

Exposures to metals in airborne particulate matter, soil and settled dust in Windsor, Ontario

WOEAS & DEARS Air Quality Meeting
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Pat Rasmussen,
Leader of Metals and Airborne PM Research Laboratories
Exposures & Biomonitoring Division,
Health Canada/University of Ottawa

Collaborators/Co-authors

**Amanda Wheeler, Jianjun Niu, Michelle Nugent, Marc Chénier,
Nouri Hassan, Dave Gardner, Monique Lanouette**

Ron Williams (US-EPA)

Special Thanks to

**Iris Xu (U of Windsor), Alain Filiatreault, Keith Van Ryswyk,
Christine Levesque, Hongyu You, Alberta Research Council**

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NSERC Metals in the Human Environment Research Network
(www.nserc-sn.org)**

Purpose of Our Research: Address Gaps in Metals Exposure Assessment

- **Improve the accuracy of exposure assessments**
 - **For risk assessments**
 - **For epidemiological studies**
- **Focus on exposure measurement errors**
 - **Crude exposure assessments a major weakness**
 - **Profound effect on predicted risks and public policy**
- **Identify sources and pathways of exposure**
 - **For risk management**

Canadians are exposed to metals in various ways

- through the **inhalation of airborne metals** in the workplace or **polluted neighbourhoods**
- through the ingestion of food and water containing metals (e.g. certain seafood)
- **childhood ingestion of dust, soil** and paint chips that contain lead

Outline of Windsor Metals Research

- 1. Challenges in obtaining reliable elemental data**
(Rasmussen, Wheeler et al. (2007) Monitoring personal, indoor, and outdoor exposures to metals in airborne particulate matter: risk of contamination during sampling, handling and analysis. *Atmospheric Environment*. 41 (28): 5897-5907)
- 2. ICP-MS and XRF: Method comparison**
Collaboration with Ron Williams, US-EPA
(Niu et al. manuscript under internal review)
- 3. Indoor, outdoor and personal exposures (Mn and Pb)**
(progress)
- 4. Soil and Dust: Sources/Sinks for Metals**

The challenge: lightly loaded filters

24-hr low flow samples often less than 100 μg

- Extreme caution is required to avoid contaminating the filter samples during sampling, handling and analysis.
- The contribution of metals from contamination can easily exceed the contribution from the airborne particulate matter being sampled.
- Focus on Quality



Buoyancy-corrected mass measurement of lightly-loaded PM filters

Rasmussen et al. (2007) *Atmos Environ* 41 (28): 5897-5907



- Environmental chamber
- 24 h conditioning before pre- and post- weighing
- Temperature $21^{\circ}\text{C}\pm 0.5^{\circ}\text{C}$
- RH at $40\%\pm 1\%$ continuous
- 7 decimal place Mettler UMX2 Microbalance
- Soft-walled clean room
- Dust-free, vibration-free
- Elimination of static charge
- Correction for changes in air density at 1 min intervals

USA Patent April 2008; ARCHIMEDES M3™

XRF & ICP-MS determination of metals in outdoor urban air

% samples >LOD

Element	ED-XRF*	ICP-MS**
	No. Samples > LOD	No. Samples > LOD
Mn	100 %	100 %
Pb	100%	100 %
Zn	100%	100%
Fe	100%	100%
Cu	97 %	100 %
V	80 %	100%
As	69 %	100%
Ni	59 %	96 %
Sr	56 %	92%
Cr	33 %	100 %

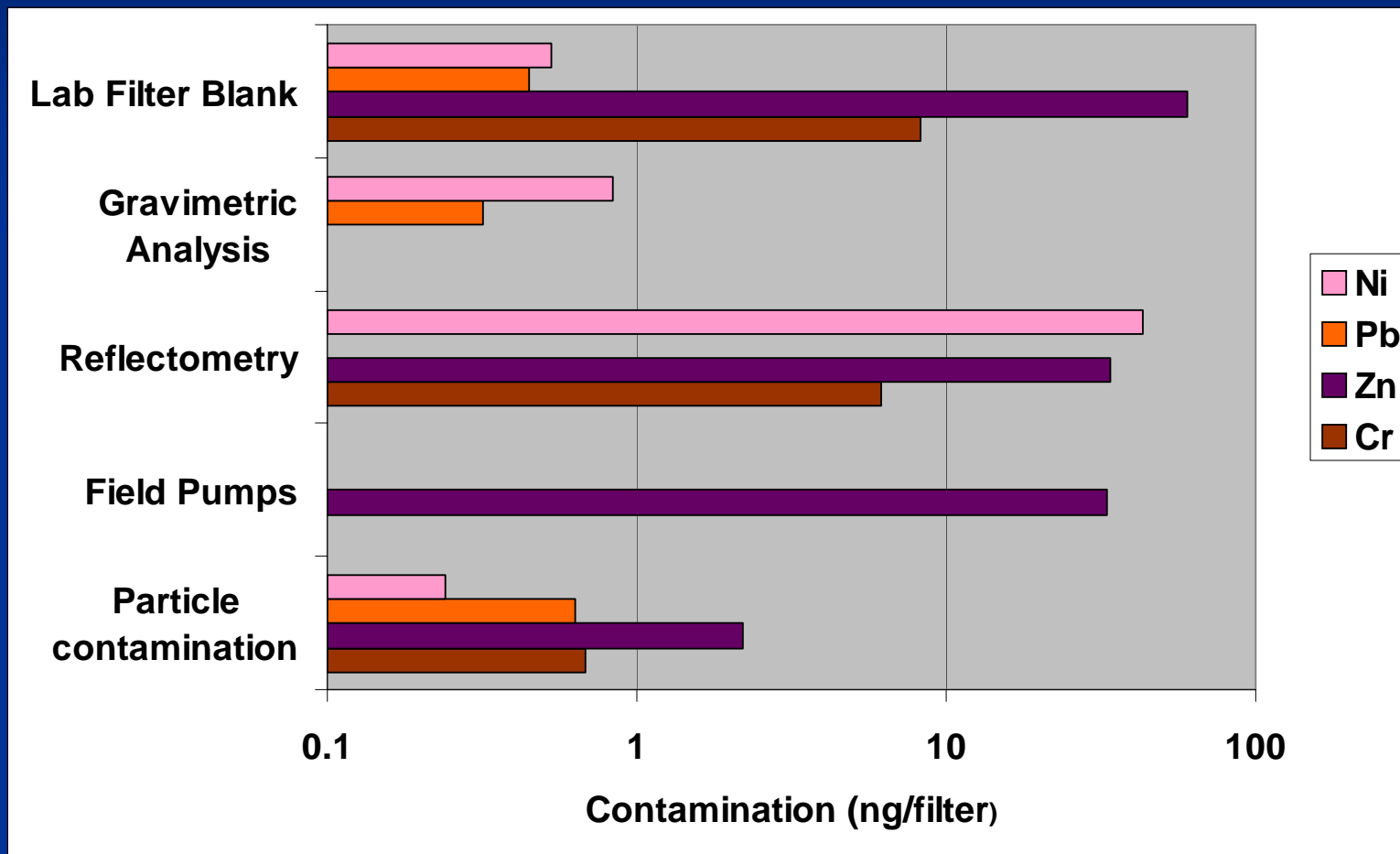
***XRF by Williams US-EPA ** ICP-MS by Rasmussen HC Lab**

N = 39 outdoor air sampled across Windsor ON (2 wk samples)

From: Niu et al. manuscript under internal review.

Metals Introduced During Sampling, Handling and Processing

Rasmussen et al. *Atmos Environ* 41 (28): 5897-5907.



Interpretation of ICP-MS data

Rasmussen et al. *Atmos. Environ.* (2007) 41: 5897-5907.

- Sources and magnitude of contamination differ from element to element.

Acceptability of results must be assessed on an element by element basis.

- Certified Reference Materials, reagent blanks, lab filter blanks, detection limits, field blanks and co-located duplicates are all assessed to determine whether or not a given element should be reported.

Next paper (Niu et al. internal review): Co-located duplicate study and XRF/ICP-MS method comparison

Manganese in Air

- Health Canada 1994 reference concentration

$$= 0.11 \mu\text{g}/\text{m}^3$$

- Proposed Health Canada reference concentration for inhaled manganese

$$= 0.05 \mu\text{g}/\text{m}^3$$

Lead in Air

- New National Ambient Air Quality Standard (NAAQS)
- October 15, 2008
- Lead $0.15 \mu\text{g}/\text{m}^3$ Rolling 3-Month Average
- $1.5 \mu\text{g}/\text{m}^3$ Quarterly Average

Progress in analysis of 24-hr Windsor samples (WOEAS campaigns 2005 & 2006)

All PM_{2.5} and PM₁₀ mass measurements
for WOEAS completed and reported
January 2007



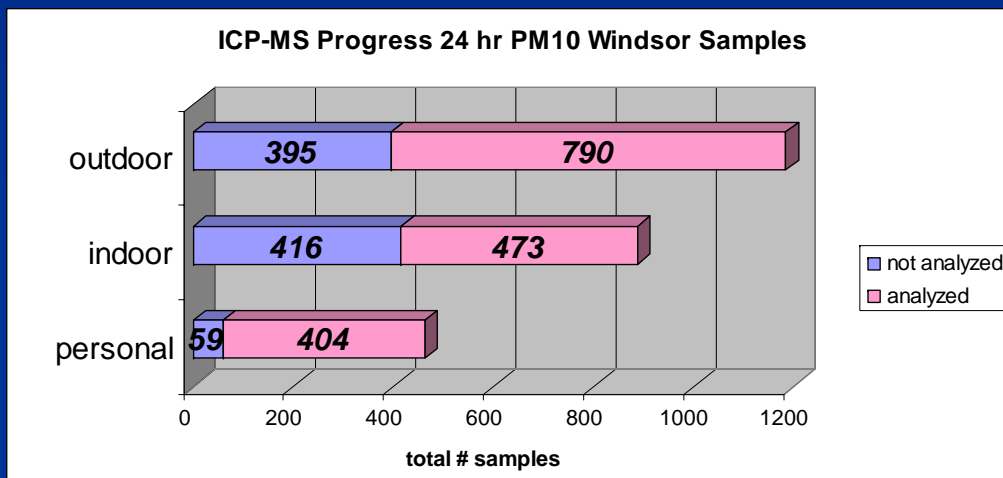
- Personal, Indoor & Outdoor

- 24-hr low-flow samples

- Two seasons each year; 8 weeks per season

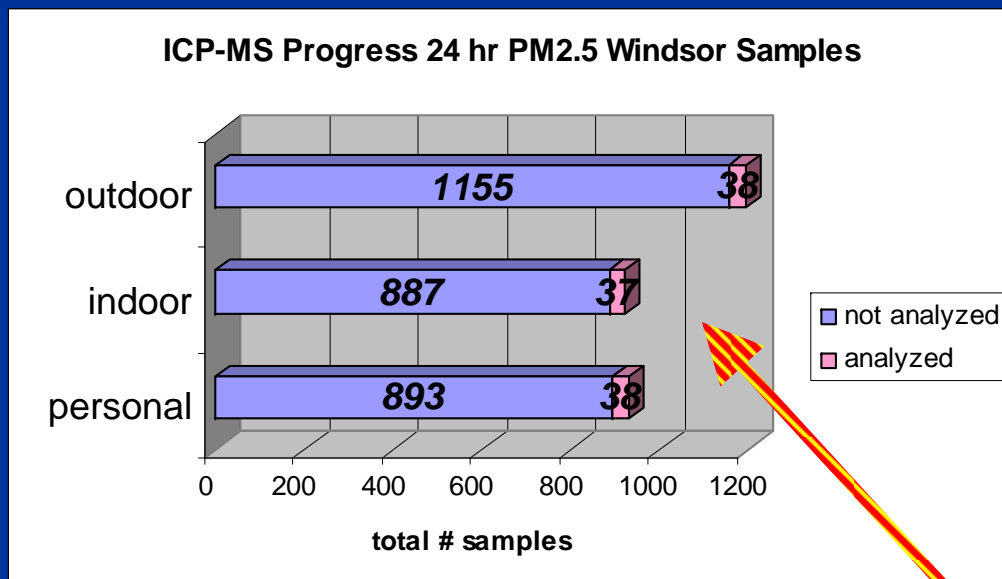
- 48 participants

Progress in ICP-MS Analysis – PM₁₀



	Total samples collected	% Analyzed by ICP-MS
PM ₁₀ outdoor	1185	67%
PM ₁₀ indoor	889	53%
PM ₁₀ personal	463	87%

Progress in ICP-MS Analysis – PM_{2.5}



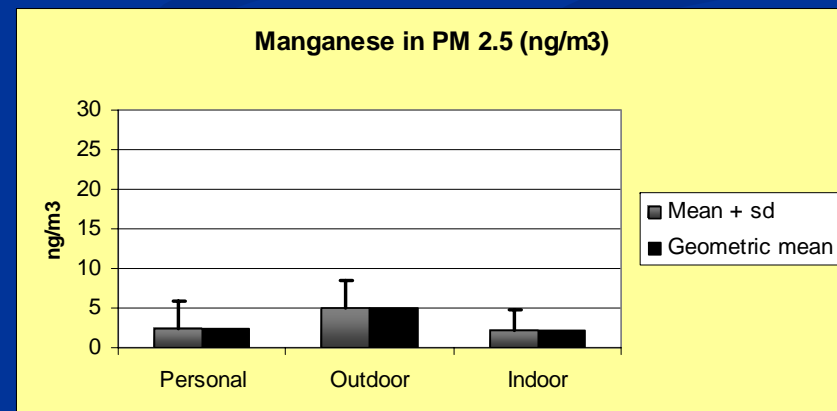
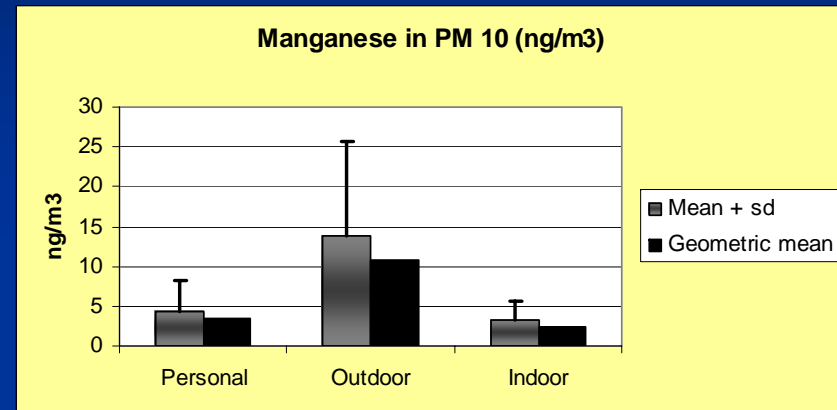
	Total samples collected	% Analyzed by ICP-MS
PM _{2.5} outdoor	1155	3%
PM _{2.5} indoor	887	4%
PM _{2.5} personal	893	4%

Subset of matched I-O-P samples

Mn results to date (partial datasets)

Proposed HC reference level 50 ng/m³

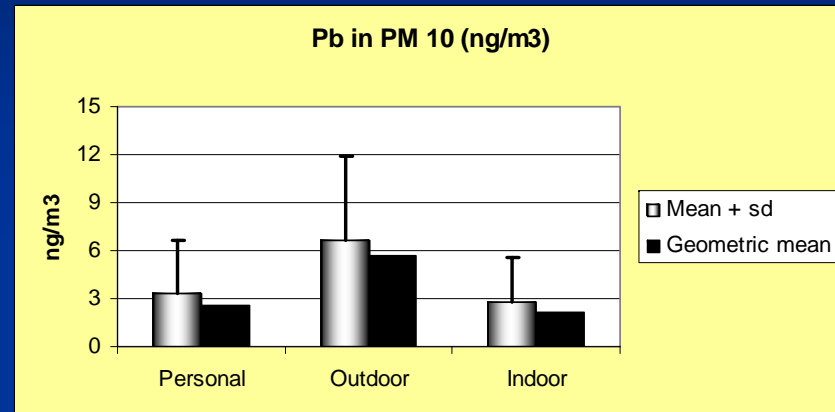
- After analyzing 60% of PM₁₀ samples
- After analysing 4% of PM_{2.5} samples



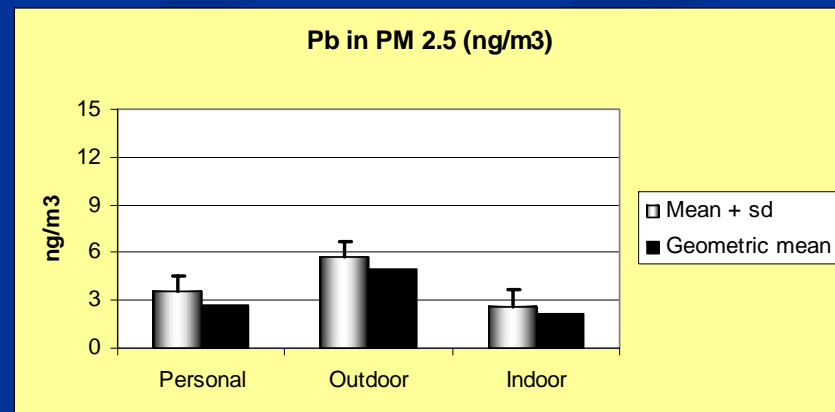
Pb results to date (partial datasets)

NAAQS for Pb 150 ng/m³

- After analyzing 60% of PM₁₀ samples



- After analyzing 4% of PM_{2.5} samples



Windsor-Detroit Method Comparison

ICP- MS for Windsor Exposure Studies

(Rasmussen's HC Lab)

- Aggressive acid digestion
- HF/HNO₃ ultrasonication; 60°C for 5-7 days

ED-XRF for Detroit Exposure Studies

(Williams' US-EPA Lab)

- Non-destructive
- no acid digestion required

Method Comparison: Metals in PM_{2.5} XRF versus ICP-MS

- Number of samples = 39
- Backyards of volunteers who participated in 24-hr personal indoor and outdoor sampling WOEAS Study, plus EC sites
- 2 week samples
- Summer sampling only



Method Comparison for Metals in Airborne Particles on Teflon Filters

Sample Collection in Windsor HC

Gravimetric Analysis HC

Non-destructive ED-XRF US-EPA



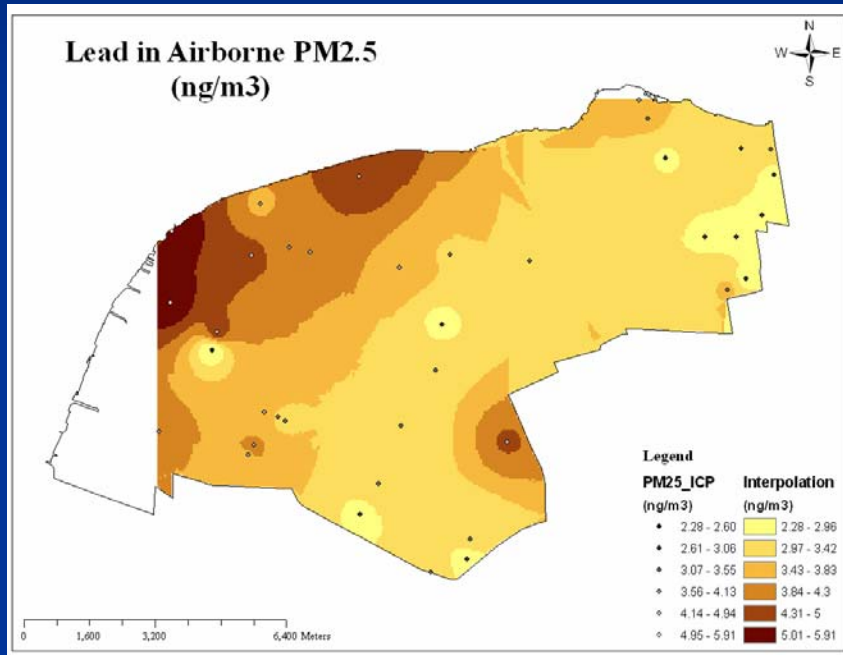
Acid digestion HC



ICP-MS HC

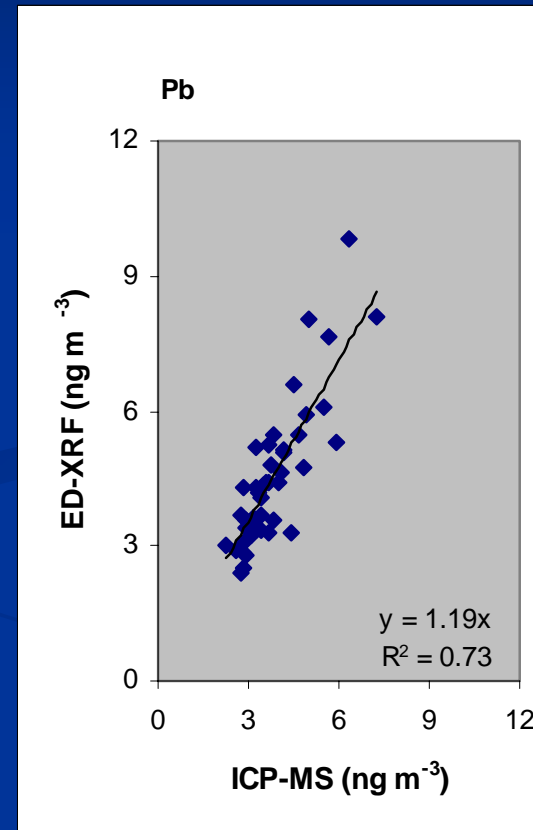
Total (ICP-MS) *should equal* Total (XRF)

Method comparison (XRF and ICP-MS) Lead in PM_{2.5} across Windsor, Ontario



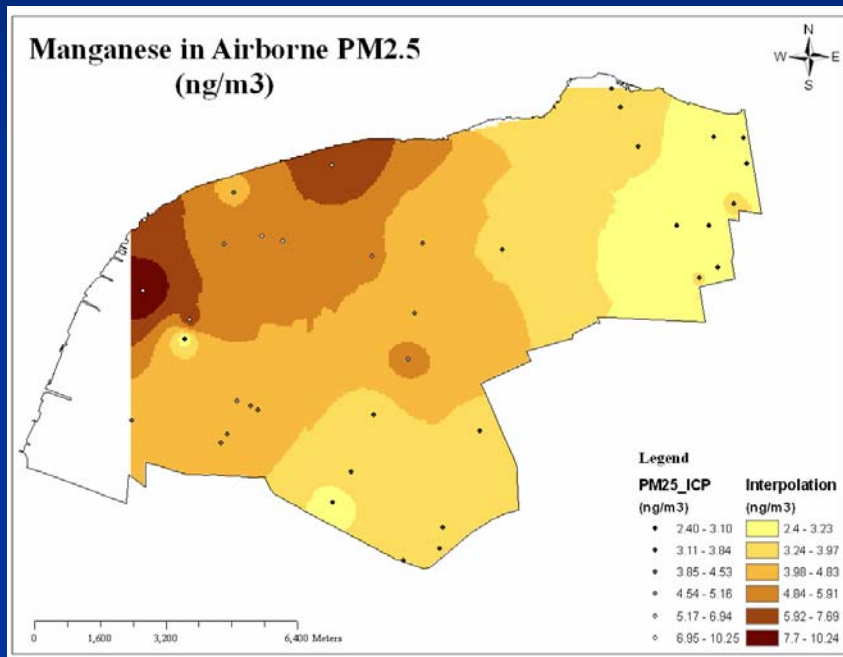
N=39; Rasmussen Lab ICP-MS data; 2-wk summer samples; Spatial data interpolated by M. Nugent using geographical information system (GIS) ArcGIS version 9.2

US – EPA Lab



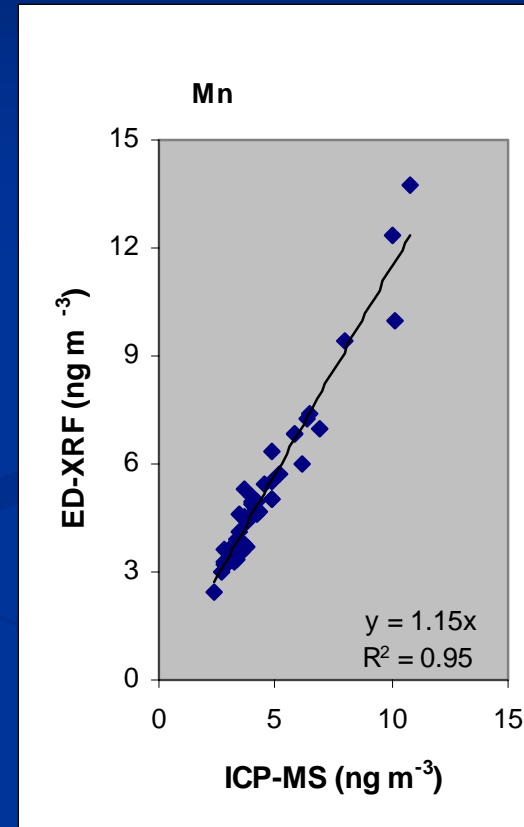
HC Metals Lab

Method comparison (XRF and ICP-MS) Manganese in PM_{2.5} across Windsor, Ontario



N=39; Rasmussen Lab ICP-MS data; 2-wk summer samples; Spatial data interpolated by M. Nugent using geographical information system (GIS) ArcGIS version 9.2

US – EPA Lab



HC Metals Lab

Water Soluble & Total Extraction of PM_{2.5} Pulmonary Bioaccessibility

Stage 1

- 0.01 M ammonium acetate;
37°C; pH = 7 (buffered)
- ICP-MS
- Simulates solubility of metals
in neutral pH of lung
environment.
- Reference: Thomassen et al.
(2001) JEM 3:555-559.

Stage 2

- HF/HNO₃ ultrasonication
- ICP-MS
- Quantitative (total) extraction of
metals from particulate matter
trapped on Teflon filter

Airborne Particles on Teflon Filters



Verification of 2-Stage Extraction

Pre-measurement of each filter by
non-destructive ED-XRF



Stage 1

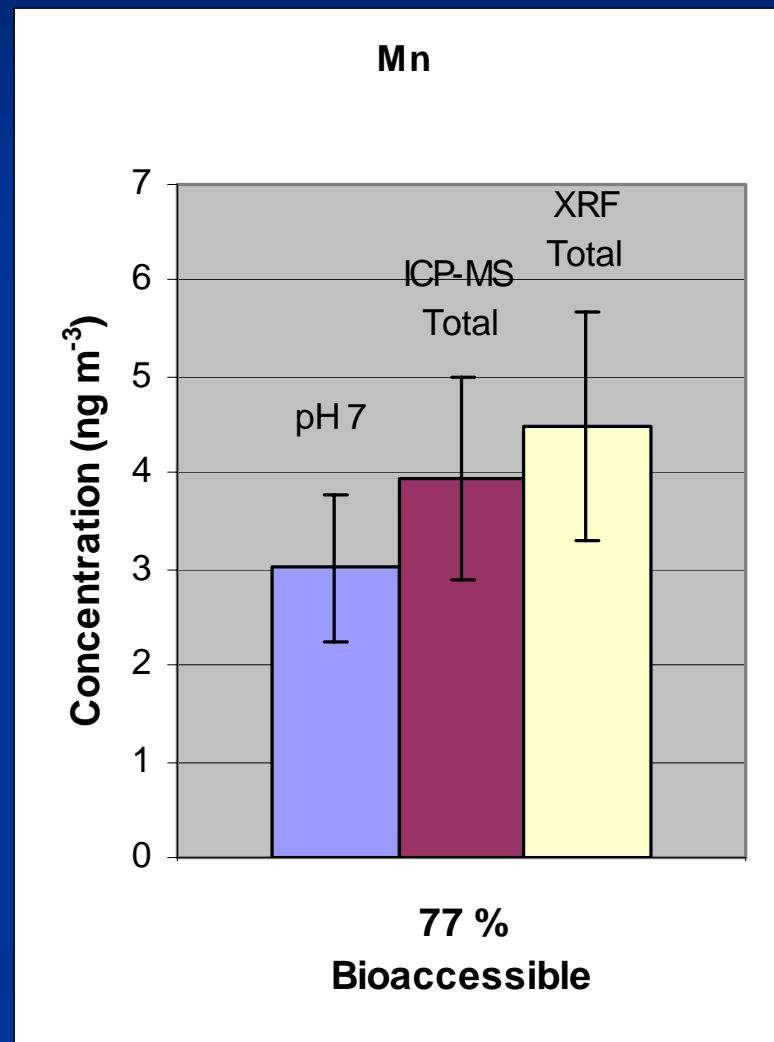
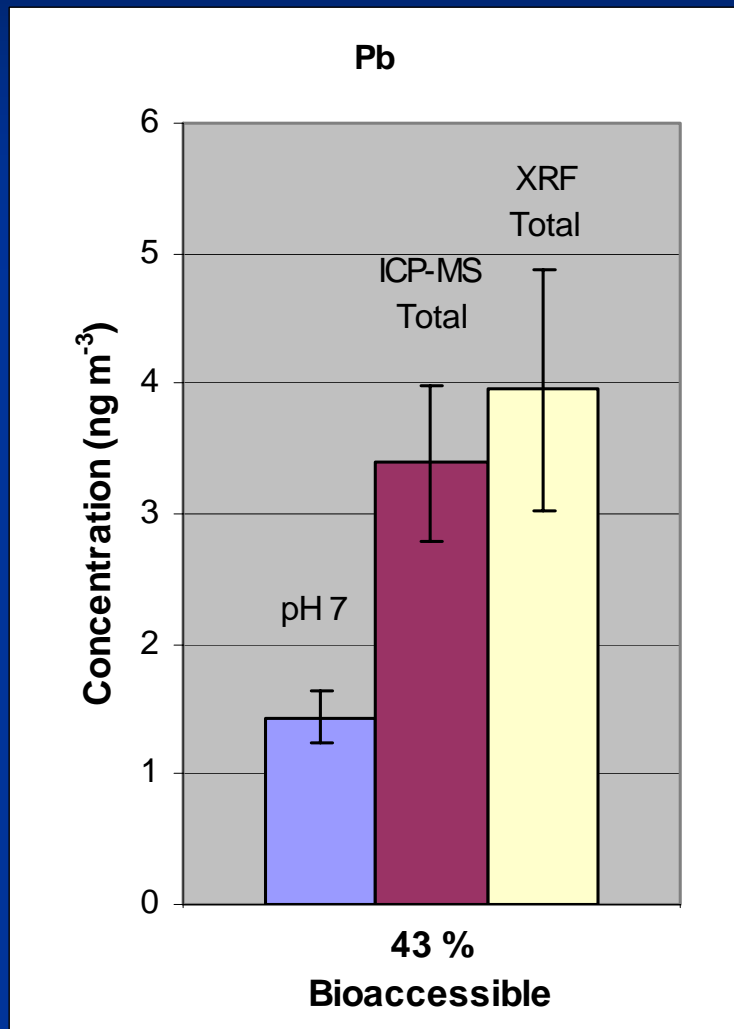


Stage 2

Total_(Stage 1 + Stage 2) *should equal* Total_(ED-XRF)

Pulmonary bioaccessibility of Pb & Mn

Windsor outdoor PM_{2.5} (n= 36; mean ± sd)

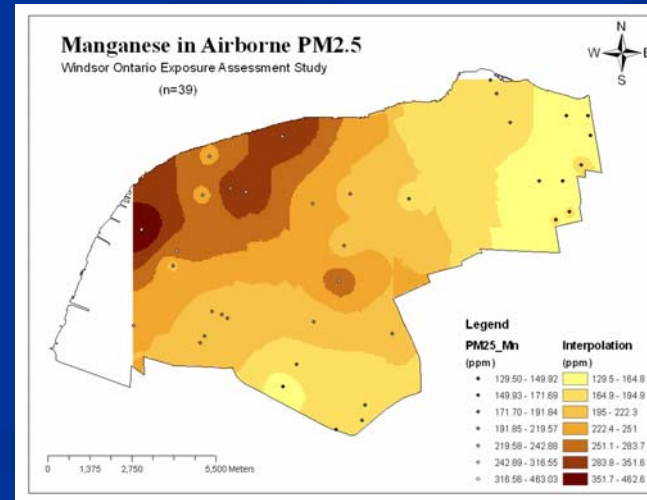


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(progress)
4. **Soil and Dust: Sources/Sinks for Metals** ←

University of Ottawa PhD thesis “Spatial and Geochemical Techniques for Assessment of Manganese in Windsor, Ontario, Canada”

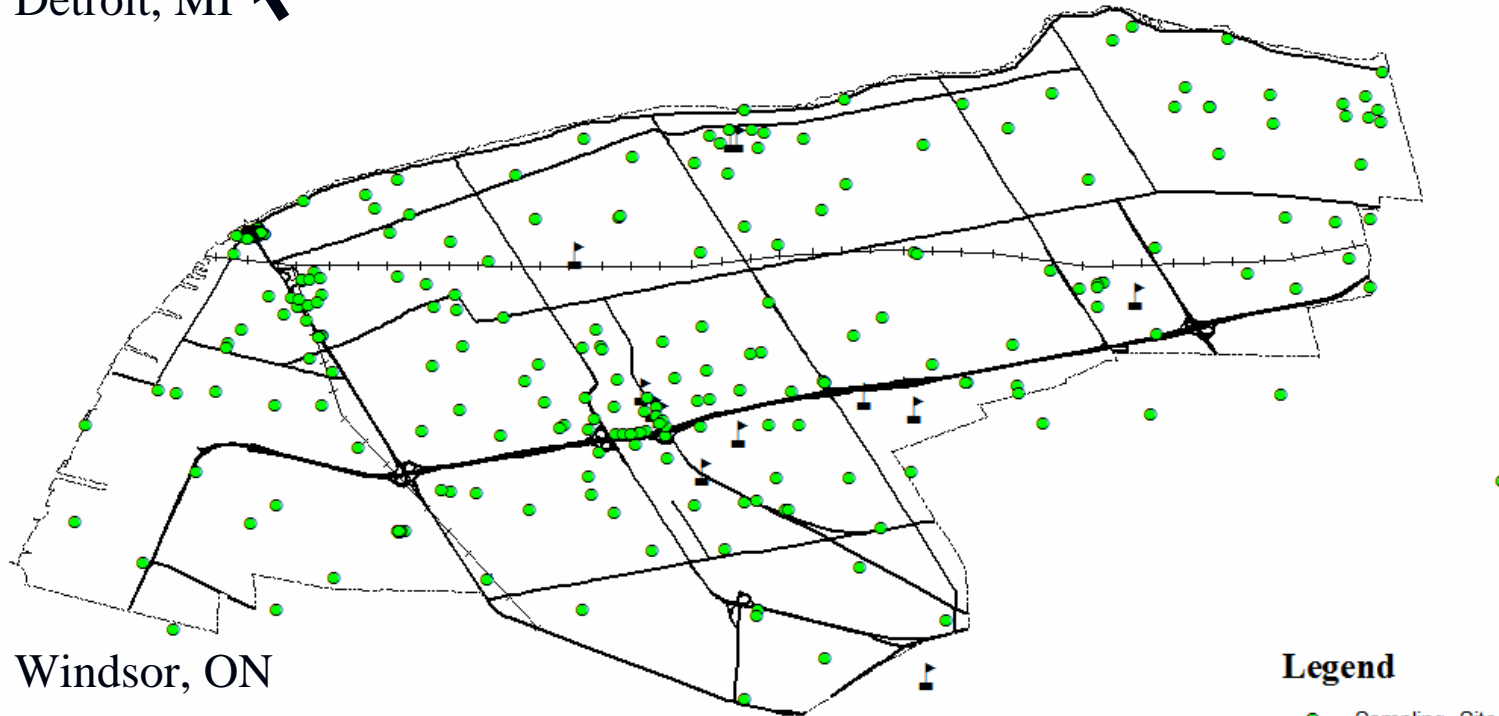
Michelle Nugent (PhD candidate)





2007-2008 Soil Sampling Sites

Detroit, MI



Windsor, ON

0 1,750 3,500 7,000 Meters

Legend

- Sampling_Sites
- Mn_Industries
- Railroads
- Hwy
- Major_Roads
- Expressway

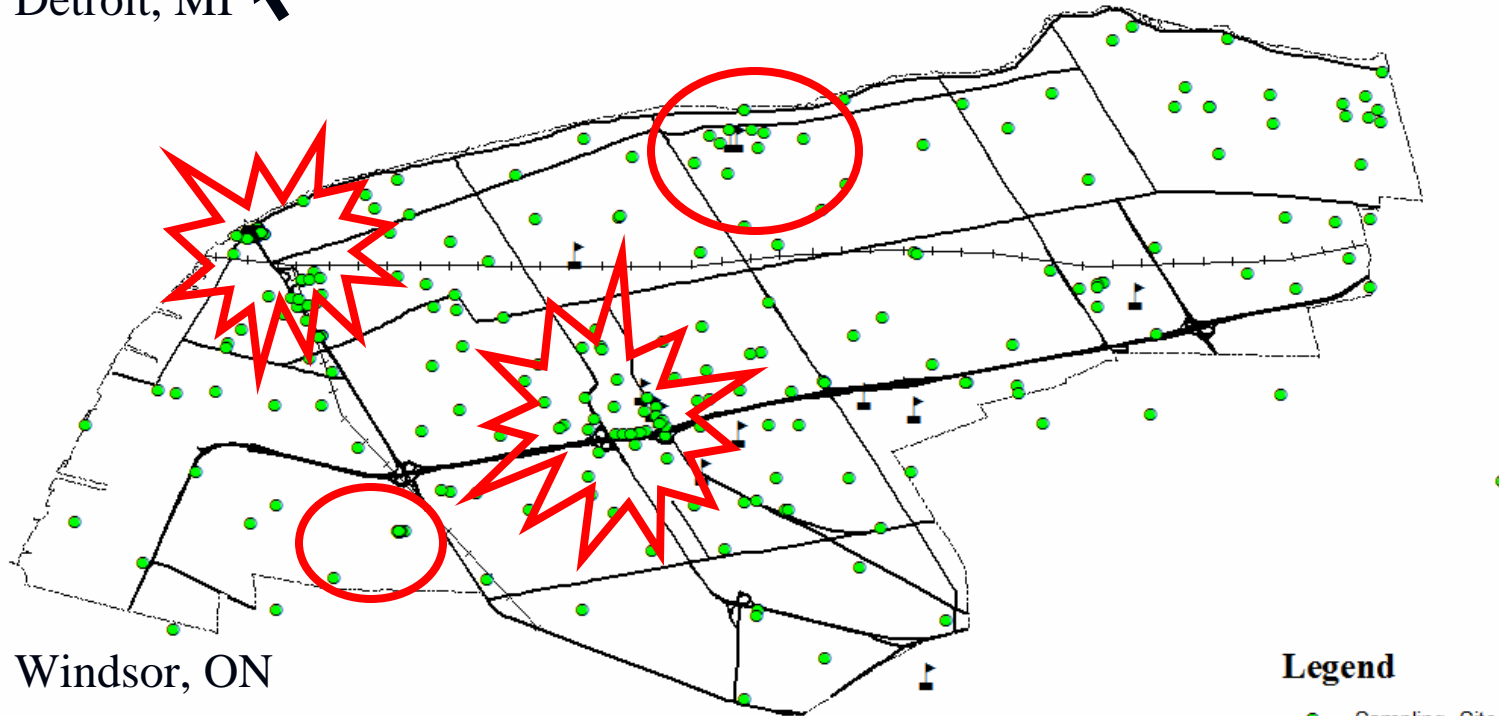
502 sampling sites from Nugent PhD thesis in prep

Rasmussen et al Detroit Oct 29 2008



2007-2008 Soil Sampling Sites

Detroit, MI



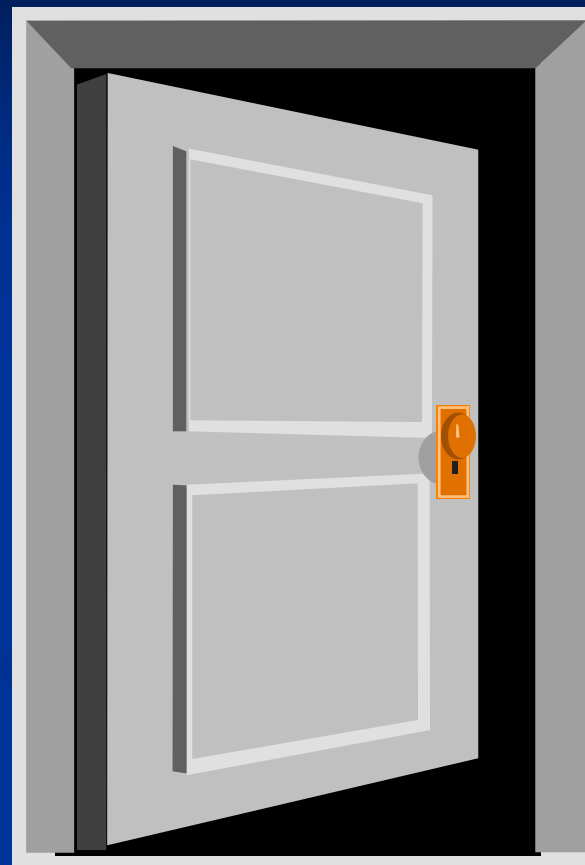
Windsor, ON

0 1,750 3,500 7,000 Meters

Legend

- Sampling_Sites
- ▲ Mn_Industries
- +— Railroads
- Hwy
- Major_Roads
- Expressway

Sources of Metals in Indoor Residential Environments



Sources of Metals Indoors

- Tracking in soil and dirt
- Windblown dust
- Industrial sources
- Vehicle emissions
- Combustion processes (wood, coal, kerosene)
- Occupational (“take-home Pb”)

- Consumer products
- Carpets, furnishings
- Paint, building materials
- Cooking
- Fireplaces
- Cigarette smoke
- Crafts & hobbies

Rasmussen, P.E. (2004) Elements and Their Compounds in Indoor Environments.

In 2nd Edition. Elements and Their Compounds in the Environment, Editors. E. Merian, M. Anke, M. Ihnat and M. Stoepler. V.I(1).Chap. 11; Wiley-VCH, Weinheim. 20p.

Metals in Household Dust

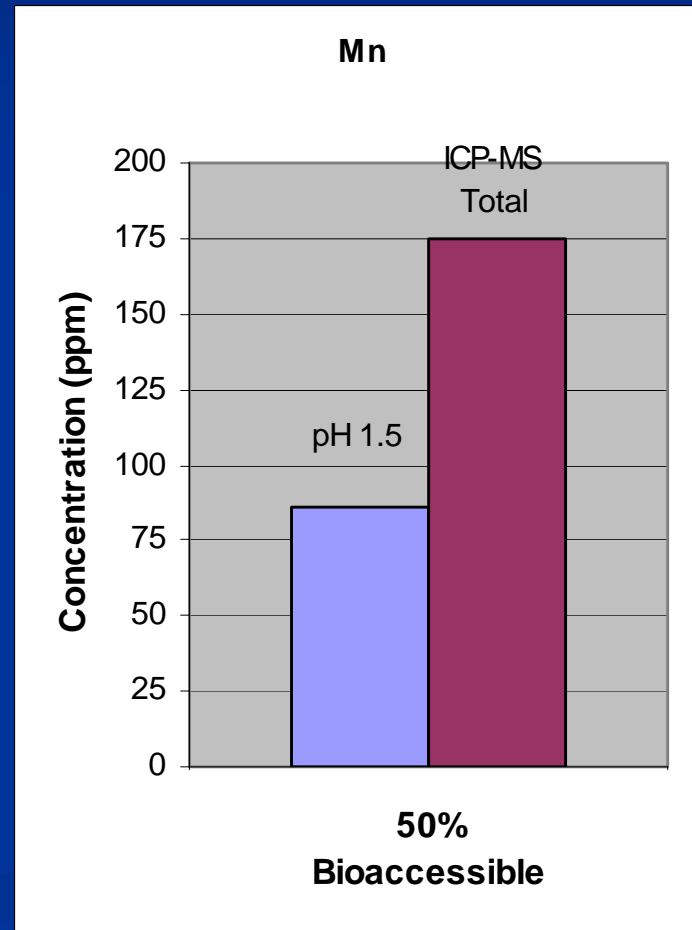
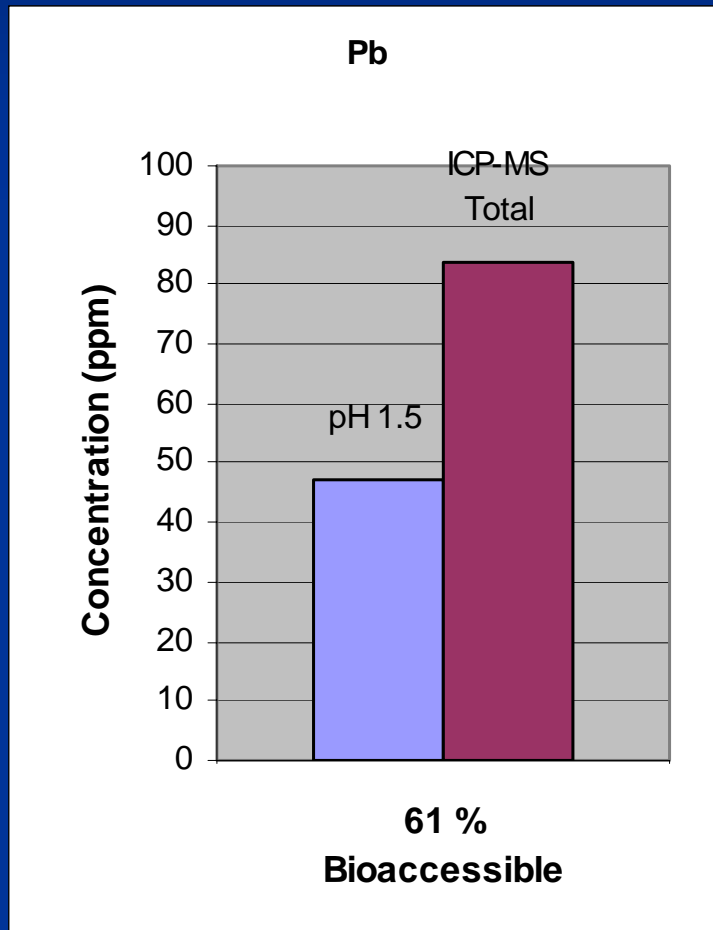
Oral Bioaccessibility (Ingestion Pathway)

- Adaptation of European Standard EN 71 (Safety of Toys)
- Reference: Rasmussen et al. (2008) Human and Ecological Risk Assessment 14(2) 351-371
- Simulates solubility of metals in stomach acid
- 0.07 M HCl; 37°C for 2 hr; pH = 1.5 (monitored)

$$\% \text{ bioaccessible} = \frac{\text{soluble metal value}}{\text{total metal value}} \times 100$$

Windsor indoor settled dust Pb & Mn

Oral bioaccessibility (n= 45; geomean; <150 μm)



Summary of progress

Successes: PM mass measurement

- Tight environmental controls including correction for air buoyancy allowed very sensitive measurement of particle mass.
- 100% of the samples and 98% of the field blanks are above gravimetric laboratory detection limit
- Analyses completed and reported January 2007

Good agreement US-EPA method (XRF) and HC ICP-MS method

Importance of Soil and Indoor Settled Dust as metal sources/sinks

Remaining challenges: metals on lightly loaded filters

- 10% of PM_{2.5} samples and 60% of PM₁₀ samples analyzed to date
 - For filter samples > 60 ug particle mass, certain elements may be reported reliably (depends on magnitude and variability of contamination)
 - Filter samples < 60 ug particle mass require new analytical approaches

Thank you!



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