Review of the manuscript No. acp-2014-419

The manuscript presents scavenging efficiencies for a number of parent PAHs, alkylated PAHs and DBTs. The scavenging efficiencies were compared with those reported by previous studies. In addition, the authors investigated the effect of snow vs. rain on analyte gas and particle scavenging processes.

General Comments:

Introduction: The introduction is long and rather repetitive. Good background information about PAH toxic effects are provided; however, the authors do not really need to convince readers that PAHs are carcinogenic. This study is not about carcinogenicity of PAHs but the processes involved in their removal from the atmosphere. The introduction lacks a short description of these processes. In addition, authors need to provide more information about alkylated PAHs and DBTs. Why these were selected and why it is important to study them? Were they detected in any previous studies conducted at similar locations?
The authors need to narrow down the introduction in a better way, define their objectives more clearly, and highlight the novelty of the work? How this study is going to contribute to the existing knowledge about SOC wet scavenging? Perhaps they need to put more emphasis on the alkylated analytes that they studied because, as far as I can see, that is the main novel contribution.

Methods: The authors need to include a table containing meteorological data related to their sampling sites. This is a standard practice when presenting environmental data. This is particularly important for this manuscript because of the unusual sampling method applied - i.e. averaging PAC air concentrations from each set of five samples (air sampling once every 6 days) and relating them to PAC concentrations in monthly rainwater samples. Were the air samples related to rain events in those specific months? In another word, did the authors consider if they had rainfall after collecting the air samples? If so, this information should be provided in a table. Otherwise, how did they verify if PAC concentrations in rainwater were related to those in air samples? Change in air mass over the sites is expected in cases where there is a gap between the end of air sampling and start of rainfall. The authors need to provide the relevant information.

Results and discussion: More stress should be put on alkylated analytes - do their scavenging ratios relate to the degree of alkylation or their physical-chemical properties? I see some interesting trends in the reported ratios for the individual analytes, which have not been discussed in the manuscript.

Specific comments:

Abstract

P. 1, Line 5: Please avoid using the term "washout", unless you are referring specifically to "below-cloud scavenging". See the following article for details: Cousins, I. T., Beck, A. J., and Jones, K. C.: A review of the processes involved in the exchange of semi-volatile organic compounds (SVOC) across the air–soil interface, Sci. Total Environ., 228, 5-24, 1999.

1 Introduction

P. 1, Line 5-6: "*The number of rings and the molecular weight of the PACs affect their physical and chemical properties,*"

The physical-chemical properties of an organic compound are determined by its molecular structure and not necessarily by "molecular weight". Please revise the sentence.

P. 2, Line 17: "benzo(a)pyrene"

For PAH congener names, the letter/s in brackets should be italicized. Please revise throughout the text.

P. 3, line 6-11: "*However, wet deposition was only collected for a two-year period at three of the 17 sites, and the spatial coverage is not enough for mapping wet deposition. The scavenging (or washout) ratio (Wt) parameter, defined as the ratio of the concentration of a chemical species in precipitation to that in air, is an alternative means of estimating the wet deposition amount when only surface air concentration is monitored.*"

This statement needs to be revised. What authors are exactly trying to say here? Are they implying that they intend to determine the analyte scavenging ratios for a limited number of sites (i.e. three) so that they can estimate analyte concentrations in precipitation at sites for which precipitation samples were not collected? If so, this approach would be limited to compounds that are mainly present in gas phase, as they used passive air sampling for the sites with no precipitation samples.

If this is a general reference to the possible applications of scavenging ratios, then the approach is limited by the potential variability in parameter controlling SOC scavenging, such as aerosol and rainwater chemical and physical properties related to the sampled air mass, which could be different spatially. In any case, the statement needs to be revised and the limitations of the suggested approach should be highlighted.

In addition, "*is not enough for mapping wet deposition."* Or "*estimating the wet deposition amount*"

What wet deposition? Please be specific.

"The scavenging (or washout) ratio (Wt) parameter,"

Please remove the word *washout* as well as *parameter* – use only scavenging ratio.

P. 4, line 18-21: "*Therefore in the absence of wet deposition measurements, the wet deposition can be estimated based on other scavenging ratio values of similar particle sizes (Galloway et al., 1993). To date, knowledge of precipitation scavenging of PACs is still very limited.*"

Redundant, authors did mention this before in the introduction (see my comment above) – why repeating? Most importantly, are they discussing particle size distribution or any other physical-chemical properties of aerosols in their study? Without this data, how the scavenging ratios determined by this study are going to be used in the future to determine analyte concentrations in precipitation? Did authors have access to this data? If so, this should have been included in the manuscript in order to improve comparability of the data for future applications. Otherwise, no such claim can be made for the use of scavenging ratios.

2 Methods

2.1.2 Sampling procedures

P. 2: Please mention how often the field blanks were collected and what procedure was followed.

2.1.3 Analysis procedure (better to say analytical procedures)

P. 1, line 3: "*d8-dibenzothiophene*"

The correct form is d_8-dibenzothiophene. Please revise throughout the text.

P. 1, line 4: "*deuterated PAH surrogates*"

Please specify the names of the individual PAH surrogates.

P. 1, line 6: "*The aqueous phase is re-extracted with DCM*"

What do authors mean by aqueous phase?

P.1, line 9-10: "*the GFFs and PUF plugs were spiked with a solution containing PAH and DBT surrogates. The GFFs and PUF plugs samples are then…*"

Why abbreviating dibenzothiophene if the abbreviation was going to be used once throughout the text? In any case, every abbreviation needs to be defined the first time used, which is not the case with DBT.

"*The GFFs and PUF plugs samples…*"

Please change to GFF and PUF samples…

P. 2. Is there any reference for the applied analytical method/s? If so, that needs to be mentioned in the text. It might be interesting for readers to know what the PAH recoveries were when eluted from silica column with benzene (considering that the same solvent was used to complete the elution of alkanes in the previous step!!). Readers could access this information if a proper reference is provided.

What were the LOQs for this method? Authors need to mention these values - this is a standard practice.

P. 2, line 17-18: "*Sample measurements with surrogate recoveries from 50–150% were corrected for surrogate recoveries.*"

Please re-phrase this sentence – it is confusing. Does this imply that other samples were excluded from data analysis? If so, that should be mentioned. This falls under quality control criteria - I suggest the authors to put all QC related information under a separate section.

2.2. Data analysis

P. 1, line 4: "… ($W = C_{prec}/C_{air}$)."

There is no need to mention this here because it is discussed later in the same section. Please try to avoid repetition.

P. 2, line 4: "*Air samples collected approximately every 6 days were averaged to correspond with the monthly precipitation samples collected between 30 April 2011 and 30 August 2012.*"

This is not a two-year period, as claimed in the introduction - please clarify.

P. 2, line 13: "*Wt includes both the **gas** and particulate phase concentrations in precipitation and in air*"

Dissolved phase is the correct form when used for precipitation.

P. 2, line 15: "*and PAC particulate fraction in air (') are known.*"

PAC particulate mass fraction is the correct form.

P. 3, line 5: "… *and PAC air concentrations below MDL as discussed above.*"

There is no need to repeat this - you mentioned it once before!

P. 4, line 1: *"Using the particulate PAC fractions in air measured at the AMS5 site, the PACs were categorized into predominantly gas-phase (i.e. > 0.7 gas fraction) and particulate phase (> 0.7 particle fraction) PACs in order to analyze differences in the precipitation scavenging of gases and particles.*"

Particulate mass fraction is a temperature-dependent parameter (apart from other factors that affect analyte gas-particle partitioning, such as aerosol chemical properties). What were the ambient temperature ranges across these three sites? The readers deserve to know how comparable these sites were. The authors should make a comment about potential uncertainties, which could arise as a result of extending the particulate mass fractions, determined for AMS5, to the other two sites. In addition, median values for particulate mass fraction should be listed for all PACs in one of the tables.

P. 4, line 4: "*There were 18 gas-phase PACs of lower molecular weight and 15 particulate-phase PACs of higher molecular weight.*"

Please specify what the cut-off was for the low and high molecular mass PACs. Besides, the compounds that were not dominant in gas- or particulate-phase need to be listed in the text.

3 Results and discussion

Please be consistent with the number of decimal places when reporting analyte concentrations.

Analyte groups (e.g. C1 phenanthrene/anthracene, etc.) need to be defined either in the text or table captions. Authors should explain why these are reported as groups and not individually – e.g. limitations in current analytical methods/co-eluted peaks in chromatograms??

Since there are many co-eluted compounds on the list, it makes more sense to report the concentrations as sums (i.e. sum PAHs, sum C-PAHs, sum DBTs) and only highlight those compounds that stand out because, for instance, they showed high concentrations, detection frequencies, or contribution to the sums. This would help readers to follow the sentences more easily and reduces the congestion of information, which authors are trying to get across. I also suggest using either median or mean values when describing analyte concentrations in the text.

The sentences like "*Median air concentrations at AMS5, AMS11, and AMS13 were 0.02–14.6 ngm−3, 0.03–16.9 ngm−3, and 0.01–7.7 ngm−3, respectively.*" should be avoided. What median air concentrations? Please be specific. The authors should not expect readers to guess what the sentence is trying to say! Where the readers are supposed to look for this data? I cannot see them anywhere in the tables!!

Similarly, "*Median precipitation concentrations for parent PAHs ranged from 0.3–184.9 (chrysene) ng L−1 and air concentrations ranged from 0.01–3.9 (naphthalene) ngm−3 at the three sites, which were lower than the concentration ranges that included the alkylated PAHs and dibenzothiophenes.*"

Are these presenting concentrations for the sums or individual analytes? What are you implying by "*from 0.3–184.9 (chrysene)"* or "*0.01–3.9 (naphthalene)"*. Such sentences are ambiguous and should be re-phrased. Authors could do a better job in describing the data.

3.2 Comparison of gas-phase dominant and particulate-phase dominant PACs by snow scavenging

Wouldn't it be more informative if the title is changed to snow scavenging of gas-phase and particulate-phase dominant PACs or something along this line? I suggest the same change for 3.3.

The biggest problem that I see with this manuscript is the way the results and discussion sections are organized, particularly section 3.2, 3.3, 3.4, and 3.5. These sections appear to be repetitive. I suggest reorganizing these sections in such way to have three sections, instead. First, discuss snow scavenging of gas- and particulate-phase PACs. Second, rain scavenging of gas- and particulate-phase PACs, and third compare PAC snow vs. rain scavenging processes.

In-depth review of the results and discussion can only be done after the above-mentioned sections are re-organized.