



Scavenging ratio of polycyclic aromatic compounds in rain and snow

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

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## Abstract

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, in precipitation and in air at three near-source sites in the Fort MacKay and Fort McMurray area during May 2011 to August 2012 were analyzed 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)  $\text{ng L}^{-1}$  and 0.01–3.9 (naphthalene)  $\text{ng m}^{-3}$ , respectively, which were comparable to literature values. Higher concentrations in precipitation and air were observed for alkylated PAHs and dibenzothiophenes. The median precipitation and air concentrations were 11.3–646.7 (C3-fluoranthene/pyrene)  $\text{ng L}^{-1}$  and 0.21–16.9 (C3-naphthalene)  $\text{ng m}^{-3}$ , respectively, for alkylated PAHs, and 8.5–530.5 (C4-dibenzothiophene)  $\text{ng L}^{-1}$  and 0.13–6.6 (C2-dibenzothiophene)  $\text{ng m}^{-3}$  for dibenzothiophenes and their alkylated derivatives.

Median  $W_t$  over the measurement period were 6100– $1.1 \times 10^6$  from snow scavenging and 350– $2.3 \times 10^5$  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  $\sim 9$  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

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PACs, and Henry's Law constant of gas-phase dominant PACs explained, to a large extent, the different  $W_i$  values among the different PACs and precipitation types. 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 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. 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 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.

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

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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-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 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). 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. 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

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on a monthly schedule. The XAD resin columns were shipped to the Canada Centre for Inland Waters (Environment Canada, Burlington, Ontario) for the determination of PACs in precipitation samples.

5 Simultaneously, air samples were collected for 24 h every 6 days at the three sites using a modified high-volume air sampler. A vacuum pump draws in 700–1000 m<sup>3</sup> of air through a Teflon-coated glass fibre filter (GFFs) 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 h air samples were also recorded.

### 2.1.3 Analysis procedures

15 For the analysis of PACs in precipitation, the XAD 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 d8-dibenzothiophene spike and deuterated PAH surrogates are added prior to XAD column elution. The elution solvents are combined in a separatory funnel to separate the DCM phase. The aqueous 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 GFFs and PUF plugs samples are then extracted by Soxhlet apparatus for a period of 16 to 20 h 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.

25 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



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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 d10-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, and their alkyl derivatives. 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.

## 2.2 Data analysis

The scavenging of gaseous and particulate PACs by rain and snow have been studied using scavenging 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 ( $W = C_{\text{prec}}/C_{\text{air}}$ ).

Total scavenging ratios ( $W_i$ ) 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 April 2011 and 30 August 2012. 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) + 3x standard deviation (field blanks). The total



scavenging ratios were determined as follows (Škrdlíková et al., 2011):

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

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

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

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

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 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 and 15 particulate-phase PACs of higher molecular weight. The median particulate fraction of the gas-phase and particulate phase PACs were 0.073 and 0.92, respectively. 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.

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## 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. Median precipitation concentrations measured between May 2011 and August 2012 ranged from 0.4–302.8 ng L<sup>-1</sup> at the AMS5 site, 0.4–646.7 ng L<sup>-1</sup> at AMS11, and 0.3–236.6 ng L<sup>-1</sup> at AMS13 for PAHs, dibenzothiophenes, and their alkylated derivatives. The most abundant PACs (highest median concentration) in precipitation was C3-fluoranthene/pyrene at the three sites. 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<sup>-1</sup> (max: C1-benz(a)anthracene/triphenylene/chrysene) in snow and 0.1–260 ng L<sup>-1</sup> (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.

Median air concentrations at AMS5, AMS11, and AMS13 were 0.02–14.6 ng m<sup>-3</sup>, 0.03–16.9 ng m<sup>-3</sup>, and 0.01–7.7 ng m<sup>-3</sup>, respectively. 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 °C and 8.9 ± 8.6 °C, respectively, with an average temperature difference of 17.5 °C (Table 1). The median air concentrations ranged from 0.04–18.3 ng m<sup>-3</sup> for the snow data subset and 0.03–11.8 ng m<sup>-3</sup> 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<sup>-1</sup> and air concentrations ranged from 0.01–3.9 (naphthalene) ng m<sup>-3</sup> at the three sites, which were lower than the concentration ranges that included the alkylated PAHs and dibenzothiophenes. The parent PAH median

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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  $3.9 \times 10^5$  and  $4.6 \times 10^5$ , respectively, for snow events. In the rain events, the overall median and mean scavenging ratios were  $8.3 \times 10^4$  and  $1.1 \times 10^5$ . The median and mean scavenging ratios were within the range of values reported in literature (Tables 3 and 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). 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 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 scavenging ratios for the gas and particle phases ranged from  $8.52$ – $8.97 \times 10^5$  (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, 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

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(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 (December 2011 at AMS13 site).

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

The scavenging ratios for snow samples were larger for particulate-phase PACs than gas-phase at the oil sands sites. The median total snow scavenging ratios were  $8.0 \times 10^5$  for particulate-phase PACs and  $6.7 \times 10^4$  for gas-phase PACs (Table 2), which were within those from previous studies (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  $6.3 \times 10^5$ – $9.8 \times 10^6$  and 1400– $1.4 \times 10^6$ , respectively. These results are also in agreement with the strong relationship between  $\text{Log}W_t$  and particulate fraction of PACs in air ( $\text{Log}\varphi$ ). According to the regression equation, larger  $\varphi$  or particulate-phase PACs have higher total scavenging ratios than lower  $\varphi$  (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 lower molecular weight PACs tend to have 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  $W_g$ . 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. This is 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, the gas scavenging ratio ( $W_g$ ) in snow was 385 times smaller than  $W_p$  in literature (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 of gas-phase dominant and particulate-phase dominant 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  $1.8 \times 10^5$  for particulate-phase PACs and  $1.1 \times 10^4$  for gas-phase PACs (Table 2). This

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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  $27.7 \text{ ng L}^{-1}$  and  $26.9 \text{ ng L}^{-1}$ , respectively. The scavenging ratios were within those reported in literature, which ranged from 5100– $1.2 \times 10^6$  for particulate-phase PACs and  $450\text{--}2.8 \times 10^5$  for gas-phase PACs (Table 4). The larger  $W_t$  of particulate-phase PACs compared to gas-phase PACs is consistent with the empirical relationship between  $\text{Log}W_t$  and the particulate fraction of PACs in air ( $\text{Log}\varphi$ ) (Table 4) (Franz and Eisenreich, 1998; He and Balasubramanian, 2009). The slopes of the regression equation were similar in the two studies, indicating that the relationship between  $W_t$  and  $\varphi$  does not appear to be dependent on the location (He and Balasubramanian, 2009). This relationship suggests that particulate-phase PACs (with larger  $\varphi$ ) are associated with larger  $W_t$  in rain than gas-phase PACs (with smaller  $\varphi$ ), similar to the result for snow.

Although the gas-phase PACs have very low particulate fraction in air, Table 4 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  $W_g$  were more comparable in the literature (up to 1 order of magnitude difference). 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

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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 Sect. 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 ( $> 6 \mu\text{m}$ ) 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 ( $W_{g,\text{diss}}$ ) 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 ( $W_{g,\text{ads}}$ ) 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), 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; Henzing et al., 2006).

### 3.4 Comparison of snow and rain scavenging for gas-phase dominant PACs

The median snow scavenging ratio of gas-phase PACs ( $6.7 \times 10^4$ ) was greater than that for rain scavenging ( $1.1 \times 10^4$ ), which is also observed in previous studies. Based on the data in Table 1, the overall median concentrations of gas-phase dominant PACs



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in snow and rain were  $208.2 \text{ ng L}^{-1}$  and  $27.7 \text{ ng L}^{-1}$ , respectively, which is  $\sim 7.5$  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:  $11.6\text{--}11.8 \text{ mm month}^{-1}$ , rain:  $10.8\text{--}12.3 \text{ mm month}^{-1}$ ), the median snow and rain scavenging ratios for gas-phase PACs were  $1.2 \times 10^5$  and 8300, respectively. For gas-phase PACs, the total snow and rain scavenging ratios reported in literature ranged from  $1400\text{--}1.4 \times 10^6$  and  $450\text{--}2.8 \times 10^5$ , 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. No relationship between the Henry's Law constant and total scavenging ratios was observed for rain samples. This suggests that some of the less volatile gas-phase PACs (i.e. lower Henry's Law constant in  $\text{Pa m}^3 \text{ mol}^{-1}$  units) is associated with higher total snow scavenging ratios. But 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



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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  $5.5 \times 10^3$ – $2.7 \times 10^7$ , while theoretical and measured  $W_g$  ranged from 25–3300 in literature (Table 4). Therefore, even though gas-phase PACs have very low particulate fraction in air, the particle scavenging contribution to snow and rain can still be important because the particle scavenging ratios can be much greater than the gas scavenging ratios. 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

For the particulate-phase PACs, snow scavenging ratios are higher than rain scavenging ratios. The median scavenging ratios for snow and rain were  $8.0 \times 10^5$  and  $1.8 \times 10^5$ , respectively, for all precipitation events (Table 2). 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  $635.7 \text{ ng L}^{-1}$  and  $26.9 \text{ ng L}^{-1}$ , 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  $6.3 \times 10^5$ – $9.8 \times 10^6$  for snow and  $5100$ – $1.2 \times 10^6$  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.

If only snow and rain events with similar precipitation rates are considered (e.g, snow:  $11.6$ – $11.8 \text{ mm month}^{-1}$ , rain:  $10.8$ – $12.3 \text{ mm month}^{-1}$ ), 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:  $13.0$ – $15.3 \text{ mm month}^{-1}$ , rain:  $13.2$ – $16.5 \text{ mm month}^{-1}$ ) 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

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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  $\sim 10$  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 ( $< 0.01 \mu\text{m}$ ) 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 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

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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





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**Table 1.** Descriptive statistics of precipitation and air concentrations ( $\text{ng m}^{-3}$ ) of PACs and temperature and precipitation amount at the oil sands sites. (G) and (P) denote predominantly gas-phase and particulate-phase PACs, respectively. S.D. is the standard deviation.

PAC	Median precipitation concentration		Mean precipitation concentration		S. D. of precipitation concentrations		Median air concentration		Mean air concentration		S. D. of air concentrations	
	Snow	Rain	Snow	Rain	Snow	Rain	Snow	Rain	Snow	Rain	Snow	Rain
Naphthalene (G)	$2.4 \times 10^5$	$4.3 \times 10^4$	$1.4 \times 10^5$	$1.0 \times 10^5$	$1.9 \times 10^6$	$2.8 \times 10^6$	4.56	1.67	6.20	1.90	4.89	1.24
Acenaphthylene (G)	$2.5 \times 10^5$	$1.4 \times 10^5$	$3.2 \times 10^5$	$7.5 \times 10^5$	$3.2 \times 10^5$	$1.9 \times 10^5$	0.39	0.13	0.49	0.20	0.47	0.23
Acenaphthene (G)	$7.2 \times 10^3$	$1.7 \times 10^3$	$1.3 \times 10^4$	$5.1 \times 10^3$	$1.8 \times 10^4$	$1.2 \times 10^4$	0.86	0.55	0.97	0.51	0.43	0.27
Fluorene (G)	$3.6 \times 10^4$	$3.0 \times 10^3$	$5.3 \times 10^4$	$1.1 \times 10^4$	$6.4 \times 10^4$	$3.2 \times 10^4$	0.84	0.68	0.91	0.75	0.40	0.47
Phenanthrene (G)	$3.4 \times 10^5$	$2.6 \times 10^4$	$5.0 \times 10^5$	$9.2 \times 10^4$	$5.7 \times 10^5$	$2.8 \times 10^5$	2.14	2.06	2.22	2.91	1.11	3.06
Anthracene (G)	$1.2 \times 10^5$	$4.5 \times 10^3$	$2.3 \times 10^5$	$3.7 \times 10^4$	$3.0 \times 10^5$	$1.4 \times 10^5$	0.16	0.13	0.23	0.23	0.22	0.29
Fluoranthene	$1.0 \times 10^5$	$7.4 \times 10^3$	$1.6 \times 10^5$	$2.5 \times 10^4$	$1.7 \times 10^5$	$6.9 \times 10^4$	0.37	0.18	0.41	0.33	0.30	0.40
Pyrene	$3.6 \times 10^5$	$2.6 \times 10^4$	$5.5 \times 10^5$	$1.0 \times 10^5$	$6.0 \times 10^5$	$3.1 \times 10^5$	0.48	0.36	0.72	0.55	0.63	0.61
Retene	$5.1 \times 10^4$	$1.2 \times 10^4$	$7.9 \times 10^4$	$2.4 \times 10^4$	$7.1 \times 10^4$	$2.5 \times 10^4$	1.09	0.40	1.13	0.92	0.84	0.31
Benz(a)anthracene (P)	$5.0 \times 10^5$	$2.1 \times 10^4$	$6.8 \times 10^5$	$1.6 \times 10^5$	$7.0 \times 10^5$	$4.6 \times 10^5$	0.23	0.12	0.40	0.45	0.54	0.68
Chrysene (P)	$6.4 \times 10^5$	$2.7 \times 10^4$	$9.7 \times 10^5$	$2.0 \times 10^5$	$1.0 \times 10^6$	$6.3 \times 10^5$	0.37	0.24	0.67	0.57	0.80	0.83
Benzo(b)fluoranthene (P)	$1.7 \times 10^5$	$8.8 \times 10^3$	$2.9 \times 10^5$	$4.6 \times 10^4$	$4.0 \times 10^5$	$1.4 \times 10^5$	0.16	0.10	0.24	0.24	0.25	0.34
Benzo(k)fluoranthene (P)	$3.0 \times 10^4$	$1.7 \times 10^3$	$6.4 \times 10^4$	$1.0 \times 10^4$	$7.3 \times 10^4$	$2.9 \times 10^4$	0.04	0.03	0.06	0.06	0.06	0.09
Benzo(a)pyrene (P)	$3.8 \times 10^5$	$2.2 \times 10^4$	$8.6 \times 10^5$	$1.3 \times 10^5$	$1.3 \times 10^6$	$3.9 \times 10^5$	0.20	0.10	0.39	0.30	0.62	0.47
Perylene	$3.4 \times 10^4$	$4.9 \times 10^3$	$5.6 \times 10^4$	$1.5 \times 10^4$	$6.2 \times 10^4$	$3.7 \times 10^4$	0.02	0.02	0.04	0.03	0.06	0.04
Indeno(1,2,3-cd)pyrene (P)	$8.3 \times 10^4$	$4.3 \times 10^3$	$1.2 \times 10^5$	$2.2 \times 10^4$	$1.2 \times 10^5$	$6.3 \times 10^4$	0.07	0.05	0.12	0.11	0.16	0.13
Dibenzo(a,h)anthracene (P)	$1.5 \times 10^5$	$7.7 \times 10^3$	$2.3 \times 10^5$	$4.0 \times 10^4$	$2.7 \times 10^5$	$1.2 \times 10^5$	0.06	0.04	0.14	0.11	0.24	0.18
Benzo(ghi)perylene (P)	$2.8 \times 10^5$	$1.3 \times 10^4$	$4.1 \times 10^5$	$7.2 \times 10^4$	$4.2 \times 10^5$	$2.1 \times 10^5$	0.16	0.10	0.31	0.21	0.48	0.35
C1 Naphthalenes (G)	$1.6 \times 10^5$	$2.1 \times 10^4$	$2.0 \times 10^5$	$6.4 \times 10^4$	$1.7 \times 10^5$	$1.7 \times 10^5$	8.63	3.12	9.47	3.44	5.43	1.58
C2 Naphthalenes (G)	$2.1 \times 10^5$	$2.1 \times 10^4$	$2.1 \times 10^5$	$5.3 \times 10^4$	$1.8 \times 10^5$	$1.2 \times 10^5$	11.46	4.18	12.11	5.02	5.61	2.22
C3 Naphthalenes (G)	$2.1 \times 10^5$	$3.3 \times 10^4$	$2.3 \times 10^5$	$6.0 \times 10^4$	$1.7 \times 10^5$	$1.2 \times 10^5$	18.53	12.97	18.30	11.90	6.21	5.58
C4 Naphthalenes (G)	$1.2 \times 10^5$	$3.0 \times 10^4$	$1.1 \times 10^5$	$4.4 \times 10^4$	$7.0 \times 10^4$	$6.5 \times 10^4$	10.03	10.98	10.73	11.55	4.71	6.67
C1 Fluorenes (G)	$1.5 \times 10^5$	$1.2 \times 10^4$	$1.5 \times 10^5$	$2.8 \times 10^4$	$1.2 \times 10^5$	$6.7 \times 10^4$	2.18	2.67	2.54	3.05	1.24	1.99
C2 Fluorenes (G)	$3.7 \times 10^5$	$4.1 \times 10^4$	$3.7 \times 10^5$	$9.4 \times 10^4$	$2.7 \times 10^5$	$2.2 \times 10^5$	3.91	6.48	4.38	6.87	2.14	4.59
C3 Fluorenes (G)	$7.8 \times 10^5$	$1.1 \times 10^5$	$8.4 \times 10^5$	$2.1 \times 10^5$	$6.2 \times 10^5$	$4.7 \times 10^5$	3.35	5.89	4.12	6.30	2.22	4.14
C4 Fluorenes (G)	$4.0 \times 10^5$	$7.6 \times 10^4$	$4.1 \times 10^5$	$1.3 \times 10^5$	$2.9 \times 10^5$	$2.3 \times 10^5$	1.85	3.60	2.22	3.85	1.08	2.58
C1 Phenanthrene/Anthracene (G)	$1.0 \times 10^5$	$7.6 \times 10^4$	$1.0 \times 10^5$	$2.1 \times 10^5$	$7.8 \times 10^5$	$6.1 \times 10^5$	2.15	2.54	2.91	3.32	1.89	2.69
C2 Phenanthrene/Anthracene	$1.6 \times 10^5$	$1.8 \times 10^5$	$1.5 \times 10^5$	$4.5 \times 10^5$	$1.1 \times 10^6$	$1.2 \times 10^6$	2.84	4.06	3.95	5.27	2.52	4.91
C3 Phenanthrene/Anthracene	$1.1 \times 10^6$	$1.9 \times 10^5$	$1.1 \times 10^6$	$4.0 \times 10^5$	$7.6 \times 10^5$	$9.0 \times 10^5$	2.29	3.04	2.76	4.48	1.44	4.99
C4 Phenanthrene/Anthracene	$5.7 \times 10^5$	$8.9 \times 10^4$	$6.0 \times 10^5$	$2.0 \times 10^5$	$4.1 \times 10^5$	$4.4 \times 10^5$	1.54	1.21	1.73	4.47	0.96	9.27
C1 Fluoranthenes/Pyrene	$6.6 \times 10^5$	$4.6 \times 10^4$	$7.0 \times 10^5$	$1.8 \times 10^5$	$5.5 \times 10^5$	$5.4 \times 10^5$	0.49	0.50	0.84	0.78	0.98	0.99
C2 Fluoranthenes/Pyrene (P)	$1.9 \times 10^6$	$1.7 \times 10^5$	$2.1 \times 10^6$	$5.7 \times 10^5$	$1.4 \times 10^6$	$1.6 \times 10^6$	1.31	1.33	2.47	2.24	2.70	2.86
C3 Fluoranthenes/Pyrene (P)	$2.3 \times 10^6$	$2.6 \times 10^5$	$2.5 \times 10^6$	$7.6 \times 10^5$	$1.9 \times 10^6$	$2.1 \times 10^6$	1.64	1.80	2.90	2.88	3.17	3.65
C4 Fluoranthenes/Pyrene (P)	$1.6 \times 10^6$	$1.9 \times 10^5$	$2.0 \times 10^6$	$5.7 \times 10^5$	$1.5 \times 10^6$	$1.5 \times 10^6$	1.11	1.04	2.03	1.93	2.38	2.62
C1 Benz(a)anthracenes/Chrysene/Triphenylenes (P)	$2.4 \times 10^6$	$1.5 \times 10^5$	$2.8 \times 10^6$	$7.8 \times 10^5$	$2.1 \times 10^6$	$2.4 \times 10^6$	1.23	1.14	2.60	2.13	3.52	3.08
C2 Benz(a)anthracenes/Chrysene/Triphenylenes (P)	$1.4 \times 10^6$	$1.1 \times 10^5$	$1.6 \times 10^6$	$4.8 \times 10^5$	$1.3 \times 10^6$	$1.4 \times 10^6$	0.87	0.90	1.66	1.51	2.19	2.13
C3 Benz(a)anthracenes/Chrysene/Triphenylenes (P)	$1.3 \times 10^6$	$1.3 \times 10^5$	$1.4 \times 10^6$	$4.3 \times 10^5$	$1.1 \times 10^6$	$1.2 \times 10^6$	0.82	0.91	1.48	1.56	1.89	2.02
C4 Benz(a)anthracenes/Chrysene/Triphenylenes (P)	$7.4 \times 10^5$	$1.0 \times 10^5$	$9.0 \times 10^5$	$3.1 \times 10^5$	$6.9 \times 10^5$	$8.4 \times 10^5$	0.62	0.55	1.05	0.97	1.26	1.22
Dibenzothiophene (G)	$1.9 \times 10^5$	$8.1 \times 10^3$	$2.0 \times 10^5$	$3.8 \times 10^4$	$1.8 \times 10^5$	$1.3 \times 10^5$	0.64	0.43	0.79	0.59	0.64	0.58
C1 Dibenzothiophenes (G)	$9.2 \times 10^5$	$5.0 \times 10^4$	$9.6 \times 10^5$	$1.8 \times 10^5$	$8.0 \times 10^5$	$5.8 \times 10^5$	2.22	2.23	3.45	2.94	3.12	2.36
C2 Dibenzothiophenes (G)	$1.8 \times 10^6$	$1.3 \times 10^5$	$1.7 \times 10^6$	$4.0 \times 10^5$	$1.4 \times 10^6$	$1.3 \times 10^6$	3.90	3.56	5.03	4.42	4.47	3.36
C3 Dibenzothiophenes	$1.4 \times 10^6$	$1.4 \times 10^5$	$1.3 \times 10^6$	$3.9 \times 10^5$	$1.0 \times 10^6$	$1.0 \times 10^6$	3.05	2.56	4.16	3.15	3.35	2.33
C4 Dibenzothiophenes	$1.2 \times 10^6$	$1.8 \times 10^5$	$1.2 \times 10^6$	$4.2 \times 10^5$	$8.4 \times 10^5$	$8.5 \times 10^5$	2.99	2.20	3.85	2.74	2.94	2.11
Temperature ( $^{\circ}\text{C}$ )	-11.3	12.4	-8.6	8.9	7.2	8.6	-11.3	12.4	-8.6	8.9	7.2	8.6
Precipitation (mm)	9.4	22.6	10.8	33.2	6.4	27.5	9.4	22.6	10.8	33.2	6.4	27.5

## Scavenging ratio of polycyclic aromatic compounds in rain and snow

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**Table 2.** Descriptive statistics of the total scavenging ratios ( $W_t$ ) at the oil sands sites. (G) and (P) denote predominantly gas-phase and particulate-phase PACs, respectively.

PACs	# of samples		Median		Mean		Min		Max	
	Snow	Rain	Snow	Rain	Snow	Rain	Snow	Rain	Snow	Rain
Naphthalene (G)	19	15	$4.7 \times 10^4$	$3.6 \times 10^4$	$4.6 \times 10^5$	$5.3 \times 10^5$	$1.7 \times 10^3$	$1.2 \times 10^2$	$2.5 \times 10^6$	$4.7 \times 10^6$
Acenaphthylene (G)	19	27	$6.8 \times 10^3$	$3.5 \times 10^3$	$9.9 \times 10^3$	$7.8 \times 10^3$	$7.2 \times 10^2$	0	$2.9 \times 10^4$	$5.3 \times 10^4$
Acenaphthene (G)	19	28	$6.1 \times 10^3$	$3.5 \times 10^3$	$1.4 \times 10^4$	$9.1 \times 10^3$	$4.8 \times 10^2$	0	$8.2 \times 10^4$	$8.9 \times 10^4$
Fluorene (G)	19	28	$3.2 \times 10^4$	$5.8 \times 10^3$	$7.8 \times 10^4$	$1.0 \times 10^4$	$3.2 \times 10^3$	0	$5.5 \times 10^5$	$1.1 \times 10^5$
Phenanthrene (G)	19	28	$1.1 \times 10^5$	$1.5 \times 10^4$	$2.5 \times 10^5$	$2.2 \times 10^4$	$1.6 \times 10^4$	$3.2 \times 10^3$	$9.1 \times 10^5$	$1.1 \times 10^5$
Anthracene (G)	18	28	$4.1 \times 10^5$	$3.5 \times 10^4$	$1.4 \times 10^6$	$8.5 \times 10^4$	$5.1 \times 10^4$	$1.7 \times 10^3$	$7.8 \times 10^6$	$5.5 \times 10^5$
Fluoranthene	18	27	$2.5 \times 10^5$	$3.8 \times 10^4$	$4.5 \times 10^5$	$6.3 \times 10^4$	$7.1 \times 10^4$	$8.4 \times 10^3$	$1.6 \times 10^6$	$2.6 \times 10^5$
Pyrene	17	24	$3.4 \times 10^5$	$7.1 \times 10^4$	$1.1 \times 10^6$	$1.2 \times 10^5$	$1.1 \times 10^5$	$1.8 \times 10^4$	$4.7 \times 10^6$	$5.8 \times 10^5$
Retene	18	27	$6.6 \times 10^4$	$2.1 \times 10^4$	$1.2 \times 10^5$	$4.5 \times 10^4$	0	0	$5.8 \times 10^5$	$2.0 \times 10^5$
Benz(a)anthracene (P)	17	16	$8.2 \times 10^5$	$2.1 \times 10^5$	$2.9 \times 10^6$	$2.8 \times 10^5$	$2.5 \times 10^5$	$2.2 \times 10^4$	$1.2 \times 10^7$	$9.8 \times 10^5$
Chrysene (P)	17	20	$6.0 \times 10^5$	$1.7 \times 10^5$	$2.3 \times 10^6$	$2.8 \times 10^5$	$1.9 \times 10^5$	$2.0 \times 10^4$	$8.4 \times 10^6$	$1.3 \times 10^6$
Benzo(b)fluoranthene (P)	18	21	$5.3 \times 10^5$	$1.2 \times 10^5$	$1.6 \times 10^6$	$1.5 \times 10^5$	$1.2 \times 10^5$	$1.3 \times 10^4$	$7.3 \times 10^6$	$6.4 \times 10^5$
Benzo(k)fluoranthene (P)	19	22	$5.1 \times 10^5$	$4.8 \times 10^4$	$1.5 \times 10^6$	$1.3 \times 10^5$	$9.3 \times 10^4$	0	$6.0 \times 10^6$	$9.0 \times 10^5$
Benzo(a)pyrene (P)	18	21	$9.8 \times 10^5$	$1.9 \times 10^5$	$4.3 \times 10^6$	$3.8 \times 10^5$	$1.9 \times 10^5$	$2.3 \times 10^4$	$1.9 \times 10^7$	$1.9 \times 10^6$
Perylene	16	20	$6.4 \times 10^5$	$2.1 \times 10^5$	$2.7 \times 10^6$	$3.8 \times 10^5$	$1.8 \times 10^5$	$3.0 \times 10^4$	$1.3 \times 10^7$	$1.5 \times 10^6$
Indeno(1,2,3-cd)pyrene (P)	17	21	$5.3 \times 10^5$	$9.1 \times 10^4$	$1.8 \times 10^6$	$1.7 \times 10^5$	$1.2 \times 10^5$	$1.0 \times 10^4$	$6.8 \times 10^6$	$8.0 \times 10^5$
Dibenzo(a,h)anthracene (P)	18	20	$1.1 \times 10^6$	$1.9 \times 10^5$	$3.5 \times 10^6$	$3.7 \times 10^5$	$2.2 \times 10^5$	$1.1 \times 10^4$	$1.3 \times 10^7$	$1.7 \times 10^6$
Benzo(ghi)perylene (P)	17	20	$5.7 \times 10^5$	$1.5 \times 10^5$	$2.6 \times 10^6$	$2.2 \times 10^5$	$1.6 \times 10^5$	$2.1 \times 10^4$	$1.0 \times 10^7$	$9.1 \times 10^5$
C1 Naphthalenes (G)	19	16	$1.6 \times 10^4$	$6.2 \times 10^3$	$2.2 \times 10^4$	$1.9 \times 10^4$	0	0	$6.7 \times 10^4$	$1.8 \times 10^5$
C2 Naphthalenes (G)	19	23	$1.8 \times 10^4$	$5.0 \times 10^3$	$1.9 \times 10^4$	$1.0 \times 10^4$	$7.2 \times 10^2$	0	$4.9 \times 10^4$	$7.4 \times 10^4$
C3 Naphthalenes (G)	19	28	$1.1 \times 10^4$	$2.9 \times 10^3$	$1.3 \times 10^4$	$4.8 \times 10^3$	$4.1 \times 10^2$	$9.7 \times 10^2$	$3.8 \times 10^4$	$2.9 \times 10^4$
C4 Naphthalenes (G)	19	28	$1.2 \times 10^4$	$3.1 \times 10^3$	$1.2 \times 10^4$	$4.5 \times 10^3$	$1.1 \times 10^3$	$7.2 \times 10^2$	$3.8 \times 10^4$	$1.7 \times 10^4$
C1 Fluorenes (G)	19	28	$5.2 \times 10^4$	$4.3 \times 10^3$	$5.8 \times 10^4$	$8.5 \times 10^3$	$6.5 \times 10^3$	$1.2 \times 10^3$	$1.5 \times 10^5$	$4.3 \times 10^4$
C2 Fluorenes (G)	19	28	$8.2 \times 10^4$	$6.6 \times 10^3$	$9.1 \times 10^4$	$1.4 \times 10^4$	$2.1 \times 10^4$	$2.3 \times 10^3$	$2.3 \times 10^5$	$7.4 \times 10^4$
C3 Fluorenes (G)	19	28	$1.5 \times 10^5$	$1.6 \times 10^4$	$2.3 \times 10^5$	$3.6 \times 10^4$	$4.0 \times 10^4$	$4.6 \times 10^3$	$6.4 \times 10^5$	$2.5 \times 10^5$
C4 Fluorenes (G)	19	28	$1.5 \times 10^5$	$2.1 \times 10^4$	$2.2 \times 10^5$	$3.8 \times 10^4$	$3.0 \times 10^4$	$5.6 \times 10^3$	$7.8 \times 10^5$	$2.4 \times 10^5$
C1 Phenanthrene/Anthracene (G)	19	27	$2.2 \times 10^5$	$2.5 \times 10^4$	$3.8 \times 10^5$	$5.4 \times 10^4$	$4.5 \times 10^4$	$5.9 \times 10^3$	$9.9 \times 10^5$	$3.6 \times 10^5$
C2 Phenanthrene/Anthracene	19	25	$2.5 \times 10^5$	$4.3 \times 10^4$	$4.6 \times 10^5$	$8.3 \times 10^4$	$9.8 \times 10^4$	$9.9 \times 10^3$	$1.4 \times 10^6$	$6.5 \times 10^5$
C3 Phenanthrene/Anthracene	19	23	$2.9 \times 10^5$	$6.6 \times 10^4$	$4.6 \times 10^5$	$8.9 \times 10^4$	$8.6 \times 10^4$	$9.9 \times 10^3$	$1.2 \times 10^6$	$2.5 \times 10^5$
C4 Phenanthrene/Anthracene	18	28	$3.1 \times 10^5$	$7.7 \times 10^4$	$4.8 \times 10^5$	$1.1 \times 10^5$	$4.6 \times 10^4$	$2.2 \times 10^3$	$2.1 \times 10^6$	$6.4 \times 10^5$
C1 Fluoranthenes/Pyrene	18	23	$5.6 \times 10^5$	$1.0 \times 10^5$	$1.3 \times 10^6$	$1.9 \times 10^5$	$1.9 \times 10^5$	$2.0 \times 10^4$	$5.5 \times 10^6$	$9.1 \times 10^5$
C2 Fluoranthenes/Pyrene (P)	16	19	$6.5 \times 10^5$	$1.5 \times 10^5$	$1.4 \times 10^6$	$2.0 \times 10^5$	$2.0 \times 10^5$	$2.5 \times 10^4$	$5.3 \times 10^6$	$8.8 \times 10^5$
C3 Fluoranthenes/Pyrene (P)	18	20	$7.7 \times 10^5$	$1.8 \times 10^5$	$1.4 \times 10^6$	$2.1 \times 10^5$	$2.3 \times 10^5$	$2.8 \times 10^4$	$4.7 \times 10^6$	$9.6 \times 10^5$
C4 Fluoranthenes/Pyrene (P)	17	19	$8.2 \times 10^5$	$2.3 \times 10^5$	$1.9 \times 10^6$	$2.6 \times 10^5$	$2.3 \times 10^5$	$3.0 \times 10^4$	$8.4 \times 10^6$	$9.8 \times 10^5$
C1 Benz(a)anthracenes/Chrysene/Triphenylenes (P)	17	19	$8.0 \times 10^5$	$1.8 \times 10^5$	$2.1 \times 10^6$	$3.0 \times 10^5$	$2.4 \times 10^5$	$2.3 \times 10^4$	$1.0 \times 10^7$	$1.4 \times 10^6$
C2 Benz(a)anthracenes/Chrysene/Triphenylenes (P)	18	21	$1.0 \times 10^6$	$1.7 \times 10^5$	$1.9 \times 10^6$	$3.0 \times 10^5$	$2.1 \times 10^5$	$2.3 \times 10^4$	$8.7 \times 10^6$	$1.9 \times 10^6$
C3 Benz(a)anthracenes/Chrysene/Triphenylenes (P)	18	20	$9.7 \times 10^5$	$2.3 \times 10^5$	$1.7 \times 10^6$	$2.2 \times 10^5$	$2.3 \times 10^5$	$2.7 \times 10^4$	$6.2 \times 10^6$	$8.9 \times 10^5$
C4 Benz(a)anthracenes/Chrysene/Triphenylenes (P)	19	22	$8.3 \times 10^5$	$2.3 \times 10^5$	$1.5 \times 10^6$	$3.6 \times 10^5$	$2.1 \times 10^5$	$3.3 \times 10^4$	$5.4 \times 10^6$	$2.7 \times 10^6$
Dibenzothiophene (G)	15	28	$2.2 \times 10^5$	$1.7 \times 10^4$	$4.2 \times 10^5$	$4.7 \times 10^4$	$1.5 \times 10^4$	$9.7 \times 10^2$	$3.1 \times 10^6$	$4.2 \times 10^5$
C1 Dibenzothiophenes (G)	15	28	$2.2 \times 10^5$	$2.0 \times 10^4$	$4.3 \times 10^5$	$5.0 \times 10^4$	$2.1 \times 10^4$	$2.1 \times 10^3$	$2.1 \times 10^6$	$3.9 \times 10^5$
C2 Dibenzothiophenes (G)	15	28	$3.0 \times 10^5$	$3.2 \times 10^4$	$1.1 \times 10^6$	$7.9 \times 10^4$	$4.0 \times 10^4$	$1.0 \times 10^4$	$1.1 \times 10^7$	$6.2 \times 10^5$
C3 Dibenzothiophenes	14	27	$2.9 \times 10^5$	$6.6 \times 10^4$	$4.1 \times 10^5$	$1.3 \times 10^5$	$7.8 \times 10^4$	$1.6 \times 10^4$	$1.4 \times 10^6$	$1.0 \times 10^5$
C4 Dibenzothiophenes	14	26	$2.9 \times 10^5$	$9.7 \times 10^4$	$4.3 \times 10^5$	$1.9 \times 10^5$	$9.4 \times 10^4$	$2.6 \times 10^4$	$2.1 \times 10^6$	$1.9 \times 10^5$
Overall			$3.9 \times 10^5$	$8.3 \times 10^4$	$4.6 \times 10^5$	$1.1 \times 10^5$				

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**Table 3.** Total ( $W_t$ ), particulate ( $W_p$ ), and gas ( $W_g$ ) scavenging ratios for snow reported in literature.  $\varphi$  is the particulate PAC fraction in air.

PAC	$W_t$	$W_p$	$W_g$	Reference
Acenaphthylene	$0.025 \times 10^5$ $0.014 \times 10^5$	$2.5 \times 10^5$	$0.0065 \times 10^5$ Wania et al. (1999)	Franz and Eisenreich (1998)
Acenaphthene	$3.2 \times 10^5$ $0.58 \times 10^5$	$4 \times 10^6$	$0.64 \times 10^5$ $2.7\text{--}3.0 \times 10^5$ $0.4\text{--}0.46 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
Fluorene	$2.0 \times 10^5$ $0.30 \times 10^5$	$2 \times 10^6$	$0.45 \times 10^5$ $1.2\text{--}1.8 \times 10^5$ $0.21\text{--}0.24 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
Phenanthrene	$11 \times 10^5$ $1.6 \times 10^5$	$2.5 \times 10^6$	$1.7 \times 10^5$ $8\text{--}10 \times 10^5$ $1.0\text{--}1.2 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
Anthracene	$14 \times 10^5$ $2.4 \times 10^5$	$2.5 \times 10^6$	$1.2 \times 10^5$ $9.9\text{--}14 \times 10^5$ $1.5\text{--}1.9 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
Fluoranthene	$19 \times 10^5$ $5.2 \times 10^5$	$2 \times 10^6$	$2.8 \times 10^5$ $0.6\text{--}17 \times 10^5$ $3.1\text{--}4.6 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
Pyrene	$37 \times 10^5$ $5.6 \times 10^5$	$2.51 \times 10^6$	$2.3 \times 10^5$ $22\text{--}38 \times 10^5$ $3.5\text{--}5.3 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
Retene	$3.8 \times 10^5$ $0.59 \times 10^5$	$3.6 \times 10^5$	$0.21 \times 10^5$ Wania et al. (1999)	Franz and Eisenreich (1998)
Benz(a)anthracene	$110 \times 10^5$ $5.1 \times 10^5$	$1.1 \times 10^6$	$27 \times 10^5$ $290\text{--}1930 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
Chrysene	$53 \times 10^5$ $5.7 \times 10^5$	$1 \times 10^6$	$12 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
Benzo(b+k)fluoranthene	$51 \times 10^5$ $8.8 \times 10^5$	$1.1 \times 10^6$ $51 \times 10^5$ $8.8 \times 10^5$		Franz and Eisenreich (1998) Wania et al. (1999)
Benzo(e)pyrene	$49 \times 10^5$ $9.3 \times 10^5$	$1.1 \times 10^6$ $49 \times 10^5$ $9.3 \times 10^5$		Franz and Eisenreich (1998) Wania et al. (1999)
Benzo(a)pyrene	$98 \times 10^5$ $14 \times 10^5$	$1.6 \times 10^6$ $98 \times 10^5$ $14 \times 10^5$	$230\text{--}380 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
Indeno(c,d)pyrene	$50 \times 10^5$ $8 \times 10^5$	$1 \times 10^6$ $50 \times 10^5$ $8 \times 10^5$		Franz and Eisenreich (1998) Wania et al. (1999)



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Table 3. Continued.

PAC	$W_t$	$W_p$	$W_g$	Reference
Dibenz(a,h)anthracene	$81 \times 10^5$	$1.3 \times 10^6$	$24\text{--}81 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
	$10 \times 10^5$	$81 \times 10^5$		
Benzo(g,h,i)perylene	$30 \times 10^5$	$7.9 \times 10^5$		Franz and Eisenreich (1998) Wania et al. (1999)
	$6.3 \times 10^5$	$30 \times 10^5$		
1-methylfluorene	$1.2 \times 10^5$	$6.3 \times 10^5$	$0.18 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
	$0.18 \times 10^5$		$0.22\text{--}0.91 \times 10^5$	
2-methylphenanthrene	$7.4 \times 10^5$	$0.044\text{--}0.091 \times 10^5$	$0.78 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
	$0.98 \times 10^5$		$2.7\text{--}6.3 \times 10^5$	
4,5-methylenephenanthrene	$15 \times 10^5$	$0.44\text{--}0.64 \times 10^5$	$1.6 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
	$2.2 \times 10^5$		$10\text{--}14 \times 10^5$	
1-methylphenanthrene	$10 \times 10^5$	$1.4\text{--}1.8 \times 10^5$	$1.1 \times 10^5$	Franz and Eisenreich (1998) Wania et al. (1999)
	$1.2 \times 10^5$		$5.6\text{--}9.2 \times 10^5$	
Overall range	$10^3$ to $10^7$			Franz and Eisenreich (1998)
Overall avg		$30\text{--}98 \times 10^5$		Wania et al. (1999)
Overall total		$6.3\text{--}9.3 \times 10^5$		
Enrichment factor (measured $W_t$ /theoretical $W_g$ )	$\log W_T = 0.89 \log \varphi + 6.07$ ( $r = 0.73$ )		$0.43\text{--}20$	Franz and Eisenreich (1998) Franz and Eisenreich (1998)

**Table 4.** Total ( $W_t$ ), particulate ( $W_p$ ), and gas ( $W_g$ ) scavenging ratios for rain reported in literature.  $\varphi$  = particulate PAC fraction in air; diss = theoretical gas scavenging due to dissolution; ads = theoretical gas scavenging due to surface adsorption.

PAC	$W_t$	$W_p$	$W_g$	Reference
Naphthalene	$1.6 \times 10^5$	$2.7 \times 10^7$	24.3 (diss) 0.2 (ads)	He and Balasubramanian (2009)
Acenaphthylene	600 $11-1.0 \times 10^4$ $1.7 \times 10^5$	$2.1 \times 10^3$ $1.4 \times 10^7$	$1 \times 10^4$ 160	Franz and Eisenreich (1998) Škrdlíková et al. (2011)
Acenaphthene	450 $30-9.0 \times 10^3$ $2.8 \times 10^5$	$5.5 \times 10^3$ $5.5 \times 10^6$	$1.4 \times 10^2$ (diss) 2.2 (ads) $3.2 \times 10^4$ 290	He and Balasubramanian (2009) Franz and Eisenreich (1998) Škrdlíková et al. (2011)
Fluorene	$1.3 \times 10^3$ $120-1.3 \times 10^5$ $1.6 \times 10^6$	$1.6 \times 10^4$ $4.7 \times 10^6$	$1.2 \times 10^2$ (diss) 1.6 (ads) $2.5 \times 10^4$ 710	Franz and Eisenreich (1998) Škrdlíková et al. (2011)
Phenanthrene		$1.8 \times 10^5$	$2.6 \times 10^2$ (diss) 5.3 (ads) $0.05 \times 10^5$	He and Balasubramanian (2009)
	$6.1 \times 10^3$ $990-9.1 \times 10^4$ $1.2 \times 10^5$	$1.8 \times 10^4$ $4.3 \times 10^6$	$2.5 \times 10^4$ $3.3 \times 10^3$	Birgöl et al. (2011)
Anthracene	$1.8 \times 10^3$ $2.8-5.1 \times 10^4$ $1.4 \times 10^6$	$6.3 \times 10^3$ $4.0 \times 10^6$	$7.1 \times 10^2$ (diss) 21.4 (ads) $0.05 \times 10^5$ $3.2 \times 10^4$ 270	He and Balasubramanian (2009) Birgöl et al. (2011) Franz and Eisenreich (1998) Škrdlíková et al. (2011)
Fluoranthene	$3.1 \times 10^4$ $4.7 \times 10^2-$ $3.4 \times 10^5$ $8.9 \times 10^4$	$2.0 \times 10^4$ $3.3 \times 10^6$	$8.2 \times 10^2$ (diss) 24.7 (ads) $0.05 \times 10^5$ $2.5 \times 10^4$ $2.5 \times 10^4$	Birgöl et al. (2011) Franz and Eisenreich (1998) Škrdlíková et al. (2011)
Pyrene	$1.6 \times 10^4$ $42-1.0 \times 10^5$ $5.4 \times 10^5$	$1.3 \times 10^4$ $2.1 \times 10^6$	$1.6 \times 10^2$ (diss) 2.6 (ads) $0.05 \times 10^5$ $3.2 \times 10^4$ $9.9 \times 10^3$	He and Balasubramanian (2009) Birgöl et al. (2011) Franz and Eisenreich (1998) Škrdlíková et al. (2011)
Retene			$7.2 \times 10^3$ (diss) $2.6 \times 10^3$ (ads) $4 \times 10^4$	He and Balasubramanian (2009)
Benz(a)anthracene		$0.1 \times 10^5$	$0.5 \times 10^5$ $1.1 \times 10^4$ $3.3 \times 10^3$	Franz and Eisenreich (1998) Birgöl et al. (2011) Franz and Eisenreich (1998) Škrdlíková et al. (2011)
	$5.1 \times 10^3$ $15-3.5 \times 10^5$ $6.9 \times 10^6$	$4.3 \times 10^3$ $1.2 \times 10^6$	$9.6 \times 10^3$ (diss) $7.7 \times 10^4$ (ads)	He and Balasubramanian (2009)

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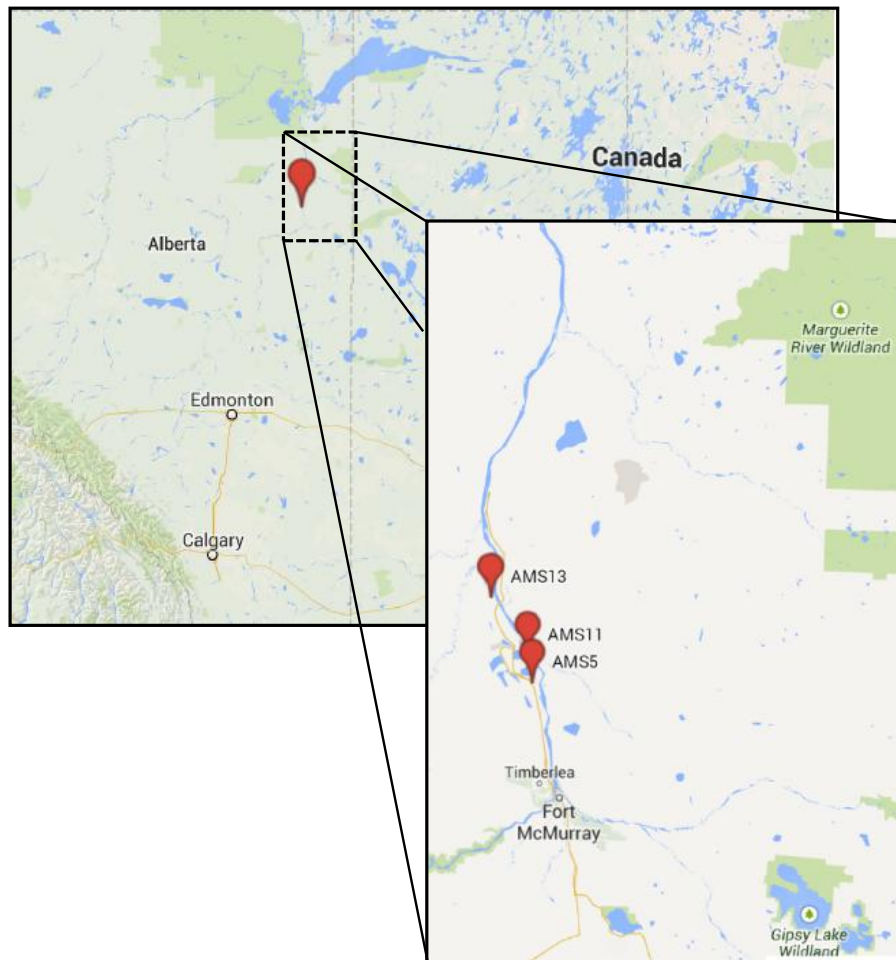
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Table 4. Continued.

PAC	$W_i$	$W_p$	$W_g$	Reference
Chrysene		$0.2 \times 10^5$	$0.1 \times 10^5$	Birgöl et al. (2011)
	$1.1 \times 10^4$	$7.9 \times 10^3$	$1.1 \times 10^4$	Franz and Eisenreich (1998)
	$32\text{--}2.4 \times 10^6$		$1.5 \times 10^4$	Škrdlíková et al. (2011)
Benzo(b+k)fluoranthene	$1.2 \times 10^6$	$2.0 \times 10^6$	$1.0 \times 10^4$ (diss)	He and Balasubramanian (2009)
			$9.2 \times 10^3$ (ads)	
			$1 \times 10^4$	Franz and Eisenreich (1998)
Benzo(b)fluoranthene		$0.1 \times 10^5$	$1.2 \times 10^5$	Birgöl et al. (2011)
	$1.5 \times 10^4$	$1.5 \times 10^4$	$5.5 \times 10^3$	Škrdlíková et al. (2011)
	$260\text{--}9.3 \times 10^5$			
Benzo(k)fluoranthene	$7.7 \times 10^5$	$8.9 \times 10^5$	$3.4 \times 10^3$ (diss)	He and Balasubramanian (2009)
			$1.9 \times 10^4$ (ads)	
			$1.7 \times 10^5$	Birgöl et al. (2011)
Benzo(e)pyrene		$0.2 \times 10^5$	$2.0 \times 10^4$	Škrdlíková et al. (2011)
			$2.2 \times 10^3$ (diss)	He and Balasubramanian (2009)
	$6.6 \times 10^5$	$7.8 \times 10^5$	$2.5 \times 10^4$ (ads)	
Benzo(a)pyrene			$1 \times 10^4$	Franz and Eisenreich (1998)
		$0.1 \times 10^5$	$2 \times 10^5$	Birgöl et al. (2011)
			$2.5 \times 10^4$	Franz and Eisenreich (1998)
Indeno(c,d)pyrene	$7.4 \times 10^5$	$8.2 \times 10^5$	$3.0 \times 10^3$	Škrdlíková et al. (2011)
			$2.8 \times 10^4$ (diss)	He and Balasubramanian (2009)
			$5.6 \times 10^4$ (ads)	
Dibenzo(a,h)anthracene		$0.1 \times 10^5$	$1.8 \times 10^5$	Birgöl et al. (2011)
			$6.3 \times 10^3$	Franz and Eisenreich (1998)
	$2.7 \times 10^5$	$2.5 \times 10^5$	$6.2 \times 10^3$	Škrdlíková et al. (2011)
Benzo(g,h,i)perylene			$2.6 \times 10^3$ (diss)	He and Balasubramanian (2009)
			$6.9 \times 10^2$ (ads)	
		$0.1 \times 10^5$	$1.7 \times 10^5$	Birgöl et al. (2011)
Overall range			$1.3 \times 10^4$	Franz and Eisenreich (1998)
	$5 \times 10^2$ to $2.5 \times 10^4$		$2.2 \times 10^3$	Škrdlíková et al. (2011)
	$8.9 \pm 4.3 \times 10^4$ to $1.2 \pm 0.4 \times 10^6$		$2.7 \times 10^5$	Birgöl et al. (2011)
Overall avg			$5 \times 10^3$	Franz and Eisenreich (1998)
		$8.97 \times 10^5$	$5.6 \times 10^3$	Škrdlíková et al. (2011)
			$3.3 \times 10^3$ (diss)	He and Balasubramanian (2009)
Avg of low MW PACs (Phe, Ant, Flt, and Pyr)			$9.8 \times 10^2$ (ads)	
		$231\ 215 \pm 387\ 550$	$2675 \pm 3125$	Birgöl et al. (2011)
		$20\ 670 \pm 25\ 790$	$170\ 845 \pm 244\ 015$	Birgöl et al. (2011)
Overall total				
	$9.9 \times 10^3$	$1.4 \times 10^4$	$6.1 \times 10^3$	Škrdlíková et al. (2011)
Enrichment factor (measured $W_p$ /theoretical $W_g$ )				
	$\log W_T = 0.94 \log \phi + 6.09$ ( $R^2 = 0.74$ )		0.14	He and Balasubramanian (2009) Franz and Eisenreich (1998)



**Figure 1.** Precipitation and air monitoring sites in the Athabasca oil sands region.

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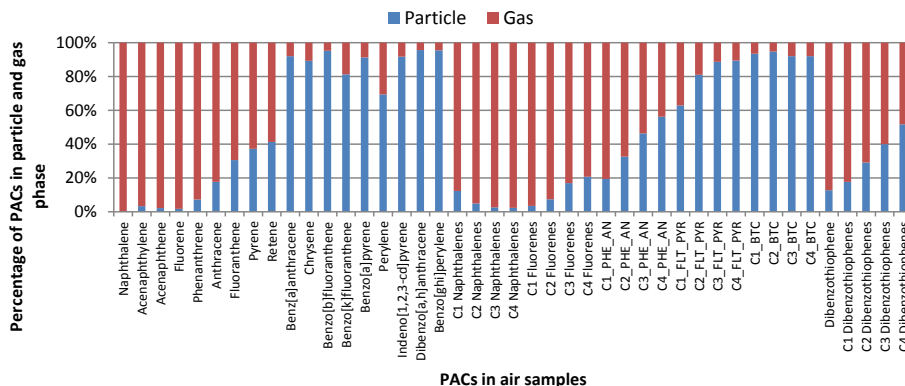
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**Figure 2.** Distribution of PACs in the gas and particle phases in air samples (PHE\_AN = phenanthrene/anthracene; FLT\_PYR = fluoranthene/pyrene; BTC = benz(a)anthracene/triphenylene/chrysene).

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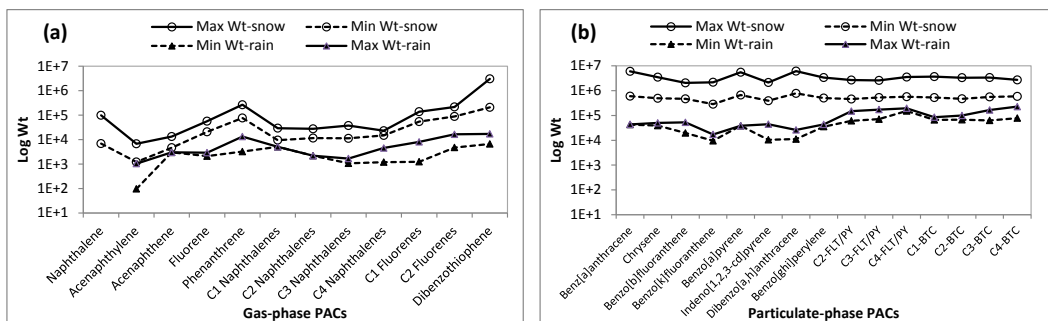
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**Figure 3.** Range of total scavenging ratios ( $W_t$ ) in snow and rain samples with similar precipitation rates (snow: 11.6–11.8 mm, rain: 10.8–12.3 mm month<sup>-1</sup>) for **(a)** gas-phase PACs and **(b)** particulate-phase PACs. Note the use of log scale for  $W_t$ , which indicates the range of  $W_t$  for snow is much larger than what is shown on the graph. FLT/PY = fluoranthene/pyrene; BTC = benz(a)anthracene/triphenylene/chrysene.

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