Joint Canada | Alberta Implementation Plan for Oil Sands Monitoring

Atmospheric Deposition of Contaminants to the Athabasca Oil Sands region

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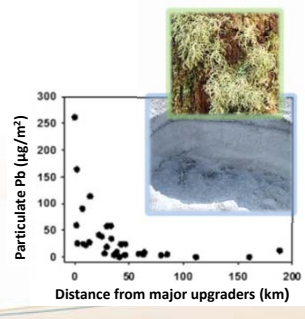
Development of the Joint Oil Sands Monitoring (JOSM) program Design

- Kelly et al. (2009, 2010) used snow measurements at 30 sites to show that polycyclic aromatic carbons (PACs) and the 13 elements considered Priority Pollutant Elements (PPEs) were deposited within 50 km of the major upgraders.
- Similar findings by Studabaker et al. and Graney et al. (2012) for PACs (20 analytes and metals Al, V and Pb).



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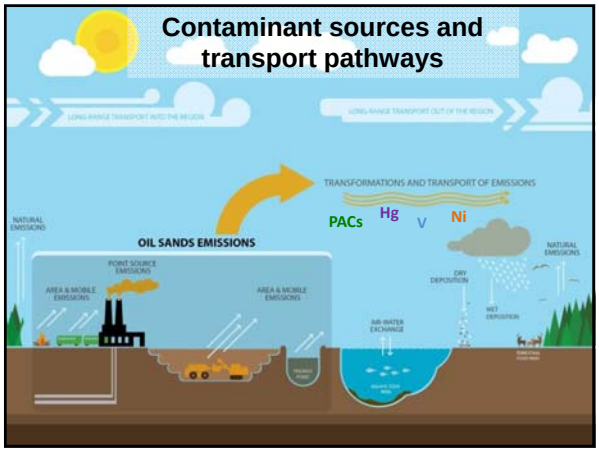
Contaminant sources and transport pathways



Methods

SPATIAL: Snow in early March

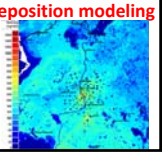
TEMPORAL: Sediment cores from 28 isolated lakes

Air Quality Research Division

Passive air sampling

Precipitation sampling

Deposition modeling

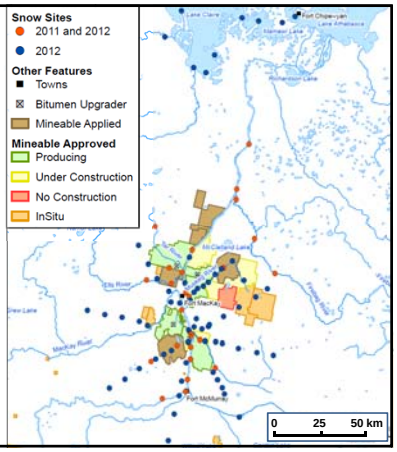


Analytes

- Polycyclic aromatic compounds (PACs): 52 analytes + 25 individual compounds
- 2D-GC-TOF MS to identify other alkylated PAHs, as well as thia-arenes, and aza-arenes
- Multielements: 45 including the 13 priority pollutant elements (PPEs)
- Mercury and methyl mercury
- Complete suite water chemistry parameters: POC, PON, TP, etc
- Paleo-chemical indicators in sediment cores : chlorophyll a and DOC via visible near infrared reflectance spectroscopy (VNIRS)
- Paleo-ecological indicators: Cladocera, fossil diatoms, chironomids

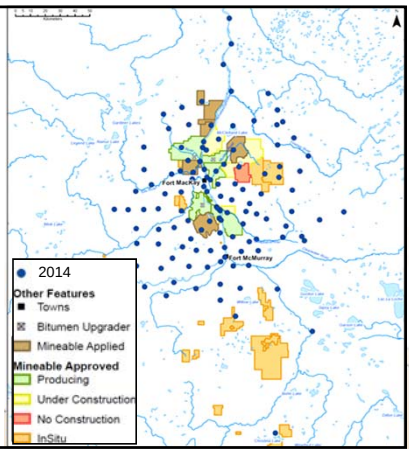
March 2011-12 Snowpack Sampling Design

- ~30 Kelly/Schindler sites.
- Transects moving away from major developments following 2011 Alberta Environment design.
- Fort Chipewyan residents: 9 sites in the Peace Athabasca Delta.



March 2014-15 Snowpack Sampling Design

- Gridded sampling design gives better regional coverage.
- Allowed for a better fit of interpolations via kriging to measured values.

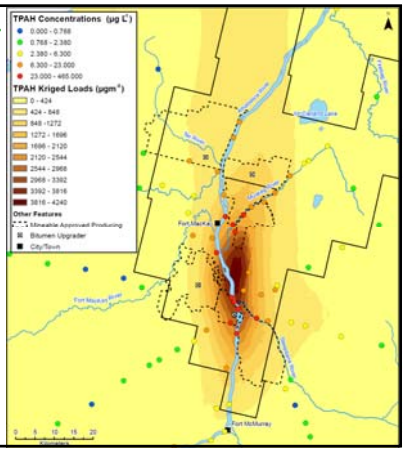


Collaboration with Fort Chipewyan residents

- Snow sampling at ~10-12 sites 2012-2016 in collaboration with Parks Canada and Fort Chipewyan residents.
- Sampled sites where bird egg collections are carried out by *Hebert et al.*.
- These sites are one of our methods for establishing background for the region.

2012 *net* winter-time PACs deposition

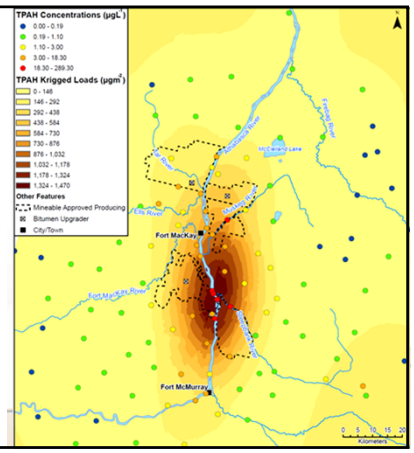
- Rather than just describing spatial patterns, our goal was to interpolate measurements to create a deposition map for ~20, 000 km^2 region of the Athabasca Oil Sands region.



2014 *net* winter-time PACs deposition

- Deposition pattern unchanged with improved spatial coverage on the landscape.

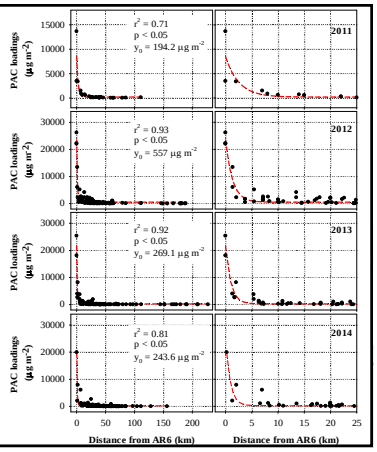
Published in Manzano et al. Environmental Monitoring and Assessment 2016



What is background for the region?

Max loads are up to ~1000X higher than background with background determined by:

- The Peace- Athabasca Delta ~200 km from major developments.
- Loads in remote US national parks and the Austrian Alps.
- Load where the exponential decay function flattens out.



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- In the absence of pre-industrial monitoring, a robust method for determining background is needed to quantify the extent of the industrial footprint.
- The algal and invertebrate communities will be suited to background conditions and changes must be assessed against this background.

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Comparison of two methods to estimate winter PACs deposition within 50 km of major developments

PACs	2008 Kelly et al.	2011	2012	2013	2014
	kg	kg	kg	kg	Kg
# sites	31	27	98	91	119
1. From the exponential decay function	560	1240	1800	810	1370
2. From kriging			3390	1920	1970

Method 1. Integration of the exponential decay function describing the data
Method 2. From the kriged deposition map.

Net net spring-time contaminant loads can now be paired with river water monitoring using GIS and hydrological modeling to determine the extent to which winter-time atmospheric deposition alters contaminant concentrations and loads in rivers.

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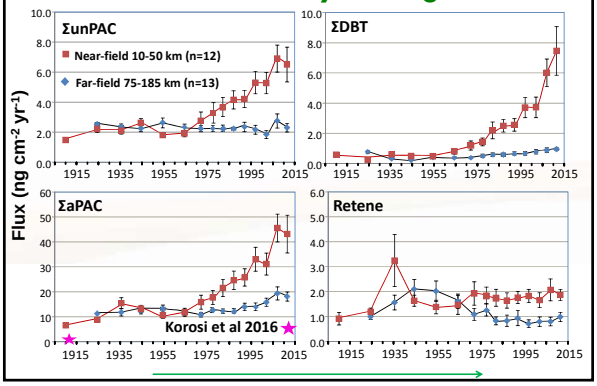
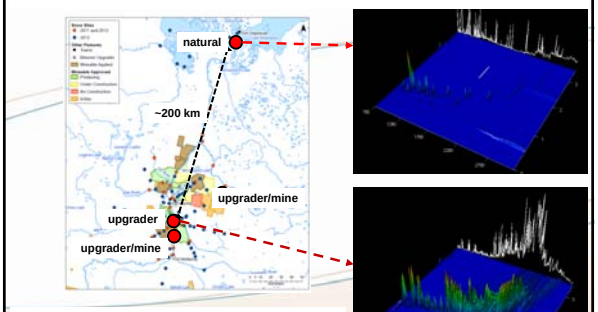
PACs (52 analytes) in 25 lake sediment cores decadally averaged



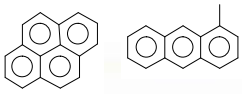
PACs source identification using 2D-GC



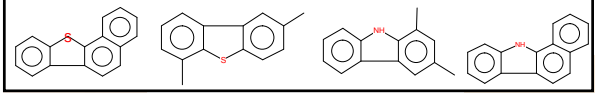
Method published in Manzano et al. International Journal of Environmental Analytical Chemistry, 2016

Identification of thia-arenes and aza-arenes as a major components of the PACs in snow, sediments and air

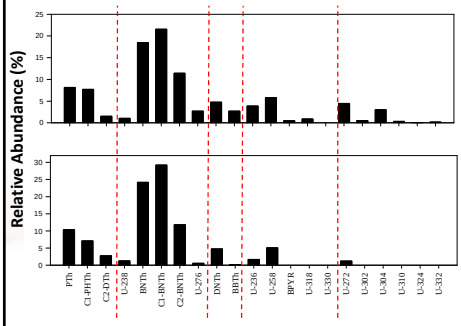
- Polycyclic aromatic hydrocarbons (PAHs): Structure based on benzene rings
  Natural and anthropogenic sources: forest fires, heating, traffic



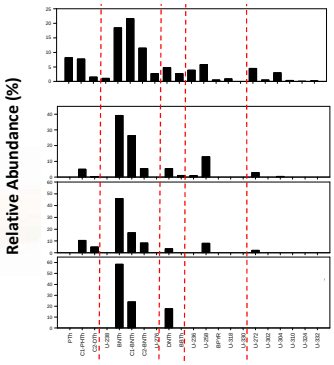
- Thia-arenes and aza-arenes: Lower concentration than PAHs
  Sources include fossil fuels, soot, shale oils, engine exhaust.



Distribution of novel PACs in snow compared to a pet coke sample



Distribution of novel PACs lake sediments compared to a pet coke sample



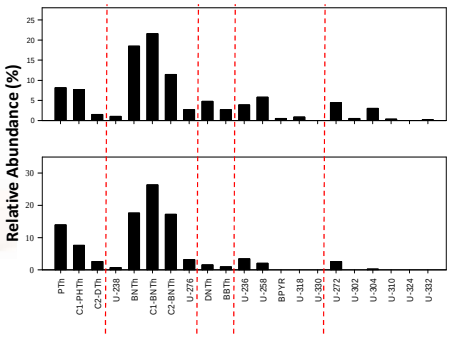
DELAYED PET COKE: from Jon Martin, U. Alberta

SURFACE SEDIMENT: from Lake NW35

PRE-1985 SEDIMENT: from Lake NW35

PRE-1950 SEDIMENT: from Lake NW35

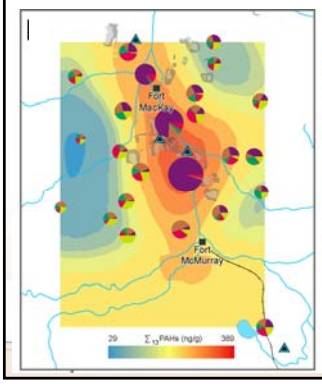
Distribution of novel PACs in passive air samples compared to a pet coke sample

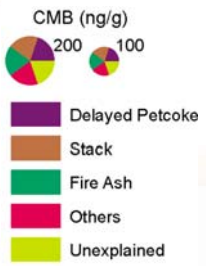


DELAYED PET COKE

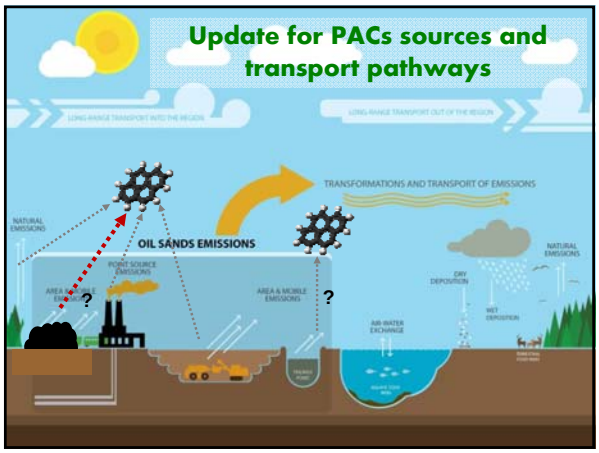
POLYUROTHANE FOAM PASSIVE AIR SAMPLERS: ~30 km from major developments

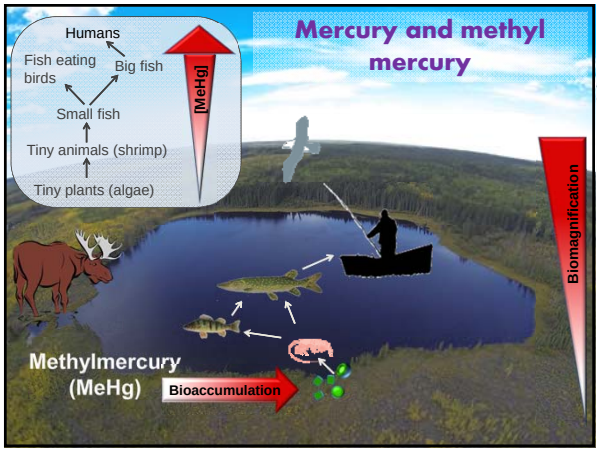
Pet coke pattern also observed in moss from bogs in the OS mining region





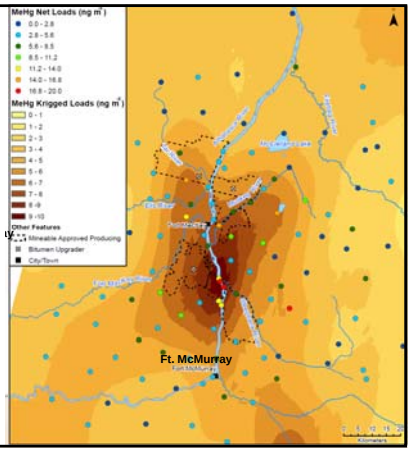
Published in Zhang et al. Environmental Science and Technology, 2016





2014 *net* winter-time methyl Hg deposition

- Max mercury and methyl mercury ~10x above background.
- Beyond ~50 km and in the Peace Athabasca Delta, both were near background levels.



Examining potential sources of methyl mercury to snowpacks

- Using Hg stable isotope tracer experiments to determine potential rates of Hg(II) methylation in snowpacks/melt.

$^{198}Hg(II) \rightarrow Me^{198}Hg$ (methylation)

Distance from developments (km)	Snowpack k_d (d^{-1})	Snowpack k_m (d^{-1})
0	0.07	0.001
7	0.23	0.004
25	0.14	0.003
134	0.42	0.003

From Willis et al. In preparation

Analyses of pet coke and snowpack particulates for methyl mercury

Company	MeHg (n/g)
*PET COKE Canadian Natural Resources Ltd	0.041
*PET COKE: Syncrude	0.002
*PET COKE: ANZAC	0.005
AVERAGE SNOWPACK PARTICULATE MeHG	2.47

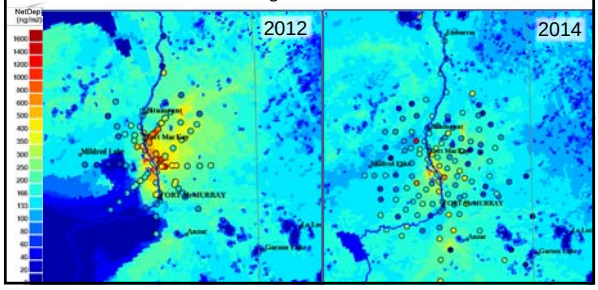
*Pet coke obtained from Jon Martin, U of Alberta

- Results suggest that although snowpack methylation is possible, rates are too low to account for the quantity of methyl mercury in the snowpack.
- Unlike PACs, pet coke is not an important source of atmospheric mercury deposition.

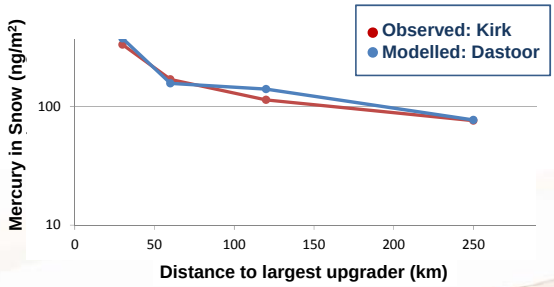
From Willis et al. In preparation

Using the snowpack measurements to validate the mercury deposition model

- Model simulated net deposition of mercury to snow on March 10th, 2012 and 2014 compared to measured mercury in snow.
- Model is based on the Canadian weather forecast model, which simulates all of the meteorological variables.



Do the model and the data match?



- With a verified mercury deposition model for the region, deposition can be predicted under future projected emission and climate scenarios.

Final Thoughts

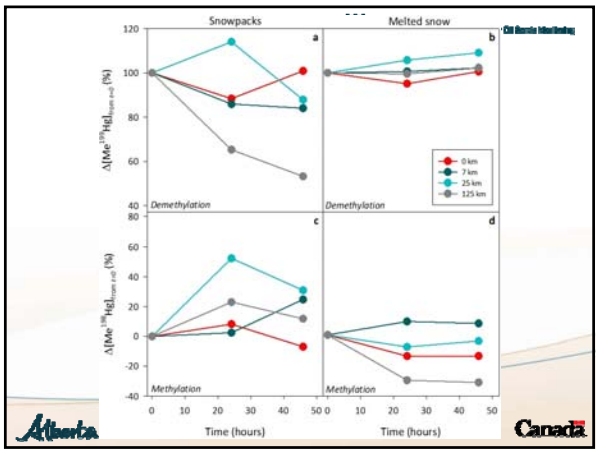
- Have obtained an understanding of the extent of the industrial footprint and % increase above background in atmospheric contaminant deposition.
- Deposition estimates can be directly inputted into contaminant mass balances, for example to individual tributaries.
- Have developed tools for source identification; continuing this work with additional source materials and a "nearest to fence line" approach.

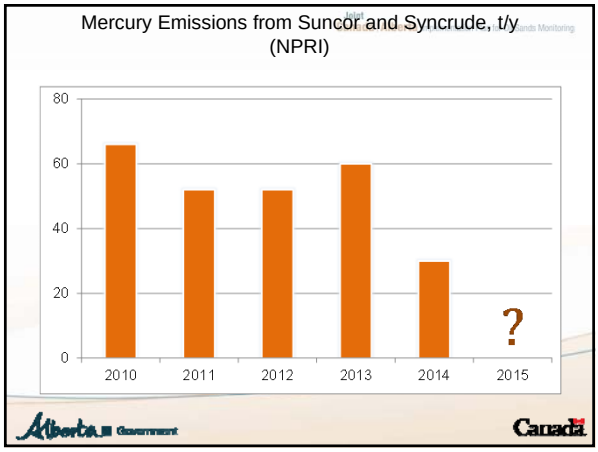
Does atmospheric deposition matter?

- Working now on understanding the fate of contaminants deposited from the atmosphere after spring melt.
- Working on understanding the impact on biological communities: Paleo-ecological indicators including cladocera, fossil diatoms, chironomids through collaborations with Queens University.
- Ultimately will link this work to measurements of contaminants in invertebrates, fish and fish eating birds.

Acknowledgements

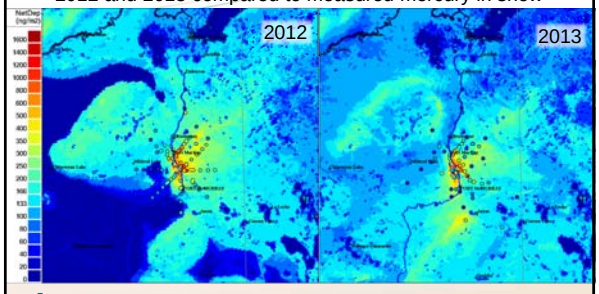
- The community of Fort Chipewyan and Bruce Maclean.
- Joint Oil Sands Monitoring program.
- All field and laboratory support.
- Parks Canada.
- The Wood Buffalo Environmental Association.





Putting it together: Air to Snow Modeling

Model simulated net deposition of mercury to snow on March 10th, 2012 and 2013 compared to measured mercury in snow



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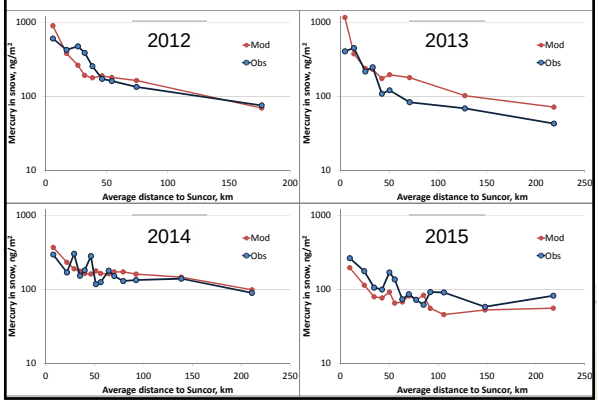
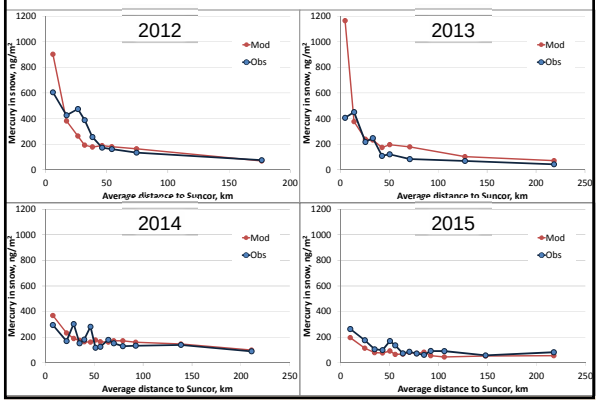
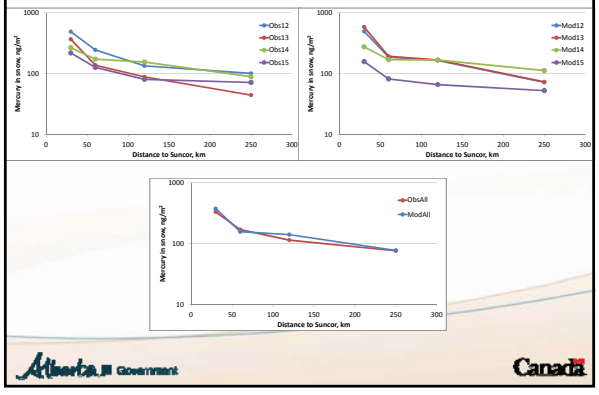
Mercury in snow as a function of distance to Suncor



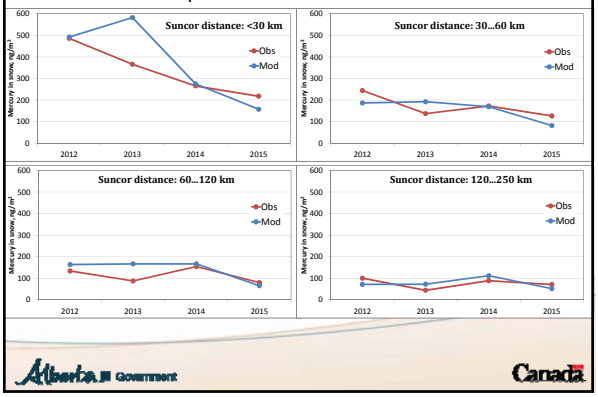
Mercury in snow depending on distance to Suncor



Mercury in snow as a function of distance to Suncor for all years (2012-2015)



Change (2012-2015) in mercury in snow (measured and modeled) sampled as distance from Suncor.



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