



Rotary Kiln, Almaden
Quicksilver County Park



Investigating mercury uptake, release, chemical speciation, and isotope fractionation in native and transplanted lichens at legacy mercury mine and background locations

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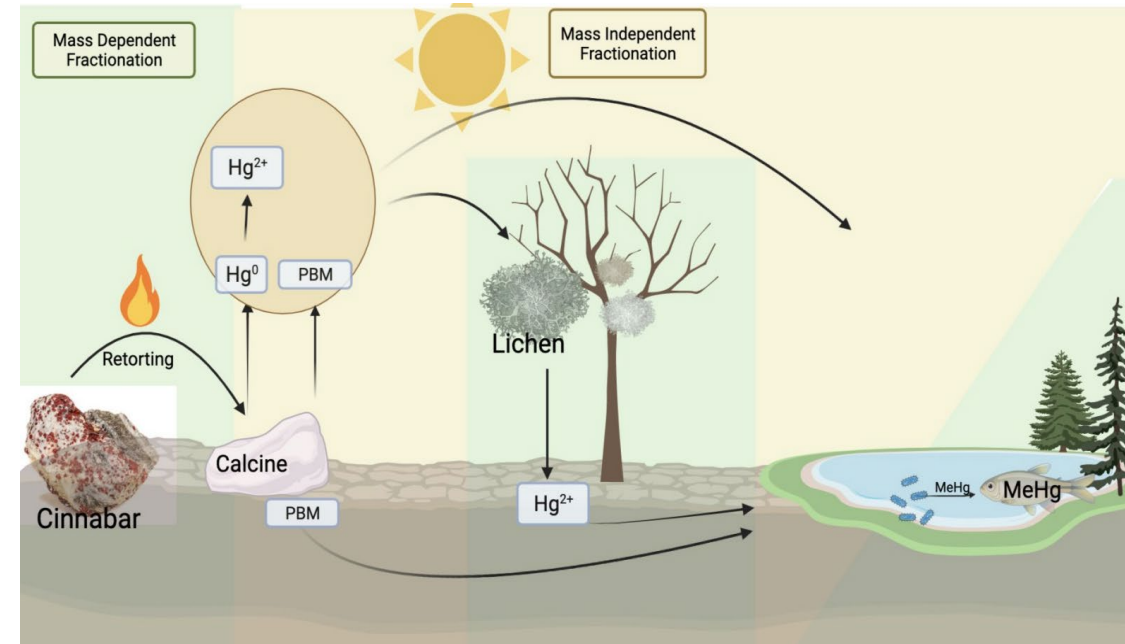
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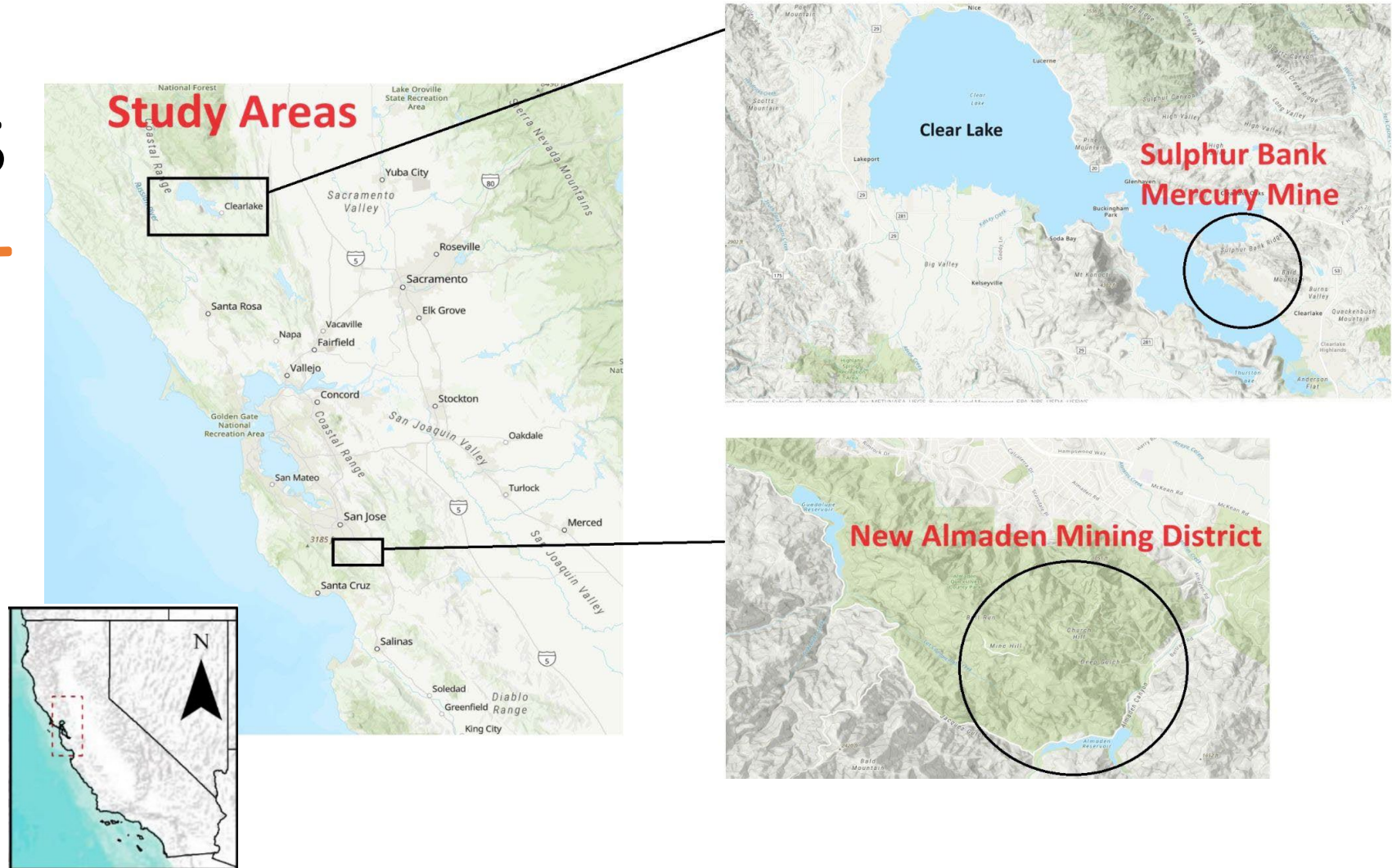
Goals of the study

- Determine the locations of Hg emission hotspots.
- Quantify Hg uptake and/or release rates at different locations.
- Compare Hg uptake rates between lichens and commercially available passive samplers.
- Estimate dry deposition flux to lichens in the mining district.
- Discuss benefits and limitations of using lichens as a bioindicator for this application.



Study areas

- The New Almaden Mining District (NAMD) was North America's largest and most productive mine (1846-1977), producing 38,000 metric tons of mercury, or 5 percent of the world's total mercury.
- The Sulphur Bank Mercury Mine (1865-1957) produced ~7000 metric tons of Hg and caused mine waste to enter Clear Lake. Since 1990 it is an EPA Superfund site.



Ramalina farinacea



Ramalina leptocarpha



Lichens commonly found in the California Coast Range



Ramalina menziesii



Flavopunctelia sp.



Evernia prunastri



Usnea sp.

Sample processing and analysis methods



Lichen homogenization with liquid N₂ and a mortar and pestle

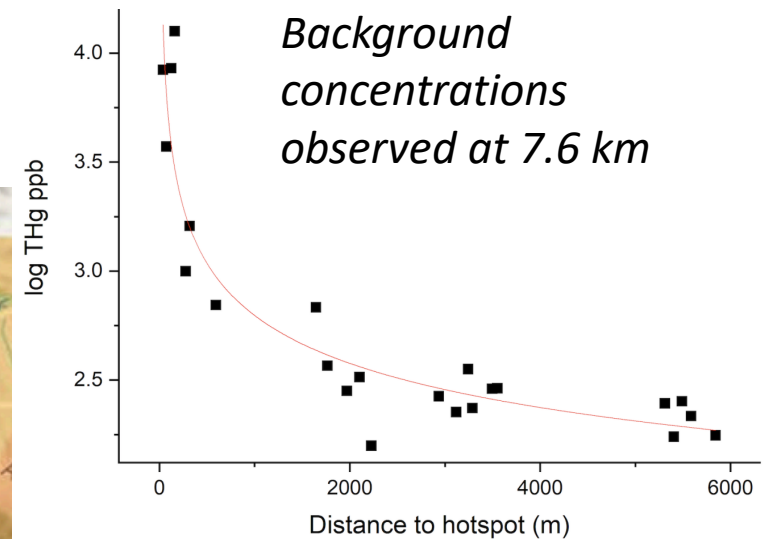
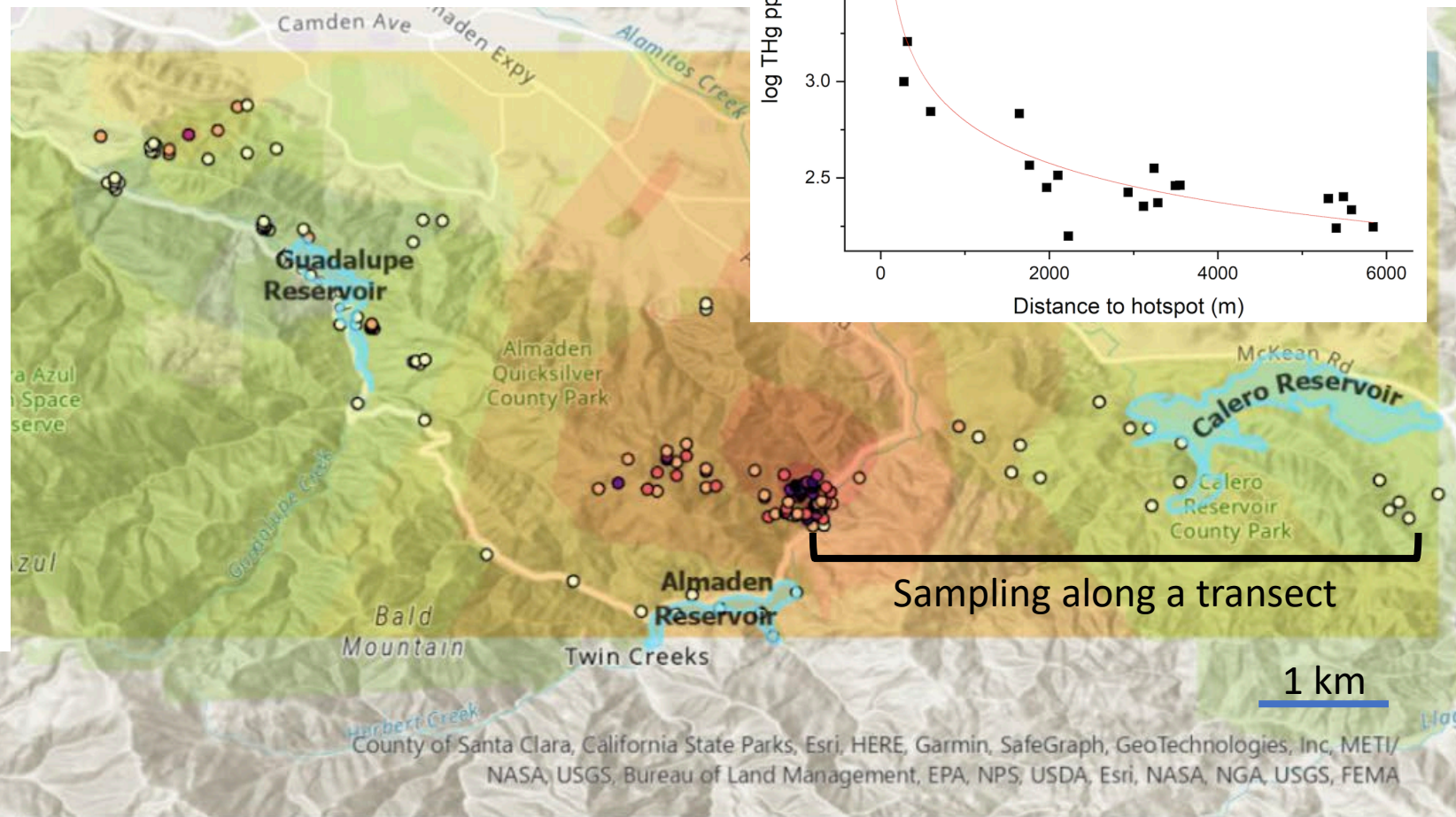
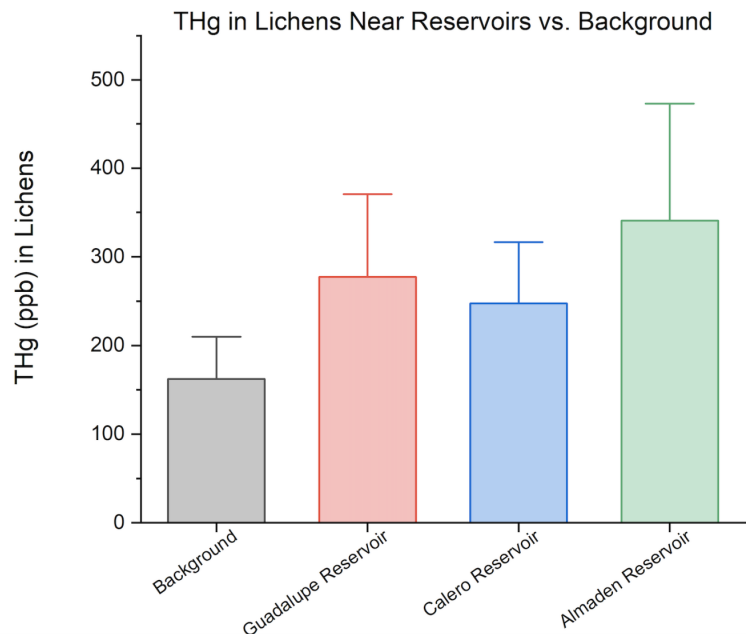


Freeze-drying with a lyophilizer

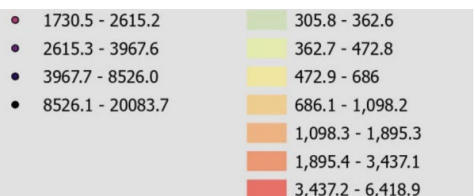


Total Hg quantification with a DMA-80

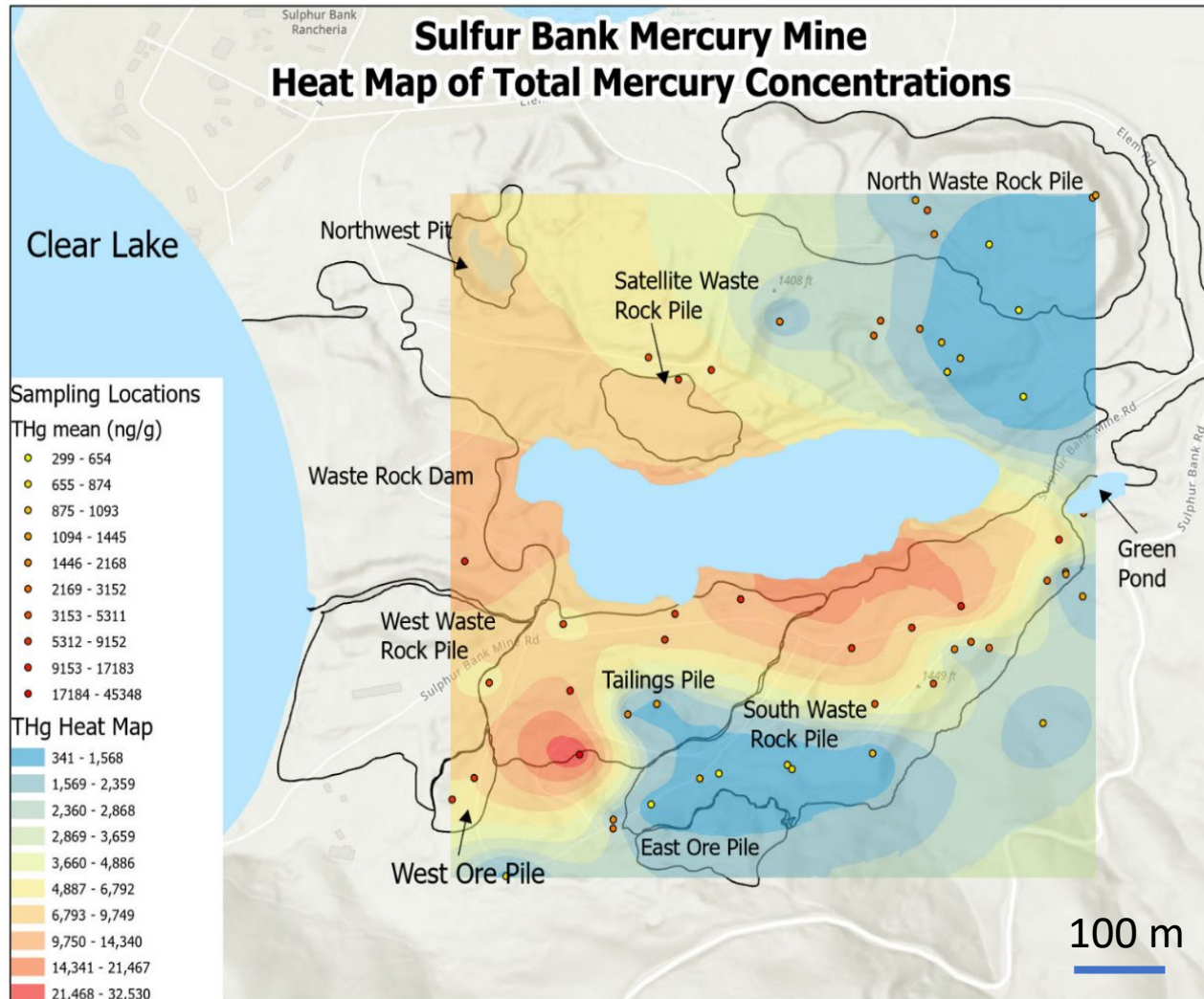
Sampling locations and spatial interpolation of THg in lichens at the NAMMD



Atmospheric deposition from local sources impacting the area's reservoirs

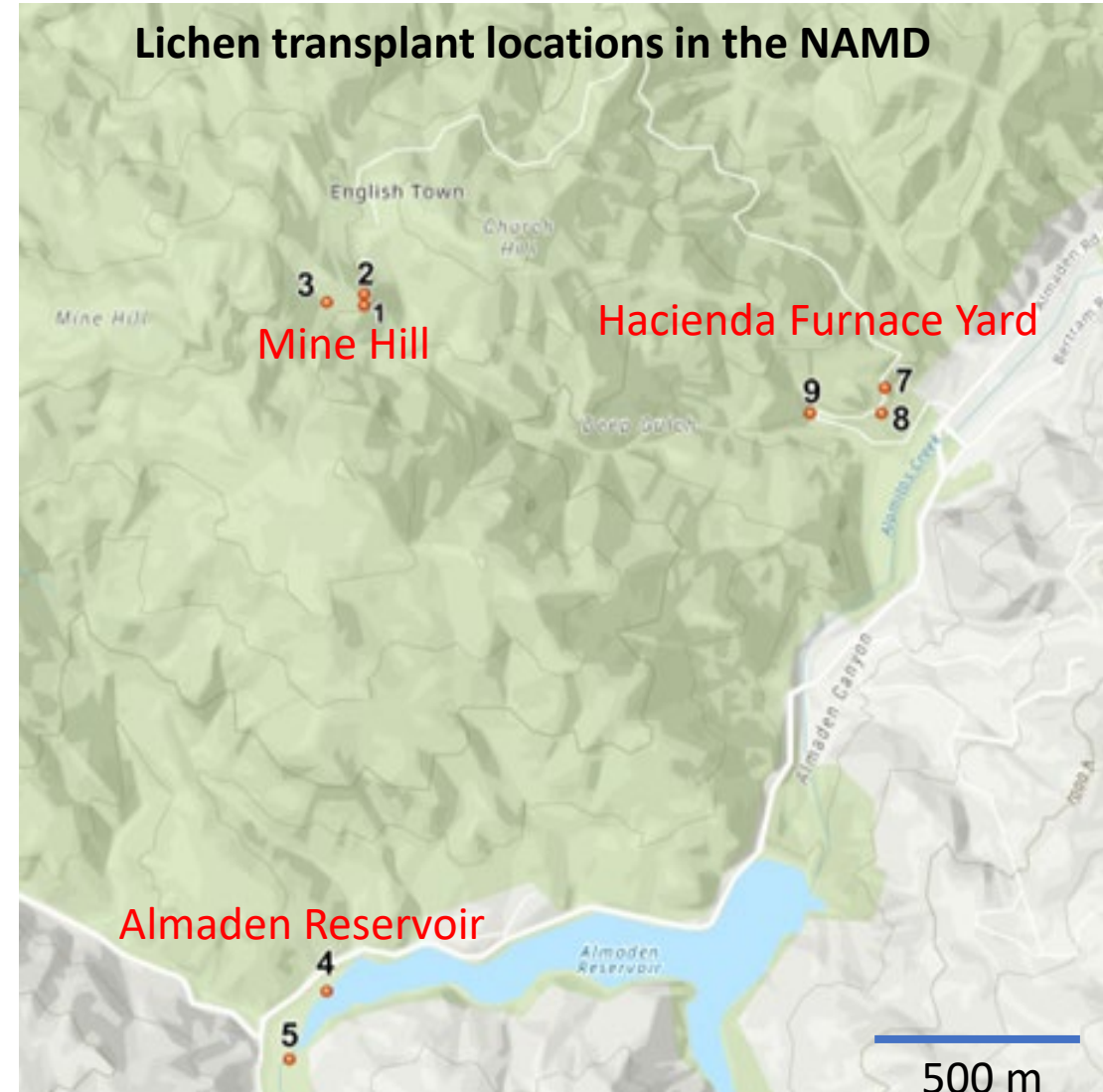


Sampling locations and spatial interpolation of THg in lichens at the Sulphur Bank Hg Mine



- Lichens reveal emissions hotspots.
- Resolve order-of-magnitude Hg gradients with a resolution of ~10's of m.

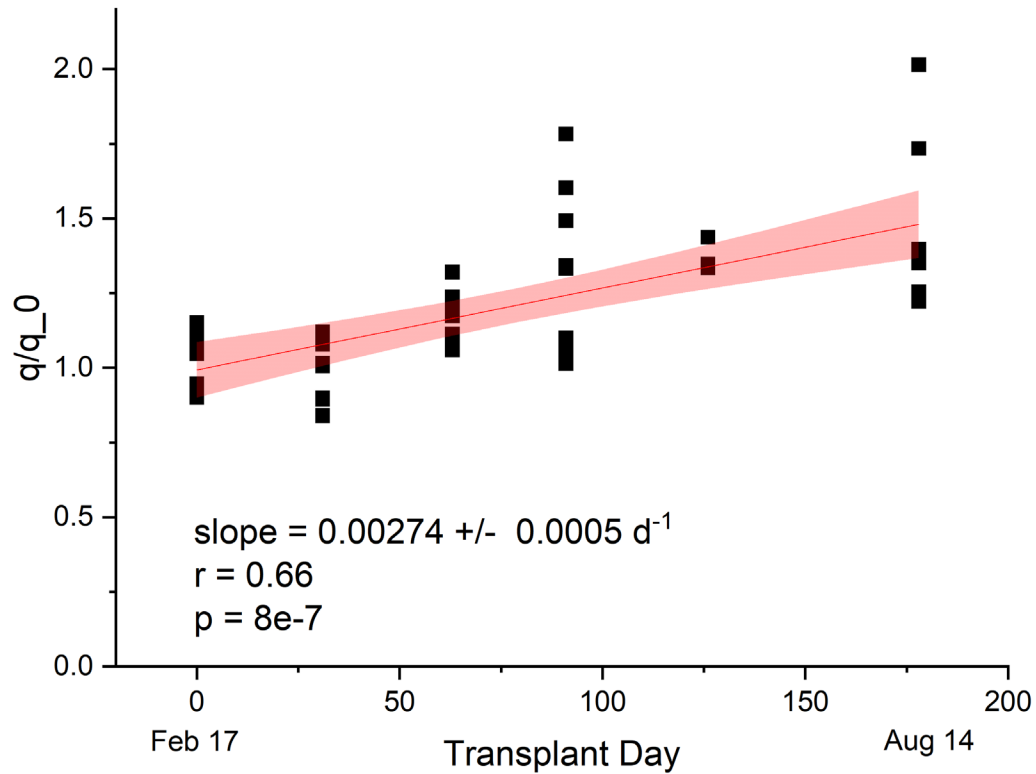
Lichen transplantation and MerPAS experiment



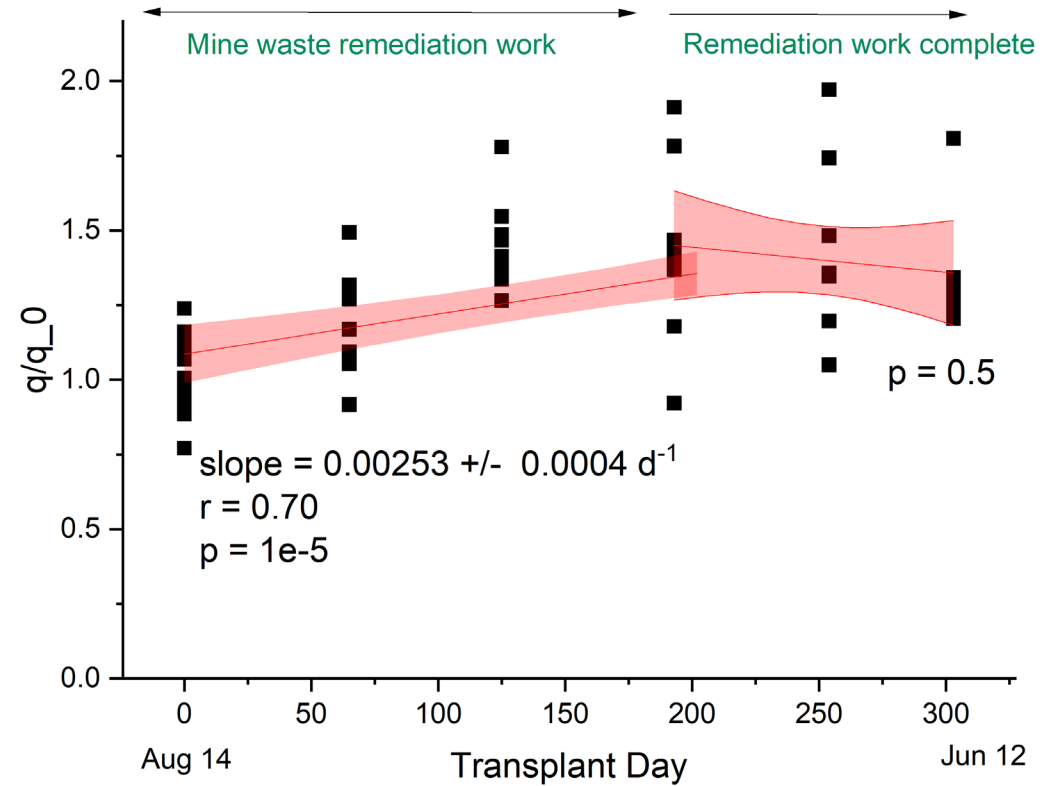
- Lichen picked at background location, sorted by species, washed with spring water, patted dry, placed in nylon bags suspended under rain shields from oak trees in the NAMD (Vanini et al., 2021).
- One bag was a control containing lichen picked at each transplant location.
- Two MerPAS were deployed at each location.
- Transplant #1: Jan 18-Sep 13, 2023. Transplant #2: Aug 14, 2023 – Jun 12, 2024.
- Uptake rates constants given by q/q_0 (Lopez-Berdonces et al., 2017).

THg uptake at the most contaminated location in the NAMD (Hacienda Furnace Yard)

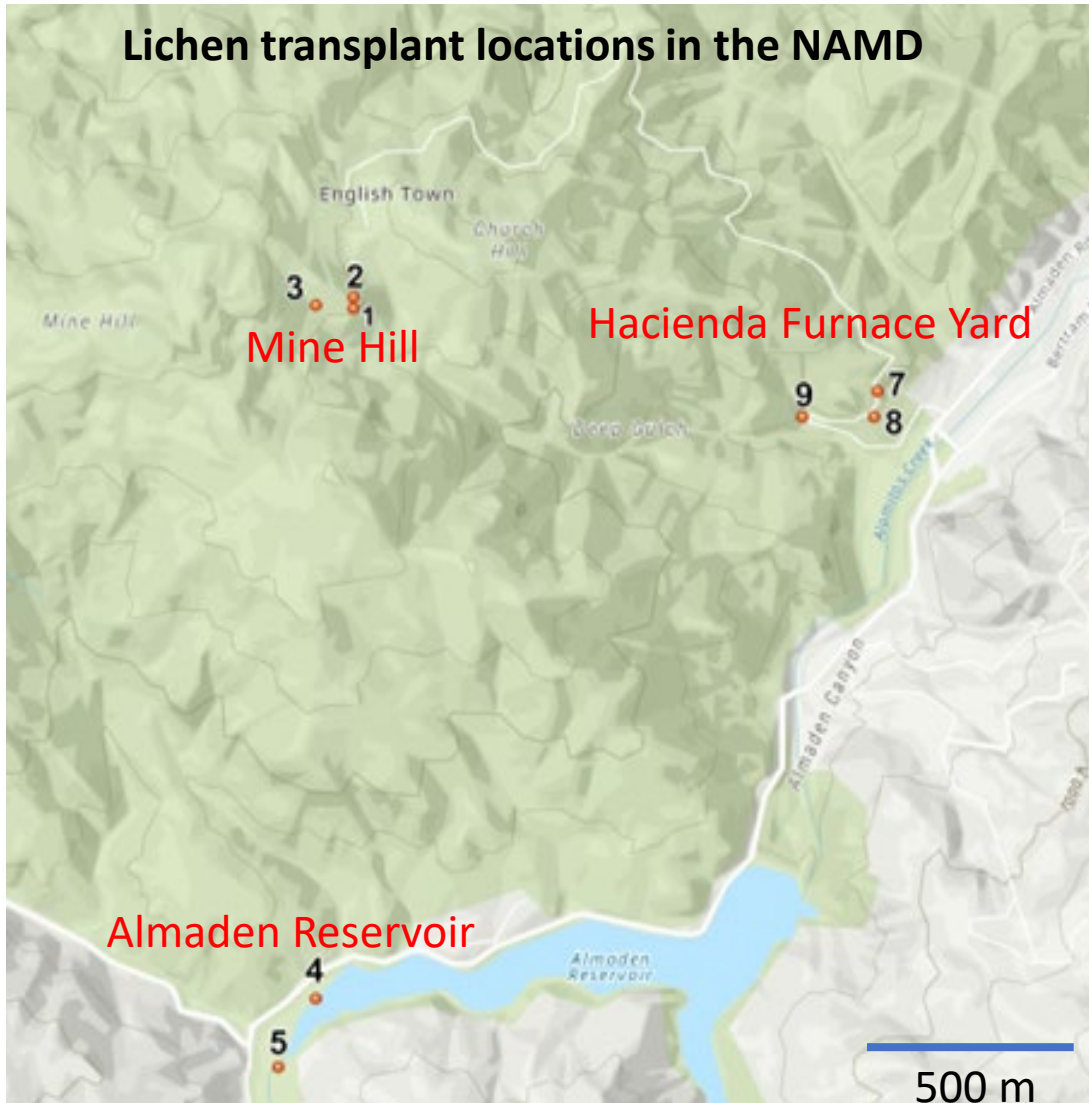
Transplant #1 – *Ramalina leptocarpha*



Transplant #2 – *Evernia prunastri*



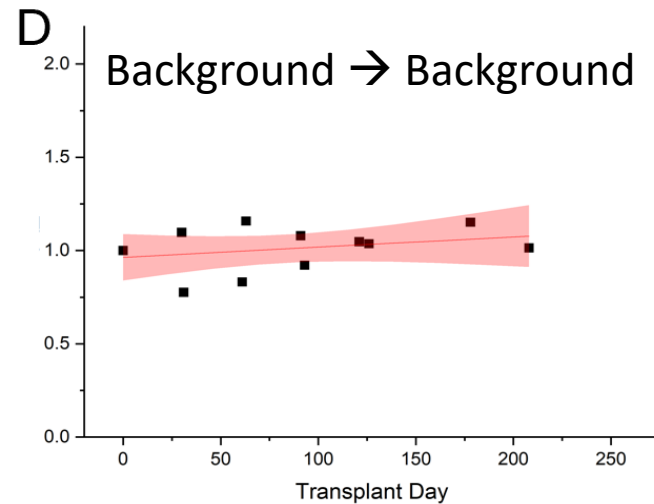
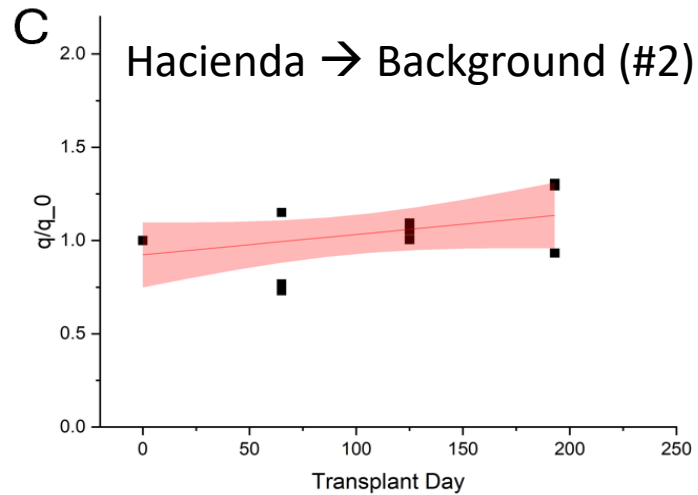
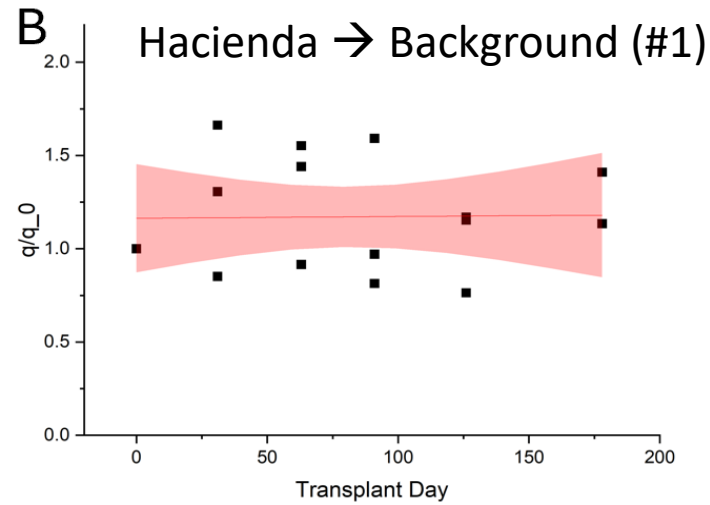
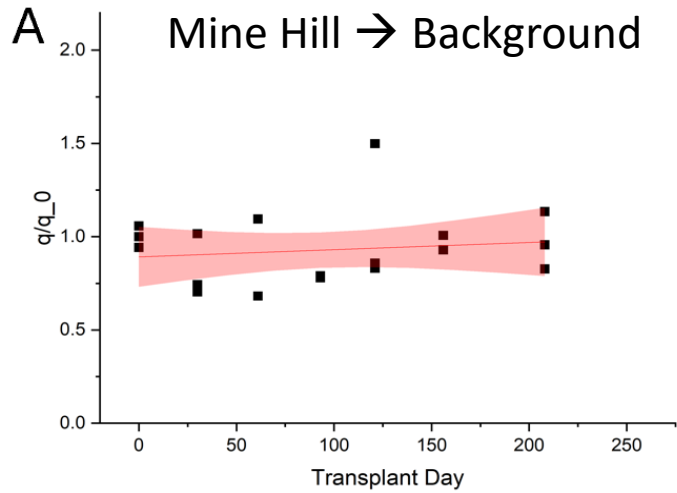
Comparison of THg uptake rates across sites



Location	Contamination Level	THg (ng g ⁻¹) in lichen	Uptake Rate Const q/q ₀ (d ⁻¹)
Lexington Reservoir	Background	76-203	0
Almaden Reservoir	Low	188-241	0.0011 ± 0.0004
Mine Hill	Medium	335-372	0.0021 ± 0.0004
Hacienda Furnace Yard	High	647-1127	0.0027 ± 0.0005

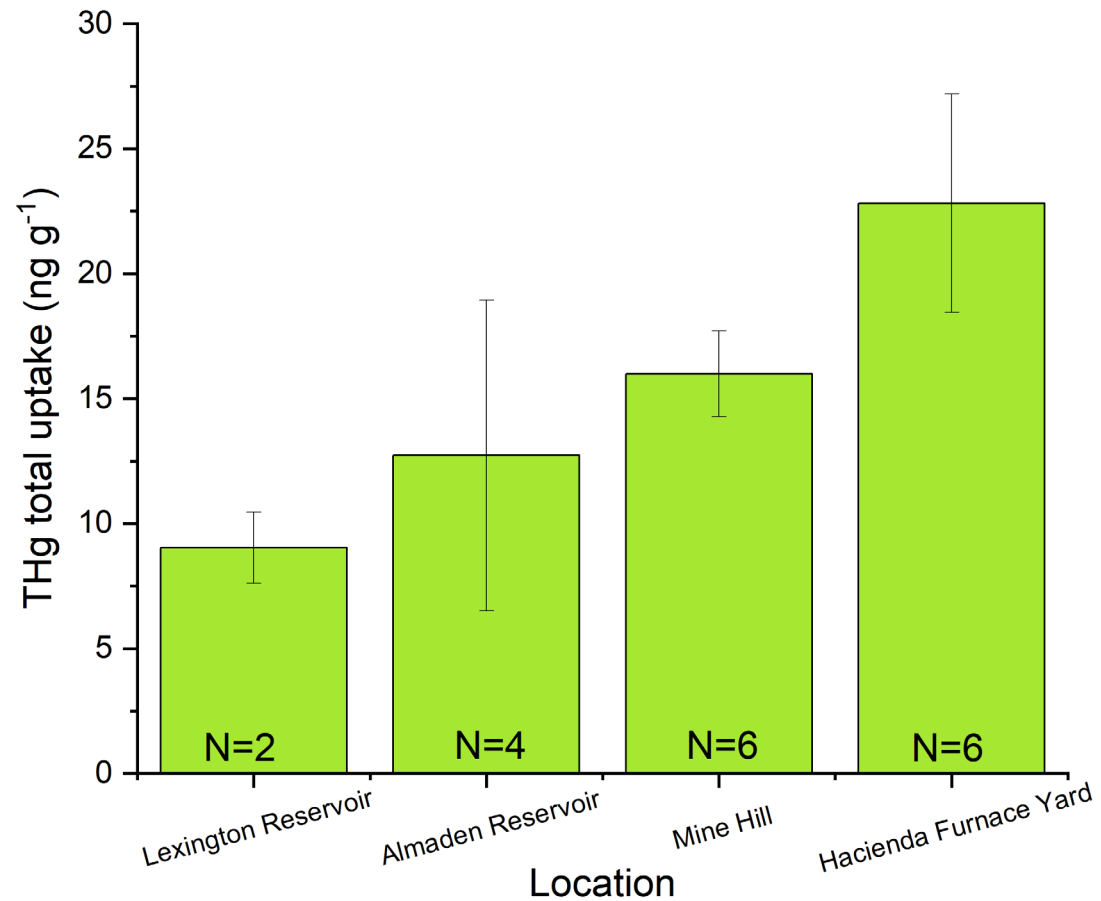
- Uptake rates generally scale with the ambient lichen concentration.

THg release and control transplants



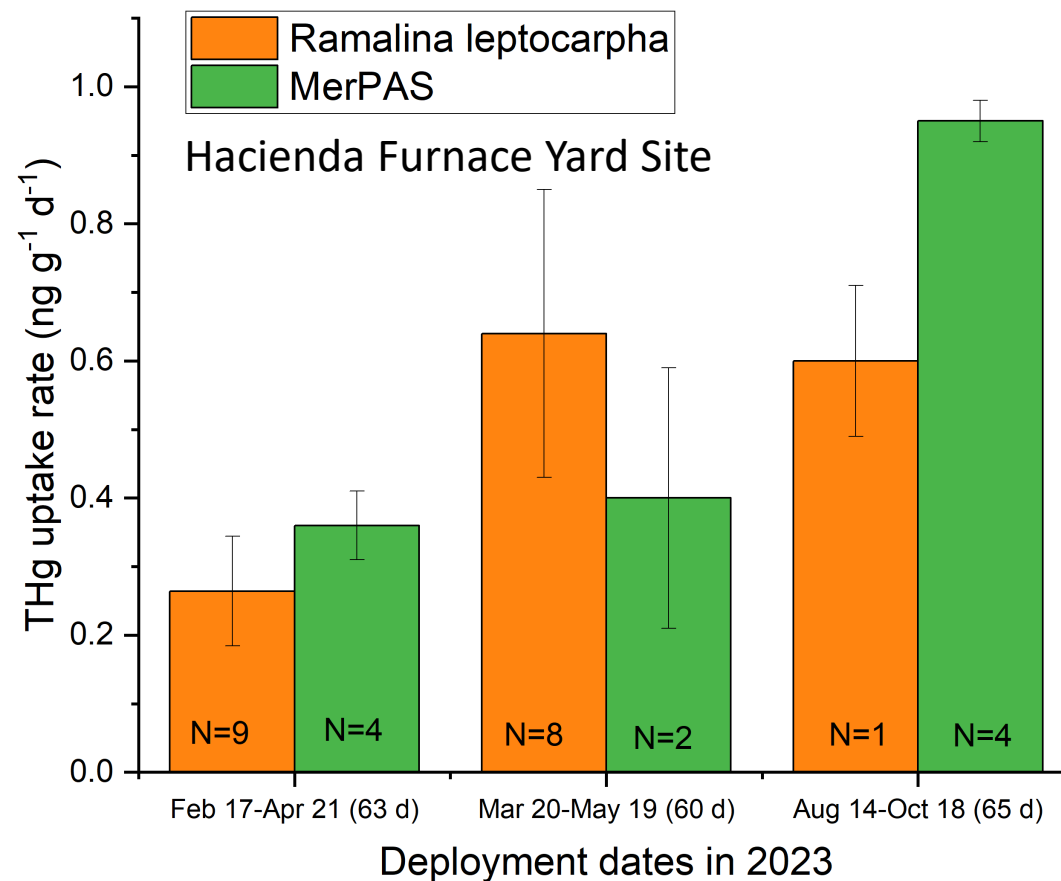
- No significant trends in Hg release.
- No significant trends in any of the control transplants.

Passive Hg⁰ sampler (MerPAS) results



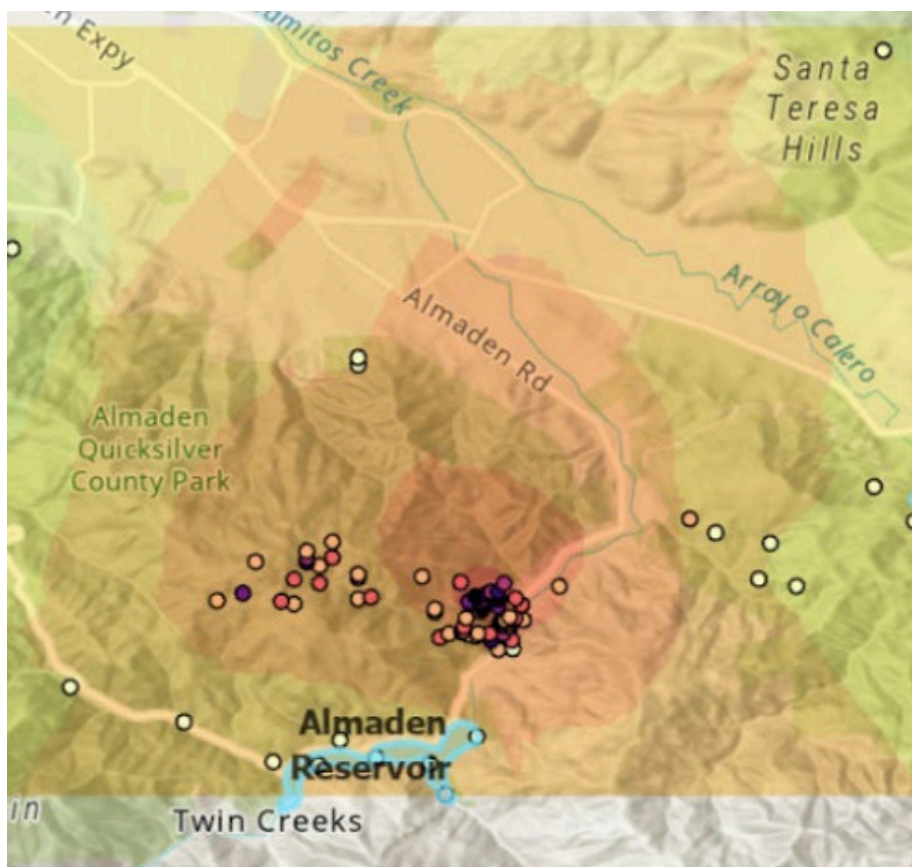
- Blank corrected
- 60-d deployments, winter/spring 2023.
- Pattern matches expected contamination levels from prior lichen survey.

Comparison of uptake rates between lichens and passive samplers



- Lichen uptake rate = $([THg]_t - [THg]_0) / \text{days}$
- MerPAS more sensitive than lichen at detecting uptake.
- “Lichens provide additional independent data that increase the confidence in the MerPAS results (Gačnik et al., 2024).

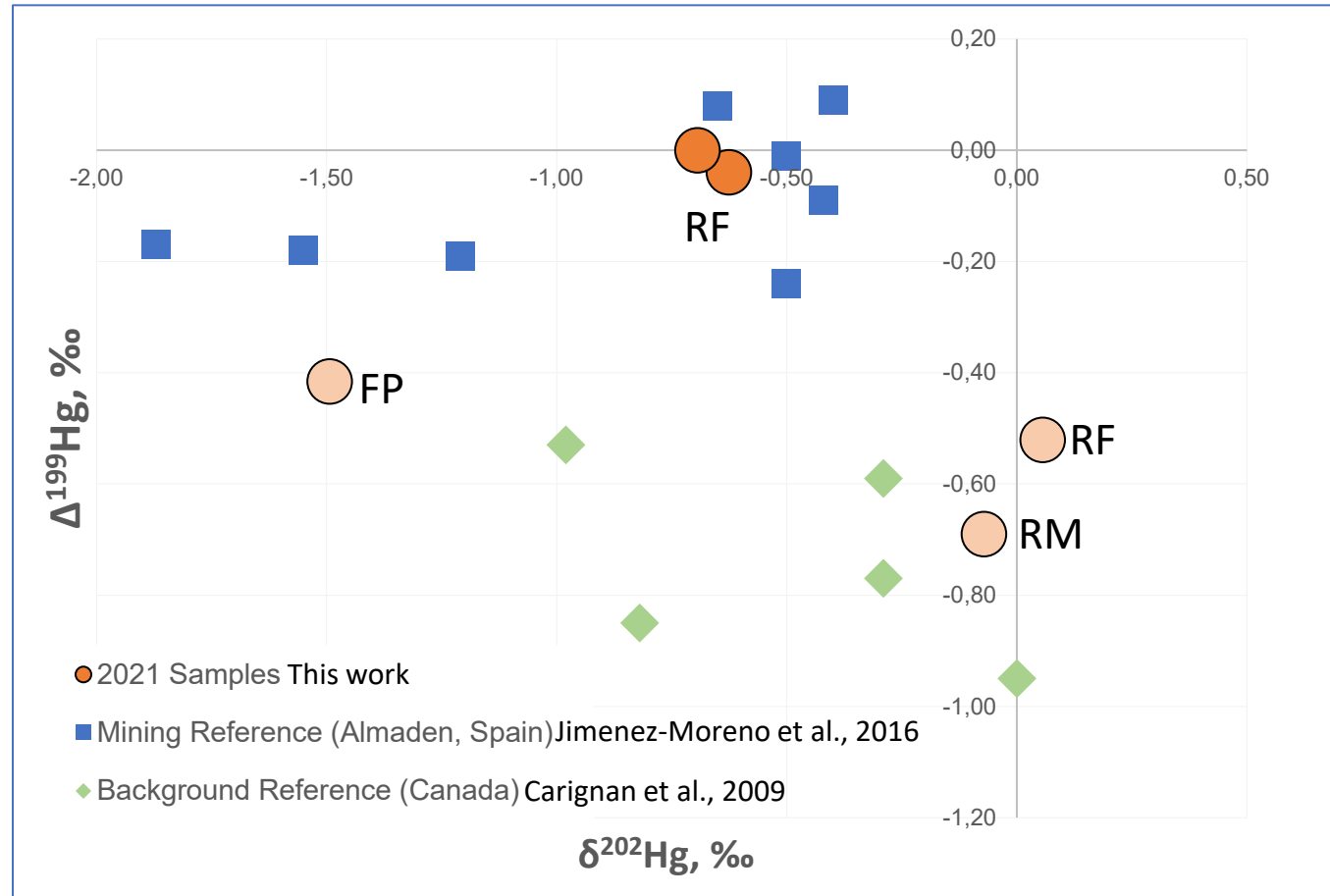
Estimates of total Hg deposition to lichen in the NAMD for three regions



Region represented by:	Lichen uptake rate (ng g ⁻¹ d ⁻¹)	Mass of lichen (g m ⁻²)	Deposition flux (ng m ⁻² d ⁻¹)	Area of each region (m ²)	Total deposition (g y ⁻¹)
Hacienda Furnace Yard	0.5	10	5	1.00E+06	1.8
Mine Hill	0.25	10	2.5	3.65E+06	3.3
Almaden Reservoir	0.1	10	1	2.54E+07	9.3
U.S. Dry Deposition Est.*			8-63		

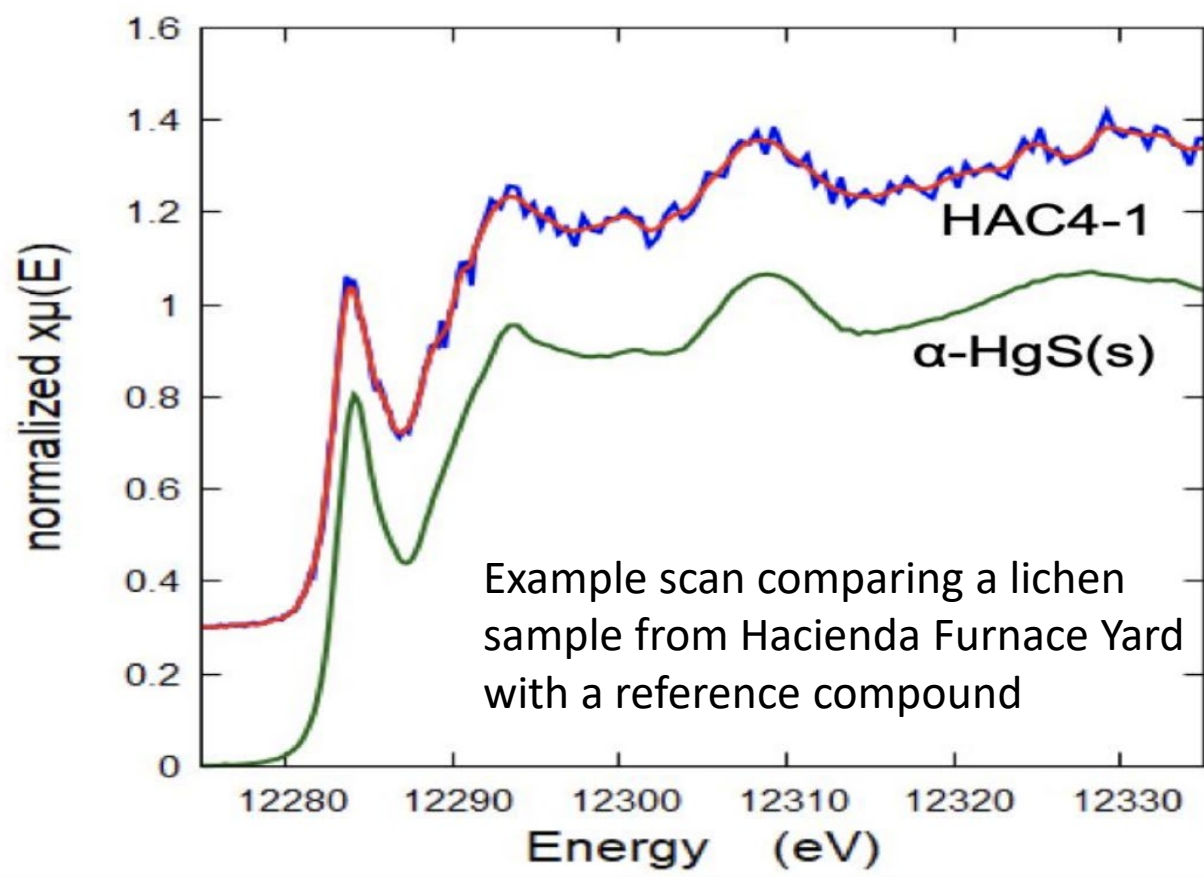
*Zhang et al., 2016

Lichen Hg Stable Isotopes



- Large range of $\delta^{202}\text{Hg}$ values likely due to MDF during uptake of Hg by different species of lichen.
- Lichens with elevated concentrations show close to 0 $\Delta^{199}\text{Hg}$.
- Lichens at background locations show more negative $\Delta^{199}\text{Hg}$.
- Still awaiting 2023 results from transplant.

XANES-HERFD analysis on Hg in lichen



- $\sim 200 \mu\text{m} \times 700 \mu\text{m}$ beam area.
- Hg concentrations were variable on a scale of ~ 10 – $100 \mu\text{m}$.
- Spatial heterogeneity within lichen samples.
- Several lichen samples had spectra nearly identical to mine waste.
- Lichen had higher amounts of organically associated Hg and minor fractions of reduced Hg in addition to α - or β -HgS.
- Still awaiting results from 2023 samples.

Conclusions

- Hg in lichens are useful indicators for identifying emissions hotspots on spatial scales of 10's of meters.
- Lichen transplants are a cost-effective complement to passive samplers for measuring uptake (deposition).
- Care must be taken in determining q_0 lichen Hg concentrations for calculating uptake rate constants.
- Hg in lichen is not released quickly, although may be sensitive to decreasing emissions resulting from remediation work.



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