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Atmospheric
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Interactive comment on "Record high peaks in PCB concentrations in the Arctic atmosphere due to long-range transport of biomass burning emissions" *by* S. Eckhardt et al.

S. Eckhardt

sec@nilu.no

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We thank R. Lohmann for his positive review of our paper.

Page 6231, lines 9/10 - 'Finally, a fractionation of a PCB mixture on a regional/global scale are both predicted and observed' - this is not fully accurate - most studies over the open Ocean do not reflect this (e.g., Jaward et al., 2004); further even the soil studies only observed fractionation in the northernmost samples, but not below 60 N (Meijer et al., 2003).

Yes you are right, we corrected our statement about global fractionation that it reads as following: Furthermore, fractionation of a PCB mixture on a global scale has been pre-

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dicted (Wania and Mackay, 1993) and indeed observed in some studies (e.g. Agrell et al. 1999; Gioia et al., 2006), but not all (e.g. Jaward et al. 2004). For example, a study of PCBs in global surface soils observed fractionation only in the northernmost subset of samples (Meijer et al. 2003). Still, differences in key physical-chemical properties among the PCBs (Li et al., 2003) are recognised among the key factors that dictate LRAT behaviour (e.g. Beyer et al., 2003).

new reference: Jaward FM, Barber JL, Booij K, Dachs J, Lohmann R, Jones KC, 2004. Evidence for dynamic air-water coupling and cycling of persistent organic pollutants over the open Atlantic ocean. Environ. Sci. Technol. 38: 2617-2625.

Page 6236: The authors used a 20 day retroplume, yet the air took only 4-5 days to reach the Arctic. Why was a 20 day retroplume warranted?

A 20-days backward calculation was used by default, as it is our standard set-up for these types of calculations. In a case like ours, with a strong source contribution only a few days back, sources further back in time become negligible. Therefore, the source contributions would have been almost exactly the same when using only a, say, 5-day duration for the backward calculation. Also, extending the calculation even further back in time to 30 days or more would not have increased the source contributions noticeably. In summary, our results are not sensitive to the duration of the backward calculation.

Page 6240 Low OH-radical concentrations are claimed for the Arctic atmosphere. But what about depletion reactions en route? After all, the authors suggest that PCBs have traveled for 3-4 days before reaching the northern site.Both fire episodes were in or close to the Arctic summer - what effect would have OH-radical degradation have had on the composition of the PCBs during transport?

Indeed, the reaction with OH is an important removal factor, especially for less chlorinated congener. For the transport episode in spring 2006 we estimated an e-folding lifetime of PCB 52 of around 154 days. (with average OH concentration typically for this region and season of 2.2E5 mol/cm^3, transport height 1.5km, -10 degrees). Assuming OH as the only removal mechanism after 3 days of transport still 98% should be in the atmosphere. During July the lifetime would be 40 days, which would give 60% of the mass of PCB 52 after 20 days. (OH concentration: 1.1E6 mol/cm^3, transport height 4km, temperature -20 degree). (calculation based on Wania and Daly, 2002) We added a paragraph with the calculation of the lifetime.

Page 6236, line 24 - how realistic is it to have a transport time of 3-4 week, but still being able to detect enhanced PCBs in the atmosphere from the original source?

Other substances, such as carbon monoxide and black carbon aerosols, showed enhancements, too (Stohl et al., 2004). PCBs have a longer lifetime in the atmosphere than CO or aerosols and, thus, it is not so surprising that enhancements can still be seen after 3-4 weeks of transport. It just means that the source was strong enough to yield observable enhancements over the "background", even after accounting for dilution, which was significant for this case. But this was the case for carbon monoxide and black carbon aerosols, so why not for the longer-lived PCBs?

Page 6237, lines 18 ff - The authors considered all other PCB measurements as background - how can they be sure that some of these measurements were not affected by long-range transport from biomass burning?

Well, admittedly an influence of biomass burning on other episodes cannot be excluded. However, biomass burning is highly episodic and, therefore, it is not very likely that a large fraction of the data were strongly affected by biomass burning. But even if some of the other data were influenced by biomass burning, this would only lower our reference background and would make the two reported episodes even more important. It would also increase our estimated emission strengths. However, since the two episodes were so extreme and enhancements over the background so large, the results are not strongly sensitive to the assumed background.

Page 6240 - how do the PCB profiles in the Arctic air compare to measured emissions *from wood/biomass burning? How certain can we be that this is really volatilization and not production (e.g., Lee et al., 2006).*

It is difficult to compare the emission profile with the profile at Zeppelin mountain, because we cannot estimate the exact removal of the specific congeners. What we see is, that in 2004 a great amount of the heavier congener is removed, this is due to the wet and dry deposition occurring during the 3-4 weeks of transport. Comparing the fire influenced period and mean condition we find that the relation between the single congeners does not vary so much, as it reflects the general pattern of atmospheric concentrations with a maximum in the less chlorinated congeners and a minimum in the higher chlorinated ones.

To be able to exclude formation of PCBs during the burning, specific experiments would be needed. An indication, that it is volatilization could be the fact, that also substances such as DDT were enhanced during the fire-influenced periods, which cannot be formed during the burning. We added a comment at li 25 page 6240, that there could be a possibility of new formation during the biomass burning.

Page 6241 - shouldn't this EF be better called a volatilization factor?

We have chosen the term emission factor because our method to calculate it was very similar to the methods used in studies done for other species (i.e., rationing versus a reference biomass burning product; CO, in our case). In our case, for PCBs, revolatilization may also have been important (or even dominant). However, with the available data, we cannot distinguish between emissions from the fire or revolatilization from heated soil. Therefore, we will keep the nomenclature but will insert a remark saying that the term "emission factor" is not used in a strict sense and does include revolatilization.

We performed the technical corrections: we substituted mid-latitudes with middle latitudes and quite strongly enhanced with substantially enhanced.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 6229, 2007.

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