

General Comments: This manuscript describes an effort to apportion PM_{2.5} elements to different sources in the Athabasca Oil Sands Region. Two types of data were used: 24-hr filter samples from three near-mine monitoring stations over a two-year period from Dec. 2010 to Nov. 2012, and hourly elemental concentration from a portable elemental analyzer and 24-hr filters during an intensive study (Aug. 2013). Source apportionment was accomplished by Positive Matrix Factorization (PMF). Correlations with gases, time series, conditional probability function, and trajectory analyses were used to support the rationality the PMF factors. Elevated concentrations of elements have been observed in snow, river water, and lichen samples in the oil sands region (Bari et al., 2014; Graney et al., 2012; Huang et al., 2016; Kelly et al., 2010; Landis et al., 2012). Understanding the concentrations and sources of elements in PM_{2.5} in the region is important for assessing their environmental impacts and implementing control strategies. Therefore, the topic described in this manuscript is of great interest to the environmental science community, particularly to stakeholders in the oil sands region.

I have three major concerns on the data and results:

- 1. The source apportionment only used elemental composition. As can be seen from Figs. 2 and 3, many elements are present in multiple PMF factors, and most PMF factors are lacking specific elemental source markers. This collinearity make source identification and contribution apportionment less specific and more uncertain. The similarity in the temporal trend (e.g., Fig. S10) of different PMF factors is an indication of the difficulty in resolving these similar factors. The authors indicate that follow up analyses will include other chemical components (Page 20). I would prefer a source apportionment paper using all available chemical species (e.g., ion, carbon, isotopes, organic speciation, etc.) to create more specific and confident source apportionment results.*

We thank the reviewer for their helpful comments. The difficulty in adding other species lies in the variance of the sampling strategies and techniques between and within the two campaigns. In order to include as much data as possible, which increases the accuracy of the PMF analysis as it provides the program with more patterns to analyse, the filter data from all three sites and both campaign periods were included in the PMF run. However, only elemental composition data were available for these filters thus only trace element data was used for the high time-resolution study as well. As a main goal of the paper was to compare the source apportionment identified through a long-term, low time-resolution study and a short-term, high time-resolution study, the species analysed were kept as similar as possible. Follow-up research examining far more species would likely have to focus on the intensive period, when far more species were studied.

- 2. The Xact malfunctioned during the intensive study. While the authors tried their best to retain the Xact data as much as possible, the data quality is still in question for the following reasons:*
 - a) There was a drop in the internal measurement values for Pd, Pb, Cr, and Cd between 8/25 and 9/2/2013. It was assumed that the regression Eqns in Fig. S1 were applicable to all metals within its energy level. However, Fig. S2 shows that such correction caused the slope of Xact sulfur vs. AMS sulfur to change from 2.75 to 3.57, a significant 30% difference. The authors speculate that “could have been due to an increase in sulfate size distribution” but did not provide such evidence. Did the dichotomous sampler coarse channel show higher sulfate after 8/25?*

As stated in the Supplementary, estimated AMS PM1 sulfur and AIM-IC PM2.5 sulfur data were used to evaluate the instrument performance and the correction of Xact internal signals. We found more than 60% differences between AMS and AIM-IC sulfur data. Different cut-diameters and collection efficiencies of these two instruments could be a main reason for the difference. Thus we speculated that the change of the slope between AMS sulfur and Xact sulfur also might be related to a poor collection efficiency of the AMS as sulfate size distribution increases between near PM1 and PM2.5. The dichot sampler provides fine (PM2.5) and coarse mode (PM2.5-10) speciation data. However, the coarse mode sulfate data did not provide any stronger evidence of a shift in the sulfate size distribution between near PM1 and PM2.5.

Another possible explanation of the slope change before and after the Xact correction was identified and explored: the range of sulfur concentrations was quite different between the two periods. Before August 25, AMS sulfur increased to $\sim 3500 \text{ ng/m}^3$, which was almost one order of magnitude higher than the sulfate range after August 25. In order to examine the effect of sulfur concentrations, AMS sulfur data before the 25th were regrouped into two ranges, $< 300 \text{ ng/m}^3$ and $> 300 \text{ ng/m}^3$. As shown in Figure R1a, the slope for the lower concentrations range was closer to the slope after Aug. 25 (3.26 vs. 3.57). At the high range the agreement between Xact and AMS sulfur was better (Figure R1b), which was close to the slope for the entire concentrations ranges (2.71 vs. 2.75). The reason of the concentration dependency is unclear, it could be due to the change of the Sulfate/Sulfur ratio varying by sources. However, the agreement of the Xact with the AMS is not the key point here as the agreement between these two instruments is still not well established. Rather, it is the similarity in the agreement of the Xact before and after the correction that is the point. Here the similar slope ($\sim 10\%$ difference) for S before and after the Xact correction clearly supports the Xact correction is valid. Furthermore, Xact daily sulfur averages were compared to the filter XRF data before and after the correction. As shown in Figure R2, the corrected Xact S data lie in the range of the 95% prediction interval, indicating they are in the uncertainty levels of the analytical methods. In the revised supplement, Figure S2 was changed to display the slope at the lower range and we revised the statement on the comparison of the Xact data with SP-AMS.

“Overall, there was a large change in the slope of the line from 2.75 before August 25 to 3.57. However, the corrected slope was comparable to the slope in a similar concentration range (Figure S2b) before August 25 (3.26 vs. 3.57), suggesting that the Xact data correction was reasonable.”

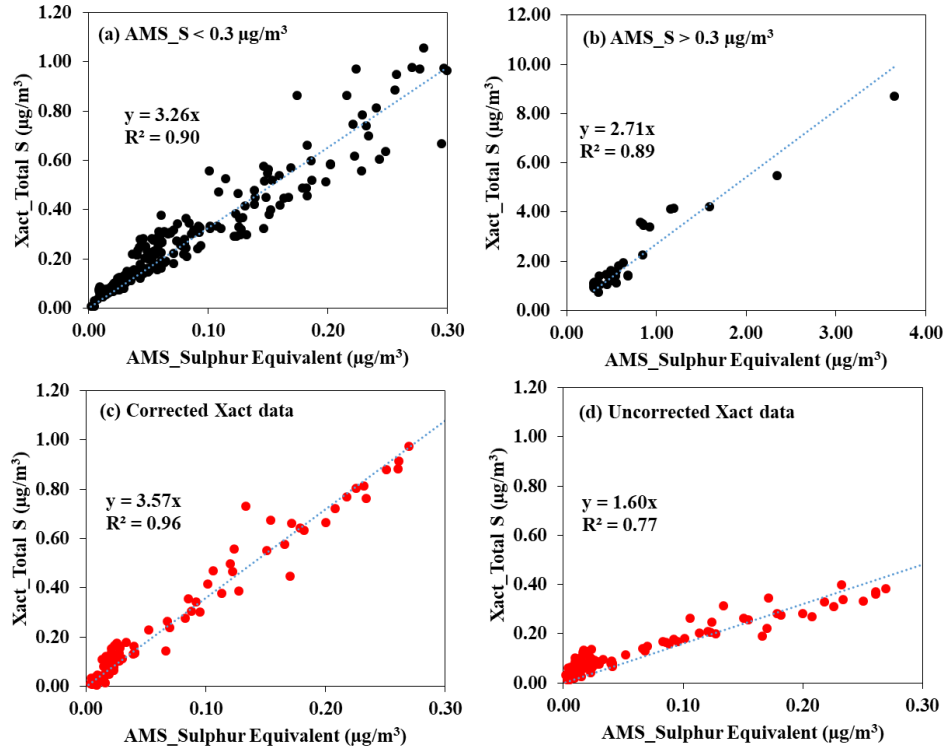


Figure R1. Comparison of SP-AMS sulphur equivalent to Xact S before Aug. 25, 2013 (a, b) and after Aug. 25, 2013 (c, d). All SP-AMS sulphate concentrations were divided by three to determine equivalent sulphur mass concentrations.

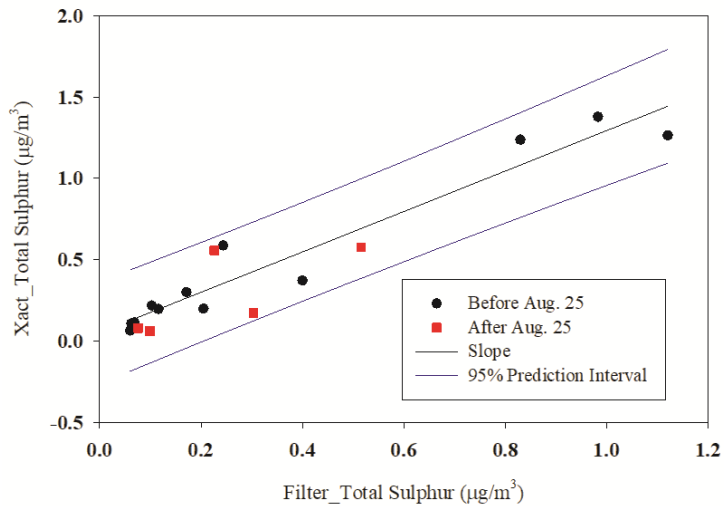


Figure R2. Comparison of daily integrated filter sulphur to Xact sulphur before and after August 25, 2013.

b) Figs. S3d and S3e show that sulfur from filter and AIM-IC measurements were comparable (indicating non-sulfate sulfur may not be significant), but Xact was ~40% higher. Such discrepancies also exist for several other high concentration elements (Fig. S3d), causing concerns about the Xact data quality. c) The Xact and filter data had various regression slopes according to concentration ranges (0.77 to 1.43; Figs. S3b-3d). From the assumption of using Fig. S1 to correct elements in the same energy level, I would expect the slopes to be similar for those within the same energy level, but not for those in the same concentration range. Both K and S belong to Energy Level 1 (Table S1), but the slopes are 0.77 and 1.43, respectively (Fig. S3c and 3d). This data is puzzling. Any explanations?

We agree that some hourly element concentrations measured by Xact were higher than the 23-hr integrated filter measurements. This difference is puzzling and thus we probed it in as many ways as we could and documented this in the supplementary. There could be many reasons for the discrepancy due to possible measurement biases of both methods (i.e., sampling time, inlet location, internal calibration factor). A further study for the comprehensive comparison of Xact and filter measurements is required to resolve confounding factors. In this study, the correlations between Xact and Filter for high concentration elements were very good ($r^2 > 0.85$), which was higher than the correlation between AIM-IC and Filter sulfur ($r^2 = 0.68$). We believe that this possible inaccuracy in the Xact data did not detract from the PMF analysis and the majority of elements included agreed well based on the filter comparison result.

The upscaling correction using Figure S1 equally affected all elements in the same energy level as the reviewer pointed out. However, each element in the Xact data has a specific internal calibration factor determined by standard element checks. Thus, the slope could be changed by elements and instruments.

- 3. While trying to explain the results, there are quite a few hand waving speculations, which shows insufficient understanding of the potential pollution sources in the oil sands region. For example, the high sulfur in the stack flue gas was assumed to be caused by #4 boiler fuel instead of the sulfur origin from upgrading process. Several other speculations are commented later. More specific and detailed comments are given below.*

We have tightened up the language. In particular, we agree that Boiler Fuel #4 was added as an example of a potential source. This has been edited for clarity and accuracy as follows:

“The profile is suggestive of a mixed-combustion source (Lee et al., 2000; Van et al., 2008), such as coke, or the process gasses, which are comprised of effluent from the sulphur recovery units (Wang et al., 2012).”

Specific Comments:

- 1. Title: “Source of Particulate Matter. . .” This is paper is about PM2.5 elements. Modify the title to be accurate.*

Since we didn't use major PM2.5 chemical speciation in PMF and multi linear regression of the source contributions against the total PM2.5 mass, the source apportionment and contributions are just related to the total metal mass, which are trace amounts within PM2.5. As such, the use of “Particulate Matter” encapsulates the purpose of the study for the title, as metals comprise such a small amount.

- 2. The authors generally referred the elements as metal (e.g., Page 3 last paragraph), which is not accurate because there are non-metal elements (e.g., S and Si). I would suggest to call them element to be accurate.***

Agreed, and done

- 3. There is a gap between the long-term filters and intensive study (Dec. 2012-July 2013). It would be logic to have the long-term sampling overlap the intensive study.***

It is agreed that it would be have been ideal to have a complete time series between the intensive and long-term campaign. However, at time of research and writing, these data were not available.

- 4. Page 3, 2nd paragraph. The review of past PM_{2.5} research in the oil sands is missing a large body of studies organized by the Wood Buffalo Environmental Association, such as air quality trend, emission source characterization, and elemental composition in lichen (Landis et al., 2012; Landis et al., 2017; Percy et al., 2012; Wang et al., 2012; 2015a; 2015b; 2016; Watson et al., 2012). These are very relevant to this manuscript.***

It is agreed that the second paragraph of page three does not include a full account of all studies done in the area, as it is simply an introduction to some of the work done in the area, not a full synopsis. Some of these papers had been added to other parts of the paper, some have been added as per further comments. In order to provide a more full reference to the amount of research in the area, the section have been altered as follows:

“Past research on PM_{2.5} within the Athabasca Region has included overall and comparative emission and air quality analyses (Kindzierski and Bari, 2011; Kindzierski and Bari, 2012; Wang et al., 2012; Percy et al., 2012; Howell et al., 2014; Wang et al., 2015; Landis et al., 2017). Further studies have developed into modelling the emission sources through both computer-based (Cho et al., 2012) and measurement-based methods (Landis et al., 2012)”

- 5. Page 4 Line 3. “. . . V and Ni are often indicative of oil combustion. . .” While this statement might be true in general, it may not be accurate in the oil sands region because bitumen is enriched with V and Ni (Shotyk et al., 2016). Attributing V and Ni to oil combustion will not reflect the bitumen-rich environment of the oil sands region. Citation of marker species should consider the local sources and chemical nature in the study area. This also raises question about the reason for attributing the factor “Upgrader Emission to oil combustion due the higher percentage of V and Ni. This may not be due to oil combustion, but due to bitumen processing. Therefore, it is important to find out if oil is largely used in combustion in the mining/upgrading facilities.***

This paragraph is intended as an example of how metals can and have been grouped together for source apportionment in the past, not as evidence of results. As bitumen is an oil derivative, this similarity would not be unexpected. Paragraph reworded to elucidate:

“However, compositional analysis of PM_{2.5} has helped elucidate sources and processes that contribute to PM_{2.5} mass concentrations in other regions. The element species in PM_{2.5} are of particular importance because they can be source-specific and are typically preserved in the aerosol phase during transport. For

example, V and Ni are often indicative of oil combustion (Becagli et al., 2012), as well as oil derivatives (Shotyk et al., 2016),”

6. ***Page 4 Line 3-4. “Al, K, Mg, and Cr are indicative of road dust. . .” This sentence was cited from a Mediterranean study, and the statement contradicts the results. For example, Al is abundant in almost all dust sources in the oil sands region (Wang et al., 2015a), K is a marker for biomass burning (Fig. 3) and Cr is not abundant in the haul road dust factor (Fig. 2).***

It is agreed that this is a source from a Mediterranean study. The purpose of this paragraph is to introduce how metals have been grouped together in the past for source apportionment, this has been edited for clarity as follows:

“while Al, Mg, and Cr, when grouped together have been indicative of dust, in the past specifically that associated with transportation (Amato et al., 2014)”

7. ***In the quality assurance and quality control sections (maybe in corresponding supplemental materials), I suggest adding: a) A comparison of overlapping elements that were measured by both ICP-MS and XRF. b) Describe in more details about how PMF factors were optimized and their uncertainties were estimated (e.g., Landis et al., 2017; Reff et al., 2007). Each PFM factor should show uncertainty based on bootstrapping. The similarity of profiles may be examined with Chi-square in addition to correlation coefficients.***

Scatter plots for Al, Ti, V, Mn, Fe, and Zn measured by ICP-MS and ED-XRF have been added in the supplementary. The correlation coefficients (r^2) ranged from 0.81 to 0.96 with good agreements.

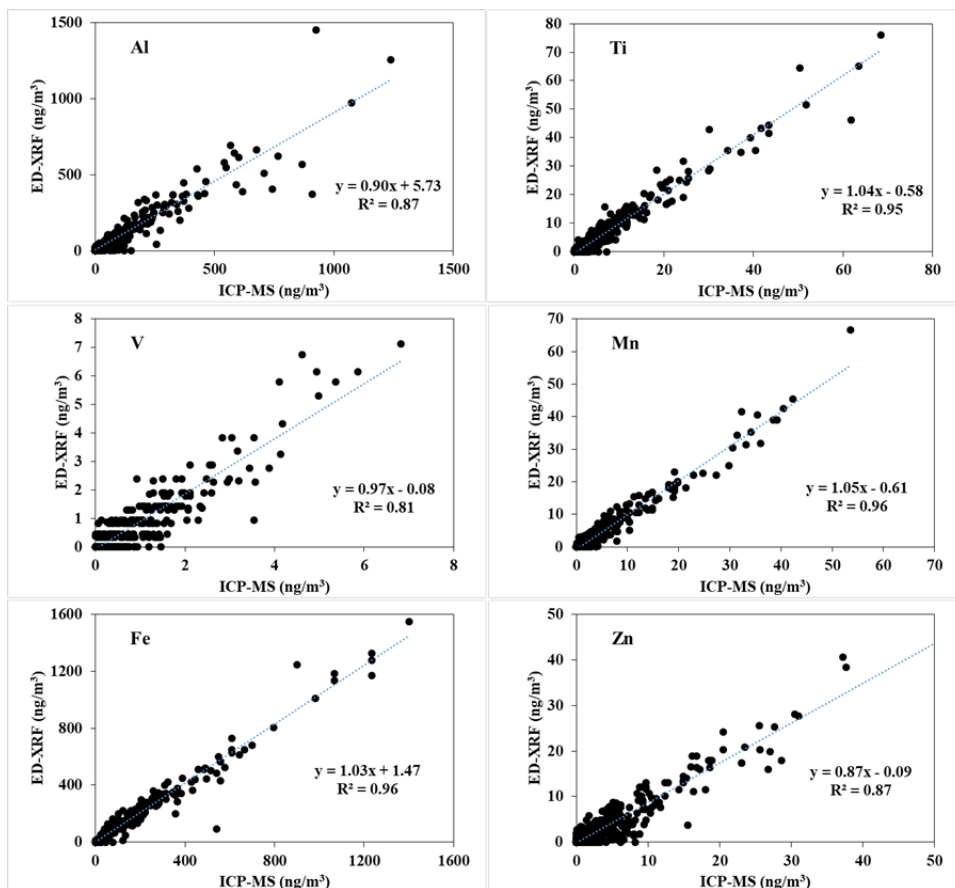


Figure R3. Comparison of ED-XRF and ICP-MS measurements at AMS 5, 11, and 13 from Dec. 16, 2010 to Nov. 29, 2012. Nine elements with more than 80% of data below the minimum detection limit were excluded from the comparison.

In the revised manuscript, we re-examined the PMF solution using EPAPMF 5 and calculated comprehensive error estimates of the PMF solution. Possible solutions were compared to determine the best solution based on their stabilities and uncertainties. Detailed information about the solution evaluation has been added in supplementary as follows:

“In order to estimate uncertainties and evaluate the robustness and rotational ambiguity of PMF modeling results, the solutions were evaluated using the error estimation methods of EPA PMF 5; bootstrap analysis (BS), displacement analysis (DISP), and bootstrap enhanced by displacement (BS-DISP). Bootstrap analysis (BS) was performed to quantify the uncertainty of a PMF-resolved solution. In addition, 100 bootstrap iterations were conducted to obtain the percentage of factors assigned to each base case factor (i.e. bootstrap mapping) and determine unstable factors in the PMF solutions. With the displacement analysis (DISP), each element in source profile is displaced from its fitted value in a PMF solution to estimate the uncertainties for each element in each factor profile. Based on the result of the displacement analysis of a PMF solution, the rotational ambiguity of PMF solutions was assessed (i.e. number of swaps at the lowest predetermined Q levels). BS-DISP, a combination of BS and DISP, estimates the error associated with both random and rotational ambiguity (Paatero et al., 2014; Brown et

al., 2015). A discussion of diagnostic results of the error estimation methods for possible PMF solutions is provided in Supplement S.3.”

“The bootstrap (BS) analysis was conducted to evaluate the uncertainties (i.e. random error in data values) of the source profiles and the reproducibility of factors in every bootstrap (Paatero et al., 2014; Brown et al., 2015). In the BS analysis, the BS factors are compared with the base run factors and then mapped to the base factor if the correlation is higher than a threshold ($r^2=0.8$ in this study). Tables S4 and S5 summarize the diagnostics of the error estimation for three PMF solutions (i.e. 4-, 5-, 6-factor solution) for the intensive Xact data and the long-term filter data, respectively. In the 5-factor solution of both Xact and filter data, we found most bootstrap factors were well assigned to base factors in >96% of every bootstrap. Overall reproducibility (i.e. average BS mapping percentages) for each factor in the 5-factor solution was higher than other solutions, suggesting the 5-factor solution was very reproducible and the optimal solution. The displacement (DISP) analysis was conducted to evaluate rotational ambiguity in the PMF solution as well. Multiple solutions may be generated with the same value of the object function Q due to rotational ambiguity. In DISP, each fitted element (only good species) in a source profile is displaced in turn from its fitted value until Q increases by a predetermined maximum change in Q. An uncertainty estimate for each element in each factor profile is thereby yielded and factor swaps may occur if factors change too much. A comprehensive error estimate method, bootstrap enhanced by displacement (BS-DISP) combine the strengths of BS and DISP, which evaluate both the robustness to data errors and rotational uncertainty. Overall, no change in DISP Q (%dQ) was found for the 5-factor solutions. Furthermore, no swapped factor was found in DISP BS-DISP runs, indicating the 5-factor solution was a global minimum and well-defined PMF solution.”

“The source profiles of the 4- and 6-factor solution for the intensive Xact PMF analysis are shown in Figures S5 and S6. In the 4-factor solution, the Soil and Haul Road Dust factors can be combined, but the reproducibility of the solution was poor and there were factor swaps in the BS-DISP runs. In the 6-factor solution, the Soil factor from the 5-factor solution split into two similar soil factors which have poor BS mapping reproducibility and very high factor swaps in the BS-DISP analysis. Another solution could be possible in the 6-factor solution which was characterized by additional resolution of the Mixed sources in the 5-factor solution. As shown in Figure S6b, two Mixed sources were characterized by high loadings of Cu (Mixed Sources I) and Br and Se (Mixed Sources II). Thus, due to the robustness of the solution and the physically meaningfulness of the factor profiles, the 5-factor solution was clearly acceptable for the intensive campaign.”

“In the long-term campaign the Haul Road Dust and Soil factors in the 5-factor solution can be combined into one factor in the 4-factor solution (Figure S7a). However, there was an alternative solution including a combined factor of Mixed and Upgrader Emissions (Figure S7b). Due to the instability, there were factor swaps in BS-DISP and the reproducibility of the 4-factor solution was poor. With 6 factors, an additional Soil factor characterized by high loadings of rare earth elements and vanadium was found. However, this second Soil factor is only found 56% of the BS resamples and 85% of the BS-DISP runs were accepted with high factor swaps. In the 7-factor solution, additional factor containing high Pb and Br can be isolated from the Upgrader Emissions factor, but it’s stability was very poor and there was no reasonable source for Pb and Br only. The BS resamples and BS-DISP runs of the 5-factor solution was better than the 4- and 6-factor solutions for the long-term filter data (Table S5). These results indicate that the 4- and 6-factor solution are much less certain than the 5-factor solution. As a result, the 5-factor solution was chosen as the most reasonable and stable solution for the filter data.”

“In order to determine the relative weights of the different factors, a multiple linear regression of the time series of each factor for both campaigns was run against both the summed metal concentrations as well as

the PM_{2.5} concentrations (obtained from WBEA). As trace metals only account for a small percentage of the overall PM_{2.5} mass, the results of the PM_{2.5} regression proved to be a poor fit both statistically ($r^2 < 0.8$) and physically, as it resulted in negative relative weights, to the metal speciation factor solutions. Because of this, the total metals concentration was used to determine the relative weights of the different factors, which resulted in a much better fit ($r^2 > 0.99$).”

The chi-square value is the weighted sum of squares of the differences between the measured (i.e., Landis et al. 2012) and PMF-modelled element concentrations. However, no Chi-square values are available in this study since the Landis’s source profiles were reported as relative contributions (i.e., $\mu\text{g/g PM}$). In the revised manuscript, uncentered correlation coefficient has been used as an unbiased metric to evaluate the level of similarity between the profiles of sources. This metric is particularly useful as it takes into account the similarity of minor peaks.

Table S4. Summary of error estimation diagnostics for intensive Xact data.

	4-Factor Solution	5-Factor Solution	6-Factor Solution
Robust Mode	Yes		
Seed Value	Random		
# of Bootstraps in BS	100		
R ² in BS	0.8		
DISP active species	Si, S, K, Ca, Ti, V, Mn, Fe		
BS-DISP active species	S, K, Ti, V, Fe		
Factors with BS mapping < 100%	Upgrader Emissions II(51%), Mixed (99%)	Upgrader Emissions II (98%)	Soil (53%), Soil II (93%)
DISP %dQ	0	0	0
DISP # of swaps	0	0	0
BS-DISP % of Cases Accepted	95	97	27
BS-DISP # of swaps	4	0	198

Table S5. Summary of error estimation diagnostics for long-term combined filter data.

	4-Factor Solution	5-Factor Solution	6-Factor Solution
Robust Mode	Yes		
Seed Value	Random		
# of Bootstraps in BS	100		
R ² in BS	0.8		
DISP active species	Si, S, K, Ca, Ti, Fe, Cu, Sr, Al, Cd, Ce, La, Pr, Nd, Sm, Gd, Pb, U		
BS-DISP active species	Si, S, K, Ca, Fe, Cu, La		
Factors with BS mapping < 100%	Mixed (29%), Biomass Burning (98%)	Mixed (96%), Soil (99%)	Soil (56%), Haul Road Dust (97%), Mixed (99%)
DISP %dQ	9.3E-5	0	1.8E-5
DISP # of swaps	0	0	0
BS-DISP % of Cases Accepted	87	97	85
BS-DISP # of swaps	10	0	12

8. *The calibration with metals standards showed good accuracy (Table S1) after the Xact returned to the laboratory after field campaign. Was there anything done to fix the Pd signal drop during the field campaign? If so, what was cause of the problem and what was the fix? If not, did the instrument somehow fix by itself sometime between 8/25 and laboratory tests?*

Many parts including high voltage power supply (HVPS), x-ray tube, and filament cables had to be checked. We finally found a loose wire connection from the National Instruments AD converter and suspected that the position of the Pd rod changed slightly because of vibration during shipping. After the field campaign the HVPS had to be replaced. It appears that shipping can be tough on this instrument.

9. *Page 11 Line 17-19. Please verify if No. 4 boiler fuels were used in upgrading facilities. From an earlier publication on oil sands stack emission (Wang et al., 2012), the boilers were fired with natural gas, process gas, and/or coke. Process gases (e.g., effluent from the sulfur recovery units) and coke, instead of No. 4 fuels, are likely the main sources of sulfur in that area. Careful survey and understanding of the industrial operations are required to reduce speculations.*

We agree and thank the reviewer. The comparison was simply to show an example of a mixed source combustion fuel, this section has been edited for accuracy and clarity as follows:

“The profile is suggestive of a mixed-combustion source (Lee et al., 2000; Van et al., 2008), such as coke, or the process gasses, which are comprised of effluent from the sulphur recovery units (Wang et al., 2012).”

10. *Page 12. “It is speculated that this factor may have arisen from short term changes in fuel, such as a switch to oil combustion for heat/energy or the burning of coke. . .” This speculation of the source of “Upgrader Emission II” is not supported by hard evidence.*

We agree and had worked this text accordingly so as to emphasise that this was speculation and that this was raising possibilities rather than making any definitive claim

For clarity, this has been changed to: “It is speculated that this factor may have been due to two different stacks from within the upgrading process/facility. A less likely, but more fortuitous, possibility is that the Upgrader Emissions II factor was due to a short-term change in upgrader fuel that occurred only during the intensive measurement campaign and not during the long-term campaign”

11. *Sections 3.2.3 and 3.2.4. I am not convinced that the soil factor and haul road factor can be reliably separated based on elemental composition. The profiles Figs. 2-3 are very similar. The overburden itself is stable and is not a large source of fugitive dust (Wang et al., 2015b). Dust is emitted from dikes built by overburden when heavy haulers are travelling on them. Then the emissions are similar to the haul road. Emissions of haul road dust occur when heavy haulers are moving on the unpaved haul road and when wind speed is high. Since diesel-fueled heavy haulers are the largest emitters of NO_x, I would expect the haul road dust to better correlate with NO_x than the “Soil” factor. Large dust plumes are often observed from tailings beaches under high wind conditions. Also there are several unpaved roads around the sampling sites, which are large dust sources. As shown in Figure 6 and its related discussion, both Soil and*

Haul Road factors increased during the day with very similar temporal patterns and are not driven by wind speed. These indicate that these two factors are likely driven by road dust. A single “dust” factor instead two may be more appropriate.

While there are overlaps in the elements within the haul road dust and soil factors, there are enough differences to separate them as two separate sources. In fact, the source profiles for the Soil and Haul Road Dust were only weakly correlated (uncentered $r=0.129$), as is stated in the paper. Figure 6 simply shows the averaged-daily trends, not the overall hour-by-hour trends that PMF used, which are seen in Figure S9. These overall temporal trends do show clear differences in the time series of the two factors. Further, the speculated sources of the Haul Road Dust and Soil factors are due to on and off-road transportation. As the overburden dump is comprised of the overburden (top soil) in the area, it would be expected that any off-road transportation, whether on the dikes made of the overburden dump, or undisturbed overburden (top soil), would kick up dust comprised of the same material as the overburden dump. However, dust kicked up by vehicles on a road would be expected to have a slightly different elemental composition than that of the dust kicked up by the off-road vehicles, thus the two factors. Further the two factors, particularly in the intensive campaign, were very stable. These two factors can be combined in the 4-factor solution, but the reproducibility of the solution was poor and there were more factor swaps (please refer to the uncertainty analysis as shown earlier). This stability, along with lack of correlation, justifies the separation into two factors.

12. Table 2. Have the correlations between PMF factors and CO been looked at? CO is an indicator of biomass burning and/or vehicle emissions and may offer added evidence to the PMF factors.

While this would be a useful comparison, of the species available to us at the sites, as well as during the two campaigns, CO was not a gas that available to us.

13. Page 20 Line 16-17. It is not accurate to categorize the Soil and Haul Rod Dust factors as “two with the transportation of the bitumen-rich oil”. This excludes on-road vehicle and other dust sources.

We agree that “the transportation of bitumen-rich oil” does not entirely encapsulate all of the transportation. To account for this, the sentence has been adjusted to read as follows:

“two with on and off-road transportation”

14. Figure 6 and S10. It might be useful to examine the diurnal variation each factor.

While the Soil and Haul Road Dust Factors showed what appeared to be regular, diurnal trends (See Figure S9), the other three factors did not exhibit any patterns that resemble a daily trend. Taking daily averages of such episodic occurrences would not aid in the identification of the factor.

Technical Details

1. Figs 1, 7, S14 etc. All maps should have a scale bar to infer distances.

Agreed, and they have been added to the Figures.

- 2. Figs. 2, 3, S5, and S6. Add a note to indicate if the bar and symbol refers to the left or right hand side of the Y-axis.**

Agreed. For clarity, the following has been added to the figure descriptions:

“Factor concentrations depicted as bars, percentages depicted as circles.”

- 3. Page 6 Line 4. I suggest changing “dirt” to “oil sands”.**

While this wording was constructed in a way to describe what “oil sand” is, the paper has been adjusted as follows:

“Bitumen-rich dirt” has been converted to “Oil Sands”

- 4. Page 6 Lines 7-10. Each oil sands mining facility has multiple stacks that are connected to different upgrading processes. For example, Syncrude has a main stack, a FGD stack, and several smaller stacks. Furthermore, most stacks are equipped with pollution control devices. Some particles, e.g., ammonium sulfate, are formed in the FGD process designed to remove SO₂ (Wang et al., 2012). Rewrite this sentence to accurately reflect this information.**

It is agreed that while there are numerous stacks, our comparison was to the measurements of the main stack taken by (Landis et al., 2012). However, in order to better reflect the totality of what happens, the wording has been changed to the following:

“Once at the upgrading facility the bitumen is separated from the slurry in large settling vessels, after which it is upgraded into different hydrocarbon streams using steam, vacuum distillation, fluid cokers, and hydrocrackers, these processes produce aerosol particles which are emitted to the air through both the main stack (Landis et al., 2012), as well as numerous other secondary stacks. Within these stacks, some particles are directly emitted from the upgrading processes, while others are created by the pollution control devices installed within the stacks (Wang et al., 2012).”

- 5. Page 6 Lines 10-13. Evaporative emissions from tailings ponds may be an importance source of VOCs and secondary particles, but may not be an important source for primary particles. Instead, windblown dust from tailings beaches and dikes is a significant particle source (Wang et al., 2015b).**

It is agreed that evaporative emissions is likely not a significant source of primary particles. As such, the sentence has been altered to read:

“Other known sources of particles are: the large fleets of on and off-road vehicles, dust re-suspended by mining activities, windblown dust from the tailings ponds and dikes (Wang et al., 2015), and dust re-suspended from open petroleum coke piles.”

6. Fig. S3b-S3d showed 9 metals. Where are other metals?

In order to do a comparison, hourly measurements were turned into daily averages. If in the course of the day over 50% of the hourly measurements were below detection limit or if the average itself was below detection limit, this daily average data point was removed due to increase unreliability associated with below detection limit measurements. In some cases this removed all daily average measurements for a metal.

7. Write “Eqn 1” in supplemental materials in an equation form.

Equations have been denoted as Arabic numerals in parentheses as suggested by the journal guideline.

8. There are two Table S4

Agreed, in sections S.5 and S.6, the table numbers have been altered to be “Table S6 and Table S7”

9. Page 10 Section 3.1 and Section 3.5. I don’t think it is fair to compare the 90th percentile in the oil sands to the average city values. If such comparison should be done, the 90th percentile of city values should be used. Also the three monitoring stations are considered as near-source monitoring due to their close distance to mining facilities. It is not surprising that their elemental concentrations are higher than many cities, considering the abundance of dust in the region (Shotyk et al., 2016).

We agree that the 90th percentile does provide a different comparison than a straight mean comparison table. The main reason for including this table was to provide some context for the levels of PM2.5 metals relative to other sites in Canada where this type of data is available, which all happen to be cities. The second reason is to identify which metals are likely related to activities in the region. To do this we looked at the 90th percentile values which are more likely representative of intermittent plumes, than day to day averages.

To increase the clarity of these points, we made the following changes:

Within Section 3.1:

In order to clarify that the only reason that the oil sands concentrations were compared to the cities alone was due to lack of Canadian trace element data for remote sites, “cities” has been changed to “sites” in many places in order to clarify the intent of the comparison. For example, the first sentence, which reads “Average metal concentrations from the filter data were compared to measurements taken by the NAPS program at seven different Canadian sites (Environment and Climate Change Canada, 2015) (Table S6), which, due to a lack of comparable rural or remote baseline data, corresponded to different Canadian cities.”

In order to clarify the use of the 90th percentile as a means to predict which metals come from anthropogenic sources, the end of section 3.1 has been altered to read:

“In the oil sands, large swaths of forest are broken up by the occasional mine or upgrader. When the wind comes from one of these directions, particularly the upgraders, there is a noticeable difference in the air quality. To illustrate this large variability, the 90th percentile of the various elements was calculated and

analysed, as species that show a high degree of variability are more likely from these intermittent pollution sources. The results of this showed that the previously discussed elevated elements showed peaks indicating large variability. Additionally, at the highest peaks the concentrations of S, Ba, Br, and Mn also showed large increases, which indicates that in the Oil Sands, they are likely caused by anthropogenic sources.”

Within Section 3.5:

The second and third sentences have been altered to read “In particular, the concentrations of Si, Ti, K, Fe, Ca, and Al were, on average, higher than those measured in major Canadian cities. At their highest peaks the concentrations of S, Ba, Br, and Mn also exhibited large increases in concentrations.”

10. Page 13 Line 17. “lower concentrations of Mn and Fe” should be “higher. . .”

We agree that the “lower” should be changed to “higher”. This has been changed.

The sentence in the “Haul Road Dust” Section now reads as “What differentiated this factor from the Soil factor were the higher concentrations of Mn and Fe, and Ca. (Fig. 2).”

11. Page 20 Line 4. Incomplete sentence: including. . .

We agree that this is an incomplete sentence. And the “including” has been dropped from that sentence.

The sentence in “Implications of the Source Identification for Element Species” section now reads “As these factors represented a combination of multiple sources, the individual sources causing elevation of these elements is still not known; this limitation may help direct further studies.”

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Interactive comment on “Sources of Particulate Matter in the Athabasca Oil Sands Region: Investigation through a Comparison of Trace Element Measurement Methodologies” by Catherine Phillips-Smith et al.

Anonymous Referee #3

Received and published: 16 May 2017

The manuscript by Phillips-Smith et al. investigated sources of PM_{2.5} in the Athabasca Oil Sands region based on PMF analyses of particulate metals. The metal species were derived from a long-term campaign in which filter-based measurements were conducted at three sites, and also from an intensive campaign in which semi-continuous measurements were performed at one of the long-term sites. Interestingly, PMF results were compared between these two campaigns. The topic of this manuscript is within the scope of the special issue “Atmospheric emissions from oil sands development and their transport, transformation and deposition”. However, I cannot support its publication in the current form. As can be seen from my detailed comments given below, my major concerns are about the PMF results.

- 1. Page 3, line 25-28. It is not appropriate to list “modelling”, “airborne studies” and “comparison of PM_{2.5} concentrations” successively in one sentence.***

We thank the reviewer for their feedback. In order to provide a brief overview of work completed on the topic of PM_{2.5} in the Oils Sands Region, the examples were simply listed. To better structure this, this section has been reworded as follows:

“Past research on PM_{2.5} within the Athabasca Region has included overall and comparative emission and air quality analyses (Kindzierski and Bari, 2011; Kindzierski and Bari, 2012; Wang et al., 2012; Percy et al., 2012; Howell et al., 2014; Wang et al., 2015; Landis et al., 2017). Further studies have delved into modelling the emission sources through both computer-based (Cho et al., 2012) and measurement-based methods (Landis et al., 2012).”

- 2. Page 4, line 9-13. The authors implied that no source apportionment study had been performed for the oil sands region using metal species of PM_{2.5}. However, it is unclear whether there are any previous source apportionment studies using other PM_{2.5} components (e.g., water-soluble ions, organic carbon, elemental carbon and etc.). Please clarify.***

It is true that there has been another PMF study done in the Oil Sands, based on PM_{2.5} (Bari and Kindzierski, 2017). However, it did not focus on the metal analysis, or use high time resolution data to compare and contrast the results.

The section of the paper has been adjusted as follows:

“In past receptor modeling, open pit mining, upgrading, and fugitive dust have been identified as major emission factors in the oil sands region (Landis et al., 2012; Bari and Kindzierski, 2017). However, these emission factors were identified based solely on long-term, low time-resolution data.”

- 3. Page 4, line 24-26. No content in the results and discussion section corresponds to the second purpose presented here.***

In order to reduce the length of the paper, findings relating to the accuracy, precision, and consistency of the Xact™ 625 instrument are introduced in section 2.5 and described in detail in the supplementary.

- 4. Line 29 in Page 4 to line 8 in page 5. This paragraph should be presented much more briefly, since all the descriptions involved here are repeated in the methods section.**

The text has been shortened by removing details related to the method as follows:

“Since December 2010, under the Enhanced Deposition Component of the Joint Canada-Alberta Implementation Plan for Oil Sands Monitoring (JOSM) Program, 24-hr integrated filter samples have been collected by Environment and Climate Change Canada in PM_{2.5} at three sites (Fig. 1) operated by the Wood Buffalo Environmental Association (WBEA). As part of a 2013 summer intensive field campaign, hourly measurements were also made at one of the sites (Fort McKay South, AMS13) for one month (Aug. 10- Sept. 10) using a semi-continuous metal monitoring system.”

- 5. Page 9, line 6-9. Please provide (representative) scatter plots comparing ICP-MS and ED-XRF measurement results on the same metals.**

Scatter plots for Al, Ti, V, Mn, Fe, and Zn measured by ICP-MS and ED-XRF have been added in the supplementary (Figure S3f). The correlation coefficients (r^2) ranged from 0.81 to 0.96 with good agreements. Please find our responses to the reviewer #1.

- 6. Page 11, line 12-15. It is unclear which PMF profile (i.e., Upgrader Emissions I shown in Figure 2 or 3) was used for the comparison to the profile reported by Landis et al. (2012). In addition, it is quite surprising that the regression analysis could show an r value of 1.00. Does this mean that the two profiles are exactly the same?**

In order to confirm that both campaigns identified the same factor, both profiles were compared to the same upgrader emission profile published by Landis et al. (2012).

The intensive campaign is referenced Figure 2, while the long-term campaign is referenced Figure 3.

Further, while surprising, both profiles so closely resembled the reported profile of Landis et al. (2012), that to 2 significant digits, their r values reported as 1.00. In the revised manuscript, uncentered correlation coefficient has been used as an unbiased metric to evaluate the level of similarity between the profiles of sources. This metric is particularly useful as it takes into account the similarity of minor peaks. Spearman ranked correlation analysis was performed on the comparison of temporal variations (i.e., time series).

The paper has been adjusted to clarify which correlation relates to which figure as follows:

In Section 2.4.2., “Spearman ranked correlation analysis was performed on the comparison of temporal variations, whereas uncentered correlation coefficient was used to evaluate the level of similarity between factor profiles.”

In Section 3.2.1., “This factor was attributed to typical emissions from the upgrading processes based on the correlation (uncentered $r=1.00$ for the intensive campaign (Figure 2): uncentered $r=1.00$ for the long-

term campaign (Figure 3)) of its elemental profile with an average profile derived from samples of PM_{2.5} taken from main upgrader stacks in the area (Landis et al., 2012).”

“There were strong correlations in: i) the PMF factor profiles derived from the two methodologies and ii) the time series between the co-measured Xact and filter data of this factor (profile (uncentered $r=1.00$); time series (Spearman $r=0.74$, $p<0.01$)).”

- 7. Page 11, line 29-30. V and Ni were used to indicate oil combustion. However, as shown in Figure 2, the majority of Ni was attributed to the Mixed Sources factor; on the other hand, negligible V was seen in the Mixed Sources factor. These results mean that the major sources of V and Ni are different. Consequently, I don't think it is reliable to attribute the Upgrader Emissions II factor to oil combustion, unless the authors could demonstrate that the V to Ni ratio calculated for this factor was comparable to that measured in source emissions from oil combustion.**

We agree that while the Upgrader II factor does not contain the highest percentage of Ni of all the factors, it does contain a significant amount (around 30% of the total). Further, the ratio of V to Ni for this factor is 5.5, which is very similar to the known ratio for heavy oil combustion ($V/Ni = 5-7$) (Huffman et al., 2000).

This section has been adjusted to account for this as follows:

“More specifically, this factor was attributed to oil or bitumen based fuel combustion because of the higher percentages of V and Ni, (Fig. 2), which are typical of oil combustion (Huffman et al., 2000; Lee et al., 2000). On average, the ratio of V to Ni in this factor profile was 5.5, which was comparable to heavy oil combustion with high sulphur contents reported by Huffman et al., 2000 ($V/Ni=5-7$).”

- 8. Page 13, line 17. According to Figure 2 and 3, concentrations of Mn and Fe were higher in the Haul Road Dust factor compared to the Soil factor.**

We agree that the “lower” should be changed to “higher”. This has been changed to agree.

The sentence in the “Haul Road Dust” Section now reads as “What differentiated this factor from the Soil factor were the higher concentrations of Mn, Fe, and Ca (Fig. 2).”

- 9. Page 13, section 3.2.5. Figure 3 indicates that biomass burning was the major source of Cd. Moreover, the biomass burning contribution to Cd (~80%) was more significant than its contribution to K (~60%). However, previous source emission studies typically suggest that biomass burning is not a strong source of Cd (e.g., Schmidl et al., Atmos. Environ., 42, 126-141, 2008 and references therein). The authors are required to provide references to support their discussions here, i.e., biomass burning could be the major source of Cd.**

Since the correlation between K and Cd was strong ($r=0.74$, w/o an outlier on Feb 9, 2012), Cd cannot be separated from the biomass factor. Although the high loading of Cd in biomass burning is not commonly found in other areas, source apportionment studies in Edmonton, Alberta reported the presence of Cd in biomass burning factors including our previous PMF study in Edmonton (~20% of total mass, Jeong et

al., 2011). Kindzierski and Bari (2015) and Bari et al., (2015) also found the high loading of Cd (37%-62%) as marker species of biomass burning in this area.

This section has been altered to address the above as follows:

“All of these elements, to different degrees, have been associated with different types of biomass burning in this (Jeong, et al., 2011; Kindzierski and Bari, 2015; Bari et al., 2015) and other regions (Van et al., 2008; Vassura et al., 2014; Alves et al., 2011).”

10. Page 14, section 3.2.6. High abundance of Ni observed in the Mixed Sources factor should be discussed.

Due to the nature this factor, we have concluded that it is from a mixture of sources, for which there was not sufficient data to resolve into their own, separate sources.

Regardless, the largest known emitter of Ni, at 2.5 tonnes in 2013, according to the 2013 NPRI data from near Wood Buffalo, is the Mildred Lake Plant Site of Syncrude. This facility also co-emitted Cu, Cr, Zn, and Se, which were more of the marker elements of the Mixed Sources Factor.

This section has been adjusted to reflect this information as follows:

Addition of “Ni” into the marker elements descriptions of the two campaigns for this factor.

“as well as Ni, K and Se, which suggested the inclusion of biomass, oil, or coal burning, perhaps the burning of scrap-brush”

Addition of the following sentence:

“Other elements within these Mixed Sources could have been the result of further industrial activity at the different plant sites, which are known to be large emitters of elements such as Ni, Cu, Cr, Zn, and Se (Environment and Climate Change Canada, 2015).”

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Interactive comment on “Sources of Particulate Matter in the Athabasca Oil Sands Region: Investigation through a Comparison of Trace Element Measurement Methodologies” by Catherine Phillips-Smith et al.

M. A. Bari

mdaynul@ualberta.ca

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In this manuscript the authors investigated sources of ambient concentrations of elements in fine particulate matter (PM_{2.5}) at three industrial locations in the Athabasca Oil Sands Region (AOSR) using 24-h (Dec. 2010 – Nov. 2012) and 1-h (August 2013) data. The receptor model EPA PMF3.0 was applied and seven emission sources were identified. In general, the results appear to be impressive and interesting for the international scientific community. However, I would like to raise some points that would be needed to address to better understand and reveal the sources of PM_{2.5} in the AOSR.

Some assumptions and interpretations have been made particularly in the methodology and result sections, which make the findings more uncertain. I would therefore suggest that the authors should consider major revisions as outlined in the specific comments.

Specific comments:

1. The authors investigated sources of PM_{2.5} using trace element concentrations that accounted for only a small fraction of PM_{2.5} mass. The authors should consider using all available chemical components e.g., cations (K⁺, Ca²⁺), anions (SO₄²⁻, NO₃⁻). It is reported that additional chemical composition data would be available in the follow-up analysis (page 20). To the best of my knowledge, carbonaceous aerosol (EC/OC) measurements were not performed at oil sands region. Therefore, checking PM_{2.5} mass closure is helpful to identify the proportion of unaccounted mass, which can be included as an input variable (missing mass) in the model as suggested by Larson et al (2006) and have been applied in several other studies (e.g., Wu et al., 2007; Bari and Kindzierski, 2017). This helps to better explain some source factors.

We agree that PM_{2.5} source apportionment using comprehensive chemical speciation data including major inorganic/organic aerosol will provide a better insight into PM_{2.5} sources in terms of the quantification of PM_{2.5} source contributions. However, as stated in the study objectives, we focused on the source identification of trace metal elements related to short-term sporadic events using high-time resolution data during the intensive campaign period. Furthermore, long-term filter data were used to evaluate the trace metal source apportionment from the intensive hourly measurements. However, only the trace and not the major component speciation data was available for the filter data. This the PMF analysis was done for the trace element data only so as to allow direct comparison between the findings from the two methods. Thus, while we agree with the reviewer’s suggestion, it is beyond the possible scope of this current study and we may need a further study as stated in the manuscript”

“More generally, the elements used to create the factor profiles and thereby identify sources accounted for only a small portion of the total PM_{2.5} mass. This limitation will be addressed in follow-up analysis combining the Xact data with other concurrent, time-resolved, measurements of non-refractory components. Combining these data will provide a more complete mass reconstruction so as to allow apportionment of PM_{2.5} and further sources may be revealed by leveraging the perspective given by the additional composition information.”

2. It is not clear how the authors come up with the 5-factor solution using EPA PMF3.0. The authors provided justification for choosing the optimum number of factors screening basic criteria e.g., Q-values, G-space plots, Fpeak values. However, they didn't report any error estimation techniques such as bootstrapping (BS) analysis. The authors should apply the current version of the PMF model (EPA PMF5.0) that allows to better assess the uncertainty of PMF solutions, using three error estimation methods i.e., BS, displacement (DISP) and bootstrapping with displacement (BS-DISP) analysis.

In the revised manuscript, EPAPMF 5 was used to calculate the error estimates of the PMF solution. Possible solutions were compared to determine the best solution based on their stabilities and uncertainties. Detailed information about the solution evaluation has been added in supplementary. Please find our responses to the reviewer #1.

3. The selection of chemical elements for PMF analysis was based on the frequency of detection and species only >10% of the measurements above the detection limit were chosen. This may increase more uncertainty in PMF-resolved sources. It is suggested to exclude the elements with more than 70% of samples below the detection limit. The authors should include data quality information (including percentage of detection, below detected and missing values) in the supplemental. It is also suggested to provide QA/QC for laboratory analysis.

Since air quality in the monitoring areas were frequently influenced by short-term episodic events lasting for several hours, we included trace elements containing a high percentage of below the detection limit data to identify the short-term sources, that exhibited strong, plume-like behaviour. Compared to integrated filter samples, hourly measurements are advantageous to detect the sporadic events and below detection limit data can be useful to identify local sources. Furthermore, below detection limit data were down-weighted based on their signal-to-noise ratios to minimize modeling errors. While most elements that fulfilled this requirement had over 10% above detection limit data, a couple of metals had less than this, however, when these metals were above the detection limit, they were significantly higher for several hours, suggesting a plume.

As suggested, we have added the percentage of data below the detection limit and missing data in Table S2, and clarified the description as follows.

“or data that exhibited strong, “plume-like” behaviour when it was above detection limit,”

All NAPS filter samples across the sites were routinely maintained and analyzed by Environment Canada in Ottawa. We briefly described the filter sampling and analytical method in the manuscript as more detailed information is available elsewhere (Celo et al., 2011; Dabek-Zlotorzynska et al., 2011). A comparison of overlapping elements (i.e., Al, Ti, V, Mn, Fe, and Zn) measured by both ICP-MS and ED-XRF has been added in the supplementary (Please find our responses to the reviewer #1). The correlation coefficients (r^2) ranged from 0.81 to 0.96 with good agreements.

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4. The authors identified seven sources including two types of upgrader emissions, soil, haul road dust, biomass burning and two sources of mixed origin. It is suggested to improve the interpretation for describing some specific sources that are related to oil sands development. For example, adding secondary ions (SO₄²⁻, NO₃⁻) in PMF analysis will help to better characterize the input of oil sands emissions.

As discussed previously, the main objective of the study is to identify sources related to the increase of trace metal species. Since organic aerosol can be the largest PM contributor in this area (~70% of total PM_{2.5} mass were unidentified as shown in Bari and Kindzierski 2017), a follow-up source apportionment study including high resolution organic species measured by aerosol mass spectrometry would provide a better estimation of source contributions.

5. Recent studies in the AOSR indicated fugitive dust (e.g., from oil sands tailings, unpaved roads and hauling fleet emissions) as a dominant source contributing ~20%– 40% to PM_{2.5} (Landis et al., 2017, 2012; Bari and Kindzierski, 2017). The authors should check ‘soil’ and ‘haul road dust’ factors to better interpret the influence of fugitive dust.

We agreed that the two “crustal” factors found in this study, soil and haul road dust, likely encompass a large portion of the “fugitive dust”. As combined, our soil and dust factors make up between 31 and 38 % of the total metal element mass, this would agree. However, it should be noted that this is soil and dust factor contribution to the total metal mass in PM_{2.5} and care must be taken to compare with PM_{2.5} source contributions as shown in the references (Landis et al., 2017, 2012; Bari and Kindzierski, 2017).

Because the term “fugitive dust” encapsulates so much of the different sources of dust (such as from the oil sands tailings, unpaved roads (or off-road vehicles), and Hauling Fleet Emissions (or on-road vehicles), it makes more sense to keep them separate, as they describe two parts of the overall fugitive dust.

6. The authors tried to compare the observed levels of PM_{2.5} elements in the industrial locations in the AOSR with other Canadian cities. Elemental levels at oil sands communities (e.g., Fort McKay and Fort McMurray) were not investigated here. Due to the unique nature of emission sources (not available in other Canadian region), the comparison analysis may not be informative and therefore suggested to exclude from the manuscript.

We agree that in order to get a full idea of how the element levels in the Oil Sands compares to other areas, the concentrations would have ideally be compared to baseline rural and remote measurement sites with no industrial activity. However, we wanted to compare the oil sands data to sites in Canada where

this type of information has been measured, which happens to be the sites included, within the cities. Despite this limitation, a comparison to cities, urban sites known to be more polluted, some even with other industrial emissions nearby, do provide some context for the levels observed.

Further, while the measurements taken in the long-term study do not include Fort McMurray, one of the sites, AMS 13, is located in the south of Fort McKay, and would thus be representative of that community. Further the three sites do cover a range of the area, so their average provides an indication of how the area as a whole compares to other Canadian sites.

The paper has been adjusted to refer to the comparison cities as “sites”.

Sources of Particulate Matter in the Athabasca Oil Sands Region: Investigation through a Comparison of Trace Element Measurement Methodologies

Catherine Phillips-Smith¹, Cheol-Heon Jeong¹, Robert M. Healy², Ewa Dabek-Zlotorzynska³, Valbona Celo³, Jeffrey R. Brook⁴, Greg Evans¹

¹ Southern Ontario Centre for Atmospheric Aerosol Research, University of Toronto, Toronto, Ontario, Canada

² ~~Analysis Air Monitoring and Transboundary Air Quality Sciences~~ Section, ~~Air Quality Research Division, Ministry of the Environment and Climate Change Canada, 335 River Road, Etobicoke~~, Ontario, Canada

³ Analysis and Air Quality Section, Air Quality Research Division, Environment and Climate Change Canada, 335 River Road, Ottawa, Ontario, Canada

⁴ Air Quality Processes Research Section, Air Quality Research Division, Environment and Climate Change Canada, 4905 Dufferin Street, Toronto, Ontario, Canada

Correspondence to: Greg Evans (greg.evans@utoronto.ca)

Abstract. The province of Alberta, Canada is home to three oil sands regions which, combined, contain the third largest deposit of oil in the world. Of these, the Athabasca Oil Sands Region is the largest. As part of Environment and Climate Change Canada's program in support of the Joint Canada-Alberta Implementation Plan for Oil Sands Monitoring program, concentrations of trace metals in PM_{2.5} elements in PM_{2.5} (particulate matter smaller than 2.5 µm in diameter) were measured through two campaigns that involved different methodologies: a long-term filter campaign and a short term intensive campaign. In the long-term campaign, 24-hr filter samples were collected one-in-six days over a two-year period (Dec. 2010 - Nov. 2012) at three air monitoring stations in the Regional Municipality of Wood Buffalo. For the intensive campaign (Aug. 2013), hourly measurements were made with an on-line instrument at one air monitoring station; daily filter samples were also collected. The hourly and 24-h filter data were analysed individually using positive matrix factorization. Seven emission sources of PM_{2.5} trace elements were thereby identified: two types of Upgrader Emissions, Soil, Haul Road Dust, Biomass Burning, and two sources of mixed origin. The Upgrader Emissions, Soil, and Haul Road Dust sources were identified through both the methodologies and both methodologies identified a mixed source, but these exhibited more differences than similarities. The second Upgrader Emissions and Biomass Burning sources were only resolved by the hourly and filter methodologies, respectively. The similarity of the receptor modeling results from the two methodologies provided reassurance as to the identity of the sources. Overall much of the PM_{2.5} related metal was trace elements were found to be anthropogenic, or at least to be aerosolized through anthropogenic activities. These

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emissions may in part explain the previously reported higher levels of metal trace elements in snow, water, and biota samples collected near the oil sands operations.

1 Introduction

The Athabasca Oil Sands Region, located in the north-east corner of the province, is the largest of the three oil sands deposits in Alberta, Canada (Bytnerowicz et al., 2010). This area contains an estimated 1.7 trillion barrels of oil, located tens of meters below the ground (Kean, 2009),
5 composed of a highly viscose mixture of high molecular weight hydrocarbons, bitumen, clay, sand, and water (Bytnerowicz et al., 2010). As of 2009, the oil was extracted at a rate of 0.825 million barrels per day (Moritis, 2010), predominantly through two methods: open pit mining and steam assisted gravity drainage (Canadian Association of Petroleum Producers, 2014). Combined, these methods have rendered 10% of the bitumen in the oil sands economically recoverable, making
10 Alberta home to the third largest known oil deposit in the world after Venezuela and Saudi Arabia (Xu and Bell, 2013).

The various processes involved in bitumen extraction are believed to have environmental impacts on the area's water (McMaster et al., 2006), soil (Whitfield et al., 2009), and ecology (Goff et al., 2013). While air quality studies are much more limited (Hodson, 2013; Bari and Kindzierski,
15 2015), gaseous emissions such as SO₂ and NO_x are known pollutants associated with oil sands activities (Charpentier and Bergerson, 2009; Bytnerowicz et al., 2010; McLinden, 2012). These gases have been linked to several oil sands extraction processes such as mining, transportation, and upgrading (Howell et al., 2014). Of current interest are aerosol particles below 2.5 µm in diameter (PM_{2.5}), which affect the environment through transport of pollutants, visibility
20 reduction, and by directly or indirectly shifting the earth's radiation balance (Dusek et al., 2006; Posfai and Buseck, 2010; Jeong et al., 2013). Further, PM_{2.5} has been linked to adverse health outcomes (Docker et al., 1993; Burnett et al., 1995; Schlesinger, 2007) due to its propensity to penetrate deep down to the alveolar region of the lungs (Borm and Kreyling, 2004; Alfoldy et al., 2009). PM_{2.5} is produced both by natural and anthropogenic sources such as motor vehicles, wind-blown dust, industrial processes, and biomass burning (Jeong et al., 2013). Past research on PM_{2.5}
25 within the Athabasca Region has included ~~modelling (Cho et al., 2012), airborne studies (Howell et al., 2014), overall, and comparisons of the regions PM_{2.5} concentrations to other areas of Canada~~ comparative emission and air quality analyses (Kindzierski and Bari, 2011; Kindzierski and Bari, 2012; ~~Hsu and Clair,~~ Wang et al., 2012; Percy et al., 2012; Howell et al., 2014; Wang et al., 2015); Landis et al., 2017). Further studies have developed into modelling the emission
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sources through both computer-based (Cho et al., 2012) and measurement-based methods (Landis et al., 2012).

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No previous studies have examined short term variability in the ~~metal~~elemental composition of PM_{2.5} in this region. ~~Compositional~~However, ~~compositional~~ analysis of PM_{2.5} ~~can help~~has helped

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5 elucidate sources and processes that contribute to PM_{2.5} mass concentrations. ~~The metal in other~~ regions. ~~Trace element~~ species in PM_{2.5} are of particular importance because they can be source-

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specific and are typically preserved in the aerosol phase during transport. For example, V and Ni are often indicative of oil combustion (Becagli et al., 2012), ~~as well as oil derivatives (Shotyk et al., 2016).~~ while Al, ~~K,~~ Mg, and Cr ~~are, when grouped together have been~~ indicative of ~~road dust~~

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10 ~~in the past, specifically that associated with transportation~~ (Amato et al., 2014). ~~This source~~ specificity allows for the identification of sources of PM_{2.5} with great resolution (Moreno et al., 2009). Receptor models are often used to determine these sources in areas where the chemical

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composition of the various sources is unknown. One such receptor model is Positive Matrix Factorization (PMF), which uses a weighted multivariate statistical approach to identify pollution

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15 sources (called factors) by examining the correlations in the PM_{2.5} ~~metal~~ speciation matrix over time (Paatero, 1996). In past receptor modeling, open pit mining, upgrading, and fugitive dust have

been identified as major emission factors in the oil sands region (Landis et al., 2012); ~~Bari and~~ Kindzierski, 2017). However, these emission factors were identified based ~~on metal species~~

20 ~~measured in lichen, which is not necessarily representative of PM_{2.5} solely on long-term, low time-~~ resolution data.

Previous studies also provide indirect indications of higher levels of ~~metals~~trace elements ~~s~~ in this region. Through dry and wet deposition, such as snowfall (Bari et al., 2014), it is possible for the

~~metal~~trace elements contained in the particulate matter to reach the soil and surface waters in the area (Amodio et al., 2014). Metals, such as Cu, Zn, Ni, Cr, and Pb have been found to be higher

25 in the Athabasca River, its tributaries, and snowpack near the oil sands developments than several hundred kilometers away (Kelly et al., 2010). Furthermore, epiphytic lichens have experienced

increases in Ti, Al, Si, and Ba (Landis et al., 2012). In summary, the available evidence suggests that ~~metal~~-contamination may already be occurring in this region and that some of this may be due

to transport of ~~metal~~trace elements present within PM_{2.5}.

Due to these gaps in knowledge, the purpose of this work was threefold: (1) To fill the knowledge gaps that exists about the sources of PM_{2.5} ~~metals~~trace elements in this region, (2) to assess the accuracy, precision, and consistency of the Xact™ 625 instrument (Cooper Environmental Services, 2013) used for the intensive hourly measurements versus that of the more standard 24-hr filters, and (3) to determine what can be learned from receptor modelling using higher time-resolved vs. 24-hr filter data.

Since December 2010, under the Enhanced Deposition Component of the Joint Canada-Alberta Implementation Plan for Oil Sands Monitoring (JOSM) Program, ~~trace elements-24-hr integrated filter samples~~ have been ~~measured~~collected by Environment and Climate Change Canada in PM_{2.5} at three sites (Fig. 1) operated by the Wood Buffalo Environmental Association (WBEA), ~~in close proximity to oil sands processing activities (Fig. 1). The 24-hr integrated filter samples are collected every 6 days (midnight-midnight) following the procedure used in the National Air Pollution Surveillance (NAPS) program. Furthermore, as~~ a part of the a 2013 summer intensive field campaign, hourly measurements were also made at one of the sites (Fort McKay South, AMS13) for one month (Aug. 10- Sept. 10) using a semi-continuous metal monitoring system; ~~daily 23-hr filter measurements were also collected.~~

A comprehensive protocol was developed to analyze the data from the two methodologies individually with PMF, which made it possible to identify the sources of PM_{2.5} affecting the measurement sites (Jeong et al., 2013; Sofowote et al., 2014; Jeong et al., 2016). The identity of these sources was supported by comparing the resolved source profiles with existing profiles for the postulated sources along with temporal patterns of measured gaseous species. Meteorological data (courtesy of the WBEA) was used to further improve interpretation and identify probable source locations. By comparing the PMF results of the 24-hr and hourly measurements, a deeper understanding of the long and short term temporal variability of the sources, and the applicability of the two measurement methodologies to receptor modelling was achieved.

2 Methods

2.1 Field Measurement Sites

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Under the Air Component of JOSM, the Municipality of Wood Buffalo was selected for the monitoring of air pollutants associated with oil sands activities because it is home to both mining and in situ extraction operations. In the long-term filter study, ~~metalelement~~ concentrations were monitored around the Athabasca river valley at three WBEA air monitoring stations (AMS):
5 AMS13- Fort McKay South (SYN); AMS5- Mannix (MAN); and AMS11- Lower Camp (LOW) (Fig. 1). The AMS13 site is located between three oil companies in the area, all of which perform extensive mining, upgrading, and in-situ processing (Fig. 1): Canadian Natural Resources Limited (CNRL) is to the north, Syncrude is to the south, and Suncor is to the southeast. All three companies extract bitumen through both open pit mining and in situ methods within the Athabasca
10 Region. The other two measurement sites are located farther south, directly between Syncrude and Suncor, with AMS11 to the north of AMS5.

Within the Municipality of Wood Buffalo, open pit mining is the predominant method of bitumen extraction. In open pit mining, large hydraulic shovels lift the ~~bitumen rich dirt~~ oil sand into trucks for transport to a nearby wet crusher which reduces the size of the soil and adds water, allowing
15 the soil-slurry to be piped to an upgrading facility (Syncrude Canada Ltd., 2015; Canadian Association of Petroleum Producers, 2014). Once at the upgrading facility the bitumen is separated from the slurry in large settling vessels, after which it is upgraded into different hydrocarbon streams using steam, vacuum distillation, fluid cokers, and hydrocrackers, these processes produce aerosol particles which are emitted to the air through ~~the main upgrader stack (Landis et al., 2012)~~ both the main stack (Landis et al., 2012), as well as numerous other secondary stacks. Within these stacks, some particles are directly emitted from the upgrading processes, while others are created by the pollution control devices installed within the stacks (Wang et al., 2012). Other
20 known sources of particles are: the large fleets of on and off-road vehicles, dust re-suspended by mining activities, ~~evaporative emissions~~ windblown dust from the tailings ponds, and dikes (Wang et al., 2015), and dust re-suspended from open petroleum coke piles.
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2.2 Instrumentation

2.2.1 Filter Monitoring Setup

PM_{2.5} samples were collected at the three sites on 47 mm polytetrafluoroethylene (PTFE)
30 membrane filters (Pall Corporation, New York) using Thermo Fisher Partisol 2000-FRM samplers

at 16.7 L/min. The samplers were operated once every six days with a 24-hr sampling time (midnight-midnight) according to the NAPS protocol. All samples, including laboratory, travel, and field blanks, were subjected to gravimetric determination of PM mass and were subsequently analyzed for 22 elements using non-destructive x-ray fluorescence (ED-XRF). PM_{2.5} samples were then analyzed for 37 trace elements including 14 lanthanoids by inductively-coupled plasma mass spectrometry (ICP-MS) combined with microwave-assisted acid digestion, which provides superior detectability for trace metal(oids) (Celo et al., 2011). [A comparison of overlapping elements \(i.e., Al, Ti, V, Mn, Fe, and Zn\) measured by both ICP-MS and ED-XRF \(Fig. S3f\) confirmed good agreement with correlation coefficients \(r²\) from 0.81 to 0.96.](#) The PMF analysis applied 2-yr of filter data from Dec. 16, 2010 to Nov. 29, 2012 (Long-term Filter, Table 1).

2.2.2 Intensive Campaign Setup

During the intensive campaign in August, 2013, daily PM_{2.5} samples were also collected at AMS13 site using a dichotomous sampler (Partisol 2000-D, Thermo Scientific, Waltham, MA) on 47 mm PTFE filters (Pall Corporation, New York). The sampler was operated with a 23-hr sampling time (8:30 am – 7:30 am) so as to allow an hour for filter switching. In the dichotomous PM sampler, a virtual impactor splits the incoming PM₁₀ sample stream into fine (PM_{2.5}) and coarse (PM_{10-2.5}) fractions. Mass flow controllers maintained the flow rates of the fine and coarse particle streams at 15 L/min and 1.7 L/min, respectively. Elemental composition of PM_{2.5} was analyzed following the procedure described above. Due to the limited number of samples taken (sample number, n=29), these PM_{2.5} data were combined with those of the long-term campaign for PMF analysis.

In addition to the filter measurements, an Xact 625 (Cooper Environmental Services, 2013) made hourly measurements of 23 ~~metalelement~~ [metalelement](#) species at AMS13 between August 10 and September 5, 2013 (n=489). This semi-continuous instrument was installed in a trailer and sampled air through a PM₁₀ head fitted with a PM_{2.5} cyclone located 4.55 m above ground level. The Xact used a two-step “semi-continuous” process. In the first step, particles were pumped through a section of PTFE filter tape at a flow rate of 16.7 L/min, which was regulated through measurement of the inlet temperature and pressure. The section of filter tape was then analyzed in the second phase, which employs the same measurement technique as ED-XRF. Both the sampling and the measurement phase occurred simultaneously, producing data for all 23 ~~metalelement~~ [metalelement](#)s every hour.

2.3 Quality Assurance and Quality Control

The filter measurements were carried out in accordance with the standard operating protocols that were in place and care was taken to ensure that quality assurance and control programs (ISO17025 accredited) were followed.

Quality assurance and quality control (QA/QC) for the Xact measurements was based on protocols implemented before, during, and after the intensive campaign. Prior to the intensive campaign, the Xact was calibrated using 12 high-concentration metal standards. Three metal standards: Cr, Pb, and Cd, were selected to represent the three energy levels employed by the Xact. These metal standards were measured on site at the beginning of the intensive measurement campaign (Table S1). Throughout the campaign, the internal Pd, Cr, Pb, and Cd upscale values were recorded after the instrument's daily programmed test, and the PM₁₀ and PM_{2.5} cyclones were cleaned weekly. A sample of filtered air was measured daily to determine both the detection limits (DL) and baseline biases of the metals the instrument measured. Further QA/QC that occurred during the campaign can be found in the Supplementary. After the campaign, the performance of the Xact metals monitor was further evaluated through three methods: re-testing with the high-concentration standards, new medium-concentration standards, and a comparison of the Xact data to co-measured data from filter samples and other collocated high time resolution instruments (Supplementary S.1).

2.4 Data Analysis

2.4.1 Positive Matrix Factorization

The metalelement speciation data of the two measurement methods were analyzed using Positive Matrix Factorization (PMF). Developed by Paatero and Tapper, PMF is a least squares regression model that inputs the data (X) and uncertainty (σ) matrices of the receptor site, resolving them into factor profiles (F), factor contributions (G), and residuals (E) (Paatero and Tapper, 1993; 1994) (Equation 1). Each factor corresponds to pollution sources or processes that may co-occur, contributing to particles at receptor site; the profile displays the concentration of metalelement

species within each factor, and the time series displays the normalized contribution of each factor to the total metalelement concentration over time (Norris and Duvall, 2014).

$$X = GF + E \quad (1)$$

Marker elements within the factor profiles were identified based on their high concentrations and/or percent segregations. These marker elements enabled the initial attribution of these PMF factors to probable sources. The identity of these sources was then supported by comparing, where possible, the resolved PMF profiles with source profiles for the suspected sources along with temporal patterns of measured gaseous species.

Prior to running the PMF algorithm, the data were screened to exclude metalelements for which fewer than 10% of the measurements were above the detection limit (DL) (Table S2). The data for metalelements measured with both ED-XRF and ICP-MS were then compared so as to select the optimal set of measurements based on the percentage of data above the DL and the signal-to-noise ratio (S/N). For a full description of the PMF algorithm and pre-treatment, refer to Supplementary S.2. The diversity of the elements among the factors was examined using Shannon Entropy (Healy et al., 2014) (Supplementary S.5). Elements with Shannon entropy above 3.5 were discounted as marker elements in the factor profiles due to their relatively equal segregation into the different factors.

The filter and Xact data were analyzed separately using PMF due to their different sampling intervals. Filter data from Dec. 2010-Nov. 2012 (Long-term Filter) and Aug. 2013 (Intensive Filter) were combined (total n= 351) to produce a single data matrix as the Aug. 2013 data alone were insufficient to support a separate PMF analysis. Measurements taken by ICP-MS were combined with those taken by ED-XRF in order to create a full metalelement profile. In instances where the ICP-MS and ED-XRF both measured the same species, the data measured by ICP-MS were selected as this resulted in the most above DL data. PMF solutions with four to six factors were considered as candidates and five-factor solutions were selected for both the filters and the Xact data; these solutions had three common factors and two factors that differed (Figs. S5-S8S7). Furthermore, the five-factor solution for the combined filter data was similar to five-factor solutions produced when the filter data from each site was run independently (AMS5, AMS11, and AMS13) (Supplementary S.2-3).

In order to estimate uncertainties and evaluate the robustness and rotational ambiguity of PMF modeling results, the solutions were evaluated using the error estimation methods of EPA PMF 5: bootstrap analysis (BS), displacement analysis (DISP), and bootstrap enhanced by displacement (BS-DISP). Bootstrap analysis (BS) was performed to quantify the uncertainty of a PMF-resolved solution. In addition, 100 bootstrap iterations were conducted to obtain the percentage of factors assigned to each base case factor (i.e. bootstrap mapping) and determine unstable factors in the PMF solutions. With the displacement analysis (DISP), each element in source profile is displaced from its fitted value in a PMF solution to estimate the uncertainties for each element in each factor profile. Based on the result of the displacement analysis of a PMF solution, the rotational ambiguity of PMF solutions was assessed (i.e. number of swaps at the lowest predetermined Q levels). BS-DISP, a combination of BS and DISP, estimates the error associated with both random and rotational ambiguity (Paatero et al., 2014; Brown et al., 2015). A discussion of diagnostic results of the error estimation methods for possible PMF solutions is provided in Supplement S.3.

2.4.2 Supporting Analyses

To further investigate the results, linear regression analyses were performed for each factor time series against NO, NO₂, NO_x, and SO₂ concentrations (obtained from the Wood Buffalo Environmental Association) in order to identify relationships. Spearman ranked correlation analysis was performed on the comparison of temporal variations, whereas uncentered correlation coefficient was used to evaluate the level of similarity between factor profiles. The time series of each factor resulting from both methodologies were run through a conditional probability function (CPF) to determine the most likely direction of the relevant sources. As described in Equation 2, the CPF is the ratio between the number of times the mass contribution surpasses a certain threshold percentile (i.e. 75%) when the wind comes from a certain direction ($m_{\Delta\theta}$) and the number of times the wind came from that direction ($n_{\Delta\theta}$) (Kim and Hopke, 2004).

$$CPF = \frac{m_{\Delta\theta}}{n_{\Delta\theta}} \quad (2)$$

In this study, the wind direction (obtained from the WBEA) was divided into 24 bins, each encompassing 15°, and time periods with wind speeds below 1 m/s were removed. Given the varied topography within the Athabasca River Basin, favouring transport of local emissions along the

river valley, the CPF only gave approximate indications of the source directions. Finally, a back trajectory model, Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) was run on potential non-local factors (Stein et al., 2015).

5 3 Results and Discussion

3.1 Elemental Species Overall Trends

Average ~~metalelement~~ concentrations from the filter data were compared to measurements taken by the NAPS program at seven different Canadian ~~cities~~ sites (Environment and Climate Change Canada, 2015) (Table ~~S4~~,~~S6~~), ~~which, due to a lack of comparable rural or remote baseline data, corresponded to different Canadian cities.~~ Prior to averaging, blank values were removed as described in Supplementary S.2, and Below Detection Limit (BDL) values were replaced by half the detection limit. Overall, the average concentrations of some of the ~~metalelements~~ measured through the long-term campaign were lower than those observed in the ~~Canadian cities~~ sites as shown in Table ~~S4~~~~S6~~. This is not overly surprising as ~~these~~ the cities are impacted by a range of anthropogenic activities such as heavy traffic and industrial factories. What was surprising was the number of ~~metalelements~~ measured in the largely unpopulated oil sands region, which exhibited similar or higher concentrations to those seen across the various ~~cities~~ sites. In particular, levels of Si, Ti, K, Fe, Ca, and Al appeared to be higher near the oil sands operations. However, these averages do not fully ~~encapsulate~~ capture the differences between the ~~cities~~ sites and the oil sands region. In the oil sands, large swaths of forest are broken up by the occasional mine or upgrader. When the wind comes from one of these directions, particularly the upgraders, there is a noticeable difference in the air quality. ~~This is in contrast to a city where levels fluctuate less.~~ To illustrate this large variability, the 90th percentile of the various ~~metalelements~~ was calculated and ~~compared to the averages~~ analysed, as species that show a high degree of the ~~various cities~~ variability are more likely from these intermittent pollution sources. The results of this showed that ~~at its highest peaks,~~ the previously discussed elevated ~~metals~~ further surpass the ~~average city values.~~ elements showed peaks indicating large variability. Additionally, at the highest peaks the concentrations of S, Ba, Br, and Mn also ~~surpass those typically seen in the cities~~ showed large increases, which indicates that in the Oil Sands, they are likely caused by anthropogenic ~~sources.~~

3.2 PMF Results

Each technique identified five unique factors through PMF analysis. Comparison of these factors led to the identification of seven factors: two types of Upgrader Emissions, Soil, Haul Road Dust, Biomass Burning, and two factors of presumably mixed origins. Three of these factors were identified by both methodologies, two by only one of the methodologies, and the two mixed sources showed more differences than similarities between the two methodologies. The results of the PMF factor profiles (F matrix) from the two methodologies can be seen in Fig. 2 (hourly data from the intensive campaign in Aug., 2013) and in Fig. 3 (24-hr filter data from the combined long-term campaign, Dec. 2010 - Nov. 2012 and intensive filter campaign in Aug. 2013). Distinctive marker elements were evident in some profiles while other elements were surprisingly ubiquitous, appearing in most or all of the factors. Here the low diversity (high Shannon Entropy) of Ni and Se across the source profiles is interesting as it implies that these metal(oid)s are present in most of the sources, perhaps as a result of greater natural homogeneity in this region or contamination of the region through anthropogenic activities.

3.2.1 Upgrader Emissions I

This factor was attributed to typical emissions from the upgrading processes based on the correlation (uncentered $r=1.00$, $p<0.05$ for the intensive campaign; (Fig. 2); uncentered $r=1.00$, $p<0.05$ for the long-term campaign) (Fig. 3) of its elemental profile with an average profile derived from samples of PM_{2.5} taken from main upgrader stacks in the area (Landis et al., 2012). Specifically, the elemental profile contained significant portions of the S, V, As, Br, and Pb (Fig. 3). The very high S contribution in its profiles distinguished it from the second upgrader related factor. The profile is suggestive of a mixed-combustion source ~~as these characteristic elements have been previously seen in No.4 boiler fuels, a mix still used in many parts of Canada~~ (Lee et al., 2000; Van et al., 2008), such as coke, or the process gasses, which are comprised of effluent from the sulphur recovery units (Wang, et al., 2012). Further, the high correlation of this factor with SO₂ (Table 2) was consistent with the increased SO₂ observed in fresh industrial plumes in the area (Hsu and Clair, 2015; Zhang et al., 2015). There were strong correlations in: i) the PMF factor profiles derived from the two methodologies and ii) the time series between the co-measured Xact and filter data of this factor (profile (uncentered $r=1.00$, $p<0.05$); time series (Spearman

r=0.8774, p<0.0501). These observations support the assertion that this factor resulted from combustion of a range of fuels in support of upgrading processes.

3.2.2 Upgrader Emissions II

This factor was hypothesized to be a less common type of emissions originating from upgrading processes; it was only resolved through the hourly data of the intensive measurement campaign.

More specifically, this factor was attributed to oil or bitumen based fuel combustion because of the higher percentages of V and Ni, (Fig. 2), which are typical of oil combustion (Huffman et al., 2000; Lee et al., 2000).

~~Other metals~~ On average, the ratio of V to Ni in this factor profile was 5.5, which was comparable to heavy oil combustion with high sulphur contents reported by Huffman et al., 2000 (V/Ni=5-7).

~~Other elements~~ associated with oil combustion such as S, Ti, Zn, and Fe (Huffman et al., 2000; Lee et al., 2000) were also evident. The temporal correlation of this factor to SO₂ in the intensive measurement campaign suggested the combustion of high sulphur fuel

(Table 2) (Van et al., 2008; Zhang et al., 2015). ~~Correlation~~ Uncentered correlation (r=0.90, p<0.0599) between the chemical profile for this factor and the average ~~meta~~ element profile seen

in upgrader stacks around the region (Landis et al., 2012) was ~~not as strong as~~ slightly lower than the correlation for the Upgrader Emissions I factor. In addition, the time series of this factor exhibited short-term peaks that occurred during the intensive measurement campaign at different

times than those of the first Upgrader Emissions factor- (Fig S9). The lower mole ratio of particulate sulphur to SO₂ (Upgrader Emissions I: 0.44, Upgrader Emissions II: 0.22) evaluated

during these short-term peaks suggests that while both sources were relatively local, Upgrader Emissions II may have been closer to the receptor site. This, in addition to the small contribution of this factor relative to that of the first Upgrader factor, indicated that this factor may have been

due to occasional smaller plumes that occurred for too short a duration or too rarely to be differentiated through the long-term 24-hr filter data. In contrast, the Xact data's time resolution

allowed isolation of this more-specific process/emission occurring as part of the upgrading processes. In this case the Upgrader Emissions factor for the long-term campaign likely included

the Upgrader Emissions II factor. It is speculated that this factor may have arisen been due to two different stacks from short term changes in fuel, such as a switch to oil combustion for heat/energy

~~or within the burning of coke upgrading process/facility.~~ A less likely, but more fortuitous,

possibility is that the Upgrader Emissions II factor was due to a short-term change in upgrader fuel

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that occurred only during the intensive measurement campaign and not during the long-term campaign. _

3.2.3 Soil

The Soil factor exhibited high concentrations of crustal elements such as Si, Ti, and K (Figs 2 and 3). Additionally, both the filter and the Xact's chemical profiles exhibited a high correlation with samples taken of the area's overburden dump (Intensive Measurement campaign (uncentered $r=0.99$, $p<0.05$); Filter (uncentered $r=0.83$, $p<0.0593$)) (Landis et al., 2012) which supported identifying this factor as a soil factor. The overburden dump is comprised of the top soil of the area, a mixture of the soil and glacial till overlying the oil deposits (Landis et al., 2012). The Soil factor derived from the long-term campaign data exhibited high concentrations of additional crustal elements not measured by the Xact such as Al, and lanthanoids such as Pr, Sm, and Nd (Fig. 3). Interestingly, this factor also exhibited high concentrations of Fe (both campaigns) and S (intensive campaign). This may have been due to the presence of bitumen in the soil in the Athabasca region, or may indicate that this natural crustal material was being aerosolized through anthropogenic means. Specifically, the soil may have been emitted through entrainment by off-road transportation, or crushing of bitumen-rich sand. This hypothesis was supported by the high correlation of this factor with NO_2 and NO_x (Table 2), which are related to engine emissions (Almeida et al., 2014). In fact, it is probable that this Soil factor represents a combination of emissions: (1) directly through entrainment by off-road vehicular traffic on-site and (2) indirectly through "track-out", where the dust temporarily sticks to vehicles travelling within the mining sites, only to be aerosolized on-road later after leaving the site. In summary, the Soil factor's chemical profile was consistent with natural soils but its rate of emission may have been enhanced by anthropogenic processes. This factor was identified through both methodologies; the source profiles for the two campaigns and time series between the co-measured Xact and filter data were highly correlated (profile (uncentered $r=1.00$, $p<0.0599$); time series (Spearman $r=0.8786$, $p<0.0501$)).

3.2.4 Haul Road Dust

Much like the Soil factor, this factor exhibited high concentrations of crustal elements such as Ca and Fe (Fig. 2), and the PMF outputs derived from the intensive and long-term campaign data were highly correlated to each other (profile (uncentered $r=0.81$, $p<0.0588$); time series (Spearman

$r=0.7980$, $p<0.0501$). What differentiated this factor from the Soil factor were the ~~lower~~higher concentrations of Mn, ~~Fe~~, and ~~Fe~~, as well as its lower correlations with both NO_2 and NO_x . ~~Ca~~. (Fig. 2 and Table 2). ~~Despite this, the~~. The strength of the correlations with NO_2 and NO_x are indicative of vehicular traffic (Moreno et al., 2013; Almeida et al., 2014). In fact, the source profiles for the Soil and Haul Road Dust were only weakly correlated (uncentered $r=0.15$, ~~$p=0.62923$~~). Furthermore, the ~~meta~~element profiles of this factor were similar to that of samples taken by WBEA of the Athabasca Region's haul road dust (intensive campaign (uncentered $r=0.93$, ~~$p<0.0567$~~); long-term campaign (uncentered $r=0.91$, ~~$p<0.0585$~~)). As haul roads are made of a mixture of overburden material combined with limestone and low-grade oil sand, it is reasonable that the Soil and Haul Road Dust factors exhibit some similarities in chemical composition.

3.2.5 Biomass Burning

Only observed in the long-term campaign, this factor was characterized by its high S, K, Zn, Br, Cd, and Pb. All of these elements, to different degrees, have been associated with different types of biomass burning in this (Jeong, et al., 2011; Kindzierski and Bari, 2015; Bari et al., 2015) and other regions (Van et al., 2008; Vassura et al., 2014; Alves et al., 2011). Furthermore, this combination of elements associated with different types of biomass combustion was consistent with a forest fire (Landis et al., 2012) in which all types of plants are burned. Finally, this factor's profile displayed a high correlation (uncentered $r=0.89$, ~~$p<0.0599$~~) with the measured profile of an Alberta forest fire, and in fact experienced its highest peak during a period of intense forest fires in northern Alberta (USDA Forest Service, 2011). Combined, these similarities suggested that this factor originated from biomass burning, with smaller possible contributions year-round from the scrap-brush burning for land clearing that is performed in the area.

3.2.6 Mixed Sources

The PMF results of each campaign yielded a factor that appeared to be a combination of anthropogenic and crustal sources. While the Mixed factors from the two campaigns were not correlated to each other (profile (uncentered $r=0.05$, ~~$p>0.8026$~~); time series (Spearman $r=-0.03$, ~~$p=0.04$, $p>0.8091$~~)), they both appeared to originate from multiple sources. The Mixed factor from the intensive measurement campaign was characterized by elements such as Cu, Zn, and Mn, which suggested the presence of mechanical abrasion (Zhang et al., 2011; Gietl et al., 2010; Bukowiecki et al., 2007), as well as Ni, K and Se, which suggested the inclusion of biomass, oil.

or coal burning, perhaps the burning of scrap-brush (Van et al., 2008; De Santiago et al., 2014). In contrast, the marker elements from the long-term campaign were included Zn, Cu, as well as K, and Ca, suggesting as possible sources mechanical abrasion and activities aerosolizing crustal elements, respectively. The conflicting nature of these two different Mixed-source factors suggested the presence of further factors. This was further evidenced by the unstable temporal trends these factors exhibited and the relative stability of the alternate 6-factor solutions (Supplementary S.3 Fig. S6). For example, some of the characteristic elements identified in the intensive measurement campaign, such as Br and Se, proved to be less stable, and would separate from the intensive measurement campaign's Mixed factor when the number of factors was increased (Supplementary S.3 Fig. S6b). However, these 6-factor solutions were less stable than the 5-factor solutions, and did not yield additional, clearer factors. This suggested that these Mixed factors were a result of insufficient data that prevented full separation into more distinct source profiles. More detailed evaluation of the PMF solutions are described in Supplementary. The combination of anthropogenic and crustal metalelements present in these factors could have arisen from mining-related activities such as mechanical abrasion of excavated materials within crushers. Activities such as combustion powered mechanical abrasion could result in a full-range of PM, from ultrafine to coarse, part of which would be considered as PM_{2.5} (Okuda et al., 2007; Martins et al., 2015). Other elements within these Mixed Sources could have been the result of further industrial activity at the different plant sites, which are known to be large emitters of elements such as Ni, Cu, Cr, Zn, and Se (Environment and Climate Change Canada, 2015).

3.3 Spatial and Temporal Trends

After analysis with PMF, the resultant factor time series (G matrix) of the combined filter data was split into 3 distinct factor time series, one corresponding to each site (AMS5, AMS11, or AMS13), in order to examine both the temporal and spatial trends (Supplementary S.6 Fig. S10). The time-series contributions were then averaged by to assess each site's seasonality (Fig. 4) from Dec. 2010 to Nov. 2012. Finally, the factor contributions derived from the Xact data were compared to the averaged contributions from the Aug. 2013 portion of the long-term campaign at AMS13 (Fig. 5).

As can be seen from Fig. 4, there were clear differences in mass contributions between the three sites. Of the three sites, AMS5 consistently exhibited the highest metalelement concentrations,

followed by AMS11, then AMS13, which was largely due to the high amounts of Haul Road Dust measured at AMS5. In contrast, AMS11 had higher average contributions from the Upgrader Emissions and Soil than both AMS5 and AMS13. This can be explained by the prevalent winds at AMS11, which were often from the south-east, the direction of the upgrader processes (Fig. 1).

5 Overall, these local differences between the sites may have been due to a combination of the proximity of the sites to the various emission sources, as well as the direction of the prevailing winds at each site ([Supplementary S-12 Fig. S11](#)) In particular, the predominant winds at AMS13 came from the North and the Southeast, which point towards the Syncrude and the more distant CNRL mines. In contrast, at AMS5 the wind came from many directions in which there were roads
10 and open mines.

Also Fig. 4 depicts the seasonal trends of the 5 factors identified in the long-term campaign. The total contribution was largest in the spring, then lower in the winter, then summer, then fall. A major part of this overall trend was due to the higher contribution from Biomass Burning, a natural source, in the spring. However, even without the inclusion of Biomass Burning, the combined
15 mass loading of the 4 remaining factors followed the same overall seasonal trend. Of the 5 factors, only the Mixed factor was relatively consistent throughout the seasons (within $0.08 \mu\text{g}/\text{m}^3$). Both the Soil and the Haul Road Dust factors were notably lower in the winter than in the other seasons, presumably due to freezing of the ground and snow cover in the winter. The concentrations were higher in spring than in fall. In the fall, the temperatures drop below 0°C quickly ([Supplementary
20 S-13 Fig. S12](#)) which could result in the lower Soil and Haul Road Dust concentrations. In contrast, temperatures are higher in the spring (Fig. [S13 S12](#)) and there is a surplus of sand on paved roads from ice treatment in the winter. Interestingly, the Upgrader Emissions factor's contribution to the total $\text{PM}_{2.5}$ mass was highest in the winter and spring, which may be due to the differences in mixing height and wind direction and speeds across the seasons, or it may reflect true changes in
25 upgrader activity. Overall, the combined seasonal concentration of the factors follows the same trend as the strength and directionality of the prevailing winds, in which the most prevalent, fast winds are present in the spring, then winter, then summer, then fall (Fig. [S12 S11](#)).

In addition to the wind speeds, mixing height plays a vital role in the impact of various factors throughout the seasons. In the colder months, inversions can occur, increasing concentrations and channeling emissions horizontally based on the local topography (Davison et al., 1981; Celso and
30

Dabek-Zlotorzynska, 2010). This may result in higher contributions from emissions sources, such as Soil and Haul Road Dust, which occur close to the ground. In contrast, in the warmer months, more vertical mixing tends to occur, which may result in the observance of higher contributions from tall emission stacks. Thus, the seasonality apparent within the source contributions is presumably in part due to this seasonality in mixing. However, the low contributions of the Soil and Haul Road Dust factor in winter, when mixing is the lowest, is not likely due to low mixing, unless the mixing was so low that it prevents transport from the sources to the nearby measurement sites. This indicates it is more likely that emissions of Soil and Haul Road Dust are lower in winter.

A closer look at the contributions during the summer of 2013 is shown in Fig. 5. Good agreement of the Upgrader I and II Emissions can be seen between the PMF factor contributions to the total ~~metals concentration~~ element concentrations calculated from the AMS13, Aug. 2013 filter and hourly data (~~52% and 53% and 54%~~, respectively). While there is disagreement between the two independent PMF runs in the magnitude of the contribution from Soil and Haul Road dust, (~~38% for Filter vs. 31% for Xact~~), the time series for the Soil and Haul ~~road~~ Road Dust factor from the filter measurements taken at AMS13 during Aug. 2013 vs. that from the Xact measurements did exhibit good temporal correlations (~~Spearman $r = 0.7977$~~). It is possible that the filter data only allowed limited separation of the Haul Road Dust factor from the Soil factor: the 24-hr time scale of the filter data would not enable distinguishing changes that occur on a smaller time scale, such as the changing mixing height and/or wind direction throughout the day. Alternatively, by combining the data from the three sites prior to running PMF, the factor contributions may have been biased towards sites more impacted by the crustal factors. Despite these differences in relative contributions, the factors identified by the two different methodologies were broadly similar. Finally, as the filter data measured at AMS13 during Aug. 2013 was added to those measured between Dec. 2010 and Nov. 2012 prior to analyzing it with PMF, the ~~very~~ small contribution (~~~26%~~) of the Biomass Burning factor seen in this figure arose from the forest fire factor resolved through other times in the long-term campaign, and given its low magnitude it is uncertain if this is an accurate indication of emissions from Biomass Burning during the intensive measurement campaign.

Whereas the long-term campaign was able to identify the overall seasonal trends of the factors, the lower time resolution made identification of some sources more difficult (Fig. ~~S14S9~~). In contrast,

the higher time resolution employed during the intensive measurement campaign revealed diurnal patterns (Fig. 6 and Fig. S10S9). From Fig. S10S9, it is clear that both the Upgrader Emissions were observed episodically, which indicates that they likely came from specific point sources and could thus be measured only when the wind was favourable. Interestingly, both the Haul Road Dust and Soil exhibited similar, but slightly offset, diurnal trends (Fig. 6). This is in contrast to the daily trends of the mixing height in the area, which are highest during the day and lowest during the night (Davies, 2012). This trend also disagrees with the average diurnal wind speeds that occur at AMS13, which experience their peak at 15:00, while both the Soil and the Haul Road Dust factors experienced their highest peaks at 11:00 (Fig. 6). Overall, this suggests that the daytime increases for both the Soil and the Haul Road Dust factors were not due to natural processes such as decreases in mixing height or increases in windblown dust. Further, the daytime increase pointed to on-road vehicles (e.g. through track-out) rather than off-road mining activities as the more dominant source, as off-road operations at most mining sites occur around the clock.

In addition to diurnal patterns, the higher time resolution used by the Xact resulted in more detailed CPF plots (Fig. 7 and Fig. S14S13). Whereas the Xact data was able to point towards distinct emission sources with the CPF plots, the filter data time resolution was too low. Despite this, the multiple sites used by the filter study allowed for approximate triangulation of the sources (Fig. S14S13). The results of the two CPF profiles indicate that both the Upgrader I and II Emissions came from the direction of known upgraders and that the Mixed factors came from the direction of known mines. The Haul Road Dust factor appeared to come from the direction of the three major roads closest to the receptor site(s). Further, the CPF profile of the Soil factor exhibited broad peaks which surrounded known mines, perhaps as a result of vehicular traffic leading to and from the mines. Finally, the Biomass Burning factor appeared to come into the valley from the north and south. Because of this, HYSPLIT analysis was run on the three highest-concentration days for both the Biomass Burning and the Soil factors in order to determine if they were local or regional in origin. The long-range winds of the Biomass Burning factor, which experienced its highest concentration days during periods of known biomass burning just north of the measurement sites (USDA Forest Service, 2011), appeared to largely come from specific regions in northern Alberta that contained additional forest fires (Fig. S15S14). Combined, the local and regional forest fires greatly affected the air quality, as during this period (May-June, 2011), the average PM_{2.5} concentration increased by 328%. Back trajectory analysis of the highest

concentration soil days of each receptor site suggested that it predominantly came from the direction of known mines (Fig. S16S15); these trajectories largely crossed uninhabited, forested, areas in northern Canada prior to reaching the open pit mines. Overall, these findings support the conclusions that the Upgrader Emissions came from the bitumen upgrading process, the Soil and the Haul Road Dust factors came from on road transportation coupled with “track out”, and the Mixed factors likely originated in the open pit mines.

3.4 Long-term vs. Intensive Campaign Methodologies

The methodologies employed in the long-term and the intensive campaigns each had their own strengths and weaknesses. The lower DL and higher number of metalelement species measured by the filter samples resulted in more detailed factor profiles (Fig. 2 and Fig. 3). Further, the longer duration enabled identification of seasonal trends, while the use of multiple sampling sites improved geographic resolution of sources. However, the limited number of co-measured aerosol and gaseous species enabled fewer comparisons. Additionally, the longer 24-hr sampling time of the filter limited the separation of close proximity sources, such as Upgrader Emissions I and II.

In contrast, the higher time resolution employed by the Xact resulted in better defined temporal patterns which supported the separation of similar sources (Fig. 6 and Fig. S10S9), which in turn led to more precise CPF profiles and gaseous species comparisons (Fig. 7, Table 2). Furthermore, the higher time resolution measurements accomplished all this within a much shorter time frame. However, without the long-term filter sampling, it would have been unclear how representative this intensive period was of the norm. Because of this, it is important to take more time-resolved metalelements measurements in this area in order to see if there are further, unresolved sources. This is important as it can help to guide decisions made about regulation and control in the area.

In addition to their measurement capabilities, each campaign had its own requirements in terms of energy, difficulty in set up and measurement, and quality control. While the intensive measurements by the Xact had more energy and housing requirements on site, the filter analysis required much more follow-up laboratory analysis. Finally, despite the quality assurance and control measures employed by the Xact, comparison to co-measured species indicated a possible linear bias in certain metalelements measured. In contrast, the filter protocol employed was well

established, and followed stringent quality assurance and quality control protocols. This led to a high level of confidence in these measurements.

3.5 Implications of the Source Identification for Element Species

5 Overall, the average concentration of some ~~metalelement~~ species measured in the Athabasca region was either equal to or higher than that measured in urban/industrial locations in Canada (Table ~~S4S6~~). In particular, the concentrations of Si, Ti, K, Fe, Ca, and Al were, on average, higher than those measured in major Canadian cities. At their highest peaks the concentrations of S, Ba, Br, and Mn ~~were also higher than the city averages-exhibited large increases in concentrations.~~ Of
10 these ~~metalselements~~, Ti, Fe, Cu, and Zn all showed periods of higher concentration during the intensive measurement campaign. Of these species, Al, Ca, Si, Mn, Ba, and Fe were predominantly observed in the Soil and Haul Road Dust factors, suggesting that they originated from vehicle-related emissions or associated anthropogenic dust production in the area. These species have been
15 previously seen to be elevated in epiphytic lichens (Landis et al., 2012). The elements As, Pb, and Tl were associated with Upgrader Emissions, and Be and Ba with the Haul Road Dust; these metals and metalloids were also previously found to be higher in snow or biota near the oil sands operation (Landis et al., 2012).

There were some differences between the campaign data as to the dominant source(s) of some
20 ~~metalselements~~. For example, V was apportioned to Soil and Upgrader Emissions I in the long-term campaign while based on the intensive measurement campaign it was almost entirely apportioned to the Upgrader Emissions II factor. While this difference appeared to create some ambiguity it actually highlighted the enhanced separation of factors allowed by the higher time resolution Xact data: V was associated with a type of anthropogenic emissions that the filter sampling had trouble identifying. Interestingly, Ni, Zn, Cr, Ag, and Cu were grouped into Mixed
25 factors. As these factors represented a combination of multiple sources, the individual sources causing elevation of these ~~metalselements~~ is still not known; this limitation may help direct further studies ~~including~~. More generally, the ~~metalselements~~ used to create the factor profiles and thereby identify sources accounted for only a small portion of the total PM_{2.5} mass. This limitation will be addressed in follow-up analysis combining the Xact data with other concurrent, time-resolved,

measurements of non-refractory components. Combining these data will provide a more complete mass reconstruction so as to allow apportionment of PM_{2.5} and further sources may be revealed by leveraging the perspective given by the additional composition information.

5 4 Conclusions

In conjunction with JOSM, seven sources of PM_{2.5} related metalelements were identified through two measurement technologies: two types of Upgrader Emissions, Soil, Haul Road Dust, Biomass Burning, and two sources of mixed origin. Of the seven factors obtained by the PMF analysis, two were directly associated with oil sands upgrading, two with the on and off-road transportation of the bitumen rich oil, one with natural processes, and two with mixed anthropogenic-natural activities. Thus, much of the PM_{2.5} related metalelements were found to originate from anthropogenic sources or activities. Interestingly, it was only through the time-resolved measurements taken by the Xact that some of these anthropogenic activities became better defined and understood, which can help guide further studies. This work describes the influence of the development activities on PM in the part of the Athabasca Oil Sands Region near open pit mining and upgrading activities. Finally, determining the relative contributions of these sources to the different metalelements in PM_{2.5}, helped to better resolve their potential contributions to the higher concentrations of metalelements in snow, water, and biota that have been previously reported for samples collected near the oil sands operations.

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Table 1. Summary of the measurement strategy used during the two campaigns.

Campaign	Sampling Interval	Monitoring Site		
		AMS5	AMS11	AMS13
Long-term Filter (Dec. 2010- Nov. 2012)	24-hr Integrated Filters (one in six days)	ED-XRF /ICP-MS	ED-XRF /ICP-MS	ED-XRF /ICP-MS
Intensive Filter (Aug. 13- Sep. 10, 2013)	23-hr Integrated Filters (daily)	N/A	N/A	ED-XRF /ICP-MS
Intensive (Aug. 10- Sep. 5, 2013)	1-hr continuous	N/A	N/A	Xact metals monitor

Table 2. Pearson/Spearman correlation (r) of gaseous pollutants with PMF-resolved factors.

Campaign	Factor	Correlated Gases (r>0.43, p<0.0501)
Long-term Filter	Upgrader Emissions I	SO ₂ (r=0.52), NO ₂ (r=0.46), NO _x (r=0.41)
	Soil	none
	Haul Road Dust	none
	Mixed Sources	none
	Biomass Burning	none
Intensive	Upgrader Emissions I	SO ₂ (r=0.84), NO ₂ (r=0.44), NO _x (r=0.34)
	Upgrader Emissions II	SO ₂ (r=0.60), NO ₂ (r=0.40)
	Soil	SO ₂ (r=0.36), NO ₂ (r=0.63), NO _x (r=0.54)
	Haul Road Dust	SO ₂ (r=0.52), NO ₂ (r=0.61), NO _x (r=0.49)
	Mixed Sources	none

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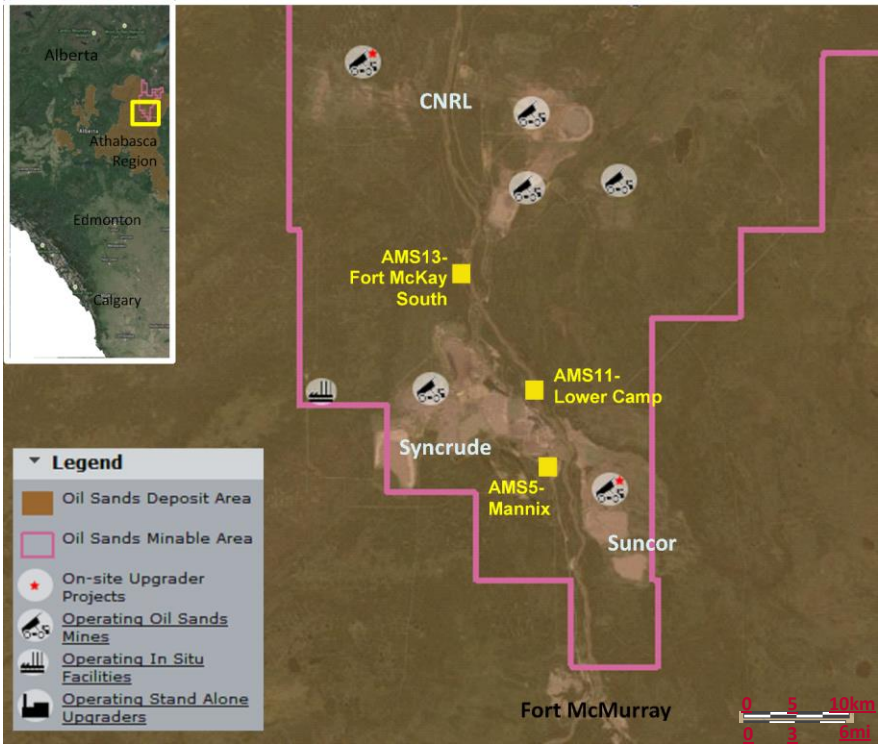
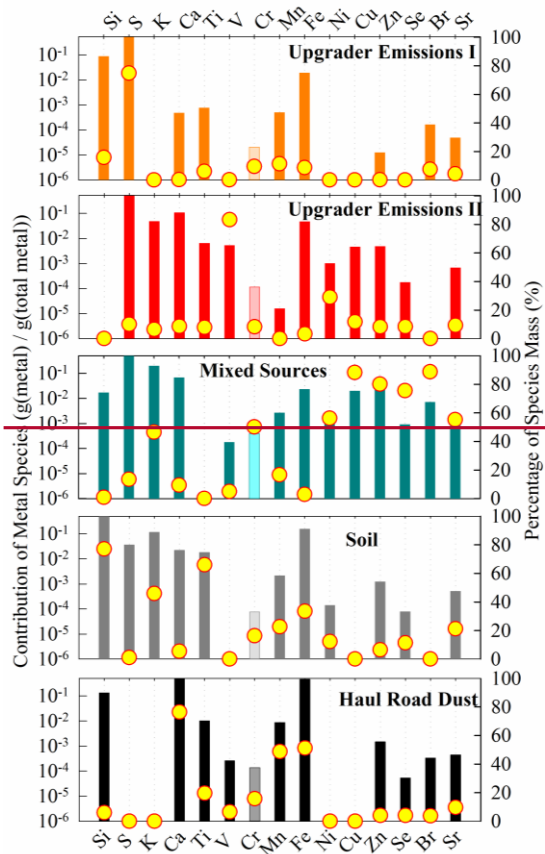


Figure 1. Locations of the various extraction processes and three measurement sites (triangles) within the Municipality of Wood Buffalo in the Athabasca Region of Alberta, Canada. Map courtesy of Alberta: Environmental and Sustainable Resource Development. Available: <http://osip.alberta.ca/map/>

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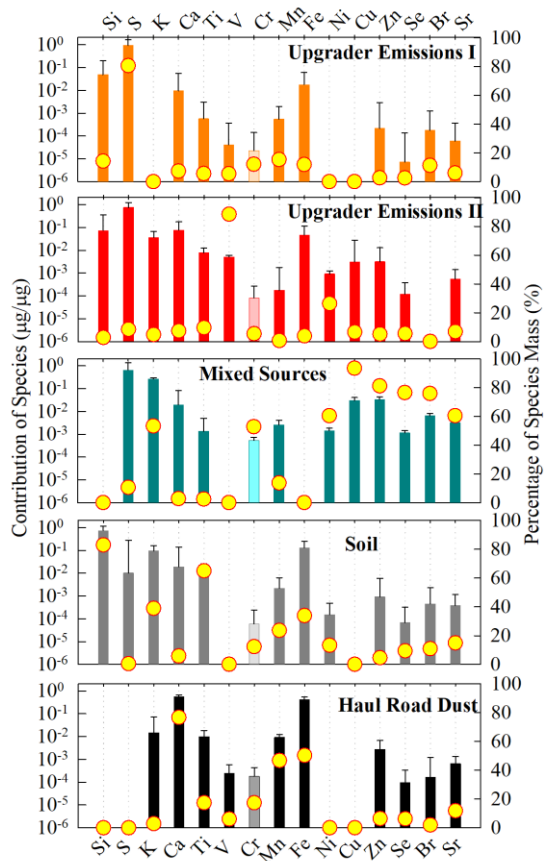
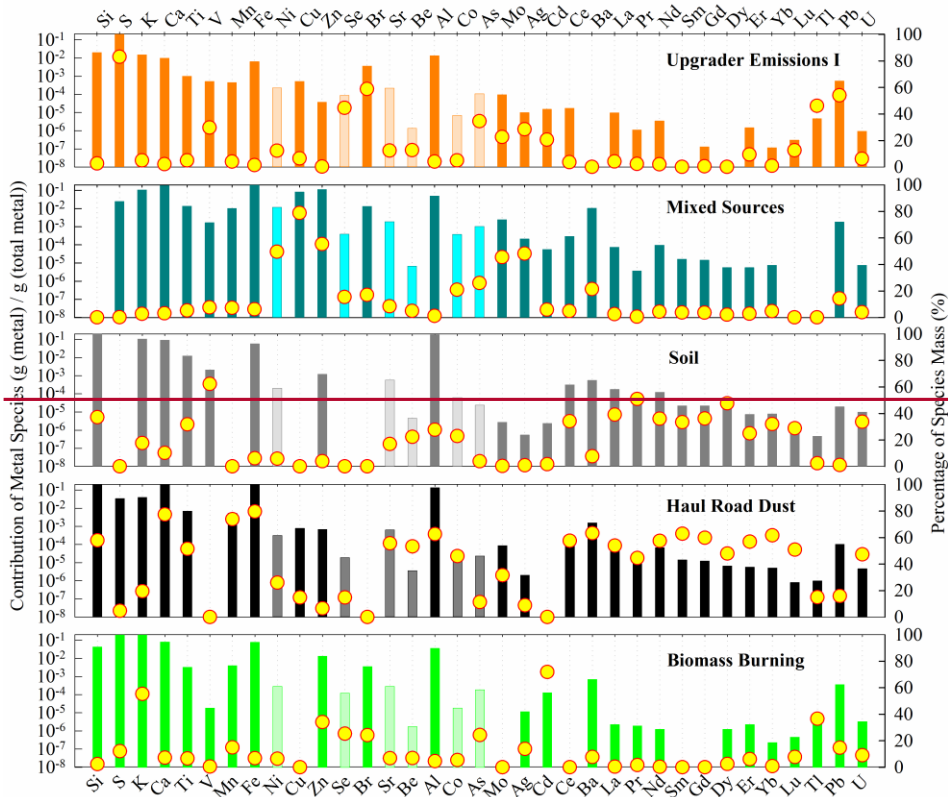


Figure 2. Factor profiles from the hourly measurements by the Xact, August 10- September 5, 2013. The percentage of species is defined as the percentage of mass of each ~~meta~~element apportioned to each factor. Factor Concentrations depicted as bars, percentages depicted as circles. Error bars represent standard deviations estimated by 100 bootstrap runs. Elements with Shannon entropy below 3.5 have been given a higher transparency than the remaining elements.

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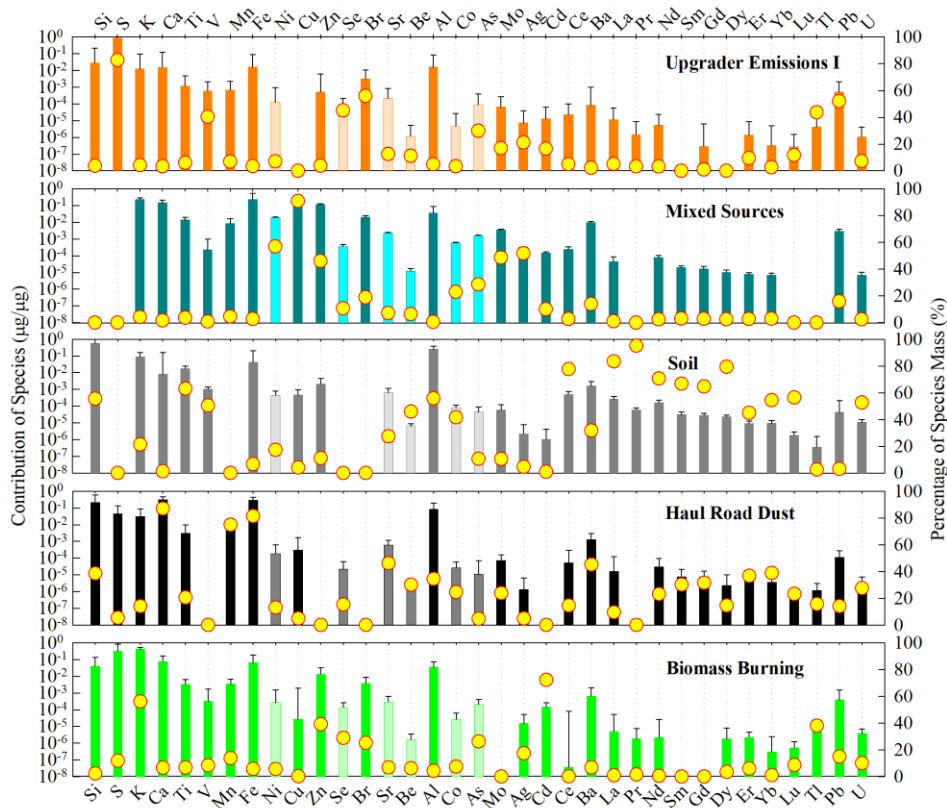
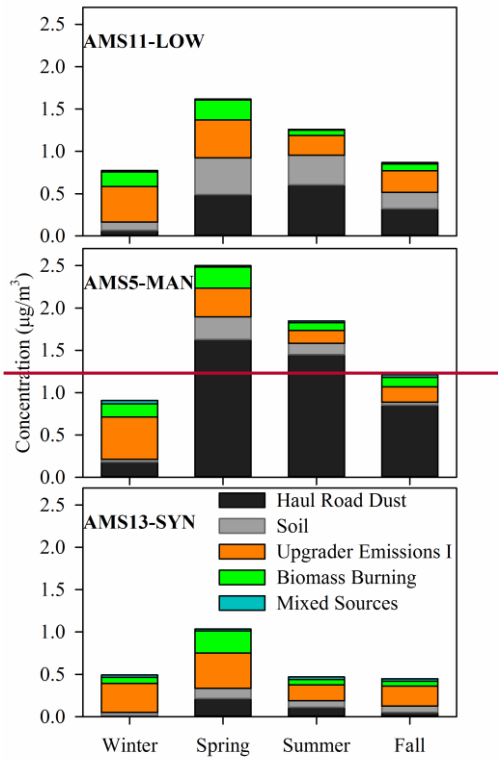


Figure 3. Factor profiles of the combined filter data. Filters were collected one in six days at three sites for two years (Dec.2010-Nov. 2012) and daily at one site in Aug 2013. **Factor Concentrations** depicted as bars, percentages depicted as circles. Error bars represent standard deviations estimated by 100 bootstrap runs. Elements with Shannon entropy below 3.5 have been given a higher transparency than the remaining elements.

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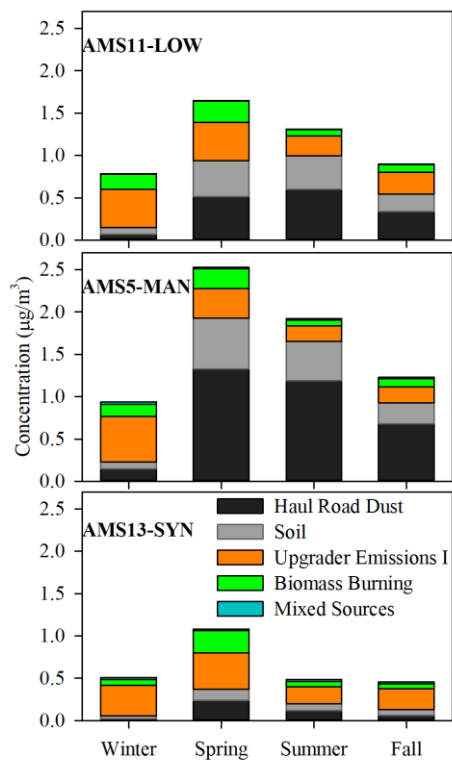


Figure 4. Average seasonal contribution at the three sites from the combined long-term filter campaign data. The contributions are averaged by the season: winter (December 21- March 19), spring (March 20- June 20), summer (June 21-September 21), and fall (September 22-December 20) from December 16, 2010 to November 29, 2012.

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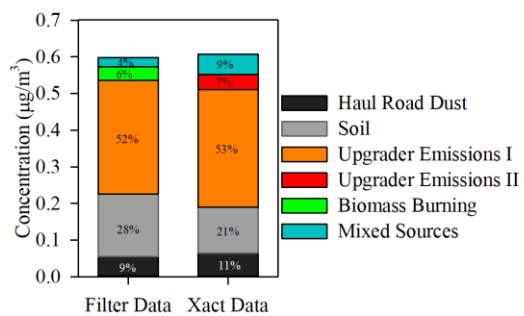
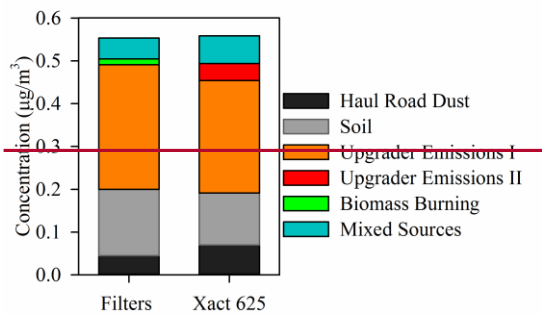


Figure 5. Average mass contributions at AMS13 of each factor derived from the hourly Xact and 23-hr integrated filter data during the intensive campaign from August 13 to September 4, 2013.

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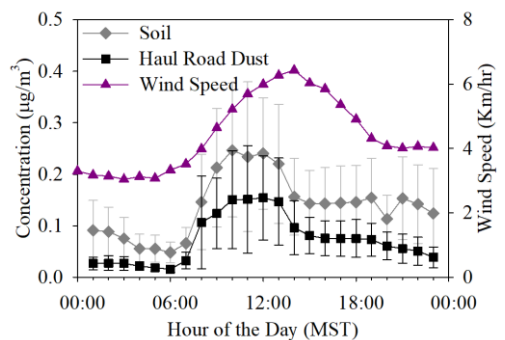
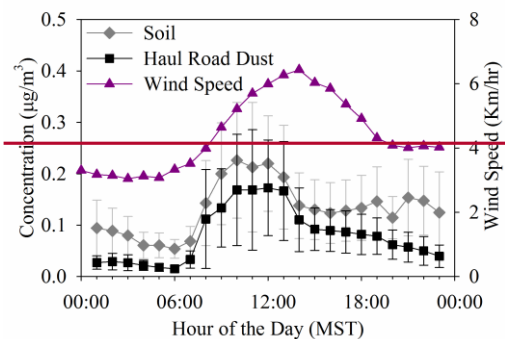
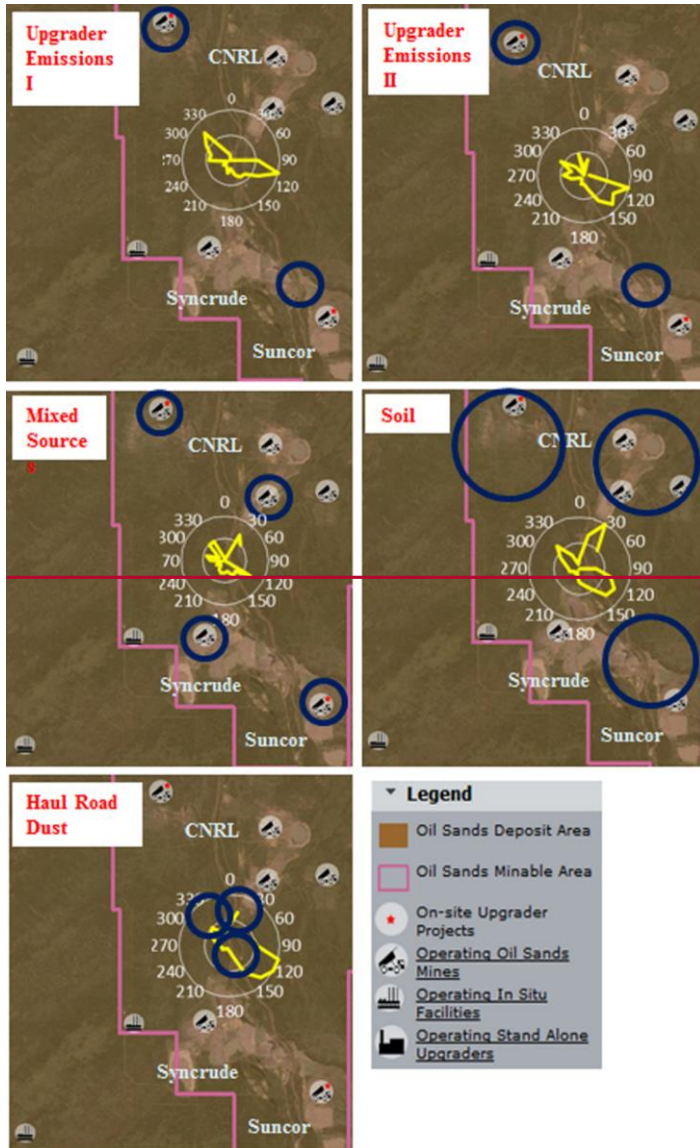


Figure 6. Average concentrations displaying the diurnal trends the Soil factor (grey) and the Haul Road Dust factor (black) at AMS13 during the intensive campaign, and the average wind speeds between Dec., 2010 and Sept., 2012 (green). Error bars represent 95% confidence intervals.

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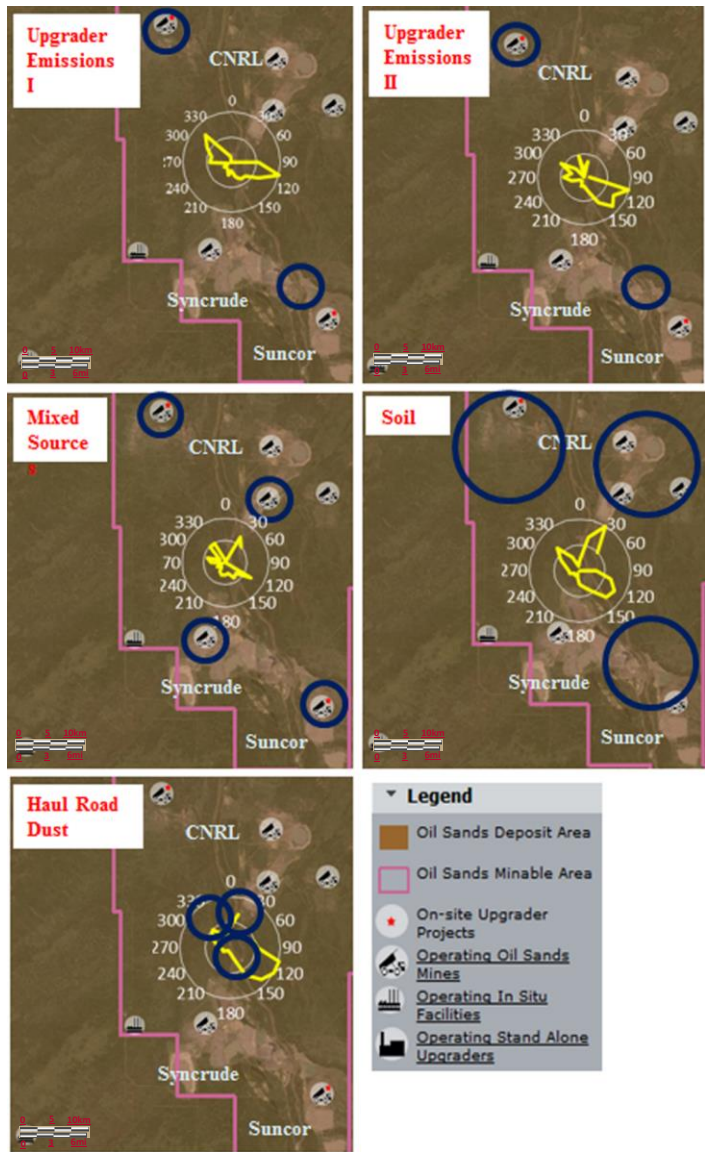


Figure 7. CPF profiles of the 5 factors identified by hourly Xact data during the intensive campaign in August 2013. Blue circles indicate possible source locations. Map courtesy of Alberta: Environmental and Sustainable Resource Development. Available: <http://osip.alberta.ca/map/>.

Supporting Information

Sources of Particulate Matter in the Athabasca Oil Sands Region: Investigation through a Comparison of Trace Element Measurement Methodologies

Catherine Phillips-Smith¹, Cheol-Heon Jeong¹, Robert M. Healy², Ewa Dabek-Zlotorzynska³, Valbona Celo³, Jeffrey R. Brook⁴, Greg Evans¹

¹ Southern Ontario Centre for Atmospheric Aerosol Research, University of Toronto, Toronto, Ontario, Canada

² ~~Analysis Air Monitoring and Transboundary Air Quality Sciences~~ Section, ~~Air Quality Research Division, Ministry of the Environment and Climate Change~~ Canada, ~~335 River Road, Etobicoke~~, Ontario, Canada

³ Analysis and Air Quality Section, Air Quality Research Division, Environment and Climate Change Canada, 335 River Road, Ottawa, Ontario, Canada

⁴ Air Quality Processes Research Section, Air Quality Research Division, Environment and Climate Change Canada, 4905 Dufferin Street, Toronto, Ontario, Canada

Correspondence to: Greg Evans (greg.evans@utoronto.ca)

S.1 Quality Control and Analysis

The Xact incorporates several Quality Assurance and Quality Control measures. With each measurement the instrument takes, it simultaneously measures the concentration of a Pd rod that is located within the instrument to ensure measurement stability (Batelle, 2012). Additionally, every day at midnight, the instrument completes several tests. In one of these tests, the Xact measured the concentrations of metals located within an upscale rod made of Pd, Pb, Cr, and Cd. The three metals, Pb, Cr, and Cd, in the upscale rod represent each energy level the instrument (Batelle, 2012). When the instrument is operating under normal conditions, these measurements are constant with each test. This feature was invaluable during the August, 2013 campaign when there was a drop in the internal Pd measurement values between August 25 and September 2, 2013. As this had the potential to alter the measured metal concentrations, the changing Pd upscale value was linearly regressed against the upscale values of Cr, Pb, and Cd, which were found to have slopes of 0.63, 8, and 3.3, respectively (Figure S1). These relationships were assumed to be the same for all metals within that energy level, and measurements made August 25 to September 2 were then adjusted assuming a constant ratio between the upscale metal concentration and the various metals within its energy level. To validate this assumption, a linear comparison of the sulphur (S) data before, as well as both the raw and corrected S data during the incident was

compared to the collection-efficiency corrected PM_{1.0} SO₄ data measured by a soot particle aerosol mass spectrometer SP-AMS (Willis et al., 2014); the AMS sulphate was divided by three to determine the equivalent sulphur mass. Prior to August 25 the slope of the line was 2.75 (Figure S2S2a); a slope greater than 1.0 was expected given that PM_{2.5} and PM_{1.0} mass values were being compared. However, the slope of 2.75 was greater than that expected due to the difference in size cutpoints alone. For example, comparison of the ambient ion monitor ion chromatograph's (AIM-IC) PM_{2.5} to the AMS's PM_{1.0} data yielded a slope of 1.66 (Figure S3a), which suggested that there is 66% more sulphate in PM_{2.5} than in PM_{1.0}. The difference in the slopes of 2.75 vs. 1.66 implied that the Xact might be measuring additional sulphur that was not in the form of sulphate. However, comparison of the Xact sulphur with the AIM-IC or PM_{2.5} filter data, as described below, indicated that the Xact sulphur values were on average only 40% too high. The additional 17% divergence with the AMS data could not be resolved. As described below, the accuracy of most other metal(oid)s determined by the Xact was much better than that for sulphur.

Correcting the Xact S data for Aug 25-Sept 2 based on the concentration-dependent equations seen in Figure S1 raised the r² value from 0.9277 to 0.9896, and changed the slope of the line from 1.60 to 3.57 (Figure S2). The Figures S2c and S2d). Overall, there was a large change in the slope of the line from 2.75 before August 25 to 3.57 ~~could have been due~~. However, the corrected slope was comparable to an increase in the slope in sulphate size distribution a similar concentration range (Figure S2b) before August 25 (3.26 vs. 3.57), suggesting that the Xact data correction was reasonable. It is more likely that the data after August 25, 2013 may have been over corrected by up to 20%. This represented 35% of the total Xact data used in the PMF analysis.

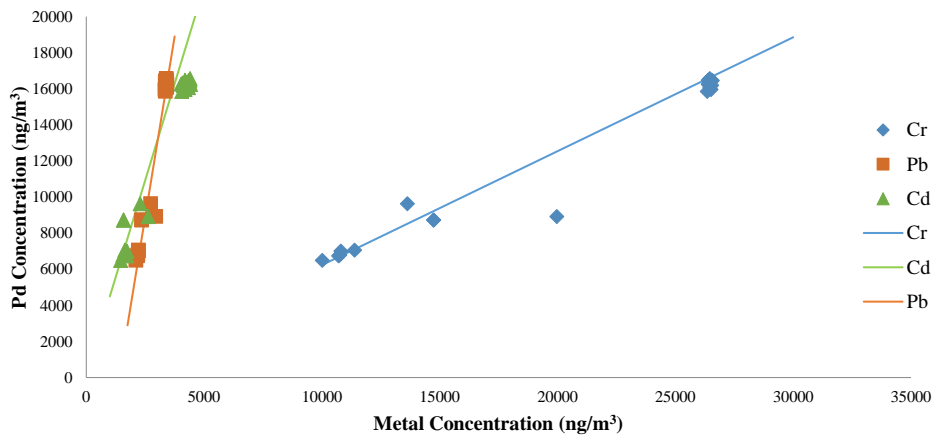
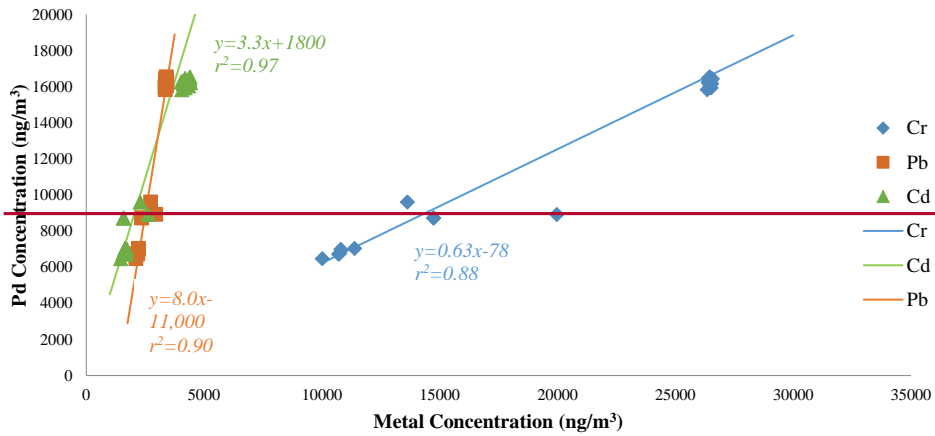


Figure S1. Comparison of Pd rod concentration to the three measured upscale metals: Cr, Cd, and Pb that were measured throughout the intensive campaign.

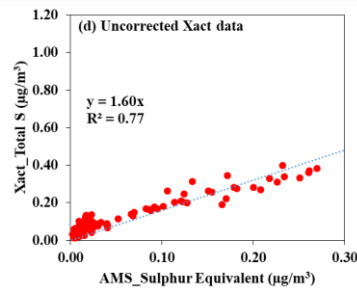
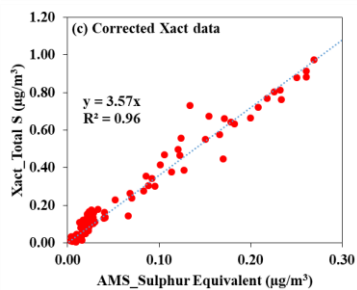
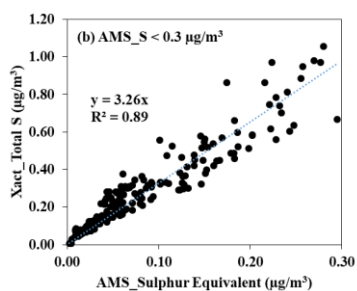
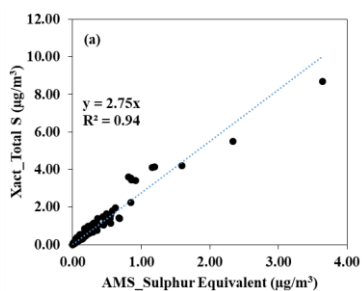
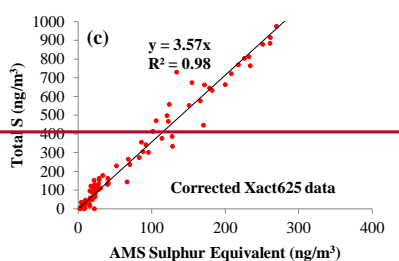
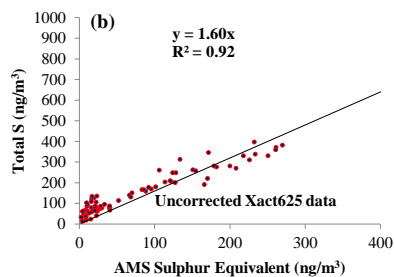
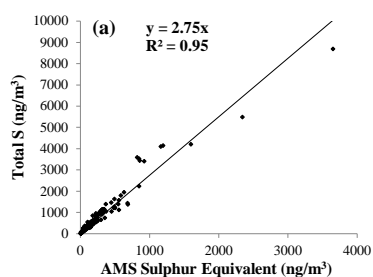
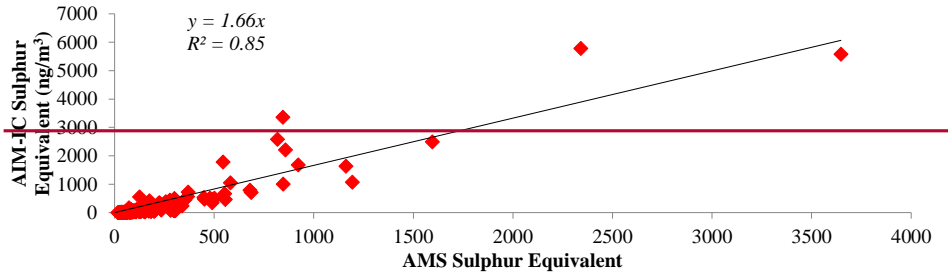


Figure S2. a) Comparison of SP-AMS sulphur equivalent to Xact S before Aug. 25, 2013, b) comparison of SP-AMS sulphur equivalent lower than 300 ng/m³ to raw Xact S data after before Aug. 25, 2013, and c) comparison of SP-AMS sulphur equivalent to corrected Xact S data after Aug. 25, 2013, and d) comparison of SP-AMS sulphur equivalent to raw (uncorrected) Xact S data after Aug. 25, 2013. All the SP-AMS sulphate values were divided by three to determine equivalent sulphur mass values.

A comparison of the 1-hr instrumentation data against the coincident 23-hr filter data was conducted to ensure the data measured with the Xact was equivalent to that measured with the filters. The 1-hr data was averaged between 8:30 am and 7:30 am to correspond with the period during which the filter sample was taken. Any averaged values that were below the detection limit (DL), or calculated using data more than 50% of which were below the DL, were removed. The data was then divided into three groups: low, medium, and high concentrations. Low-concentration metals, those with average values <10 ng/m³ (Figure S3b), exhibited excellent agreement, with a linear slope of 1.03 and an r² value of 0.95 (Xact to Filter data). This represented 63% of the metals measured by the Xact used in the PMF analysis. The medium-concentration metals, those with averages between 10 ng/m³ and 50 ng/m³ (Figure S3c), had a slope of 0.77 and an r² of 0.99, while the high-concentration elements, with averages above 50 ng/m³, such as sulphur, had a slope of 1.43 and an r² of 0.99 (Figure 3d). The sulphur data was also linearly regressed against the SO₄ data measured with an ambient ion monitor ion chromatograph (AIM-IC), which was divided by three to estimate the S equivalent concentration (Markovic et al., 2012). The result was a line with a slope of 1.42 and an r² of 0.84 (Figure 3), this further indicated the likely presence of a 40% bias in the Xact sulphur measurements.



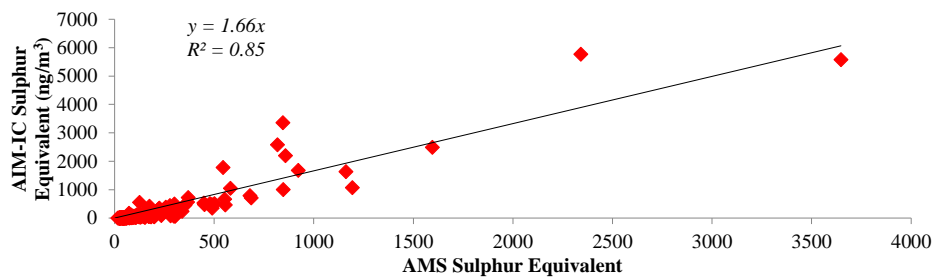


Figure S3a. PM_{2.5} concentrations measured by the AIM-IC to PM_{1.0} concentrations measured by the AMS comparison S before Aug. 25, 2013.

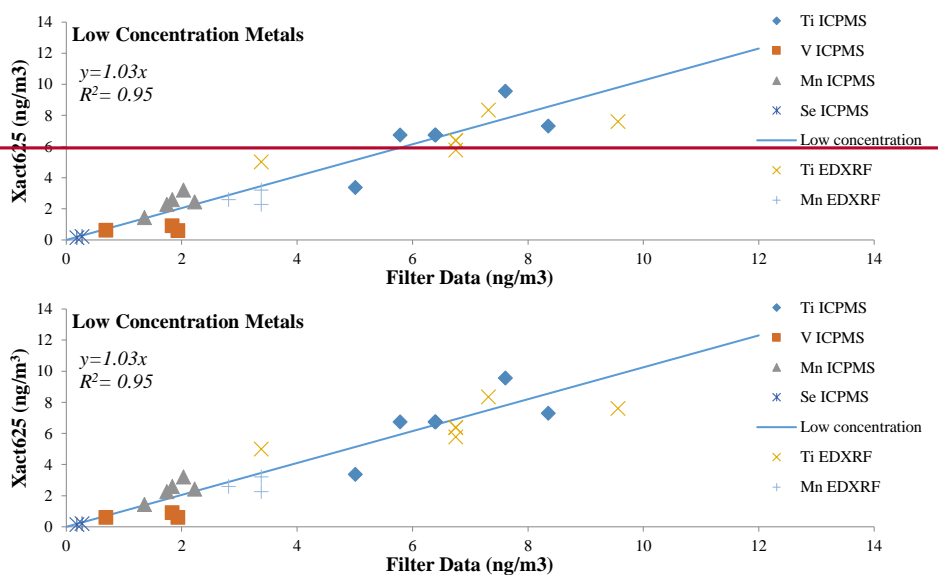


Figure S3b. Filter-Xact comparison for metals with average concentrations < 10 ng/m³.

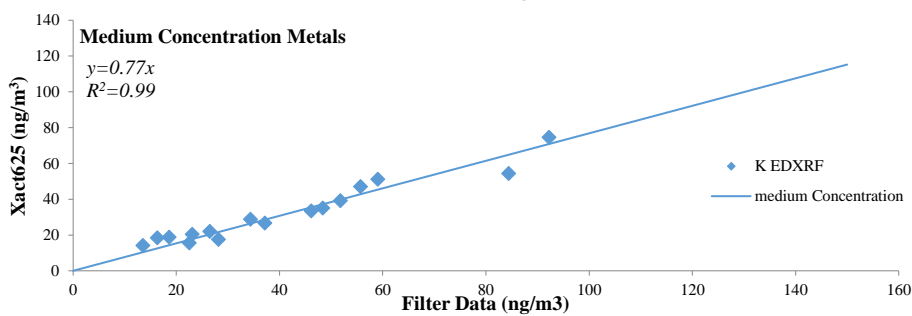
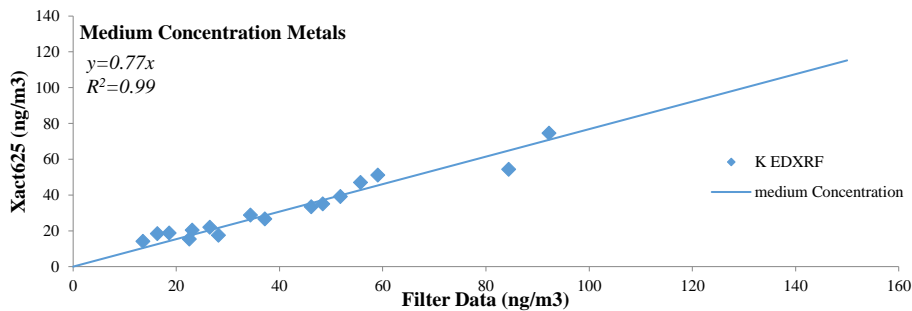


Figure S3c. Filter-Xact comparison for metals with average concentrations $>10 \text{ ng/m}^3$ and $<50 \text{ ng/m}^3$.

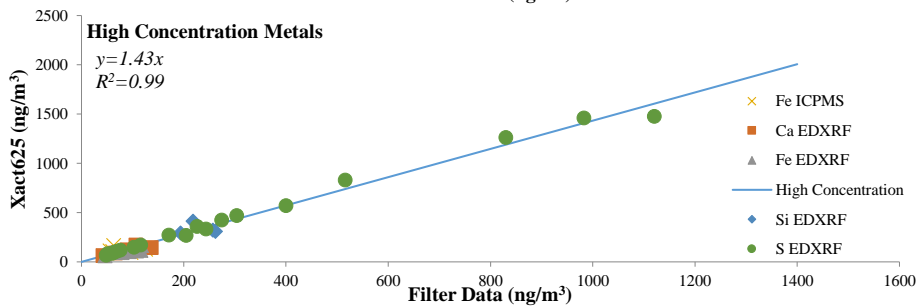
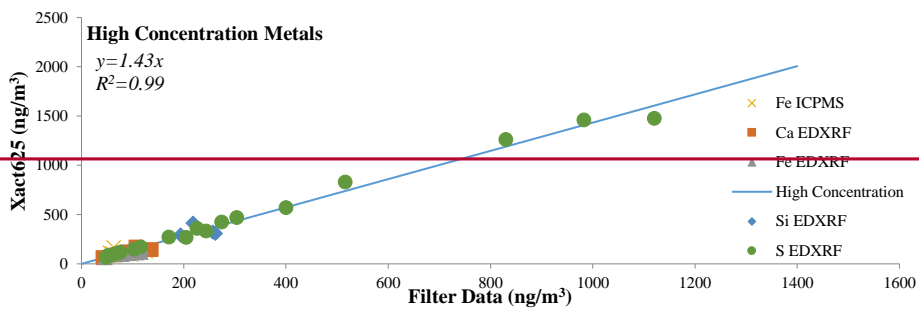


Figure S3d. Filter-Xact comparison for metals with average concentrations $>50 \text{ ng/m}^3$.

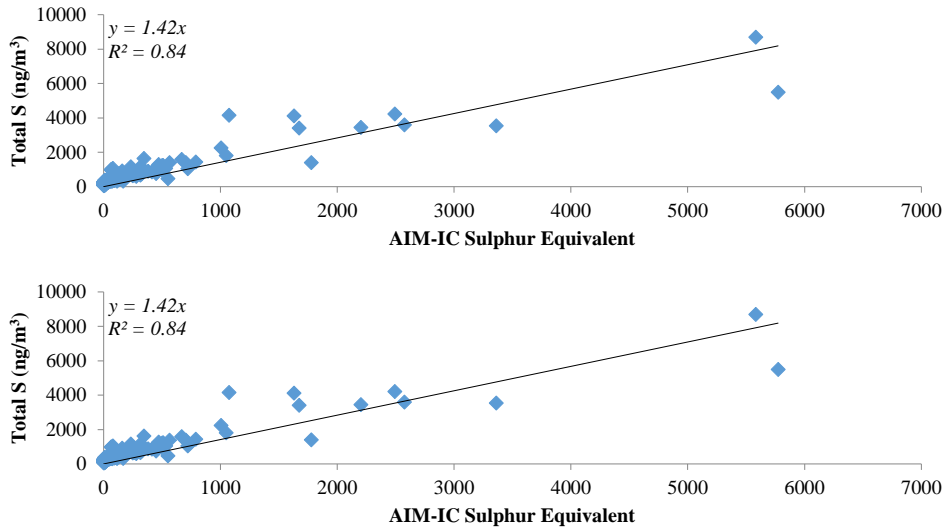


Figure S3e. AIM-IC/Xact comparison for sulphur before Aug. 25, 2013.

After the instrument was returned to the laboratory, all metal standards were run to assess the accuracy, precision, and uncertainty of each metal. High-concentration metal standards, between 7650 and 40852 ng/cm² in concentration, were initially run for each metal between 3 and 7 times, and each metal was found to have an accuracy and precision in the range of 98-113% and 0.3-17%, respectively (Table S1). The metal-specific analytic uncertainty was then calculated based on the sum of the average ratio of the difference between the target (T) and measured (X) values of each run (α) divided by the target value multiplied by the total number of runs (A), the uncertainty of the flow rate accuracy, set to be 10%, and additional metal-specific uncertainties (M), as seen in Equation 1. If the resulting uncertainty of any metal was less than 10%, it was raised to 10%; if there was no metal standard available for a measure metal, it was assigned an uncertainty based on the average uncertainties of the rest of the metals in the corresponding energy level. The results of this can be seen in Table S1.

$$\left\{ \left| \frac{\sum_{a=1}^A (X-T)}{A \cdot T} \right|^2 + 0.1^2 \right\}^{1/2} + M$$

Equation _____ (1: uncertainty calculation)

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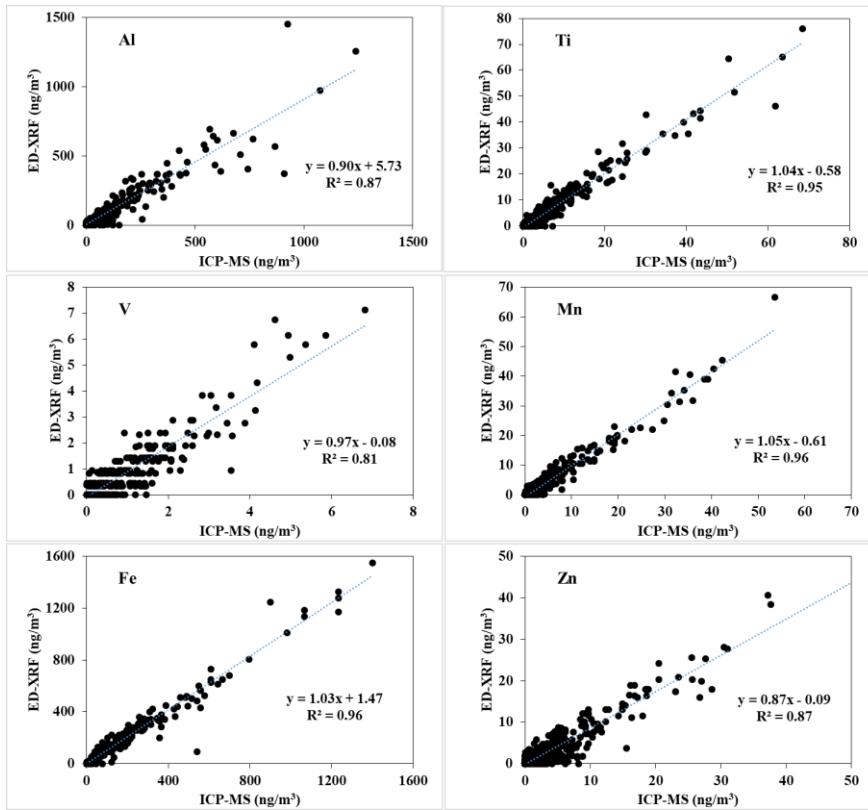


Figure S3f. Comparison of ED-XRF and ICP-MS measurements at AMS 5, 11, and 13 from Dec. 16, 2010 to Nov. 29, 2012. Nine elements with more than 80% of data below the minimum detection limit were excluded from the comparison.

S.2 PMF

Prior to analysis with PMF, the data for both the filter and intensive monitoring campaigns were pre-treated for Quality Control. In addition to only allowing metals which had >10% above DL data, or data that exhibited strong, “plume-like” behaviour when it was above detection limit, into the PMF matrices, the data matrices were also treated for biases. As the intensive monitoring campaign measured one blank value every 24 to 48 -hr, these blank values were averaged to create a single ‘baseline bias’ for each metal from which every datum was subtracted. This was possible as the blank values did not vary from measurement to measurement. This was not the case in the filter campaign. As the blank measurements were spaced a large temporal distance apart, and the values had wide variances, the data measured in this campaign were subtracted from the blank value which was the closest temporally. In order to quantitatively compare the contributions of PMF-resolved sources for the filter and Xact campaigns, the concentrations of major elements (i.e., Si, S, Ca, Fe) measured using Xact were corrected based on the intercomparison of filter and Xact data as described in the previous section.

Special consideration was given to the input data (X) and uncertainty (σ) matrices by sorting the data into three categories: above the DL, below the DL, and missing values (Xie et al., 1999). Data above the DL was input directly, with an uncertainty of $\sigma_{ij} + DL/3$. Data below the DL was replaced with $DL/2$, and given an uncertainty of $5(DL)/6$. Missing values were replaced with the geometric mean of the measured concentrations (v), and had the highest uncertainty of the three categories ($4v$) (Xie et al., 1999). Additionally, each remaining metal species was classified as good, weak, or bad depending on the S/N ratio (Equation 2). Metal species with an S/N ratio above 2 were classified as good, while weak data had an S/N ratio between 0.2 and 2, and were down-weighted by a factor of 3 (Paatero and Hopke, 2003, Norris and Duvall, 2014) (Table S2). Data with an S/N ratio below 0.2 were classified as “bad” and given a weight of zero (Paatero and Hopke, 2003). The only exception to this was Cu, which had an S/N ratio of 2.76, but was classified as ‘weak’. This was done as all measurements that were above the DL were very close to the DL, raising their uncertainties. Finally, the data set were all given an additional 10% “Extra Modelling Uncertainty” to further reduce the effects of noise within the data (Norris and Duvall, 2014).

$$S/N = \sqrt{\sum_{i=1}^n x_i^2 / \sum_{i=1}^n \sigma_i^2} \quad \text{Equation (2)}$$

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Table S2. Minimum detection limits (DL), S/N ratios, and average values of elements measured by the Xact and analyzed using PMF.

Element	DL (ng/m ³)	S/N Ratio	Average Value (ng/m ³)	Percentage of Missing Data	Percentage of Data Below Detection Limit
Si	107.0	3.72	143	21.13%	45.16%
S	26.7	8.10	468	21.13%	0.97%
K	11.1	4.29	31	21.13%	16.94%
Ca	26.2	3.89	54	21.13%	46.29%
Ti	1.9	4.79	3.4	21.13%	39.35%
V	0.3	3.22	0.21	21.13%	60.81%
Cr	5.1	1.82	0.04	21.13%	69.35%
Mn	0.4	2.40	1.12	21.13%	53.71%
Fe	21.8	4.78	60	21.13%	41.29%
Ni	0.3	0.80	0.08	21.13%	73.55%
Cu	1.8	2.76	2.04	21.13%	59.52%
Zn	1.4	0.75	0.88	21.13%	77.74%
Se	0.2	1.50	0.07	21.13%	59.68%
Br	0.2	4.79	0.54	21.13%	16.7%
Sr	0.9	0.82	0.23	21.13%	71.77%

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S.3

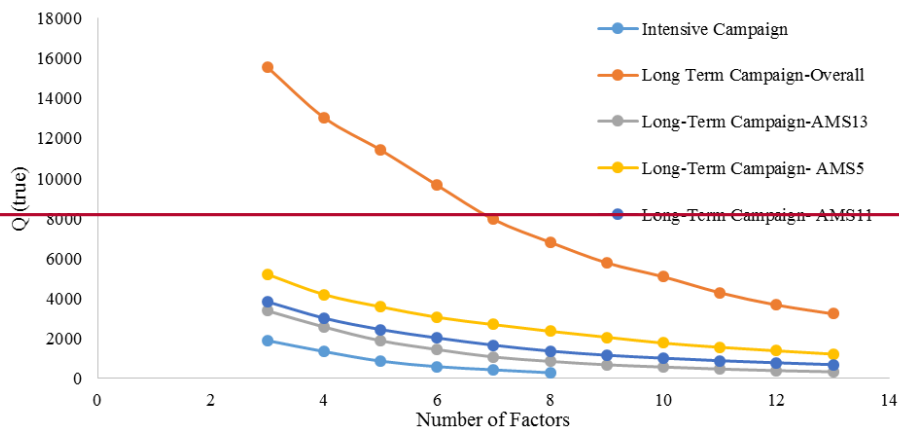
Evaluation of the PMF solution

The Q value (Equation 3) calculated by PMF algorithm was used to determine the number of resolvable factors affecting the receptor site, through its stability and inflection point. Because different pseudorandom numbers are selected by the algorithm at the initiation of each run, a stable solution with a preset number of factors will not experience a change in the Q value through a series of runs (Xie et al., 1999). Also, since the ratio of Q value to the expected Q (Q_{exp} , Equation 4) of the solution decreases with an increase in the preset number of output factors, an inflection point in the rate of decrease will indicate the most central, or optimal, solution (Xie et al., 1999) (Figure S4). The optimal number of factors was also determined by examination of the G-space plot, a direct comparison of the time series (G matrix) of one factor against that of another factor, and the scaled residuals of the results. Factor solutions that contain metals with a non-normal distribution in the scaled residual could signify that the uncertainty of the metal is too low, that there is noise in the data, or that there is another pollutant source of the metal not separated in the

factor solution (Paatero, 1996). It should also be noted that a linear relationship between two factors in the G-space plot could signify either a co-aligned or identical source (Paatero et al., 2005).

$$Q = \frac{\sum_{i=1}^n \sum_{j=1}^m E_{ij}^2 / \sigma_{ij}^2}{\sum_{i=1}^n \sum_{j=1}^m e_{ij}^2 / \sigma_{ij}^2} \quad \text{Equation (3)}$$

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$$Q_{exp} = nm - p(n+m) \quad (4)$$

where n is the number of samples and m is the number of species, e_{ij} is the residual concentration of the j th species in the i th sample; σ_{ij} is the uncertainty of the j th species in the i th sample, and p is the number of factors.

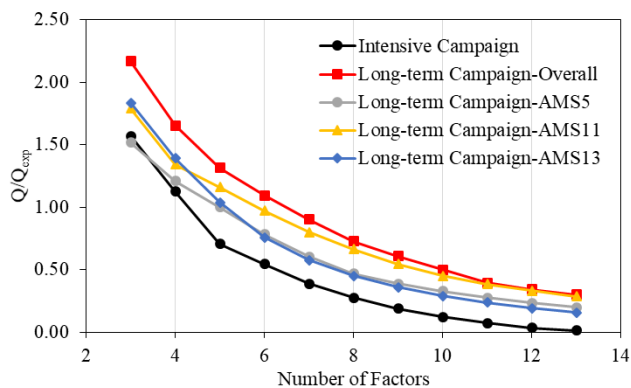


Figure S4. Q analysis of the intensive and long-term campaigns.

The final parameter examined in the selection of the optimal solution for the receptor site was the user-specified rotational parameter, Φ , chosen for the FPEAK analysis. When the PMF algorithm is run normally, i.e. with $\Phi=0$, it finds the optimal solution the farthest away from any zeros in both the G and the F matrices (Paatero et al., 2002). When the value of Φ is changed to lie between -2 and 2, in the FPEAK analysis, the rotation of the algorithm is altered to allow for zeros or negative numbers in either the G or the F matrix. A stable solution will not change radically when the rotation, Φ , is changed, but the change in rotation may “clean” the solution by allowing the minor elements of the factor to go to zero. Throughout this study, the value of Φ was selected to be 0.

Both the filter and the Xact data were analyzed separately using PMF due to their difference in the sampling intervals. Filter data from the monitoring and the filter campaign were combined to produce a single data matrix. Additionally, the filter data from all three sites were combined into one data set prior to running the PMF algorithm. The goal of this was to take advantage of the close proximity and remote nature of the three sampling locations, assuming most, if not all aerosol sources are common among the sites, at the expense of independent PMF solutions. The spatial variability of the sites may also add extra factor-discriminating power, as each site is in a different direction to the various sources. [ThisAs shown in Table S3, this](#) technique succeeded in producing a stable 5-factor solution, which was similar to the [4- or 5-factor](#) solutions produced when the filter data from each site was run independently (AMS 5, AMS 11, and AMS 13). Not only did the 5-factor solution exhibit the most central and stable Q factor, but also proved to be

analysis was conducted to evaluate rotational ambiguity in the PMF solution as well. Multiple solutions may be generated with the same value of the object function Q due to rotational ambiguity. In DISP, each fitted element (only good species) in a source profile is displaced in turn from its fitted value until Q increases by a predetermined maximum change in Q. An uncertainty estimate for each element in each factor profile is thereby yielded and factor swaps may occur if factors change too much. A comprehensive error estimate method, bootstrap enhanced by displacement (BS-DISP) combine the strengths of BS and DISP, which evaluate both the robustness to data errors and rotational uncertainty. Overall, no change in DISP Q (%dQ) was found for the 5-factor solutions. Furthermore, no swapped factor was found in DISP BS-DISP runs, indicating the 5-factor solution was a global minimum and well-defined PMF solution.

The source profiles of the 4- and 6-factor solution for the intensive Xact PMF analysis are shown in Figures S5 and S6. In the 4-factor solution, the Soil and Haul Road Dust factors can be combined, but the reproducibility of the solution was poor and there were factor swaps in the BS-DISP runs. In the 6-factor solution, the Soil factor from the 5-factor solution split into two similar soil factors which have poor BS mapping reproducibility and very high factor swaps in the BS-DISP analysis. Another solution could be possible in the 6-factor solution which was characterized by additional resolution of the Mixed sources in the 5-factor solution. As shown in Figure S6b, two Mixed sources were characterized by high loadings of Cu (Mixed Sources I) and Br and Se (Mixed Sources II). Thus, due to the robustness of the solution and the physically meaningfulness of the factor profiles, the 5-factor solution was clearly acceptable for the intensive campaign.

In the long-term campaign the Haul Road Dust and Soil factors in the 5-factor solution can be combined into one factor in the 4-factor solution (Figure S7a). However, there was an alternative solution including a combined factor of Mixed and Upgrader Emissions (Figure S7b). Due to the instability, there were factor swaps in BS-DISP and the reproducibility of the 4-factor solution was poor. With 6 factors, an additional Soil factor characterized by high loadings of rare earth elements and vanadium was found. However, this second Soil factor is only found 56% of the BS resamples and 85% of the BS-DISP runs were accepted with high factor swaps. In the 7-factor solution, additional factor containing high Pb and Br can be isolated from the Upgrader Emissions factor, but it's stability was very poor and there was no reasonable source for Pb and

Br only. The BS resamples and BS-DISP runs of the 5-factor solution was better than the 4- and 6-factor solutions for the long-term filter data (Table S5). These results indicate that the 4- and 6-factor solution are much less certain than the 5-factor solution. As a result, the 5-factor solution was chosen as the most reasonable and stable solution for the filter data.

In order to determine the relative weights of the different factors, a multiple linear regression of the time series of each factor for both campaigns was run against both the summed metal concentrations as well as the PM_{2.5} concentrations (obtained from WBEA). As trace metals only account for a small percentage of the overall PM_{2.5} mass, the results of the PM_{2.5} regression proved to be a poor fit both statistically ($r^2 < 0.8$) and physically, as it resulted in negative relative weights, to the metal speciation factor solutions. Because of this, the total metals concentration was used to determine the relative weights of the different factors, which resulted in a much better fit ($r^2 > 0.99$).

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Table S4. Summary of error estimation diagnostics for intensive Xact data.

	<u>4-Factor Solution</u>	<u>5-Factor Solution</u>	<u>6-Factor Solution</u>
<u>Robust Mode</u>	<u>Yes</u>		
<u>Seed Value</u>	<u>Random</u>		
<u># of Bootstraps in BS</u>	<u>100</u>		
<u>R² in BS</u>	<u>0.8</u>		
<u>DISP active species</u>	<u>Si, S, K, Ca, Ti, V, Mn, Fe</u>		
<u>BS-DISP active species</u>	<u>S, K, Ti, V, Fe</u>		
<u>Factors with BS mapping < 100%</u>	<u>Upgrader Emissions II(51%), Mixed (99%)</u>	<u>Upgrader Emissions II (98%)</u>	<u>Soil (53%), Soil II (93%)</u>
<u>DISP %dQ</u>	<u>0</u>	<u>0</u>	<u>0</u>
<u>DISP # of swaps</u>	<u>0</u>	<u>0</u>	<u>0</u>
<u>BS-DISP % of Cases Accepted</u>	<u>95</u>	<u>97</u>	<u>27</u>
<u>BS-DISP # of swaps</u>	<u>4</u>	<u>0</u>	<u>198</u>

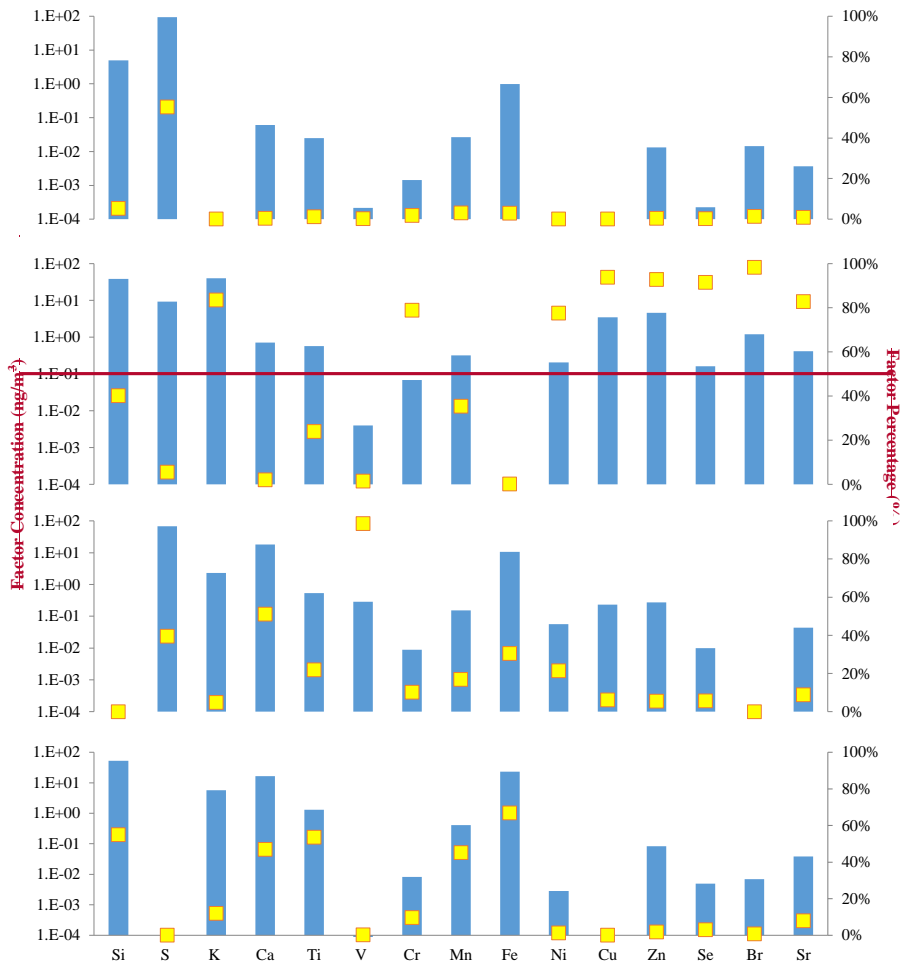
Table S5. Summary of error estimation diagnostics for long-term combined filter data.

	<u>4-Factor Solution</u>	<u>5-Factor Solution</u>	<u>6-Factor Solution</u>
<u>Robust Mode</u>	<u>Yes</u>		
<u>Seed Value</u>	<u>Random</u>		
<u># of Bootstraps in BS</u>	<u>100</u>		
<u>R² in BS</u>	<u>0.8</u>		
<u>DISP active species</u>	<u>Si, S, K, Ca, Ti, Fe, Cu, Sr, Al, Cd, Ce, La, Pr, Nd, Sm, Gd, Pb, U</u>		
<u>BS-DISP active species</u>	<u>Si, S, K, Ca, Fe, Cu, La</u>		
<u>Factors with BS mapping < 100%</u>	<u>Mixed (29%), Biomass Burning (98%)</u>	<u>Mixed (96%), Soil (99%)</u>	<u>Soil (56%), Haul Road Dust (97%), Mixed (99%)</u>
<u>DISP %dQ</u>	<u>9.3E-5</u>	<u>0</u>	<u>1.8E-5</u>
<u>DISP # of swaps</u>	<u>0</u>	<u>0</u>	<u>0</u>
<u>BS-DISP % of Cases Accepted</u>	<u>87</u>	<u>97</u>	<u>85</u>
<u>BS-DISP # of swaps</u>	<u>10</u>	<u>0</u>	<u>12</u>

S.4

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S.3 PMF Factor Solutions



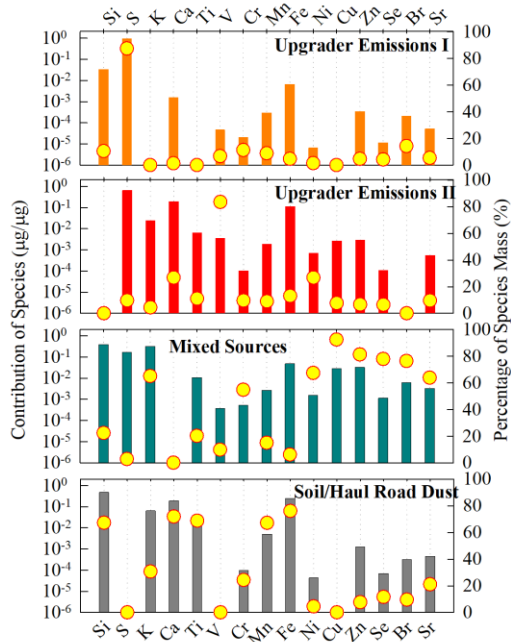
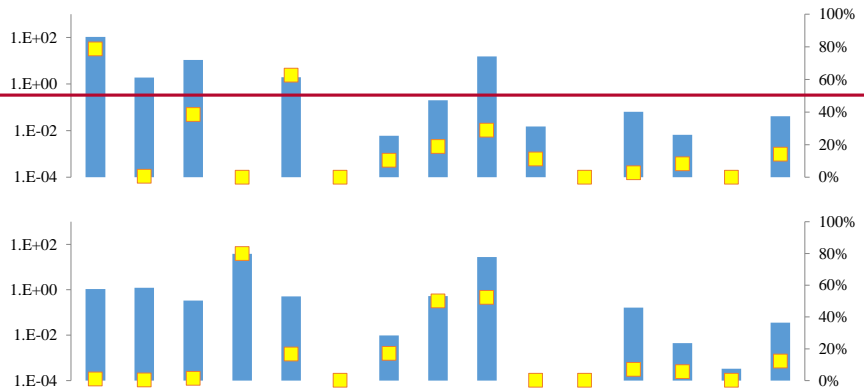
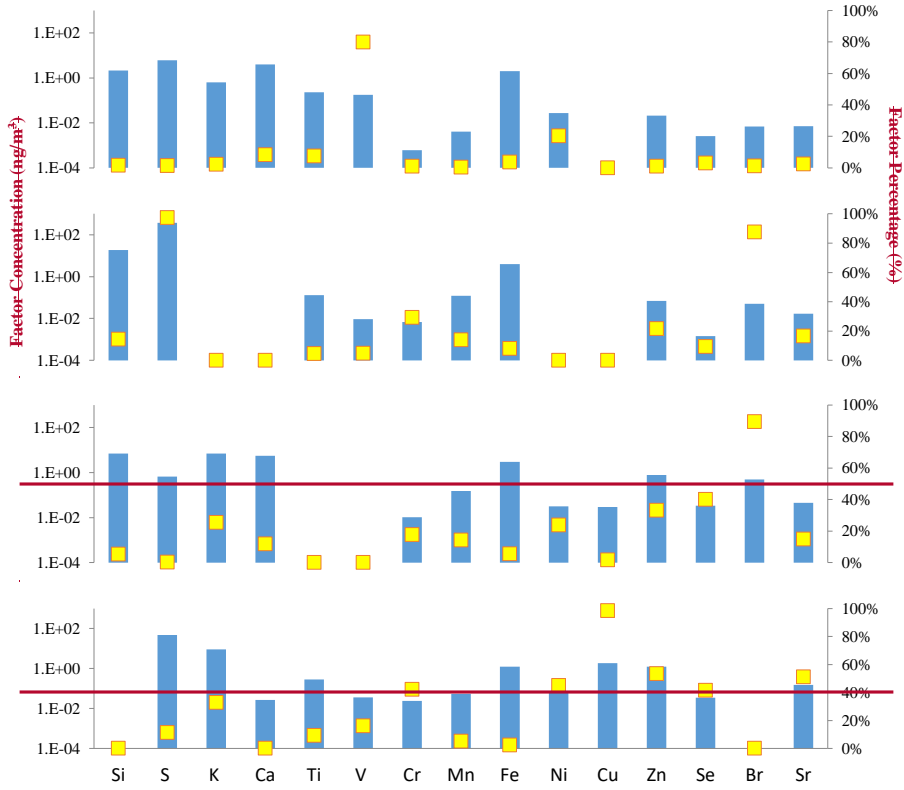


Figure S5. Alternative 4-factor solution calculated using PMF for the intensive campaign (Xact metal data).
Factor Concentrations depicted as bars, percentages depicted as circles.





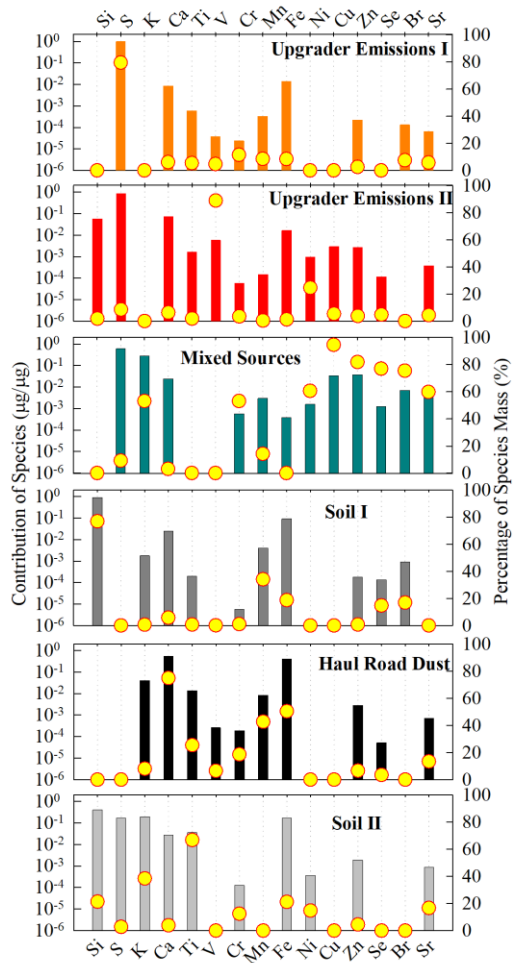


Figure S6S6a. Alternative 6-factor solution calculated using PMF for the intensive campaign (Xact metal data). Factor Concentrations depicted as bars, percentages depicted as circles.

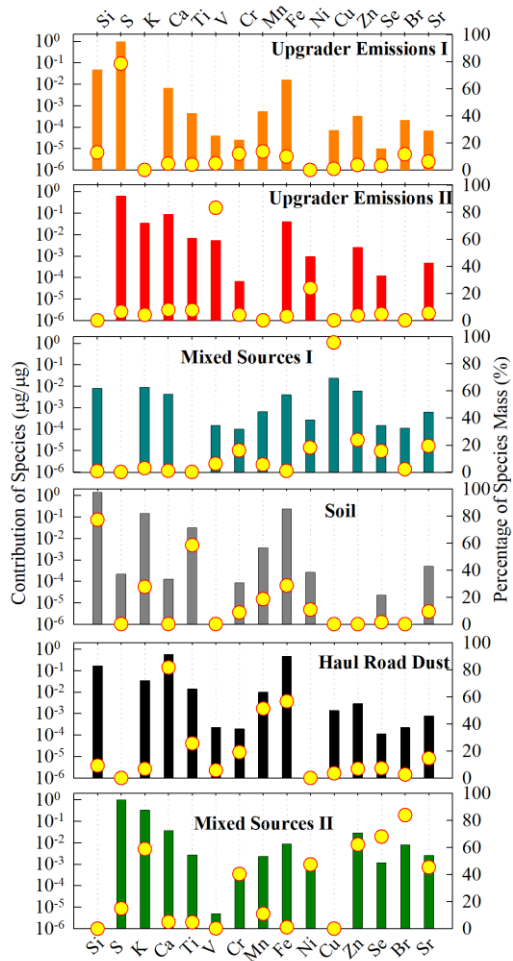


Figure S6b. Alternative 6-factor solution calculated using PMF for the intensive campaign (Xact metal data). Factor Concentrations depicted as bars, percentages depicted as circles.

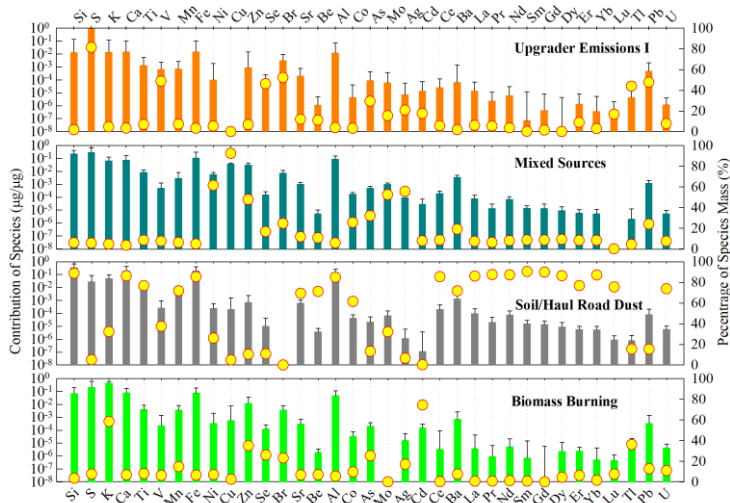


Figure S7a. Alternative 4-factor solution calculated using PMF for the long-term campaign (Filter data). Error bars represent standard deviations estimated by 100 bootstrap runs. Factor Concentrations depicted as bars, percentages depicted as circles.

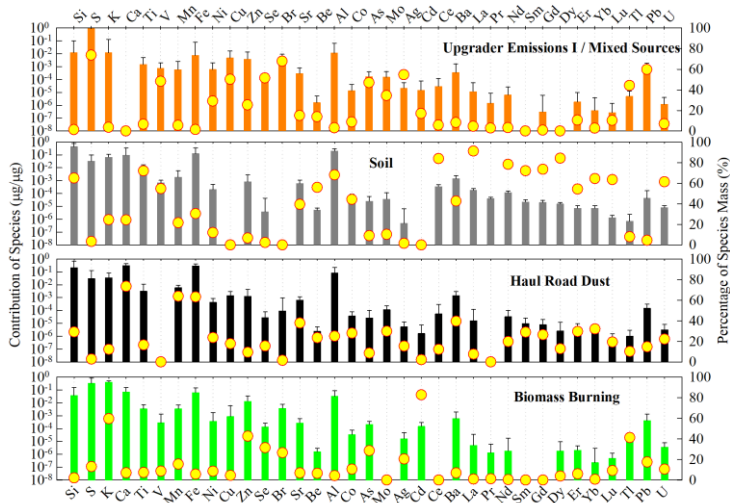


Figure S7b. Alternative 4-factor solution calculated using PMF for the long-term campaign (Filter data). Error bars represent standard deviations estimated by 100 bootstrap runs. Factor Concentrations depicted as bars, percentages depicted as circles.

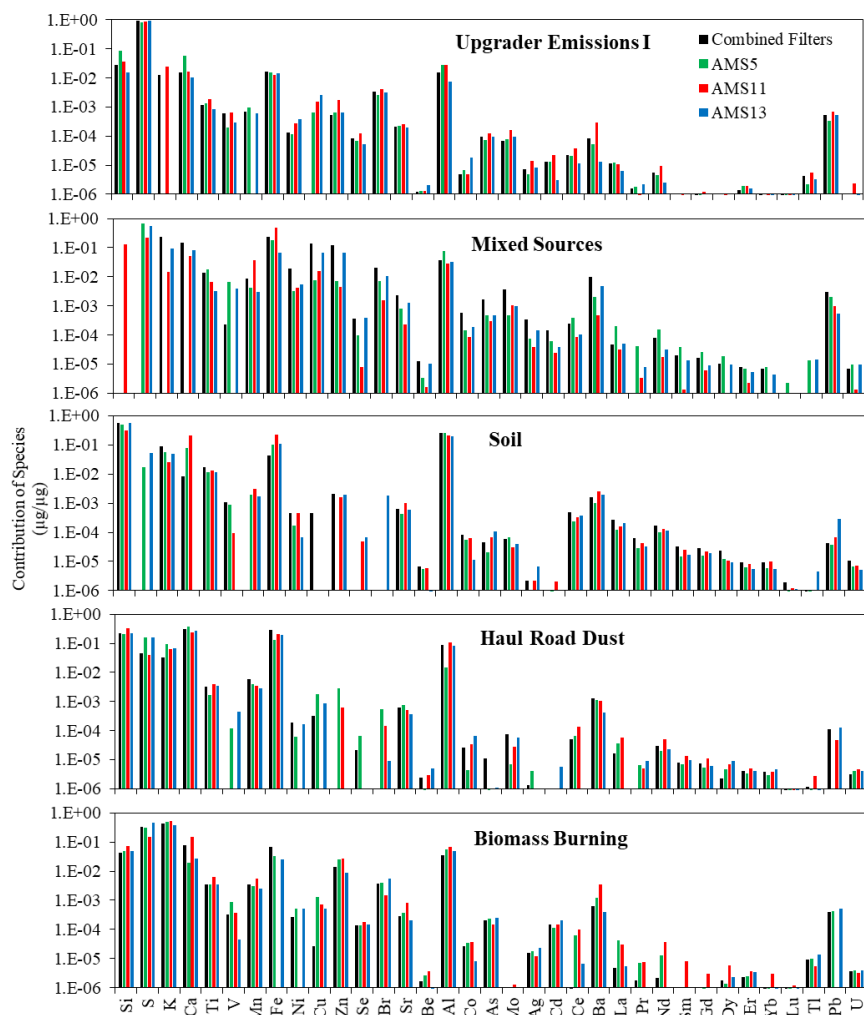
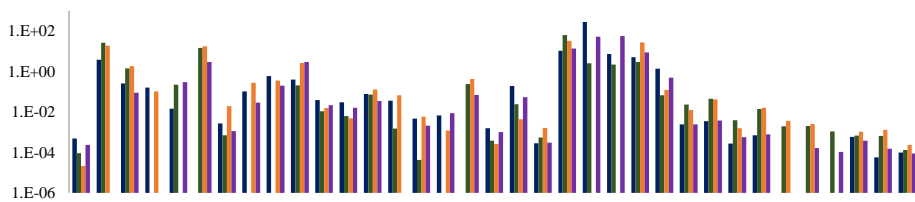


Figure S8.



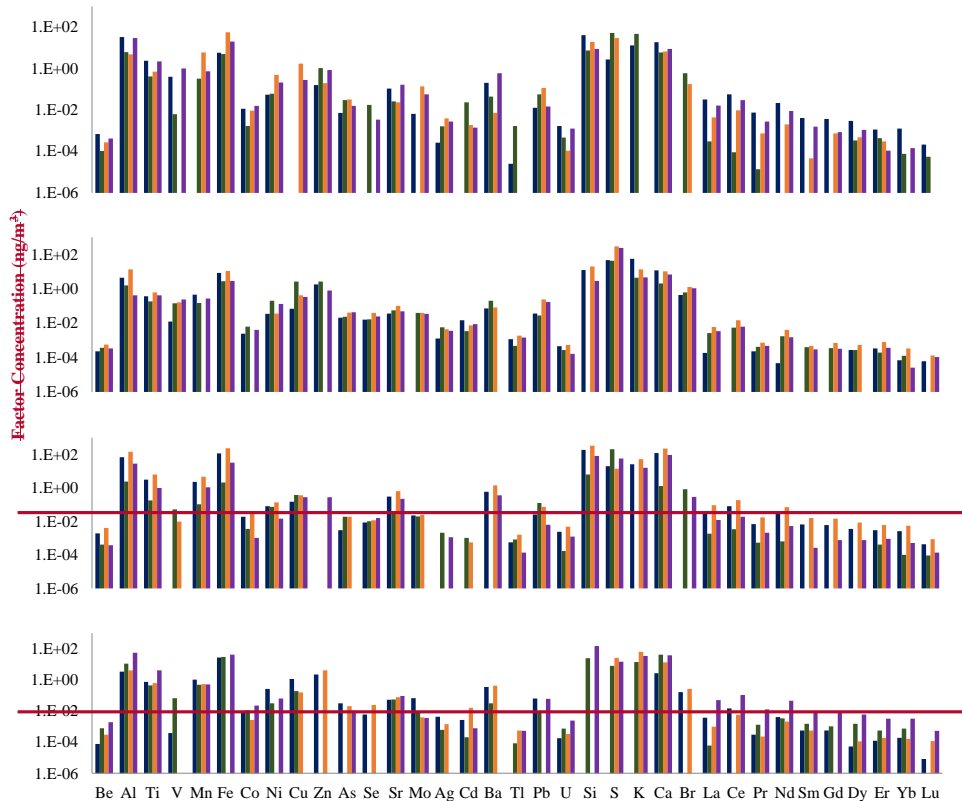
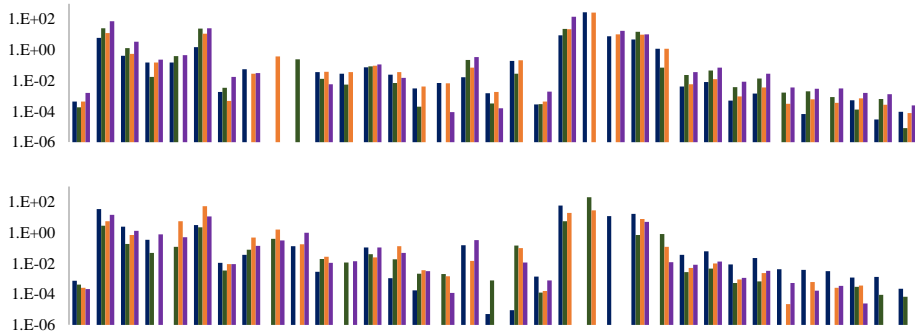


Figure S7. 5-factor solutions for 4 independently run PMF analyses of the long-term campaign data (Integrated filter data). **Dark blue/black** is the overall solution run after combining the data from all three sites; **green** is the independently run **AMS13** data; **orange** is the independently run **AMS5** data; and **purple** is the independently run **AMS11** data; and **blue** is the independently run **AMS13** data.



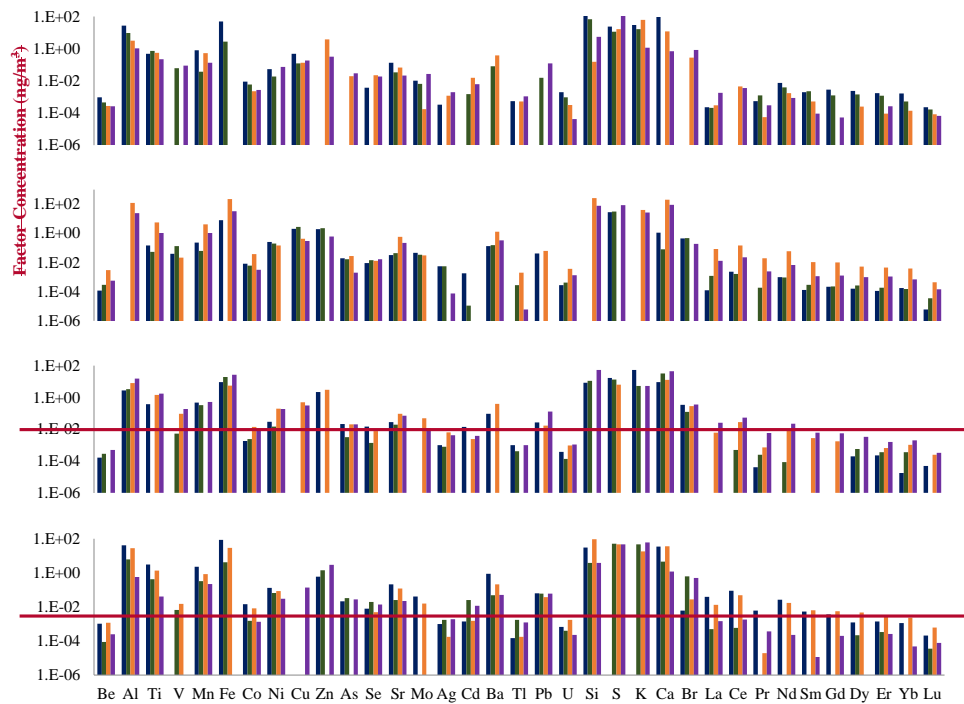


Figure S8. 6-factor solutions for 4 independently run PMF analyses of the long-term campaign data (Integrated filter data). Dark blue is the overall solution run after combining the data from all three sites; green is the independently run AMS13 data; orange is the independently run AMS5 data; and purple is the independently run AMS11 data.

S.45 Overall Species comparison

Table S4S6. Average concentrations of elements used in the PMF analysis of the long-term campaign average and 90th percentile (Dec. 2010-Nov. 2012, Aug. 2013) for all three sites compared to average metal concentrations in Halifax, St John, Montreal, Windsor, Toronto, Edmonton, and Vancouver (Environment Canada, 2015). All metal(oids) are measured either by acid digested ICP-MS ⁽¹⁾ or ED-XRF ⁽²⁾.

Element (ng/m ³)	Oil Sands - Average	Oil Sands-90 th Percentile	Halifax, NS	St John, NB	Montreal, QC	Windsor, ON	Toronto, ON	Edmonton, AB	Vancouver, BC
Ag ¹	0.02	0.02	0.02	0.02	0.04	0.03	0.03	0.03	0.03
Al ²	121	290	36	31	43	29	31	47	29
As ¹	0.12	0.25	0.25	0.25	0.83	1.0	0.48	0.41	0.51
Ba ¹	1.4	3.5	1.2	0.88	1.79	2.26	2.45	2.87	2.42
Be ¹	N/A	N/A	0.005	0.004	0.005	0.005	0.004	0.005	0.004
Br ²	2.1	4.3	2.0	1.8	2.5	2.7	2.0	2.6	2.0
Ca ²	154	390	23	14	58	69	45	60	19
Cd ¹	0.04	0.08	0.03	0.04	0.19	0.16	0.08	0.13	0.07
Ce ¹	0.16	0.35							
Co ¹	0.05	0.11	0.12	0.02	0.03	0.02	0.03	0.15	0.03
Cr ¹	N/A	N/A	0.23	0.21	0.54	0.43	0.37	1.6	0.55
Cu ¹	2.7	6.0	2.0	1.2	3.2	3.3	2.8	3.6	2.7
Dy ¹	0.01	0.02							
Er ¹	0.01	0.02							
Fe ²	151	350	32	20	59	123	51	120	52
Gd ¹	0.01	0.03							
K ²	97	200	51	42	75	70	48	66	56
La ¹	0.08	0.17							
Lu ¹	N/A	L/A							
Mn ¹	5.1	13	0.91	0.60	2.2	4.5	1.6	7.7	2.6
Mo ¹	0.21	0.39	0.11	0.09	0.31	0.33	0.18	0.40	0.22
Ni ¹	0.94	1.4	2.3	0.76	0.73	0.75	0.46	1.5	1.4
Nd ¹	0.06	0.14							
Pb ¹	0.42	0.99	1.5	0.85	3.9	4.3	2.0	1.4	2.5
Pr ¹	0.02	0.04							
S ²	373	760	334	357	415	720	455	331	248
Se ¹	0.09	0.15	0.19	0.20	0.63	1.1	0.57	0.15	0.15
Si ²	265	670	46	29	54	53	40	14	26
Sm ¹	0.01	0.03							
Sr ¹	N/A	N/A	0.50	0.48	0.69	0.78	0.58	0.50	0.62
Ti ¹	7.3	15	0.85	0.32	1.6	0.52	0.35	0.61	0.38
Tl ¹	0.01	0.03	0.02	0.02	0.02	0.03	0.02	0.01	0.01
U ¹	N/A	N/A							
V ¹	0.84	1.9	2.9	1.2	0.81	0.71	0.23	0.35	2.4
Yb ¹	N/A	N/A							

<i>Zn^l</i>	6.4	14	6.5	8.6	16	22	10	12	8.9
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S.56 Shannon Entropy

Shannon entropy is a theoretical measure of the uncertainty associated with a random variable (Healy et al., 2014). Shannon entropy was used to quantify how each species was partitioned across various factors. The bulk population diversity (D_i) for each species (i) was determined based on the mass fractions of each species (p^a) for each factor (a) across the total number of factors (A). A species equally distributed across all five factors would have a diversity of 5: a species with a value of 1 is considered to be entirely distributed to a single factor. Overall, Shannon Entropy is an information-theoretic measure that has been previously used to indicate biodiversity (Whittaker, 1965), genetic diversity (Rosenburg et al., 2002), and economic diversity (Attaran, 1986). More recently, Shannon entropy has been used to analyze how chemical species present in particles are distributed in an aerosol population (Healy et al., 2014; Reimer and West, 2013). In this study, Shannon entropy was used to analyze how the metals species were distributed across the various factors. A metal species with a diversity value above 3.5 was considered to be equally distributed, and, therefore, that species could not be used as a characteristic species for factor identification.

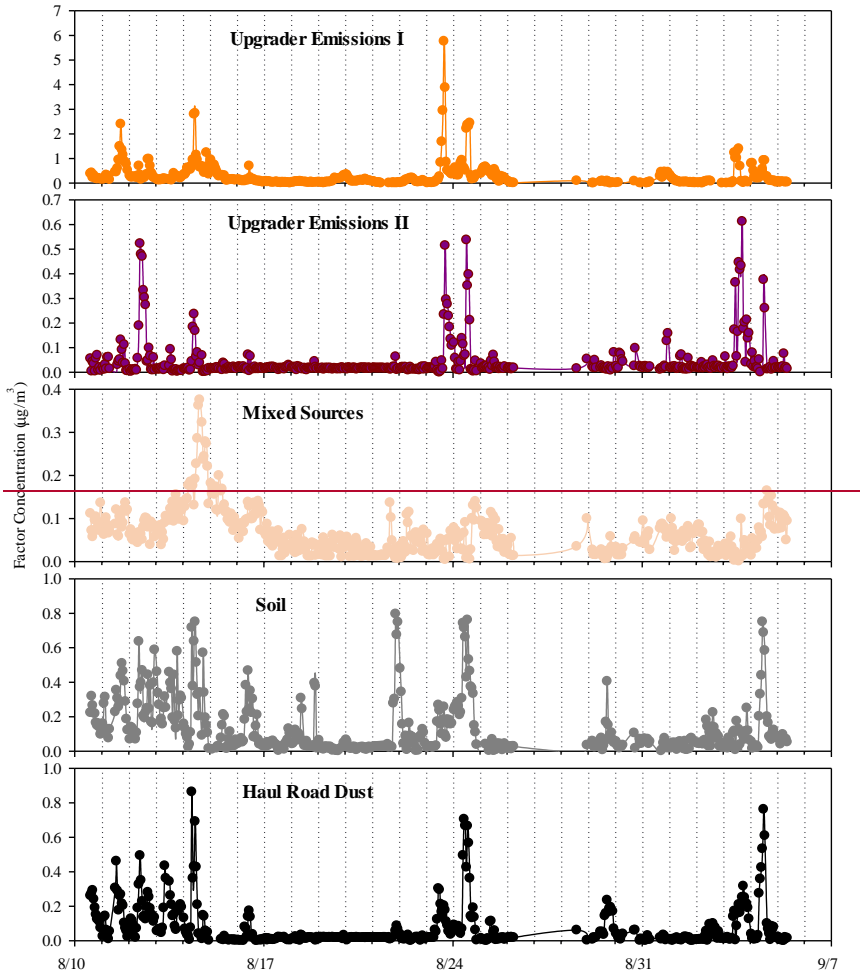
$$D_i = e^{\sum_{a=1}^A -p^a \ln p^a}$$

Equation 4(5)

Table S4S7. Diversity values for the elements analyzed in the intensive monitoring and long-term campaigns. Species in bold had diversity values greater than 3.5 and thus were too diverse to be used to distinguish between factors.

Elements	Intensive Campaign	Long-term Campaign
<i>Si</i>	2.0	2.4
<i>S</i>	2.1	1.8
<i>K</i>	2.4	3.3
<i>Ca</i>	2.3	2.2
<i>Ti</i>	2.6	3.3
<i>V</i>	1.6	2.4
<i>Cr</i>	3.9	
<i>Mn</i>	3.5	2.3
<i>Fe</i>	3.1	2.1
<i>Ni</i>	2.6	3.7
<i>Cu</i>	1.4	1.9
<i>Zn</i>	2.0	2.8
<i>Se</i>	2.2	3.6
<i>Br</i>	1.5	2.6
<i>Sr</i>	3.5	3.6
<i>Be</i>		3.5
<i>Al</i>		2.6
<i>Co</i>		3.8
<i>As</i>		4.2
<i>Mo</i>		2.9
<i>Ag</i>		3.4
<i>Cd</i>		2.2
<i>Ce</i>		2.6
<i>Ba</i>		2.8
<i>La</i>		2.6
<i>Pr</i>		2.4
<i>Nd</i>		2.5
<i>Sm</i>		2.2
<i>Gd</i>		2.3
<i>Dy</i>		2.4
<i>Er</i>		3.2
<i>Yb</i>		2.4
<i>Lu</i>		3.2
<i>Tl</i>		3.0
<i>Pb</i>		3.4
<i>U</i>		3.4

S.67 Temporal trends



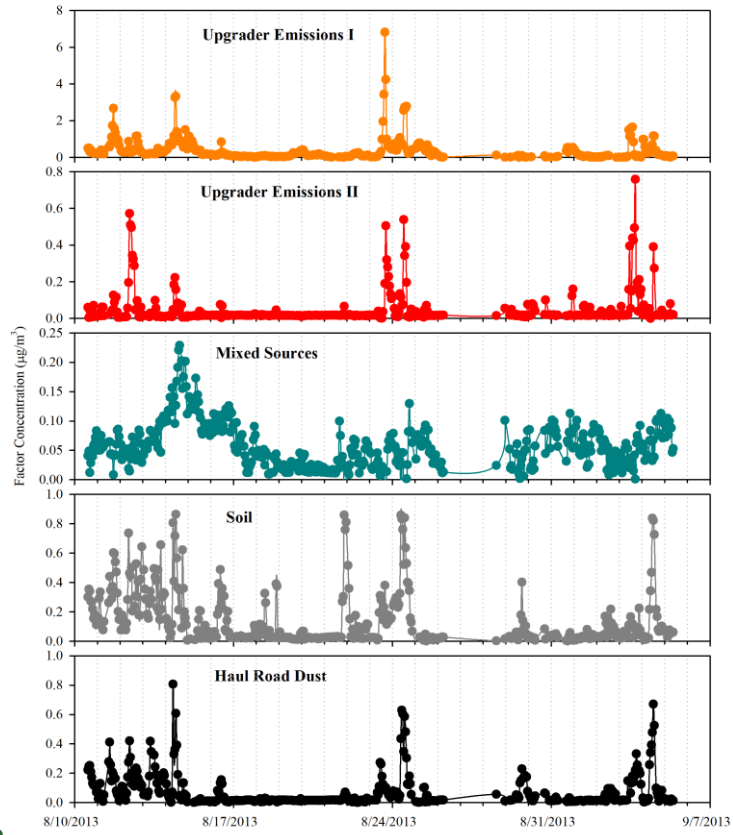


Figure S10.

Figure S9. Concentration time series of PMF-resolved 5 factorfactors during the intensive campaign.

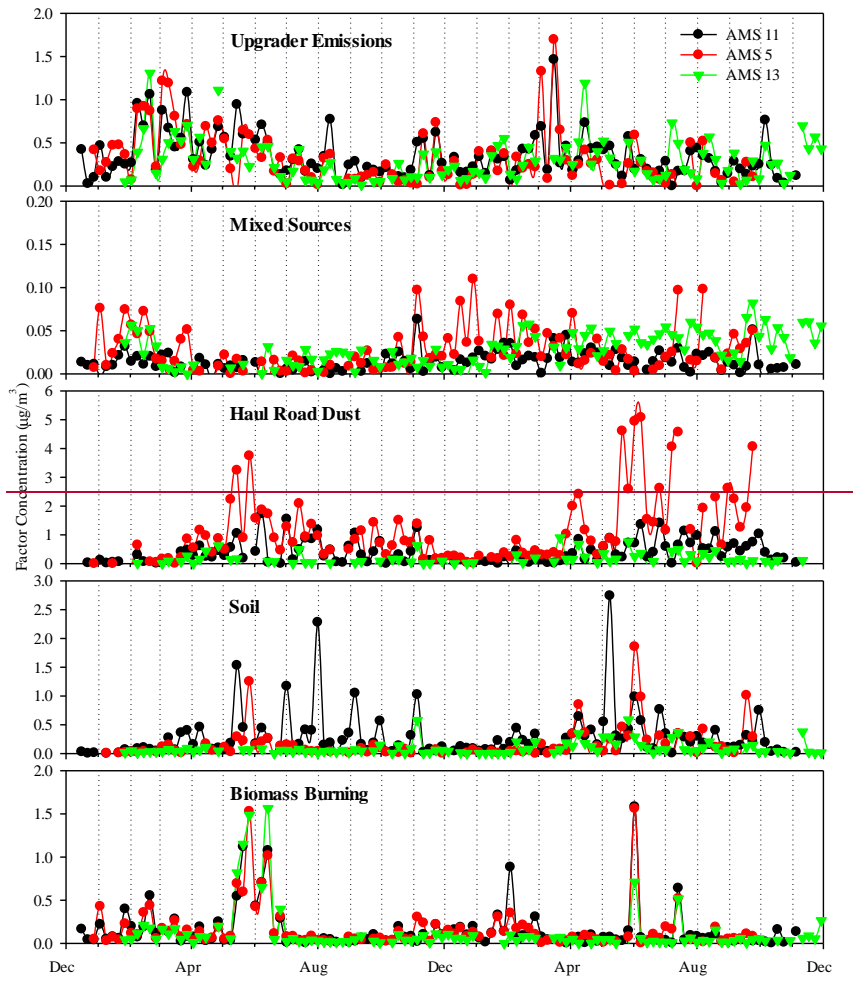


Figure 11.

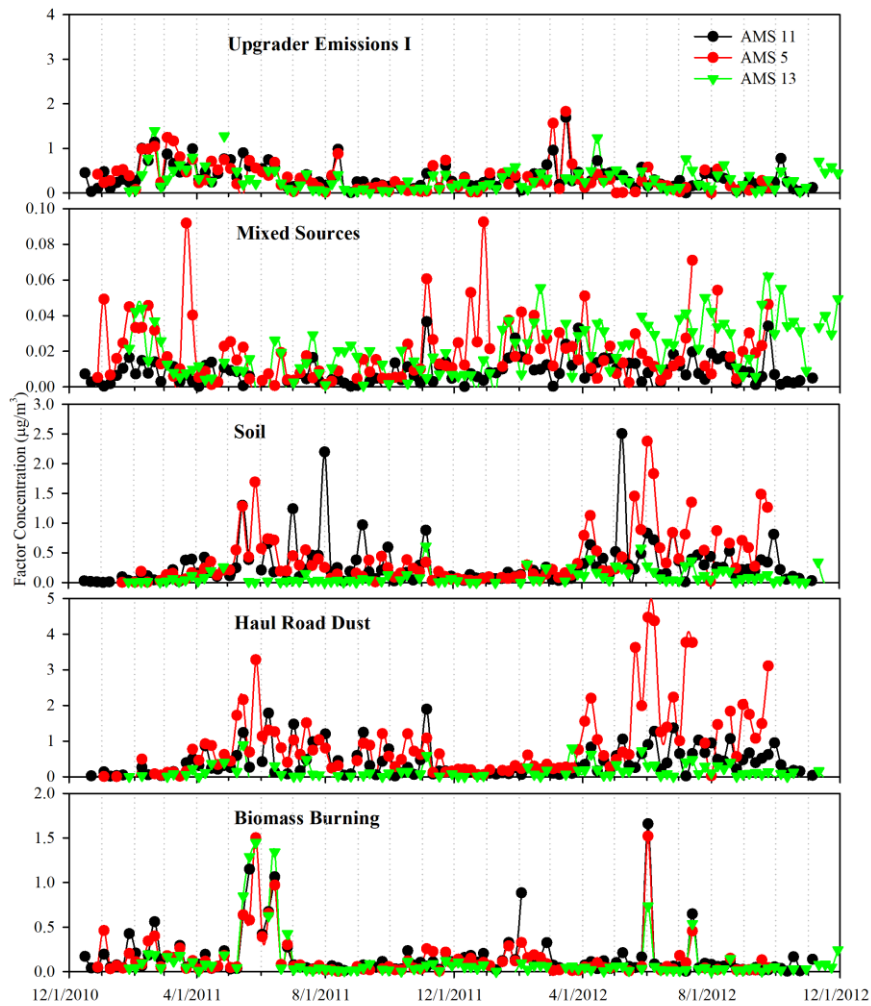


Figure S10. Concentration time series of PMF-resolved 5 factors during the long-term campaign from December, 2010 to November, 2012 for AMS13, AMS5, and AMS11.

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S.78 Seasonal and Geographical Wind Directions

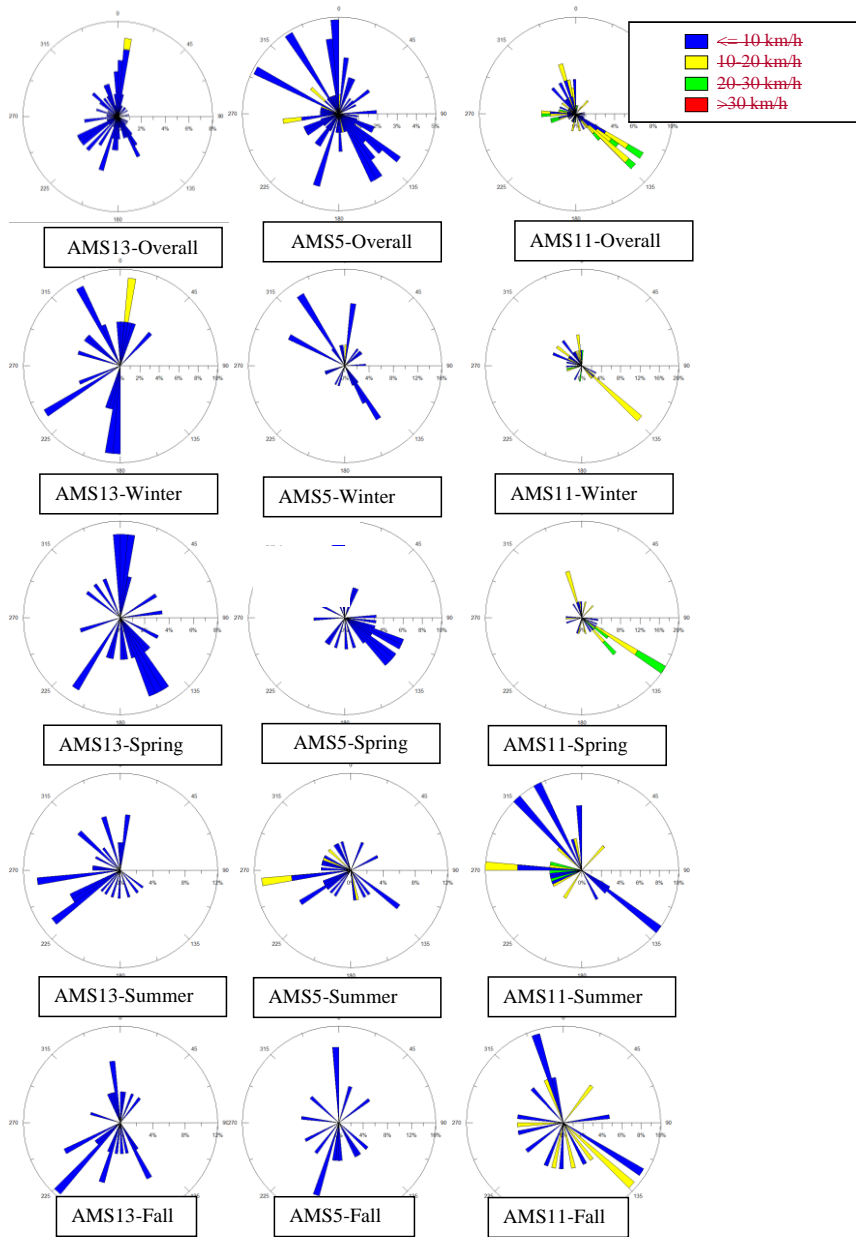


Figure S12S11. Overall and seasonal wind roses of the three sites analyzed in the long-term campaign.

S.89 Seasonal Temperatures

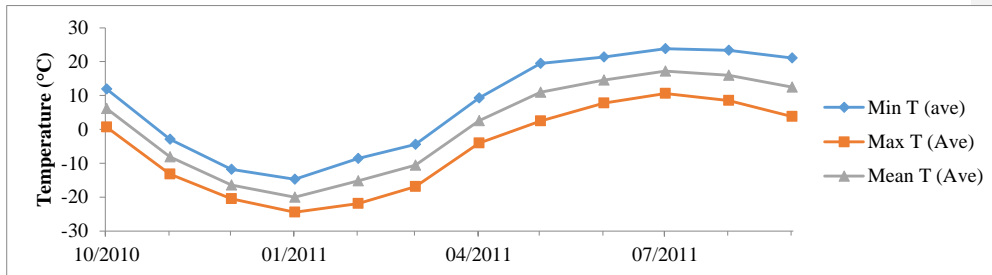


Figure S13.

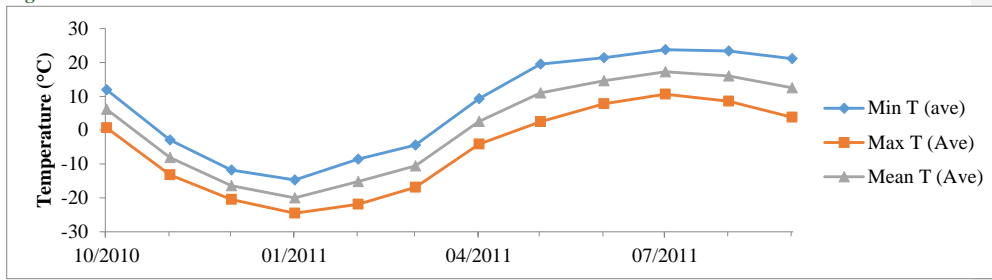
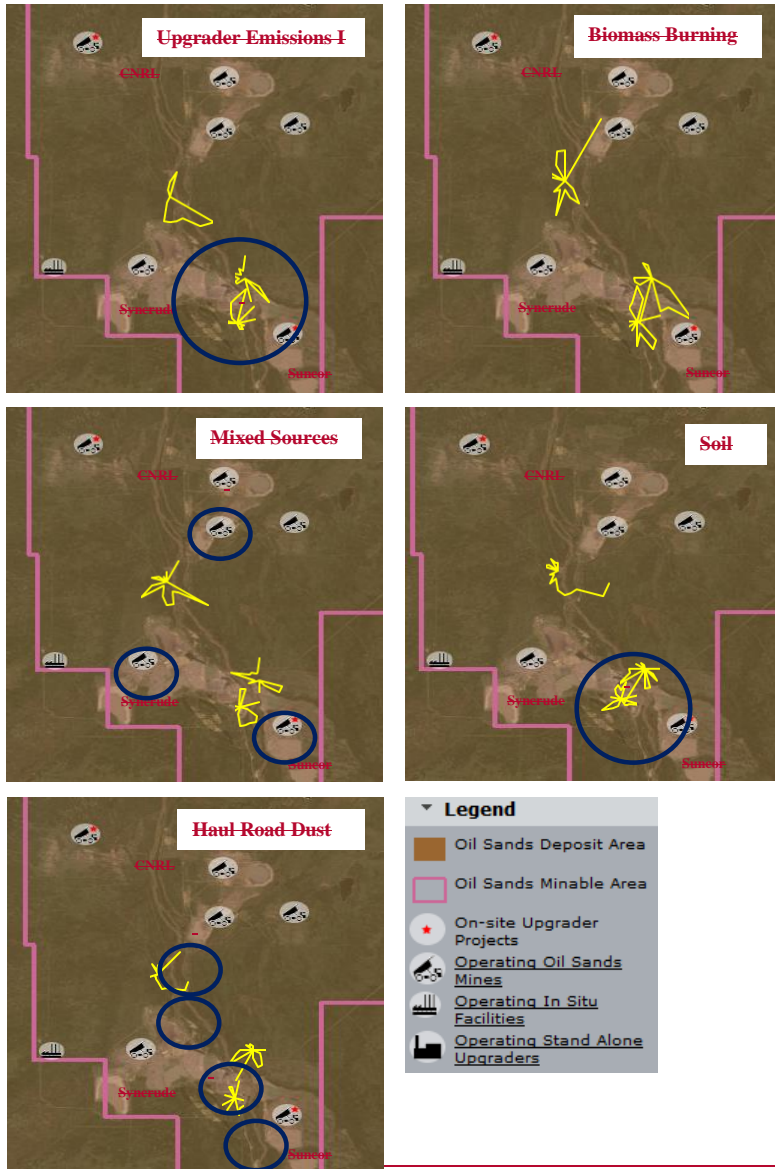


Figure S12. Typical average monthly temperatures for Fort McMurray, AB for the year 2010-2011.

S.910 Long-Term Campaign CPF Plots



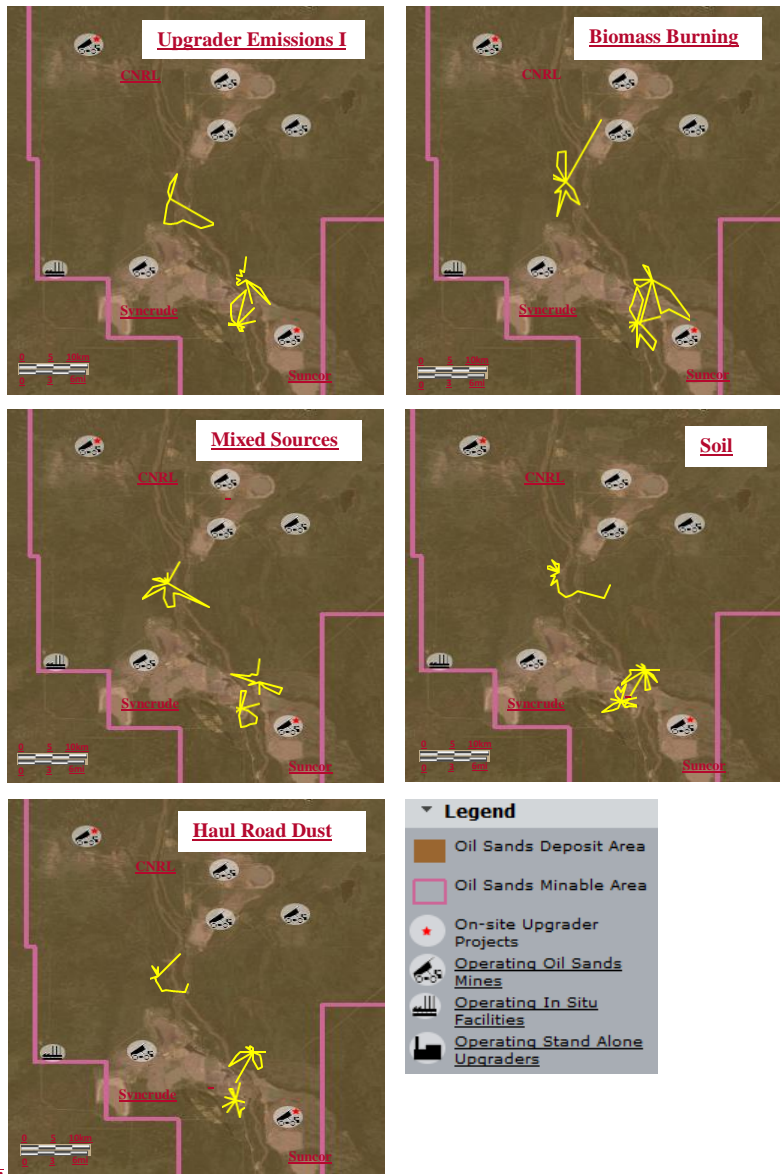
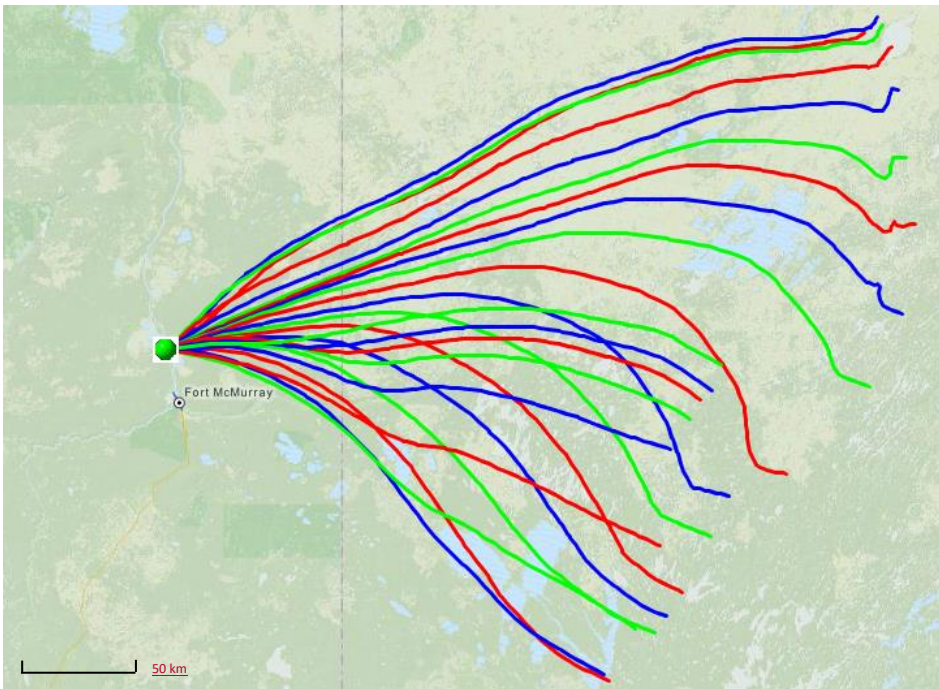
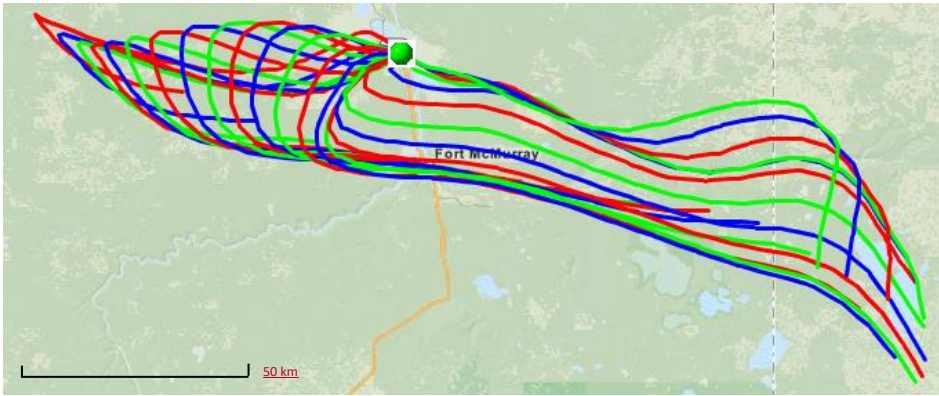


Figure S14.

Figure S13. CPF plots from all three sites; AMS13, AMS5, and AMS11 for each factor identified using PMF on the long-term campaign's data. Blue Circles indicate the location of potential sources. 'Gaps' in the yellow wind rose are due to a lack of wind data coming from certain directions. Map courtesy of Alberta: Environmental and Sustainable Resource Development. Available: <http://osip.alberta.ca/map>

S.1011 HYSPLIT Analysis



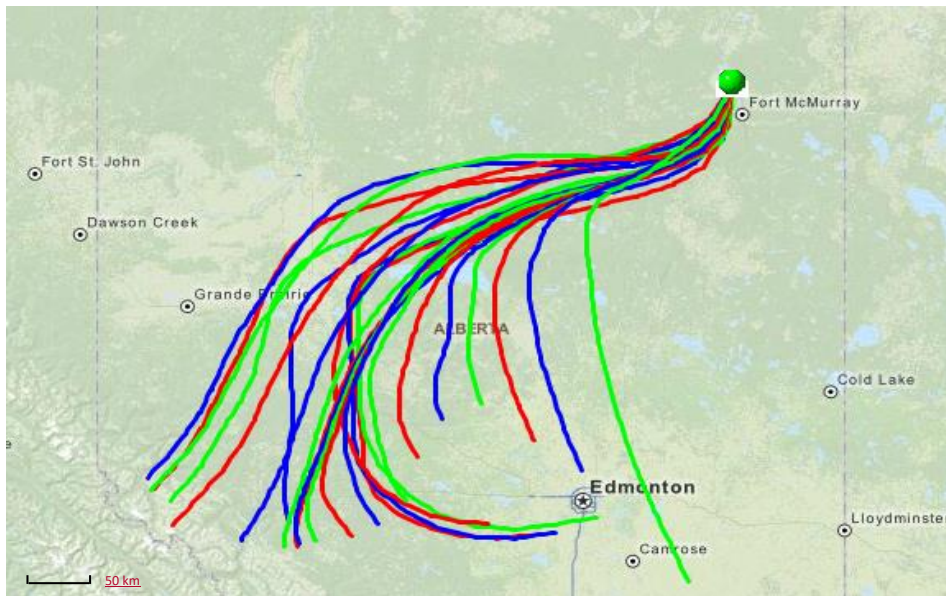
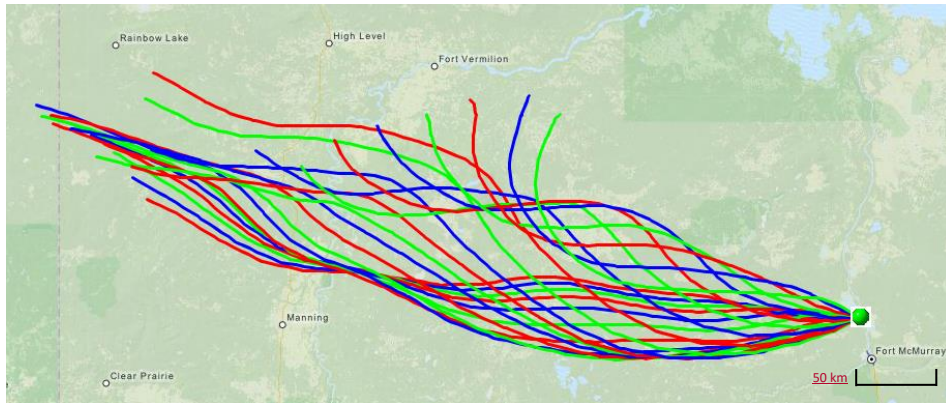


Figure S15S14. HYSPLIT Analysis diagrams of the 4 days with the overall highest contributions of the biomass burning factor: June 2, 2011; June 14, 2011; May 27, 2011; May 21, 2011.

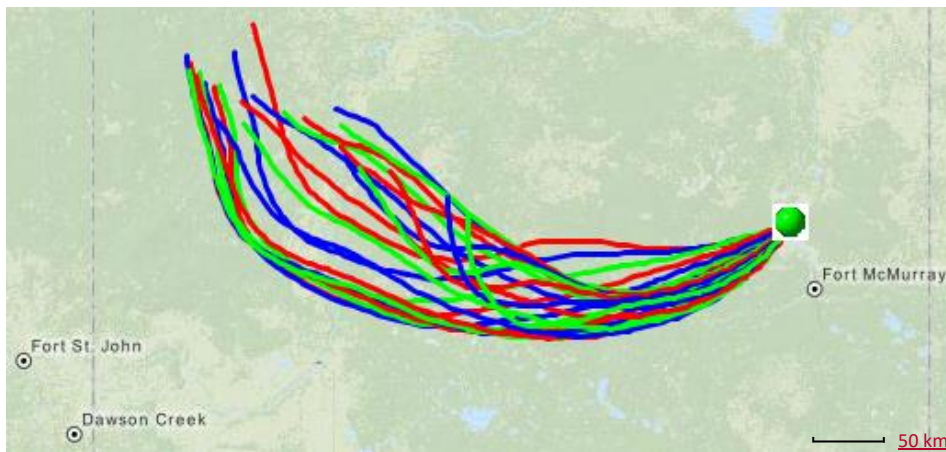
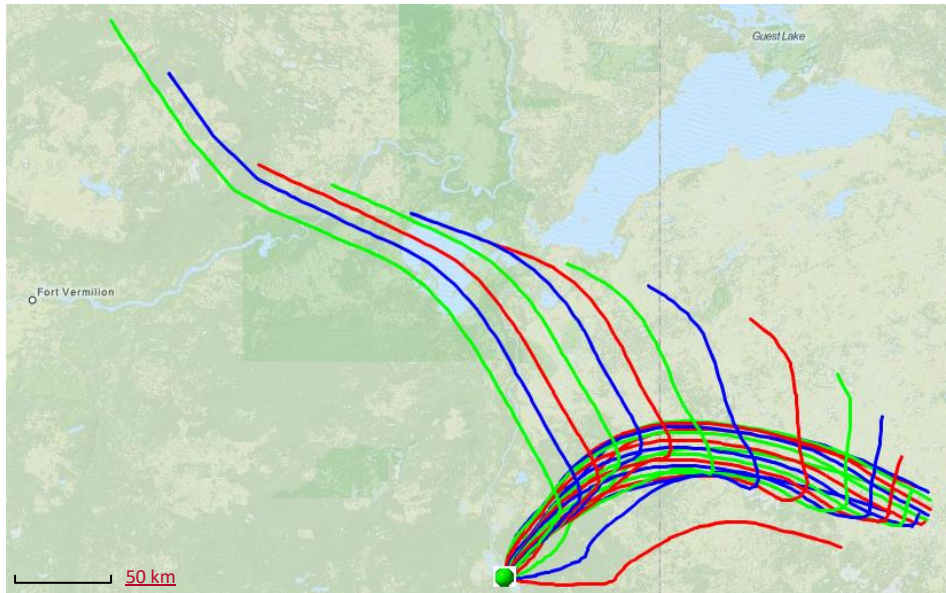


Figure S16S15. HYSPLIT analysis diagrams of the 2 days with the highest overall soil contributions: June 8, 2011; March 22, 2012.

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