

Response to Reviewer #1

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

General comments:

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

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

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

Specific comments:

Title: "ratio" should be "ratios".

Response: Will be revised according to your suggestion.

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

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

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

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

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

Response: The introduction in the revised paper will be more concise and focus more on the literature related to wet scavenging processes and scavenging ratios for PACs. The objective of this study is to compare wet scavenging of PACs at the oil sands sites to other locations using scavenging ratios and to examine differences between snow and rain scavenging and between gas phase and particulate phase scavenging, since this makes up the majority of the results in sections 3.1-3.5. Previous studies have estimated PAH wet deposition in the Athabasca oil sands region in order to assess the impacts of the oil sands industry. Compared to these studies, the novel contribution of our study is the emphasis on how different species of PACs and precipitation types could affect the wet deposition of PACs in the Athabasca oil sands region. The introduction will include more information about alkylated PAHs and dibenzothiophenes because these compounds are associated with petrogenic sources which are highly relevant to the oil sands sites. The scavenging ratio results for alkylated PAHs and dibenzothiophenes will help improve the novelty of the study.

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

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

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

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

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

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

Response: The wet deposition samplers have been in the field for at least two years now; however this study has so far analyzed the data measured between 2 January 2011 and 31 May 2012. This is about 1.5 years of data. The period of data analyzed in this study will be corrected in the revised paper.

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

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

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

Response: The particulate mass fraction could vary with the air temperature, relative humidity, and chemical composition of particles because these parameters could affect gas-particle partitioning. These are potential uncertainties associated with the particulate mass fractions that will be discussed in the revised paper. The particulate fractions measured at AMS5 are thought to be representative of those at AMS11 and AMS13 because the sites are within 30 km of each other and they are all near-source sites. Thus, the meteorological conditions and particle composition should be similar for the three sites, which suggest the particulate mass fractions should be similar as well.

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

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

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

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

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

compared to those reported in other references (Franz and Eisenreich, 1998; Wania et al., 1999). This discussion will be provided in the revised paper.

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

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

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

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

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

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

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

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

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

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

Technical corrections:

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

Response: Will be revised according to your suggestion.