Dear Prof. Bertram,

Thank you very much for editing the paper. We have revised the paper carefully and addressed all the comments provided by the reviewers. Our detailed replies are attached below.

For your and the reviewers' convenience to review the changes, a copy of the text with highlighted changes (from track changes) is also attached here.

We hope you and the reviewers will find the revised paper meets the standard of the journal.

Sincerely,

Leiming Zhang and coauthors

Response to Reviewer #1

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

General comments:

Characterization of chemical transport and fate in the Athabasca oil sands region has increased in recent years due to controversy over oil sands development and its poorly characterized environmental impacts. Zhang et al. add to this body of knowledge by describing the deposition of a particular group of hazardous air pollutants, PACs, in this region. The authors do a thorough job placing their results in the context of other similar work. Recent measurements of PACs in the Athabasca oil sands environment highlight the necessity of including alkylated PAHs in any study concerning PAC transport and fate as they are present in much higher quantities in this region relative to unsubstituted PAHs, and Zhang et al. accordingly include these PACs in their work. The authors' inclusion of alkylated PAHs is notable considering these chemicals remain relatively poorly characterized despite suspicions that they may be more toxic than their parent homologues. Though the data are notable in this respect, the work as presented in its current form is not substantial with respect to new concepts, ideas, or methods. As the other reviewer noted in their initial review, reporting and comparing values is not enough, and the novelty in the work needs to be better stressed. Finally, though Zhang et al. present a manuscript that makes good use of the English language, there are some key methodological details missing that take away from the flow of the manuscript.

Response: We agree with both reviewers that the novelty of the paper can be improved by including the scavenging ratio results for the alkylated PAHs and dibenzothiophenes. In addition to this, we will incorporate the details suggested in the specific comments in the methodology.

We'd also like to point out that the motivation of this study came from a few angles. The first one is on the relative efficiencies of snow versus rain scavenging for aerosol particles, an idea that was generated from a series of below-cloud aerosol scavenging studies we conducted recently (Wang et al., 2010, 2014; Zhang et al., 2013). In those studies, we only found limited evidence that snow scavenging is likely more efficient than rain scavenging based on equivalent water content. Field measurements on this topic are very rare and this data set provides us a good opportunity to verify the assumptions made in the previous studies. In this study, we further managed to extend this type of investigation to gaseous pollutants. Thus, comparing scavenging ratios (between snow and rain cases and between aerosol and gas pollutants) already added new knowledge on the topic of wet removal. The second motivation is to investigate precipitation scavenging of PACs – a group of pollutants for which only limited data are available in literature, and build a database of scavenging ratios for PACs. We noticed that both reviewers emphasized this aspect and we will revise the paper accordingly. The third motivation is to use the PACs scavenging ratios database for future wet deposition estimation using monitored surface air concentration at locations where wet deposition is not monitored. This will be accommodated in a separate study. These motivations will be reflected in the revised Introduction of the paper.

Specific comments:

Title: "ratio" should be "ratios".

Response: Will be revised according to your suggestion.

What is the meaning of the names of the chemicals given in parentheses next to reported e.g. precipitation and air concentrations as in Line 10? Clarify.

Response: The concentrations will be reported differently in the revised paper. Based on suggestions from Reviewer 2, the concentrations in the abstract and section 3.1 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. The analytes that contributed the most to the sums will be discussed.

Line 37: Is it really the number of rings and molecular weight or more the structure of a PAC that affects its phys-chem properties and, in particular, bioaccumulation potential and toxicity?

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.”

The introduction in general is not concise – the expected narrowing of focus leading up to the statement of objectives is lacking, and thus there is not such a clear link between context and objectives.

Response: The introduction in the revised paper will be more concise and focus more on the literature related to wet scavenging processes and scavenging ratios for PACs. 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 introduction will include more information about alkylated PAHs and dibenzothiophenes because these compounds are associated with petrogenic sources which are highly relevant to the oil sands sites. The scavenging ratio results for alkylated PAHs and dibenzothiophenes will help improve the novelty of the study.

More details will also be provided on how the database of scavenging ratios could be used in future wet deposition studies of PACs in the Athabasca oil sands region. According to Duce et al. (1991), the total wet deposition flux is the product of the total scavenging ratio, total air concentration, and precipitation rate. In a previous study, Sakata and Asakura (2007) determined the wet deposition of atmospheric particulate mercury from the scavenging ratios of particulate trace metals, particulate mercury air concentrations, and precipitation. Also see our responses to the general comments above.

As noted, PAHs vary widely in terms of their phys-chem properties, and thus also their behavior. For this reason, please specify which deuterated PAH surrogates were used during sample extraction. Provide also recoveries in a table, and as other reviewer noted, detection limits.

Response: A table containing a list of the deuterated PAH surrogates and the average and standard deviation of the percent recoveries, and detection limits of the target analytes will be included in the revised paper.

The separation between gas and particulate phases in the HVAS is clear, but not so clear with the deposition samplers. Please clarify in description of sampler itself and in lines 139-150 describing extraction.

Response: The wet deposition sampler does not include a filter unit for separating the particulate phase from the dissolved phase in precipitation. Therefore, both the dissolved and particulate PACs are collected on the XAD column. It will be clarified in the sampling and extraction descriptions in the revised paper that total PACs were collected and measured.

In section 2.2, it is stated that air concentrations were estimated for a period of a little over a year while earlier in the introduction, it is stated that wet deposition samplers were deployed for two years. Why the discrepancy? Also, is it common practice to use air samples taken every 6 days, and averaging them over a month, and using them in conjunction with precipitation samples resolved on a monthly basis?

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 1.5 years of data. The period of data analyzed in this study will be corrected in the revised paper.

The use of average concentrations in precipitation or in air to determine the scavenging ratios is a common practice in literature (Barrie, 1985; Duce et al., 1991; Galloway et al., 1993; Sakata and Asakura, 2007). Scavenging ratios determined for individual precipitation events are highly variable. As the averaging time decreases (i.e. shorter time scale), the variability in the scavenging ratios tends to increase (Barrie, 1985; Galloway et al., 1993). The monthly average scavenging ratios can vary by a factor of 2-5, whereas the variability increases to an order of magnitude for daily scavenging ratios (Galloway et al., 1993). It is recommended that for the estimation of wet deposition flux, scavenging ratios based on aerosols and precipitation concentrations averaged over a two year period are considered reliable (Galloway et al., 1993).

Ideally, monthly average concentrations should be obtained from daily data of all the days in a month. However, due to the extensive cost of high-volume sampling, only data for one in every six days are collected. We believe that the uncertainties using this averaging approach should not be larger than uncertainties caused by other sources (e.g., measurements itself and/or laboratory analysis). Also, the median and mean scavenging ratios shown in Table 2 are based on the monthly scavenging ratios averaged over the snowfall and rainfall periods (5-7 months) and should have smaller variability. These explanations will be provided in the revised paper.

Line 197-199: How representative is AMS5 when it comes to particulate fractions at the other two sites, in addition to the locations of the other passive samplers in the AOSR that are intended to be used in future for estimating deposition? Also, provide more details about the measurements used to estimate these fractions: e.g. was it five measurements taken in one month, or a few measurements every 3 months? These fractions likely vary seasonally for many PACs.

Response: 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. These are potential uncertainties associated with the particulate mass fractions that will be discussed in the revised paper. The particulate fractions measured at AMS5 are thought to 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. Thus, the meteorological conditions and particle composition should be similar for the three sites, which suggest the particulate mass fractions should be similar as well.

Some of the passive sampling locations are 30-100 km from AMS5 and are considered remote/background sites. Besides, the domain we are planning to estimate dry and wet deposition of all the monitored PACs is larger than the area where passive sampling is currently conducted. We thus have developed a method for estimating particulate fraction for each PAC species with input parameters including particle/gas partitioning coefficient, temperature, and total suspended particle. The method has been validated using field data collected at three sites and will be presented in a separate study.

Although the particulate mass fractions at AMS5 may not be suitable for some of these passive sampling sites, the total scavenging ratios that may be used in future studies to estimate the total wet deposition of PACs at the passive sampling sites do not require particulate mass fractions. We have used the particulate mass fractions in this study to classify the PACs as predominantly gas-phase or particulate-phase in order to examine their relative scavenging efficiencies.

The particulate PAC fractions in air were measured every sixth day at the AMS5 site, which is 4-5 particulate mass fractions taken in one month. In the revised paper, a plot of the mean and standard deviation of the particulate mass fractions for all PACs will be included. It will show that while there is some variability in the particulate mass fractions over the study period, most of the particulate mass fraction measurements (i.e., mean ± 1 standard deviation) for the gas-phase dominant parent PAHs were below 0.3. For the particulate-phase dominant parent PAHs (except for benzo(k)fluoranthene), most of the particulate mass fraction measurements were above 0.7. We considered only the parent PAHs here because these are relevant to the comparisons in sections 3.2-3.5. The mean particulate mass fractions during snow (i.e. winter/spring) and rain (i.e. summer/fall) samples will also be shown in the figure to illustrate the temporal variation of the particulate mass fractions.

Line 223: what kind of environment were these snow samples taken in? Urban? Rural? Suburban? It might also be important to note how your measurement methods differ from the studies referenced and how, if at all, this might influence the differences between your data and the references.

Response: The snow samples were taken from the wet deposition samplers, which are setup in the surface mining (industrial) areas in the Athabasca oil sands region. The monthly precipitation samples were classified as snow samples based on the months when snowfall occurred. The heater inside the wet deposition samplers melts the snow collected, and snowmelt was analyzed for PACs. The method used to study the PACs in snow samples in this paper are different from those who collected snow from snowpack or snow cores from the ground (e.g., Franz and Eisenreich, 1998; Kelly et al., 2009, *PNAS*). This difference might have some influence on the comparisons between the results from this study and other references. In the case of snowpack or snow core sampling, the PACs in snow samples could be exposed to both wet and dry deposition. Due to the surface mining operations at the oil sands sites, particulate matter emissions are likely to be elevated, which may be a large contributor to the dry deposition of particulate PACs. In contrast, the collection of snow in the wet deposition sampler excludes PACs from dry deposition. This may explain the lower parent PAH concentrations in snow compared to those reported in other references (Franz and Eisenreich, 1998; Wania et al., 1999). This discussion will be provided in the revised paper.

Table 1: There are a lot of numbers here. It might make for more intuitive digestion of patterns or lack thereof/comparisons to literature if these were somehow presented in graphical format that also includes literature values. This would also allow for a more concise description of these patterns and comparisons in the lines following. The info contained in Tables 2 & 3 might also be more easily digested if presented in graphical format.

Response: Additional figures for the data in Tables 1-3 will be included in the revised paper. Tables 1-3 will be presented as supplementary material because the summary database of scavenging ratios could be useful for future modeling applications.

Again, measurement methods and how these compare to methods used in other studies – could these perhaps account for "high" ratios described in lines 244-253?

Response: As explained in one of our earlier responses, the collection of snow in the wet deposition sampler in this study excludes PACs from dry deposition, whereas snow sampling from snow packs or snow cores in previous studies may include PACs from both wet and dry deposition. Thus, the PAC concentrations in snow in this study should be lower, which would result in lower scavenging ratios. The 2-7 times higher scavenging ratios for acenaphthylene at the oil sands sites is likely not related to the different snow sampling methods.

To what extent do the three sites with wet deposition samplers allow for accurately estimating wet deposition at the other air quality monitoring sites in the AOSR considering the limited geographical extent of the wet deposition samplers in this study relative to the passive sampling network (and perhaps AOSR in general)? Can you also be clearer about how to go from using the scavenging ratios determined using HVAS to estimating wet deposition at these other sites that only have passive air samplers?

Response: The major result from our study is the analysis of the scavenging ratios to compare differences between rain and snow scavenging and between gas and particulate phase PACs. The database of PAC scavenging ratios could be used in future studies to predict the wet deposition flux at the passive sampling sites. The total wet deposition flux is the product of the total scavenging ratio, total air concentration, and precipitation rate (Duce et al., 1991; Sakata and Asakura, 2007). Although there is a better understanding on the temporal variability of scavenging ratios as discussed in an earlier response, there have not been enough studies conducted to address the spatial variability (Galloway et al., 1993). The large variability in scavenging ratios, such as cloud and precipitation types and air masses discussed in section 3.6 of the ACPD paper, could vary with location. Although it might not be feasible to account for all the factors affecting PAC wet deposition, it is possible to explore this at the passive air monitoring sites that measure both gas phase and particulate phase PACs (total PACs in air) and then validate with wet deposition measurements. We think it is a reasonable approach to provide a first-order estimation of wet deposition using scavenging ratio concept, although the uncertainties can be large.

Lines 288-290: Clarify whether the particulate and gas fractions in precipitation samples were separated in the present study in the methods section. Lines 311-313 make this clear too late.

Response: In lines 288-290 in the ACPD paper, the sentence explains why the particulate scavenging of acenaphthylene is important even though it is a gas-phase dominant PAC. The study did not separate the particulate and dissolved PACs in precipitation samples. In an earlier response, we mention that this will be clarified in the sampling and analytical procedure sections of the revised paper. The sentence will be revised to, "a small mass fraction in particulate-phase could increase its overall scavenging ratio (W_t) dramatically compared to the pure gas-phase scavenging ratio (W_g) due to the much higher value of W_p than W_g reported in literature."

Lines 454-456: Couldn't the seasonal differences in temperature and thus vapor pressure and chemical partitioning also have an influence on the variability in scavenging ratios?

Response: The seasonal differences in air temperature and chemical partitioning potentially affect the particulate mass fraction of PACs. In the revised paper, we will include the particulate fraction during snow (i.e. lower temperatures) and rain (higher temperatures) for both gas phase and particulate phase PACs in a figure and discuss how this would affect the snow and rain scavenging ratios. It is expected that at lower temperatures the vapor pressures of PACs in the particulate phase would be even lower, which causes the PACs to remain bounded to particles. Since snow is more efficient than rain at scavenging particles, these explanations should support the higher scavenging ratios of particulate phase PACs during snow. Temperature also affects gas-particle partitioning of PACs. At lower temperatures, the gas phase dominant PACs will tend to partition to particulate matter. Thus, the particulate mass fraction of gas phase dominant PACs should be higher for snow samples. Because literature values of $W_p >> W_g$, it supports the higher total snow scavenging ratios for gas-phase PACs.

Technical corrections:

Titles of sections 3.2 and 3.3. e.g. 3.2 reads Comparison of gas-phase dominant and particulate-phase dominant PACs by snow scavenging. Would something like "during" be a better replacement for "by"? Line 358, replace is with "are".

Response: Will be revised according to your suggestion.

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. Techol.*; 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 d_8-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 = Cprec/Cair)." 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^{o}C to 31.5^{o}C at AMS5, -33.9^{o}C to 31.2^{o}C at AMS11, and -39.2^{o}C to 32.8^{o}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.

Scavenging ratios of polycyclic aromatic compounds in rain and snow at the Athabasca oil sands region

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Abstract. The Athabasca oil sands industry in northern Alberta, Canada is a possible source of polycyclic aromatic compounds (PACs). Monitored PACs, including polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs, and dibenzothiophenes (DBTs), in precipitation and in air at three near-source sites in the Fort MacKay and Fort McMurray area during ~~May~~ January 2011 to ~~August~~ May 2012 were ~~analyzed~~ used to generate a database of scavenging ~~(or washout)~~ ratios (W_t) for PACs scavenged by both snow and rain. ~~Median precipitation and air concentrations of parent PAHs over the May 2011 to August 2012 period ranged from 0.3-184.9 (chrysene) ng/L and 0.01-3.9 (naphthalene) ng/m^3, respectively, which were comparable to literature values.~~ Higher concentrations in precipitation and air were observed for alkylated PAHs and ~~dibenzothiophenes~~DBTs. The sum of the median precipitation concentrations over the period of data analyzed was 0.48 µg/L for the eighteen PAHs, 3.38 µg/L for the twenty alkylated PAHs, and 0.94 µg/L for the five DBTs. The sum of the median air concentrations for parent PAHs, alkylated PAHs, and DBTs were 8.37 ng/m^3, 67.26 ng/m^3, and 11.83 ng/m^3, respectively. ~~The median precipitation and air concentrations were 11.3-646.7 (C3-fluoranthene/pyrene) ng/L and 0.21-16.9 (C3-naphthalene) ng/m^3, respectively, for alkylated PAHs, and 8.5-530.5 (C4-dibenzothiophene) ng/L and 0.13-6.6 (C2-dibenzothiophene) ng/m^3 for dibenzothiophenes and their alkylated derivatives.~~

Median W_t values over the measurement period were 6100 to ~~-~~1.1x10^6 from snow scavenging and 350 to ~~-~~2.3x10^5 from rain scavenging depending on the PAC species. Median W_t for parent PAHs were within the range of those observed at other urban and suburban locations. But W_t for acenaphthylene in snow samples was 2-7 times higher. Some individual snow and rain samples exceeded literature values by a factor of 10. W_t for benzo(*a*)pyrene, dibenz(*a*,*h*)anthracene, and benzo(*g*,*h*,*i*)perylene in snow samples had reached 10^7, which is the maximum for PAH snow scavenging ratios reported in literature. From the analysis of data subsets, W_t for particulate-phase dominant PACs were 14-20 times greater than gas-phase

dominant PACs in snow samples and 7-20 times greater than gas-phase dominant PACs in rain samples. W_t from snow scavenging was ~9 times greater than rain scavenging for particulate-phase dominant PACs and 4-9.6 times greater than rain scavenging for gas-phase dominant PACs. Gas-particle fractions of each PAC, particle size distributions of particulate-phase dominant PACs, and Henry's Law constant of gas-phase dominant PACs explained, to a large extent, the different W_t values among the different PACs and precipitation types. The trend in W_t with increasing alkyl substitutions may be attributed to their physico-chemical properties, such as octanol-air and particle partition coefficients and subcooled vapour pressure, which increase gas-particle partitioning and subsequently the particulate mass fraction. This study verified findings from a previous study of Wang et al. (2014) which suggested that snow scavenging is more efficient than rain scavenging of particles for equivalent precipitation amount, and also provided new knowledge on the scavenging of gas-phase PACs and alkylated PACs by snow and rain.

1. Introduction

Polycyclic aromatic compounds (PACs) are organic pollutants containing two or more benzene rings that are fused together and may contain additional ring structures. They are typically further classified into polycyclic aromatic hydrocarbons (PAHs) and dibenzothiophenes (DBTs), which contain sulfur. There are hundreds of PACs ranging from two ring chemical structures to over six rings. Some PACs are substituted with functional groups, such as alkyl, amino, halogen and nitro groups (Boström et al., 2002). 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~~The number of rings and the molecular weight of the PACs affect their physical and chemical properties, such as vapor pressure and water solubility, as well as the~~

~~bioaccumulation potential and toxicity~~ (Ravindra et al., 2008; CCME, 2010). These properties play a role in atmospheric processes of PACs, their environmental fate, and impacts to animals and human health (Boström et al., 2002; Banger et al., 2010; Diggs et al., 2011; Muñoz and Albores, 2011). The probable human PAH carcinogens according to the USEPA are benz(*a*)anthracene, benzo(*a*)pyrene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, chrysene, dibenz(*a*,*h*)anthracene, and indeno(*1*,*2*,*3-cd*)pyrene (ATSDR, 2008). In Canada, benzo(*a*)pyrene, benzo(*b*)fluoranthene, benzo(*j*)fluoranthene, benzo(*k*)fluoranthene, and indeno(*1*,*2*,*3-cd*)pyrene are the PAHs that may constitute a danger to human life or health under the *Canadian Environmental Protection Act* (CCME, 2010). Abnormal physical and neurological development in infants has also been linked to prenatal exposure of PAHs (Perera et al., 2009). Less is known about the cancer and other health risks of alkylated PAHs because of the limited toxicity data (Baird et al., 2007; Wickliffe et al., 2014). Due to the potential toxic effects on animals and humans when exposed to PACs, it is necessary to quantify the deposition budget of PACs to terrestrial and aquatic ecosystems at local to regional scales.

~~PACs are emitted into the atmosphere primarily from incomplete combustion and production of fossil fuels, biomass burning, and waste incineration. Industrial processes, residential coal and wood burning for heating and cooking, and vehicular emissions are also sources of PACs in the air (Ravindra et al., 2008; Banger et al., 2010; Lee and Vu, 2010; Keyte et al., 2013). PACs are found in the gas phase or bound to particulate matter in the atmosphere. Once in the air, PACs are transported in the atmosphere and ultimately deposited into soil, water, and sediment. PACs have an affinity for lipids, hence they can bioaccumulate and become increasingly concentrated higher up in the food chain (Boström et al., 2002). Development of tumors, lower reproduction rates, and abnormal development are some of the harmful effects on wildlife (Banger et al., 2010). People are exposed to PACs in industrial workplaces and in the~~

~~indoor and outdoor environment by inhalation, skin contact, and ingestion of contaminated food (Boström et al., 2002; Banger et al., 2010; Diggs et al., 2011). PACs pose a major concern to people because it can potentially cause errors in DNA replication which can lead to cancer (Perera et al., 2009; Muñoz and Albores, 2011). The probable human carcinogens according to the USEPA are benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-c,d)pyrene (ATSDR, 2008). In Canada, benzo(a)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene are the PAHs that may constitute a danger to human life or health under the *Canadian Environmental Protection Act* (CCME, 2010). Abnormal physical and neurological development in infants has also been linked to prenatal exposure of PAHs (Perera et al., 2009). Less is known about the cancer risks of alkylated PAHs because of the limited toxicity data (Baird et al., 2007). Due to the potential toxic effects on animals and humans when exposed to PACs, it is necessary to quantify the deposition budget of PACs to terrestrial and aquatic ecosystems at local to regional scales.~~

The Athabasca oil sands industry in northern Alberta, Canada is known to release significant amounts of ~~polycyclic aromatic compounds (~~PACs~~),~~ among other pollutants (Jautzy et al., 2013; Parajulee and Wania, 2014). While PAH emissions are ubiquitous among combustion and industrial sources, alkylated PAHs and DBTs are specifically found in crude oil deposits including bitumen and emissions from bitumen upgrading facilities as well as wood combustion emissions. These pollutants have been observed in lakes, rivers, sediments, and snow cores in the Athabasca oil sands region (Kelly et al., 2009; Timoney and Lee, 2011, Jautzy et al., 2013; Kurek et al., 2013). One of the major pathways for PACs to enter terrestrial and aquatic environments is via wet deposition. In order to accurately estimate wet deposition, models need to account for the differences in scavenging efficiencies of gases and aerosols and various forms of precipitation (e.g. snow versus rain) for in-cloud and below-cloud scavenging processes. Previous below-cloud aerosol scavenging studies found limited evidence that snow scavenging is likely more efficient than rain scavenging based on equivalent water content (Wang et al., 2010, 2014; Zhang et al., 2013). These findings can be verified with field measurements from the Athabasca oil sands region by determining scavenging ratios for PACs, including PAHs, alkylated PAHs, and DBTs. Furthermore, the investigation of precipitation scavenging efficiencies can now be extended to gaseous pollutants.

The scavenging ratio is a simplified measure for analyzing wet deposition and is defined as the ratio of the concentration of a chemical in precipitation to that in air (Cousins et al., 1999). In literature, scavenging ratios were determined for radioactive particles, water vapor, sea salt, non-sea salt sulfate, nitrate, methanesulfonate, sodium, sulfur dioxide, particulate matter, carbonaceous aerosols, trace metals, PACs, and mercury (Barrie, 1985; Engelmann, 1971; Duce et al., 1991; Galloway et al., 1993; Guentzel et al., 1995; Franz and Eisenreich, 1998; Sakata and Asakura, 2007; He and Balasubramanian, 2009; Rothenberg et al., 2010; Hegg et al., 2011; Škrdlíková et al., 2011; Huang et al., 2013). Scavenging ratios were compared with previous values obtained from other locations to gain insight into some of the factors (e.g., precipitation characteristics, scavenging efficiency, and changes in source emissions) that may explain the discrepancies in scavenging ratio values (Rothenberg et al., 2010; Hegg et al., 2011). The relative scavenging efficiencies of PACs between rain and snow and between gas and particulate phases have also been compared based on their scavenging ratios (Franz and Eisenreich, 1998; Wania et al., 1999). Gas and particulate scavenging ratios for PACs have also been used to estimate the relative contributions or importance of gas and particle scavenging to total wet deposition (He and Balasubramanian, 2009; Škrdlíková et al., 2011). These studies have highlighted that the knowledge of precipitation scavenging of PACs is still very limited and that more research is needed to understand the factors affecting wet deposition in order to improve model wet deposition estimates.

The objective of the present study is to compare wet scavenging of PACs at the oil sands sites to other locations using scavenging ratios and examine differences between snow and rain scavenging and between gas phase and particulate phase scavenging. This involves generating a database of scavenging ratios for PACs. The database could potentially be used in future wet deposition estimation using monitored surface air concentrations at locations where wet deposition is not monitored and will be detailed in a separate study.

~~A network including 17 passive-sampling sites has been setup since November 2010 to monitor air concentrations of polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs, and dibenzothiophenes for subsequent mapping of dry deposition. 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 (W_t) 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. The wet deposition flux is the product of the scavenging ratio, air concentration, and precipitation rate according to Duce et al. (1991). In a previous study, Sakata and Asakura (2007) determined the wet deposition of atmospheric particulate mercury from the scavenging ratios of particulate trace metals, particulate mercury air concentrations, and precipitation. In the absence of wet deposition measurements, the wet deposition can be estimated from scavenging ratios of similar particle sizes (Duce et al., 1991). This approach requires a good knowledge of W_t values for all the PAC species of interest. Fortunately, PAC air concentrations were also monitored using~~

~~high-volume samplers at the same three wet deposition sites, enabling us to calculate the scavenging ratio of PACs at these sites.~~

~~In literature, scavenging ratios were determined for radioactive particles, water vapor, sea salt, non-sea salt sulfate, nitrate, methanesulfonate, and sodium, sulfur dioxide, particulate matter, carbonaceous aerosols, trace metals, PACs, and mercury (Barrie, 1985; Engelmann, 1971; Duce et al., 1991; Galloway et al., 1993; Guentzel et al., 1995; Franz and Eisenreich, 1998; Sakata and Asakura, 2007; He and Balasubramanian, 2009; Rothenberg et al., 2010; Hegg et al., 2011; Škrdlíková et al., 2011). Scavenging ratios were compared with previous values obtained from other locations to gain insight into some of the factors (e.g., precipitation characteristics, scavenging efficiency, and changes in source emissions) that may explain the discrepancies in scavenging ratio values (Rothenberg et al., 2010; Hegg et al., 2011). The relative scavenging efficiencies of PACs between rain and snow and between gas and particulate phases have also been compared based on their scavenging ratios (Franz and Eisenreich, 1998; Wania et al., 1999). Gas and particulate scavenging ratios for PACs have also been used to estimate the relative contributions or importance of gas and particle scavenging to total wet deposition (He and Balasubramanian, 2009; Škrdlíková et al., 2011). Scavenging ratios of particles, air concentrations, and the precipitation rate have also been used to estimate the wet deposition fluxes of particles (Duce et al., 1991; Sakata and Asakura, 2007). 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.~~

~~One goal of the present study is to develop a database of scavenging ratios for the monitored 43 PAC species scavenged by both snow and rain. Other goals include a better understanding of the potential differences between gas and particulate scavenging and between~~

~~snow and rain scavenging because PACs exist as gases and bound to particles and the oil sands region experiences long winters and rainfall. The database will first be used in a separate study for producing deposition maps in the Athabasca oil sands region in combination with monitored air concentrations. The database and the new knowledge gained from the study will also be useful for improving chemical transport models that simulate the fate and transport of PACs.~~

2. Methods

2.1 Data collection

2.1.1 Description of sampling sites

~~Polycyclic aromatic compounds~~PACs in precipitation and air were sampled at three sites in the Athabasca oil sands region in northern Alberta, Canada, where large deposits of bitumen are mined. The region is highly industrial because of the surface mining activities, oil sands production facilities, and industrial traffic. The three sites, AMS5 (56°58’7.68"N, 111°28’55.2"W), AMS11 (57°1’36.73"N, 111°30’2.7"W) and AMS13 (57°8’57.12"N, 111°38’32.64"W), are air sampling sites from an existing monitoring network operated by the Wood Buffalo Environmental Association (WBEA) and are within 30 km from each other (Fig. 1). The sites are located along the Athabasca River near the Fort MacKay and Fort McMurray area and are near two upgraders, which process bitumen into synthetic crude oil. The two upgraders emit PAHs directly to the atmosphere and in tailings and waste rock disposals (Environment Canada, 2012).

2.1.2 Sampling procedures

Automated precipitation samplers (MIC Co., Thornhill, Ontario) were installed at the three sites. The wet-only samplers automatically open when rain or snow activates a sensor and contains a heated funnel and heated compartment for the XAD-2 resin column. Precipitation, including rain and snow, enters the heated funnel and through the XAD-2 column, where the dissolved and particulate PACs are collected, and then into a carboy to measure the precipitation volume. The wet deposition sampler does not include a filter unit for separating the particulate phase from the dissolved phase in precipitation. Therefore, both the dissolved and particulate PACs are collected on the XAD-2 column. Sampling of precipitation was conducted on a monthly schedule. The XAD-2 resin columns were shipped to the Canada Centre for Inland Waters (Environment Canada, Burlington, Ontario) for the determination of PACs in precipitation samples.

Simultaneously, air samples were collected for 24 hours every 6 days at the three sites using a modified high-volume air sampler. A vacuum pump draws in 700-1000 m^3 of air through a Teflon-coated glass fibre filter (GFF) followed by a pair of polyurethane foam (PUF) plugs to collect both the particulate bound and gas-phase PACs, respectively. Samples were wrapped in aluminum foil to reduce exposure to light and stored in a freezer at a temperature of -10°C or less prior to analysis. Additional details on the sampling protocols are available in Harner et al. (2013). Average air temperatures corresponding to the collection of 24-hr air samples were also recorded.

2.1.3 ~~Analysis~~ Analytical procedures

For the analysis of total PACs (dissolved and particulate phase) in precipitation, the XAD-2 resin was extracted in a clean room laboratory (HEPA and carbon filtered, positively pressured) by eluting first with acetone and then with dichloromethane (DCM). Recovery standards of ~~d_8-dibenzothiophene spike and~~ deuterated PAH and DBT surrogates are added prior to XAD-2 column elution. The elution solvents are combined in a separatory funnel to separate the DCM phase. The aqueous phase that has been separated from the DCM phase is re-extracted with DCM. The DCM is back extracted with 3% sodium chloride solution then dried by pouring through a column of sodium sulfate. The DCM is evaporated to a small volume and exchanged into cyclohexane. Prior to extraction of air samples, the GFFs and PUF plugs were spiked with a solution containing PAH and DBT surrogates. The GFF~~s~~ and PUF plug~~s~~ samples are then extracted by Soxhlet apparatus for a period of 16 to 20 hours with cyclohexane. The raw extract is then filtered through sodium sulfate and concentrated to a volume of 3 to 5 ml by rotary evaporation at 45°C.

The cyclohexane extracts were further processed by the Air Quality Research Division (AQRD) laboratory (Ottawa, Ontario). The cyclohexane was fractionated on a silica column to separate aliphatic hydrocarbons (hexane elution) from PACs (elution with benzene). The column was eluted with 5 ml of hexane, followed by 5 ml of benzene and the eluate is archived (aliphatic hydrocarbon fraction). The PACs were then eluted with two 5 ml aliquots of benzene into a calibrated centrifuge tube. The PAC fraction (benzene fraction) was concentrated to less than 0.9 ml by UHP nitrogen. After addition of the d_{10}-fluoranthene internal standard, the purified sample extract is then brought to a known volume (typically 1.0 ml) using benzene. The final purified extract was analyzed by GC-low resolution MS~~ following Environment Canada AQRD protocol 3.03/4.6/M (Environment Canada, 2009)~~, which included an Agilent 6890N or 7890A GC interfaced directly to Agilent 5973N, 5975 or 5975C mass selective detector. The samples were analyzed for PAHs, ~~dibenzothiophenes~~DBTs, and their alkyl derivatives. Some alkylated PAHs are reported as analyte groups 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 be identified individually unless individual standards are available to compare retention times or retention indexes. There are many alkylated PAH standards available in the market, but they do not complete the full set of possible isomers that are found in complex samples like those from the oil sands. The analytical procedures follow Environment Canada AQRD protocol 3.03/4.6/M (2009) and Sun et al. (2006).~~Field blanks were collected for precipitation and air samples, and the concentrations were blank corrected. Surrogate standards were added to each sample, method blanks, and control samples as part of quality assurance of analytical procedures in the AQRD protocol 3.03/4.6/M (Environment Canada, 2009). Sample measurements with surrogate recoveries from 50-150% were corrected for surrogate recoveries.~~

2.1.4 Quality control and quality assurance

Field blanks were collected for ~~precipitation and~~ air and precipitation samples. 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 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. ~~, and the concentrations~~Concentrations were blank corrected. Surrogate standards were added to each sample, method blanks, and control samples as part of quality assurance of analytical procedures in the AQRD protocol 3.03/4.6/M (Environment Canada, 2009). Surrogate recovery percentages are shown in Table 1. 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. Detection limits for the target analytes ranged from 0.1 to 2 pg/µl for air and 0.4 to 20 ng for precipitation. ~~Sample measurements with surrogate recoveries from 50-150% were corrected for surrogate recoveries.~~

2.2 Data analysis

The scavenging of gaseous and particulate PACs by rain and snow have been studied using scavenging ratios ~~or washout ratios~~, which is a simplified approach at examining the overall wet deposition process based only on the concentration of a chemical in precipitation to that in air ~~(*W* = C_{prec}/C_{air})~~.

Total scavenging ratios (W_t) were determined for 43 PACs at three oil sands monitoring sites (AMS5, AMS11, and AMS13) from precipitation and high-volume air samples. Air samples collected approximately every 6 days were averaged to correspond with the monthly precipitation samples collected between ~~30~~ 2 ~~April~~ January 2011 and ~~30~~ 31 ~~August~~ May 2012 (Supplementary Tables S1 and S2), which is the period of data analyzed in this study. Ideally, monthly average concentrations should be obtained from daily air concentrations in a month; however, due to the extensive costs, air sampling was only performed once every six days. The uncertainties from this averaging approach should not be larger than the uncertainties caused by other sources (e.g., measurements itself and/or laboratory analysis). In addition to a lack of data to link individual precipitation samples to individual air samples, scavenging ratios were not determined for every precipitation event because the shorter time scale can lead to large variability in the scavenging ratios (Barrie, 1985; Galloway et al., 1993). For instance, the monthly average scavenging ratios can vary by a factor of 2-5, whereas the variability increases to an order of magnitude for daily scavenging ratios (Galloway et al., 1993). In this study, the median scavenging ratios are based on the monthly scavenging ratios over the snowfall and rainfall periods (about 5-7 months) and should have smaller variability.

Only the air samples with PAC concentrations > MDL were averaged, similar to the data selection criteria used in Škrdlíková et al. (2011). The method detection limits (MDL) were established from the PAC air concentrations observed in field blanks: MDL = average (field blanks) + 3 x standard deviation (field blanks). The total scavenging ratios were determined as follows (Škrdlíková et al., 2011):

$$W_t = \frac{C_{prec}\left(\frac{ng}{L}\right) \times 1000\ (\frac{L}{m^3})}{C_{air}\ (\frac{ng}{m^3})} = W_p\varphi + W_g(1-\varphi)$$

$$W_p = \frac{C_{prec,p}}{C_{air,p}}$$

$$W_g = \frac{C_{prec,d}}{C_{air,g}}$$

W_t includes both the ~~gas~~ dissolved and particulate phase concentrations in precipitation and the gas and particulate phase concentrations in air and may also be determined if the particulate scavenging ratio (W_p), gas scavenging ratio (W_g), and PAC particulate mass fraction in air (φ) are known. W_p is determined from the particulate PAC concentration in precipitation ($C_{prec,\,p}$) and particulate concentration in air ($C_{air,\,p}$), while W_g is based on the dissolved PAC concentration in precipitation ($C_{prec,\,d}$) and gas-phase concentration in air ($C_{air,\,g}$).

The total scavenging ratios were categorized into snow and rain samples. Snow samples included precipitation sampling dates between 20 December and 1 April. Rain samples included the precipitation sampling dates between 30 April and 30 November. Total scavenging ratios were presented for snow and rain cases separately. The scavenging ratio calculation excluded low precipitation samples (< 1.5 mm) ~~and PAC air concentrations below MDL as discussed above~~.

Using the particulate PAC fractions in air measured every sixth day 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. 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). The median particulate mass fraction of the gas-phase and particulate phase PACs were 0.073 and 0.92, respectively. Some of the PACs in Fig. 2 were not considered gas-phase dominant or particulate-phase dominant PACs because of a small difference between the gas and particle fractions. They include fluoranthene, pyrene, retene, perylene, C2/C3/C4-phenanthrene/anthracene, C1-fluoranthene/pyrene, and C3/C4-DBTs. Fig. 2 illustrates the mean and variability in the particulate mass fractions for all PACs. The variability could be due to vapor pressure of the PACs, air temperature, relative humidity, and chemical composition of particles because these parameters could affect gas-particle partitioning (Cousins et al., 1999; Hennigan et al., 2008). Most of the particulate mass fractions (i.e., mean ± 1 standard deviation) for the gas-phase dominant parent PAHs in Fig. 2 were below 0.3, which is the criterion used to categorize gas-phase dominant PACs. For the particulate-phase dominant parent PAHs, most of the particulate mass fraction measurements were above the cut-off criterion of 0.7. The particulate mass fractions measured at AMS5 are thought to 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). The temperatures ranged from -34.2^0C to 31.5^0C at AMS5, -33.9^0C to 31.2^0C at AMS11, and -39.2^0C to 32.8^0C at AMS13, which are comparable. The temperatures at AMS5 and AMS11 were almost the same, while AMS13 was slightly colder than the other two sites based on the mean, median, and minimum temperatures

(Table 2). ~~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 fractions.~~

3. Results and Discussion

3.1 General statistics and comparison with literature

Total scavenging ratios were determined for 43 PACs at the three sites from precipitation and air concentrations. The sum of the median precipitation and air concentrations for parent PAHs, alkylated PAHs, and DBTs at each of the three sites are shown in Fig. 3a and 3b. Among the sites, the highest precipitation concentrations were observed for alkylated PAHs, followed by DBTs and then parent PAHs. ~~Median~~ The sum of the median precipitation concentrations measured between ~~May~~ January 2011 and ~~August~~ May 2012 ~~ranged from~~was ~~0.4-302.8~~0.48 µ~~n~~g/L ~~at the AMS5 site~~for PAHs, ~~0.4-646.7~~ 3.38 µ~~n~~g/L ~~at AMS11~~for alkylated PAHs, and 0.~~3-236.6~~ 94 µ~~n~~g/L ~~at AMS13~~for DBTs~~ for PAHs~~. ~~, dibenzothiophenes, and their alkylated derivatives.~~ The ~~most abundant PACs (highest median concentration) in precipitation was C3-fluoranthene/pyrene at the three sites~~PAHs contributing the most to the total PAH concentration include chrysene, phenanthrene, and naphthalene. C4-fluoranthene/pyrene contributed the most to the total alkylated PAHs, while C4-DBT contributed the most to the total DBTs. The summed concentrations in snow samples were 9 to 13 times greater than those in rain samples. ~~–~~A comparison of the summed concentrations of parent PAHs, alkylated PAHs, and DBTs in snow and rain samples are illustrated in Fig. 3c. The parent PAH concentrations in rainwater at the oil sands sites were higher than those at other suburban and rural locations (Franz and Eisenreich, 1998, Birgül et al., 2011 and references therein; Škrdlíková et al., 2011). The concentrations in snow were lower than those reported by Franz and Eisenreich (1998) and Wania et al. (1999) and at other urban locations (Birgül et al., 2011 and references therein). The different sampling methods for snow may explain the lower parent PAH concentrations compared to those from previous studies (Franz and Eisenreich, 1998; Wania et al., 1999). In previous studies, fresh snow was collected from the surface of snow packs, which could be exposed to both wet and dry deposition of PACs. In contrast, snow was collected in a wet deposition sampler in this study, which might result in lower PAC concentrations compared to literature values. ~~Median concentrations of PACs in snow were 4 to 27 times higher than those in rain. Median PAC concentrations ranged from 2.5-2400 ng/L (max: C1-benz(a)anthracene/ triphenylene/chrysene) in snow and 0.1-260 ng/L (max: C3-fluoranthene/pyrene) in rain (Table 1). From the same table, the average and standard deviation of the precipitation collected during the snow and rain sampling events were 10.8±6.4 mm and 33.2±27.5 mm, respectively.~~

Air concentrations of alkylated PAHs are significantly higher than DBTs and parent PAHs at each of the three sites (Fig. 3b). Overall, the sum of the median air concentrations for parent PAHs, alkylated PAHs, and DBTs ~~Median air concentrations at AMS5, AMS11, and AMS13~~ were ~~0.02-14.6~~8.37 ng/m^3, ~~0.03-16.9~~67.26 ng/m^3, and ~~0.01-7.7~~11.83 ng/m^3, respectively. The air concentrations of parent PAHs at the oil sands sites were within the range of those reported in literature (Franz and Eisenreich, 1998, Wania et al., 1999; He and Balasubramanian, 2009; Birgül et al., 2011 and references therein). Among the parent PAHs, naphthalene and phenanthrene concentrations in air were the highest. Elevated air concentrations were also observed for C3/C4-naphthalenes and C2/C3-DBTs. Unlike precipitation, the air concentrations of PACs associated with snow samples were only slightly higher than associated with rain samples (Fig. 3c). ~~The highest median air concentration was C3-naphthalene at the three sites.~~

~~The ratio of the median air concentration of PACs of snow to rain samples ranged from 0.5 to 2.9. During the monthly snow and rain sampling events, the average and standard deviation of~~

~~the air temperatures were -8.6±7.2 ºC and 8.9±8.6 ºC, respectively, with an average temperature difference of 17.5 ºC (Table 1). The median air concentrations ranged from 0.04-18.3 ng/m^3 for the snow data subset and 0.03-11.8 ng/m^3 for the rain data subset.~~

~~Due to the lack of data for alkylated PAHs and dibenzothiophenes in air and precipitation samples in literature, only the parent PAH concentrations were compared with literature values. Median precipitation concentrations for parent PAHs ranged from 0.3-184.9 (chrysene) ng/L and air concentrations ranged from 0.01-3.9 (naphthalene) ng/m^3 at the three sites, which were lower than the concentration ranges that included the alkylated PAHs and dibenzothiophenes. The parent PAH median precipitation concentrations at the oil sands sites were higher than those in rain samples at other suburban and rural locations (Franz and Eisenreich, 1998, Birgül et al., 2011 and references therein; Škrdlíková et al., 2011), but lower than the range for snow samples (Franz and Eisenreich, 1998; Wania et al., 1999) and other urban locations (Birgül et al., 2011 and references therein). The median air concentrations at the oil sands sites were within the range of those reported in literature (Franz and Eisenreich, 1998, Wania et al., 1999; He and Balasubramanian, 2009; Birgül et al., 2011 and references therein).~~

~~The median, mean, and range of the total scavenging ratios (W_t) for the 43 PACs are shown in Table 2. Overall, the median and mean scavenging ratios of the PACs were 3.9 x 10^5 and 4.6 x 10^5, respectively, for snow events. In the rain events, the overall median and mean scavenging ratios were 8.3 x 10^4 and 1.1 x 10^5.~~ The median ~~and mean~~ total scavenging ratios of parent PAHs for snow and rain scavenging were within the range of values reported in literature (~~Tables 3 and 4~~Fig. 4), which typically ranged from 10^3 – 10^7 for snow scavenging (Franz and Eisenreich, 1998; Wania et al., 1999) and 10^2 – 10^6 for rain scavenging (He and Balasubramanian, 2009; Birgül et al., 2011; Škrdlíková et al., 2011). The comparison with literature values applies mainly to parent PAHs due to a lack of literature values for alkylated

PAHs and DBTs. Two orders of magnitude difference in W_t was observed ($8.3 \times 10^4 – 1.2 \times 10^6$) at a coastal-urban site in Singapore (He and Balasubramanian, 2009). The ~~total~~ median total scavenging ratios for PACs also varied by two orders of magnitude ($4 \times 10^2 – 3.1 \times 10^4$) at a suburban location in the Czech Republic (Škrdlíková et al., 2011). At an urban site in Turkey, the average total scavenging ratios for the gas and particle phases ranged from 8.52-8.97 x 10^5 (Birgül et al., 2011). ~~The comparison with literature values apply mainly to the non-alkyl PACs. The median and mean scavenging ratios of each PAC were lower or comparable to those reported in literature.~~ Only the acenaphthylene snow scavenging ratio was 2 to 7 times higher at the oil sands sites than the snow scavenging ratios at other locations.

When the individual snow and rain samples were analyzed (Supplementary Table S3), the snow scavenging ratio for a particular snow sample exceeded the literature values by an order of magnitude for acenaphthylene (March 2011 at AMS11 site), benzo(*b*+*k*)fluoranthene (March 2011 at AMS5 site), benzo(*a*)pyrene (April 2011 at AMS5 site), dibenz(*a*,*h*)anthracene (March 2011 at AMS5 site), benzo(*g*,*h*,*i*)perylene (April 2011 at AMS5 site), and 2-methylphenanthrene (February 2011 at AMS11 site). Scavenging ratios of 10^7 were observed in some snow samples for benzo(*a*)pyrene, dibenz(*a*,*h*)anthracene, and benzo(*g*,*h*,*i*)perylene, which is the higher end for snow scavenging ratios reported in literature. The scavenging ratio for a particular rain sample was an order of magnitude higher than literature values for naphthalene (May 2011 at AMS11 site) and benzo(*a*)pyrene (Dec 2011 at AMS13 site).

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

The scavenging ratios for snow samples were larger for particulate-phase than gas-phase PACs at the oil sands sites. The median total snow scavenging ratios were 8.0 x 10^5 for particulate-phase ~~PACs~~ PAHs and 6.7 x 10^4 for gas-phase ~~PACs~~PAHs ~~(Table 2)~~, which were within those from previous studies (Fig. 4~~Table 3~~). ~~The scavenging ratios were greater for particulate-phase dominant PACs because the concentration of particulate-phase PACs in snow was about 3 times higher than gas-phase PACs, while the air concentration of particulate-phase PACs was about 6 times lower than gas-phase PACs (Table 1). Table 3 shows that the total snow scavenging ratios for the particulate-phase and gas-phase PACs ranged from 6.3 x 10^5-9.8 x 10^6 and 1400-1.4 x 10^6, respectively.~~ These results are ~~also~~ in agreement with the strong relationship between LogW_t and particulate mass fraction of PACs in air (Logφ) (Franz and Eisenreich, 1998; He and Balasubramanian, 2009). According to the regression equation, larger φ or particulate-phase PACs have higher total scavenging ratios than lower φ (or gas-phase PACs). Particulate-phase PACs tend to have higher molecular weights and lower vapor pressure and volatility. Thus, they are more likely bound to particles. The order of magnitude higher scavenging ratio in the individual snow sample for the higher molecular weight PACs at the oil sands sites was likely due to the efficient scavenging of particles by snow. Furthermore, higher molecular weight PACs are typically associated with ultrafine and fine particles (He and Balasubramanian, 2009; Škrdlíková et al., 2011), which have larger scavenging coefficients than medium size particles (Zhang et al., 2013; Wang et al., 2014).

~~Acenaphthylene is predominantly found in the gas-phase in air because~~Gas-phase dominant PACs, like acenaphthylene, have lower molecular weight ~~PACs tend to have~~and higher vapor pressures and therefore are more volatile. However, a small mass fraction in particulate-phase could increase its overall scavenging ratio (W_t) dramatically compared to the pure gas-phase scavenging ratio (W_g) due to the much higher value of W_p than W_g in literature (Fig. 5a). Thus, this may be the reason for the higher snow scavenging ratio of acenaphthylene. The more volatile PACs will likely partition to existing particles of various sizes including large particles (Franz and Eisenreich, 1998; He and Balasubramanian, 2009; Škrdlíková et al., 2011). This typically results in a larger particulate scavenging ratio (W_p) for lower molecular weight PACs like acenaphthylene because large particles are scavenged more efficiently by precipitation ~~than medium size particles~~(Ligocki et al., 1985b). This is also supported by the higher semi-empirical scavenging coefficients of snow for large particles compared to medium size particles (Zhang et al., 2013; Wang et al., 2014). ~~Gas-particle partitioning is a potential explanation for the larger scavenging ratio (by a factor of 2-7) of acenaphthylene at the oil sands sites than those in literature because of the variability in scavenging efficiencies of different particle sizes. Even though the gas fraction of acenaphthylene in air is very large,~~ In a previous study, the gas scavenging ratio (W_g) of acenaphthylene ~~-~~in snow was 385 times smaller than W_p in literature, resulting ~~(Franz and Eisenreich, 1998). This resulted~~ in a larger particle scavenging contribution (74%) to snow than gas scavenging (26%) (Franz and Eisenreich, 1998). In this study however, the concentration of acenaphthylene sorbed to particles in precipitation was not measured at the oil sands sites to estimate W_p and the contribution of particle scavenging of acenaphthylene to snow.

3.3 ~~Comparison~~ Rain scavenging of gas-phase dominant and particulate-phase dominant ~~PACs~~ PACs ~~by rain scavenging~~

Similar to the snow scavenging results, the scavenging by rain was greater for particulate-phase than gas-phase PACs by an order of magnitude. The median W_t was 1.8 x 10^5 for particulate-phase ~~PACs~~ PAHs and 1.1 x 10^4 for gas-phase ~~PACs~~ PAHs~~(Table 2)~~. ~~This difference was attributed to the air concentrations of gas-phase PACs, which was about 11 times higher than the median air concentrations of particulate-phase PACs (Table 1). The higher air concentrations of gas-phase PACs associated with the rain samples is expected because they were collected during the months with higher air temperatures, which increases the volatilization of gas-phase PACs. Meanwhile, the differences in the median concentrations in rain samples between gas-phase and particulate-phase PACs were almost negligible, with values of 27.7 ng/L~~

~~and 26.9 ng/L , respectively.~~ The scavenging ratios were within those reported in literature, which ranged from 5100-1.2 x 10^6 for particulate-phase ~~PACs~~ PAHs and 450-2.8 x 10^5 for gas-phase ~~PACs~~ PAHs (~~Table~~ Fig. 4). The larger W_t of particulate-phase PACs compared to gas-phase PACs is consistent with the empirical relationship between LogW_t and the particulate mass fraction of PACs in air (Logφ) ~~(Table 4)~~ (Franz and Eisenreich, 1998; He and Balasubramanian, 2009), similar to the result for snow. ~~The slopes of the regression equation were similar in the two studies, indicating that the relationship between W_t and φ does not appear to be dependent on the location (He and Balasubramanian, 2009). This relationship suggests that particulate-phase PACs (with larger φ) are associated with larger W_t in rain than gas-phase PACs (with smaller φ), similar to the result for snow.~~

Although the gas-phase PACs have very low particulate mass fraction in air, ~~Table 4~~Fig. 5b illustrates that the particulate scavenging ratios (W_p) can be 1-4 orders of magnitude larger than the theoretical and measured gas scavenging ratios (W_g) in literature. Similar to snow scavenging, it has led to larger particulate scavenging contribution of gas-phase PACs to rain than gas scavenging. For particulate-phase PACs, W_p and W_g for both rain and snow scavenging were more comparable in the literature (up to 1 order of magnitude difference, Fig. 5). Thus, the particle scavenging contribution to snow and rain will dominate the gas scavenging contribution because of the larger particle fraction. The data needed to determine W_p and W_g were not available at the oil sands sites to confirm literature findings and estimate the relative gas and particle scavenging contributions to rain. In previous studies, the contributions of particle scavenging to rain were 99.41-99.99% for gas-phase PACs and 86.35-99.58% for particulate-phase PACs (He and Balasubramanian, 2009). In comparison, the contributions from gas scavenging were estimated to be up to 0.59% for gas-phase PACs and 13.7% for particulate-phase PACs (He and Balasubramanian, 2009). In a different study, the contribution of particle scavenging to rain for gas-phase PACs (17-59%) were lower than particulate-phase PACs (97-

100%) (Škrdlíková et al., 2011). Higher volatility PACs, such as acenaphthylene and anthracene, were associated with larger particles, whereas non-volatile PACs tend to be associated with smaller particles (Škrdlíková et al., 2011). ~~As discussed in section 3.2, the more volatile PACs are likely to partition to the particulate phase, while less volatile PACs will likely remain bound to the particles emitted from primary sources.~~ Based on predicted scavenging coefficients for rain, the scavenging of very large particles (> 6 µm) is more efficient than fine and ultrafine particles (Wang et al., 2014).

The higher scavenging ratio for naphthalene in the individual rain sample at the oil sands sites compared to literature must be attributed to gas scavenging, since $\varphi = 0$ for naphthalene resulting in $W_t = W_g$. Gas scavenging can occur by dissolution of gaseous PACs to the surface of raindrops. The gas scavenging ratio from the dissolution process ($W_{g,diss}$) depends on temperature-corrected Henry's Law constant, temperature, and the universal gas constant (Franz and Eisenreich, 1998). Another theory is the gas scavenging by vapor adsorption to the surface of raindrops. This scavenging ratio ($W_{g,ads}$) can be determined from the air-water interface coefficient and diameter of raindrops (Simcik, 2004; He and Balasubramanian, 2009). However, the theoretical W_g for naphthalene reported in literature was only 24.5 (~~Table 4~~Fig. 5b), which is 10^5 times lower than the measured W_g in the individual rain sample at the oil sands sites. The differences between measured W_g at the oil sands site and theoretical W_g in literature for naphthalene may be attributed to the different cloud and precipitation characteristics and are considered the major sources of uncertainties for precipitation scavenging (Galloway, 1993; Franz and Eisenreich, 1998).

3.4 Comparison of PAC snow and rain scavenging ~~for gas-phase dominant PACs~~processes

Overall, t~~T~~he ~~median~~ snow scavenging ratio of gas-phase and particulate-phase PACs ~~(6.7 x 10^4) was~~ were greater than that for rain scavenging ~~(1.1 x 10^4)~~. Median total scavenging ratios over the period of data analyzed were 6100 to 1.1x10^6 from snow scavenging and 350 to 2.3x10^5 from rain scavenging depending on the PACs. ~~Similarly, for the particulate-phase PACs, snow scavenging ratios are higher than rain scavenging ratios. The median scavenging ratios for snow and rain were 8.0 x 10^5 and 1.8 x 10^5, respectively, for all precipitation events (Table 2)., which is also observed in previous studies.~~ Since snowfall and rainfall intensities potentially affect precipitation scavenging, comparisons between snow and rain scavenging should be conducted between snow and rain samples associated with similar precipitation intensity (Zhang et al., 2013; Wang et al., 2014). Based on selected snow and rain events with similar precipitation rates (snow: 11.6-11.8 mm/month, rain: 10.8-12.3 mm/month), the median snow and rain scavenging ratios for gas-phase PACs were 1.2 x 10^5 and 8300, respectively. The median snow scavenging ratios for particulate-phase PACs was 40 times greater than that for rain for similar precipitation rates (snow: 11.6-11.8 mm/month, rain: 10.8-12.3 mm/month). For another set of snow and rain events (e.g, snow: 13.0-15.3 mm/month, rain: 13.2-16.5 mm/month) at a different oil sands site, the median snow scavenging ratio for particulate-phase PACs was only 2 times larger than that for rain. ~~For gas-phase PACs, the total snow and rain scavenging ratios reported in literature ranged from 1400-1.4 x 10^6 and 450-2.8 x 10^5, respectively (Tables 3 and 4). Based on the data in Table 1, the overall median concentrations of gas-phase dominant PACs in snow and rain were 208.2 ng/L and 27.7 ng/L, respectively, which is ~7.5 times higher concentration in snow. The median air concentration of gas-phase PACs associated with snow samples was only slightly lower than the rain samples. Since snowfall and rainfall intensities potentially affect precipitation scavenging, comparisons between snow and rain scavenging should be conducted between snow and rain samples associated with similar precipitation intensity (Zhang et al., 2013; Wang et al., 2014). Based on selected snow and rain events with similar precipitation rates (snow: 11.6-11.8 mm/month, rain: 10.8-12.3 mm/month), the median snow and rain scavenging ratios for gas-phase PACs were 1.2 x 10^5 and 8300, respectively. For~~

~~gas-phase PACs, the total snow and rain scavenging ratios reported in literature ranged from 1400-1.4 x 10^6 and 450-2.8 x 10^5, respectively (Tables 3 and 4).~~

Potential explanations for the efficient snow scavenging of gas-phase PACs have been proposed in previous studies. Franz and Eisenreich (1998) had observed a stronger correlation between measured gas scavenging ratios and those calculated from gas scavenging by dissolution for snow events than rain events. In this study, a moderate correlation ($r = -0.5$) was observed between Henry's Law constant based on experimental and theoretical values (Reid et al., 2013) and total snow scavenging ratios of gas-phase PACs, which suggests some influence of gas scavenging by dissolution for snow samples. No relationship between the Henry's Law constant and total scavenging ratios was observed for rain samples, and might be due to a lack of temperature-corrected Henry's Law constants (Ligocki et al., 1985a)~~.~~ ~~This suggests that some of the less volatile gas-phase PACs (i.e. lower Henry's Law constant in Pa m^3/mol units) is associated with higher total snow scavenging ratios~~. ~~But t~~The water solubility of the gas-phase PACs had almost no effect on the total scavenging ratios in snow and rain ($r < 0.02$) likely because organic compounds are only slightly water soluble. This further implies that there is another mechanism involved in the gas scavenging of gas-phase PACs besides the dissolution process or that particle scavenging makes a larger contribution to the total wet deposition of gas-phase PACs.

~~Given the relationship between Henry's Law constant and water solubility, an effective Henry's Law constant as described in Zhang et al. (2002) may be a more suitable parameter for comparison with the total scavenging ratios because it combines vapor pressure, solubility, and dissociation in water into one parameter.~~

~~Although the scavenging of gas-phase PACs by dissolution can occur in rain and snow, the process is more efficient for large raindrops than snow because the liquid water film on the snow surface can be very thin (Franz and Eisenreich, 1998).~~ Snow scavenging of gaseous PACs may be better modelled by surface or interfacial adsorption ($W_{g,ads}$). ~~Franz and Eisenreich (1998) obtained $W_{g,ads}$ ranging from 10^3 to 10^{10} for the snow events.~~ Measured Log(W_g) were strongly correlated with theoretical Log($W_{g,ads}$) for snow events, but not correlated in the rain events. This indicates that interfacial adsorption likely occurred in the snow events (Franz and Eisenreich, 1998). Wania et al. (1999) proposed that the scavenging of gas phase PACs likely occurred by adsorption to the air-ice interface because W_g was a strong function of both the partition coefficient for the air-ice interface and vapor pressure of the supercooled liquid. It suggests that snow scavenging of gas-phase PACs is potentially the dominant scavenging process for lower molecular weight or predominantly gas-phase PACs (Wania et al., 1999). Compared to snow scavenging, rain scavenging of gas-phase PACs yielded much lower scavenging ratios in field and theoretical studies. For gas phase PACs, W_g derived from field measurements ranged from 160-3300, while the ranges for W_g due to dissolution and surface adsorption scavenging were only 24.3-710 and 0.2-21.4, respectively (~~Table 4~~Fig. 5b). Thus, the scavenging of gas-phase PACs by surface adsorption is evidently much lower for rain than snow and may explain the difference in snow and rain scavenging ratios at the oil sands sites.

~~The ratio of the maximum to minimum W_t for snow and rain scavenging of the gas-phase dominant PACs ranged from 2.4-14.6 and 1.4-10.8, respectively, based on snow and rain events with similar amounts of precipitation (Fig. 3a). Both gas and particle scavenging are relevant to the total wet deposition of gas-phase PACs and both contribute to the uncertainties in W_t. The uncertainties in the snow scavenging of gas-phase PACs were larger than those of rain scavenging in this study. The uncertainties from gas scavenging by snow can be very large as shown in the estimated W_g for the interfacial adsorption process (10^3 to 10^{10}, Franz and Eisenreich, 1998). Field measurements of W_g can also be 0.43-20 times greater than the theoretical W_g for snow scavenging (Franz and Eisenreich, 1998). There are several factors that can contribute to the uncertainties of measured W_g, such as the higher than expected dissolved~~

~~concentration of gas-phase PACs due to the presence of colloids in the filtrate (Franz and Eisenreich, 1998; He and Balasubramanian, 2009) and the repartitioning of dissolved PAHs to particles in snowmelt (Wania et al., 1999). The unfiltered submicron particles in the filtrate led to a measured W_g that was 100 times larger than the theoretical estimate (Poster and Baker, 1995a, b). The W_g estimated by Wania et al. (1999), which accounts for the repartitioning of dissolved PAHs to particles, were 2-5 times higher than those measured by Franz and Eisenreich (1998) for the same set of snow events. The adsorption of gas-phase PACs to the snow surface could also be enhanced by the presence of an organic layer (Franz and Eisenreich, 1998). Differences in the snow and rain properties are also contributing factors to the gas scavenging uncertainties.~~

Besides gas scavenging, gas-phase PACs typically have very large particulate scavenging ratios (W_p) because they are more likely to partition to particles. For snow events, W_p can be 15-385 times larger than measured W_g in literature for gas-phase PACs ~~(Table 3)~~. For rain events, W_p ranged from 5.5 x 10^3-2.7 x 10^7, while theoretical and measured W_g ranged from 25-3300 in literature ~~(Table 4)~~. Therefore, even though gas-phase PACs have very low particulate mass fraction in air, the particle scavenging contribution to snow and rain can still be important because ~~the particle scavenging ratios~~W_p can be much greater than the ~~gas scavenging ratios~~W_g. Furthermore, the snow samples are associated with lower air temperatures, which may increase the partitioning of gas-phase PACs to the particulate phase (Pankow, 1991; Cousins et al., 1999). The average and standard deviation of the air temperatures corresponding to snow and rain samples were -8.6±7.2 ^oC and 8.9±8.6 ^oC, respectively, with an average temperature difference of 17.5 ^oC. As shown in Fig. 2, the average particulate mass fraction corresponding to snow samples were 2.5-4 times higher than those of rain samples for phenanthrene and anthracene. The combination of higher W_p and particulate mass fraction would yield higher total snow scavenging ratios. Particulate mass fractions for alkylated fluorenes, DBT, and C1/C2-DBTs during cold temperatures were also higher. Almost no differences in the particulate mass fractions between snow and rain samples were observed for the other parent gas-phase dominant PAHs.

Particle scavenging ratios for PACs in snow events were also observed to be larger than rain events. Average W_p ranged from 10^5-10^6 for the snow events and 10^3-10^4 for the rain event for particulate-phase PACs (Franz and Eisenreich, 1998). Snow is more efficient than rain at scavenging particles because of its larger surface area (Franz and Eisenreich, 1998). The relative scavenging efficiency between snow and rain depends on particle sizes and precipitation intensity (Wang et al., 2014). For particulate-phase PACs which are likely associated with ultrafine and fine particles, the snow scavenging coefficient is predicted to be ~10 times larger than the rain scavenging coefficient at low precipitation rates (Wang et al., 2014). The temperature dependence of the particulate mass fractions can also explain the larger total scavenging ratios for snow than those for rain. The average particulate mass fractions associated with snow samples were 1-14% higher than in rain samples among the particulate-phase dominant PACs (Fig. 2). This is likely because at lower temperatures the vapor pressures of PACs in the particulate phase would be even lower, which causes them to remain bounded to particles.

~~The efficient snow scavenging of particles will be discussed further in the next section on particulate-phase dominant PACs because it is largely dependent on the particle size distribution. Since gas-phase dominant PACs are likely bound to large particles as shown in previous studies, the scavenging coefficient uncertainties for large particles are expected to be a factor of 10 smaller than those for medium size particles (Zhang et al., 2013).~~

~~3.5 Comparison of snow and rain scavenging for particulate-phase dominant PACs~~

~~Overall, more efficient scavenging of particulate-phase PACs by snow were observed at the oil sands sites and can be attributed to the higher median concentrations of particulate-phase PACs in snow than in rain. The median concentrations in snow and rain samples were 635.7 ng/L and 26.9 ng/L, respectively, among the particulate-phase PACs (Table 1). No differences in the air concentrations were observed between snow and rain samples. These values were within the ranges of total scavenging ratios reported in literature, which were 6.3 x 10~~^{5}~~-9.8 x 10~~^{6} ~~for snow and 5100-1.2 x 10~~^{6} ~~for rain scavenging (Tables 3 and 4). Since the gas and particle scavenging ratios of particulate-phase PACs were more comparable (up to a factor of 10 difference in literature, Table 4), the particle scavenging contribution to snow and rain will dominate the gas scavenging contribution because of the larger particle fraction. Unlike gas-phase PACs, particulate-phase PACs have lower volatility and will likely remain in the particle phase. Thus, it is sufficient to examine only the~~ W_p ~~when comparing the snow and rain scavenging of particulate-phase PACs. Franz and Eisenreich (1998) observed higher particle scavenging ratios for PACs in snow events than rain events. Average~~ W_p ~~ranged from 10~~^{5}~~-10~~^{6} ~~for the snow events and 10~~^{3}~~-10~~^{4} ~~for the rain event for particulate-phase PACs. The temperature dependence of the particulate mass fractions can also explain the larger total scavenging ratios for snow than those for rain. The average particulate mass fractions associated with snow samples were 1-14% higher than in rain samples among the particulate-phase dominant PACs (Fig. 2). This is likely because at lower temperatures the vapor pressures of PACs in the particulate phase would be even lower, which causes them to remain bounded to particles.If only snow and rain events with similar precipitation rates are considered (e.g, snow: 11.6-11.8 mm/month, rain: 10.8-12.3 mm/month), the median snow scavenging ratio turned out to be 40 times greater than that for rain. For another set of snow and rain events (e.g, snow: 13.0-15.3 mm/month, rain: 13.2-16.5 mm/month) at a different oil sands site, the median snow scavenging~~

~~ratio was only 2 times larger than that for rain. Snow is more efficient than rain at scavenging particles because of its larger surface area (Franz and Eisenreich, 1998). The relative scavenging efficiency between snow and rain depends on particle sizes and precipitation intensity (Wang et al., 2014). For particulate-phase PACs which are likely associated with ultrafine and fine particles, the snow scavenging coefficient is predicted to be ~10 times larger than the rain scavenging coefficient at low precipitation rates (Wang et al., 2014).~~

~~The uncertainties in snow scavenging of particulate-phase PACs were larger than those for rain scavenging as shown in the range of scavenging ratios for snow and rain events with similar precipitation rates (Fig. 3b). The ratio of the maximum to minimum snow and rain scavenging ratios were up to 10 and 4.3, respectively, which were within the range of semi-empirical scavenging coefficients. For small particles (<0.01 μm) which particulate-phase PACs are typically bound to, Zhang et al. (2013) predicted the range of scavenging coefficients are up to two orders of magnitude for snow and one order of magnitude for rain. Measurements are needed to confirm the particle size distribution of particulate-phase PACs because scavenging coefficient uncertainties for medium size particles are predicted to be at least a factor of 10 larger than small and large particles (Zhang et al., 2013). Aside from particle sizes, the variability and uncertainties in the scavenging ratios could be due to the properties of snow and raindrops, such as snow shape and size of raindrops (Zhang et al., 2013). For example in snow, the porosity of snowflakes and dendrites is considered effective for capturing small particles while allowing air to pass through (Franz and Eisenreich, 1998).~~

3.5 Role of alkylation and PAC physico-chemical properties on snow and rain scavenging

Alkylated naphthalenes, fluorenes, phenanthrenes/anthracenes, fluoranthenes/pyrenes, benz(*a*)anthracenes/triphenylenes/chrysenes, and DBTs were measured at the three oil sands sites. For most of these PACs except for naphthalenes, total snow and rain scavenging ratios increased with the degree of alkylation (Fig. 6). These trends appeared to have some relationship with their physico-chemical properties, such as Henry's Law constant, octanol-air partition coefficient (K_{oa}), subcooled vapor pressure (p^0_L), water solubility, and particulate mass fraction (φ) and gas-particle partition coefficient (K_p), obtained from Reid et al. (2013). For naphthalene, the snow and rain W_t for parent naphthalene was much higher than alkylated napthalenes. With increase alkylation, snow and rain W_t decreased. This trend is consistent with the increase in Henry's Law constant (Pa m^3/mol), which leads to lower gas scavenging by dissolution (Franz and Eisenreich, 1998). This is further supported by the decrease in water solubility with increase alkyl substitutions. The large decrease in water solubility from parent napthalene to C1 napthalene is also reflected in the W_t.

The other physico-chemical properties play a more prominent role in the precipitation scavenging of other alkylated PACs. For fluorenes and alkylated phenanthrenes/anthracenes, snow and rain W_t increased with alkylation. This trend is consistent with an increase in K_{oa}, φ, and K_p as the number of alkyl substitutions increase. These physic-chemical properties are related to gas-particle partitioning (Pankow, 1994; Harner and Bidleman, 1998), which leads to a larger particulate mass fraction and thus, higher W_t. The large increase in K_{oa} from C3 to C4 fluorene corresponds to the large increase in W_t. p^0_L is another physical property affecting gas-particle partitioning (Pankow, 1994), but is also related to snow scavenging of gas-phase PACs by interfacial adsorption. As p^0_L decreases with alkyl substitutions, the interfacial adsorption coefficient (K_{ia}) increases (Franz and Eisenreich, 1998). This results in higher contribution of gas scavenging by snow to the total scavenging ratio. The physico-chemical properties that have the most influence on the precipitation scavenging on alkylated fluoranthenes/pyrenes and benz(*a*)anthracenes/triphenylenes/chrysenes are φ and K_p because these are particulate-phase dominant PACs. Thus, particle scavenging contributions will dominate the total wet deposition of these PACs. φ and K_p are predicted to increase with alkylation. The increase in W_t with alkyl substitutions is likely attributed to the increase in particulate mass fraction. For DBTs, the degree of alkylation increased the rain W_t, but did not have a large effect on snow W_t. The trend in W_t for rain is consistent with the increase in K_{oa}, φ, and K_p, which are properties affecting gas-particle partitioning. The decrease in p^0_L with increasing alkyl substitutions should result in an increase in gas scavenging by snow (due to adsorption on the air-ice interface); however, this was not reflected in the snow W_t.

3.6 Uncertainties in snow and rain scavenging

The ratio of the maximum to minimum W_t for snow and rain scavenging of the gas-phase dominant PACs ranged from 2.4-14.6 and 1.4-10.8, respectively, based on snow and rain events with similar amounts of precipitation (Fig. ~~3~~7a). ~~Both gas and particle scavenging are relevant to the total wet deposition of gas-phase PACs and both contribute to the uncertainties in W_t. The uncertainties in the snow scavenging of gas-phase PACs were larger than those of rain scavenging in this study.~~ The uncertainties from gas scavenging by snow can be very large as shown in the estimated W_g for the interfacial adsorption process (10^3 to 10^{10}, Franz and Eisenreich, 1998). Field measurements of W_g can also be 0.43-20 times greater than the theoretical W_g for snow scavenging (Franz and Eisenreich, 1998). There are several factors that can contribute to the uncertainties of measured W_g, such as the higher than expected dissolved concentration of gas-phase PACs due to the presence of colloids in the filtrate (Franz and Eisenreich, 1998; He and Balasubramanian, 2009) and the repartitioning of dissolved PAHs to particles in snowmelt (Wania et al., 1999). The unfiltered submicron particles in the filtrate led to a measured W_g that was 100 times larger than the theoretical estimate (Poster and Baker, 1995a, b). The W_g estimated by Wania et al. (1999), which accounts for the repartitioning of dissolved PAHs to particles, were 2-5 times higher than those measured by Franz and Eisenreich (1998) for the same set of snow events. The adsorption of gas-phase PACs to the snow surface could also be enhanced by the presence of an organic layer (Franz and Eisenreich, 1998).

Differences in the snow and rain properties are also contributing factors to the gas scavenging uncertainties.

The uncertainties in snow scavenging of particulate-phase PACs were larger than those for rain scavenging as shown in the range of scavenging ratios for snow and rain events with similar precipitation rates (Fig. ~~3~~7b). The ratio of the maximum to minimum snow and rain scavenging ratios were up to 10 and 4.3, respectively, which were within the range of semi-empirical scavenging coefficients. For small particles (<0.01 µm) which particulate-phase PACs are typically bound to, Zhang et al. (2013) predicted the range of scavenging coefficients are up to two orders of magnitude for snow and one order of magnitude for rain. Measurements are needed to confirm the particle size distribution of particulate-phase PACs because scavenging coefficient uncertainties for medium size particles are predicted to be at least a factor of 10 larger than small and large particles (Zhang et al., 2013). Aside from particle sizes, the variability and uncertainties in the scavenging ratios could be due to the properties of snow and raindrops, such as snow shape and size of raindrops (Zhang et al., 2013). For example in snow, the porosity of snowflakes and dendrites is considered effective for capturing small particles while allowing air to pass through (Franz and Eisenreich, 1998).

3.~~6~~ 7 Limitations and uncertainties of scavenging ratios

As discussed in the last section, particle size distribution and snow and rain characteristics may contribute to the uncertainties in precipitation scavenging of PACs. The scavenging ratio parameter itself also has limitations and uncertainties due to the oversimplification of the precipitation scavenging process. For example in snow scavenging, it is assumed that the snow scavenging of gaseous PACs contributed only to the dissolved phase, while PACs bound to particulate matter would stay in the particulate phase in snowmelt (Franz and Eisenreich, 1998; Wania et al., 1999). Hence, the fraction of PACs sorbed to particles in snowmelt was assumed to be the same as that in snow. Wania et al. (1999) proposed that the scavenging of gaseous PACs in snow would be important if dissolved PACs in snowmelt re-partitioned to particles in snowmelt. If this occurred, the fraction of PACs sorbed to particles in snowmelt would be greater than that in snow. Wania et al. (1999) re-analyzed the data used in Franz and Eisenreich (1998) and obtained much higher gas scavenging ratios ~~(Table 3)~~. ~~The study suggests gas scavenging by snow is potentially the dominant scavenging process for lower molecular weight PACs.~~ The large variability in the total scavenging ratios (e.g., 4-5 order of magnitude range for PACs) may be attributed to numerous factors that could not be accounted for in the scavenging ratios, such as particle size distribution, droplet sizes, cloud and precipitation type, and air mass trajectories (Duce et al., 1991; Galloway et al., 1993). ~~Particle scavenging ratios between different chemicals may be comparable as long as they are associated with particles around the same size (Duce et al., 1991; Franz and Eisenreich, 1998).~~ To minimize the variability, an average of a number of scavenging ratios should be determined over a longer time period instead of individual precipitation events (Duce et al., 1991; Galloway et al., 1993). In this study, the majority of the results were based on the median scavenging ratios from at least 14-15 monthly snow and rain samples. The scavenging ratio concept also assumes that the air concentrations measured near the surface are representative of the concentrations in the cloud, where in-cloud scavenging may occur.

4. Conclusions

A database of scavenging ratios was developed for the 43 PACs monitored in air and precipitation samples at the Athabasca oil sands region. Overall, the median total scavenging ratios of most PACs, except for acenaphthylene, were within the range of scavenging ratios reported in literature. Total scavenging ratios for some individual snow and rain samples exceeded literature values by a factor of 10. In some cases, snow scavenging ratios of 10^7 were observed for benzo(*a*)pyrene, dibenz(*a*,*h*)anthracene, and benzo(*g*,*h*,*i*)perylene, which is considered the upper limit for PAH scavenging ratios reported in literature. The large range in scavenging ratios associated with samples of similar precipitation amounts implies the large natural variability and/or uncertainties in precipitation scavenging processes. Total snow and rain scavenging ratios increased with the number of alkyl substitutions for some PACs, which were consistent with the trends in their physico-chemical properties, such as subcooled vapour pressure and octanol-air and particle partition coefficients. Henry's Law constant and water solubility might play a role in the decrease in snow and rain scavenging ratios for naphthalene with increase alkyl substitutions.

The database of scavenging ratios was also separated into subgroups to investigate the relative importance of gas and particle scavenging by snow and rain. It was found that snow scavenging is around 10 times more efficient (in terms of the scavenging ratio values) than rain scavenging for both particulate-phase dominant and gas-phase dominant PACs. It was also found that scavenging of particulate-phase dominant PACs is 5 to 10 times more efficient than scavenging of gas-phase dominant PACs under both rain and snow conditions. These findings suggest that snow scavenging of particulate-phase PACs should contribute significantly to the total wet deposition of PACs in this region.

The database of PAC scavenging ratios (Supplementary Table S3) could be used in future studies to predict the wet deposition flux at passive air monitoring sites in the Athabasca oil sands region. The total wet deposition flux is defined as the product of the total scavenging ratio, total air concentration, and precipitation rate (Duce et al., 1991; Sakata and Asakura, 2007). Although the uncertainties can be large because the factors affecting precipitation scavenging can vary with location, it may be a reasonable approach to provide a first-order estimation of wet deposition using the scavenging ratio concept. Detailed deposition budget of all the monitored PACs at the passive air monitoring sites will be investigated in a separate study ~~using knowledge generated from the present study~~.

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