Mercury and methylmercury contents in mine-waste calcine, water, and sediment collected from the Palawan Quicksilver Mine, Philippines

John E. Gray · Ian A. Greaves · Dorina M. Bustos · David P. Krabbenhoft

Abstract The Palawan Quicksilver mine, Philippines, produced about 2,900 t of mercury during mining of cinnabar ore from 1953 to 1976. More than 2,000,000 t of mine-waste calcines (retorted ore) were produced during mining, much of which were used to construct a jetty in nearby Honda Bay. Since 1995, high Hg contents have been found in several people living near the mine, and 21 of these people were treated for mercury poisoning. Samples of mine-waste calcine contain high total Hg concentrations ranging from 43–660 μg/g, whereas total Hg concentrations in sediment samples collected from a mine pit lake and local stream vary from 3.7–400 μg/g. Mine water flowing through the calcines is acidic, pH 3.1–4.3, and total Hg concentrations ranging from 18–31 μg/l in this water significantly exceed the 1.0-μg/l drinking water standard for Hg recommended by the World Health Organization (WHO). Total Hg contents are generally lower in water samples collected from surrounding domestic wells, the mine pit lake, Honda Bay, and the nearby stream, varying from 0.008–1.4 μg/l. Methylmercury concentrations in water draining mine calcines range from <0.02–1.4 ng/l, but methylmercury is highest in the pit lake water, ranging from 1.7–3.1 ng/l. Mercury methylation at the Palawan mine is similar to or higher than that found in other mercury mines worldwide. Much of the methylmercury generated in Palawan mine-waste calcines and those in Honda Bay is transferred to water, and then to marine fish and seafood. A food source pathway of Hg to humans is most likely in this coastal, high fish-consuming population.

Keywords Mercury · Methylmercury · Mine wastes · Philippines

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Introduction

The Palawan Quicksilver Mine (PQM), Philippines, is near the villages of Santa Lourdes, Tagburos, and Sitio Honda Bay (Fig. 1) where about 2,000 residents live on and near the mine. In addition, the mine is about 3 km from Honda Bay, which is a local fishery and recreational area. Since 1995, blood Hg contents were found to be in excess of a 20 ng/ml recommended tolerable level (NAS 1978; Tollefson 1989) in several people living near the mine, and 21 of these people experienced symptoms of mercury poisoning and were detoxified with chelating drugs. Approximately 2,000,000 t of mine-waste calcines were produced during mining (Fig. 2A) and about half of these calcines were transported to Honda Bay (Fig. 2B) to construct a peninsula or jetty about 600 m long by 50 m wide, which was used as an operational port for the mine. Presently, about 200 people live on the jetty in Honda Bay (the village of Sitio Honda Bay). Residents in the area continue to be concerned about Hg at the mine site and in Honda Bay. Mercury is a heavy metal of environmental concern because elevated concentrations are toxic to living organisms. In humans, mercury damages the central nervous system and is especially toxic to the fetus (USEPA 1976; WHO 1976; Clarkson 1990; Fitzgerald and Clarkson 1991). Under certain conditions, some inorganic Hg (e.g., that in

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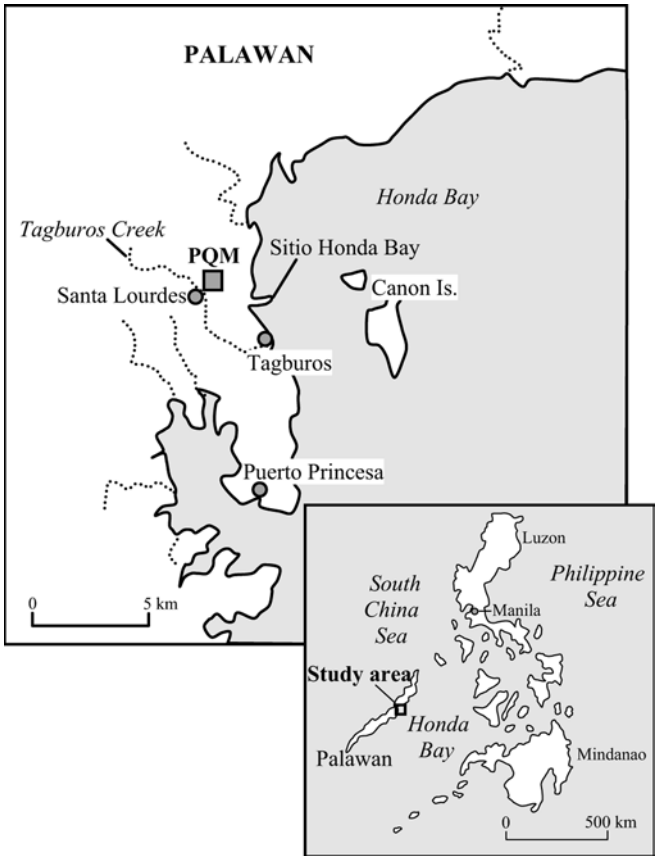

Fig. 1
Location of the Palawan Quicksilver Mine (*PQM*), Palawan, Philippines

Fig. 2A–C
Photos of PQM calcines. **A** Highly turbid water is shown flowing through PQM calcines following a rainstorm event. **B** 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. **C** This view shows human and domestic animal activity on the PQM site. A basketball court used by residents of Santa Lourdes has been built on PQM calcines, which are visible in the foreground. Cattle commonly graze on the site

ore and calcines) may be converted to organic forms of Hg (e.g., methylmercury, CH_3Hg^+). Methylmercury is a highly toxic Hg compound that is water soluble and can biomagnify with increasing trophic position in the food chain. Mercury methylation is primarily a result of anaerobic microbial activity, which is typically enhanced in sediments with high organic matter (Compeau and Bartha 1985). Mercury-contaminated sediment and water from the PQM is potentially hazardous to residents and wildlife when it enters local surface water and Honda Bay. More important, is methylmercury that has formed at the mine site or in Honda Bay because it is rapidly absorbed by biota, including fish, in this ecosystem. Mercury contamination of fish is a common problem in the USA and throughout the world. The pathway of methylmercury contamination to humans is typically through fish consumption (USEPA 1997). Because Hg-rich, mine-waste calcines from the mine were dumped into Honda Bay, Hg contamination of fish is of concern. Previous research at the PQM has focused on evaluating Hg contents around the mine and in residents in the area, but no methylmercury determinations have been reported. Because of its toxicity and bioavailability, measurement of methylmercury is critical for understanding Hg contamination. To evaluate mercury methylation in this area, total Hg and methylmercury concentrations were measured in (1) mine-waste calcines from the PQM and surface water flowing through these calcines, (2) stream sediment and stream water from Tagburos Creek, (3) sediment and water collected from the PQM pit lake, (4) mine-waste calcines and water in Honda Bay, (5) water from domestic wells in Santa Lourdes, and (6) water from a nearby commercial hot spring.

Palawan mine-site description

Palawan Quicksilver Mining Inc., Philippines, operated a mine from 1953 to 1976 that produced about 2,900 t of mercury (>80,000 flasks, 1 flask =76 lbs.). Mercury produced from this mine was significant for local economic development, but the mine ranks as only a moderate-sized mercury mine on an international scale. Nearly all of the mercury at the PQM was produced from ore containing cinnabar (HgS), however, the deposit also contains abundant pyrite (FeS_2). The combined presence of cinnabar and pyrite is potentially hazardous because pyrite is a significant acid-water producing mineral, and Hg compounds are more soluble and reactive in acidic water. Although Hg compounds, such as elemental Hg (Hg^0), and Hg salts, such as Hg chlorides and oxychlorides, were not measured in this study, they are commonly produced during the roasting of Hg-bearing ore (Kim and others 2000). Highly elevated concentrations of dissolved Hg (see Results below) were found in mine waters flowing through the PQM calcines, which suggest the presence of soluble Hg compounds in these calcines.

The PQM is within the Tagburos Creek watershed, which flows adjacent to the mine. Tagburos Creek is used by some of the local population for domestic activities (e.g., washing clothes) and by domestic animals (e.g., water buffalo). Tagburos Creek flows into Honda Bay a few kilometers downstream from the PQM. There is also a large pit lake that has formed at the mine site when water filled the mine workings following the cessation of mining. There are several homes along the perimeter of pit lake, and fish were observed in the lake, although fish in the pit lake were not collected for this study. Part of the mine pit is presently used as a landfill for refuse from the local communities, but no attempt was made to evaluate potential contamination from the landfill or its effect on the pit lake.

During our fieldwork in March 2000, there appeared to be no physical or regulatory restrictions of human activity at the PQM. There are several residential homes on or near mine-waste calcines, and at least one domestic water well that was drilled into calcines. In addition, several other domestic water wells in Santa Lourdes are within 1 km of the mine; these wells are generally shallow and <10 m deep. Children were observed playing at the PQM on mine-waste calcines, and domestic farm animals graze on grass growing in calcines (Fig. 2C). Many residents in the area conduct recreational and commercial fishing, boating, swimming, and diving in Honda Bay. Puerto Princesa City, the capital of Palawan, is about 12 km south of the mine and many residents in the region visit Honda Bay. There is also a popular commercial hot spring about 5 km north of the PQM.

Methods

Stream sediment samples were collected from channel-bed alluvium, and at each site, sediment was composited from several localities in the channel for these samples. Mine-waste calcines and pit lake sediments were collected as grab samples. Prior to analysis, the sediment samples were air-dried, sieved to minus-80-mesh (0.18 mm), and ground. Mine-waste calcines were ground but not sieved. Unfiltered water samples were collected for total Hg and methylmercury analysis in pre-cleaned, Teflon bottles and, within 8 h of collection, the water samples were acidified with ultra-pure hydrochloric acid. An additional set of filtered and unfiltered water samples were collected at each locality for total Hg analysis; these samples were collected to compare suspended (unfiltered) and dissolved (filtered) Hg concentrations in water. The filtered and unfiltered water samples for total Hg determinations were collected in pre-cleaned, ultra-pure glass bottles, and preserved with ultrex nitric acid saturated with sodium dichromate. All filtered water samples were passed through a 0.45-μm sterile membrane. Unfiltered water samples for dissolved organic carbon (DOC) were collected in glass vessels, and these samples were filtered in the lab prior to analysis. Water characteristics such as pH, conductivity, alkalinity, turbidity, temperature, Fe^{2+}, and dissolved oxygen were measured at each sample site.

Measurement of total Hg follows EPA Method 1631, and EPA Method 1630 for the analysis of methylmercury (Bloom 1989). Mercury was determined in the calcine, sediment, and water samples using cold-vapor atomic absorption spectrophotometry (CVAAS) techniques modified from Kennedy and Crock (1987), or by a cold-vapor atomic fluorescence spectrometry (CVAFS) technique developed by Bloom and Fitzgerald (1988). Methylmercury was determined in the samples using CVAFS (Bloom 1989). During methylmercury analysis, the sediment and calcine samples were extracted into methylene chloride during digestion to avoid possible methylation artifact effects (Bloom and others 1997). Loss on ignition (LOI) was determined on a subset of the sediment samples as an estimate of total organic carbon. Analysis for DOC in water was by infrared spectrometry. Quality control for Hg and methylmercury analysis was addressed with method blanks, blank spikes, matrix spikes, certified reference materials, and sample duplicates. Recoveries on blank and matrix spikes were 80–120%. The relative standard deviation was <15% on reference standards. Method blanks were below the limits of determination. Limits of determination were 2.0 ng/g for total Hg and 0.05 ng/g for methylmercury in sediment samples, and 0.2 ng/l for total Hg and 0.02 ng/l for methylmercury in water samples.

Results

Mine-waste calcine samples collected from the PQM and Honda Bay contain highly variable total Hg concentrations ranging from 43–660 μg/g (Fig. 3, Table 1). Total Hg concentrations in pit lake and Tagburos Creek sediments were generally lower, varying from 3.7–400 μg/g. Methylmercury concentrations in the calcines and sediment samples collected varied from 0.13–21 ng/g. The highest

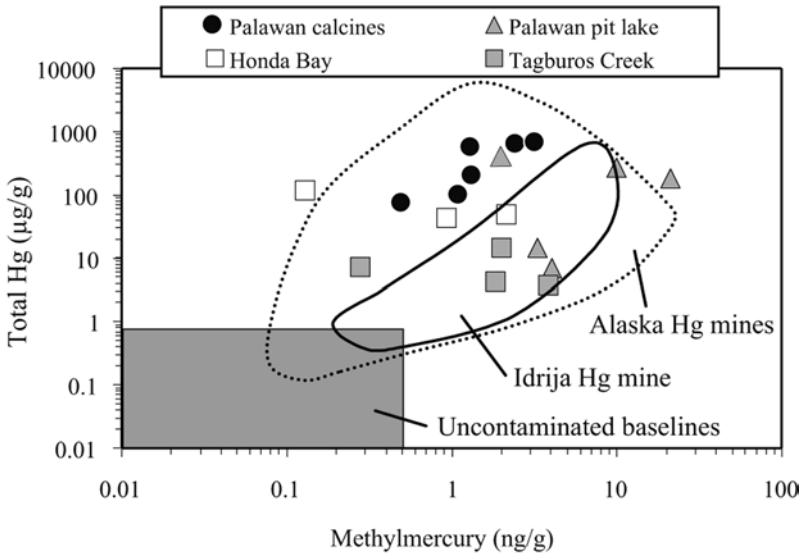

Fig. 3
Total Hg concentration versus methylmercury in PQM calcines, Honda Bay calcines, pit lake sediments, and Tagburos Creek sediments. For comparison, the range of data is shown for similar samples from Idrija, Slovenia (*solid line*; Horvat and others 2001) and southwestern Alaska (*dashed line*; Gray and others 2000). Uncontaminated baseline data (*shaded box*) are from stream sediment samples collected distant from mines (Gray and others 2000; Ullrich and others 2001

Table 1
Mercury data for sediment and mine-waste calcine samples collected in and around the Palawan Quicksilver Mine (PQM). *n.d.* Not determined

Sample no.	Location/description	Total Hg (µg/g)	Methylmercury (ng/g)
PQqple01	PQM, mine-waste calcine	560	1.3
PQqple02	PQM, mine-waste calcine	660	3.2
PQqple03	PQM, mine-waste calcine	97	1.1
PQqple04	PQM, mine-waste calcine	72	0.49
PQqple05	PQM, mine-waste calcine	200	1.3
PQqple06	PQM, mine-waste calcine	640	2.5
PQMI07ca	PQM, mine-waste calcine	70	n.d.
PQMI08ca	PQM, mine-waste calcine	28	n.d.
PQMI09ca	PQM, mine-waste calcine	170	n.d.
Hbay01s	Honda Bay, mine-waste calcine	49	2.1
Hbay02s	Honda Bay, mine-waste calcine	43	0.92
Hbay03s	Honda Bay, mine-waste calcine	120	0.13
Hbay01ca	Honda Bay, mine-waste calcine	100	n.d.
Hbay02ca	Honda Bay, mine-waste calcine	130	n.d.
Hbay03ca	Honda Bay, mine-waste calcine	70	n.d.
PQMI01ca	Honda Bay, mine-waste calcine	120	n.d.
PQMI02ca	Honda Bay, mine-waste calcine	140	n.d.
PQMI03ca	Honda Bay, mine-waste calcine	90	n.d.
PQMI04ca	Honda Bay, mine-waste calcine	180	n.d.
PQMI05ca	Honda Bay, mine-waste calcine	140	n.d.
PQMI06ca	Honda Bay, mine-waste calcine	130	n.d.
PQpit01s	PQM, pit lake sediment	180	21
PQpitd1s	PQM, pit lake sediment	270	10
PQpit02s	PQM, pit lake sediment	15	3.3
PQpitd2s	PQM, pit lake sediment	6.9	4.0
PQpit03s	PQM, pit lake sediment	400	2.0
PIT01s	PQM, pit lake sediment	170	n.d.
PIT02s	PQM, pit lake sediment	14	n.d.
TCK01s	Tagburos Creek, sediment 2.4 km above PQM	4.2	1.9
TCK02s	Tagburos Creek, sediment adjacent to PQM	15	2.0
TCKd2s	Tagburos Creek, sediment adjacent to PQM	3.7	3.9
TCK03s	Tagburos Creek, sediment 3 km below PQM	7.1	0.28

methylmercury contents were found in the pit lake sediments, which ranged from 2.0–21 ng/g (Fig. 3). Calcine samples collected from the PQM and Honda Bay contained methylmercury concentrations ranging from 0.13–3.2 ng/g (Table 1). The pit lake sediments generally contain more organic matter (Fig. 4) and the increased methylmercury in these samples is probably related to higher microbial activity in this area. Conversely, there is generally less organic material in the mine waste calcines, probably less biological activity, and lower methylmercury production in the calcines because this material is mostly crushed and retorted ore.

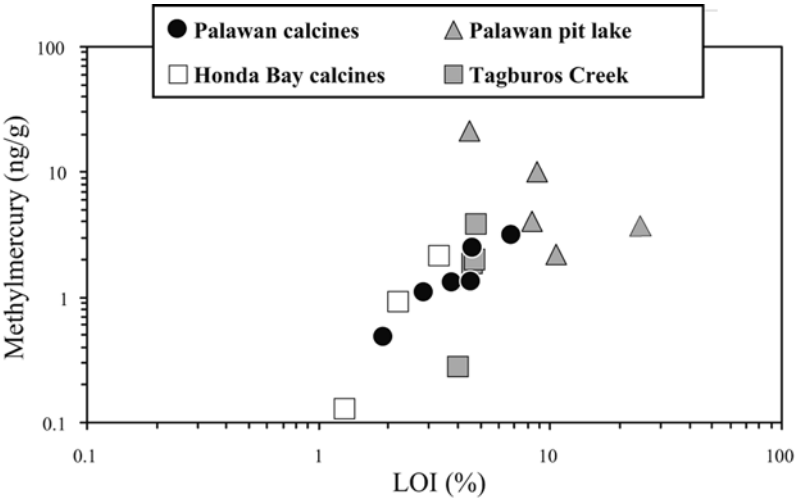

Fig. 4
Methylmercury concentrations versus loss on ignition (LOI) in PQM calcines and sediment samples

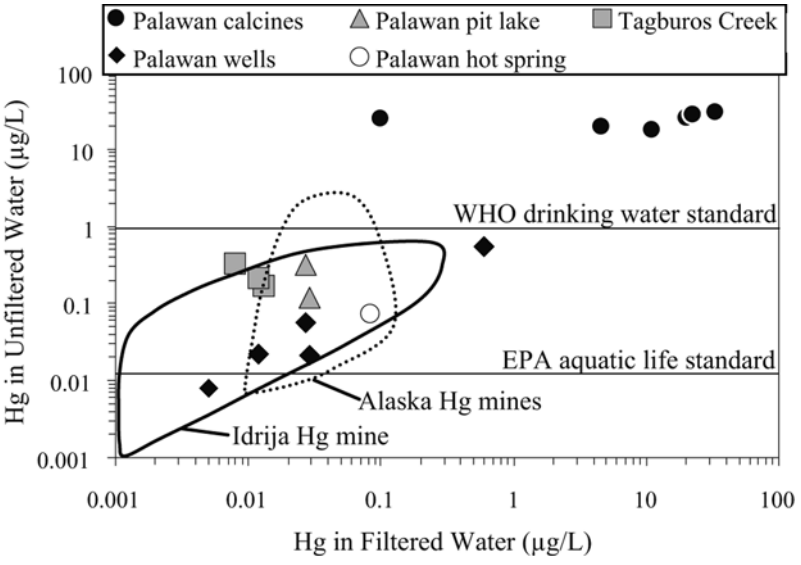

Fig. 5
The concentration of Hg in unfiltered water versus Hg in filtered water samples collected from in and around the PQM. For comparison, data are shown for similar samples collected from the Idrija Hg mine, Slovenia (Horvat and others 2001) and Hg mines in southwestern Alaska (Gray and others 2000). Also shown are the WHO 1.0-µg/l drinking water standard for total Hg, and the USEPA 0.012-µg/l standard for total Hg for the protection of adverse chronic effects to aquatic wildlife

Unfiltered water draining the calcine piles on the PQM site is acidic, pH 3.1–4.3, and total Hg concentrations ranging from 18–31 µg/l in this water significantly exceed the 1.0-µg/l drinking water standard for Hg (WHO 1984; Fig. 5). Total Hg contents in these mine waters also exceed the 10-µg/l standard for Hg recommended in the USA for watering of livestock (NDEP 2000), and because livestock are common on the PQM site, this situation is potentially adverse for such domestic animals. Such high Hg concentrations in water flowing through the mine calcines are related to the high solubility of Hg in acidic water. Most of the Hg in the mine waters was in the filtered samples suggesting dominantly dissolved Hg transport. During rain storms there is a significant volume of highly-turbid, Hg-rich water runoff that drains and flows through the mine calcines (Fig. 2A). There is a positive correlation between low pH and high Hg contents in the mine-water samples (Fig. 6). Acid water is generated on the PQM site through the oxidation of abundant pyrite waste rock that is visible throughout the calcines.

Unfiltered water samples collected from domestic wells surrounding the PQM, the mine pit lake, Honda Bay, and Tagburos Creek have near neutral pH, 6.3–8.3, and contain lower total Hg concentrations (when compared with the mine waters), varying from 0.008–1.4 µg/l (Fig. 5). Most of the Hg in the well water, pit lake, Honda Bay, and Tagburos Creek is in the unfiltered samples indicating the presence of dominantly particulate Hg. Nearly all unfiltered water samples collected in this study contain total Hg concentrations exceeding the 0.012 µg/l Hg standard recommended by the USEPA to protect against chronic effects to aquatic wildlife (USEPA 1992; Fig. 5). Methylmercury concentrations in unfiltered samples of mine water range from <0.02–1.4 ng/l, but methylmercury is higher in the pit lake water, ranging from 1.7–3.1 ng/l (Table 2, Fig. 7). Higher methylmercury contents in water generally correlated with higher DOC (Table 2). The higher methylmercury contents in the pit lake waters are consistent with those observed in the pit lake sediments, indicating transference of methylmercury from the sediment to the water column.

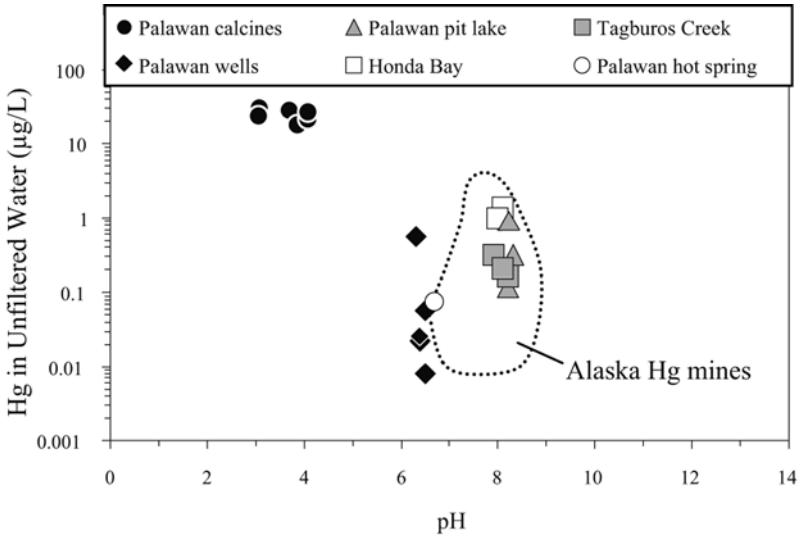

Fig. 6
The concentration of total Hg in unfiltered water versus pH for samples collected in and around the PQM. The range of data is also shown for unfiltered mine-water samples from southwestern Alaska (Gray and others 2000)

Table 2
Geochemical data for water samples collected in and around the Palawan Quicksilver Mine (PQM). *n.d.* Not determined

Sample no.	Location/description	Total Hg (µg/l)	Methylmercury (ng/l)	pH	Conductivity (µS/cm)	DOC (mg/l)
PQple01	Unfiltered water draining PQM calcines	26	1.4	4.1	360	1.1
PQple02	Unfiltered water draining PQM calcines	18	<0.02	3.9	380	0.73
PQple03	Unfiltered water draining PQM calcines	25	0.36	3.1	1,100	1.5
PQple04	Unfiltered water draining PQM calcines	31	0.39	3.7	390	0.93
PQple05	Unfiltered water draining PQM calcines	25	n.d.	4.3	220	3.3
PQple06	Unfiltered water draining PQM calcines	20	<0.02	4.1	180	1.9
PQple01F	Filtered water draining PQM calcines	21	n.d.	4.1	n.d.	n.d.
PQple02F	Filtered water draining PQM calcines	11	n.d.	3.9	n.d.	n.d.
PQple03F	Filtered water draining PQM calcines	20	n.d.	3.1	n.d.	n.d.
PQple04F	Filtered water draining PQM calcines	30	n.d.	3.7	n.d.	n.d.
PQple05F	Filtered water draining PQM calcines	0.10	n.d.	4.3	n.d.	n.d.
PQple06F	Filtered water draining PQM calcines	4.5	n.d.	4.1	n.d.	n.d.
Hbay01	Unfiltered water from Honda Bay	1.4	0.32	8.1	n.d.	1.1
Hbay02	Unfiltered water from Honda Bay	1.0	0.23	8.0	n.d.	1.0
PQpit01	Unfiltered water from PQM pit lake	0.32	1.7	8.3	980	15
PQpit02	Unfiltered water from PQM pit lake	0.12	3.1	8.2	970	16
PQpitd2	Unfiltered water from PQM pit lake	0.12	2.5	8.2	970	n.d.
PQpit03	Unfiltered water from PQM pit lake	0.94	2.6	8.2	960	16
PQpit01F	Filtered water from PQM pit lake	0.027	n.d.	8.3	n.d.	n.d.
PQpit02F	Filtered water from PQM pit lake	0.029	n.d.	8.2	n.d.	n.d.
TCK01	Unfiltered water from Tagburos Creek	0.17	<0.02	8.2	370	2.1
TCK02	Unfiltered water from Tagburos Creek	0.33	0.24	7.9	380	2.4
TCK03	Unfiltered water from Tagburos Creek	0.21	0.33	8.1	370	3.8
TCK01F	Filtered water from Tagburos Creek	0.013	n.d.	8.2	n.d.	n.d.
TCK02F	Filtered water from Tagburos Creek	0.008	n.d.	7.9	n.d.	n.d.
TCK03F	Filtered water from Tagburos Creek	0.012	n.d.	8.1	n.d.	n.d.
SLwell01	Unfiltered water, Santa Lourdes domestic well	0.021	<0.02	6.4	610	2.1
SLwell02	Unfiltered water, Santa Lourdes domestic well	0.55	0.38	6.3	540	1.2
SLwell03	Unfiltered water, Santa Lourdes domestic well	0.022	<0.02	6.4	630	1.2
SLwell04	Unfiltered water, Santa Lourdes domestic well	0.057	<0.02	6.5	840	1.9
SLwell05	Unfiltered water, Santa Lourdes domestic well	0.008	<0.02	6.5	930	1.5
SLwell01F	Filtered water, Santa Lourdes domestic well	0.021	n.d.	6.4	n.d.	n.d.
SLwell02F	Filtered water, Santa Lourdes domestic well	0.60	n.d.	6.3	n.d.	n.d.
SLwell03F	Filtered water, Santa Lourdes domestic well	0.012	n.d.	6.4	n.d.	n.d.
SLwell04F	Filtered water, Santa Lourdes domestic well	0.027	n.d.	6.5	n.d.	n.d.
SLwell05F	Filtered water, Santa Lourdes domestic well	0.005	n.d.	6.5	n.d.	n.d.
SLhot01	Unfiltered water from hot spring	0.075	0.08	6.7	4,600	6.5
SLhotd1	Unfiltered water from hot spring	0.075	0.09	6.7	4,600	n.d.
SLhot01F	Filtered water from hot spring	0.080	n.d.	6.7	n.d.	n.d.

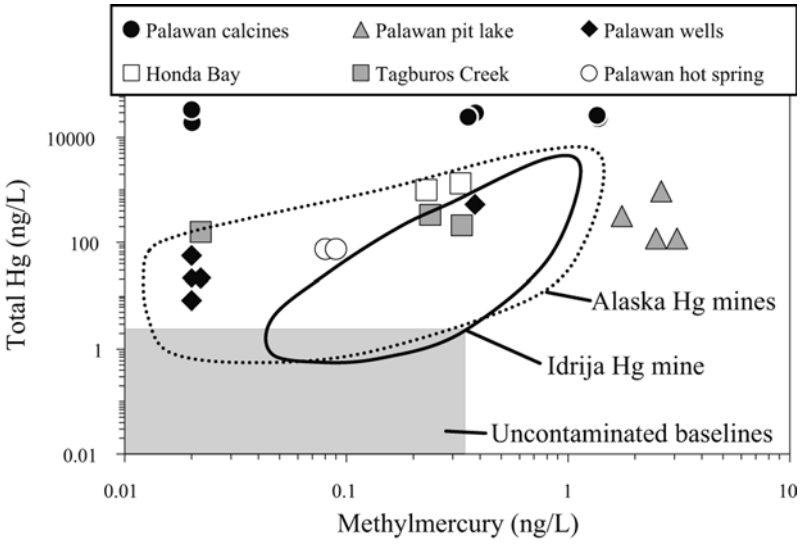

Fig. 7
Total Hg concentration versus methylmercury in unfiltered water collected from in and around the PQM site. For comparison, the range of data are shown for similar samples from the Idrija Hg mine, Slovenia (*solid line*; Hines and others 2000; Horvat and others 2001), and Hg mines in southwestern Alaska (*dashed line*; Gray and others 2000). Uncontaminated baseline data (*shaded box*) are for unfiltered water samples collected distant from mines (Watras and others 1994; Lyons and others 1999; Gray and others 2000)

Discussion

Mercury concentrations in PQM calcines are highly elevated and highly variable, which is typical of mercury mines throughout the world (Suchanek and others 1998; Kim and others 2000; Gray 2001; Horvat and others 2001). Results for total Hg in the PQM calcines (43–660 μg/g) are consistent with that previously reported (as much as 570 μg/g, Benoit and others 1994). Fine-grained and encapsulated cinnabar were observed in some calcines, and the high variability of Hg within these calcines probably indicates that retorting was not totally or uniformly efficient, which is also typical of mercury mines worldwide (Gray 2001). As a result of the high concentration of Hg in the calcines, about 400 t of Hg may remain in the mine wastes at the PQM and in Honda Bay. Some portion of this Hg is available for leaching into the environment as it is exposed to surface weathering. Highly elevated total Hg concentrations in water (Fig. 5) flowing through the PQM calcines indicate significant leaching of Hg, and suggest that the calcines contain not only cinnabar, but also soluble Hg salts.

The concentration of methylmercury in mine wastes, sediment, and water in the area is more important than total Hg contents because methylmercury is highly toxic and is a bioavialable mercury compound. There is no regulatory methylmercury standard, but methylmercury contents in the Palawan samples are similar to or higher than methylmercury in similar samples collected near other cinnabar-dominant mercury mines, such as Idrija, Slovenia, and in southwestern Alaska (Figs. 3 and 7; Gray and others 2000; Horvat and others 2001). At Idrija and in Alaska, mercury mines are within aquatic ecosystems that have been contaminated with Hg. These ecosystems support fish, and in these instances, some marine and freshwater fish collected downstream from the mines contain elevated concentrations of Hg, in excess of the 0.5 μg/g (wet weight, fish muscle) Hg standard used by many states in the USA. Similar to these mines, the data for the PQM indicate translocation of methylmercury from mine-waste calcines and sediments, to stream water, and then to Honda Bay. It is also likely that methylmercury in mine wastes and water at the PQM and in Honda Bay is transferred to biota, such as marine fish. Methylmercury is readily absorbed by and bioaccumulates in aquatic organisms, especially fish, and it is well established that most of the Hg in fish muscle is methylmercury, typically >90% of the total Hg (Friberg and Vostal 1972; NAS 1978; Clarkson 1990; USEPA 1997; Lacerda and Salomons 1998).

Kapauan and others (1982) first reported elevated concentrations of Hg in fish from Honda Bay. In their study, marine fish (alakaak, lapu-lapu, maya-maya, asohos, ayungin, malakapas, and samaral) collected from Honda Bay contained total Hg contents ranging from 0.16–1.05 μg/g (wet weight, fish muscle). Similarly, other studies have shown that marine fish in Honda Bay (malakapas, tuko, taba-taba, sap-sap, salmonete, and mackerel) contain elevated total Hg contents, varying from 0.03–1.07 μg/g (wet weight, fish muscle) (Williams and others 1999). The average Hg concentration for most of these species is below the 0.5 μg/g Hg standard commonly used in the USA, but some of these fish exceed this standard. The mean Hg content in mackerel (0.33 μg/g) from Honda Bay is higher than that found in mackerel worldwide (about 0.2 μg/g; Williams and others 1999). In addition, green mussels also collected from Honda Bay contain elevated Hg concentrations ranging from 0.86–4.4 μg/g, and average about 2.1 μg/g (wet weight; Williams and others 1999). Conversely, green mussels collected from near Canon Island, about 6 km from Honda Bay, contained much lower Hg concentrations ranging from 0.24–0.58 μg/g, averaging about 0.34 μg/g (wet weight; Williams and others 1999). These mussel data indicate significant Hg bioaccumulation in biota in Honda Bay, and possibly significant Hg methylation assuming that most of the Hg in the green mussels is methylmercury.

To evaluate methylmercury exposure among residents living near the PQM, the intake of methylmercury through

fish consumption was calculated. This dietary Hg intake was then compared with the USEPA Hg reference dose of 0.1 μg methylmercury/kg of body weight/day (USEPA 1997), which is used in the USA for protection of public health (this is a better evaluation of human Hg exposure than simply comparing Hg concentrations in fish to a Hg standard). Using this approach, it is possible to estimate the intake of methylmercury resulting from a moderate-sized meal of a commonly eaten fish. Mackerel in Honda Bay average about 0.3 μg/g methylmercury, and consumption of a 100 g mackerel fillet corresponds to an intake of about 30 μg methylmercury; assuming 95% absorption of methylmercury in the human gastrointestinal system, the methylmercury dose would be 28.5 μg. The USEPA reference dose suggesting human consumption 0.1 μg methylmercury/kg of body weight/day, corresponds to 6.5 μg methylmercury/day for a 65-kg adult. Thus, the single mackerel meal would exceed the USEPA daily recommendation, and this calculation suggests human consumption should be limited to fewer than two of such fish meals/week. Conversely, the WHO presently uses a less restrictive Hg recommendation of 0.47 μg methylmercury/kg of body weight/day, which corresponds to a daily intake of about 30 μg methylmercury for an average adult, and suggests that about one Honda Bay fish/day could be consumed. However, Filipinos are heavy fish consumers, especially those living in coastal areas, and adults may consume several types of seafood each day. In addition, Filipinos routinely consume all parts of the fish, including the skin, which generally contain high Hg concentrations (Lacerda and Salomon 1998). Residents of the Honda Bay area who rely on fish for protein in their diets could ingest as much as 100 μg of methylmercury/day, and perhaps more if they eat seafood with highly elevated Hg contents. These data suggest that the most likely pathway of Hg to residents in the Honda Bay area is through the consumption of fish and seafoods. Infants, young children, and pregnant women are at highest risk from methylmercury and are the most likely to experience adverse health effects even at low levels of exposure (USEPA 1976, 1997; Tollefson 1989).

Data presented here indicate that local Hg contamination is related to the PQM. However, a previous study concluded that the concentration of Hg in Honda Bay sediments is within the global background range, that there is low Hg bioavailability, and that the detoxification of residents in this area with blood Hg contents in excess of 20 ng/ml was difficult to justify (Williams and others 1999). The conclusion of low Hg bioavailability in and around the PQM is questionable, especially considering that the Williams and others (1999) study was based primarily on total Hg concentrations. Mercury methylation and bioavailability is more adequately addressed by the measurement of methylmercury, and Hg contamination in and around the PQM has been potentially underestimated because previous investigations did not measure methylmercury in the area. Data shown here indicate that methylmercury is generated in mine-waste calcines and transported by runoff to Honda Bay, and indicate that methylmercury is also formed in the calcines presently in Honda Bay (Figs. 3 and 7). Total Hg and methylmercury concentrations in sediment and water collected in and around the PQM are generally higher than that found in uncontaminated areas (Figs. 3 and 7). Methylmercury formation is dominantly a result of microbial activity, and Hg methylation is generally higher in tropical environments as a result of high temperatures, high organic matter, and increased biological activity (Lacerda and Salomons 1998); Hg methylation is also known in marine environments (Mason and Fitzgerald 1990; Hines and others 2000). The PQM calcines and those in Honda Bay are sources of methylmercury to marine seafood, and thus, to humans who eat fish and shellfish from the bay. Methylmercury formation will probably continue in Honda Bay as long as mine-wastes calcines remain there. Numerous studies worldwide indicate that the dominant pathway of methylmercury to humans is through fish consumption (WHO 1976; Clarkson 1990; Fitzgerald and Clarkson 1991; USEPA 1997). In the PQM area, residents with high Hg contents are most likely receiving Hg primarily through fish consumption. Total Hg in water from Santa Lourdes domestic wells is below the WHO drinking water standard (Fig. 5), and this well water is an unlikely source of significant Hg to residents living near the mine. Inhalation of significant Hg vapor or ingestion of substantial particulate Hg through hand to mouth contact of mine wastes also seems unlikely. The dominant form of Hg in the drinking water and mine-wastes is inorganic Hg (HgS and Hg salts), with a generally low proportion of methylmercury. The absorption rate of inorganic Hg in the human gastrointestinal system is much lower (about 1–7%) versus that for methylmercury (about 95%; Friberg and Vostal 1972; USEPA 1997), thus, Hg poisoning of humans by inorganic Hg exposure is less common (USEPA 1976). In and around the PQM, several adverse factors contributed to local Hg contamination of marine fish and shellfish, the most unfortunate of which was the placement of Hg-rich mine wastes into Honda Bay. The PQM is a unique example of significant methylmercury formation near a mercury mine, Hg contamination of local marine seafood, and subsequent uptake of high levels of methylmercury by humans consuming such seafood.

Conclusions

At the PQM, total Hg concentrations in mine-waste calcines are highly elevated (as much as 660 μg/g), which is similar to Hg contents at other mercury mines worldwide. These results indicate that retorting of cinnabar-rich ore was not completely or uniformly efficient. Some portion of the Hg remaining in the calcines is available for leaching into the surrounding environment, which is potentially adverse in Honda Bay where abundant mine wastes were dumped.

Total Hg contents are also highly elevated (18–31 μg/l) in unfiltered surface water flowing through the PQM calcines.

Although the dominant form of Hg in the mine waste is cinnabar, high total Hg contents in filtered mine waters suggest that soluble Hg salts are also present. The concentration of Hg in unfiltered mine waters exceeds the WHO drinking water Hg standard of 1.0 μg/l. These mine waters are probably not a source of public drinking water, but there are presently no restrictions of human or domestic animal activity at the PQM. Total Hg contents in most unfiltered water samples collected in this study also exceed the USEPA 0.012 μg/l standard for Hg established to protect against chronic effects to aquatic organisms. Although there is no regulatory standard for methylmercury, the concentration of methylmercury in water and sediment samples from the PQM area is comparable to or higher than that in similar samples from other mercury mines where Hg methylation has led to elevated Hg contents in local fish. Increased Hg methylation in the PQM area may be a result of the tropical environment and high organic contents. Data shown here indicate that methylmercury generated in mine wastes and sediments is transferred to the water column, where it is bioavailable to fish and seafood, and potentially adverse in Honda Bay. Residents in this area with elevated Hg are probably exposed to Hg through food sources, most likely fish and seafood from Honda Bay. Palawan is a coastal, high fish-consuming society, where people typically consume fish and seafood daily. Most of the Hg in fish is methylmercury, and daily consumption of fish from Honda Bay could exceed the USEPA suggested human intake of 0.1 μg methylmercury/kg of body weight/day, and the WHO recommendation of 0.47 μg methylmercury/kg of body weight/day. Based on these recommendations, residents in this area should restrict consumption of seafood from Honda Bay.

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