



ICMGP 2024

CAPE TOWN • SOUTH AFRICA • 21 - 26 JULY

Seeing the forest from the trees: Uptake, archiving, and cycling of Hg in vegetated ecosystems

Dr. David McLagan

Emerging Researcher Award winner (2024)

Asst. Prof. Environmental Geochemistry

School of Environmental Studies; Dept. Geology

Queen's University (Canada)





Gateway to terrestrial Hg research...

AGU100 ADVANCING EARTH AND SPACE SCIENCE

JGR
Atmospheres

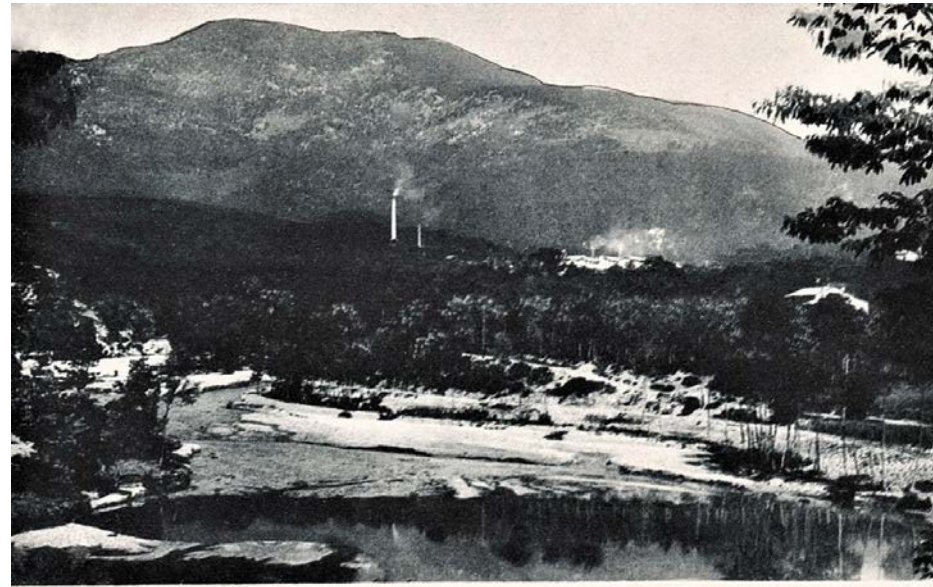
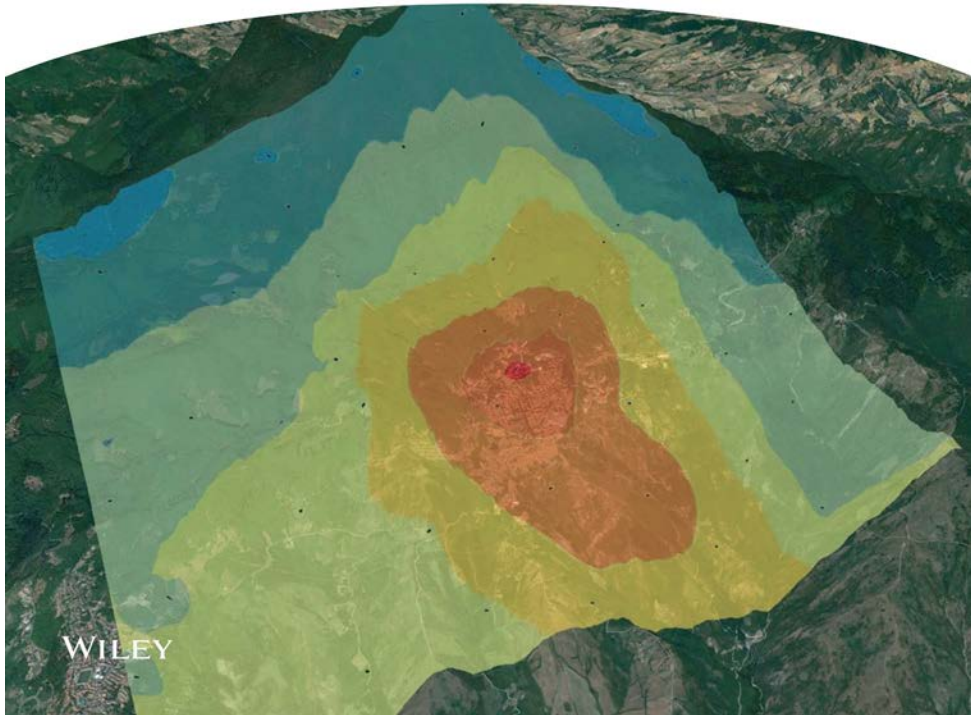
27 February 2019 • Volume 124 • Issue 4

Research Article | Free Access

Characterization and Quantification of Atmospheric Mercury Sources Using Passive Air Samplers

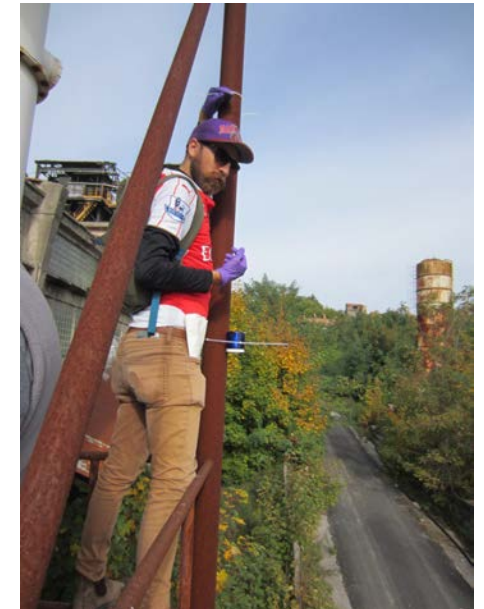
David S. McLagan, Fabrizio Monaci ✉, Haiyong Huang, Ying Duan Lei, Carl P. J. Mitchell, Frank Wania ✉

First published: 31 January 2019 | <https://doi.org/10.1029/2018JD029373> | Citations: 36



Abbadia S. Salvatore (m. 829) - Veduta del Monte Amiata e Miniera (m. 1734)

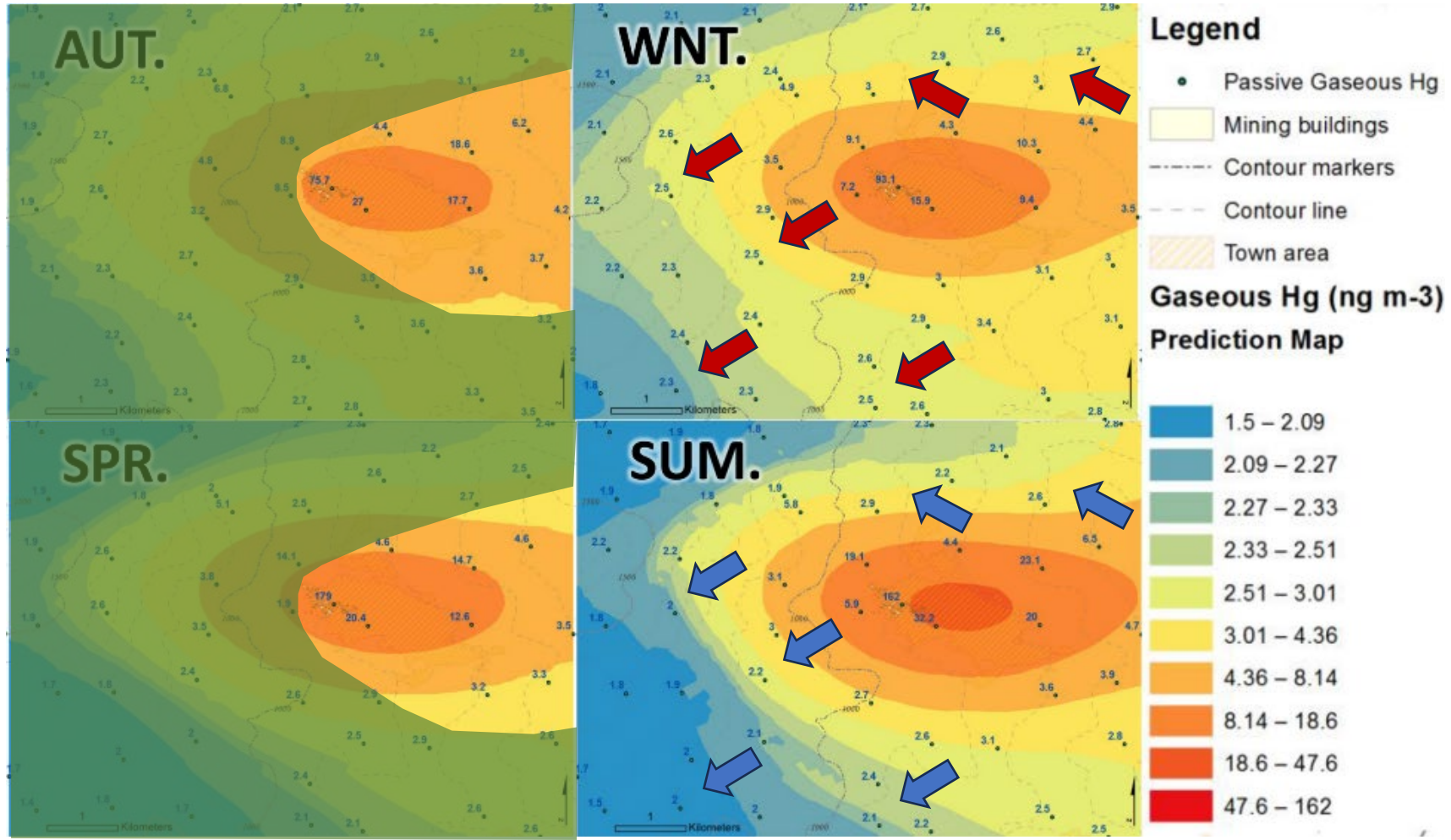
Mt. Amiata Hg mine. Modern operations: 1874-1982



Grids of MerPAS deployments across mine site (1 km²) and local region (50 km²)

Gateway to terrestrial Hg research...

Regional Monte Amiata deployments



- Demonstrated MerPAS's excellent capacity to characterize sources
- Top-down modelled emissions
- What about terrestrial Hg?
- GEM conc. higher within forested areas in winter
- Forests: oak, chestnut, beech
- **Could growing vegetation decrease GEM within canopy?**



Where there is smoke there is Hg. Fire: 1° or 2° emissions?



Atmospheric Chemistry and Physics

ACP, 21, 5635-5653, 2021 <https://doi.org/10.5194/acp-21-5635-2021>

Where there is smoke there is mercury: Assessing boreal forest fire mercury emissions using aircraft and highlighting uncertainties associated with upscaling emissions estimates

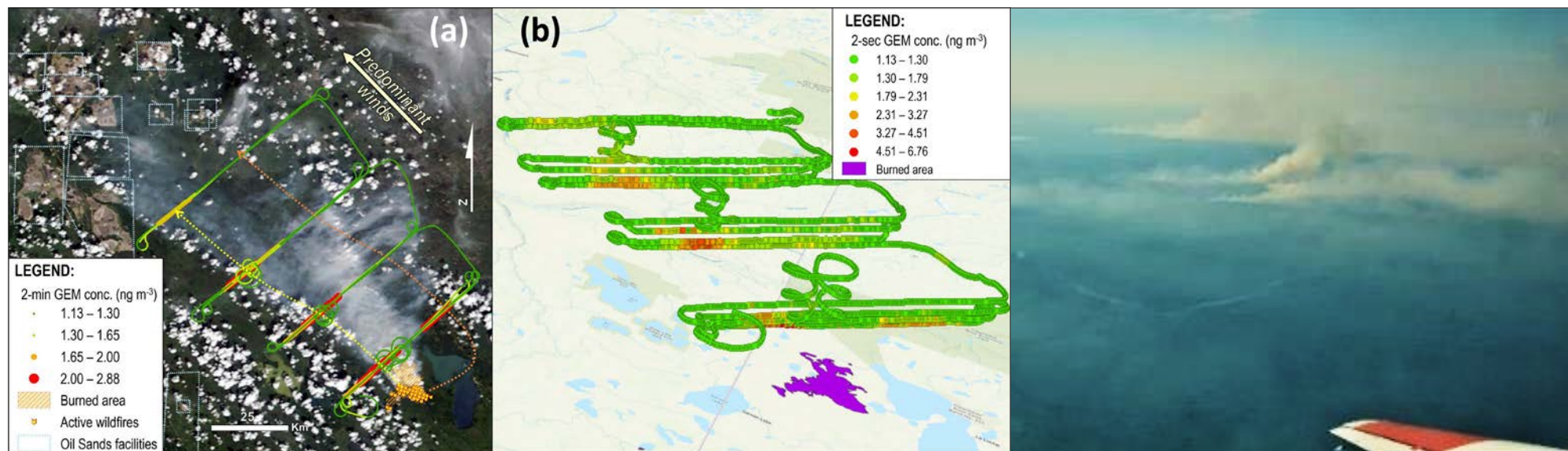
David S. McLagan, Geoff W. Stupple, Andrea Darlington, Katherine Hayden, and Alexandra Steffen ✉



Environment and
Climate Change Canada

Environnement et
Changement climatique Canada

- 2018 Boreal forest fire monitoring flight (Saskatchewan, CAN)
- National Research Council (CAN) research aircraft
 - Tekran 2537X (2-min sampling resolution)
 - Suite of other advanced gas/particulate instruments
- GEM enhanced by $\approx 2.5x$ background ($\approx 6x$ based on 2-sec CO data)
- Emissions estimate: 21 (± 10) kg of Hg released from fire
- Hg taken up from air, fire returns Hg to air: biogeochemical cycle
- Challenges: logistics, speciation data, emissions by biome?
- Climate change + wildfire suppression = bigger, more intense fire



Hg polluted sites: Field lab for Hg cycling

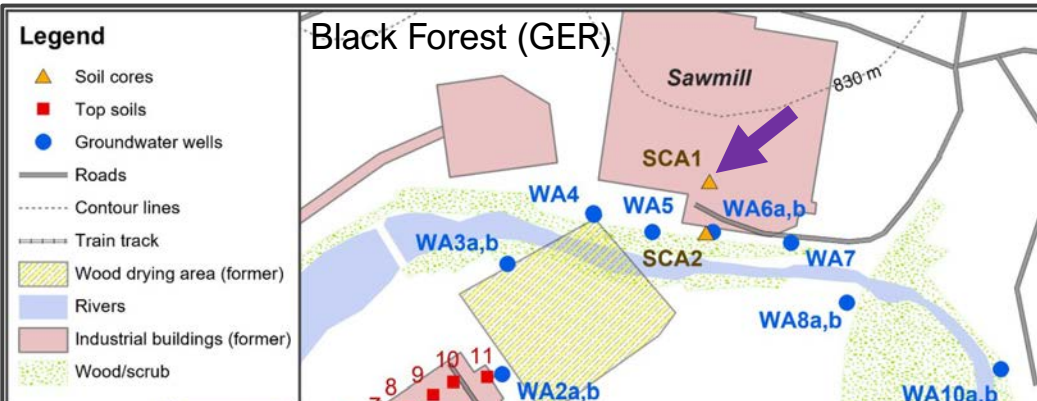


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DOI: [10.1039/D1EM00368B](https://doi.org/10.1039/D1EM00368B) (Paper) *Environ. Sci.: Processes Impacts*, 2022, 24, 1406-1429

Demystifying mercury geochemistry in contaminated soil-groundwater systems with complementary mercury stable isotope, concentration, and speciation analyses[†]

D. S. McLagan[‡], L. Schwab[‡], J. G. Wiederhold[‡], L. Chen[‡], J. Pietrucha[‡], S. M. Kraemer[‡] and H. Biester^{*‡}

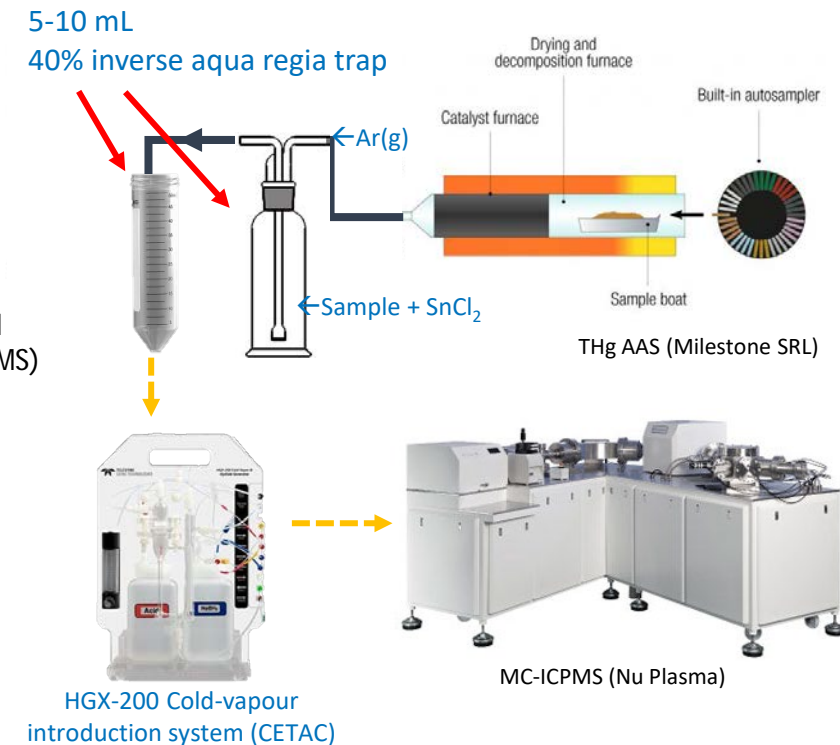


- Industrial use of HgCl₂ to prevent wood rot
 - HgCl₂ highly soluble
- Hg pollution: ≈20T of Hg lost to local soil/groundwater



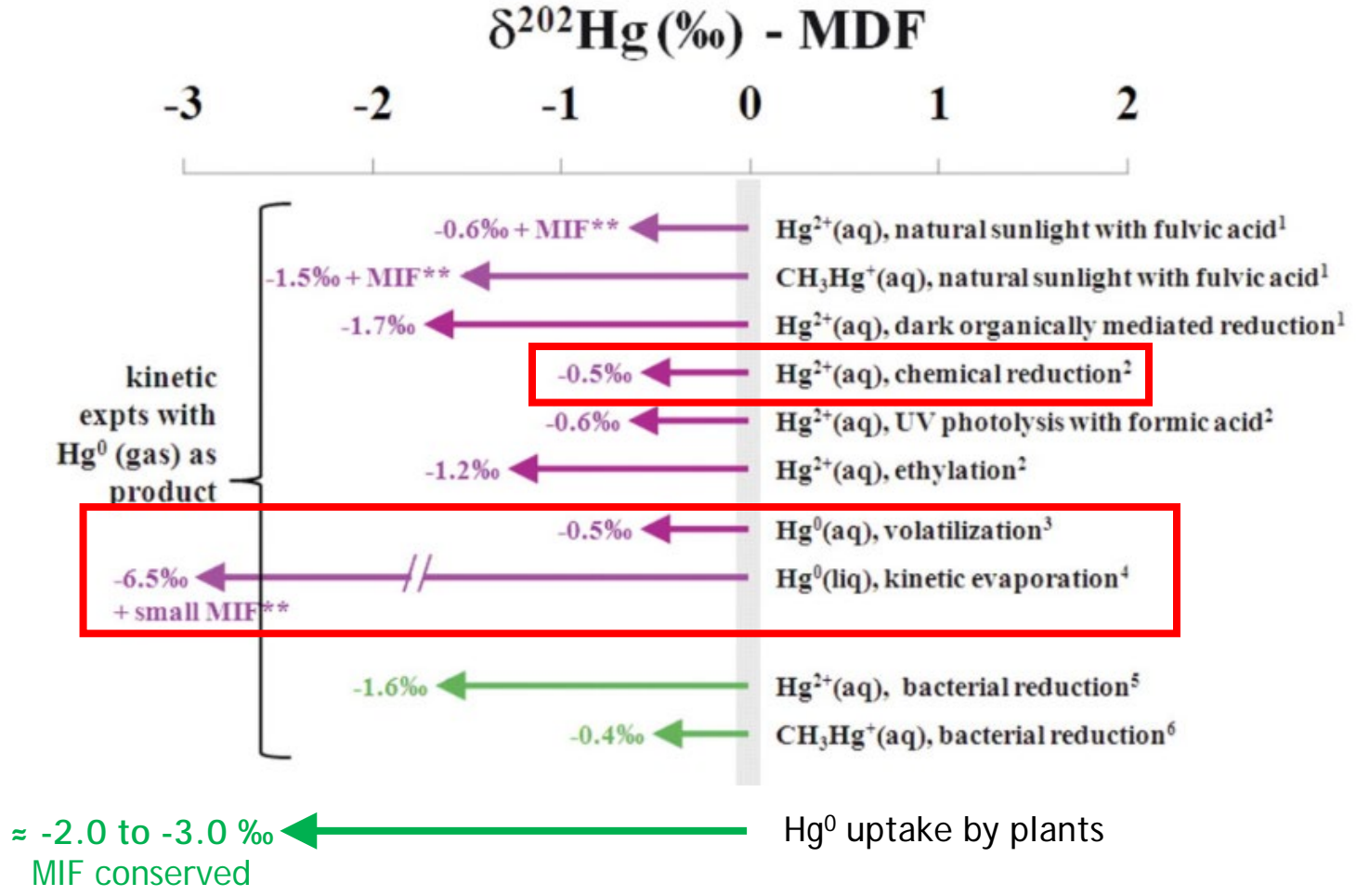
Methods:

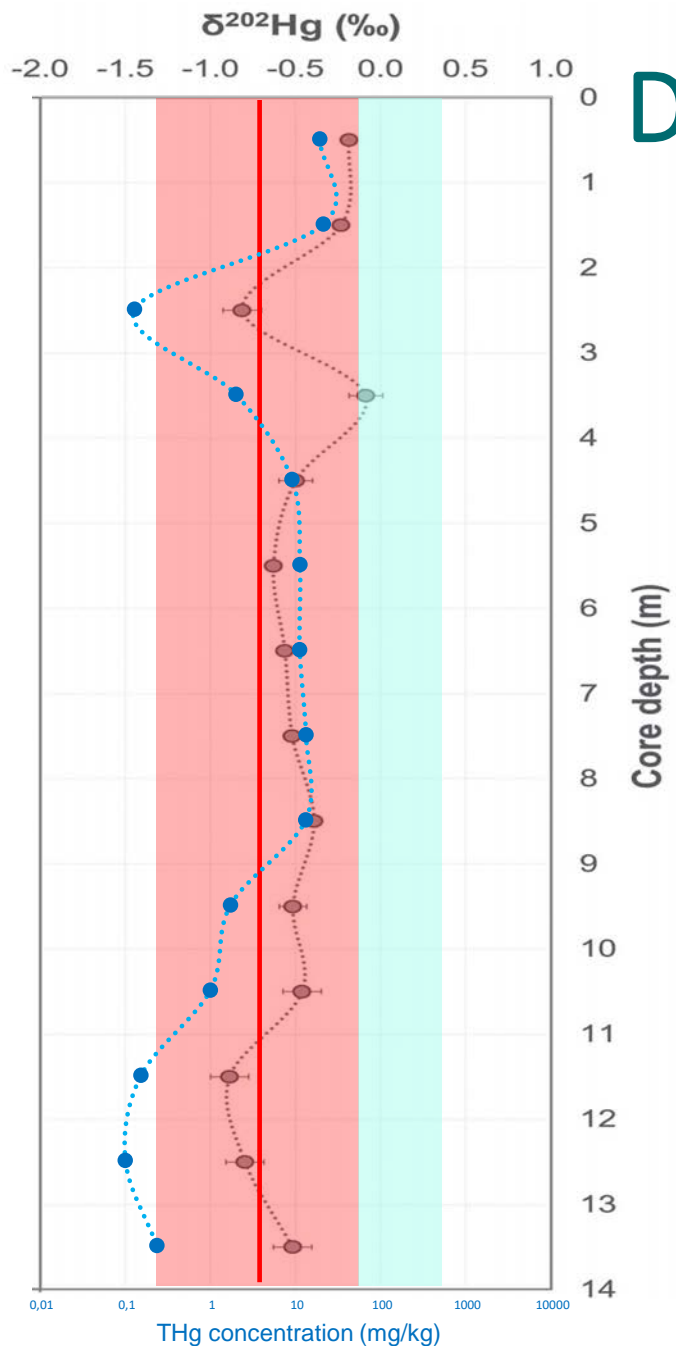
- Total Hg (THg) analyses:
 - Thermal decomp., amalgam., AAS (USEPA Method 7473)
- Hg stable isotope analyses:
 - Multi-collector, inductively coupled plasma mass spectrometer (MC-ICPMS)
- Digestion *or* Combust-and-trap Hg pre-concentration step
- Purge-and-trap used for matrix purification



[very quick] Summary of Mercury Stable Isotopes

- 7x Hg stable isotopes
(6 with measurable abundances)
- Large mass dependent fractionation (MDF) and mass independent fractionation (MIF) in the environment
- MDF - light isotopes move faster, react more, change phase more





Do current isotopes reflect historical Hg use?

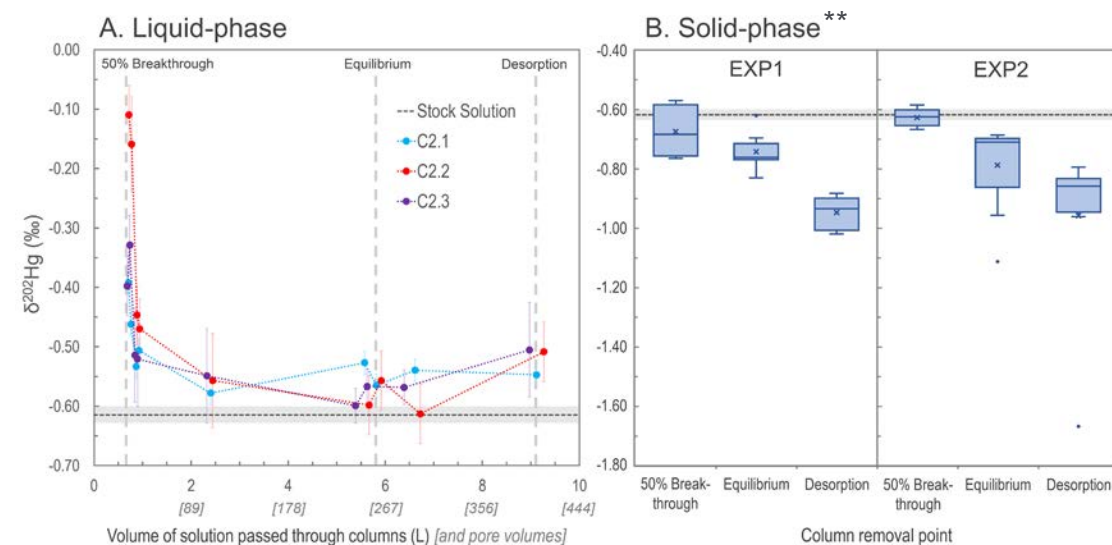
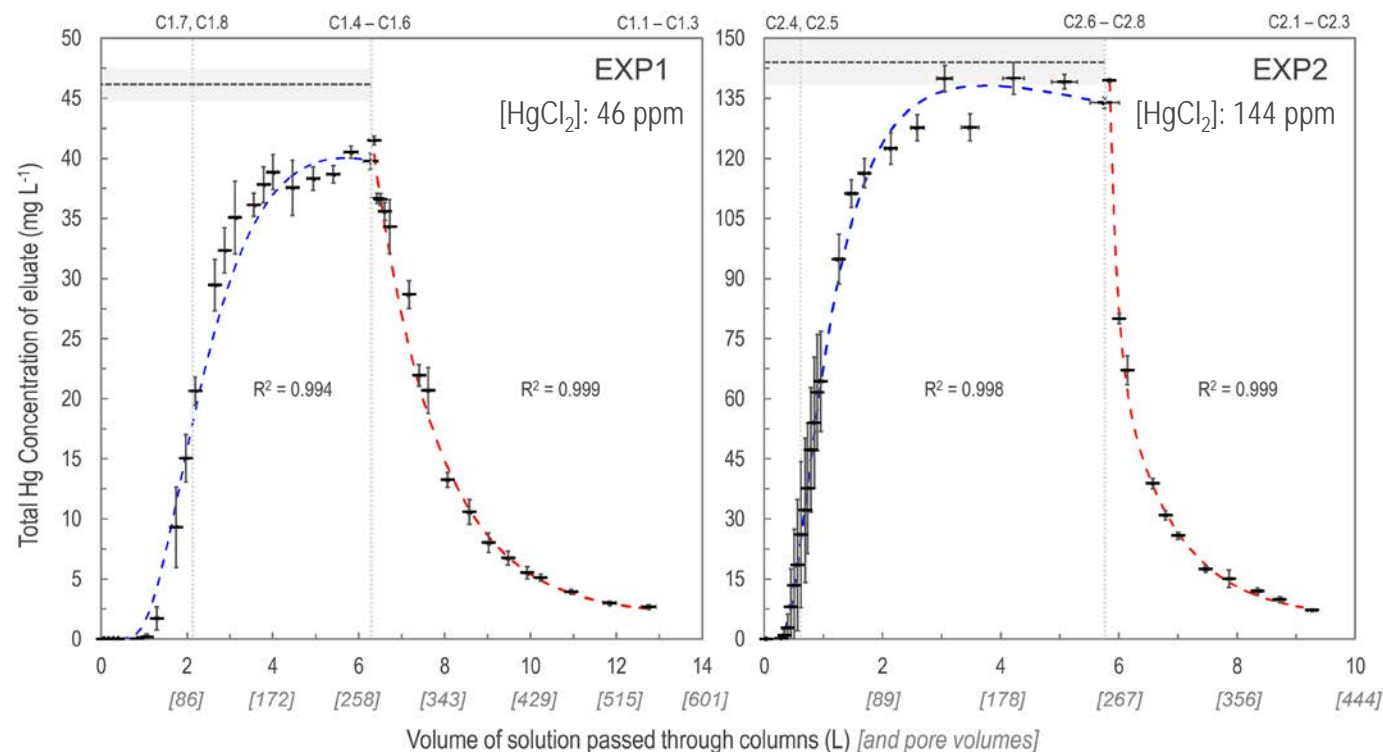
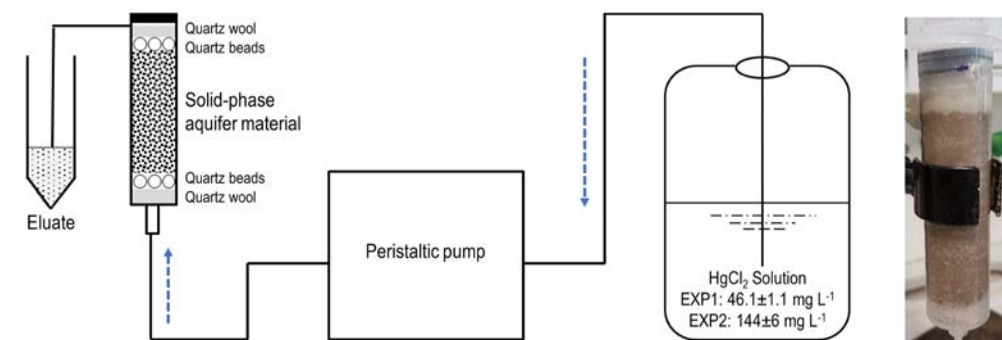
- THg up to 100-150 mg kg⁻¹ (ppm) in soil cores
- Highly polluted samples:
MDF δ²⁰²Hg ≈ -0.2 to -0.1 ‰
- Original stock from Hg mines: Hg⁰
 - MDF δ²⁰²Hg = -0.7 ± 0.6 ‰ (1SD of measured values)
- Hg stocks variable / potential change in sources
- Groundwater THg remains high
 - up to 300 μg L⁻¹ (*nearby well*)
 - MDF δ²⁰²Hg ≈ -0.1 to 0.4 ‰

Recreating contamination

- Column experiments used to simulate original contamination at HgCl_2 contaminated sites
- “S-shaped” sorption; exponential decay desorption
 - Heavy isotopes in liquid-phase
 - light isotopes in solid-phase

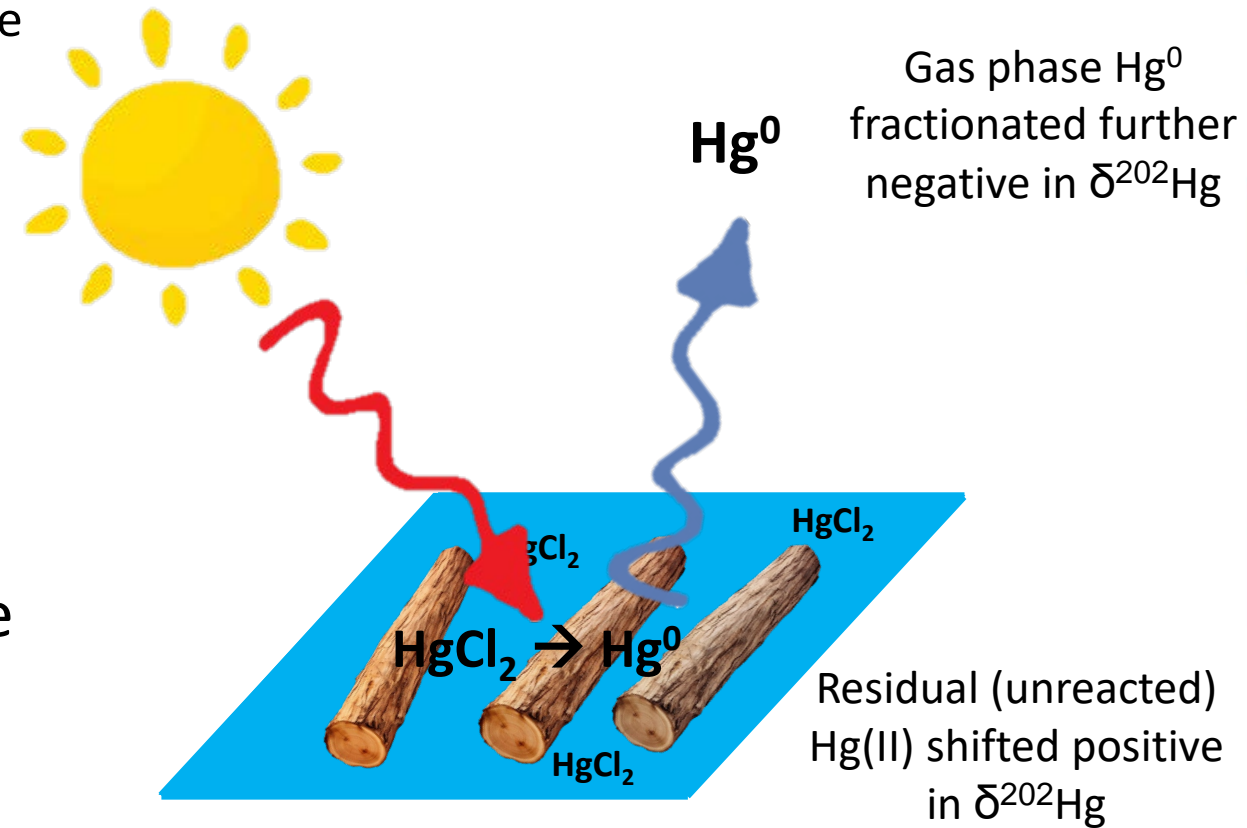
Organic matters, but inorganic matters too: column examination of elevated mercury sorption on low organic matter aquifer material using concentrations and stable isotope ratios

David S. McLagan ✉, Carina Esser, Lorenz Schwab, Jan G. Wiederhold, Jan-Helge Richard, and Harald Biester



Do processes overprint source isotopes?

- Hg(II) can readily be reduced to Hg⁰
 - Photo-, biotic-, (dark) abiotic-reduction all possible
- Hg⁰ is highly volatile escapes into the atmosphere
- Hg MDF signatures in contaminated soils and groundwater **DO NOT** represent original Hg stock used at the site.
- Highlights challenges of Hg stable isotope source tracing
- How could we find “*the smoking gun*”?



Original HgCl₂ industrial use (*Kyanisation*)

Growing archives: Hg Dendrochronology

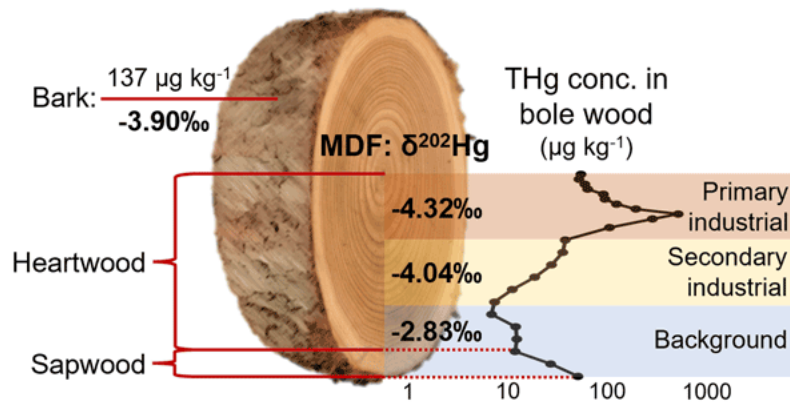


Articles / Volume 19, issue 17 / <https://doi.org/10.5194/bg-19-4415-2022>

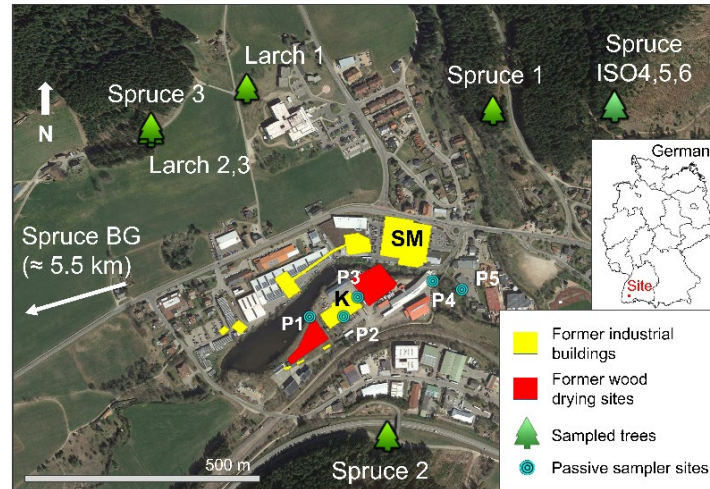
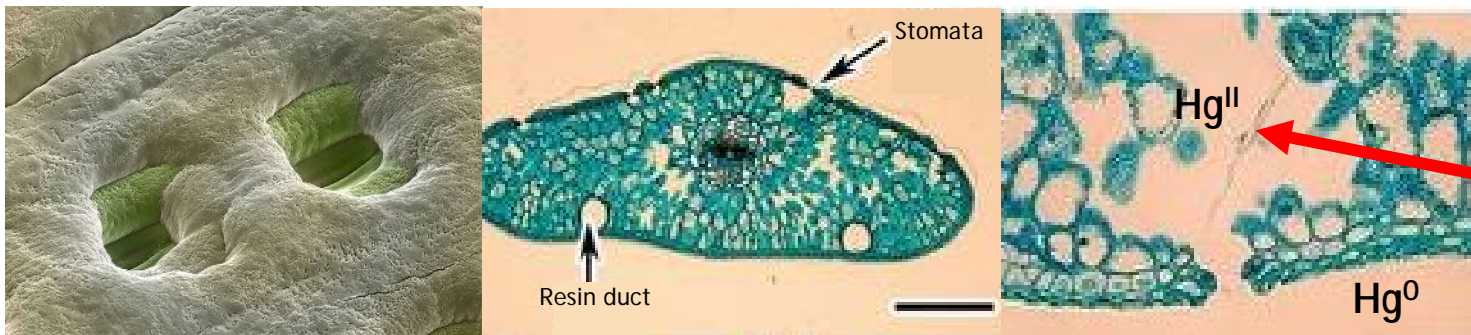
Biogeosciences

Internal tree cycling and atmospheric archiving of mercury: examination with concentration and stable isotope analyses

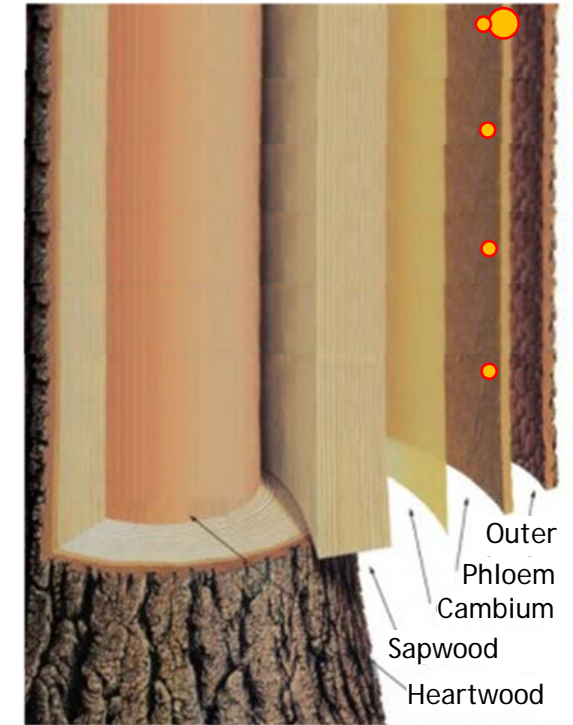
David S. McLagan ★, Harald Biester, Tomas Navrátil, Stephan M. Kraemer, and Lorenz Schwab ★



Needle of Norway Spruce (*Picea abies*)



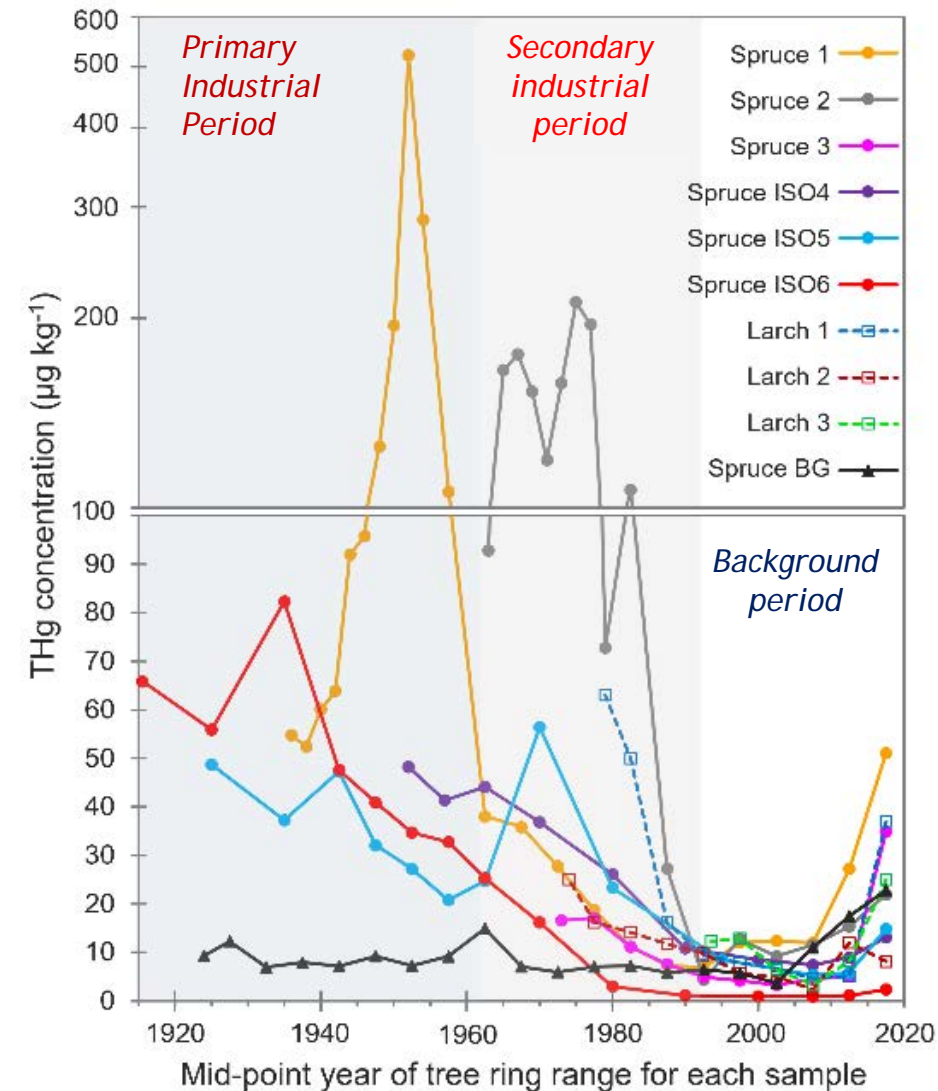
Lateral translocation of Hg^{II} to hydroactive xylem (sapwood) during phloem transport



Hg^{II} = ●
 MDF of internal transport/translocation: minimal

Does THg in tree rings correlate with historic Hg use?

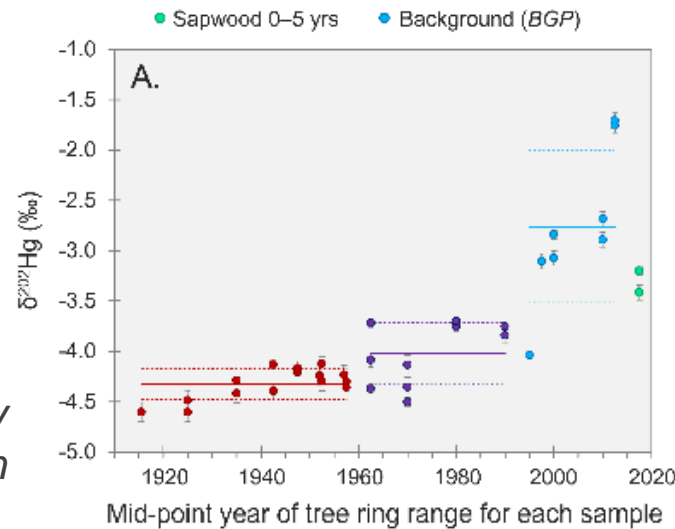
- Three distinct periods of industrial activity:
 1. Site active - timber treated w/ HgCl_2 (1892-1961)
 - Primary industrial period
 2. Site active - no HgCl_2 treatment (1962-1992)
 - Secondary industrial period
 3. Site closed (1992-present) - background period.
- Tree ring Hg reflects industrial activity
 - THg conc. up to $521 \mu\text{g kg}^{-1}$ (Spruce 1)
- Confirms there was substantial historic atmospheric Hg^0 emissions at HgCl_2 contaminated site



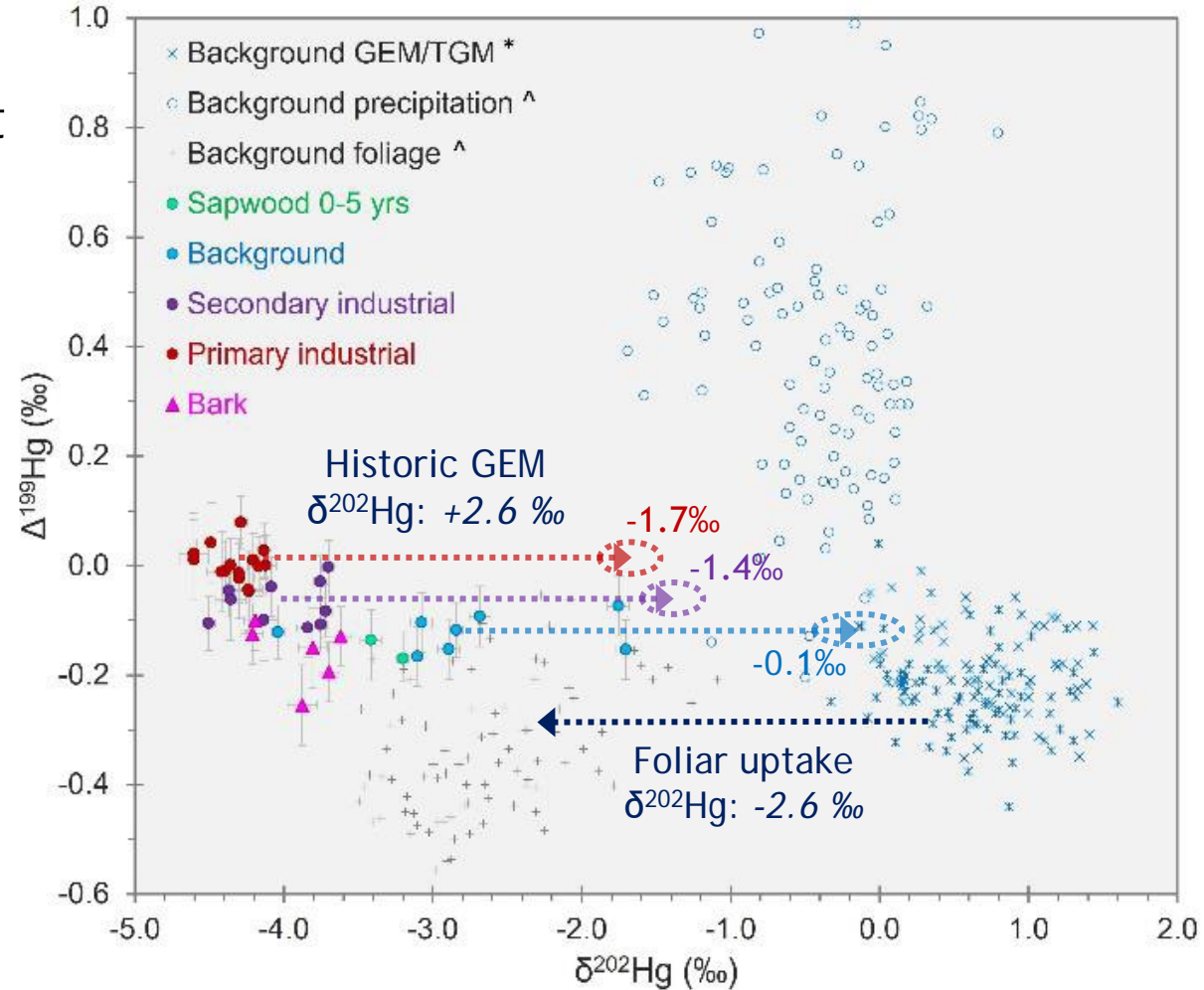
Does THg in tree rings correlate with historic Hg use?

- MIF ($\Delta^{199}\text{Hg}$): MIF from different periods is conserved
- MDF ($\delta^{202}\text{Hg}$): negative values in tree rings reflect foliar uptake
- Add the mean foliar uptake fractionation to tree ring data to estimate historical GEM isotopes
- Lighter Hg^0 in air from industrial periods (vs background period) supports reduction & evasion from site

Plot of MDF ($\delta^{202}\text{Hg}$) by year of tree ring formation

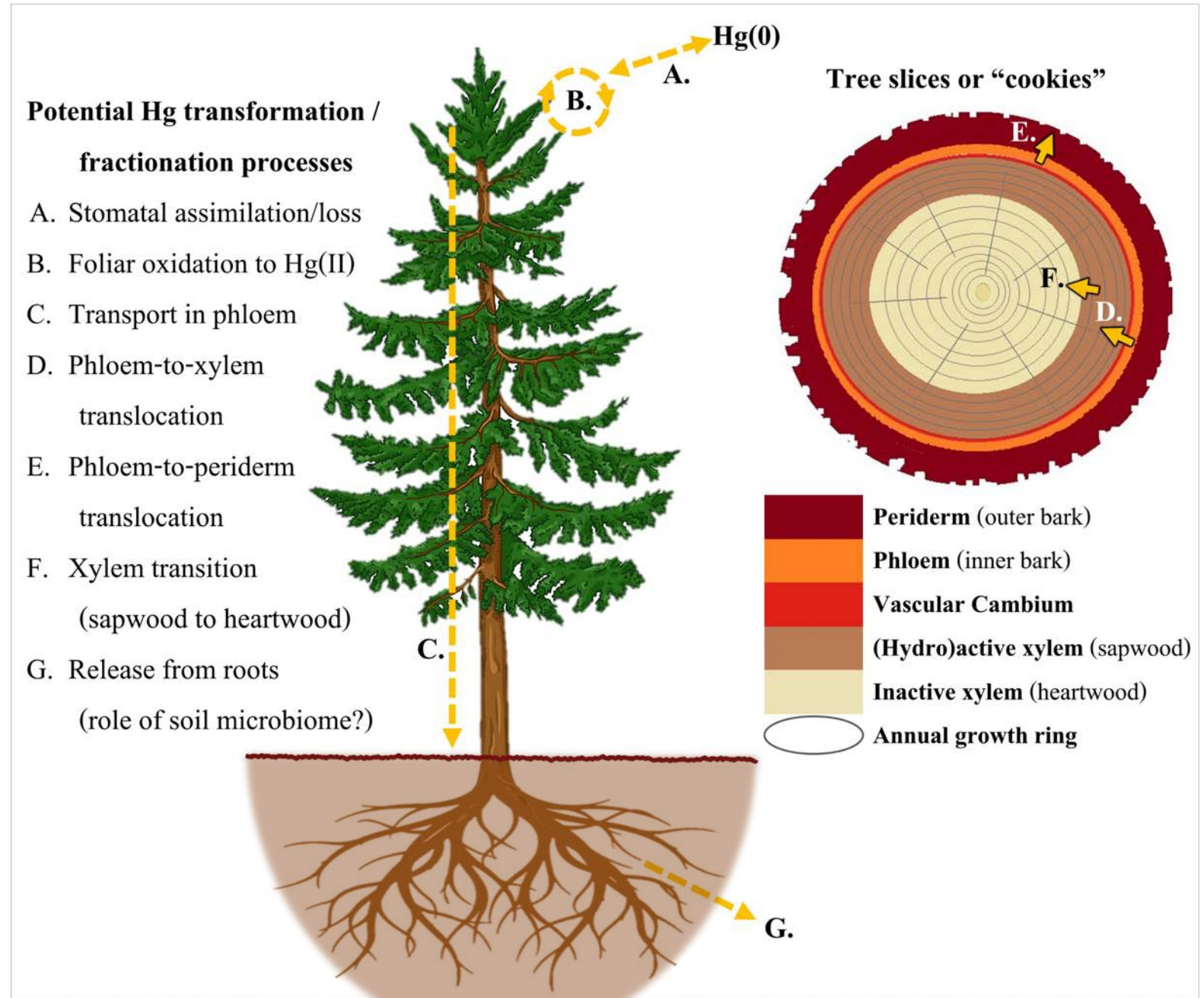


Plot of MIF ($\Delta^{199}\text{Hg}$) against MDF ($\delta^{202}\text{Hg}$)



Where to now?

- What are the key processes controlling Hg cycling in trees?
- What tree species are the best at archiving Hg?
- How else can we apply this method?
- Can we calibrate tree ring THg concentrations to give proxy data for historical GEM conc. in air?
 - *Provide model evaluation?*



Characterizing Geogenic Emissions of Hg

ACS Publications ACS Earth and Space
Most Trusted. Most Cited. Most Read. Chemistry

Measurement of Atmospheric Mercury over Volcanic and Fumarolic Regions on the North Island of New Zealand Using Passive Air Samplers

Meng Si, David S. McLagan*, Agnes Mazot, Natalie Szponar, Bridget Bergquist, Ying Duan Lei, Carl P. J. Mitchell, and Frank Wania*

Cite this: *ACS Earth Space Chem.* 2020, 4, 12, 2435–2443

Publication Date: December 4, 2020

<http://doi.org/10.1021/acsearthspacechem.0c00274>

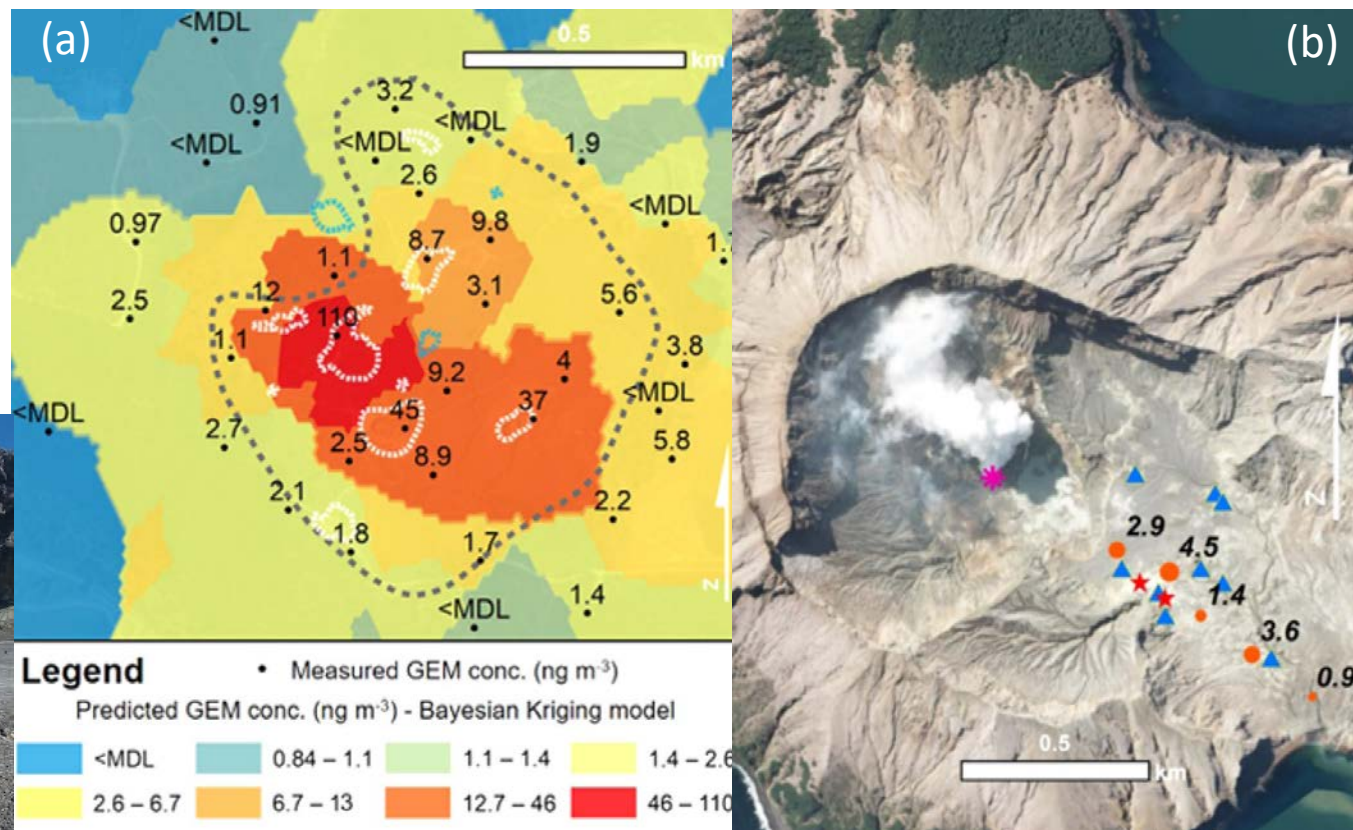
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(a) Karapiti (Craters of the Moon) fumaroles

(b) Whakaari (White Island) volcano



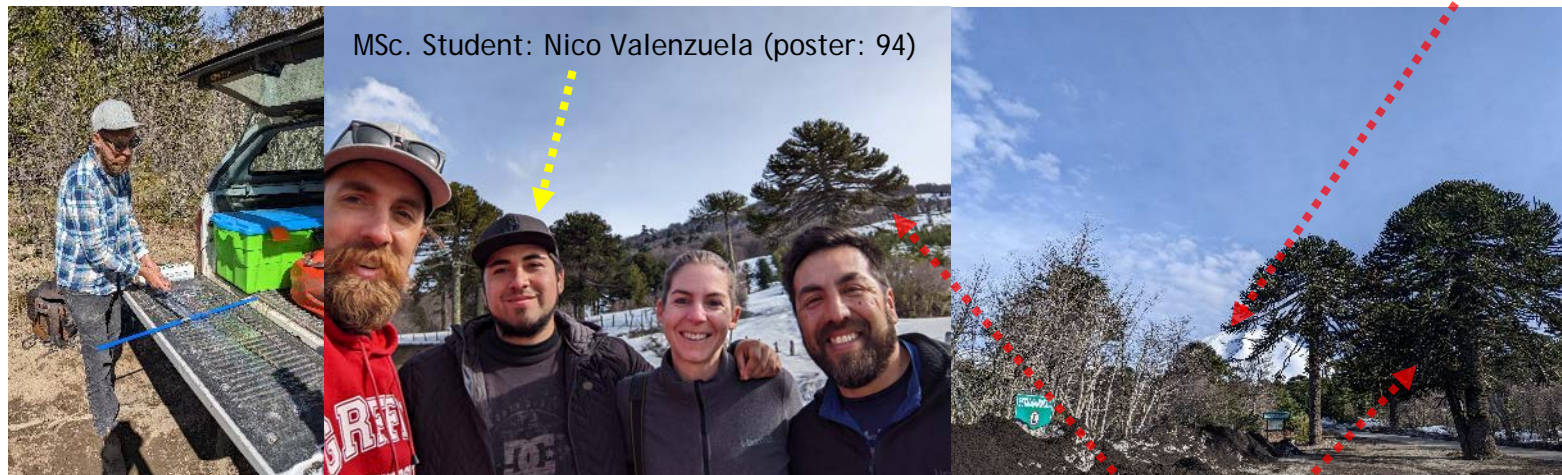
- Active and passive air measurements provide some information on current emissions
- What about past emissions?

Dendrochronologies of volcanic Hg emissions

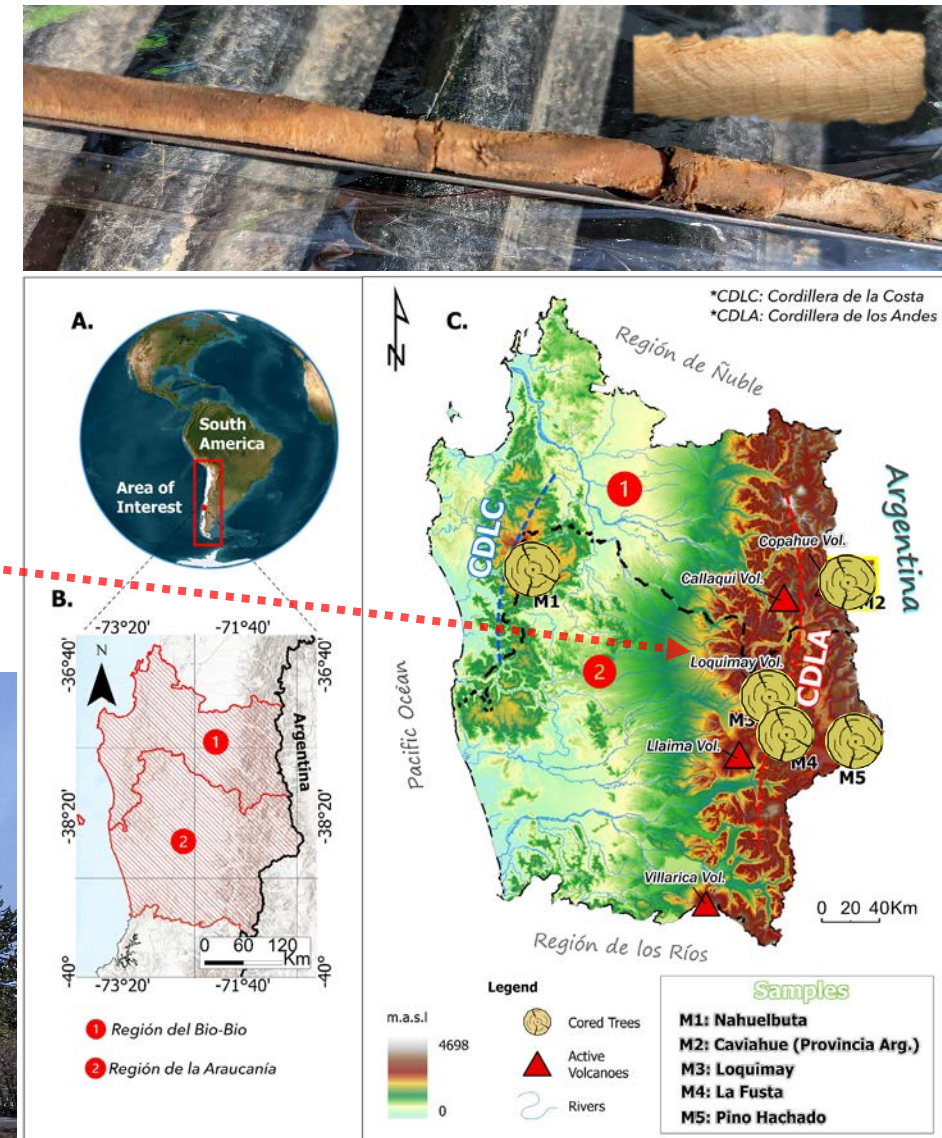
- Use *Araucaria araucana* (monkey puzzle trees) to characterize historic volcanic Hg emissions in south-central Chile (& Argentina)
 - 4 sites on leeward side of active volcanoes
 - Old (can be >1000 y.o.), high altitude (≈ 1000 -2000m a.s.l.) trees
- Assess Southern Hemisphere atmospheric Hg pre- and post-colonization and industrialisation using *A. araucana* at control site (coastal range)
- Study the impacts of eruptions and earthquakes on *A. Araucana* growth rates using ring width data
 - Seismic activity can impact tree growth

- Collaboration:  Universidad Andrés Bello

Volcán Loquimay
(Eruptions: 1887, 1933, 1988)



MSc. Student: Nico Valenzuela (poster: 94)

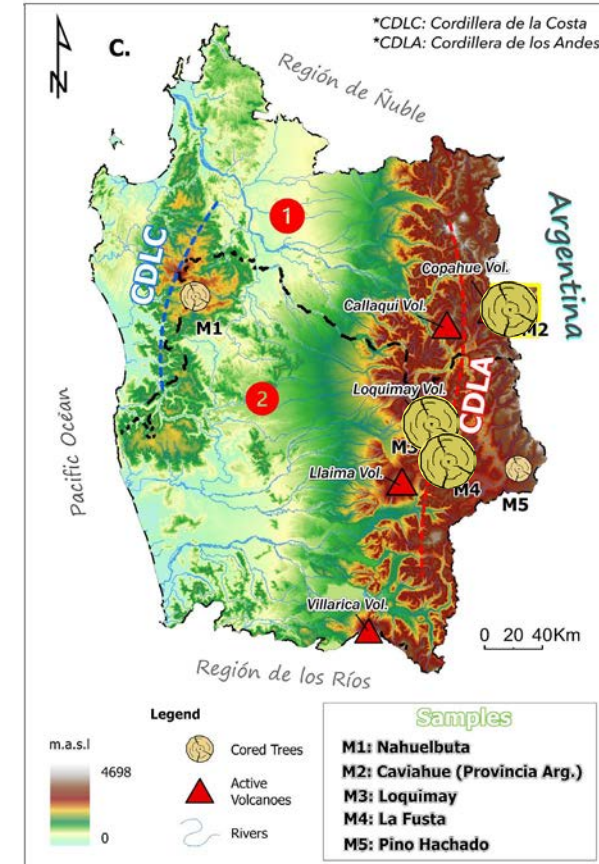
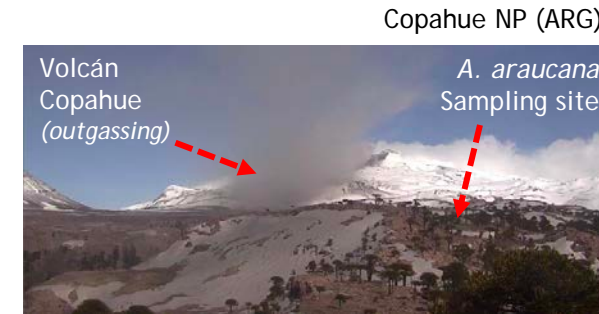
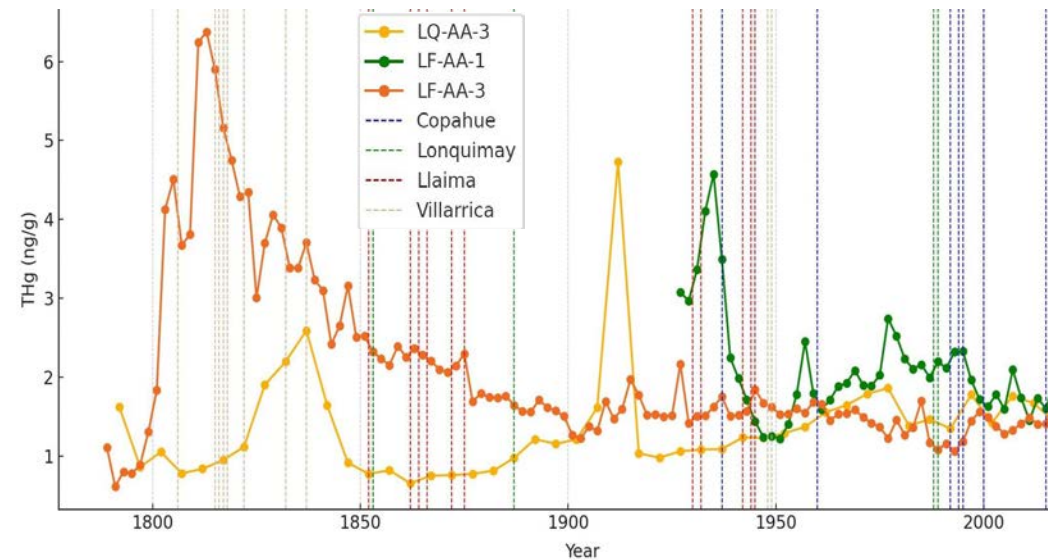


Dendrochronologies of volcanic Hg emissions

- Early focus on (non-destructive) ring widths: $\approx 35/46$ cores measured (uncorrected)
- Groupings of $\approx 2-10$ annual rings analysed for THg (*depending on period activity*)
 - Site averaging for ring widths and [THg] (*10 tree cores per site*)
- 3/46 cores analysed for THg
 - La Fusta and Lonquimay sites - little correlation with eruption records
 - Trees on mid-to-lower slopes may miss Hg signal from large, convective eruptions
 - (Non-eruptive) outgassing will be considered
- Sampling at Argentinian site (Copahue NP; *high altitude, leeward*) in Oct. 2024

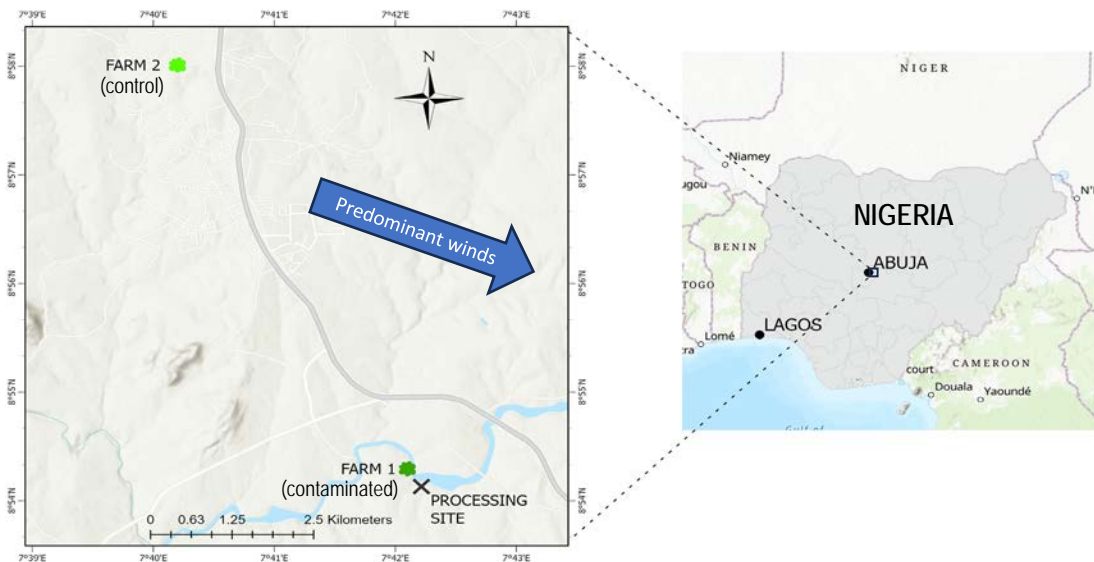
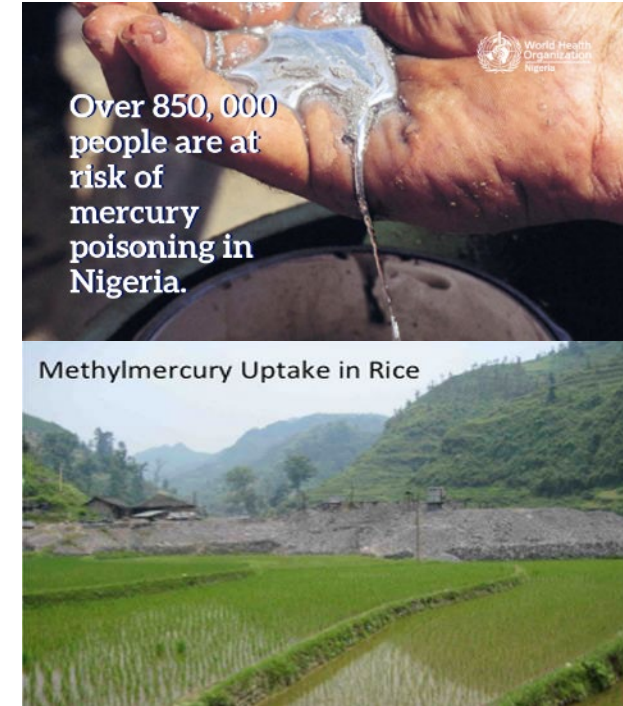


Velmex TA tree ring width measurement system



Hg uptake by crops at Nigerian ASGM site

- Artisanal Small-scale Gold Mining (ASGM) now the largest emitter of Hg to the environment globally
- Human health studies focus on fish consumption & inhalation exposures
 - Some studies on rice: Hg methylation potential in rice paddies
- What about the atmospheric pathway for other staple crops?
- Study of ASGM-derived Hg uptake in cassava, peanuts (groundnuts), and maize (corn) in Nassarawa, Nigeria



MSc. Student: Excellent Eboigbe (poster: 47)



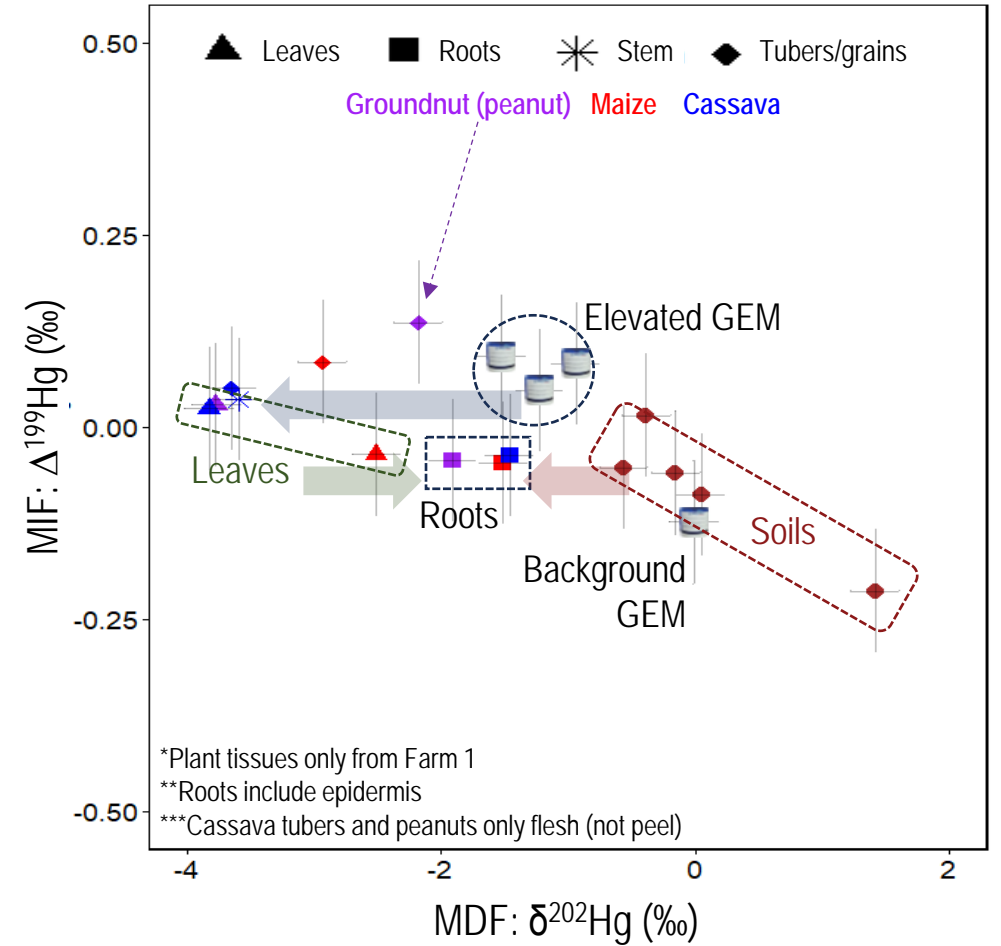
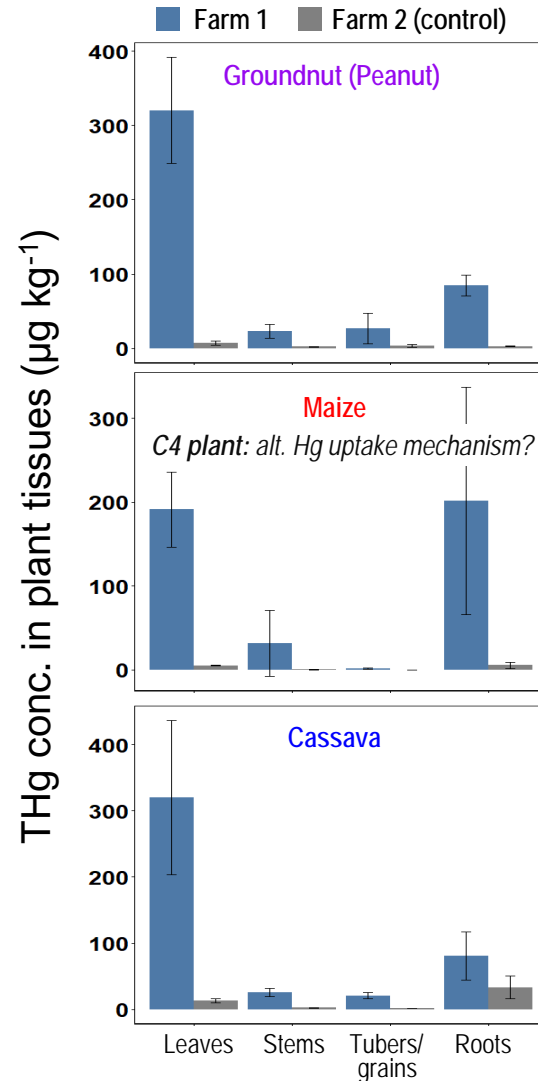
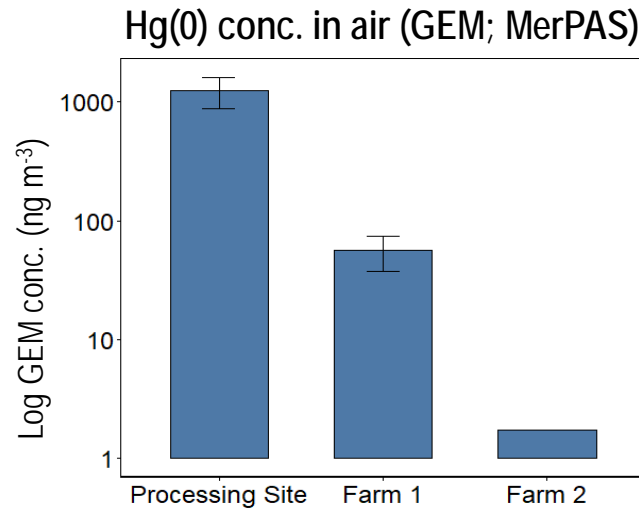
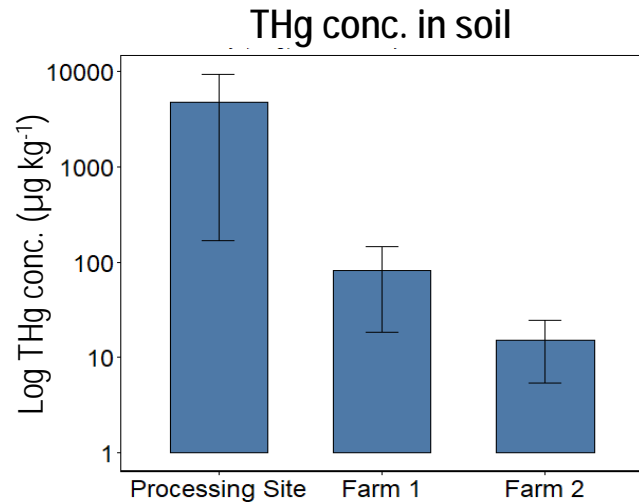
Mr. Nnamdi Anene; Dr. Mary A. Odukoya

Collaboration:



Hg uptake by crops at Nigerian ASGM site

1. Assess Hg pollution at ASGM & farms
2. Assess [THg] in plant tissues
3. Assess Hg uptake & processing with stable isotopes



Thanks and acknowledgments

My supervisors:



Dr. Bengtson-Nash (Griffith Uni)



Dr. Wania (Uni Toronto)



Dr. Mitchell (Uni Toronto)



Dr. Steffen (ECCC)



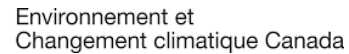
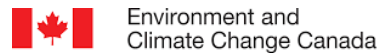
Dr. Biester (TU-Braunschweig)



Steering committee

My award nominators

My collaborators:



and funding sources:



My Research Group:



My Family:





ICMGP 2024

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Fin.

Wildfire and Hg

- Emissions ratios (ERs) used to make emissions estimates (Q):

$$Q_{GEM} = Q_{CO} * ER_{GEM:CO}$$

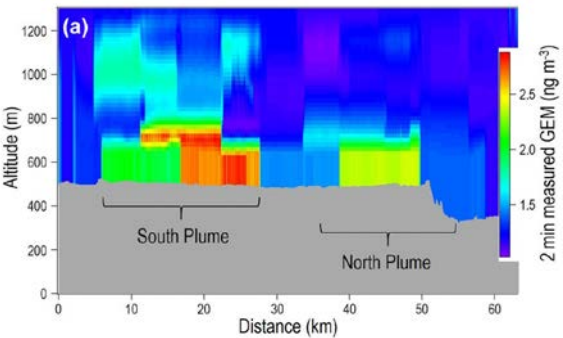
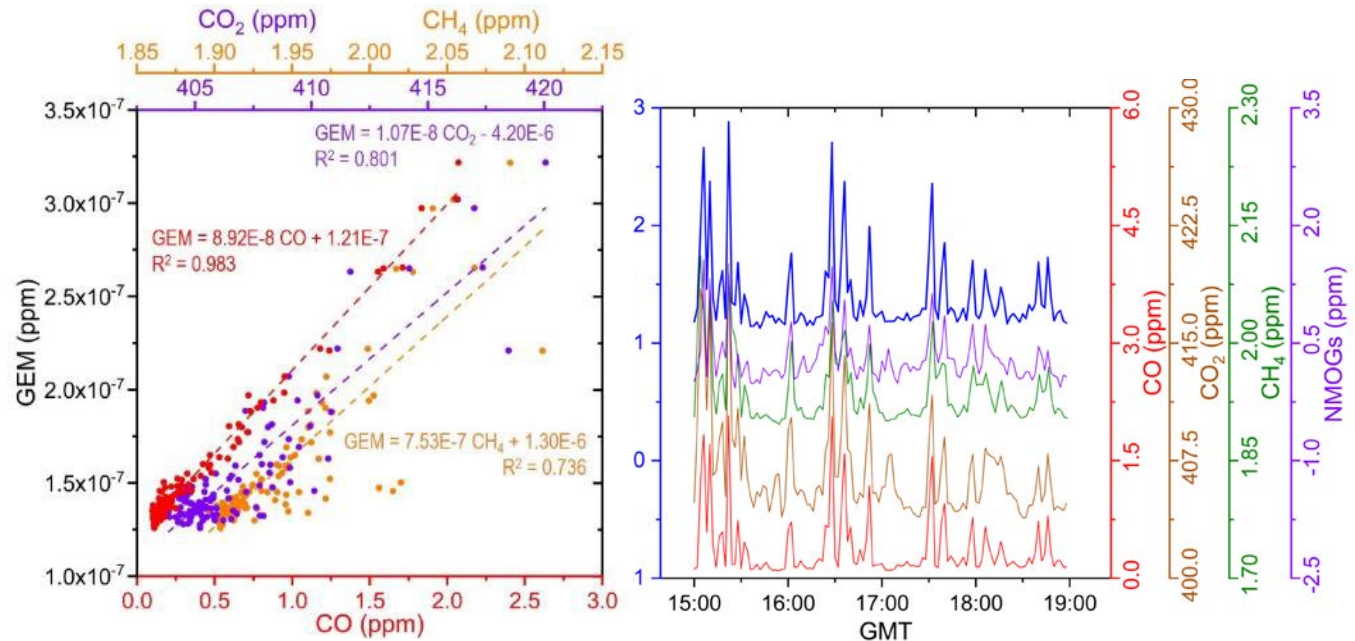
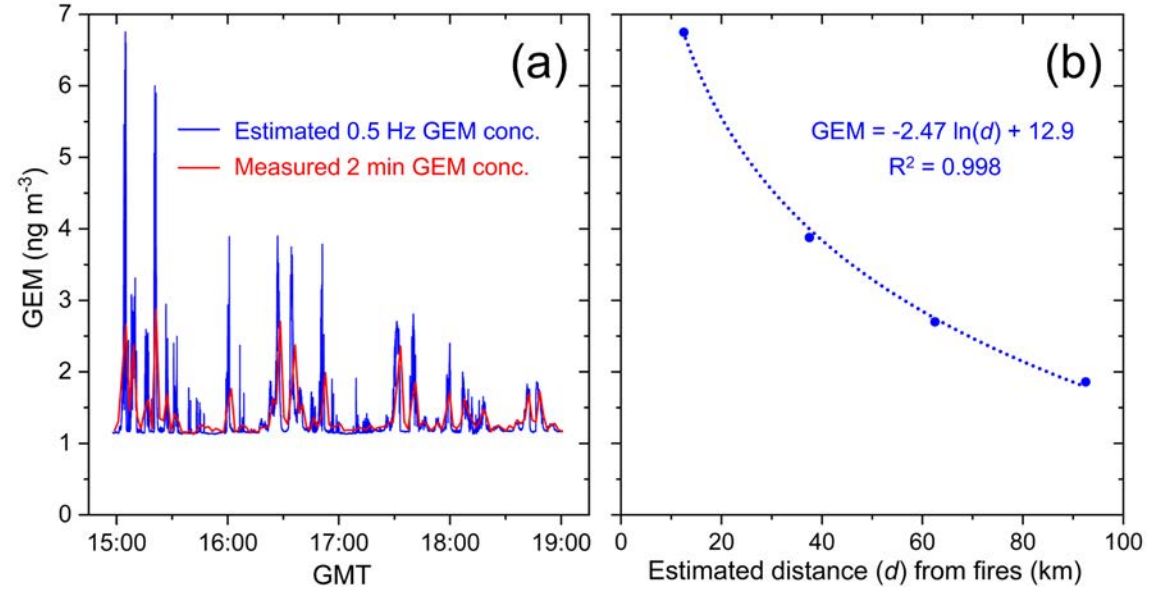
- Emissions estimates can also be calculated from emissions factors (EFs)

[mass of contaminant released per mass biomass burned (g kg⁻¹)]

$$EF_{GEM} = \frac{\Delta GEM * MW_{GEM}}{[(\Delta CO + \Delta CO_2 + \Delta CH_4 + \Delta C_{other}) * MW_C]} * C_{biomass} * 1000$$

- Emissions estimates then calculated as such:

$$Q_{GEM} = A * B * F * EF_{GEM}$$

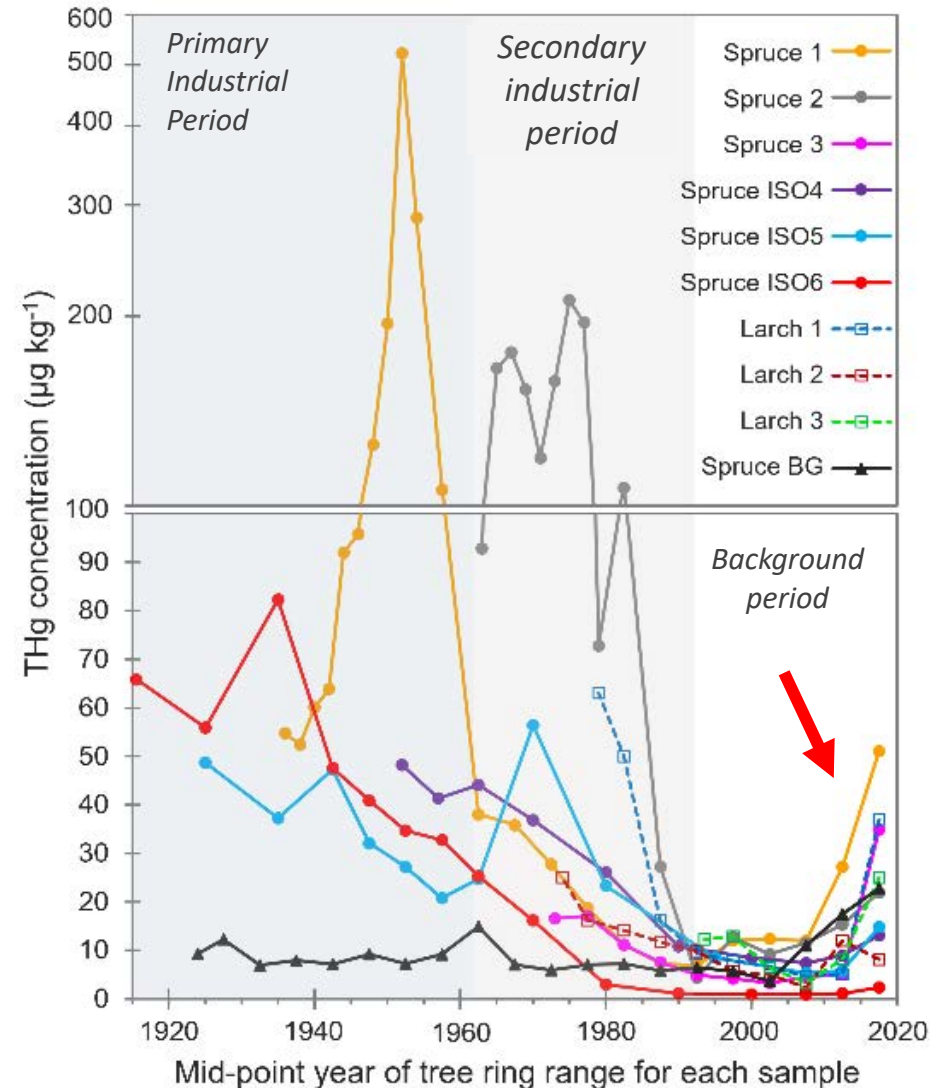
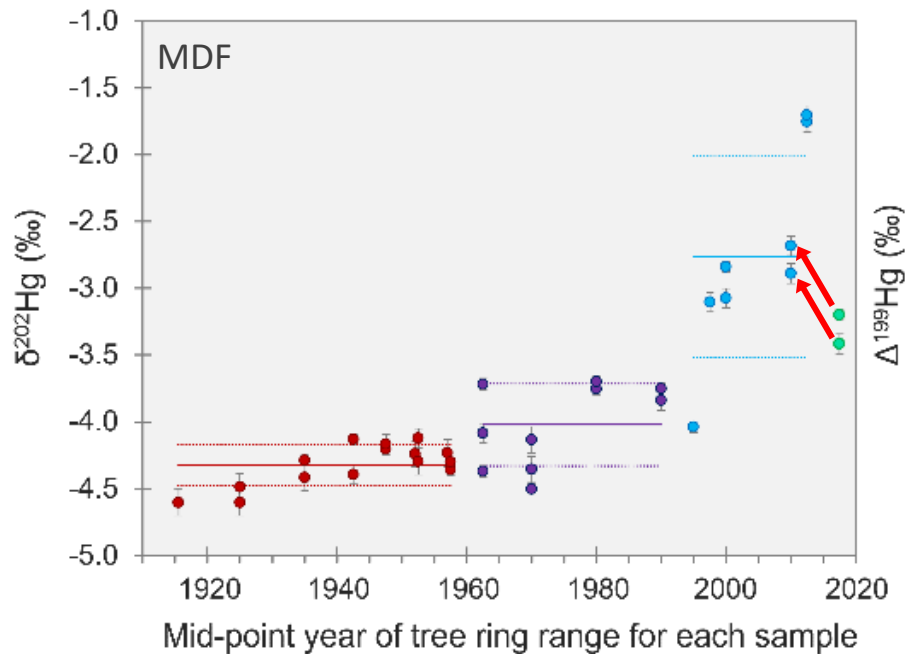


ECCC's TERRA model
(Top-down emissions Rate Retrieval Algorithm)

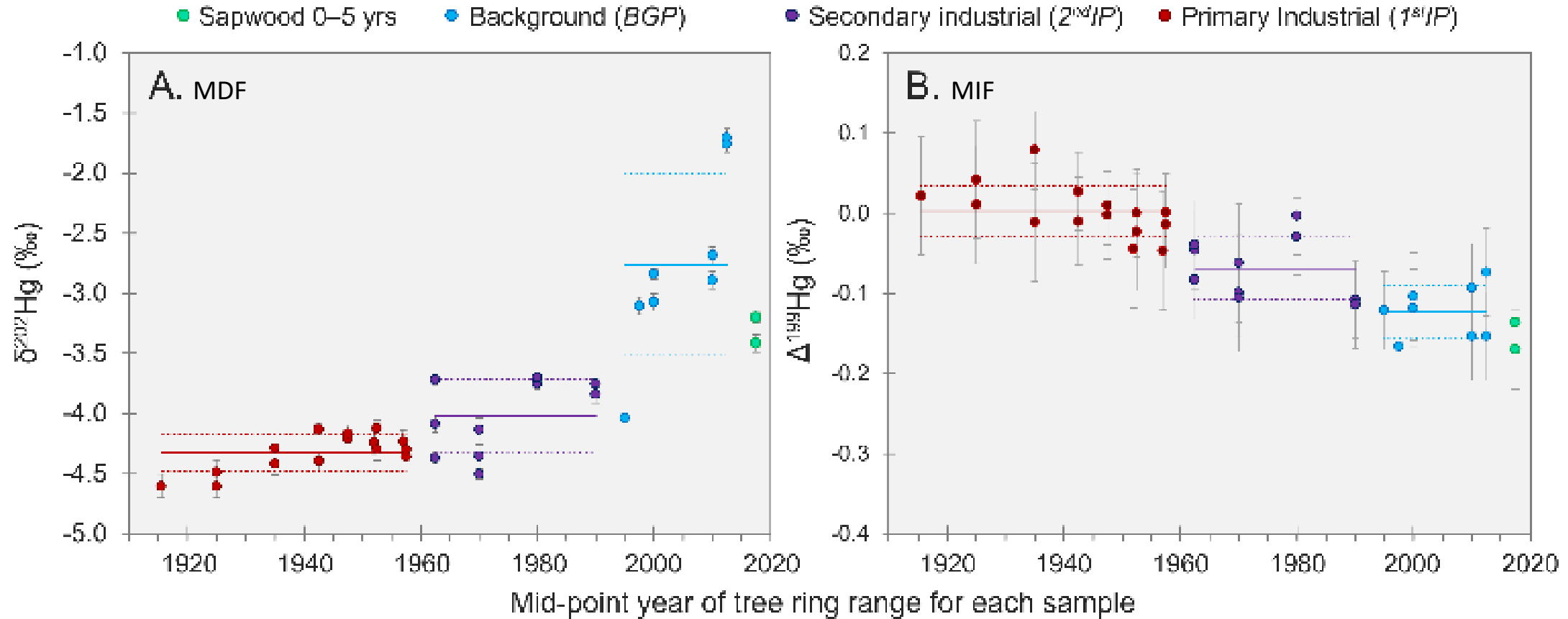
TERRA estimate: 20 (± 7) kg of Hg

Tree physiology: Sapwood enrichment

- ◆ Sapwood tree rings enriched in THg across **ALL** trees (including background spruce tree)
- ◆ More negative $\delta^{202}\text{Hg}$ than adjacent rings (by -0.4‰)



Isotopes in tree rings: source vs process tracing



Introduction → Big Thanks. Humbling award. Farm-Australia; early memory of freshly emerged snakes. Humour: Bob Dylan (literally some Australian mountain range) (1min)

ECCC → Where there is smoke, there is mercury. This made me really start to think about correctly attributing sources (these are fluxes; not emissions)

Where too now as a PI?
Maybe a quick snapshot of FEWA Lab. NZ study had me interested in geogenic sources → I lived in Chile, I have an amigo de mercurio in Chile, Gustavo Chiang. Why don't we see if we can detect volcanic mercury signals in high altitude trees growing in the Andes.

Background → maybe skim through slide automation... humour (1min)
A lot to thank for MerPAS
...maybe just skip...

TUBS → Contaminated site soil-groundwater geochemistry, really deep dive into the capacity of stable Hg isotopes.
Show slide of source attribution not explaining the in-situ measured isotopes

Nico's project: Araucaria Araucana (Monkey Puzzle) dendrochronology.
Preliminary data show some indication of THg increases around periods of elevated volcanic activity. QUESTION for audience: should THg signal in tree rings only correlate with eruptions? Changes in background (population/industry), Outgassing... (show image of Copahue) – we believe this site is our best chance. Also SH background; ring widths and eruptions/earthquakes.

How did I start researching mercury in terrestrial systems?
Mt Amiata, characterizing sources – but distinct concentration drop during the growing season for samples within the forested canopy...same time as work by Daniel Obrist and others that used stable isotopes to show the importance of dry deposition uptake of GEM by vegetations. Hmmm, maybe uptake by trees is actually impacting GEM concentrations below canopy

Hg in trees – ICMGP 14 Krakow, Lorenz and I talking to good friend Tomas Navratil. Helping us identify Larch and Norway Spruce at our site. Harald finding tree slices/cookies → isotope analysis; Low concentrations - lots of trapping. Tree physiological process information we derived inductively from this study.

What about Hg uptake by agricultural crops. Little study (a bit on rice). ASGM – unregulated, often illegal. Show image of agricultural area impacted by ASGM. Observe Hg biogeochem from source to air to crops through crops to edible parts using conc. & isotopes.
Crops near ASGM highly contaminated (control not) Isotopes: BG air heavy, ASGM air moderate; soils moderate, crops light → roots moderate-light Fits story of veg. uptake favours light; lighter industrial signals; soils potential mix of air and soil