Dear Prof. Bertram,

We have further revised the paper and addressed all the comments provided by the additional reviewer. 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.

Sincerely,

Leiming Zhang and coauthors

Response to Reviewer

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

General comments:

The present study investigated the scavenging ratios of PACs in rainfall and snow at an oil sands region. It provides a set of comprehensive and scientifically sounding data for future assessment of PAC emission from oil sands areas. Given some chemicals such as alkylated PAHs have not been well studies in previous reports, this work is very important for future studies on PACs. The observation verified previous assumption that the scavenging ratios in snow exceed those in rain, which can be regarded as the innovative finding of this manuscript. The discussion is based on previous knowledge on PAC scavenging. As section 3.6 and 3.7 stated, there are some uncertainties haven't addressed yet. Also, some issues should be discussed clearly in the manuscript.

Response: We have improved discussions on uncertainty analysis in sections 3.6 and 3.7 in the revised paper as recommended by the reviewer. We agree that some of uncertainties cannot be addressed quantitatively due to the limited knowledge and/or unavailability of data. We also like to point out that some of the uncertainties pointed out by this reviewer do not directly impact the results of our study because total scavenging ratios were determined from bulk precipitation and air concentrations. Detailed explanations are provided below.

Method

Section 2.1.2

"The wet deposition sampler does not include a filter unit for separating the particulate phase from the dissolved phase in precipitation."

The authors also mentioned the repartitioning problem in the following section. If the sampler can't separate the two phases, the uncertainties may influence the final results on scavenging.

Response: Please note that the total scavenging ratio calculated in this study is not based on separate measurements of gas- and particulate-phase PACs. Instead, total scavenging ratios were generated from bulk air concentrations and bulk precipitation concentrations. This is a standard measurement approach for wet only sampling which is also used by other precipitation monitoring programs, e.g. Integrated Atmospheric Deposition Network. When discussing the relative importance of gas-particulate-phase scavenging, the dataset was stratified into two groups; one is gas-phase dominant PACs and the other is particulate-phase dominant PACs. Thus, the uncertainties due to the measurements limitation referred by this reviewer should have minimal impact on the total scavenging ratio results.

Also, is there any measurement to prevent the exchange between air and XAD resin during each sampling procedure?

Response: The air exchange is very limited because the funnel is covered except during precipitation events and a U-shaped siphon on the XAD column outlet maintains water in the column at all times i.e.

no air flows through. This information has been added in the revised paper in section 2.1.2. This is standard operating procedure for the MIC instruments when equipped with resin columns.

The sampling volume of air sampler is large, which may lead to breakthrough. I noticed that a pair of PUF plugs was applied. Do the authors test the two PUF plugs separately? Is there any breakthrough, especially for those low molecular weight compounds like NAP?

Response: Breakthrough of the primary PUF to the backup PUF for gas-phase PACs is expected because of the large volume of air sampled. Therefore, a pair of PUF plugs was applied and analyzed. Although there is breakthrough of gas-phase PACs, optimal air sampling flow rates were used to minimize breakthrough. The mass of NAP on the backup PUF was 59% ± 2% of the total mass on the pair of PUF for air sampling volumes ranging from 595-810 m^3 at 25^oC. For the majority of the gas-phase dominant PACs (e.g., sum of acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and 2-methylfluorene), the average and standard deviation of the percent breakthrough was only 15% ± 7%. These breakthrough evaluation results will be included in the revised paper.

Section 2.1.4

"Samples with surrogate recoveries beyond this range were excluded from the calculation of scavenging ratios."

The recoveries of d8-NAP were lower than other compounds. Did the authors use those recoveries to correct alkylated NAP? Is that reasonable considering the physicochemical properties of them are different? The reported detection limits refers to method detection limits (MDLs) or instrumental detection limits (IDLs)? According to the units, it seems to be IDLs, so how about MDLs?

Response: Deuterated alkyl-PAC standards are not available from our laboratories. This is why parent PACs are still being used to calculate recoveries for each group of PACs even though the physicochemical properties for alkylated PACs are different from the parent PACs. The reported detection limits in the paper referred to the instrument detection limits. The range of the MDL has been added in the revised paper.

Results and Discussion

Section 3.4

"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." The authors have already mentioned that the snow samples are associated with lower air temperatures, which may increase the partitioning of gas-phase PACs to the particulate phase. So they shouldn't neglect the effect of temperature on the environmental behavior of PACs. Relevant data can refer the Hand Book of Physical-Chemical properties and Environmental Fate for Organic Chemicals. Although the information is limited, temperature-dependence of the Henry's Law constant and other physical-chemical properties of some PAHs is included. After checking those date, the statement of no relationship between the Henry's Law constant and total scavenging ratios will be better. Also, that information will help authors to illustrate their ideas in section 3.5, such as the decrease in water solubility or particulate mass fraction with increase alkyl substitutions.

Response: In the revised paper, correlations between the total scavenging ratios and temperature-corrected Henry's Law constant and water solubility of gas-phase PACs based on the equations in the

Handbook (Mackay et al., 2006) and theoretical values (Reid et al., 2013) are presented. Henry's Law constant and water solubility temperature-dependence equations were available for most parent PACs (except for acenaphthylene) and only a few alkyl naphthalenes. Therefore, we used the theoretical values from Reid et al. (2013) for most of the alkyl PACs and DBTs.

Weak correlations were observed between temperature-corrected Henry's Law constant (Pa m^3/mol) based on experimental data (Mackay et al., 2006) and theoretical values (Reid et al., 2013) and the total snow ($r = -0.36$) and rain ($r = -0.20$) scavenging ratios of gas-phase PACs, which suggest only minor influence of gas scavenging by dissolution. Correlation coefficients improved between water solubility of the gas-phase PACs and total rain scavenging ratios ($r = 0.56$) when temperature-corrected water solubility were analyzed, but not for total snow scavenging ratios. For the alkylated PAC discussion in section 3.5, temperature-dependence equations were only available for Henry's Law constant and water solubility for 1-methylnaphthalene and 1-ethylnaphthalene; thus, the temperature-dependence data do not cover all compounds of C1 or C2 naphthalenes. Furthermore, since analyte groups were measured for some of the alkylated PACs (e.g., fluoranthenes/pyrenes, phenanthrenes/anthracenes, and benz(*a*)anthracenes/triphenylenes/chrysenes), the temperature-dependence equations for the individual analytes are likely not applicable.

Some grammar error should be checked carefully. For example, P24, Zhang et al. (2013) predicted *that* the range of scavenging coefficients are up to two orders of magnitude for snow and one order of magnitude for rain.

Response: We have proofread the paper for grammar errors.

Section 3.6

Due the limitation of method, some problems can't be well discussed, such as the effect of temperature, colloids, repartitioning and properties of particles. Therefore the application of reported scavenging ratios seems to be limited at similar areas like oil sand region.

Response: A lack of data related to colloids in the filtrate of precipitation samples, repartitioning of dissolved PACs to particles in precipitation and particle properties (e.g. size distribution) prevented us from studying how these factors affect the uncertainties in scavenging ratios. In the revised paper, more discussion will be provided on whether air temperature affected the uncertainties of the total scavenging ratios in snow and rain samples (Fig. 7a and 7b) in section 3.6, since this data is available. As discussed in section 3.4, we found that the average particulate mass fraction corresponding to snow samples were 2.5-4 times higher than those of rain samples for phenanthrene and anthracene, which suggest the lower air temperatures increased the partitioning of some gas-phase PACs to the particulate phase. Therefore, temperature could affect the uncertainties in snow and rain scavenging.

A potential application of the reported scavenging ratios is the estimation of wet deposition in the Athabasca oil sands region. This application is spatially limited to this region because there are many factors that can affect wet deposition of PACs, which are likely location dependent (discussed in section 3.7). In this study however, the total scavenging ratios for snow and rain were within the range of those typically reported in previous studies, which were conducted in non-oil sands locations, such as urban, suburban, and rural sites. This comparability suggests that the scavenging ratios data, especially for those species that were not studied previously, are useful for applications elsewhere.

SI: The concentrations of some compounds were 0 while some were blank. Do the authors mean that blank was compounds cannot be quantified (no peak) and 0 is below method detection limits, or the concentration was below 0 after blank correction? Blank correction will influence the results of the compounds with high background (or blank) concentrations such as NAP, which will finally underestimate the values.

Response: The zero concentrations were instrument detection limits (IDL). The blank entries in the tables referred to weekly samples with surrogate recoveries below 50% or above 150% within a month, which were excluded from the total scavenging ratio calculation. No samples were collected in Jan 2011 at AMS5; therefore, the blank entries were replaced by a dash. In the revised paper, the zeroes will be replaced by IDL and we will indicate what the blank entries represent.

The data were blank corrected using an average blank from a batch of samples. The blanks from the air samples (PUF + filter) for naphthalene and alkylated naphthalene were typically higher than other PACs. For naphthalene, the average ± standard deviation of the blanks was 0.45 ± 0.26 ng/m^3 in this study, which were slightly higher than those reported by He and Balasubramanian (2009) (0.15 ± 0.07 ng/m^3). The air and precipitation concentrations and total scavenging ratios in this study were compared with those from previous studies, which had applied blank corrections to their samples as well. Applying similar quality control procedures ensure that the comparison of the results is consistent.

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 January 2011 to May 2012 were used to generate a database of scavenging ratios (W_t) for PACs scavenged by both snow and rain. Higher concentrations in precipitation and air were observed for alkylated PAHs and 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.

Median W_t over the measurement period were 6100-1.1x10^6 from snow scavenging and 350-2.3x10^5 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 increases 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 (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.

The Athabasca oil sands industry in northern Alberta, Canada is known to release significant amounts of 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 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 paper.

2. Methods

2.1 Data collection

2.1.1 Description of sampling sites

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. The wet sampler is also equipped with a U-shaped siphon on the XAD-2 column outlet that maintains water in the column at all times; thus preventing air exchange. This is also minimized by covering the funnel where precipitation is collected except during precipitation events. 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. Two PUF plugs were implemented because of potential breakthrough of low molecular weight PACs. 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 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 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 and PUF plug 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, 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, 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).

2.1.4 Quality control and quality assurance

Field blanks were collected for 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~~GFF and a pair of ~~polyurethane foam~~PUF plugs that ~~is~~ are 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. Breakthrough tests were conducted on pairs of PUF plugs. The mass of naphthalene on the backup PUF was 59% ± 2% of the total mass on the pair of PUF plugs for air sampling volumes ranging from 595-810 m^3 at 25^0C. However for most of the gas-phase dominant PACs (e.g., sum of acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and 2-methylfluorene), the average and standard deviation of the percent breakthrough was only 15% ± 7%. 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 for parent PACs are shown in Table 1. Samples were corrected for surrogate recoveries if they were within 50-150%. Parent PACs were used to calculate recovery percentages for alkylated PACs as well because deuterated alkyl PAC standards are not available from our laboratories. Samples with surrogate recoveries beyond this range were excluded from the calculation of scavenging ratios. ~~Detection~~ Instrument detection limits and method detection limits for the target analytes in air samples ranged from 0.1 to 2 pg/µl injection and 4.0 to 839.7 ng/sample, respectively. ~~for air and~~ Method detection limits for the target analytes in precipitation samples were determined to be the same as the instrument detection limits, which ranged from 0.4 to 20 ng. ~~for precipitation.~~

2.2 Data analysis

The scavenging of gaseous and particulate PACs by rain and snow have been studied using scavenging 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.

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 2 January 2011 and 31 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~~ by 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 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).

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).

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. The sum of the median precipitation concentrations measured between January 2011 and May 2012 was 0.48 µg/L for PAHs, 3.38 µg/L for alkylated PAHs, and 0.94 µg/L for DBTs. The PAHs that ~~contributing~~ contributed 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.

Air concentrations of alkylated PAHs ~~are~~ were 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 were 8.37 ng/m^3, 67.26 ng/m^3, and 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 median total scavenging ratios of parent PAHs for snow and rain scavenging were within the range of values reported in literature (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 ($8.3 \text{ x } 10^4 – 1.2 \text{ x } 10^6$) at a coastal-urban site in Singapore (He and Balasubramanian, 2009). The median total scavenging ratios for PACs also varied by two orders of magnitude ($4 \text{ x } 10^2 – 3.1 \text{ x } 10^4$) 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). 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 gas-phase dominant and particulate-phase dominant PACs

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 8.0×10^5 for particulate-phase PAHs and 6.7×10^4 for gas-phase PAHs, which were within those from previous studies (Fig. 4). These results ~~are~~ were 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).

Gas-phase dominant PACs, like acenaphthylene, have lower molecular weight 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 at the oil sands sites. 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 (Ligocki et al., 1985~~b~~). This is also supported by the higher semi-empirical snow scavenging coefficients ~~of snow~~ for large particles compared to medium size particles (Zhang et al., 2013; Wang et al., 2014). In a previous study, the gas scavenging ratio (W_g) of acenaphthylene in snow was 385 times smaller than W_p in literature, resulting 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 Rain scavenging of gas-phase dominant and particulate-phase dominant PACs

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 1.8×10^5 for particulate-phase PAHs and 1.1×10^4 for gas-phase PAHs. The scavenging ratios were within those reported in literature, which ranged from $5100\text{-}1.2 \times 10^6$ for particulate-phase PAHs and $450\text{-}2.8 \times 10^5$ for gas-phase PAHs (Fig. 4). The larger W_t of particulate-phase PACs compared to gas-phase PACs ~~is~~ was also consistent with the empirical relationship between LogW_t and the particulate mass fraction of PACs in air (Logφ) (Franz and Eisenreich, 1998; He and Balasubramanian, 2009), similar to the result for snow.

Although the gas-phase PACs have very low particulate mass fraction in air, 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, rain scavenging of particles containing gas-phase PACs contributed more ~~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~~ by gas-phase PACs (17-59%) were lower than by particulate-phase PACs (97-100%) (Škrdlíková et al., 2011). Higher volatility PACs, such as acenaphthylene and anthracene, ~~were~~ are likely associated with larger particles, whereas non-volatile PACs tend to be associated with smaller particles (Škrdlíková et al., 2011). Based on the 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~~for gas scavenging ~~by~~ is 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 (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 processes

Overall, the snow scavenging ratio of gas-phase and particulate-phase PACs were greater than that for rain scavenging. Median total scavenging ratios over the period of data analyzed were 6100-1.1x10^6 from snow scavenging and 350-2.3x10^5 from rain scavenging depending on the PACs. 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.

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, weak correlations were observed between temperature-corrected Henry's Law constant (Pa m^3/mol) based on experimental data (Mackay et al., 2006) and theoretical values (Reid et al., 2013) and the total snow ($r = -0.36$) and rain ($r = -0.20$) scavenging ratios of gas-phase PACs, which suggest only minor influence of gas scavenging by dissolution. ~~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) .~~ A moderate correlation coefficient of 0.56 was found between temperature-corrected water solubility of gas-phase PACs and total rain scavenging ratios; however, no relationship was found for total snow scavenging ratios. ~~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.

Snow scavenging of gaseous PACs may be better modelled by surface or interfacial adsorption ($W_{g,ads}$). 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 (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.

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 of gas-phase PACs can be 15-385 times larger than measured W_g in literature ~~for gas-phase PACs~~. 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. 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 W_p can be much greater than the 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 in this study were -8.6±7.2 °C and 8.9±8.6 °C, respectively, with an average temperature difference of 17.5 °C. 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 efficiencies~~y~~ between snow and rain depend~~s~~ 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.

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 s~~Snow and rain W_t for parent naphthalene ~~was~~ were much higher than those of alkylated napthalenes. With an increase in 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 naphthalene to C1 naphthalene 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 physico-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~~ of 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 with the rain W_t, but did not have a large effect on snow W_t. The trend in the rain 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~~ was used to estimate the uncertainties for snow and rain events with similar amounts of precipitation ~~(Fig. 7a)~~. The median W_t uncertainties among gas-phase PACs were a factor of 3.6 for snow scavenging and 1.9 for rain scavenging (Fig. 7a). 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. These data were not available in this study to assess their effects on the total scavenging ratio uncertainties.

Gas-phase PACs partitions to particulate matter depending on temperature, which affects the particulate mass fraction and subsequently, the total scavenging ratio. The snow events in Fig. 7a not only have similar precipitation amounts, but are also associated with similar air temperatures in order to minimize the temperature and gas-particle partitioning effects on the uncertainties of W_t. Rain events associated with similar air temperatures were also used in Fig. 7a. Despite analyzing precipitation events with similar air temperatures, particulate mass fraction differed by a factor of 1.6 and 1.5 (median among gas-phase PACs) for the snow and rain events, respectively. This may be due to other factors affecting the particle partitioning of gas-phase PACs (e.g., aerosol water content and chemical composition). When precipitation events with equivalent precipitation amounts but different air temperatures were examined, uncertainties in the total scavenging ratio increased (Fig. 7b). The median W_t uncertainties among gas-phase PACs rose to a factor of 6.6 for snow events and 2.5 for rain events (Fig. 7a and 7b). This temperature effect on the uncertainties of the W_t is also supported by the larger difference in the particulate mass fraction.

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. ~~7b~~7c). The W_t uncertainties for~~ratio of the maximum to minimum~~ snow and rain ~~scavenging ratios~~events were up to 10 and ~~4.3~~7.7, 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 that 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).

3.7 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.~~ 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), which were not determined at the oil sands sites. 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.

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