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Comment

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

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Posted below are several comments by Laurence Cool (larry.cool@sbcglobal.net), formerly at the UC Berkeley Forests Products Laboratory, Richmond, CA, where he worked with Professor Eugene Zavarin. Larry, who is now retired, is an expert in tree tissue terpenes and has carried out enantiomeric analyses for many years (see e.g. Cool, L.G. and E. Zavarin, 1992, Terpene variability of mainland *Pinus radiata*. *Biochemical Systematics and Ecology*. 20(2): p. 133-144). I am happy to post this on his behalf, and I am grateful to him for having stirred the discussion on this interesting topic. (Note that I have done some very minor editing to the text, which is otherwise a copy of an e-mail he sent to me)

In Fig. 3, peak 7 & 8 are identified as (-)- and (+)-beta-pinene, respectively. This

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agrees with Fig. 5 - Tropical, which shows only (+)-beta-pinene (corresponding to the Suriname chromatogram in Fig. 3). However, my experience with Cyclodex B is that (+)-beta-pinene precedes the (-) enantiomer, and in fact an earlier paper by Yassaa et al. (2001) shows the same order, i.e. (+) before (-). Since (+)-beta-pinene is quite rare in nature, I suspect that the Tropical analyses are actually (-)-beta-pinene. Similarly, (-)-limonene should precede (+) according to my experience (and again, according to Yassaa et al.), which would again reverse the enantiomer assignments in Fig. 3 and 5.

...

Regarding the chromatograms in Fig. 3, I am a little troubled by the variability in retention times. I understand that changing columns and/or re-setting the injector head pressure can shift the overall retention times like what is seen here. But the relative retention times should change very slightly, assuming the same temperature program was used. To me, the RRt's of peaks 6 and 8 in Hyttiälä versus Suriname look too different for the identifications to be correct in both chromatograms. An unrelated minor point: I was curious about the extra peaks in the standard chromatogram & would have liked to see them identified.

With regards to the basic question about the reason for enantiomeric distinction between the Tropical and Boreal samples: I agree with the paper's conclusion that it must be biological, not chemical. I also very much agree that "for future atmospheric chemistry, biological and ecological studies, the enantiomers of monoterpenes should be regarded and measured separately..." However, I would be tempted to say that the observed large-scale tropical/boreal difference in alpha-pinene enantiomer ratios is probably largely biologically meaningless. (Maybe that's what the authors meant by describing the presence of these compounds in the atmosphere as "background noise", p. 9591.) The biologically & ecologically significant differences in enantiomer ratios should be down at the individual species - or even individual tree-level. Thus, for example, a bark beetle will find a suitable host by "monitoring" the strength of a kairomone signal on a local level, ignoring the overall background levels of monoter-

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penes.

As to why the observed large-scale difference in atmospheric enantiomer ratios exists at all: the simplest explanation is that it is chance. So, for the Boreal sample area, where the forests consist of just a few dominant species, the chiral "coin" was flipped, say, 6 times and came up "heads" 4 times, so the (+) enantiomer won. No big surprise about that. It should be fairly easy to show that (+)-alpha-pinene predominates in foliage of enough of these trees to explain the atmospheric terpene data. (The foliar terpene composition data, including chiral, of some of these trees may have already been analyzed at some point & appeared in the literature.) For comparison, it would be interesting to look at boreal forest data from another part of the world, like N. America, where the tree species are different and where a different +/- ratio of alpha-pinene might be found.

It is harder to explain the (-)-alpha-pinene predominance in the Tropical area, which must consist of vastly more species. (If the chiral "coin" is flipped 300 times, why should "tails" come up 200 times??) However, since the foliar terpene compositions of all these tropical trees are largely or completely unknown, it may be that a relatively few species are high monoterpene emitters and that the Tropical case is similar to the Boreal one - chance dominance of the compound ratios by a few tree species.

The possibility that there are just a few dominant tropical monoterpene emitters might provide an alternative explanation of the very interesting correlation between (-)-alpha-pinene and isoprene. ... Meaning, the isoprene/(-)-alpha-P correlation may be due to presence of one or two high-isoprene/high-(-)-alpha-P emitters, rather than to light dependence of (-)-alpha-P emission. ...

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

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