

Interactive comment on “Mirror image hydrocarbons from Tropical and Boreal forests” by J. Williams et al.

J. Williams et al.

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Reply to Gunnar Schade and Laurence Cool

We would like to thank Dr Schade and Prof. Cool for their insightful comments. We will now also thank them for their input in the acknowledgements of this paper. Our replies to both posted comments are combined below.

1) The aforementioned reviewers are correct to point out two peak labelling errors in Figure 3 - the peak of plus beta pinene is incorrectly annotated as 8 rather than 7 in the top panel of Figure 3. Furthermore, the labels for plus and minus limonene have been mistakenly swapped in the legend as is correctly suggested in the comment of Prof. Cool. Following this correction the elution order does correspond to that reported by Yassaa et al. 2001 and Yassaa and Williams 2005 from the analysis of enantiomerically

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pure standards. We would like to stress that this does not affect the discussion or conclusions presented here (which focus entirely on alpha pinene), but naturally the Figure has been amended for the ACP version of this paper. We are very grateful for the experienced eye of Prof. Cool here and regret any confusion caused. The mistake was in the annotation of the Figure 3 and not in the data itself. Regarding beta pinene, (also at the request of anonymous reviewer 2), we now briefly comment on the enantiomeric enhancement ratio of beta pinene in both environments. “Interestingly, although at much lower mixing ratios beta pinene exhibited the reverse enantiomeric discrimination, namely that (+)-beta pinene predominated over the rainforest.”

2) As suggested by Dr Schade we now include a sentence (also citing the three extra references mentioned) noting that the measured relative abundances are in accordance with previous data. We gladly include the observation that the plus alpha pinene dominated emissions can be attributed to the plant leaves and include the suggested references. This indeed tallies with separate SPME-cuvette experiments we performed on the leaves at the SMEAR II site and have reported elsewhere. (Paper under review at J. Chromatography). The added text is “The relative abundance of the monoterpenes over the Boreal forest is comparable to previous measurements (Komenda et al. 2003, Komenda and Koppmann 2000, Spirig et al. 2004) and the enantiomeric distribution similar to Scots Pine leaf tissue (Persson et al. 1993, Sjödin et al. 1996, Sjödin et al. 2000).”

3) Dr Schade’s suggestion that the large peak labeled as limonene is sabinene is not correct. Sabinene elutes much earlier on this column namely before camphene, carene and beta-pinene (see Yassaa 2001). The peak was identified unambiguously by pure standards and mass spectra, and the elution order corresponds to previous studies (e.g. Yassaa 2001). Sabinene was not measured at significant quantities over either ecosystem.

4) The region surrounding the SMEAR II measurement site is not, as suggested by Dr Schade, dominated by Norway Spruce but instead Scots Pine. This was noted in the

field by ourselves and has been reported previously by Keronen 2003 whom we now cite in the revised version.

5) We agree with Prof Cool and Dr Schade that the strong enantiomeric discrimination over the Boreal forest is likely because of the predomination of the Scots pine. This was implied in the paper already but is now made clearer through the addition of the sentence, “ The strong enantiomeric preference of (+) alpha pinene over the Boreal forest could be explained by the predominance of one tree species namely Scots Pine (*Pinus Sylvestris*). “ However, the surprising finding here is that in the much more bio-diverse Tropical rainforest such a clear enantiomeric preference is exhibited. Adopting the coin flipping analogy of Prof Cool one may expect with such a large number of species present that an even distribution of plus and minus emitters would result over the rainforest. We now also include the speculative explanation of Prof. Cool that by chance the stronger terpene emitters happen to emit more (-) alpha pinene than (+) alpha pinene, as an alternative to the presented hypothesis that light dependence of (-) alpha pinene emission drives the isoprene/(-)alpha pinene correlation. The new section of text now reads: “In contrast, the spatially and temporally more extensive ecosystem scale data presented here shows a clear enantiomeric predominance in ambient air, so what could be the underlying reason for the clear dominance of the (+)-form of alpha-pinene over the Boreal forest and the (-)-form in air over the rainforest? The Boreal forest consists of a limited number of species types, predominately Scots Pine (*Pinus Sylvestris*). Thus the dominance of (+)-alpha-pinene in Finland may simply reflect the emission pattern of the Scots pine. More difficult to elucidate is the enantiomeric preference exhibited by the very biodiverse rainforest. If the enantiomeric emission predominance of any given tree species is determined by chance one may expect a more or less even distribution of (+) and (-)-alpha-pinene emitters over a very heterogeneous ecosystem such as the rainforest. An alternative explanation to the light dependence of the (-)alpha-pinene presented in the preceding section would be that the strongest monoterpene emitters in the rainforest are by chance predominately (-)alpha-pinene emitters (Prof. L. Cool, Personal communication).”

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6) We agree wholeheartedly with Prof Cool that a global assessment of the enantiomeric distribution would be very interesting, and this is already clearly stated in the conclusion section.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 9583, 2006.

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