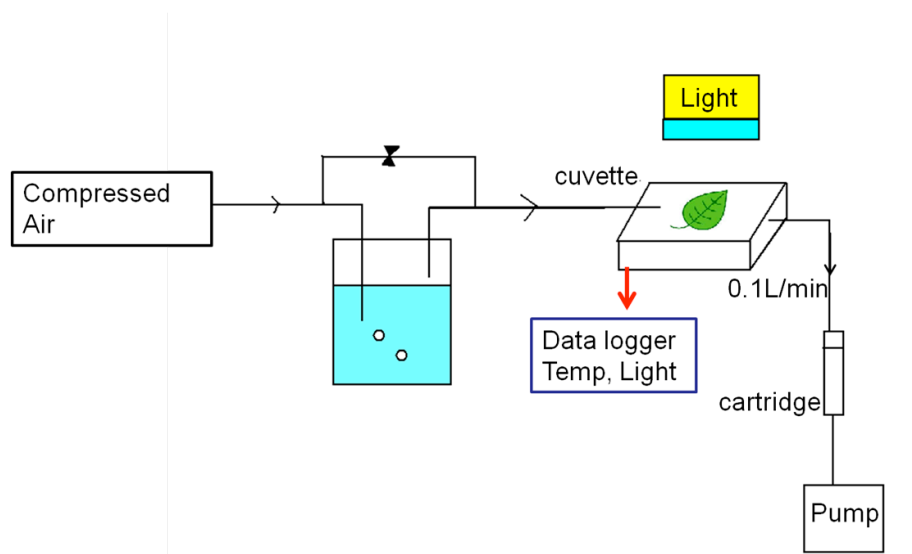
Interactive comment on Biogeosciences Discuss., 10, 16805, 2013.

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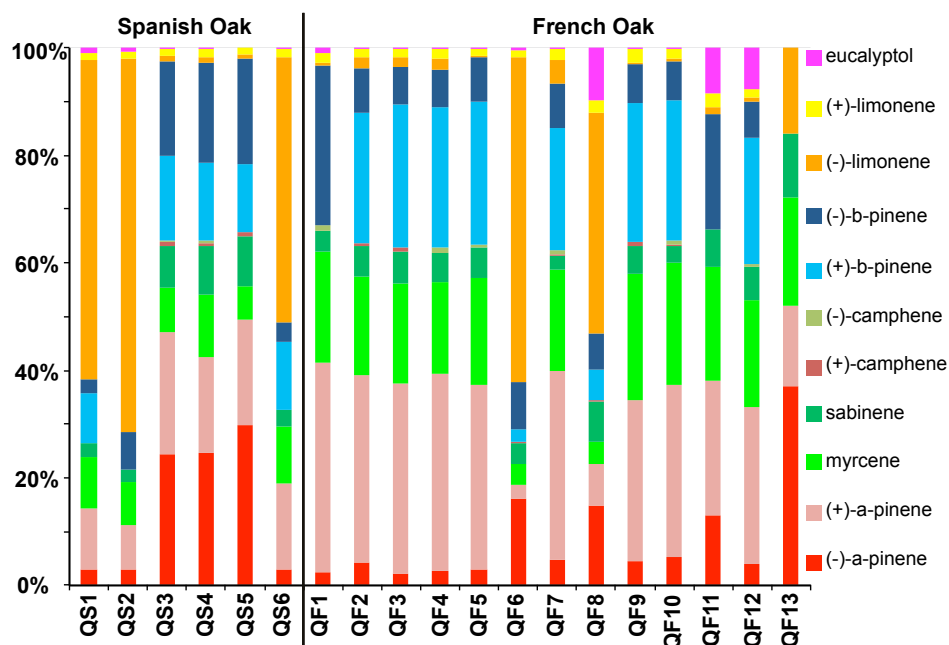
**Fig. 1.** Mirror image of α-pinene enantiomers.

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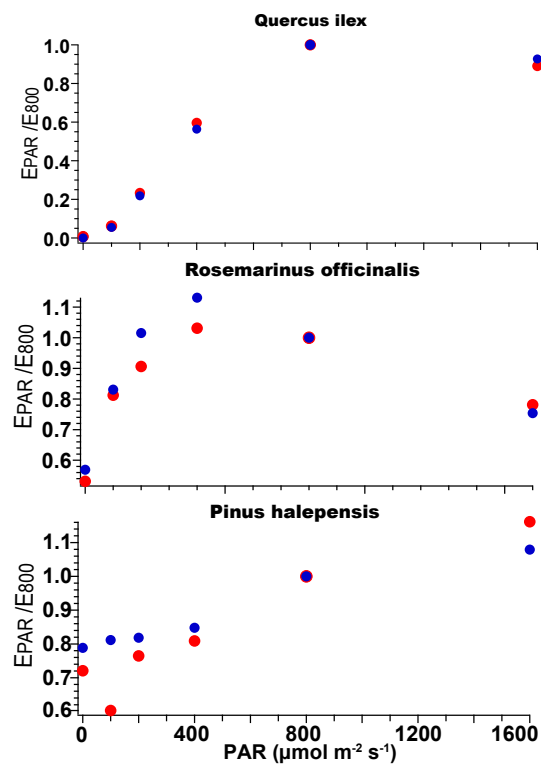
**Fig. 2.** A Schematic of the dynamic leaf enclosure cuvette set up.

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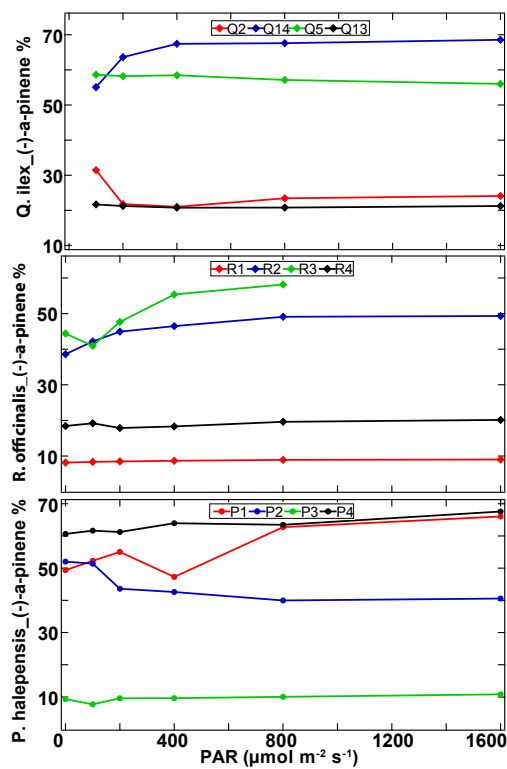
**Fig. 3.** Screening of *Quercus ilex* L. originally from different areas (Southern Spain and France) at standard conditions.

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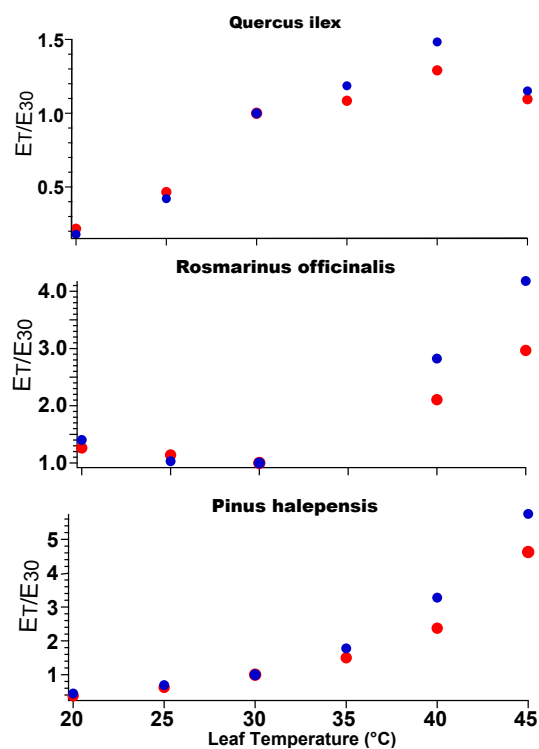
**Fig. 4.** An example of (-)/ (+)- $\alpha$ -pinene emission which was normalized by dividing with emission at 800  $\mu\text{mol m}^{-2} \text{s}^{-1}$  from three selected plant species in dependency with light (at 30°C).

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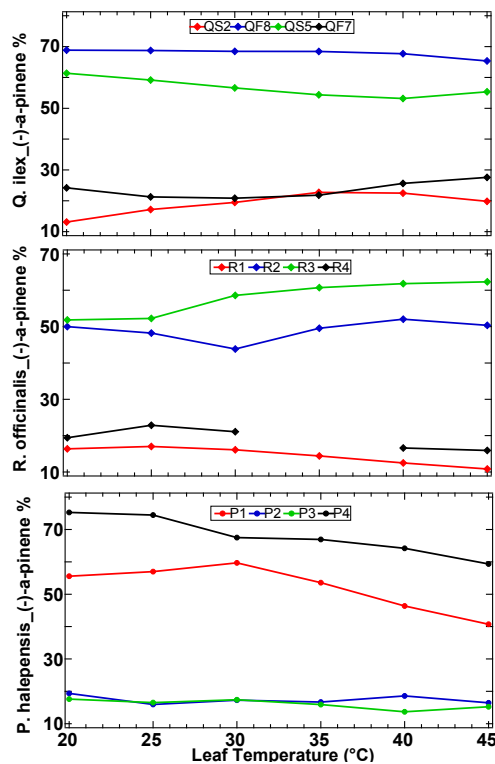
**Fig. 5.** Enantiomeric fraction of (-)- $\alpha$ -pinene of *Quercus.ilex*, *Rosmarinus officinalis* and *Pinus halepensis* as a function of light.

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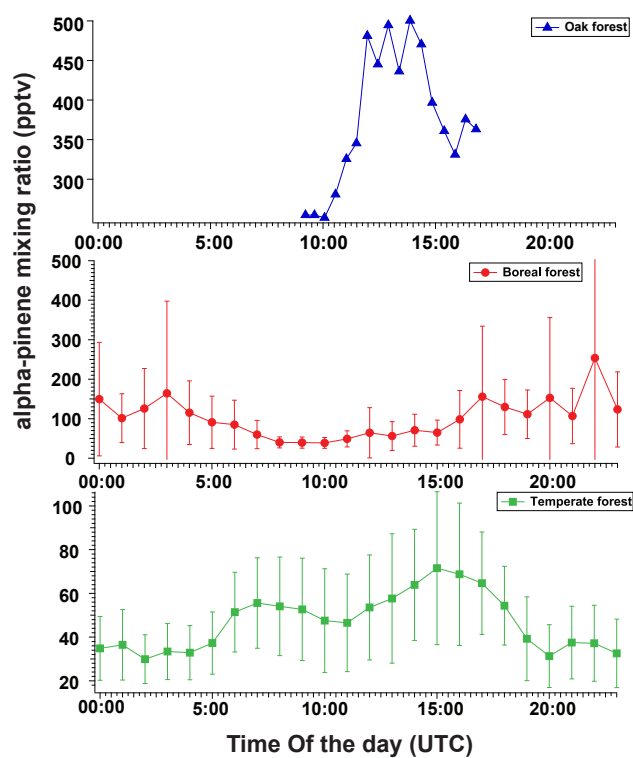
**Fig. 6.** An example of (-)/ (+)- $\alpha$ -pinene emission which was normalized by dividing with emission at 30°C from different plant species in dependency with temperature.

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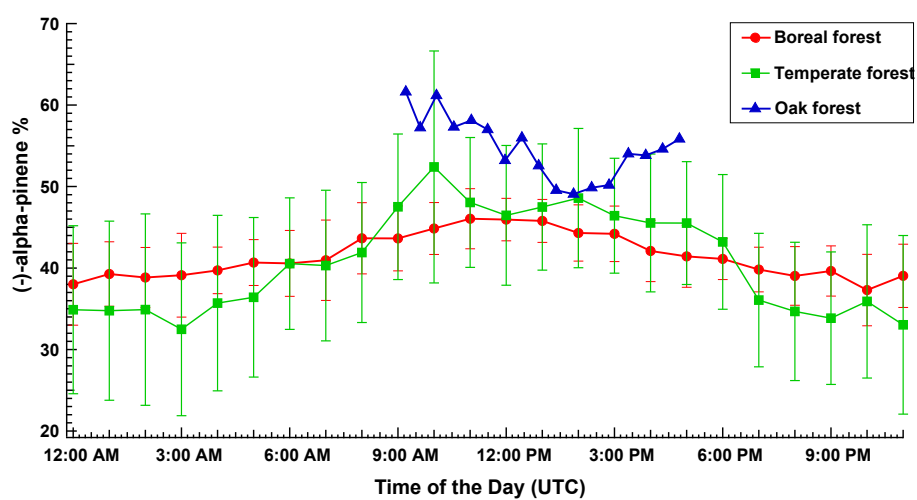
**Fig. 7.** Enantiomeric fraction of (-)- $\alpha$ -pinene in the emission of *Quercus.ilex*, *Rosmarinus officinalis* and *Pinus halepensis* as a function of temperature.

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**Fig. 8.** Diel cycle of  $\alpha$ -pinene mixing ratios during the measurement period. For boreal forest and temperate forest measurements, the marks represent the mean value of every hour,

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**Fig. 9.** Enantiomeric fraction of (-)- $\alpha$ -pinene over the *Quercus ilex* forest, boreal forest and temperate forest.

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