

Response to Reviewer #2

We greatly appreciate all of the comments, which have improved the paper. Our point-by-point responses are detailed below.

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.

Response: We totally agree with this comment. The introduction in the revised paper will be more concise, focus more on the wet scavenging processes for PACs, and explain the novel contribution of this study. The objective of this study is to compare wet scavenging of PACs at the oil sands sites to other locations using scavenging ratios and to examine differences between snow and rain scavenging and between gas phase and particulate phase scavenging, since this makes up the majority of the results in sections 3.1-3.5. Previous studies have estimated PAH wet deposition in the Athabasca oil sands region in order to assess the impacts of the oil sands industry. Compared to these studies, the novel contribution of our study is the emphasis on how different species of PACs and precipitation types could affect the wet deposition of PACs in the Athabasca oil sands region. The relative efficiency of snow versus rain scavenging of aerosol particles is also emphasized to support hypothesis provided in several of our earlier studies on the topic of aerosol scavenging by precipitation (Wang et al., 2010, 2014; Zhang et al., 2014). The alkylated PAHs and DBTs measurements are also important to the Athabasca oil sands region because these pollutants are emitted from petroleum and wood combustion sources and were used to identify natural and anthropogenic sources contributing to PAHs in the Athabasca oil sands region lakes (Jautzy et al., 2013, *Environ. Sci. Technol.*; Kurek et al., 2013, *PNAS*). The revised paper will incorporate the scavenging ratio results for alkylated PAHs and DBTs because the scavenging ratios for these analytes are rarely reported in literature and would add to the existing knowledge of PAC scavenging.

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.

Response: We understand this reviewer's concern. We agree that one particular precipitation sample might not be associated with one or more air samples collected before the rain event. However, we believe that the total PAC amounts in precipitation in any given month should be associated with monthly average air concentrations. Ideally, monthly average concentrations should be obtained from daily data of all the days in a month. Due to the extensive cost of high-volume sampling, only data for one in every six days are collected. The uncertainties using this averaging approach should not be larger than uncertainties caused by other sources (e.g., from measurement instruments and laboratory analysis). The revised paper will include tables containing the monthly precipitation concentrations, monthly average air concentrations (based on 4-5 air measurements), and meteorological data corresponding to each monthly sample (average air temperature and total precipitation). However, we do not have information to link individual precipitation samples to individual air samples (note that the study did not determine scavenging ratios from individual precipitation events because the short time scale of each precipitation event can lead to large variability in the scavenging ratios (Barrie, 1985; Galloway et al., 1993). In our study, the median and mean scavenging ratios shown in Table 2 are based on the monthly scavenging ratios averaged over the snowfall and rainfall periods (about 5-7 months) and should have smaller variability. More explanations will be added to the revised paper to explain the rationale for averaging the six day air concentrations over the month when precipitation was collected.

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.

Response: The scavenging ratio results for alkylated PAHs and DBTs were not emphasized in the ACPD paper because they were rarely reported in literature. To improve the novelty of the study, the revised paper will include a discussion on how the scavenging ratios vary with the degree of alkylation and physical-chemical properties.

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.

Response: The word "washout" will be deleted. The scavenging ratio accounts for in-cloud and below-cloud scavenging. The reference will be added in the Introduction.

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.

Response: The sentence will be revised to, “The chemical and physical properties, such as vapor pressure and water solubility, as well as the bioaccumulation potential and toxicity of PACs vary with the structure of PACs including the number of rings, molecular weight, and chemical substitutions.”

P. 2, Line 17: “benzo(a)pyrene”

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

Response: Will be revised according to your suggestion.

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.

Response: We are planning to use the scavenging ratio data generated from the measurements at the three sites to estimate the amount of wet deposition at other sites where passive PACs samples have been collected. This is based on the concept the scavenging ratio is defined (Duce et al., 1991). This comment provides us with more scientific questions that we have to consider before applying the method. In the revised paper we will remove or simplify related statements and will address the scientific concerns in future studies.

In addition, “is not enough for mapping wet deposition.” Or “estimating the wet deposition amount” What wet deposition? Please be specific.

Response: We meant the spatial coverage is not enough for estimating wet deposition fluxes in the Athabasca oil sands region. We will remove/simplify related statements on this potential application (as mentioned in the response to the previous comment).

“The scavenging (or washout) ratio (Wt) parameter,” Please remove the word washout as well as parameter – use only scavenging ratio.

Response: The words “washout” and “parameter” will be deleted.

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.

Response: The above statement (lines 18-21) will be deleted in the revised paper because it is not relevant to the current study aimed at examining differences between rain and snow scavenging and between gas and particulate phase PACs.

2 Methods

2.1.2 Sampling procedures

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

Response: The procedure for collecting field blanks will be included in the sampling procedures of the revised paper. The field blanks for the high volume air samples, collected every 4-6 months at each of the three sites, consist of a clean glass fibre filter and a pair of polyurethane foam that is placed in the sampler housing for the same duration as the samples, but without the vacuum pump turned on. For precipitation samples, field blanks were collected by exposing the XAD-2 columns to the atmosphere for 3 to 5 minutes at the site. One field blank was collected every month at a different site, which means a set of blanks for all sites were collected in a 4-month period.

2.1.3 Analysis procedure (better to say analytical procedures)

Response: The subheading will be revised to Analytical procedures

P. 1, line 3: “d8-dibenzothiophene” The correct form is d₈-dibenzothiophene. Please revise throughout the text.

Response: Will be revised throughout the text.

P. 1, line 4: “deuterated PAH surrogates” Please specify the names of the individual PAH surrogates.

Response: A table containing a list of the deuterated PAH surrogates and percent recoveries will be included in the revised paper.

P. 1, line 6: “The aqueous phase is re-extracted with DCM” What do authors mean by aqueous phase?

Response: The sentence will be revised to, “The aqueous phase that has been separated from the DCM phase is re-extracted with DCM.”

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.

Response: The abbreviation for dibenzothiophene will be defined earlier in the revised paper.

“The GFFs and PUF plugs samples...” Please change to GFF and PUF samples...

Response: It will be changed to “The GFF and PUF plug 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.

Response: A reference for the analytical methods was provided in the ACPD paper (Environment Canada, 2009), which are the protocols from the National Air Pollutants Surveillance (NAPS) network. A scientific reference will be included in the revised paper as well (Sun et al., 2006, *Environ. Sci. Technol.*).

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

Response: Detection limits for the analytical methods of the target analytes will be added to the revised paper.

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.

Response: Samples were corrected for surrogate recoveries if they were within 50-150%. Samples with surrogate recoveries beyond this range were excluded from the calculation of scavenging ratios. These details will be included in the Quality control section of the revised paper.

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.

Response: This equation will be deleted in the revised paper.

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.

Response: The wet deposition samplers have been in the field for at least two years now; however this study has so far analyzed the data measured between 2 January 2011 and 31 May 2012. This is about 1 ½ years of data. The period of data analyzed in this study will be corrected in the revised paper.

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.

Response: This will be corrected in the revised paper.

P. 2, line 15: "and PAC particulate fraction in air (ϕ) are known." PAC particulate mass fraction is the correct form.

Response: This will be corrected in the revised paper.

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!

Response: This part of the sentence will be deleted in the revised paper.

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.

Response: The temperature statistics at each of the three sites will be included in the revised paper. The temperatures ranged from -34.2°C to 31.5°C at AMS5, -33.9°C to 31.2°C at AMS11, and -39.2°C to 32.8°C at AMS13, which are comparable. The temperatures at AMS5 and AMS11 are almost the same,

while AMS13 is slightly colder than the other two sites when we compared the mean, median, and minimum temperatures. The particulate mass fraction could vary with the air temperature, relative humidity, and chemical composition of particles because these parameters could affect gas-particle partitioning. This is a potential source of uncertainty for the particulate mass fractions and will be addressed in the revised paper. The particulate mass fractions measured at AMS5 should be representative of those at AMS11 and AMS13 because the sites are within 30 km of each other and they are all near-source sites (near bitumen extraction and upgrading facilities). This suggests the meteorological conditions and particle composition should be similar for the three sites; thus, the particulate mass fractions should be similar. The mean and standard deviation particulate mass fractions for all PACs will be provided in a figure. The mean particulate mass fractions during snow (i.e. lower temperatures) and rain (i.e. higher temperatures) samples will also be shown in the figure to illustrate the temperature dependency of the particulate mass fractions.

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.

Response: The sentences will be revised as follows, “There were 18 gas-phase PACs of lower molecular weight (128.2-222.0 g/mol) and 15 particulate-phase PACs of higher molecular weight (228.3-284.4 g/mol)... Some of the PACs were not considered gas-phase dominant or particulate-phase dominant PACs because of a small difference between the gas and particle mass fractions. They include fluoranthene, pyrene, retene, perylene, C2/C3/C4-phenanthrene/anthracene, C1-fluoranthene/pyrene, and C3/C4-dibenzothiophene.”

3 Results and discussion

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

Response: A consistent number of decimal places for the analyte concentrations will be used in the revised paper.

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??

Response: Analyte groups are reported for alkylated PAHs because of co-elution and the vast amount of different congeners in the alkylated groups does not allow a more selective qualitative analysis. Alkylated PAHs have many structural isomers that share the same ion fragments, and most of them cannot really be identified individually, unless you have an individual standard to compare retention times or retention indexes. There are many alkylated PAH standards available in the market, but it doesn't complete the full set of possible isomers that can be found in a complex samples like those coming from the oil sands. These explanations will be included in the revised paper.

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.

Response: In the revised paper, the concentrations in section 3.1 and the abstract will be reported as the sum of the median parent PAHs, sum of the median alkylated PAHs, and sum of the median dibenzothiophenes. The median values are based on the monthly precipitation concentrations and monthly average air concentrations from 2 January 2011 and 31 May 2012, which is the period of data with both precipitation and air concentrations that are used to calculate the scavenging ratios. As recommended, we will discuss the analytes that contributed the most to the sums.

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.

Response: The subheadings will be revised according to your suggestion.

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.

Response: Sections 3.2 to 3.5 will be reorganized according to your suggestions because there is some overlap in the discussions.