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Comment

Interactive comment on “Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and chlorinated pesticides in background air in central Europe – investigating parameters affecting wet scavenging of polycyclic aromatic hydrocarbons” by P. Shahpoury et al.

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We appreciate the constructive comments made by the reviewer.

1] Reviewer’s comment: Page 26945/L13-14. Some of the pesticides analyzed are not as resistant to acid treatment as PCBs, for example DDTs or HCHs. Did you check that no degradation occurred due to acid treatment in the fractionation step?

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Author's response: The analytical method performance was tested prior to sample analysis. No degradation of target PCBs/OCPs due to acid treatment was detected during the fractionation steps. The following sentence will be added to the manuscript in order to address the reviewer's comment:

Page 26945, line 14: "...acid modified silica column for PCBs and CPs. The method performance was tested prior to sample analysis and no degradation of target analytes due to acid treatment was detected."

2] Reviewer's comment: Which are the recoveries from the fractionation step? Further in this comment, it is stated that recovery standards were used however no recovery results is provided at all. This data must be reported to understand the method performance. Are results corrected by method recoveries?

Author's response: We determined the compound recoveries for the entire analytical method and not for the fractionation step alone. The following sentences will be added to the manuscript in order to address the reviewer's comment:

Page 26946, line 14: "The analytical method recoveries for PCBs/CPs and PAHs ranged from 88 to 100% and 72 to 102%, respectively. The measured analyte concentrations were not recovery corrected."

3] Reviewer's comment: Page 26949/L1-4. The concentrations you reported (GAS: 0.6 -140 ng/m³ and PART: 0.1 – 190 ng/m³) do not seem to me "by far lower" than those reported by Holoubek et al (GAS: 0.4 – 208 ng/m³ and PART: 0.1 – 360 ng/m³). I would rather say that values are slightly lower. Alternatively, you can try to prove that there are statistically significant differences.

Author's response: As suggested by the reviewer, the sentence will be changed to "...but are slightly lower than those reported by Holoubek et al. (2007)..." (page 26949, lines 1-2)

4] Reviewer's comment: Page 26951/52 Ls27-28, 1-2. Couldn't be the Henry's law con-

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starts corrected by the temperature at various heights from the cloud to the ground?
Is this information available at all?

Author's response: There is no direct way to determine the gas scavenging ratios at higher altitudes through the air column. This has not been done in the past but could be the subject of a future research. Extrapolation of gas scavenging ratios based on the ground temperature and lapse rate would introduce an unknown degree of inaccuracy, which is why this approach was avoided in the present study. This is clearly explained in the manuscript (please see page 26951, line 21 – page 26952, line 8).

No changes to the manuscript.

5] Reviewer's comment: Page 26953 Ls1-3. It would have been interesting to analyze the PCB in the rain particle phase which was also collected by the precipitation sampler. Concentrations of PCBs in rainwater were below LODs most probably because only the water dissolved phase was analyzed, since the particle phase was removed due to filtration in C18 columns. Maybe relevant for higher MW PCB (e.g. 118, 138, 153 and 180)?

Author's response: The reviewer's comment is very interesting. However, this is unlikely to be the case in our study - we found a number of PAHs (e.g. BAA, CHR, BAP, IPY, BPE - log Kow 5.76 – 6.70), which mainly partition into particulate phase of the two-phase rainwater, as shown by a preceding study (Skrdlikova et al., 2011). Hence, these compounds were efficiently eluted from C18 Speedisks in our study. We think that PCBs were not detected/present in rainwater because they were mainly present in the gas phase in the atmosphere and gas scavenging is less efficient, as we have explained in the manuscript.

No changes to the manuscript

6] Reviewer's comment: P26954/Ls5-25. The discussion on the influence of PM ionic species on the scavenging of SOC is not clear to me. The sorption of SOC to PM (OC,

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EC fractions) is mostly driven by hydrophobic interactions and not ionic binding. How (mechanistically speaking) ionic species may increase the sorption of SOCs (nonionic compounds) to PM and therefore the scavenging ratios?

Author's response: We understand that the current statement is unclear and could mislead the reader. Hence, the statement "This observation could suggest that PAH scavenging by rain is more efficient in conditions where PM and rainwater contain high quantities of ionic species" (page 26954, lines 6–8) will be changed to:

"This observation suggests that PM removal by rain, and consequently wet scavenging of PAHs that are sorbed to PM, is enhanced in conditions where PM contains high quantities of soluble species. This argument is supported by considerably higher scavenging ratios found for particulate PAHs (a factor of 50 on average) in the former event. This difference was much smaller for gaseous species (a factor of five on average)."

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 26939, 2014.

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