FORMATION OF SECONDARY PM IN CAPITAL REGION

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OUTLINE

- Background (Capital Region, monitoring data)
- Modeling Methodology
- Results
- Source attribution
- Conclusion

BACKGROUND: PARTICULATE MATTER (PM)

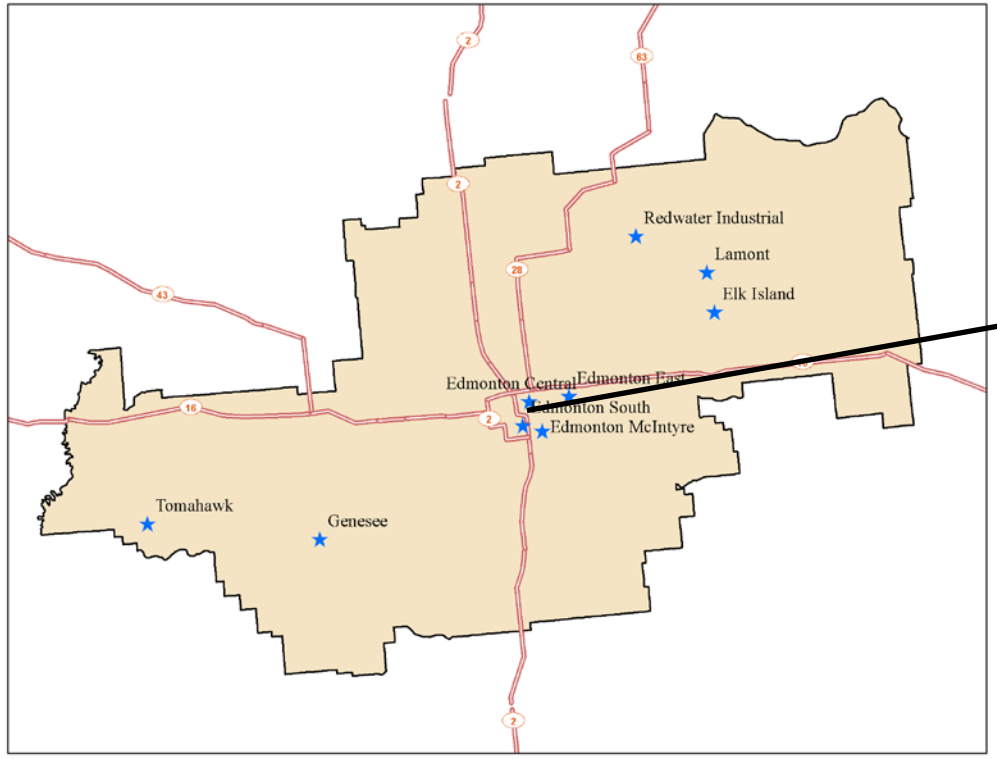
- Fine PM : diameter smaller than 2.5 μm; complex mixture consisting of *many* different *components*
- Cause health, vegetation, visibility problems
- Canadian Ambient Air Quality Standards (CAAQS)

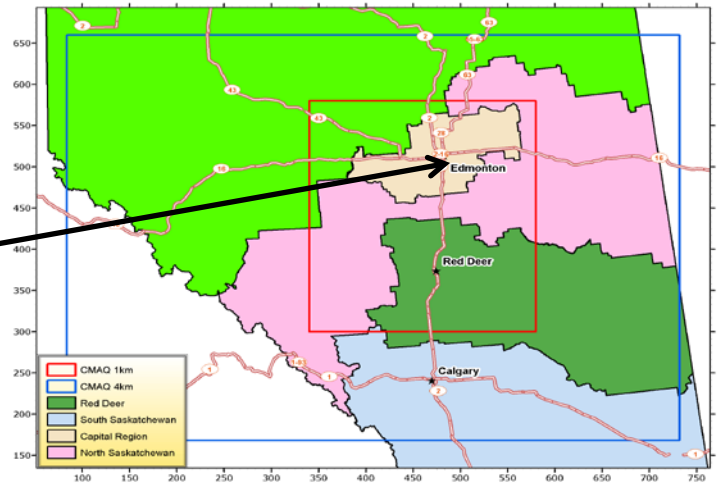
Pollutants	Old Standards	New Standards	
		2015	2020
$PM_{2.5}$ Annual	-	10 µg/m³	8.8 µg/m³
$PM_{2.5}$ 24-hour	30 µg/m³	28 µg/m³	27 µg/m³

- Origins
  - Primary: emitted from a source
  - **Secondary**: formed through chemical and physical reactions involving different precursor gases

$$SO_2, NOx, NH_3, VOC \rightarrow NH_4SO_4, NH_4NO_3, OM$$

BACKGROUND: CAPITAL REGION



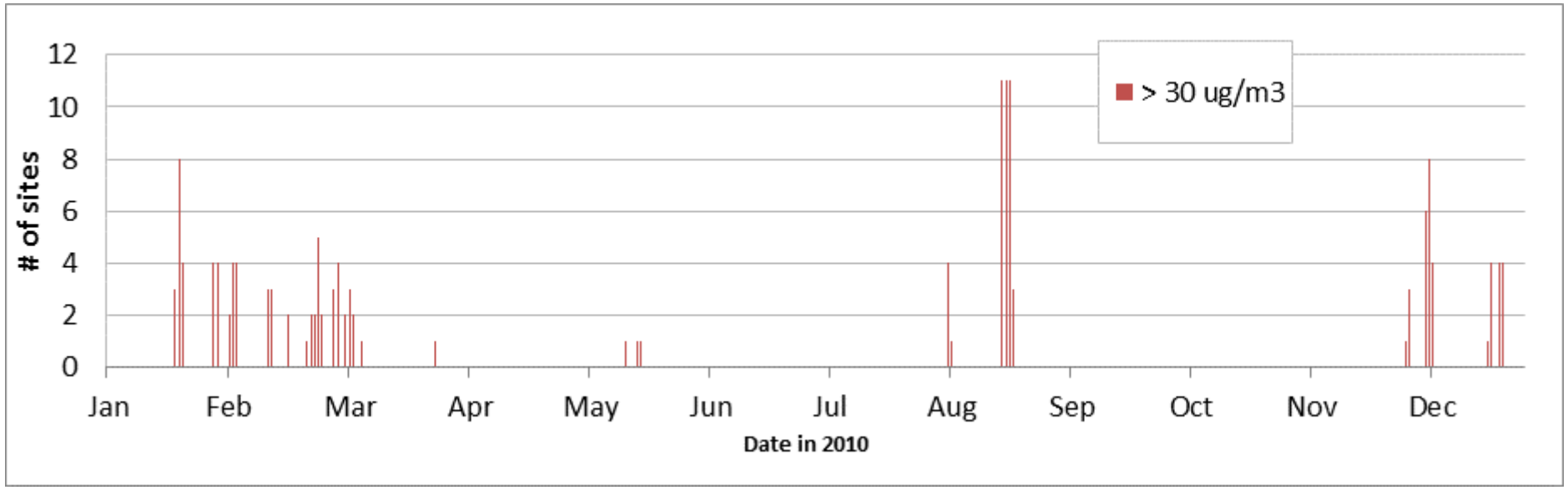


Sources in Capital Region:
Mobile, EGU, Industrial sources, Agriculture

24-hr average > 30 µg/m³

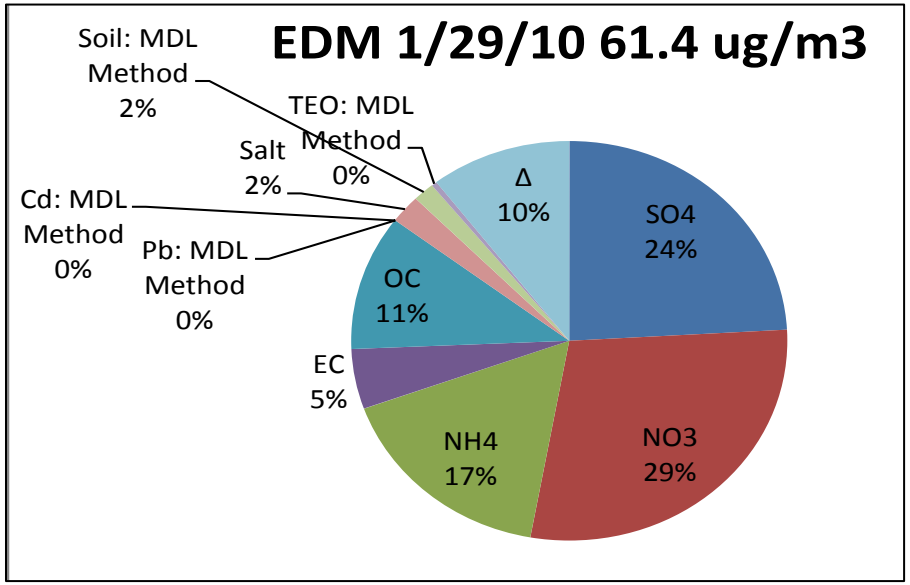
- 2008 : 9 exceedance days; all in winter
- 2009 : 7 exceedance days; 5 in winter
- 2010 : **41** exceedance days; 4 due to fires

BACKGROUND: 2010 EXCEEDANCES



- 9 winter episodes : peak on Jan 29
- Winter episodes characterized by higher than typical secondary $PM_{2.5}$

Non-event : $NH_4SO_4 + NH_4NO_3 \sim 30\%$
24-hr $PM_{2.5} < 10\ \mu g/m^3$



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BACKGROUND: SUMMER VS WINTER PM

Summer	Winter
Active Photochemistry	Slow photochemistry (scarce sunlight and low radical availability)
Strong vertical mixing	Light winds, temperature inversion → accumulation of pollution
Dominated by secondary PM OM > SO_4 > NO_3	Dominated by secondary PM OM > NO_3 > SO_4
High PM typically associated with SO_4	Colder temperatures favor NO_3 formation; less competition by SO_4 for NH_3

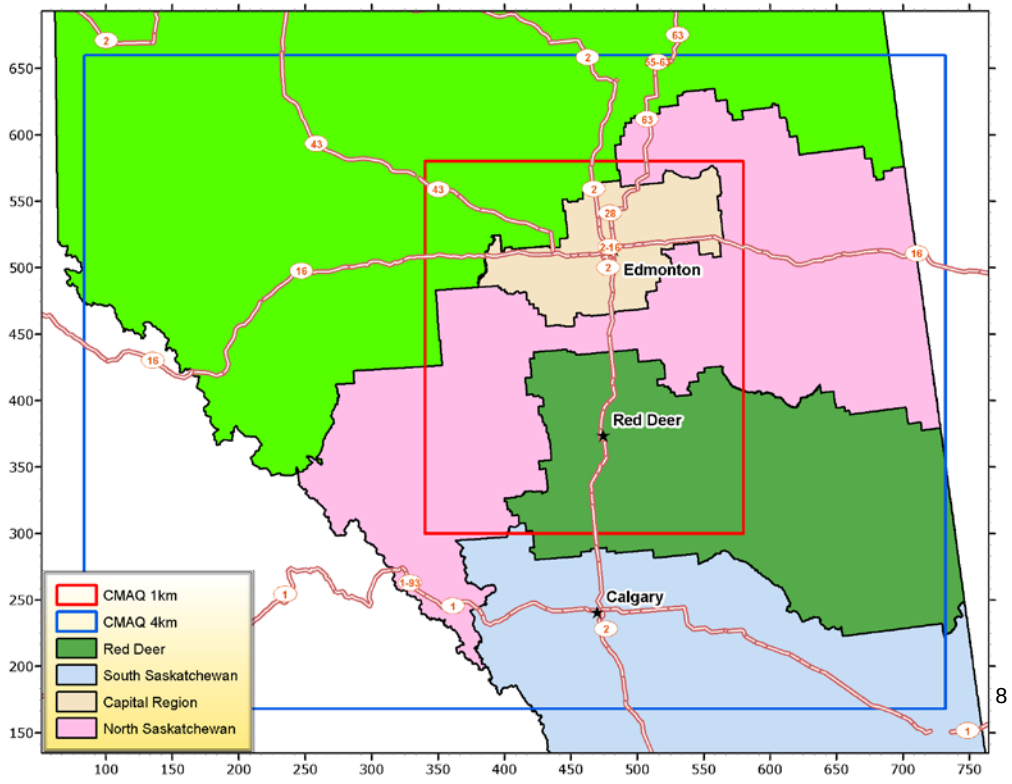
BACKGROUND: STUDY GOALS

- Develop a Photochemical Grid Model (PGM) modelling database for the Capital Region
  - Reproducing the observed winter elevated $PM_{2.5}$ sufficiently well
  - Tool for analyzing source contributions and control strategies

- Why PGM?
  - USEPA guidance (2014) requires use of photochemical models for secondary PM (e.g., sulphate and nitrate) and ozone.
  - Models with reduced form chemistry (e.g., CALPUFF) are incapable of properly simulating the chemical processes of secondary PM formation.

MODELLING : OVERALL METHODOLOGY

- Inputs focused on Capital Region
  - 2010 Alberta inventory with extensive emissions inventory updates
    - Tremendous efforts in harmonizing multiple data sources, e.g., Environment Canada 2010, AEP's Industrial Survey, NPRI, other local inventories
    - Maximum allowance in EIAs not appropriate for this application
  - WRF meteorological modeling
- CMAQ setup
  - version 5.0.1
  - Resolution : 36/12/4/1.33 km & 22 layers
- Highest ranked PM episode
  - January 26 – February 4, 2010



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MODELLING: NITRATE FORMATION IN CMAQ

- NOx conversion to HNO_3 through OH and HO_2

  $NO_2 + OH \rightarrow HNO_3$

  $NO_3 + HO_2 \rightarrow HNO_3$

  $NTR + OH \rightarrow HNO_3$ + other products

Winter: Scarce sunlight and radical availability

- Another gas-phase HNO_3 formation reaction is the reaction with aldehydes [formaldehyde (FORM) and acetaldehyde (ALD2)]:

  $FORM + NO_3^- \rightarrow HNO_3 + HO_2 + CO$

  $ALD2 + NO_3^- \rightarrow C_2O_3 + HNO_3$

Primary sources of aldehydes in the Capital Region are from mobile sources and petrochemical plants

MODELLING: NITRATE FORMATION IN CMAQ

- At night, HNO_3 formation occurs through N_2O_5 (Dinitrogen Pentoxide),

  $NO_2 + NO_3^-$ --> N_2O_5 — NO_3^- is formed through reactions involving NO_2 and ozone

  $N_2O_5 + H_2O$ --> HNO_3

  $N_2O_5 + H_2O + H_2O$ --> HNO_3 — Estimated water vapor by met. model becomes important.

- The final HNO_3 formation pathway in the CMAQ chemistry modules is the heterogeneous reaction probability (Y) of N_2O_5

  Likely most important for Capital Region, but parameterization not designed for below 0° C (frozen particles)

- Availability of ammonia (NH_3) to bind with gaseous HNO_3 to form particulate nitrate is important

  Cooler and moister conditions favors NH_4NO_3 over gaseous HNO_3

RESULTS: PHASE I INITIAL FINDINGS

- Except NO_3, all species are over-estimated

Species	Average Obs	Average Model	Fractional Bias (%)	Fractional Error (%)
EC	1.5	5.6	127.6	127.6
NH4	4.6	10.7	72.8	76.3
NO3	10.3	4.3	-58.9	90.6
OC	3.1	9.0	121.6	121.6
SO4	5.3	25.8	129.8	129.8

- Model performance evaluation
  - Individual PM species; compensating effects among species
  - Helps fine-tuning model through focused sensitivity cases

RESULTS: SENSITIVITY TESTS AND PHASE II

- Key findings from 10 sensitivity tests (Phase I)
  - Under-estimation of nitrate is not NH_3-limited
  - Don't have enough N_2O_5 to convert to HNO_3
  - More radicals are needed to improve nitrate performance
  - Predicted SO_4 is mostly secondary (conversion of SO_2); suspect WRF moister bias
- Phase II : revisit emissions inventory, meteorology and CMAQ assumptions
  - Improve emissions inventory (RWC, off-road)
  - WRF: remove moisture nudging which creates artificial cloud (7 tests)
  - CMAQ: heterogeneous pathway

RESULTS: PHASE II FINDINGS

- HNO_3 pathway via heterogeneous reactions
  a. N_2O_5 → 2.0 HNO_3
  b. NO_2 → 0.5 HONO + 0.5 HNO_3

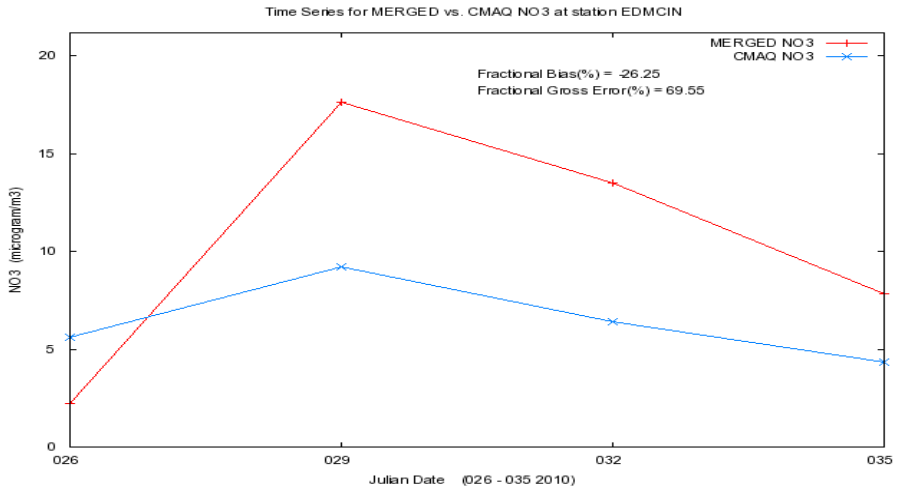
kNO_2 = 3.0e-3 [1/min] x (S/V)
Kurtenbach et al. (2001)

Rxn a. is limited by N_2O_5 availability (not enough ozone)

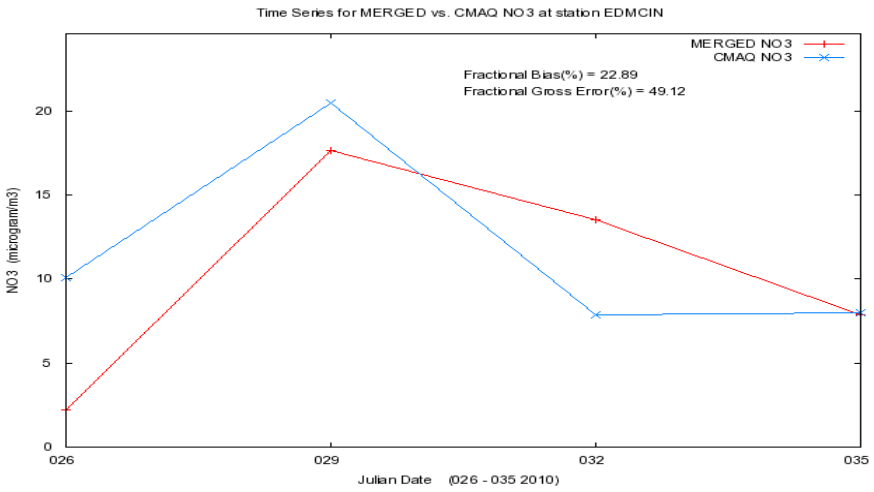
Rxn b. is important because of NO_2 is abundant

- Increasing kNO_2 by a factor of 100 increases NO_3 by a factor of two

Default kNO_2



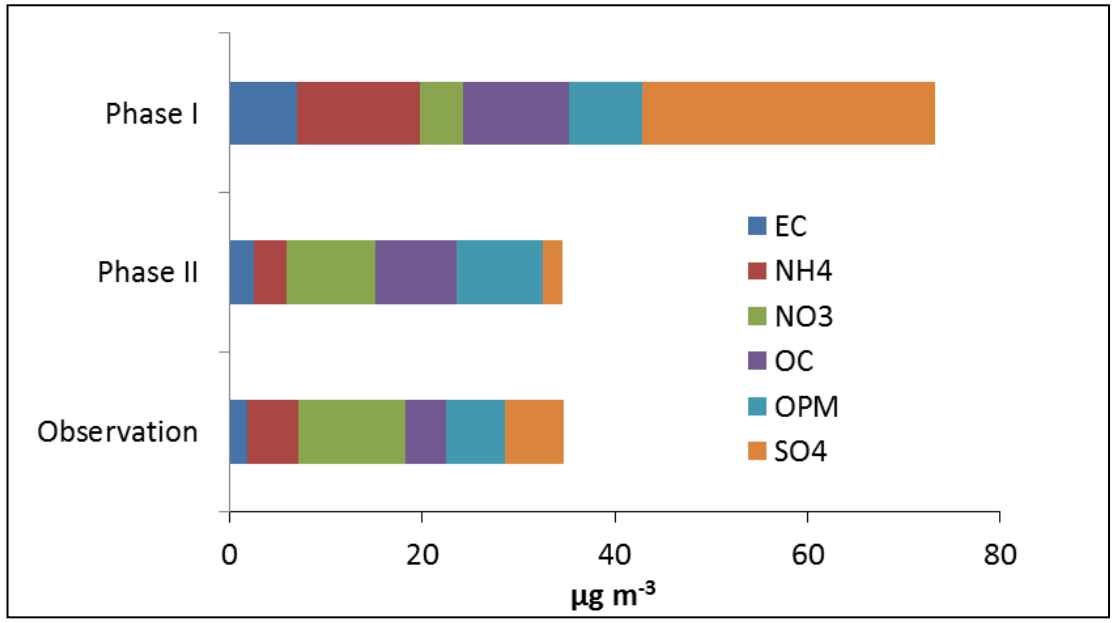
kNO_2 x 100



Blue = Model
Red = Obs.

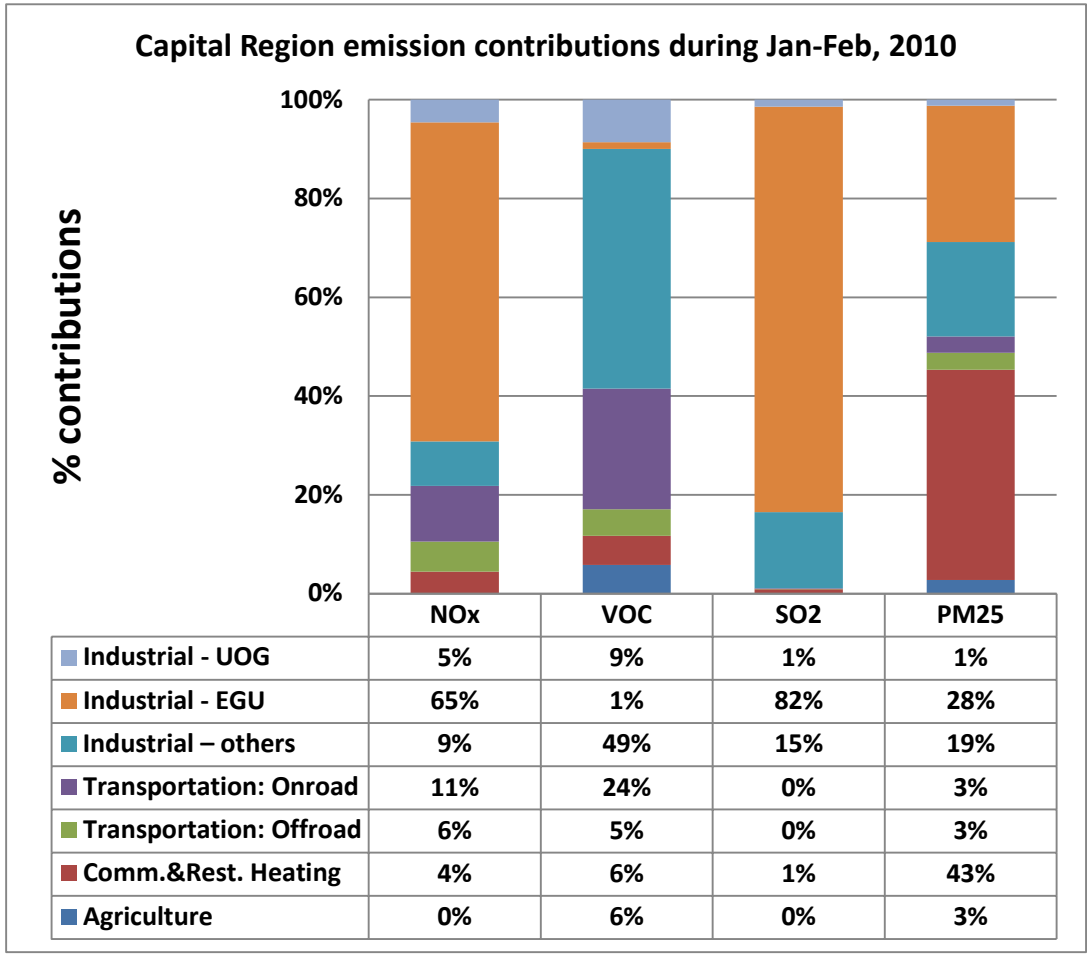
RESULTS: PHASE II FINDINGS

- Significantly improved model performance in Phase II



- Abundant NOx in Edmonton limits ozone, hence limits reactions that rely on availability of radicals (such as N_2O_5 → HNO_3)
- Need pathways that can go directly from NOx to HNO_3
  - Too low $kNO_{2,het}$ for stagnant winter condition? Missing unknown pathway(s)?

SOURCE ATTRIBUTION: CAPITAL REGION EMISSIONS (PHASE II)



	NOx	VOC	SO2	PM25
Industrial - UOG	5%	9%	1%	1%
Industrial - EGU	65%	1%	82%	28%
Industrial – others	9%	49%	15%	19%
Transportation: Onroad	11%	24%	0%	3%
Transportation: Offroad	6%	5%	0%	3%
Comm.&Rest. Heating	4%	6%	1%	43%
Agriculture	0%	6%	0%	3%

Emissions attribution alone cannot tell a complete story

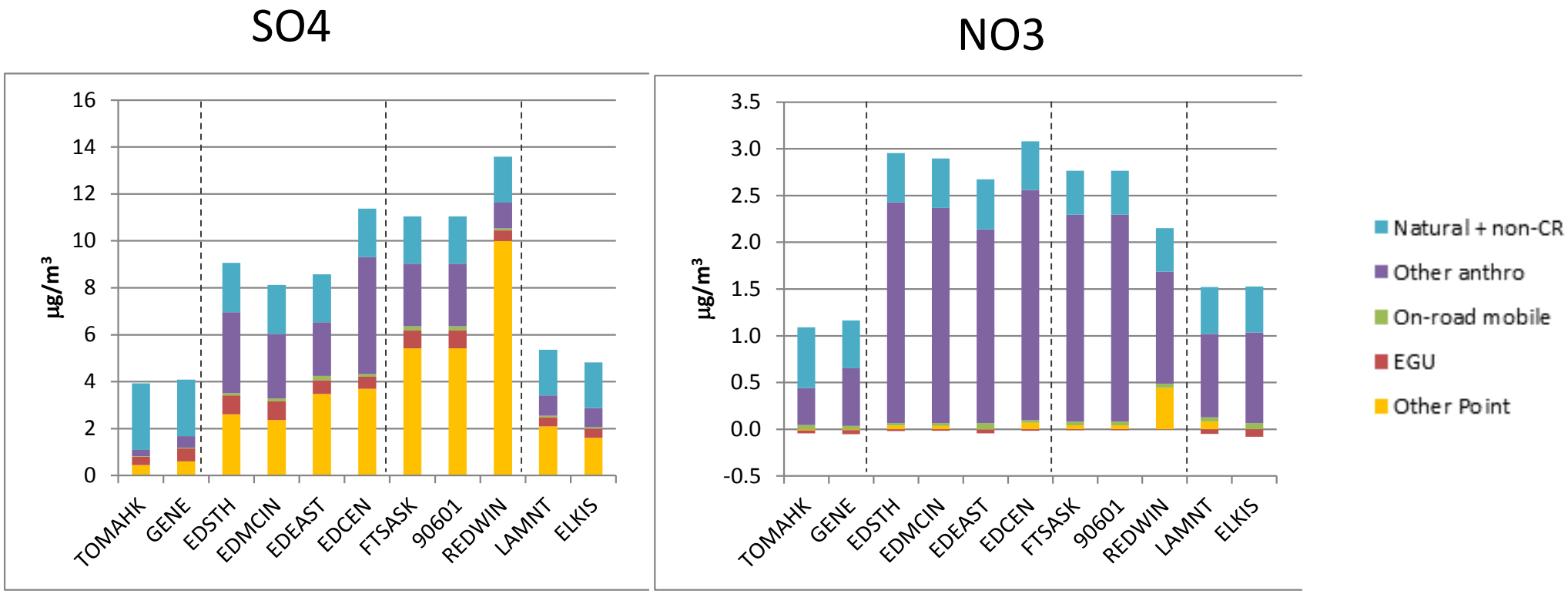
Other factors

- Source location
- Stack parameters
- Composition of VOC emissions
- Meteorological conditions

SOURCE ATTRIBITION: MODELLING

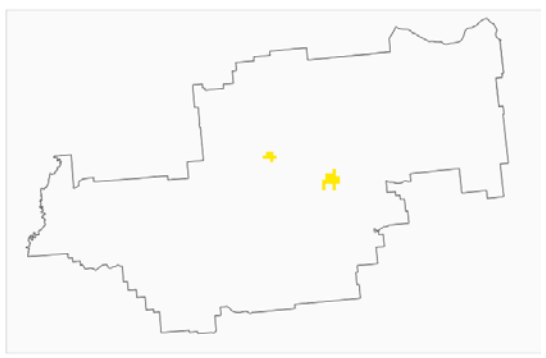
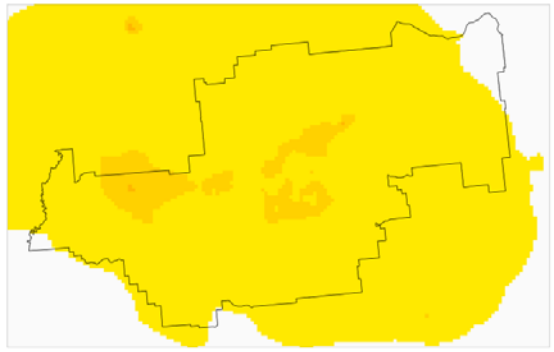
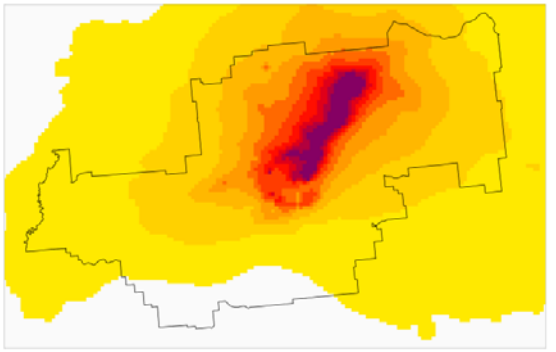
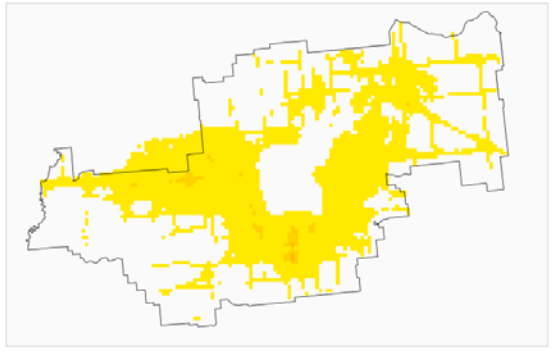
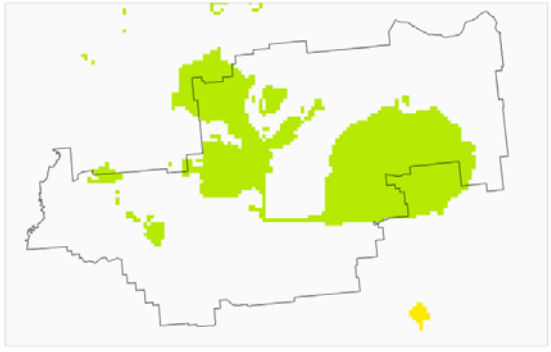
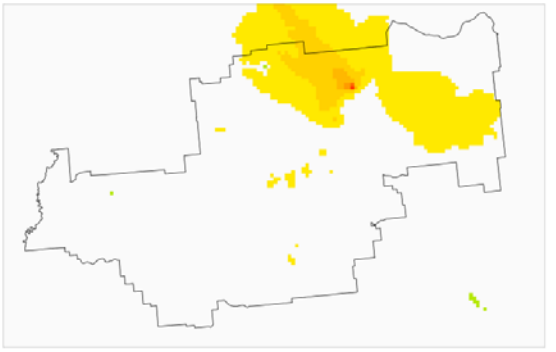
- Based on Phase I results (subject to poor model performance)
- Base Case setup with zero-out emissions to examine source contribution by sector
- Capital Region zero-out simulations:
  - On-road mobile (caveat: missing NH_3 emissions in Phase I)
  - Power Plant (EGU)
  - Other point sources - all stationary point sources except EGUs and UOG
  - All anthropogenic sources
- This approach can extend to quantify source contribution for each industrial source or sector (e.g., UOG, Refineries)

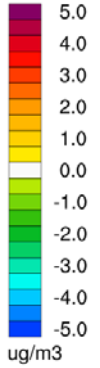
SOURCE ATTRIBUTION: JAN-FEB AVERAGE

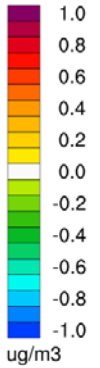


Example of contribution analysis at monitoring sites that can help identify major contributors

SOURCE ATTRIBUTION: JAN-FEB AVERAGE

	(a) On-road mobile	(b) EGU	(c) Other point sources
SO4	 Min(1,99) = 0.00, Max(95,51) = 0.38	 Min(16,1) = 0.04, Max(36,46) = 1.48	 Min(46,1) = 0.02, Max(88,51) = 19.10
NO3	 Min(144,98) = 0.00, Max(83,26) = 0.28	 Min(60,71) = -0.12, Max(120,10) = 0.11	 Min(76,81) = -0.11, Max(101,75) = 0.60





Example of contribution analysis that can help identify major contributors to the region

CONCLUSION

- PGM is a powerful tool to help understand complex air quality issues
- Modeling inputs are important (emissions and meteorology)
- Model performance evaluation is necessary
  - PM chemistry is complex
  - limited by the observation data
- Source apportionment analysis is useful for developing effective emissions control programs
  - Single sources, source groups such as sectors, and sector/geographic area combination

ACKNOWLEDGEMENT

- Funded by AEP
- Other staff at Ramboll Environ who participated in the study

For more details…

Nopmongcol, U., Johnson, J., Brasher, B., Rasmussen, DJ, Shah, Tj., Zagunis, J., Liu., Z., Morris, R. 2015.

"Formation of Secondary $PM_{2.5}$ in the Capital Region Study."

https://open.alberta.ca/publications/formation-of-secondary-pm2-5