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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 #1

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General Comments:

This manuscript describes an effort to apportion PM2.5 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

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Discussion paper

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 PM2.5 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 been 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.

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? 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?

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.

Specific Comments:

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

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.

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.

4. Page 3, 2nd paragraph. The review of past PM2.5 research in the oil sands is miss-

ing 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.

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.

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).

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.

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?

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.

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.

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 NOx, I would expect the haul road dust to better correlate with NOx 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.

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.

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.

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

Technical Details

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

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.

3. Page 6 Line 4. I suggest changing "dirt" 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.

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).

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

7. Write "Eqn 1" in supplemental materials in an equation form.

8. There are two Table S4

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).

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

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

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