Identifying the Origins of Trace Metals in Particulate Matter in the Athabasca Oil Sands Region

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Background

$PM_{2.5}$ is particulate matter that is smaller than 2.5 µm in diameter. These particles are a mixture of primary and secondary aerosols and are linked to climate and health impacts.

Metals within $PM_{2.5}$ are related to their source and some are associated with health risks (Bzdek et al.).

Metal	Source	Risks
Calcium	Crustal	
Lead	Anthropogenic	Toxic
Arsenic	Anthropogenic	Toxic
Vanadium	Anthropogenic	Lung Irritant
Strontium	Anthropogenic	Toxic
Copper	Anthropogenic/Crustal	Lung Irritant

Objectives

Identify and quantify metals in particles emitted from oil sands activities

Identify the pollutant mixture associated with oil sands activities

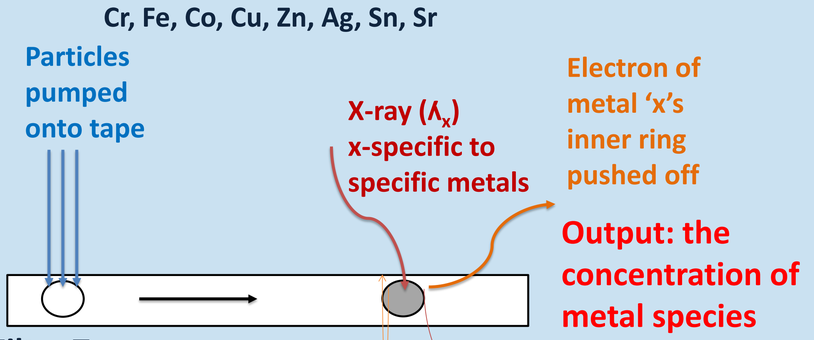
Methodology

Instrument

Xact625 (Cooper Environmental)

An X-ray Fluorescence device that takes hourly measurements of 23 aerosol metals in PM2.5:

S, Si, Rb, As, Ni, Pb, Ca, Cd, Se, Mn, Ba, K, Br, Ti, V, Cr, Fe, Co, Cu, Zn, Ag, Sn, Sr



Location

Fort McKay, Athabasca Region, Alberta

Wood Buffalo Environmental Association Site AMS 13: Fort McKay South

Image Courtesy of: Wood Buffalo Environmental Association

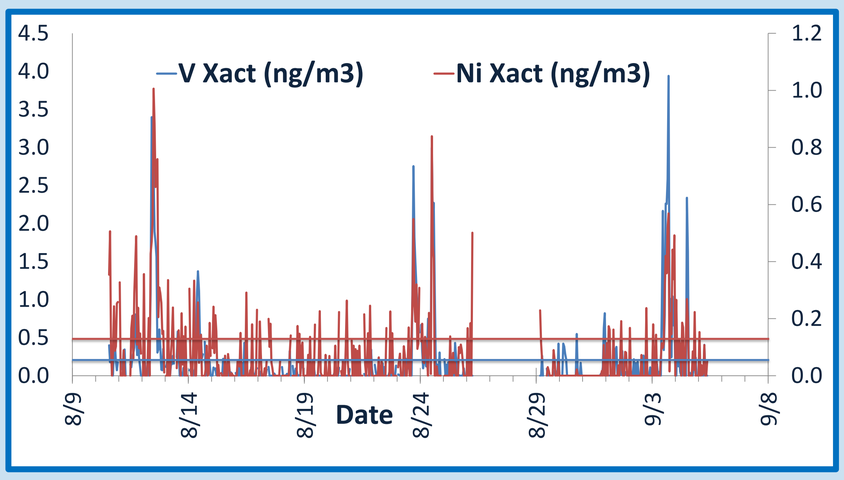
Sampling Period

August 10 - September 5, 2013

Data Output

Quality Control and Analysis

- Daily blank check to remove base line
- Comparison to metal standards and daily filter samples
- Only metals that were over 10% above the minimum detection limit were included for analysis:
  - S, Si, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Sr

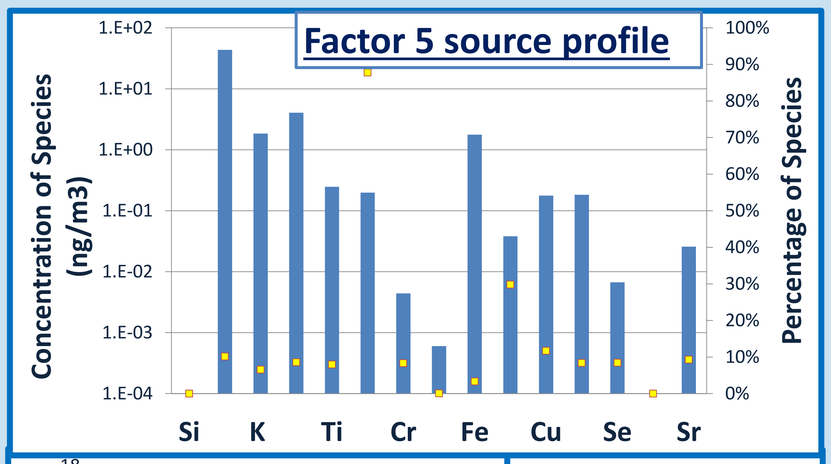


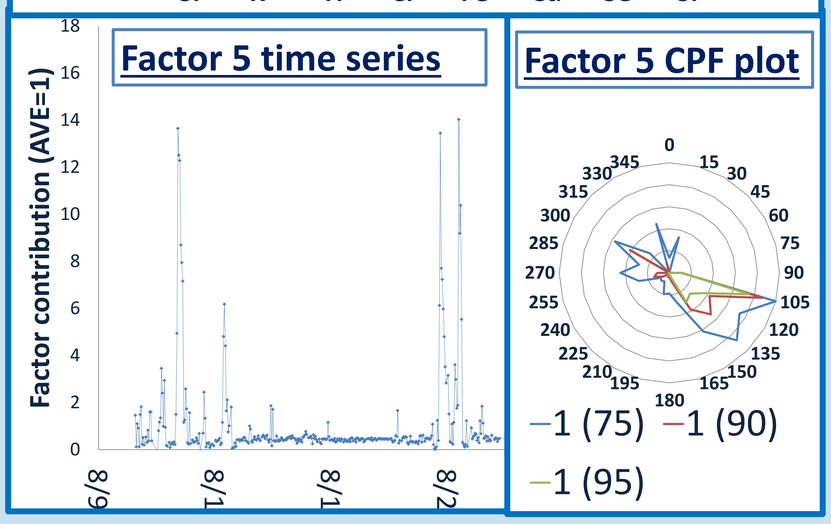
Results

Following PMF and CPF analysis 5 factors were found and were compared to other chemical species such as SO_2 and NO_2. This helps to enable source identification. The sources identified are:

1. *Elemental Sulphur*
2. *Soil*
3. *Road Dust*
4. *Mining Activities*
5. *Oil Burning*

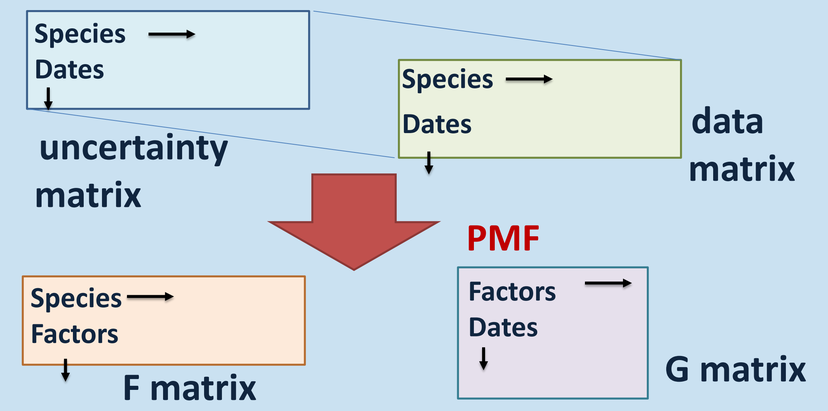
Source	Defining Metals	Correlative Aerosol
sulphur	S	SO_2
Soil	Si, K, Fe, Ca, Mn	NO_2, NO_x
Road dust	Mn, Fe, Ca	NO_2, NO_x
Mining	Cu, K, Ca	
Oil	S,V	SO_2





Data Analysis

Positive Matrix Factorization (PMF)



$$X = GF + E$$

E = residuals matrix G = factor matrix X = data matrix F = species matrix

The goal is of PMF is to separate the chemical species into factors, while minimizing the "Q" factor, as defined by the following equation (Jeong et al.):

$$Q = \sum_{i=1}^{n}\sum_{j=1}^{m} {E_{ij}}^2/{\sigma_{ij}}^2$$

σ = uncertainty matrix

Conditional Probability Function (CPF)

Taking the wind direction of a mass concentration over time allows the source direction to be found:

$$CPF = m_{\Delta\theta}/n_{\Delta\theta}$$

$m_{\Delta\vartheta}$ is the factor contribution, and $n_{\Delta\vartheta}$ is the number of times a wind came from one direction

The higher the CPF value, the more likely it comes from that direction (Wang et al.).

Conclusions

Particulate metals in the oil sands have been quantified using an Xact625 XRF device during the summer of 2013

These metals come from 5 sources; elemental sulphur, soil, road dust, mining activities and oil combustion.

Future Work

Oil Sands Campaign

- Compare campaign results to those of the 3 year off-line filter campaign results
- Compare results to those observed in literature
- Locate the sources of the 5 factors
- Compare the factor time series other chemical species

2014-2015 Arctic Campaign

- In Alert, Nunavut, each winter there are an estimated 66 snowfalls between October and May (Climatemps)
- While snow cores have been previously studies, this study will capture freshly fallen snow on a snow table.
- There will be 5 samples taken per snow fall for analysis of the following;
  - Elemental Carbon/Organic Carbon
  - Metals
  - Size, chemical composition (ATOFMS)
  - Soot (SP2)
  - Black Carbon containing particles (SP-AMS)
- Snow samples will be shipped in insulated containers from Alert to the University of Toronto, Ontario

- With these measurements, similar source apportionment can be performed across the entire season.

References

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- Bzdek et al., 2012. Single particle chemical analysis of ambient ultrafine aerosol: A review. *Journal of Aerosol Science* 52, 109-120.
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Environment Canada

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