

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.

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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.

Celo, V., Dabek-Zlotorzynska, E., Zhao, J., Okonskaia, I., and Bowman, D.: An improved method for determination of lanthanoids in environmental samples by inductively coupled plasma mass spectrometry with high matrix introduction system, *Anal. Chim. Acta.*, 706, 89-96, 2011.

Dabek-Zlotorzynska, E., Dann, T.F., Martinelango, P.K., Celo, V., Brook, J.R., Mathieu, D., Ding, L.Y., Austin, C.C., 2011. Canadian National Air Pollution Surveillance (NAPS) PM_{2.5} speciation program: methodology and PM_{2.5} chemical composition for the years 2003-2008. *Atmospheric Environment* 45, 673-686.

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”.