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

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The manuscript by Phillips-Smith et al. investigated sources of PM2.5 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 PM2.5 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 PM2.5 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 PM2.5. However, it is unclear whether there are any previous source apportionment studies using other PM2.5 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 PM2.5 (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 XactTM 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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