

Mercury legacy from historical silver refining in Hispanic America: **A tale from Guanajuato, Mexico**

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Cerro Rico in 1584 by an unknown artist, as cited in Rehren (2011)

Acknowledgements

Saúl Guerrero

Ma. Catalina Alfaro de la Torre

Debbie Armstrong

Diana Rocha

Gustavo Cruz-Jiménez

Israel Razo Soto

Diego Díaz Barriga

José Carlos Zárate Valdovinos

José Adolfo Chávez García

Fátima Nicasio Gutiérrez

María Yanely Zavala Guzman

Daniel Ramos-Matehuala

Xebastian Ramos-Alvarez

Ravi Sidhu

Mark Cooper

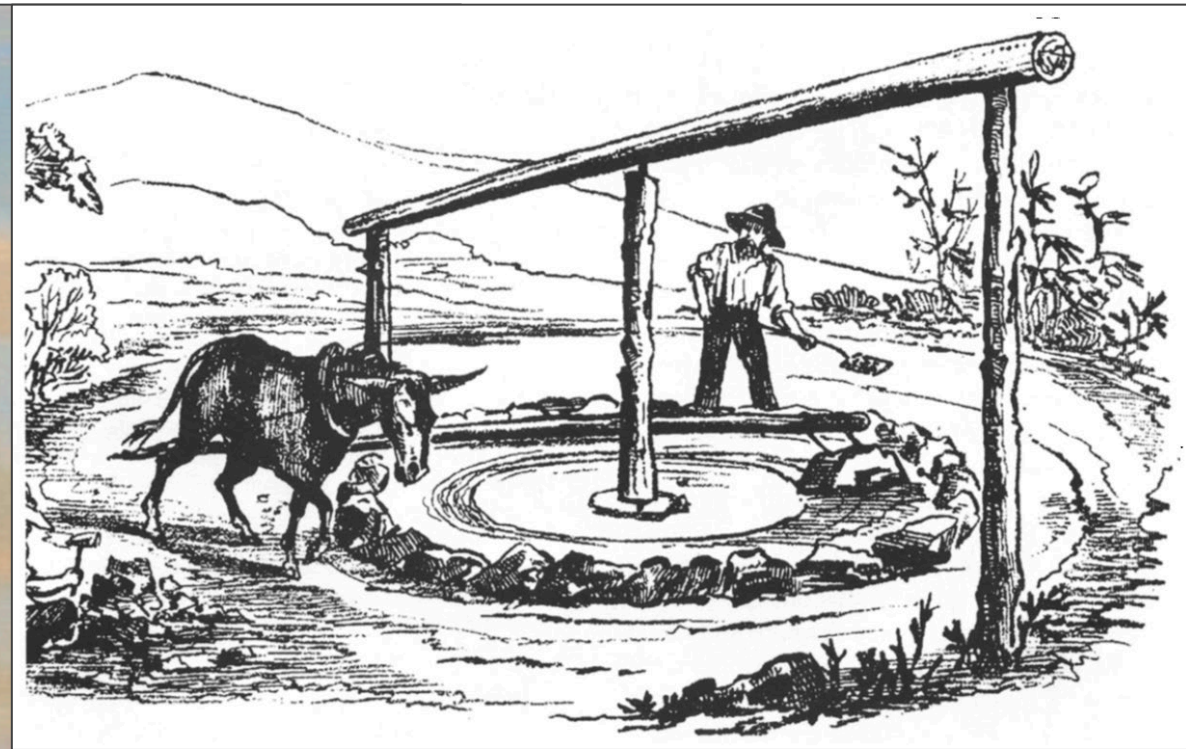


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Egleston, 1887



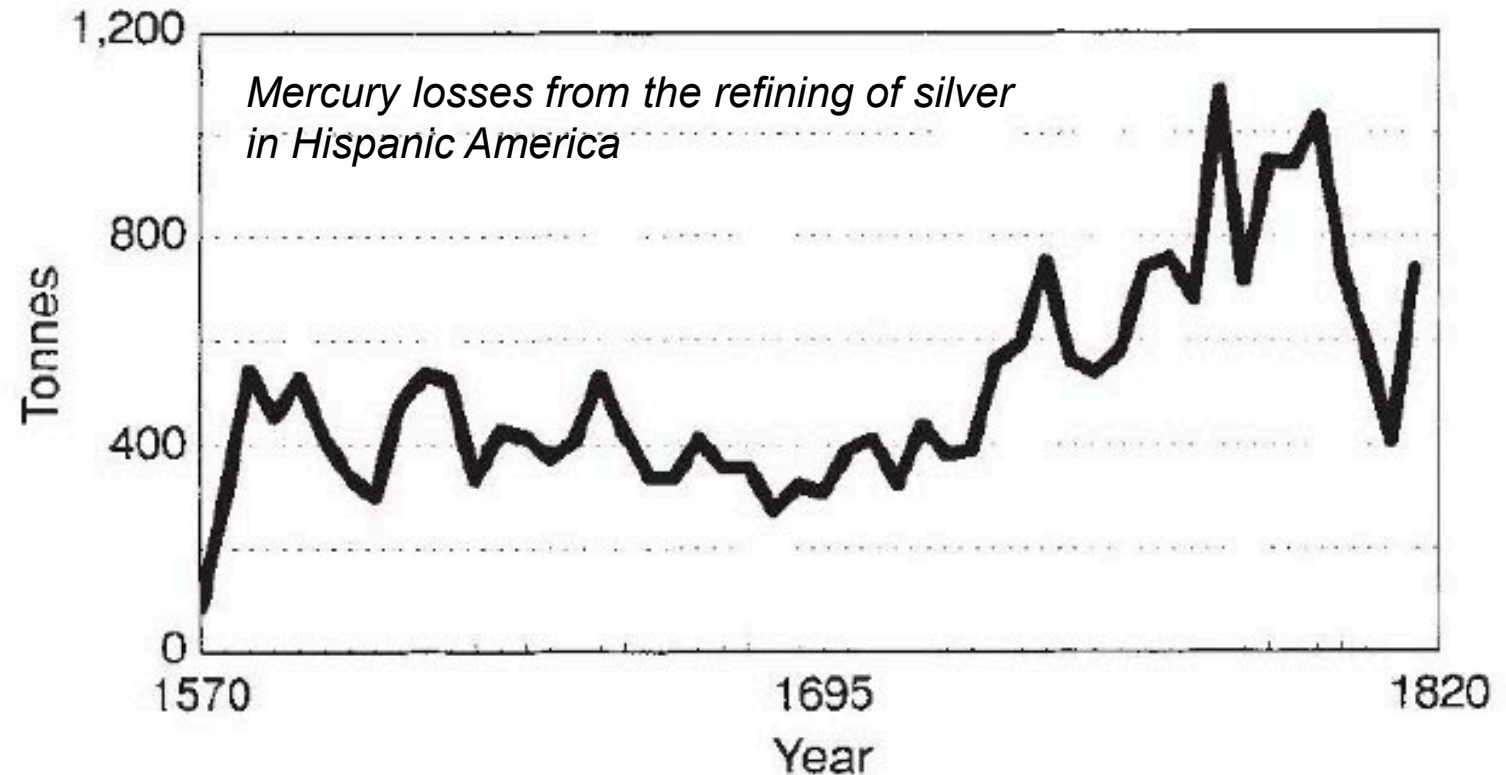
Wikipedia

From ~1570 to 1810, Hispanic America produced ~70% of the global silver output, using the “**patio method**” involving mercury amalgamation.

Legacy of mercury pollution

Jerome O. Nriagu

Nriagu (1993, 1994) estimated a total Hg loss during the period ~1570–1900 was ~196 kt (or 610 t/yr). Assuming 60% of that were emitted to the atmosphere (“emission factor”), similar to that from AGM in the Amazons, silver mining in Hispanic America would have emitted ~120 kt (or 375 t/yr) to the atmosphere.



“It is clear that the silver mines were the dominant source of [anthropogenic] atmospheric mercury pollution [in the world during that period]” – Nriagu, 1993

All-Time Releases of Mercury to the Atmosphere from Human Activities

David G. Streets,^{+,*} Molly K. Devane,[†] Zifeng Lu,[†] Tami C. Bond,[‡] Elsie M. Sunderland,[§] and Daniel J. Jacob^{||}

2011, 45, 10485–10491

Table 1. Cumulative Commodity Production Amounts and Associated Hg Emissions^a

material	pre-1850		1850–2008		all-time to 2008	
	production (Tg)	emissions (Mg)	production (Tg)	emissions (Mg)	production (Tg)	emissions (Mg)
copper	45	1240	547	3410	592	4650
zinc	50	3750	403	6520	453	10 300
lead	55	2400	268	3590	323	5990
iron	330	20	32 900	1110	33 300	1130
steel	~0	~0	44 200	388	44200	388
mercury	0.229	41 700	0.720	53 300	0.949	95 000
gold, large-scale	~0	~0	0.145	20 600	0.145	20 600
gold, artisanal	0.016	8200	0.025	10 200	0.041	18 400
silver	0.276	78 700	1.17	67 300	1.45	146 000
cement	~0	~0	61 200	3000	61 200	3000
caustic soda	~0	~0	1710	4240	1710	4240
coal	2900	868	319 000	33 900	322 000	34 800
oil	~0	~0	312 000	2620	312 000	2620
waste	~0	~0	2310	5310	2310	5310
total		137 000		215 000		352 000

^a Values are rounded to no more than three significant digits, consistent with the level of confidence.

Using a **more conservative emission factor of ~52%**, Streets et al. (2011) estimated that silver mining was the single largest anthropogenic Hg emitter to the atmosphere (146 kt), **accounting for 40% of the all-time, global total (350 kt).**

- Subsequently, recent studies have started to use a lower emission factor in global Hg modeling:
 - ❑ 17%: Zhang et al. (2014); Outridge et al., 2018; UNEP 2019
 - ❑ 3%: Streets et al. (2019)

- **But no experimental studies have examined Guerrero's postulation re calomel, specifically:**
 - ❑ Was/is calomel **present** in the local environment?
 - ❑ **How stable** is calomel as a chemical sink of legacy Hg?
 - ❑ What are the **implications** locally and globally?



Introducing Guanajuato, Mexico



A UNESCO world heritage site, Guanajuato produced over 8,000 tons of Ag from 1664 to 1805 using the patio method.

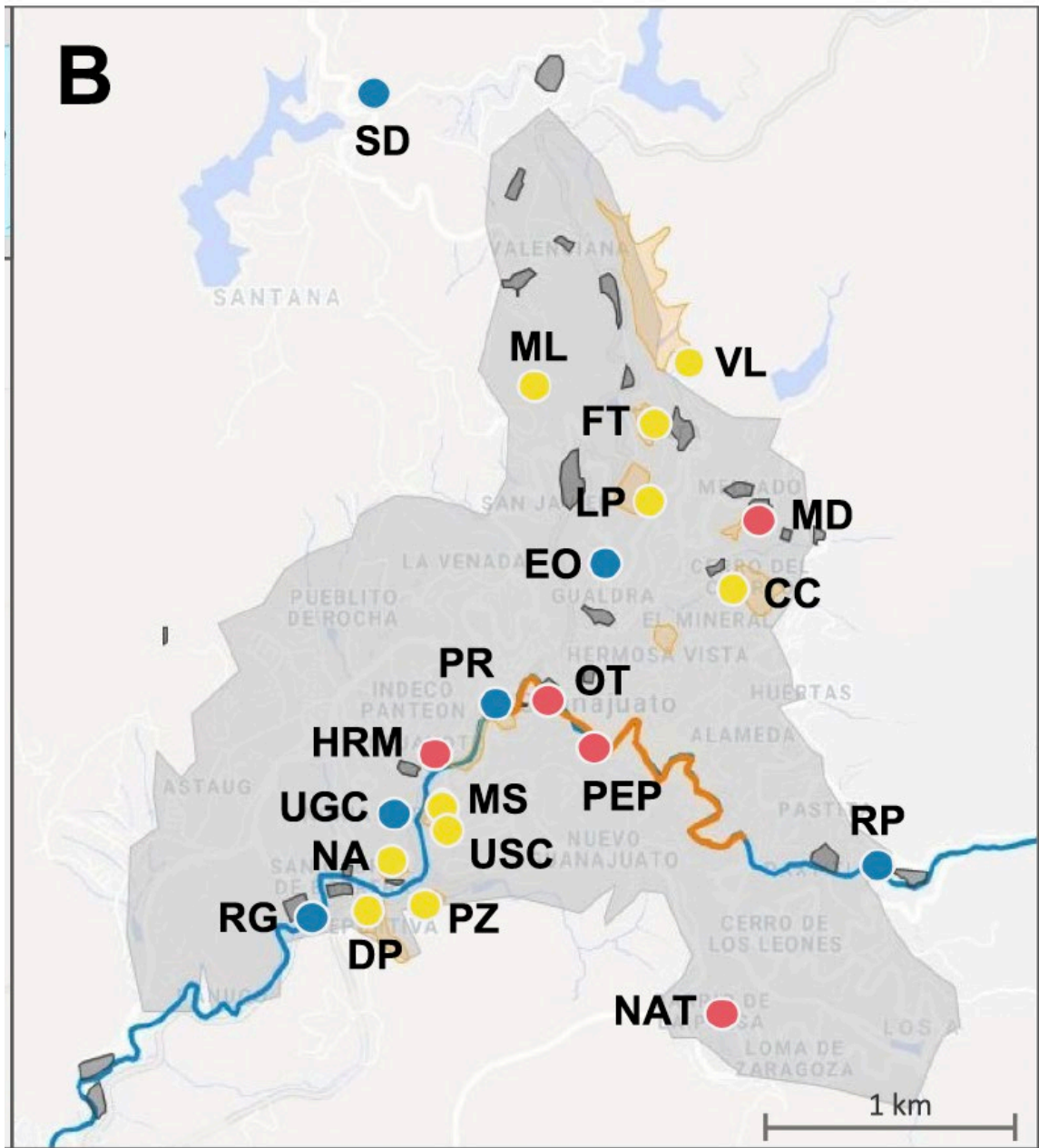
A hacienda along the river full of wastes in Guanajuato



As cited in Perez, 2019

Mineral wastes washed up post-flood in Guanajuato





Our study

26 sites in July 2019:

- Ground-level ambient air: GEM
- Soil interstitial air: GEM
- Soil Hg concentration & speciation
- Soil mineralogical analysis

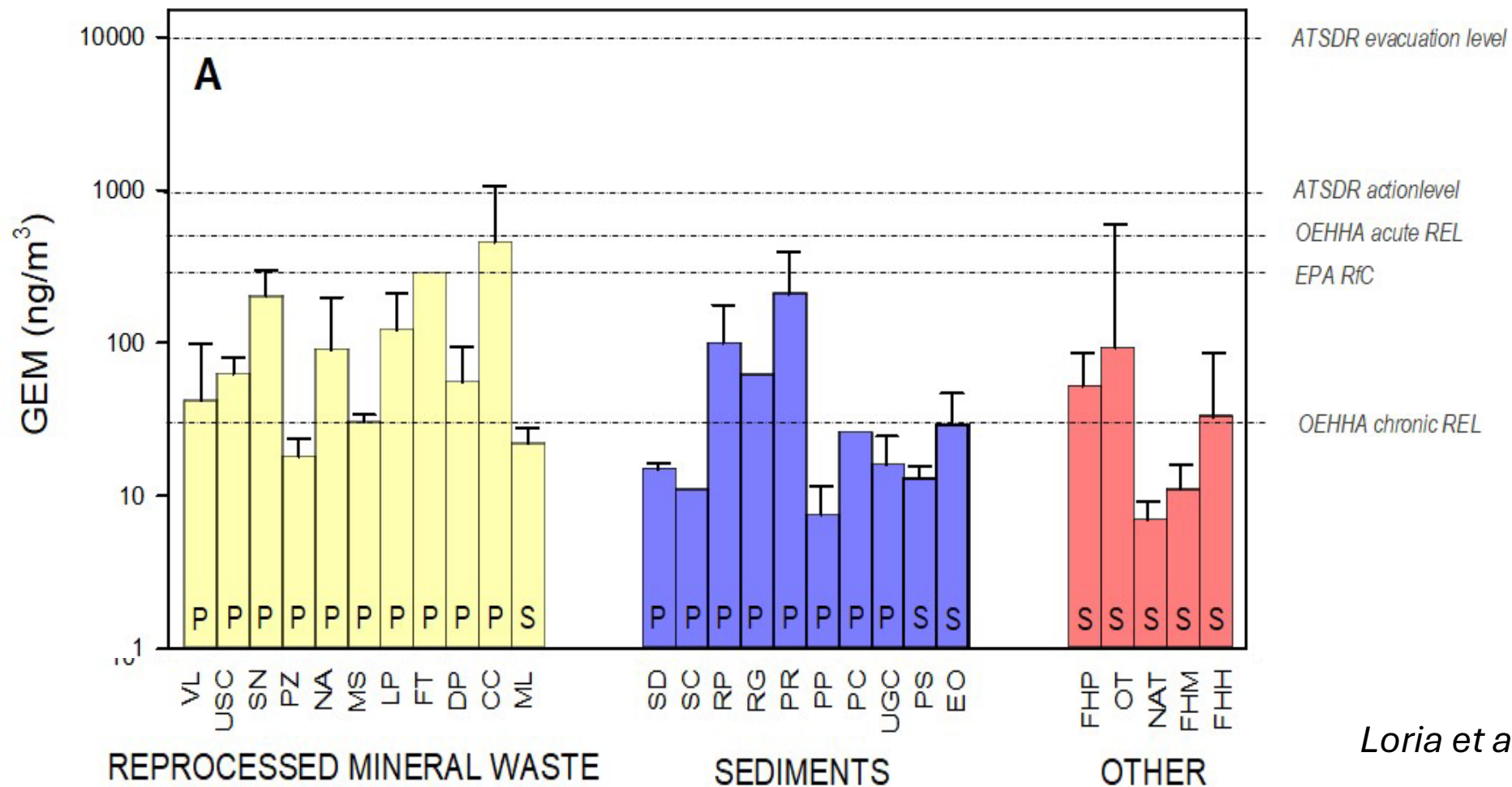
SITES

- Reprocessed mineral waste
- Sediment/Soil
- Other

- Guanajuato River
- Old Tunnel
- Waste deposits
- Haciendas
- Urban Guanajuato



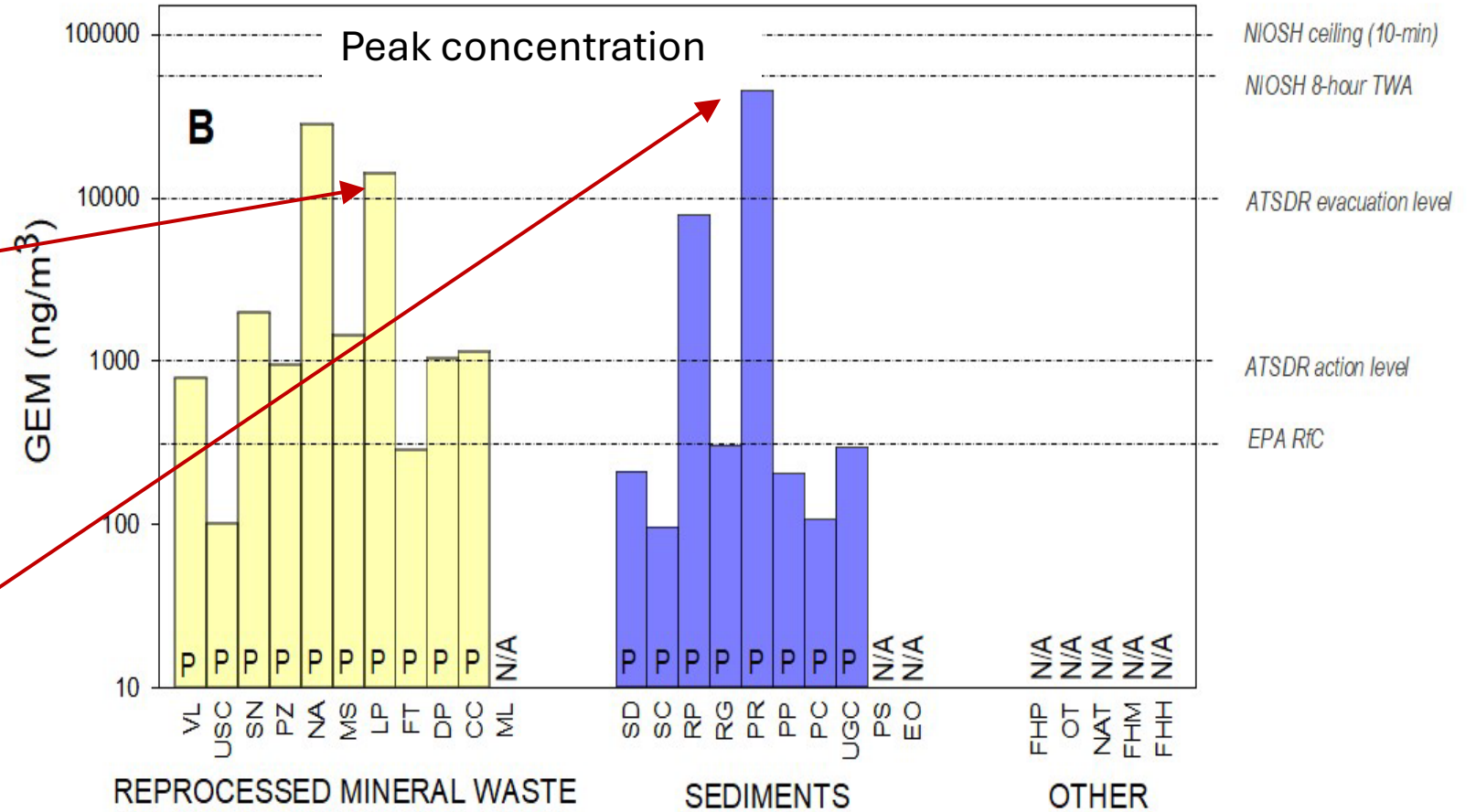
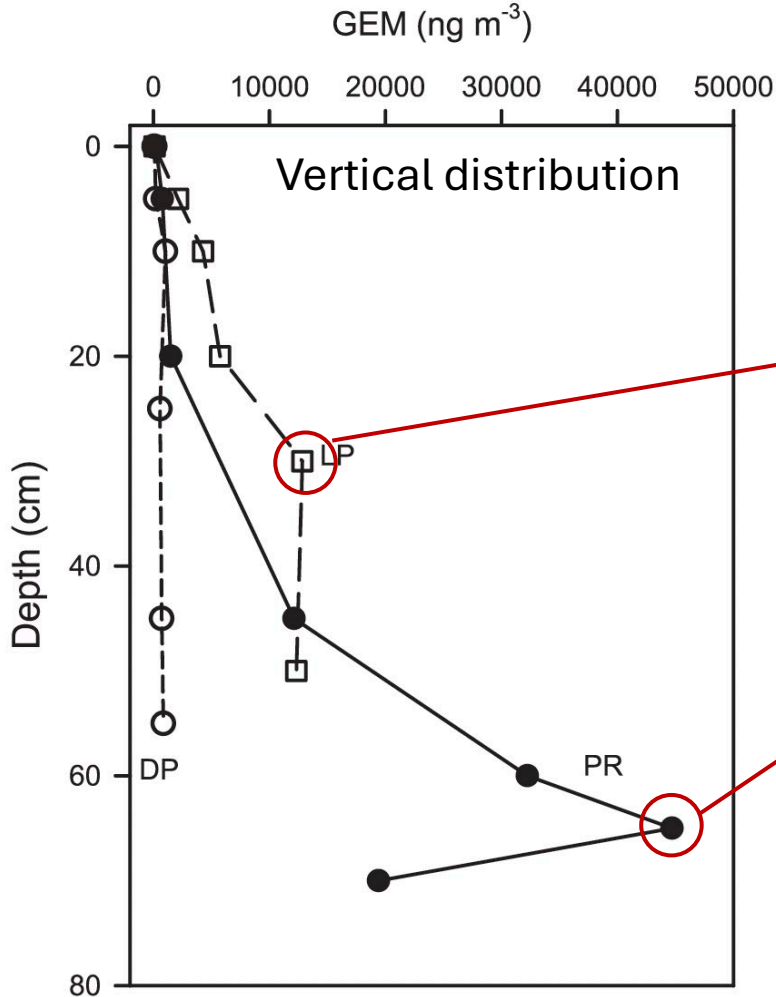
Mean GEM concentrations in ground-level, ambient air



Loria et al., 2022, STOTEN

Hg used in the patio process continues to elevate present-day concentrations of GEM throughout Guanajuato. In the ground-level air, GEM ranges from 8 to 450 ng/m³.

GEM concentrations in soil interstitial air



Loria et al., 2022, STOTEN

Extremely high GEM concentrations, up to 45,000 ng/m³, are found in the interstitial air of reprocessed mineral wastes, sediment, and soil.

Soil mineralogical analysis

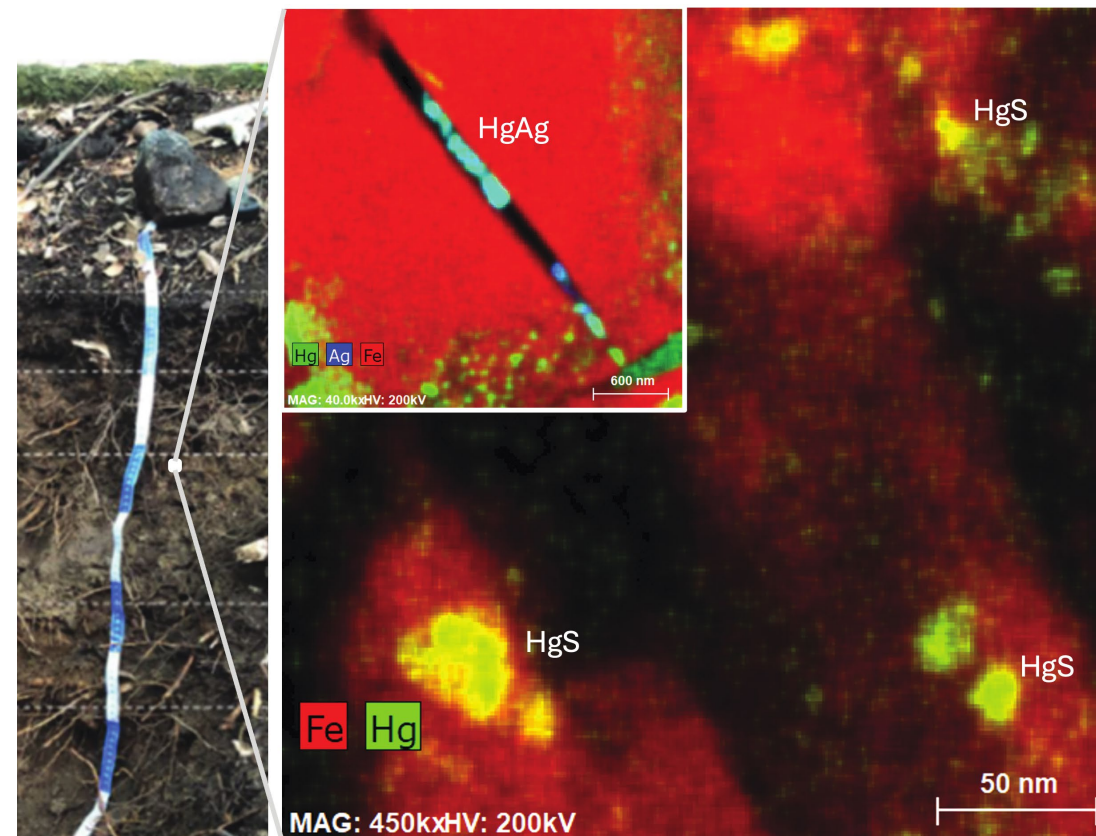
SEM/TEM analysis shows the presence of AgHg amalgam and Hg(S,Se), **but no clear evidence for the presence of calomel or HgCl₂ phases.**

Schindler et al., 2024

Environmental Science Processes & Impacts

Volume 26
Number 3
March 2024
Pages 463–646

rsc.li/espi



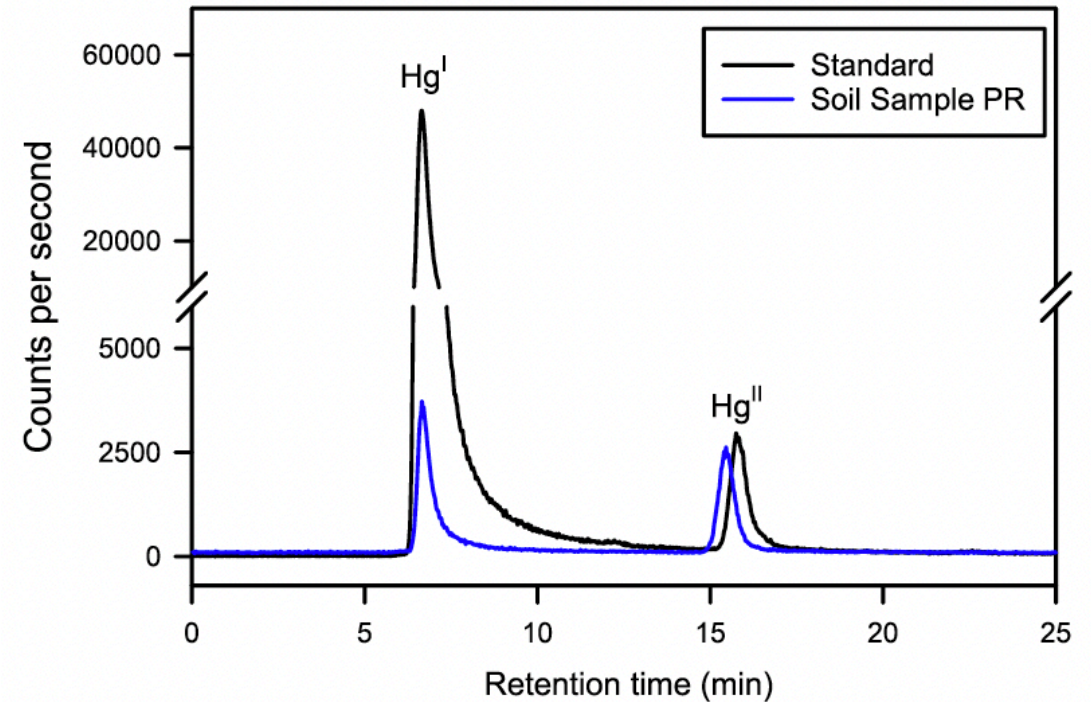
ISSN 2050-7887

Soil Hg concentration and speciation



Extraction with
2-mercaptoethanol

HPLC-ICP-MS
analysis



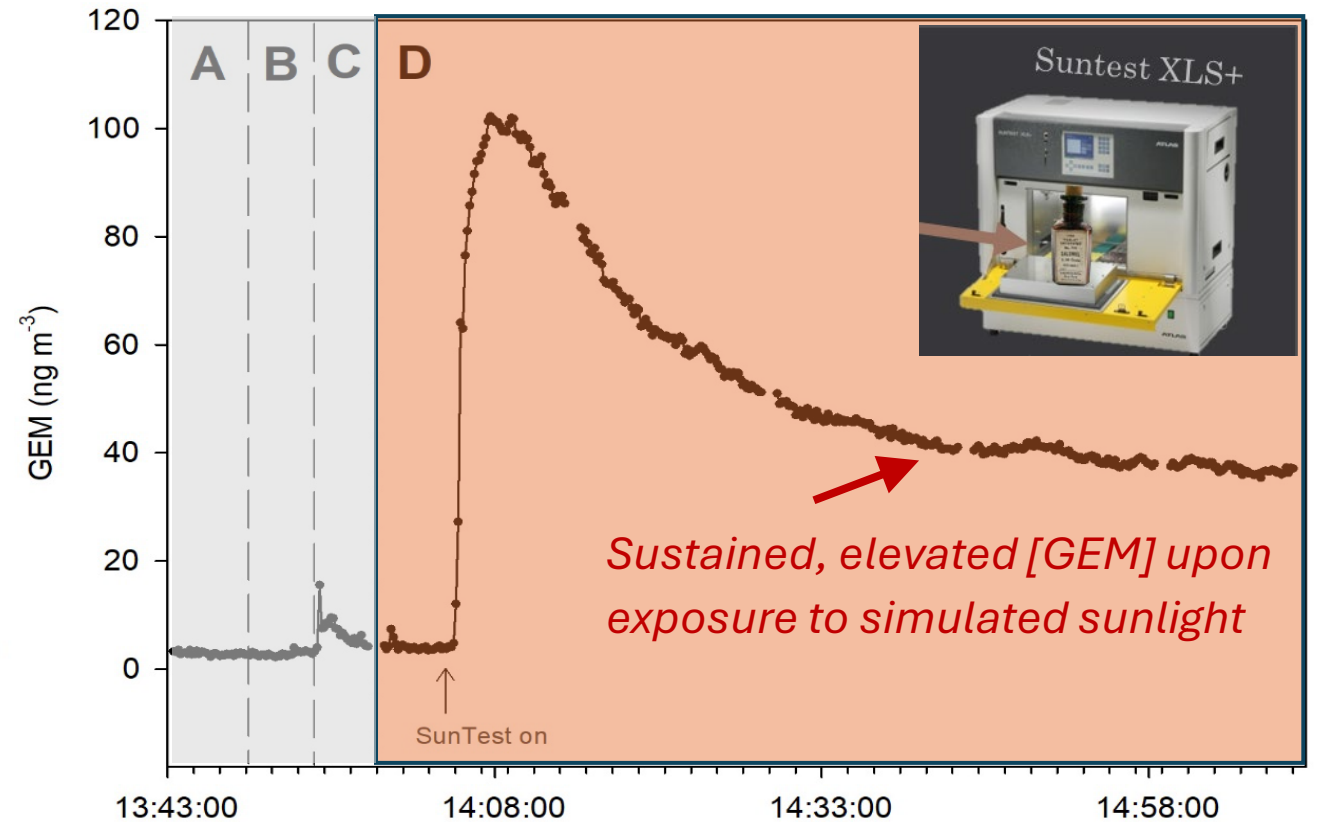
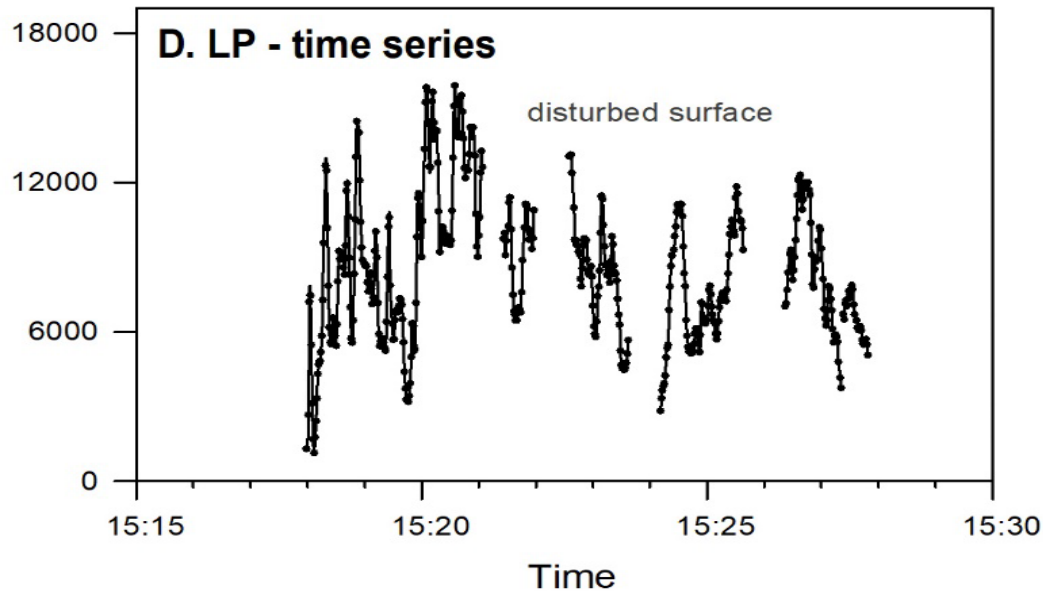
Loria et al., 2022, STOTEN

Soil total Hg concentration varies from 0.068 to 622 ug/g. **Speciation analysis shows the presence of Hg(I)**, but quantitation is not possible due to the instability.

Stability of calomel in the presence of sunlight

Lab test of calomel inside a solar simulator

Field observations

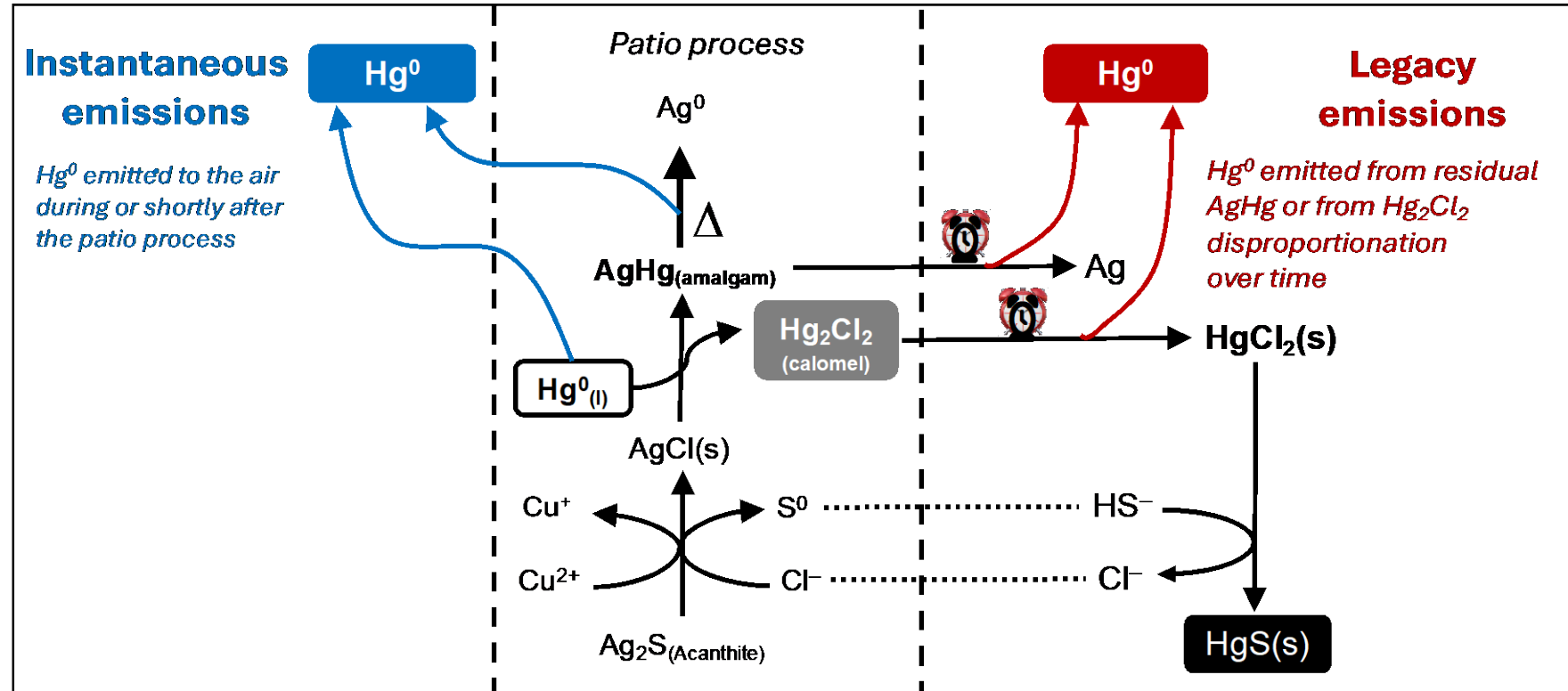


Loria et al., 2022, STOTEN

Sustained, elevated GEM levels over time when a freshly dug soil section is exposed to sunlight. A similar pattern is observed from a lab test of calomel exposed to a solar simulator.

Ending of the tale: the saga continues!

A considerable amount of legacy Hg from historical Ag refining persists in the local environment to the present day, and continues to elevate ambient air Hg concentrations.



- **Local implications:** Continuous and considerable “**legacy Hg emissions**” to the atmosphere might have been posing a health risk to local residents **for generations**.
- **Global implications:** “**Instantaneous Hg emission factor**” to the atmosphere was likely somewhere between the extreme values of 3% (Guerrero) to 60% (Nriagu).