

## *Responses to Reviewers' Comments*

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**Manuscript Title:** Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and chlorinated pesticides in background air in central Europe - investigating parameters affecting wet scavenging of polycyclic aromatic hydrocarbons

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We appreciate the constructive comments made by the reviewers. We have carefully considered all the comments and addressed them point by point. All the changes have been highlighted in yellow in the original manuscript. The line numbers mentioned in our responses to the comments refer to those in the submitted manuscript (please see attached).

### **Reviewer 1**

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?

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 has been added to the manuscript in order to address the reviewer's comment:

Lines 134-135: "*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 have been added to the manuscript in order to address the reviewer's comment:

Lines 159- 161: "The analytical method recoveries for PAHs and PCBs/CPs ranged from 72 to 102% and 88 to 100%, 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/m<sup>3</sup> and PART: 0.1 – 190 ng/m<sup>3</sup>) do not seem to me “by far lower” than those reported by Holoubek et al (GAS: 0.4 – 208 ng/m<sup>3</sup> and PART: 0.1 – 360 ng/m<sup>3</sup>). 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 has been changed to “...but are slightly lower than those reported by Holoubek et al. (2007)...” (Line 219).

4] Reviewer's comment: Page 26951/52 Ls27-28, 1-2. Couldn't be the Henry's law constants 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 lines 291-305).

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  $K_{ow}$  5.76 – 6.70), which mainly partition into particulate phase of the two-phase rainwater (as shown by a preceding study (Škrdlíková 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.

*Reference:* Škrdlíková, L., Landlová, L., Klánová, J., and Lammel, G.: Wet deposition and scavenging efficiency of gaseous and particulate phase polycyclic aromatic compounds at a central European suburban site, *Atmos. Environ.*, 45, 4305-4312, 2011.

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, 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*" has been changed to:

Lines 354-359: "*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).*"

In addition, the related statements in the abstract and conclusions were changed as follows:

Lines 26-27: "*The particulate matter removal by rain, and consequently PAH wet scavenging, was more effective when the concentrations of ionic species were high.*"

Lines 403-405: "*The results suggested that PM removal by rain, and consequently wet scavenging of PAHs sorbed to PM, could be more efficient in cases where the concentrations of ionic species in PM are high.*"

### **Reviewer 3**

1] Referee comment: The manuscript reports detailed results of wet deposition fluxes related to some semi-volatile organic compounds including PAHs and chlorines. Sampling, analyzing and reporting of deposition research involve labor and tiresome studies. Therefore this version of the manuscript can be accepted for publication.

Author response: We appreciate the positive comments made by the reviewer.

No changes to the manuscript have been suggested.