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- **ARSENIC**
- **MERCURY AND METHYLMERCURY**
- **PLANTS IN BIOGEOCHEMISTRY**



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ENVIRONMENTAL MERCURY AND METHYLMERCURY CONTAMINATION FROM THE PALAWAN QUICKSILVER MINE, PHILIPPINES

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Introduction

The Palawan Quicksilver Mine (PQM), Philippines, is located on Palawan Island near several villages where approximately 2,000 residents live, and within about 3 km of important regional fisheries and recreational areas in Honda Bay (Fig. 1). From 1953 to 1976, the PQM produced about 2,900 t of Hg, a moderate sized Hg mine on an international scale. More than 2,000,000 t of mine-waste calcines (roasted ore) was generated during mining and about half of this waste was dumped into Honda Bay to construct a jetty, which was used as a mining port ¹ (Fig. 2). Since 1995, high Hg levels have been observed in 21 people living near the mine, who also experienced symptoms of Hg poisoning and were subsequently detoxified with chelating drugs.

Mercury is a heavy metal of environmental concern because elevated concentrations are toxic to all living organisms. Mercury is one of the few pollutants where ingestion of contaminated food (primarily fish) has led to human deaths ². Mine-waste calcines can be especially hazardous because they contain highly elevated Hg concentrations and soluble Hg salts and Hg⁰, which under certain conditions, can oxidize to Hg(II) and subsequently transform into methyl-Hg (CH₃Hg⁺) through microbial processes, primarily by the action of sulfate reducing bacteria ³. Methyl-Hg is highly toxic, water soluble, and can biologically magnify with increasing trophic position in the food chain. Mercury contamination of fish and seafood is a common problem worldwide that can lead to Hg exposure to humans consuming such food sources ⁴. Mercury contaminated sediment and water from the PQM are potentially hazardous to residents and wildlife when they enter local surface water and food

webs, especially in Honda Bay. To evaluate Hg contamination and Hg methylation in this area, total Hg and methyl-Hg concentrations were measured in (1) mine wastes and mine water from the PQM, (2) stream sediment and water from a pit lake and a local stream (Tagburos Creek), (3) mine-waste calcines and water in Honda Bay, and (4) water from local domestic wells.

Results and Discussion

Mercury concentrations in PQM calcines and local sediments are highly elevated and variable (3.7–660 µg/g), which is typical of Hg mines throughout the world (Table 1; Fig. 3). Fine-grained and encapsulated cinnabar (HgS) was observed in some calcines, and the high variability of Hg within these calcines indicates that retorting was not totally or uniformly efficient, which is also typical of Hg mines worldwide. Nearly all of the Hg at the PQM was produced from ore containing cinnabar, but pyrite (FeS₂) is also abundant. The presence of pyrite is potentially hazardous because it is a significant acid-water producing mineral, and Hg compounds are more soluble and reactive in acidic water. Thus, unfiltered water draining the PQM calcines is acidic, pH 3.1–4.3, and total Hg concentrations ranging from 18,000–31,000 ng/L in this water significantly exceed the 1,000 ng/L World Health Organization (WHO) drinking water standard for Hg ⁵ (Fig. 4). Total Hg concentrations are generally lower in water samples collected from surrounding domestic wells, the mine pit lake, Honda Bay, and the nearby stream, varying from 8–1,400 ng/L. However, nearly all unfiltered water samples collected in this study contain total Hg concentrations exceeding the 12 ng/L Hg standard recommended by the U.S. Environmental Protection Agency (USEPA)

to protect against *chronic* effects to aquatic wildlife ⁶ (Fig. 4).

The concentration of methyl-Hg in mine wastes, sediment, and water in the area is more important than total Hg contents because methyl-Hg is highly toxic. Methyl-Hg concentrations in the calcines and sediment samples varied from 0.13—21 ng/g, whereas methyl-Hg contents in water from the PQM site ranged from <0.02—3.1 ng/L. There is no regulatory methyl-Hg standard, but methyl-Hg contents in the Palawan samples are similar to those found at other cinnabar-dominant Hg mines, such as in southwestern Alaska, west-central Nevada, and Idrija, Slovenia (Table 1). At Idrija and in Alaska, mines are within aquatic ecosystems that have been contaminated with Hg. These ecosystems support marine and freshwater fish, and some of these fish contain Hg concentra-

tions exceeding the 0.3 µg/g (wet weight, fish muscle) standard commonly used in the USA ⁴. Similar to these mines, the data for the PQM indicate translocation of methyl-Hg from mine-waste calcines and sediments to stream water, and then to Honda Bay. It is also likely that methyl-Hg in mine wastes and water in Honda Bay is transferred to biota, such as fish. Methyl-Hg has been shown to constitute greater than 95 % of the total Hg in consumable fish tissue ⁷. Fish in Honda Bay have been known for several years to contain elevated total Hg concentrations (0.05—1.07 µg/g, wet weight, fish muscle) ⁸⁻⁹. Residents in this area are exposed to Hg through food sources such as fish and seafood from Honda Bay. Palawan has a coastal population, where people typically consume fish and seafood daily. Daily consumption of fish from Honda Bay could exceed the USEPA suggested human intake of 0.1 µg methyl-Hg/kg bodyweight/day, and the WHO recommendation of 0.47 µg methyl-Hg/kg bodyweight/day ⁴. Based on these recommendations, residents in this area should restrict consumption of seafood from Honda Bay.

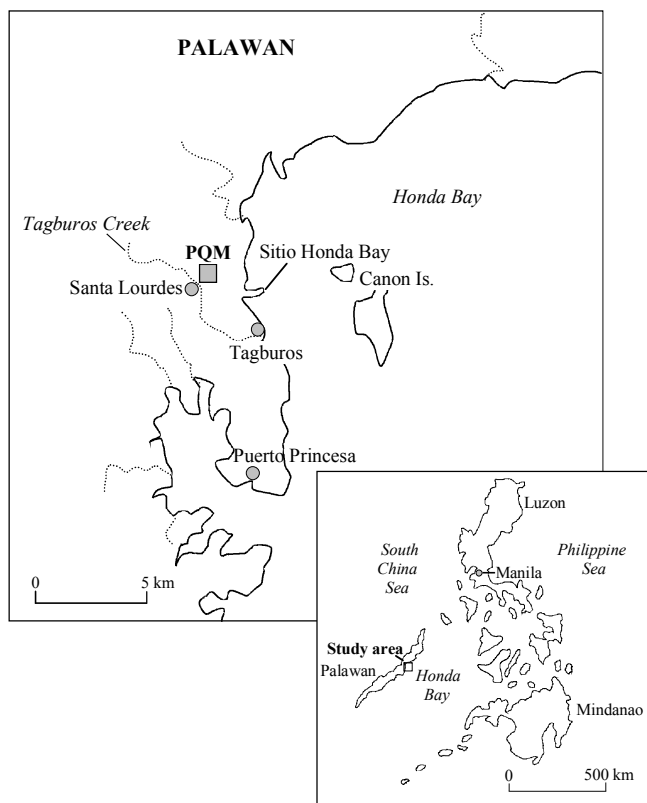


Figure 1. Location of the Palawan Quicksilver Mine (PQM), Palawan, Philippines.

Conclusions

In and around the PQM, several adverse factors have contributed to local environmental Hg contamination, one of the most unfortunate was the placement of Hg-rich mine wastes into Honda Bay. Much of the methyl-Hg generated in the PQM calcines or in Honda Bay is transferred to water, and then to higher trophic levels such as marine fish and seafood that are human food sources. The PQM is a unique example of significant methyl-Hg formation near a Hg mine, Hg contamination of local marine seafood, and subsequent uptake of high levels of methyl-Hg by local residents consuming such seafood.

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ENVIRONMENTAL MERCURY AND METHYLMERCURY CONTAMINATION (Cont.)



Figure 2. A view of mine-waste calcines that were used to construct the jetty in Honda Bay. This photo is at the waterline in Honda Bay and in the background are fish drying racks and motor vehicles.

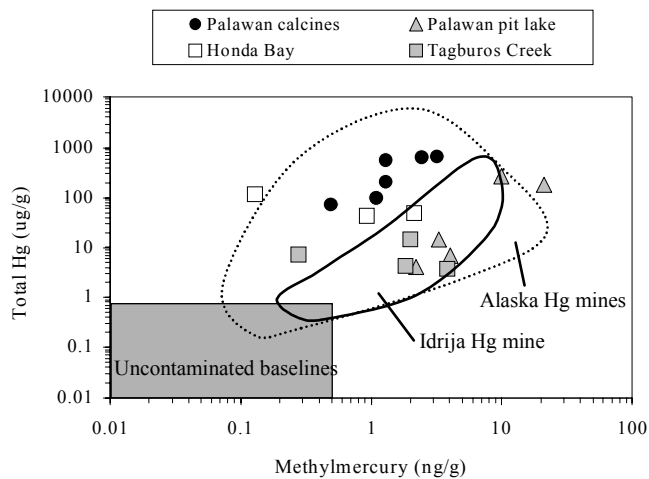


Figure 3. Total Hg concentration versus methylmercury in PQM calcines, Honda Bay calcines, pit lake sediments, and Tagbueros Creek sediments. For comparison, the range of data is shown for similar samples from Idrija, Slovenia¹⁰ (solid line) and southwestern Alaska¹¹ (dashed line). Uncontaminated baseline data (shaded box) are from stream sediment samples collected distant from mines.

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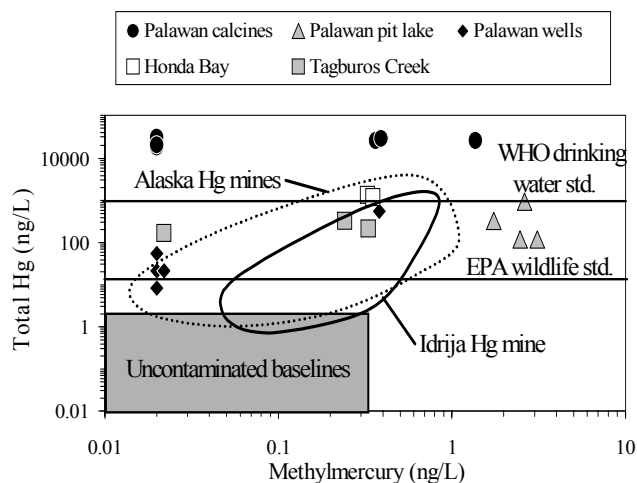


Figure 4. Total Hg concentration versus methylmercury in unfiltered water collected from in and around the PQM site. For comparison, the range of data is shown for similar samples from the Idrija Hg mine, Slovenia¹⁰ (solid line), and Hg mines in southwestern Alaska¹¹ (dashed line). Also shown is the WHO 1,000 ng/L drinking water standard for total Hg, and the USEPA 12 ng/L standard for total Hg for the protection of adverse *chronic* effects to aquatic wildlife.

ENVIRONMENTAL MERCURY AND METHYLMERCURY CONTAMINATION cont.

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Table 1. Mercury and methyl-Hg concentrations from mines discussed in this report.

Location	Unfiltered water		Sediment or soil	
	Hg (ng/L)	Methyl-Hg (ng/L)	Hg (µ g/g)	Methyl-Hg (ng/g)
Mercury mine, Palawan, Philippines ¹²				
Mine-waste calcines	18,000-31,000	<0.02-1.4	28-660	0.13-3.2
Pit lake	120-940	1.7-3.1	14-400	2.0-21
Stream below mine	170-330	<0.02-0.33	3.7-15	0.28-3.9
Water wells	8-550	<0.02-0.38	--	--
Mercury mines, southwestern Alaska ¹¹				
Streams below mines	1.0-2,500	0.01-1.2	0.90-5500	0.05-31
Untaminated baseline streams	0.10-1.4	0.04-0.2	0.02-0.78	0.10-0.30
Mercury mine, Idrija, Slovenia ¹⁰				
Mine-waste calcines	--	--	4.8-727	1.3-14
Stream above mine	8	0.1	5.4	3.6
Streams below mine	5-200	0.08-0.50	0.31-291	0.12-10
Mercury mines, west-central Nevada ¹³				
Mine-waste calcines	--	--	14-14,000	<0.05-96
Streams below mines	6.0-2000	0.039-0.92	0.80-170	0.12-0.95
Untaminated baseline streams	2.1-9.0	<0.02-0.27	0.008-0.44	<0.05-0.090

-- indicates no data or not applicable.

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