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

WOEAS & DEARS Air Quality Meeting
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Collaborators/Co-authors

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Special Thanks to

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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)

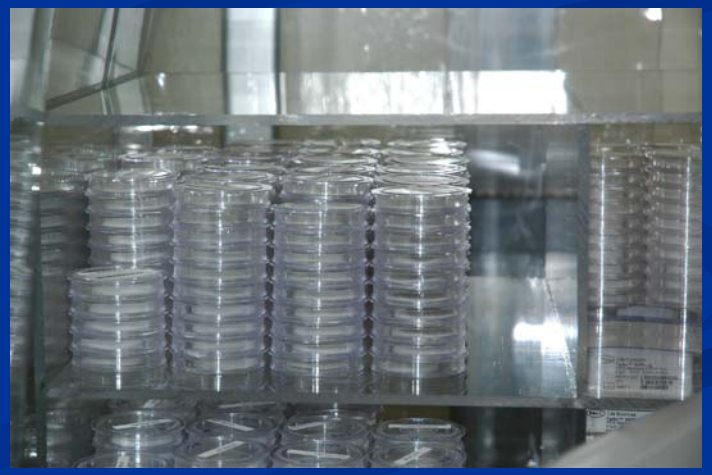
3. **Indoor, outdoor and personal exposures (Mn and Pb) (progress)**

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

USA Patent April 2008; ARCHIMEDES M3™

- Environmental chamber
- 24 h conditioning before pre- and post- weighing
- Temperature 21ºC±0.5ºC
- RH at 40%±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

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 %

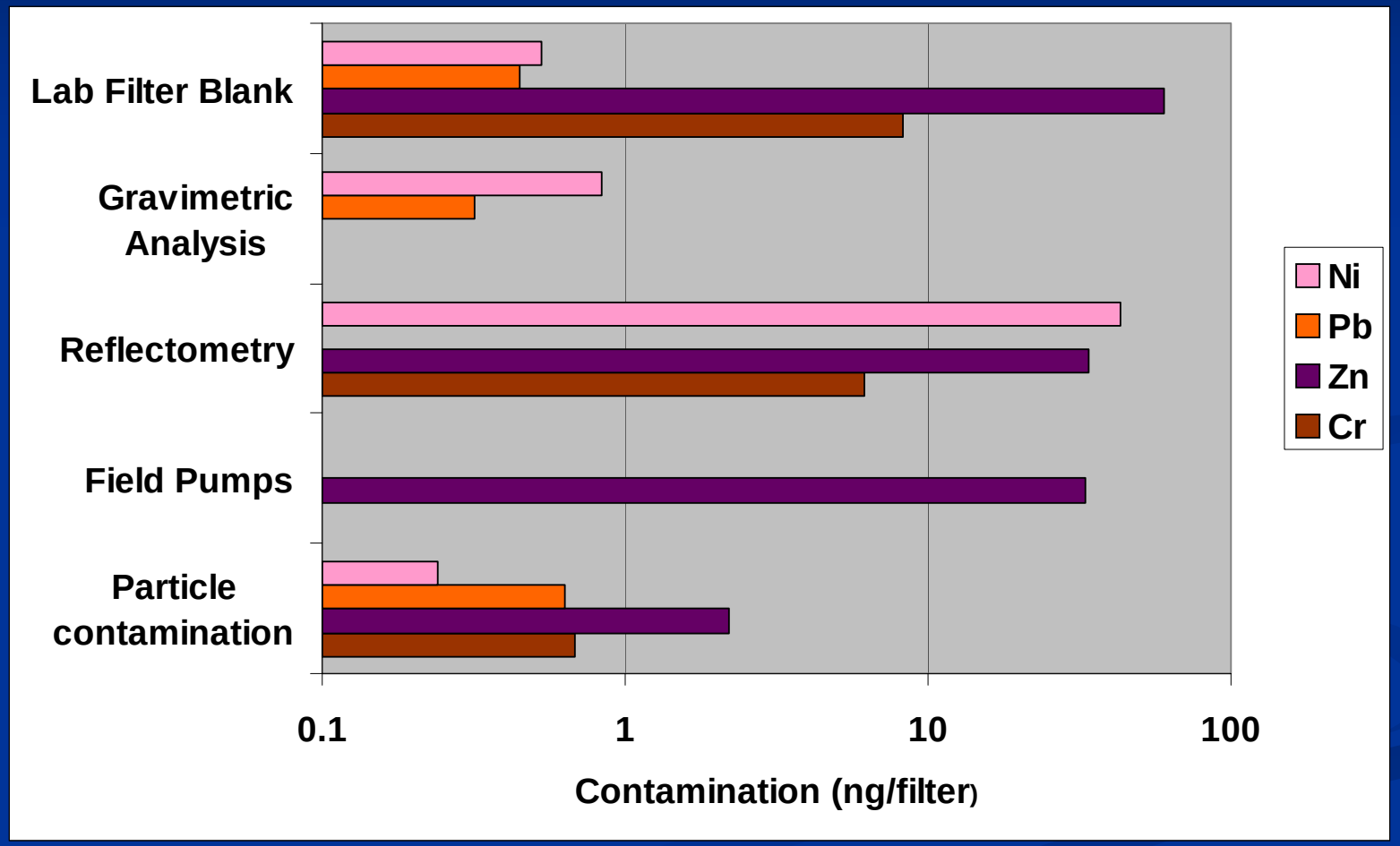
*XRF by Williams US-EPA ** ICP-MS by Rasmussen HC Lab

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 μg/m3

- Proposed Health Canada reference concentration for inhaled manganese

  = 0.05 μg/m3

Lead in Air

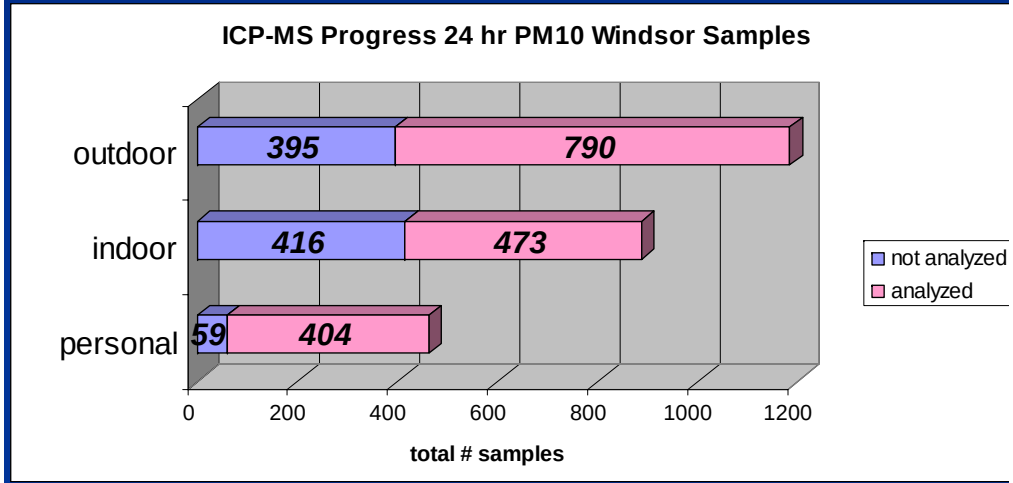
- New National Ambient Air Quality Standard (NAAQS)
- October 15, 2008
- Lead 0.15 µg/m^3 Rolling 3-Month Average
- 1.5 µg/m^3 Quarterly Average

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

All $PM_{2.5}$ and PM_{10} mass measurements for WOEAS completed and reported January 2007

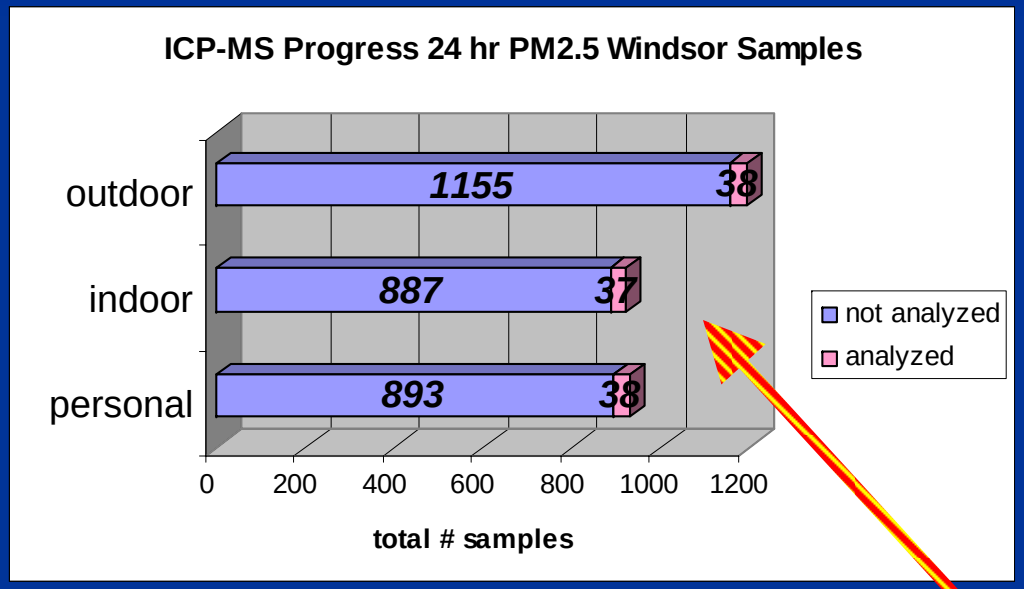
- Personal, Indoor & Outdoor
- 24-hr low-flow samples
- Two seasons each year; 8 weeks per season
- 48 participants

Progress in ICP-MS Analysis – PM_{10}



	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%

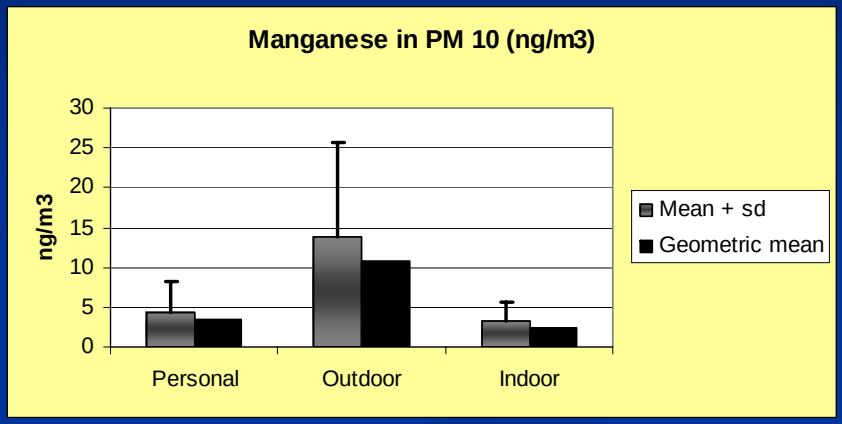
Subset of matched I-O-P samples

Rasmussen et al Detroit Oct 29 2008

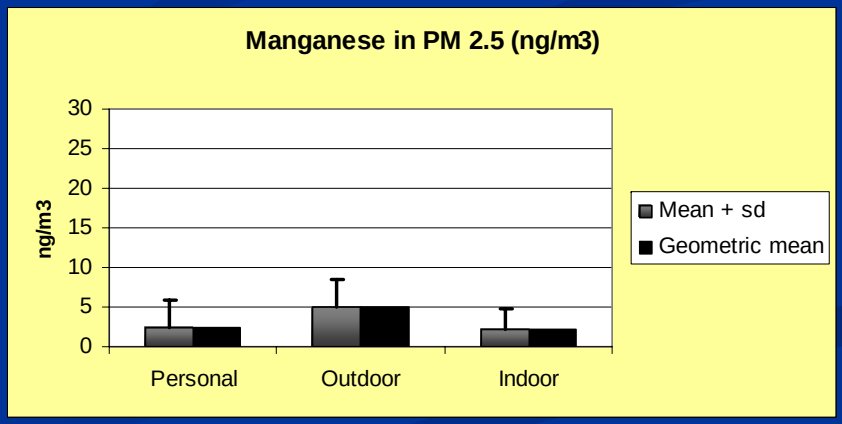
Mn results to date (partial datasets)

Proposed HC reference level 50 ng/m3

- After analyzing 60% of PM_{10} samples



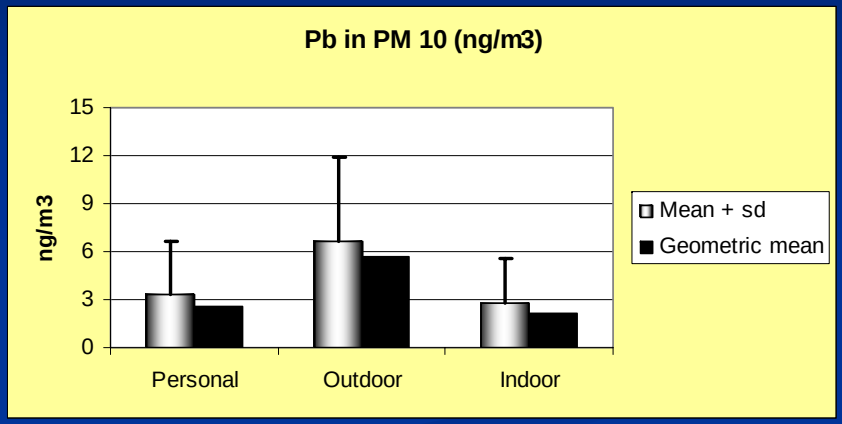
- After analysing 4% of $PM_{2.5}$ samples



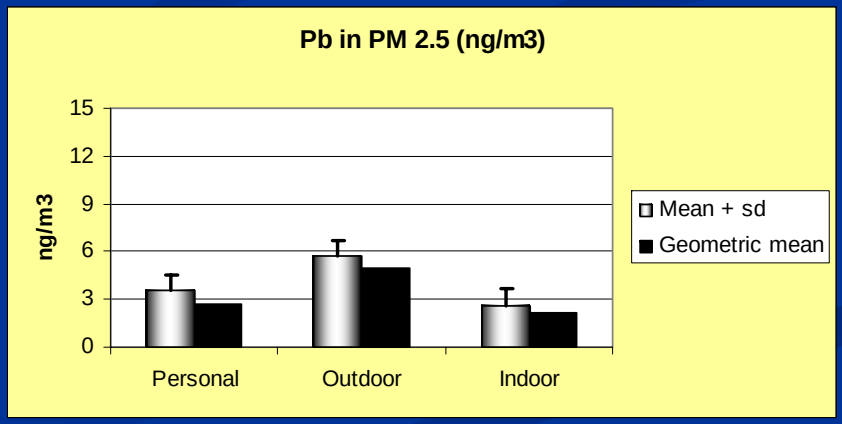
Pb results to date (partial datasets)

NAAQS for Pb 150 ng/m3

- After analyzing 60% of PM_{10} 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/HNO_3 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

↓

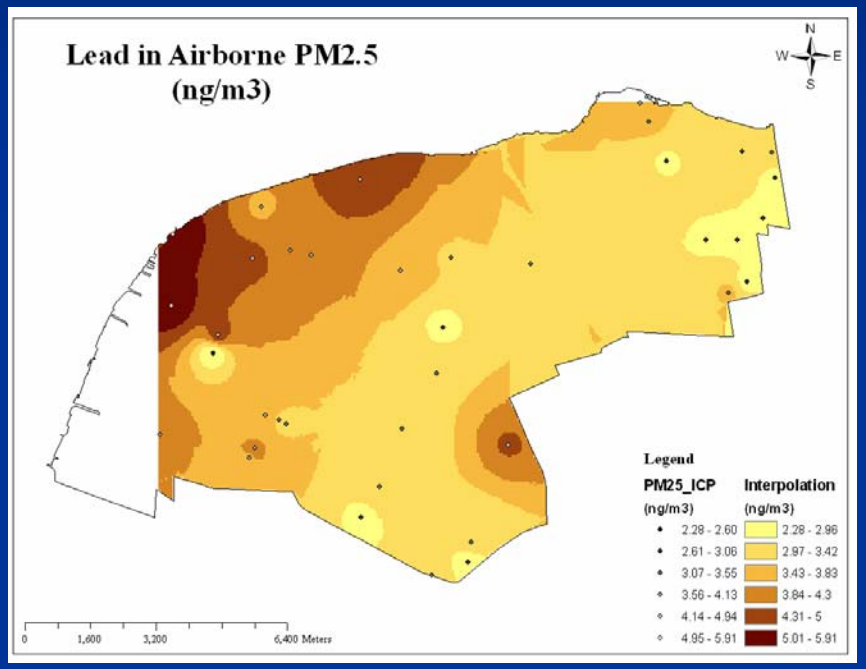
Acid digestion HC

↓

ICP-MS HC

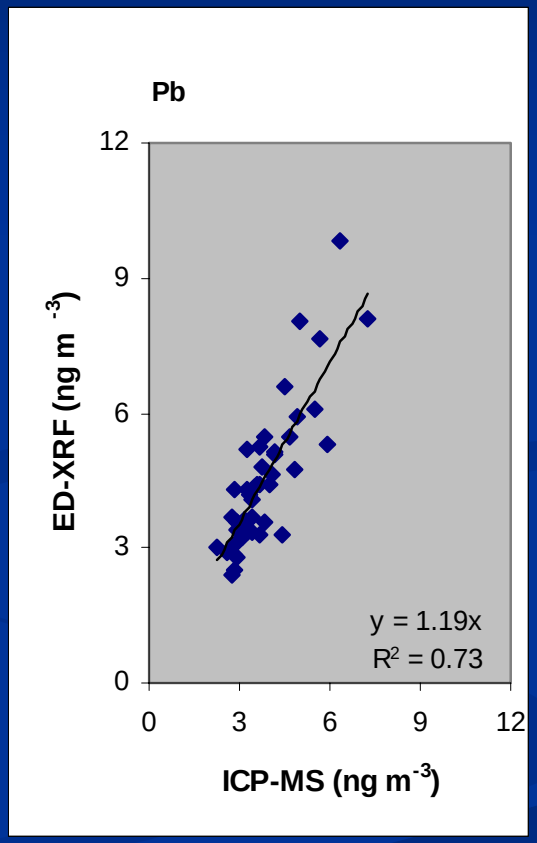
Total $_{(ICP\text{-}MS)}$ ***should equal*** Total $_{(XRF)}$

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

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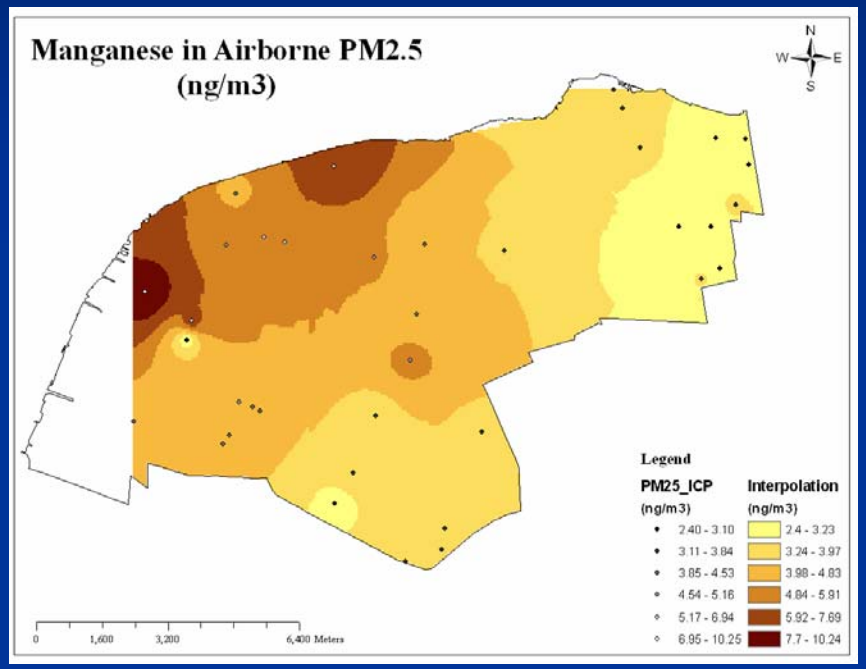
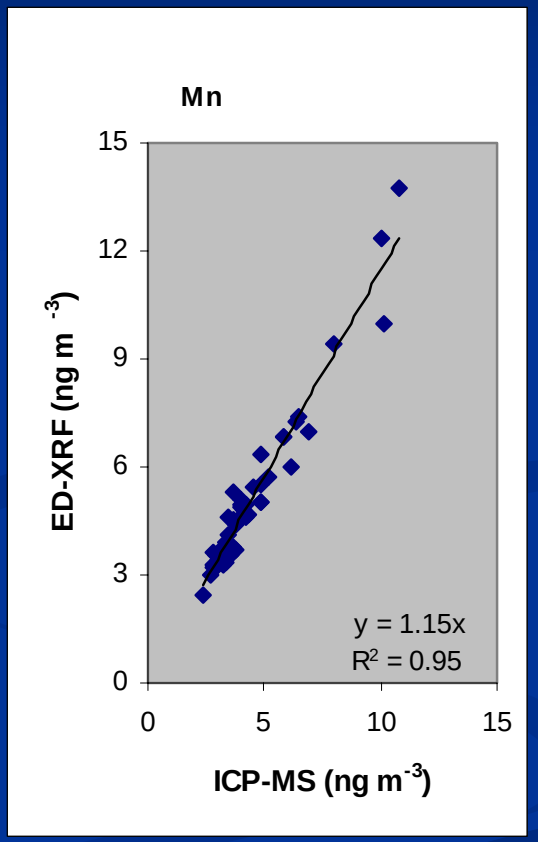
Method comparison (XRF and ICP-MS)

Manganese in $PM_{2.5}$ across Windsor,Ontario



US – EPA Lab



HC Metals Lab

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

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/HNO_3 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

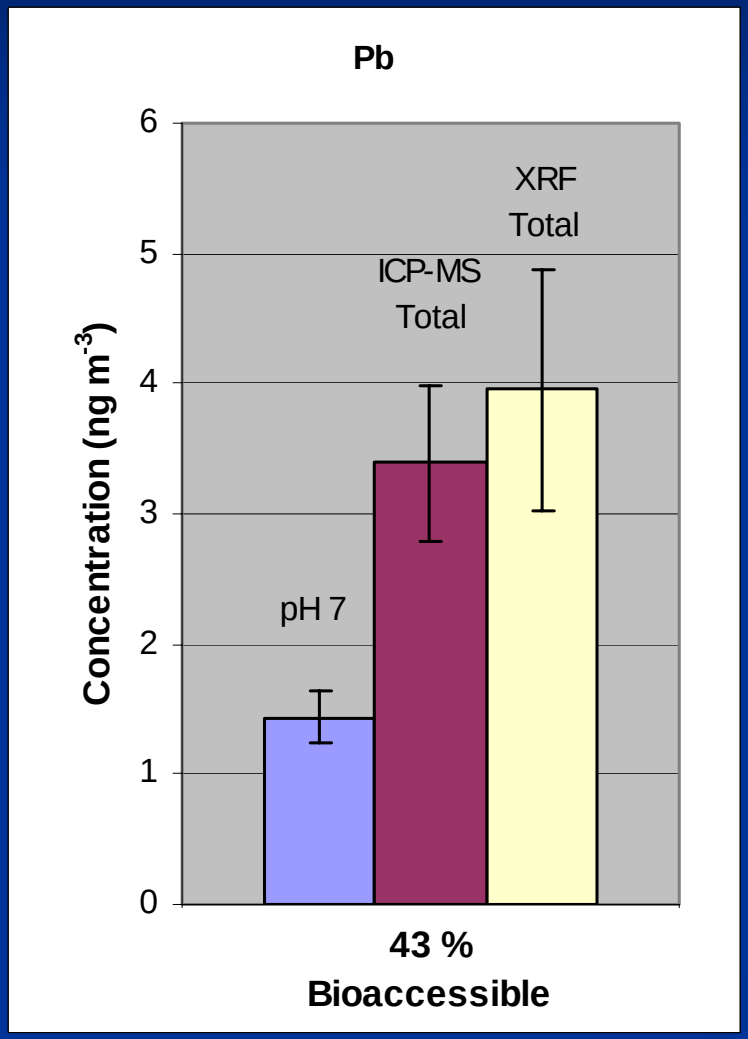
↓

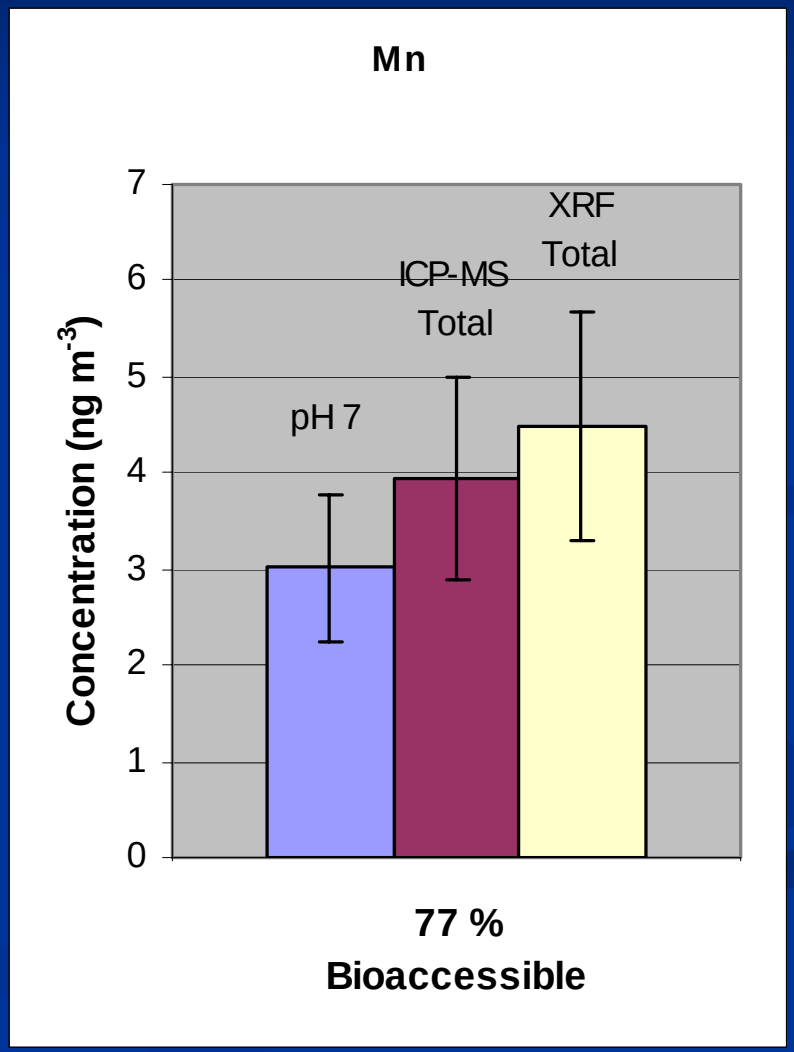
Stage 2

Total $_{\text{(Stage 1 + Stage 2)}}$ *should equal* Total $_{\text{(ED-XRF)}}$

Pulmonary bioaccessibility of Pb & Mn

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





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Outline of Windsor Metals Research

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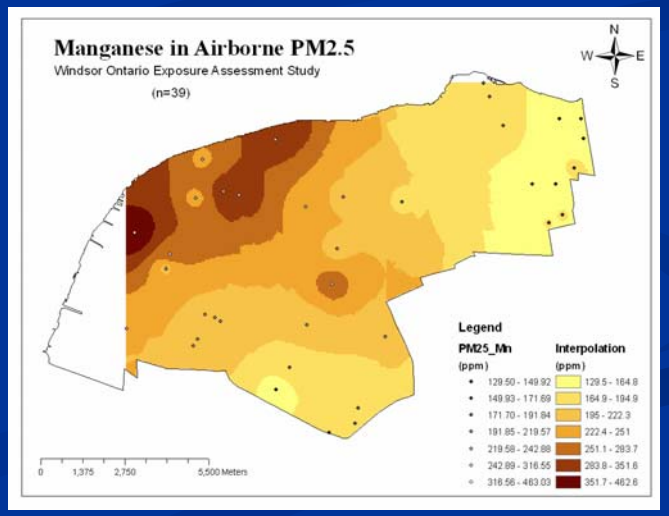
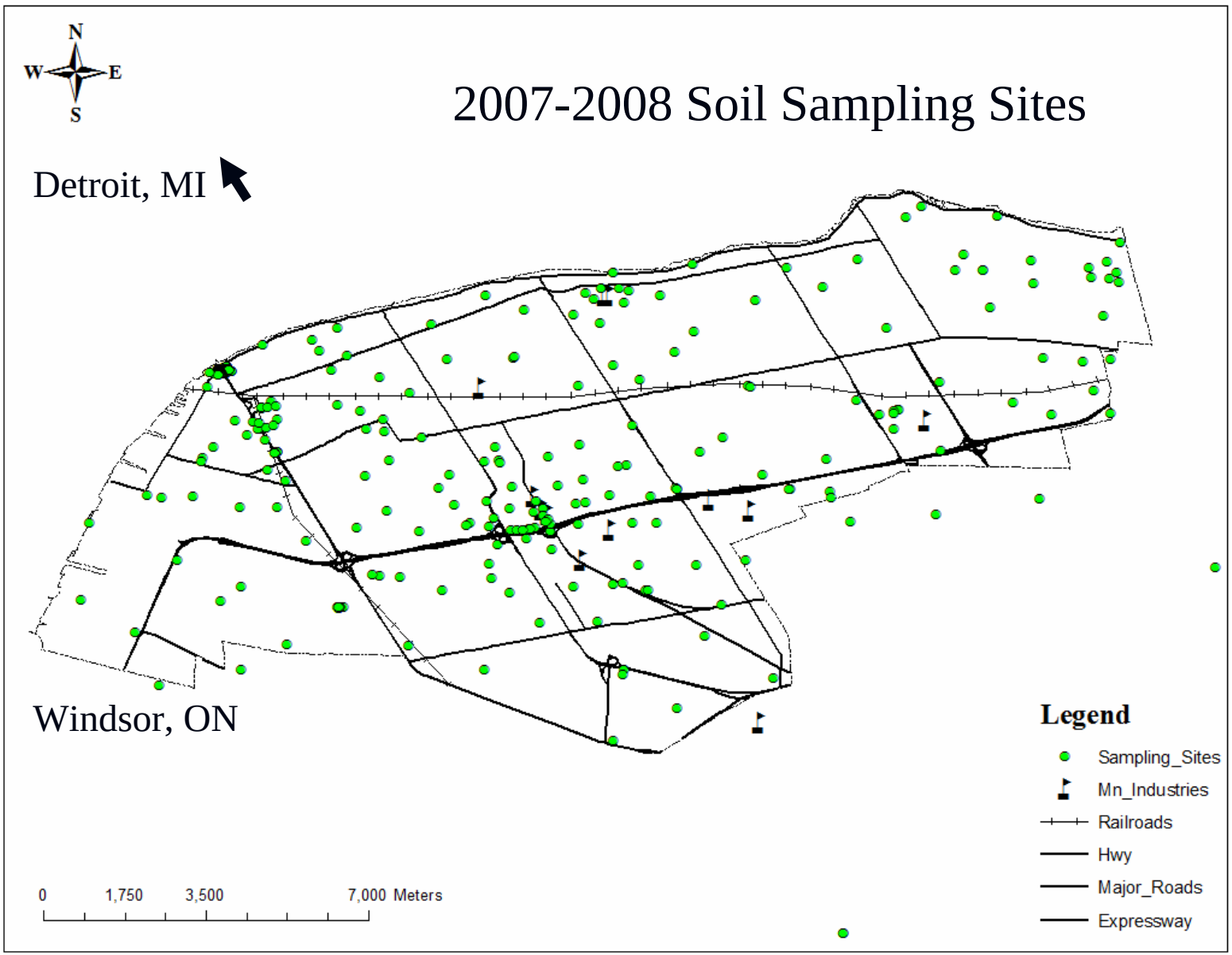
3. **Indoor, outdoor and personal exposures (Mn and Pb) (progress)**
4. **Soil and Dust: Sources/Sinks for Metals** ←

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



502 sampling sites from Nugent PhD thesis in prep

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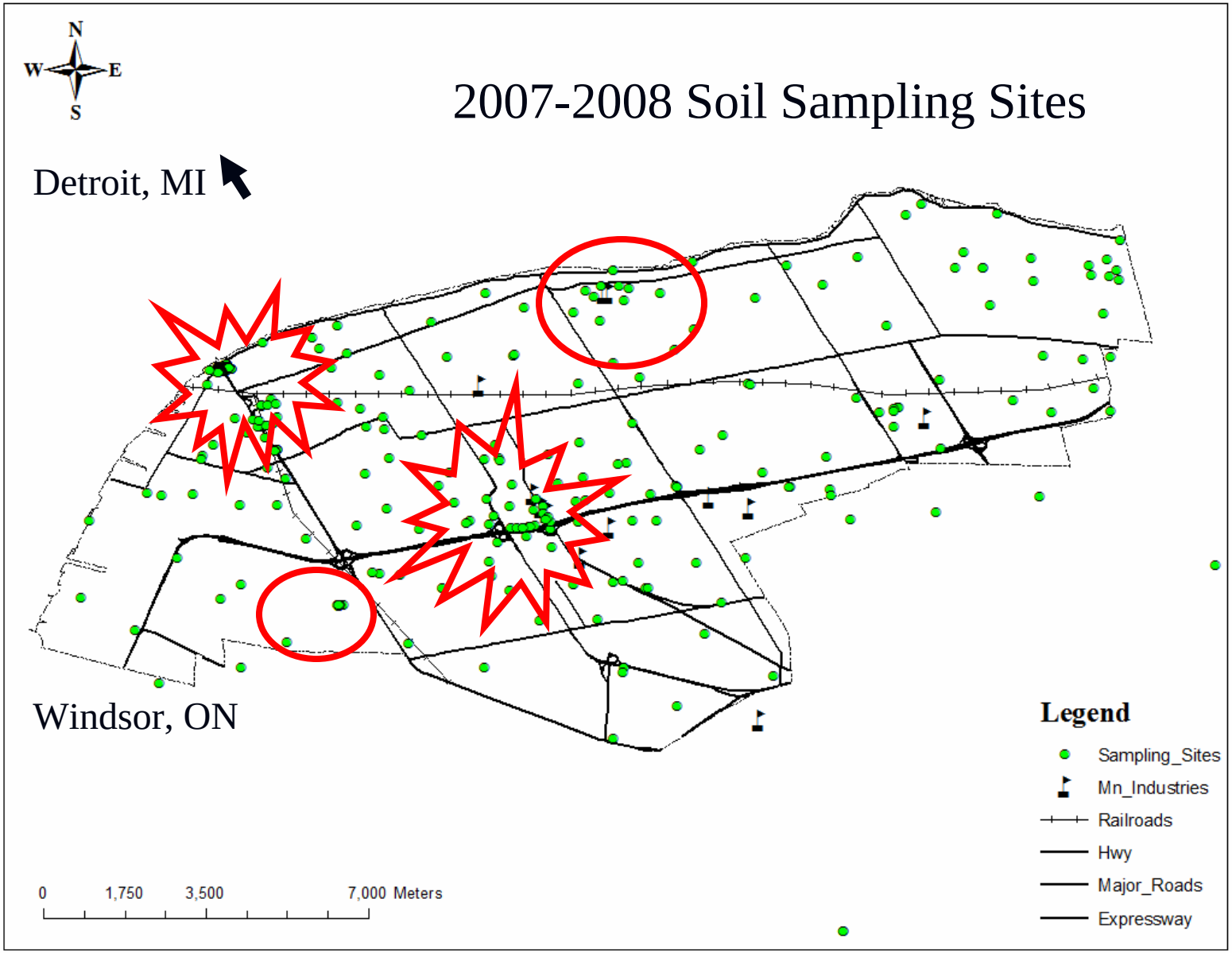
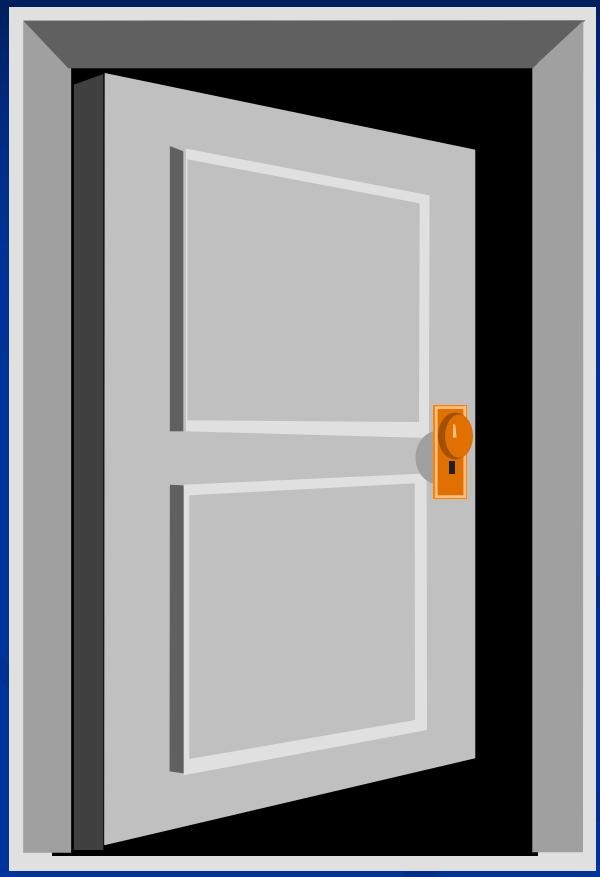
2007-2008 Soil Sampling Sites



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. Stoeppler. V.I(1).Chap. 11; Wiley-VCH, Weinheim. 20p.

Metals in Household Dust

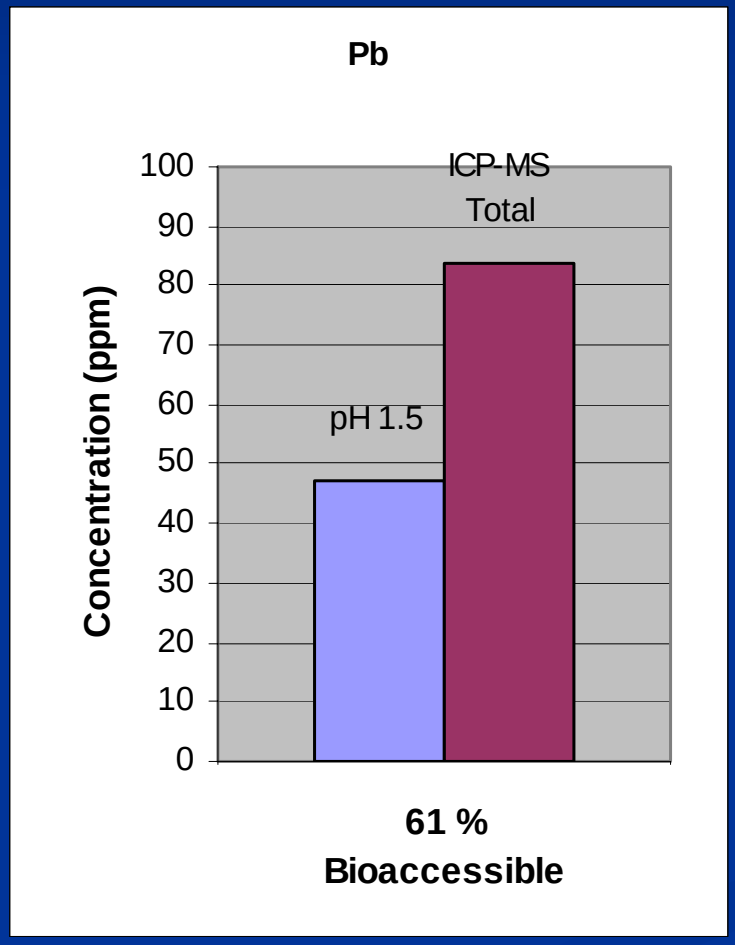
Oral Bioaccessibility (Ingestion Pathway)

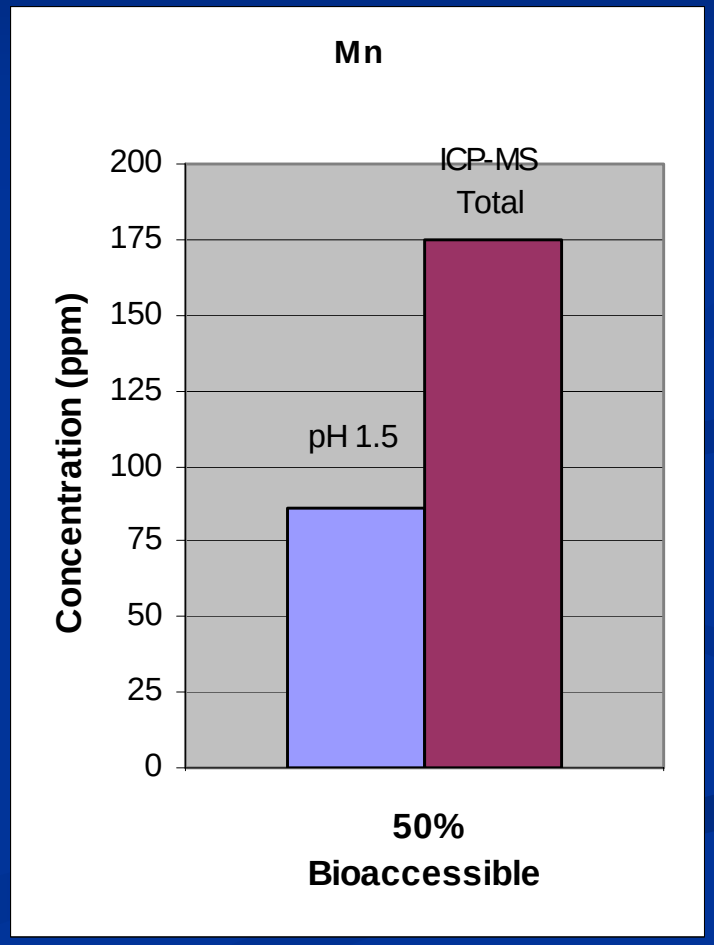
- Adaptation of European Standard EN 71 (Safety of Toys)
- Reference: Rasmussen et al. (2008) Human and Ecological Risk Assessment 14(2) 351-371
- Simulates solubility of metals in stomach acid
- 0.07 M HCl; 37°C for 2 hr; pH = 1.5 (monitored)

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

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 PM_{10} 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!