Elemental Characterization of PM$_{2.5}$ and PM$_{10-2.5}$ in Dense Traffic Areas in Toronto and Vancouver, Canada

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The Canadian National Air Pollution Surveillance (NAPS) Program
The National Air Pollution Surveillance (NAPS) Program

- NAPS is an EC-led federal-provincial-territorial monitoring program, established in 1969, focusing on urban air quality:
  - Accurate and long-term air quality data of uniform high quality standard
  - Track and understand changes in air quality and identify emerging issues
  - NAPS sites report to the Canada-Wide Air Quality Database

- NAPS Measurements
  - Continuous measurements of $O_3$, $NO_2$, $NO_x$, $SO_2$, $CO$, and fine (PM$_{2.5}$) particulate matter
  - Integrated measurements of PM mass and chemical composition
  - Volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC)
NAPS Program: PM mass and chemical composition

• NAPS has been measuring PM since 1984 using dichotomous samplers

• Originally measured mass as PM$_{2.5}$ and PM$_{10}$ and by 1986 were added:
  • **Elements** by ED-XRF
  • **Ions** by colorimetry, later used IC

• By **2000** the need to have a better understanding of PM$_{2.5}$ composition was recognized and NAPS PM2.5 Speciation started:
  • Quantify all major components of PM including ammonium nitrate, elemental carbon and organic carbon
  • Quantify important gas phase species including ammonia and nitric acid
  • Quantify important tracers for specific PM sources (e.g. metals, biomass burning markers)
  • Data for regional and source-receptor modeling
near road study


Near Road study: Background

- People living, working and going to school near highways and large transportation facilities face increased health risks.

- Recommendation from the Canadian Smog Science Assessment to monitor near road air pollution.

Measurement sites are recommended near roads to better track motor vehicle emissions as these appear to dominate observed ambient PM and O₃ precursors and can provide a platform to carry out special studies.

- 2014 launched pilot studies for Toronto and Vancouver to examine NR traffic related air pollutants (TRAP).
  - Partners in the pilot studies: University of Toronto, Ontario (MOE), Metro Vancouver, ECCC (NAPS, Pacific and Yukon Region)

- Site both Near Road and Urban Background stations to measure the excess levels.
Near-Road Monitoring Pilot Study: objectives

- To provide data needed to identify and understand the parameters governing the concentrations of traffic related air pollutants
- To better understand the linkages between traffic-related air pollution and health outcomes
- To provide information and experience needed to support the design of a national near road monitoring network
  - Monitoring site selection and design
  - Instrument selection and performance
  - Data processing and consolidation
  - Data interpretation frameworks and strategies
Parameters Measured

- Continuous CACs (CO, NO\textsubscript{X}, O\textsubscript{3}, PM\textsubscript{2.5} & SO\textsubscript{2})

- Other continuous measurements (BC, UFP, OC/EC, VOC, Metals (XACT), CO\textsubscript{2}, Aerosol speciation, Particle-bound PAH)

- Integrated samples (PM\textsubscript{2.5}/PM\textsubscript{10-2.5} speciation (metals), VOC, PAH)

- Other parameters:
  - Meteorology
  - Traffic counting
**Elements (Metals)**

- **Crustal elements**: Al, K, Ca, Fe, Ti, Si

- **Toxic metal(oids).Valves**
  - CEPA (Al, As, Cd, Cu, Cr, Hg, Ni, Pb, Zn)
  - US EPA (Ag, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Sb, Se, Tl, Zn)

- **Tracers for specific PM sources**
  - Ba, Cu, Sb, Mo, Zn: **brake and tire wear**
  - PGEs: automotive exhaust catalysts
  - Ni, V: **fuel oil combustion**
  - Lanthanoids: **oil refining industry**
Sampling: methodologies, sites and sampling period

NAPS program 24hr (00:00-24:00); 1 every 3 (6) days
**Sequential sampler (R&P) for PM$_{2.5}$ and PM$_{10-2.5}$**

<table>
<thead>
<tr>
<th>Module Description</th>
<th>Media</th>
<th>Function/Analytes</th>
<th>Method</th>
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<tbody>
<tr>
<td>Fine Fraction Filter</td>
<td>Teflon filter</td>
<td>PM$_{2.5}$ mass</td>
<td>Gravimetric</td>
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<td>ED-XRF, ICP-MS</td>
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<tr>
<td>Coarse Fraction Filter</td>
<td>Teflon filter</td>
<td>PM$_{10-2.5}$ mass</td>
<td>Gravimetric</td>
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<td><strong>Metals</strong></td>
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<td>ED-XRF</td>
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</tbody>
</table>
# Sequential R&P Chemcomb Cartridge-based Sampler for PM$_{2.5}$ Speciation

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<tr>
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<th>Media</th>
<th>Function</th>
<th>Analytes</th>
<th>Method</th>
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<tbody>
<tr>
<td>Cartridge A</td>
<td>Quartz filter</td>
<td>OC&amp;EC</td>
<td>TOR</td>
<td>Toroidal</td>
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<tr>
<td>Cartridge B</td>
<td>Teflon filter</td>
<td>PM$_{2.5}$ Mass</td>
<td>Gravimetric</td>
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<tr>
<td></td>
<td>Quartz filter</td>
<td>Positive OC artifact</td>
<td>TOR</td>
<td></td>
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<tr>
<td>Cartridge C</td>
<td>Sodium carbonate coated denuder</td>
<td>Sulfur dioxide and nitric acid</td>
<td>IC</td>
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<tr>
<td></td>
<td>Citric acid coated denuder</td>
<td>Ammonia</td>
<td>IC</td>
<td></td>
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<tr>
<td></td>
<td>Teflon filter</td>
<td>Anions, organic acids and cations</td>
<td>IC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nylon filter</td>
<td>Negative nitrate artifact</td>
<td>ICP-MS</td>
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</tbody>
</table>

**Water-soluble metals**
# Site selection

## Near Road sites (24 months)\(^a\)
- Clark Drive, Vancouver BC *(NR-VAN)*
- Highway 401, Toronto ON *(NR-TOR-HWY)*
- Wallberg, Toronto ON *(NR-TOR-DWT)*

## Background sites (12 months)\(^b\)
- Sunny Hill, Vancouver BC *(BG-VAN)*
- Hanlan’s Point, Toronto ON *(BG-TOR-S)*
- Downsview, Toronto ON *(BG-TOR-N)*

## Urban Sites (24 months)\(^a\)
- Burnaby, BC
- Edmonton, AB
- Ottawa, ON

\(\text{a. Sampling period: January 2015 to December 2016}\)
\(\text{b. Sampling period: August 2015 to August 2016}\)
Toronto Sites

NR-TOR-HWY (AADT = ~405,500); NR-TOR-DWT (AADT = ~16,000)

Image © 2018 TerraMetrics
Image NOAA
Elemental characterization of PM
**Metal Analysis: Figures of Merit**

**ED-XRF (Al, Si, Ca, K, Ti, S, Zn, Fe)**
- Instrument: Epsilon 5 (PanAlytical)
- Method detection limits: 1-10 ng m⁻³
- Recoveries for NIST 2783: 100 ± 20 %
- Frequency of detection: 50 – 100 %

**ICP-MS (trace elements)**

Methods:
- Microwave digestion: 40% (v/v) HNO₃
- Water extraction
- Instrument: ICP-MS (7900 Agilent)
- Method detection limits: 2 pg m⁻³ – 1 ng m⁻³
- Recoveries for NIST 1648a: 80 – 100% (except for Cr, La, Ce)
- Frequency of detection: 60 – 100%
PM concentrations and size distribution

Concentrations of both PM fractions are ~1.5 times higher at the NR sites compared to the respective BG sites and other urban sites.

PM$_{2.5}$ contribution to PM$_{10}$ is ~50% at all sites.
The highest concentrations of crustal elements were recorded at the NR sites and Edmonton site.

The element with the most notable increment at the NR sites was Fe.

Among crustal elements, Fe was the most abundant in PM$_{2.5}$ at all sites (average 41%), especially at the NR sites (49%).

Warm vs. cold season variations and weekday vs weekend patterns: the average ratio $\sim$2 for all elements at all sites.
Toxic elements: PM$_{2.5}$

- The highest concentrations of all toxic elements were recorded at the NR-TOR-Highway site.
- Elements with the highest increments (2-3 times) at NR sites were Cr, Cu, Zn, Sn and Sb.
- Some elements had the highest median concentrations at other sites:

<table>
<thead>
<tr>
<th>Element</th>
<th>Site with the max concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (and V)</td>
<td>Burnaby, BC</td>
</tr>
<tr>
<td>As, Cd, Pb</td>
<td>Montreal, QC</td>
</tr>
<tr>
<td>As, Se</td>
<td>All TOR sites</td>
</tr>
</tbody>
</table>
Trace Elements: Local Traffic Enhancement

\[
\Delta C(\text{traffic}) = \frac{C(\text{NR}) - C(\text{BG})}{C(\text{BG})} \times 100
\]

- Strong effect of traffic-related emissions on metals
  - **PM\(_{2.5}\)**: NR-TOR-1 (Highway) > NR-VAN > NR-TOR-2 (Downtown)
  - **PM\(_{10-2.5}\)**: NR-VAN > NR-TOR-1 (Highway) >> NR-TOR-2 (Downtown)

- The highest enhancement (>100%): Ba, Fe, Cu, Sb, Sn, Cr, Mo (both fractions)
Seasonal trends varied by location and element:

- Sites in southern ON showed concentrations of some elements (Cu, Ni, Zn, Sn, Sb) slightly higher in the warm season.

- Western sites had higher cold season concentrations for most of the elements.

- The same seasonality trends were found for PM$_{10-2.5}$ variations.
Weekend/Weekday trends

- Elements with the highest increase during the weekdays were Cr, Zn, Cu, Ni and Sn (30 to 140% increase).
- Weekday/weekend differences indicate a strong effect of local traffic emissions (especially at the NR-TOR-Highway site).
- Other elements showed either a slight decrease (As) or no significant change during the weekdays.
- The same trends were found for PM$_{10-2.5}$ variations.
Traffic-Related Metals: Diurnal Patterns

- Sharp diurnal patterns (morning rush hours):
  - NR-TOR-2 (downtown): 6-9 am
  - NR-TOR-1 (Hwy): 5-8 am

- Higher weekend traffic volume in the downtown area in the early morning

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Cheol-Heon Jeong et al, (2018), Temporal and spatial variability of traffic-related PM2.5 sources: Comparison between downtown and highway environments, *Atmos. Env.*, Submitted for publication
**Particle size distribution of elements: NR sites**

- Crustal elements reside mostly in the coarse fraction ($\text{PM}_{10-2.5}$).

- Traffic tracers (Zn, Cu, Mo, Sb and Ba) reside mostly (50 to 70%) in the $\text{PM}_{10-2.5}$ suggesting a significant contribution of non-combustion processes (non-tailpipe emissions, e.g. brake/tire ware).

- There is no significant difference between NR sites except for:
  - Zn, Se, Cd, Sn and Sb for which the %element in PM$_{2.5}$ was about 30% higher at Toronto sites than in Vancouver.

- Some of the toxic elements such as Se, As, Pb, and Cd, are mostly present in the PM$_{2.5}$ (50 – 90%).
Water-Solubility of elements: NR sites

Most of the toxic elements are more than 60% water soluble

Among other elements, Fe has the lowest solubility (less than 30%) at all sites

There is no significant difference (ANOVA, p<0.05) in the solubility of elements between sites except for Ni, Mo and Sn with slightly lower solubility at NR sites
Source apportionment: Principal Component Analysis

Method:
- Factor analysis
- Extraction: Principal components
- Extraction method: Varimax normalized
- Eigenvalues: >1

Data treatment:
- All selected sites
- Removed <MDL
- Grubbs test applied to data sets of each site to removed outliers
Principal Component Analysis: Trace Metals Sources

<table>
<thead>
<tr>
<th>Source</th>
<th>Ba</th>
<th>Cd</th>
<th>La</th>
<th>Si</th>
<th>Se</th>
<th>Fe</th>
<th>Pb</th>
<th>V</th>
<th>Ca</th>
<th>S</th>
<th>Sb</th>
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<th>Mo</th>
<th>Zn</th>
<th>Ti</th>
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<tbody>
<tr>
<td>Road traffic (34%)</td>
<td>0.97</td>
<td>0.81</td>
<td>0.88</td>
<td>0.92</td>
<td>0.77</td>
<td>0.95</td>
<td>0.81</td>
<td>0.88</td>
<td>0.69</td>
<td>0.76</td>
<td>0.95</td>
<td>0.74</td>
<td>0.78</td>
<td>0.63</td>
<td>0.93</td>
<td>0.70</td>
<td>0.59</td>
<td>0.88</td>
<td>0.84</td>
<td>0.73</td>
<td>0.66</td>
<td>0.59</td>
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<td>Industry (20%)</td>
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<td>Heavy oil combustion (e.g. marine) (11%)</td>
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<td>Re suspended road dust (7%)</td>
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<td>Coke and coal combustion (4%)</td>
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**Factor loadings (75% of total variance)**
Sources contribution: factor scores

- Traffic contribution (factor scores) is the highest at the NR Sites
  - Factor scores at NR-TOR Highway and NR-VAN were ~3 times higher than respective background sites

- Dust resuspension contributes ~2 times more at the NR sites

- Among other sources:
  - Heavy oil combustion contributes significantly at both Vancouver sites
  - Coke and coal combustion contributes 30 to 40% of elements emissions at all sites located in Southern Ontario
Summary

- Increased concentrations of traffic-related metals were observed at the near road sites relative to the urban background sites.
  - Higher weekday vs weekend concentrations and sharp diurnal patterns (morning rush hours) at the NR sites support traffic influence.
  - Different seasonal patterns in Vancouver and Toronto.

- Significant contributions of traffic emissions from brake/tire and road dust resuspension was observed at the NR sites.

- Highly water-soluble metals (>50%)
  - Growing concerns due to the high concentrations of redox active metals (e.g., Cu, Fe).

- Besides traffic (Cr, Cu, Zn, Sn and Sb emissions), other sources such as marine transportations (Ni and V emissions) and Coke/coal combustion industry (As, Se emissions) have a significant contribution to the toxicity of PM$_{2.5}$ in urban areas.
Acknowledgement

• Environment and Climate Change Canada
  – D. Johnson, D. Mathieu, L. White ……and many others

• University of Toronto
  – Prof. G. Evans and his group

• Provincial colleagues who manage the local sites and collect the samples
Thank you for your attention!