Monitoring gaseous mercury with a precise, accurate and inexpensive passive air sampler

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The Sampler

McLagan, et al., *ES&T Lett* (2016), *3*, 24-29

Rationale for passive sampling

- measuring ambient Hg levels close to the global average over extended periods of time, possibly for **long term trend monitoring**
- measuring Hg concentration variability/gradients at fine spatial resolution close to **point sources** to the atmosphere
- **Personal Hg exposure monitoring** for compliance and exposure assessment

Field Calibration

Toronto, Canada

1 year

Alongside Tekran 2537B active air sampler for gaseous Hg

Excellent linear uptake

Replicate precision

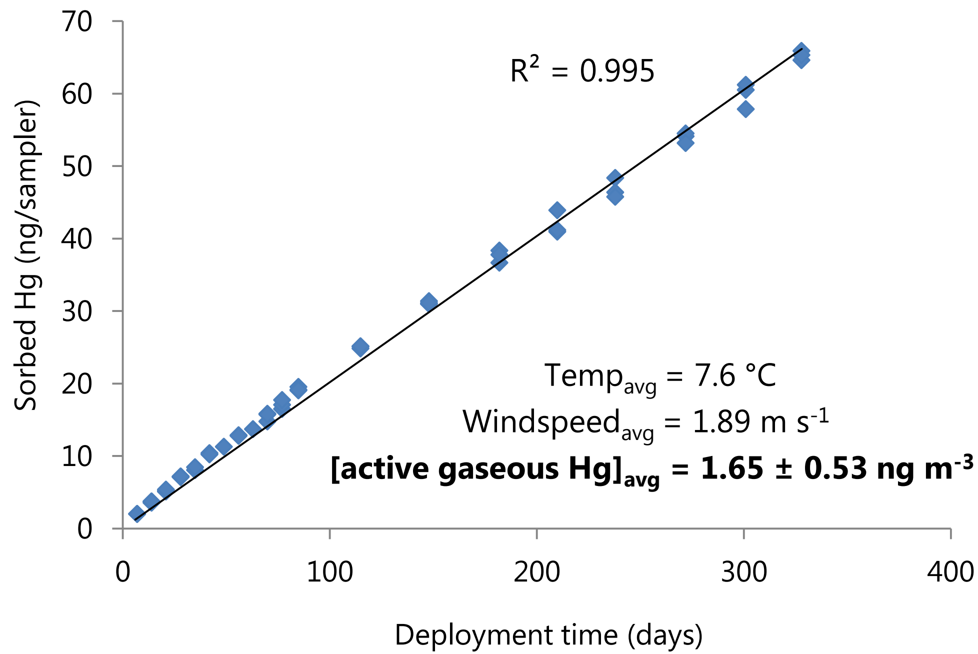
RSD_{avg} = 2.1 ± 1.3 %

Sampling rate (*SR*):

Volume of air effectively stripped of Hg per unit time

$$SR = m / (C\,t)$$

$$SR = 0.121 \pm 0.005\ m^3\ day^{-1}$$



McLagan, et al., *ES&T Lett* (2016), *3*, 24-29

Theoretical *SR* Estimation

$0.129\ m^3\ day^{-1}$

at average *T* of calibration 7.6 °C

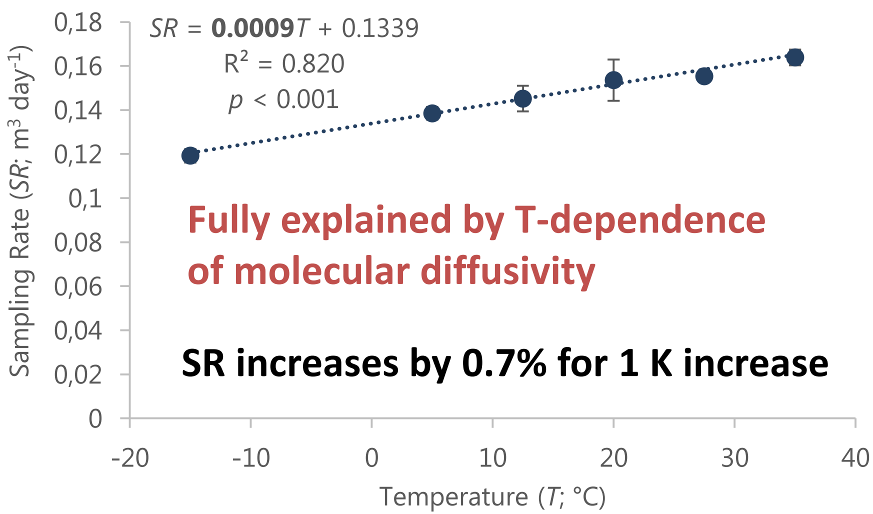
Based on:

- Temperature adjusted molecular diffusivity of mercury in air
- Molecular diffusion distance as the sum of a boundary layer, and Radiello's porous diffusive barrier and internal airspace

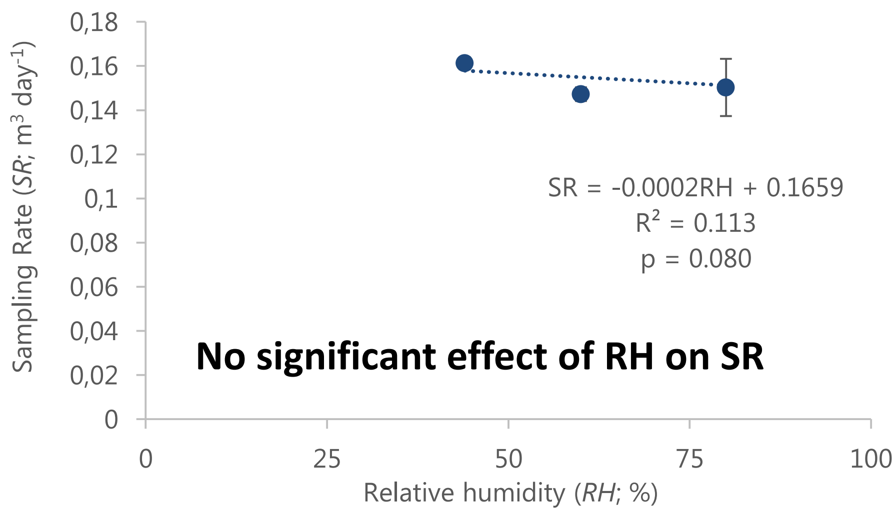
Meteorological factors and *SR*

Indoor experiments to test influence of temperature (*T*), wind speed (*WS*), and relative humidity (*RH*) on *SR*

Effect of *T* on *SR*



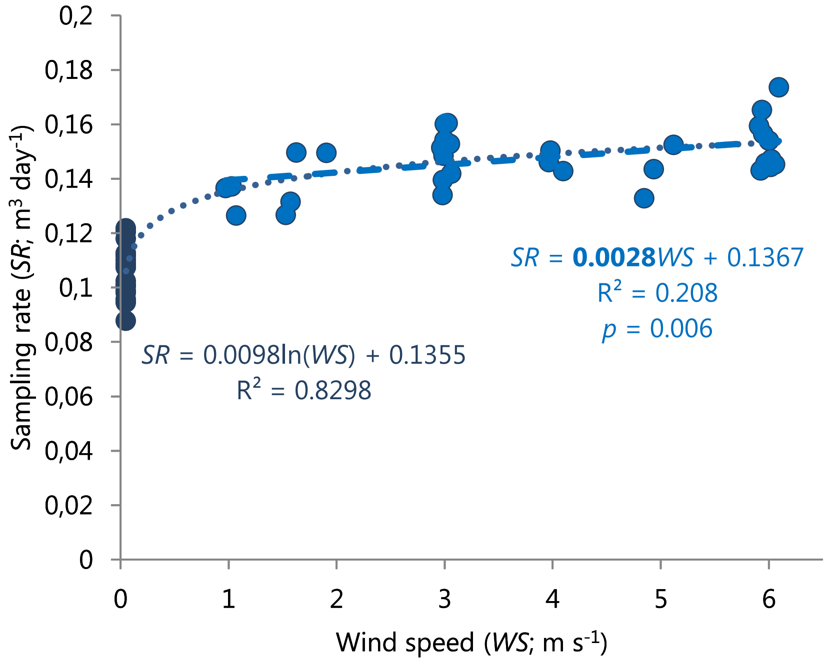
Effect of *RH* on *SR*



McLagan et al., *AMT* (2017), *In review*

Meteorological factors and *SR*

Effect of wind speed (*WS*) on *SR*



Strongest dependence at low wind speed (indoors)

At wind speeds above 1 m s^{-1} (outdoors): minor, but significant linear dependence

SR increases by 2.5% for 1 m/s increase

McLagan et al., *AMT* (2017), *In review*

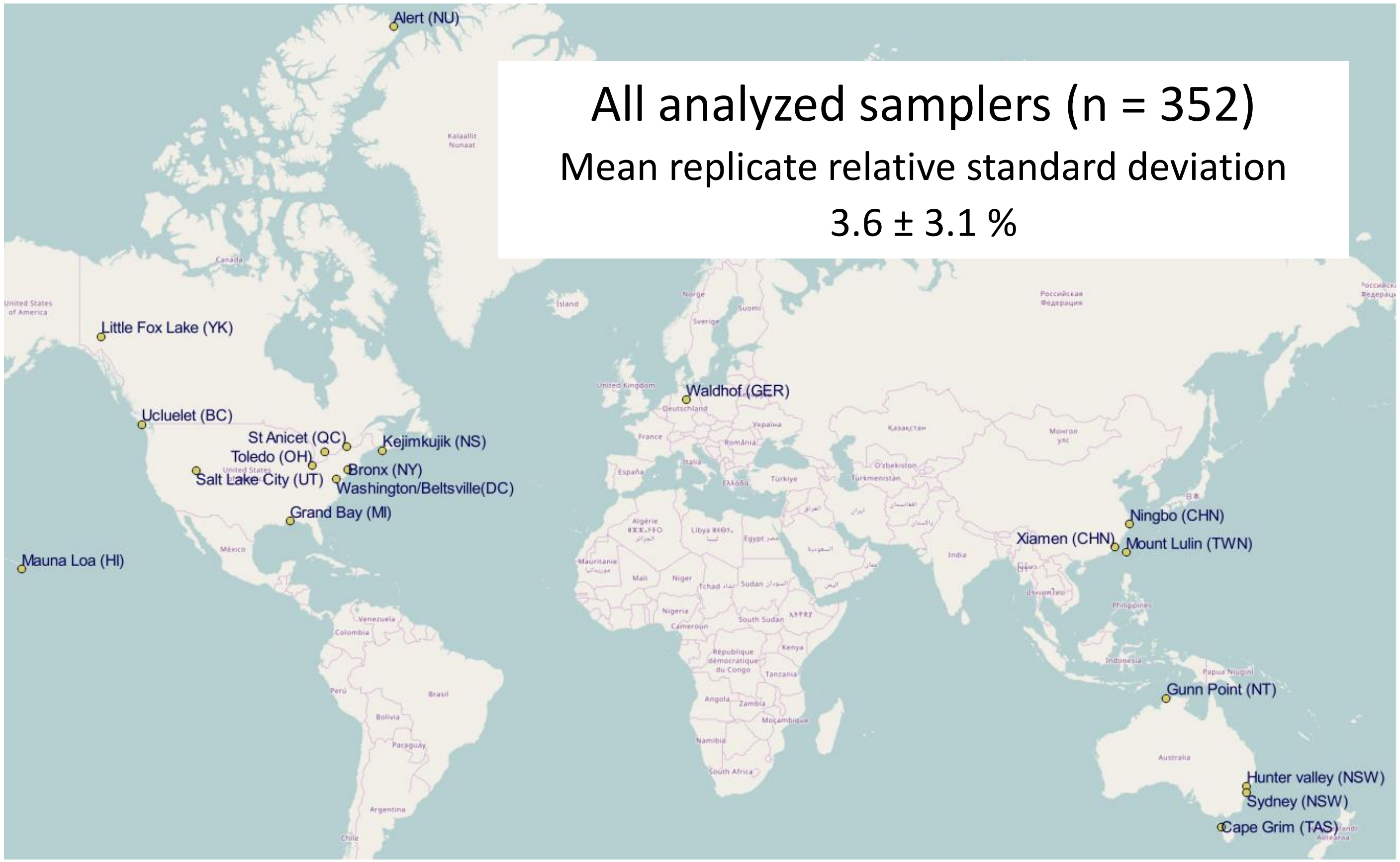
Meteorological factors and *SR*

SR adjusted for temperature and wind speed of individual deployments

$$SR_{adj} = SR_{calibration} + (T_{deployment} - T_{calibration}) * 0.0009\ \mathrm{m^3\ °C^{-1}\ day^{-1}} + (WS_{deployment} - WS_{calibration}) * 0.0028\ \mathrm{m^2\ s\ day^{-1}}$$

McLagan et al., *AMT* (2017), *In review*

Global Accuracy Testing



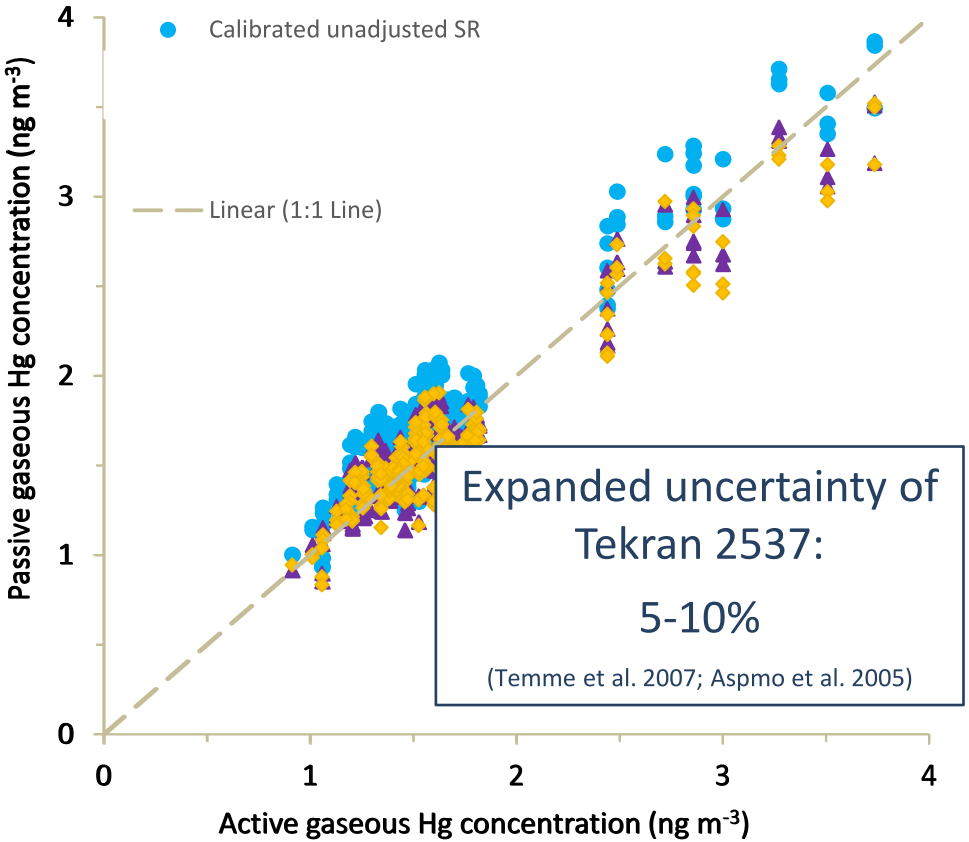
All analyzed samplers (n = 352)

Mean replicate relative standard deviation

3.6 ± 3.1 %

- 20 sites with ongoing active sampling (TEKRAN)
- Varying climate and gaseous Hg conditions
- One full year
- Varying intensity of deployments
  Monthly, seasonal, half-yearly, & yearly resolution
- Triplicates

Global Accuracy Testing



Active-Passive comparison

n = 278 (some losses due to Tekran outages)

- Previously calibrated unadjusted *SR* **0.121 m^3 day^{-1}**
  $|RPD|_{avg}$ = 11.8 ± 8.3 %
- Recalibrated *SR* from all data **0.133 m^3 day^{-1}**
  $|RPD|_{avg}$ = 7.8 ± 6.0 %
- Recalibrated *SR*: ***T* and *WS* adj.**
  $|RPD|_{avg}$ = 8.3 ± 5.9 %
- Theoretical *SR:* **0.134 m^3 day^{-1}**
  Based on average *T* = 13.0 °C

Aspmo, et al., *Atmos Environ* (**2005**), *29*; Temme, et al., *Atmos Environ* **2007**, 41,

Point Source Monitoring: Italian Hg Mine

- Monte Amiata (1738m) 3rd largest global Hg production region
- >100 000 t of Hg produced between 1847–1982
- Major mine: Abbadia San Salvatore

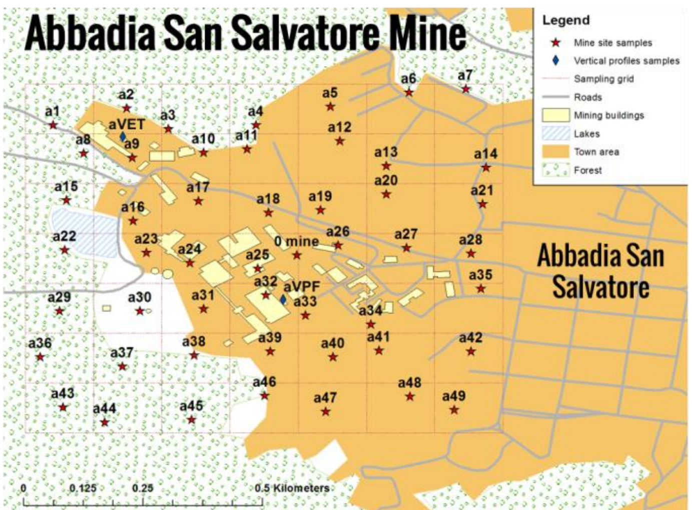


Point Source Monitoring: Italian Hg Mine

Two 7x7 PAS sampling grids

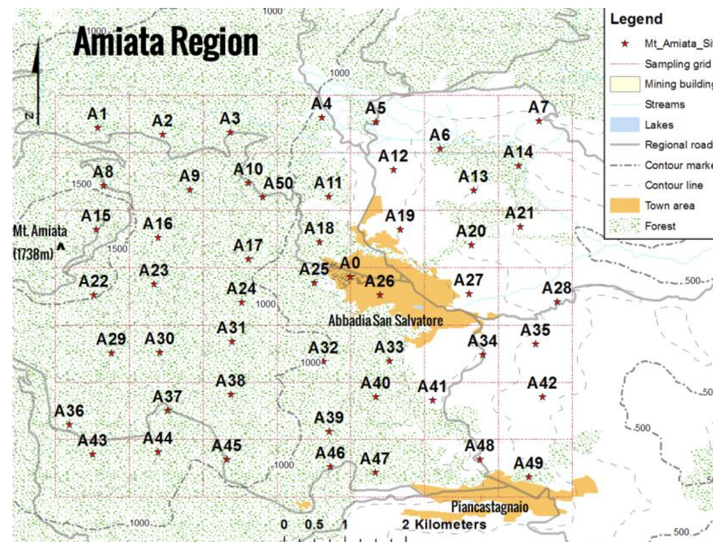
Abbadia San Salvatore Mine

two 1-week deployments Oct 2015 & July 2016



Monte Amiata region

four seasonal deployments: Oct 2015 – Oct 2016

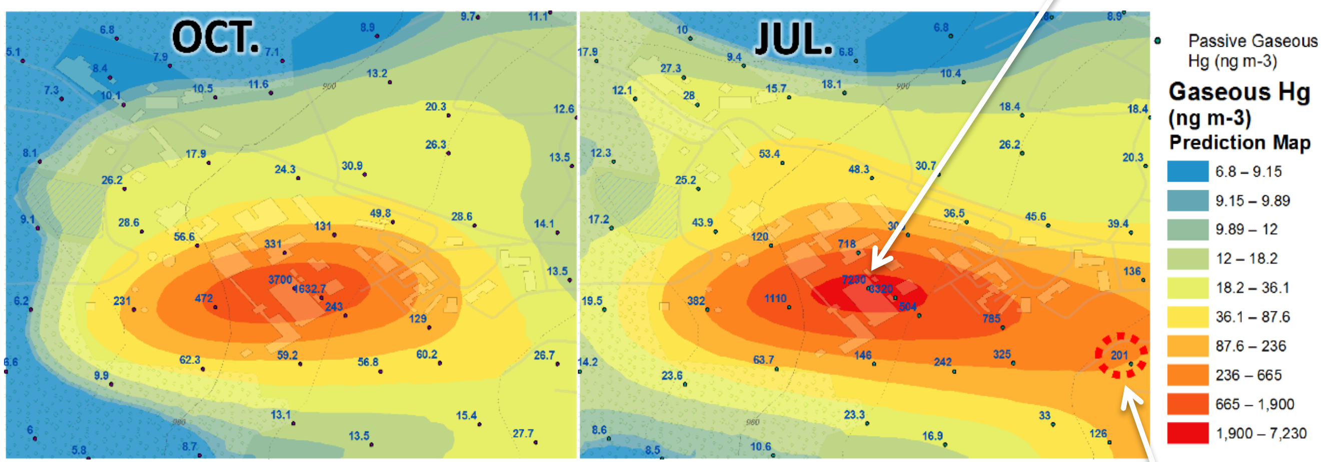


Point Source Monitoring: Italian Hg Mine

Concentrations (weekly average) **around Abbadia San Salvatore Mine**

higher Hg levels during higher summer temperatures

Maximum concentration above 7000 ng m^{-3}



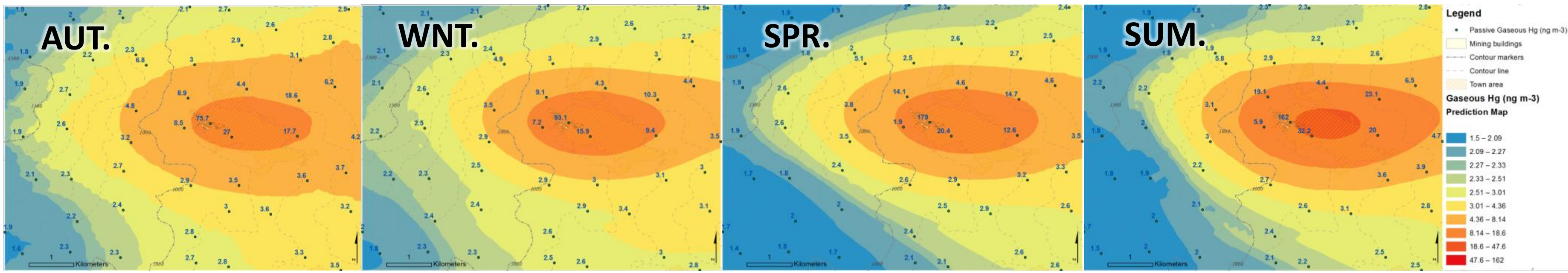
1-week measured & predicted (Kriging model) gaseous Hg conc. at ASSM

weak, but consistent westerly wind in summer advect elevated Hg levels in town

Concentration in residential area exceed 200 ng m^{-3}

Point Source Monitoring: Italian Hg Mine

Concentrations (seasonal average) **around Monte Amiata**



- Consistent spatial patterns
  - incremental increase toward source
  - predominantly westerly winds push Hg plume east into town and valley
- Concentrations at hemispheric background (~1.4 ng m^{-3}) in SW and NW corners of grid

- Source characterisation and mapping
- Population-level inhalation exposure assessment

Point Source Monitoring: Italian Hg Mine

Estimation of emission from entire mine area

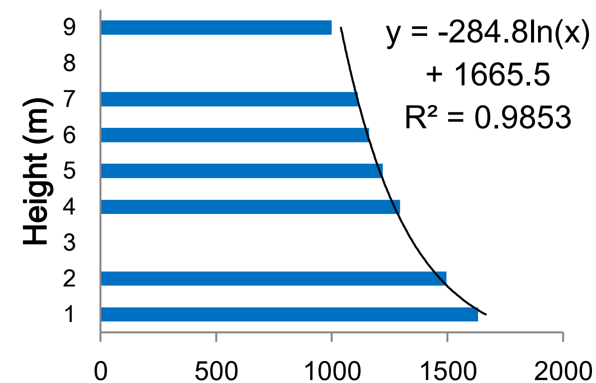
- Use spatial concentration maps and decline of concentration with height to estimate excess mercury in the air above the mine
- Estimate average residence time of air in the area based on average wind speed

E_{July} = 310 kg yr $^{-1}$

(uncertainty: 140 – 520 kg yr^{-1})

E_{Oct} = 170 kg yr $^{-1}$

(uncertainty: 120 – 220 kg yr^{-1})



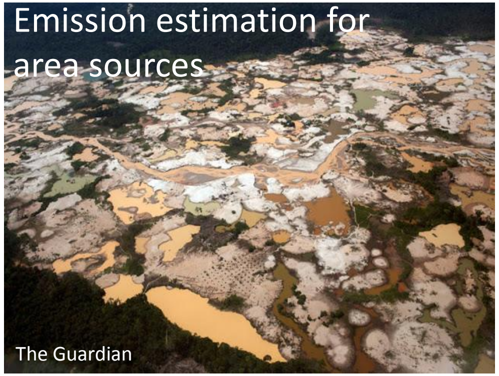
Conclusions

- Universally applicable *SR:* 0.133 m^3 day^{-1}
- Overall uncertainty: 8 ± 6 %

  with or without *T* and *WS* adjustment
- Suitable for:
  - monitoring even global background concentrations with time resolution of 1 week to >1 year
  - concurrent point source characterisation & emissions estimation
  - source identification

Future Application Potential

Artisanal and small scale gold-mining



Contaminated site remediation

Geological Hg sources

Effectiveness evaluation of Minamata Convention

etc.

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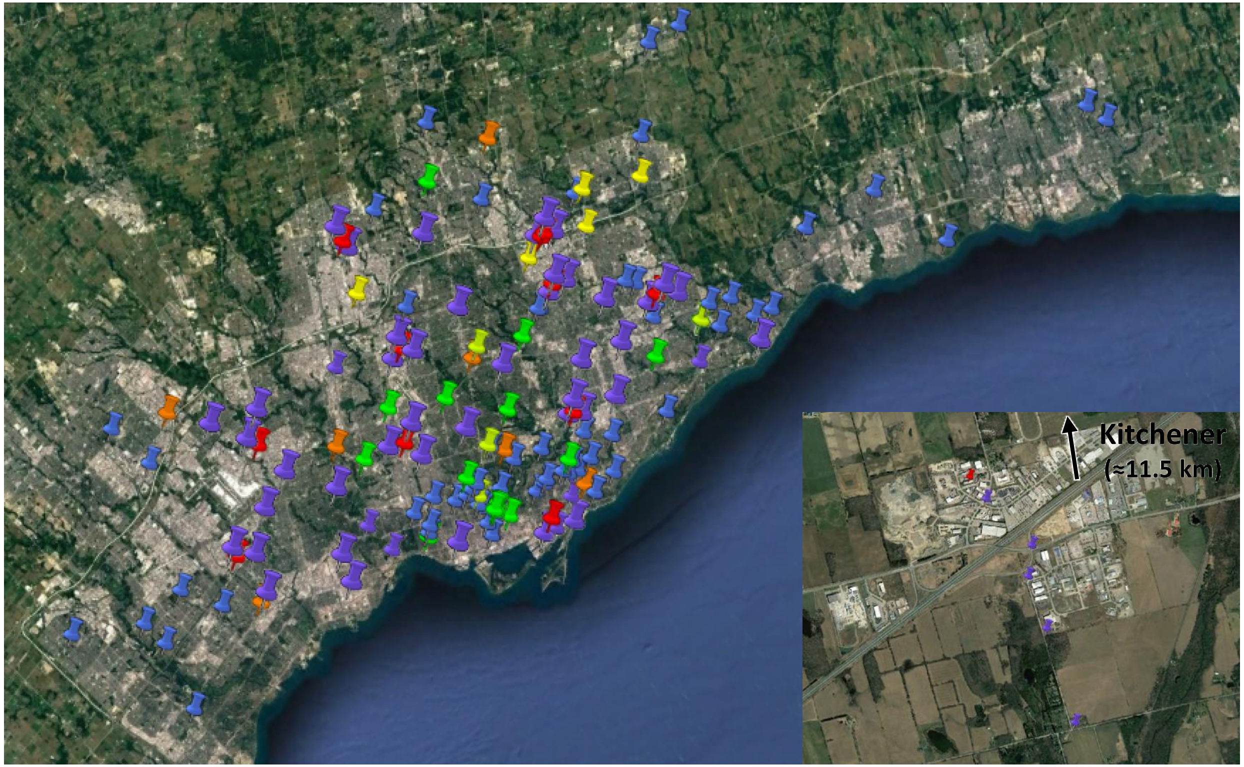
NSERC CRSNG

Environment and Climate Change Canada
Environnement et Changement climatique Canada

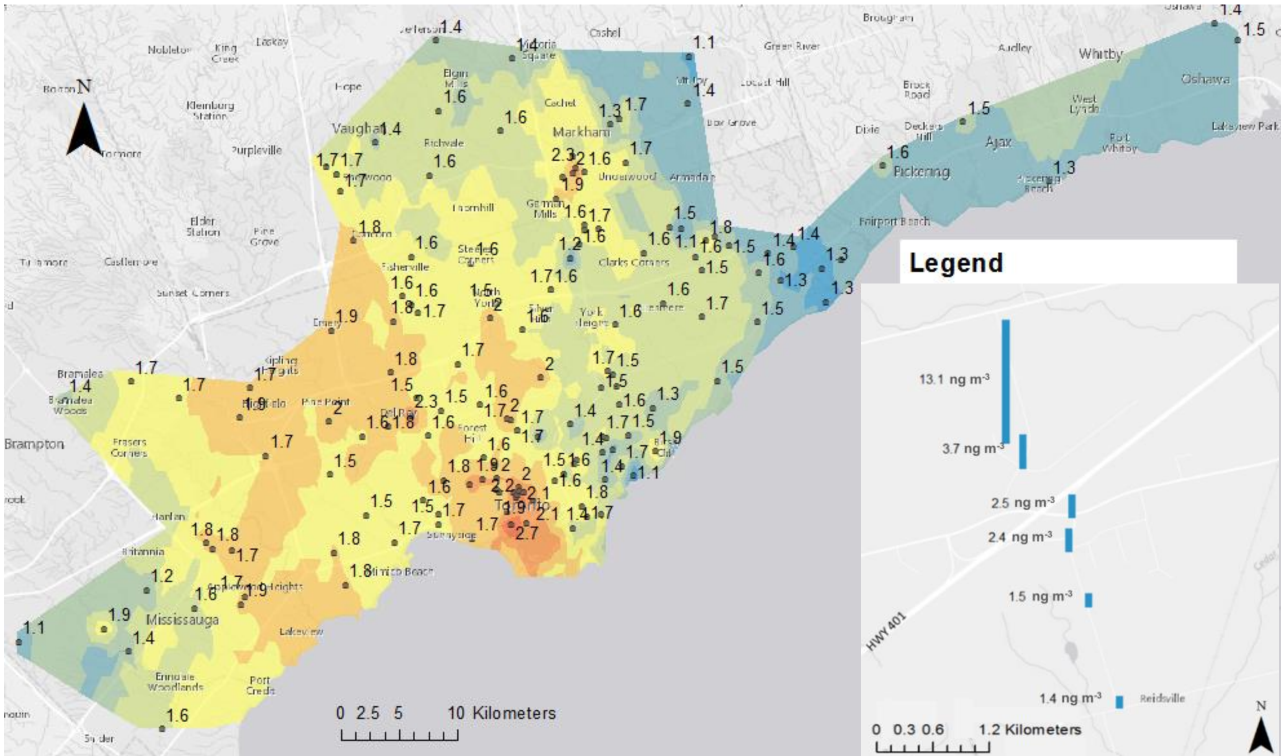
UNIVERSITY OF TORONTO SCARBOROUGH

Source Identification: Toronto



- 161 sites across city over 6-week period in Jul/Aug 2016
  - Transfer centres
  - Recycling centres
  - Crematoria
  - Hospitals and dental
  - Homes/workplaces
  - Additional sites
- Source transect at disposal site for Hg containing products (only Hg retort in Canada)

Source Identification: Toronto



6-week measured & predicted (Kriging model) gaseous Hg conc. in GTA in July/August 2016

- [Gaseous Hg]: low
  At or just above hemispheric background
- Range of [gaseous Hg]: low
- Highest in downtown
- Additional sites were significantly lower than dental/hospital, waste sites and crematoria (p<0.001)
- Disposal facility: 1 order of magnitude above background