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Mercury concentrations of fish, river water, and sediment in the Río Ramis-Lake Titicaca watershed, Peru

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Abstract

This study reports the first set of data on the concentration of mercury in muscle tissue of several varieties of fish from Lake Titicaca, including the pejerrey (*Basilichthyes bonariensis*), the carachi (*Orestias*), and 2 types of indigenous catfish (*Trichomycterus*). Approximately 27% of the pejerrey and 75% of the carachi exceeded the US EPA fish tissue-based water quality criterion level of 0.30 μg g^{-1}. Mercury levels of pejerrey increased with fish size, although this relationship was less apparent for the smaller carachi. The pejerrey and carachi are important food fish for local residents. A synoptic sampling of the Río Ramis – the largest tributary to Lake Titicaca – was conducted in an attempt to determine if mercury releases from artisanal gold mining could be an important source of Hg contamination to Lake Titicaca. Although highly elevated concentrations of Hg and other heavy metals were documented in headwater streams near the mining centers of La Rinconada and Cecilia, the quantity of Hg entering Lake Titicaca that could be attributed to mining in the Ramis watershed was below the quantifiable limit in our July 2002 study. This does not diminish the localized threat to mercury exposure for the artisanal gold miners themselves, as well as their families. Further studies of mercury dynamics in Lake Titicaca are recommended, as well as in the rivers draining into the lake. It is probable that most of the downgradient transport of Hg and other trace metals from the headwater mining centers occurs as suspended sediment during seasonal periods of high-flow.

Keywords: Mercury; Artisanal gold mining; Human health; Fish; Lake Titicaca; Peru

1. Introduction

Small-scale artisanal gold mining operations have recently been estimated to release as much as 450 tonnes of mercury annually to the environment (Lacerda, 2003). Amalgamation is illegal in most countries, but is still widely used by artisanal miners in remote locations due to the high efficiency, simplicity, and relative low cost of the method (Viega, 1997). Briefly stated, the amalgamation process involves mixing the heavy mineral fraction of mined sediment or crushed rock with liquid mercury to form a semi-solid Hg–Au amalgam. The amalgam is then roasted, driving

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off the Hg as vapor and leaving the purified Au behind. Although it is possible to capture and recycle the mercury vapors with use of a retort, artisanal miners typically bypass this step. Besides roasting, Hg can also enter the environment in liquid form from spills, or as residual Hg(l) droplets in tailings.

A growing body of literature exists on the dispersion of mercury in watersheds where amalgamation is currently used (see Lacerda, 2003, and references therein), or has been used in the past (e.g., Miller et al., 1998; Hunerlach et al., 1999). Localized mercury contamination from artisanal mining is common to the sites investigated, although the studies disagree as to the relative significance of mining vs. natural sources for mercury transport on a regional (i.e., watershed) scale. For example, Lechler et al. (2000) argued that mercury in the Madeira River basin of the Brazilian Amazon was most likely sourced from weathering of soils as opposed to artisanal mining in the headwaters of the drainage. However, in the Sierra Nevada of California, Slotton et al. (1995a,b) found a distinct mining-associated signal, with residual exposure and bioaccumulation in extensive reaches downstream of historic placer mining zones to over five times greater than in adjacent reaches impacted only by natural weathering and atmospheric deposition. Boudou et al. (2005) argued that elevated Hg concentrations of fish in rivers of the Amazon Basin of French Guiana were partly caused by gold mining, and partly by the anoxic conditions created in the deep water of a hydroelectric reservoir.

In Peru, artisanal mining of gold occurs on a relatively large scale in the La Rinconada and Ananea mining camps of the Department of Puno. These mines are located near the headwaters of the Río Ramis, the largest tributary to Lake Titicaca (Fig. 1). Very few data exist with regards to the concentrations of mercury and other heavy metals in the Lake Titicaca basin, other than internal government reports (e.g. Ministerio de Energia y Minas, 1999; Paredes et al., 2002). The objectives of the present study were three-fold: 1) to collect soil, surface water and stream sediment samples from the La Rinconada mine complex to document the extent of Hg contamination in the area; 2) to collect a set of water quality samples in the Río Ramis to see if Hg and/or other metals could be traced from the mining centers to the lake; and 3) to sample fish from Lake Titicaca for Hg concentrations. Through this work, it was our intent to evaluate whether or not artisanal mining constituted a significant threat to human and ecological health in the Lake Titicaca basin. Another objective was to provide baseline data against which future studies can be compared.

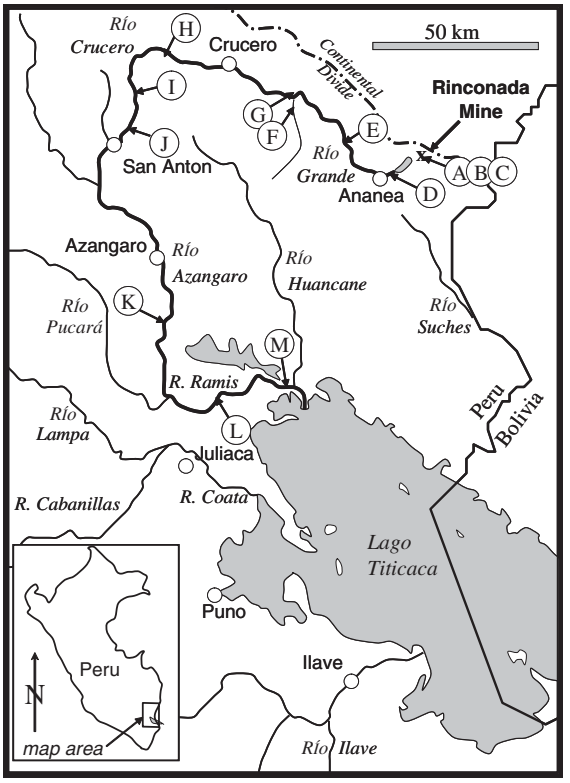

Fig. 1. Map of the Río Ramis–Lake Titicaca drainage basin. Letters refer to sampling locations discussed in the text.

1.1. Site orientation

Lake Titicaca is a large (8559 km^2), high altitude (3810 m above sea level) tropical lake that straddles the border between Peru and Bolivia. The general physical, chemical, biological, geological, and limnological characteristics of the lake and its tributaries have been extensively summarized (Newell, 1949; Richerson et al., 1975, 1986; Widmer et al., 1975; Boulangé and Jaen, 1981; Carmouze and Jaen, 1981; Carmouze et al., 1981; Vaux et al., 1988; Guyot et al., 1990). Although Lake Titicaca has a small outlet in Bolivia (the R. Desaguadero), it is estimated that over 90% of the water that enters the lake by runoff and direct precipitation is evaporated (Carmouze and Jaen, 1981). The Ramis is the largest and the longest (>200 km) of the tributary rivers draining into Lake Titicaca (Fig. 1). Other important rivers include the Ilave, Coata, Huancane, and Suches, the latter forming the boundary between Peru and Bolivia over much of its length. The name of the Río Ramis changes from source to mouth. The headwaters are called the Río Grande, which becomes the Crucero, then the Azangaro, and finally the Ramis, below the confluence with the Río

Pucará (Fig. 1). Although remote, most of the Ramis watershed is settled and accessible by dirt road. The largest cities on the river include Azangaro, San Anton, Crucero, and Ananea. Below San Anton, the river flows through a wide floodplain, which is heavily farmed.

The mining center of La Rinconada is located near the headwaters of the Río Ramis at roughly 5000 m above sea level (Fig. 1), and has a population of over 30,000 people, mostly miners and their families. Fig. 2 is a map of the La Rinconada area, showing the location of water, soil, and stream sediment samples reported below. Gold at La Rinconada is currently mined by artisanal laborers from mineralized quartz veins in meta-sedimentary bedrock. At Ananea, a smaller village located on a separate tributary, gold has been recovered for many years by hydraulic placer operations of the local river gravels. Ore from both the bedrock and placer operations is processed by mercury amalgamation. This is predominantly accomplished by small groups, often family units of all ages, without proper protection or education as to the health risks of handling mercury. At La Rinconada, the mineralized rock is crushed in a ball mill to an approximate 0.1 mm diameter. The ground ore is mixed proportionally with mercury and water in a large stone mortar and agitated manually (often by children) by standing on a stone pestle and rocking back and forth, while holding onto a rope for balance. The amalgamated mercury is separated by panning and then squeezed by hand through a fine cloth to separate the liquid mercury from the semi-solid Au–Hg amalgam. Tailings (spent ore) containing residual mercury are discarded into settling ponds or uncontrolled drainages, whereas the primary amalgam is fired in open air to drive off the mercury and produce a gold ball.

Lake Titicaca supports a commercial fishery, which is dominated by two species of non-native fish: rainbow trout *(Salmo gairdneri)* and pejerrey (*Basilichthyes bonariensis*), the latter a type of silverside introduced to Lake Titicaca from Argentina in the 1950s as a food fish (Vaux et al., 1988). Both species feed on insects, crustaceans, and small fish, although the pejerrey has a more versatile diet that includes zooplankton (Vaux et al., 1988; Hall and Mills, 2000). The rainbow trout was first introduced to Lake Titicaca in 1942 and supported a commercial fishery until 1970. However, its population has since plummeted, due in part to over-fishing, and in part to competition with the more successful pejerrey. Today, rainbow trout that are widely available in the fish markets of Puno come from fish farms. Pejerrey have advantages over rainbow trout in that they spawn throughout the lake (and therefore are not limited to spawning in tributary rivers, as is the rainbow trout), and that they have a more varied diet. Rainbow trout have migrated into the tributaries of Lake Titicaca, and are present in low numbers in the upper reaches of the Río Ramis watershed, including some of the deeper lakes such as Lago Rinconada (Fig. 2).

Unlike rainbow trout, the pejerrey have thrived in Lake Titicaca, and have become an important staple

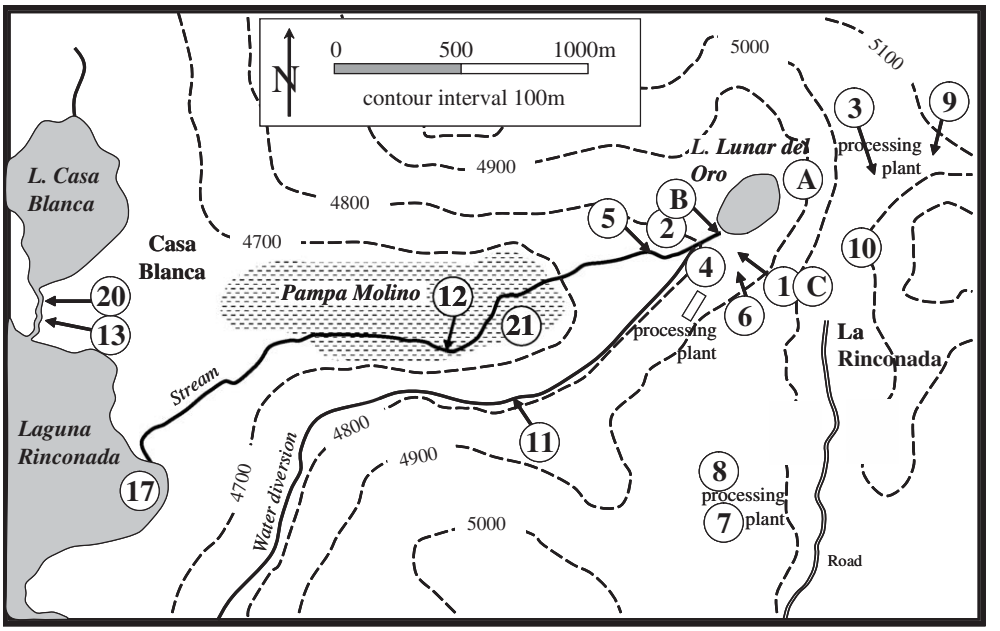

Fig. 2. Map of the area surrounding the La Rinconada mining complex. Letters and numbers refer to sampling locations discussed in the text.

for residents and a popular dish with tourists. Pejerrey reportedly grow to lengths of up to 500 mm (Vaux et al., 1988), although the majority of fish we observed in the markets and fishing boats were <350 mm in length. The pejerrey are abundant in both near shore and pelagic (open water) portions of the lake, and are littoral spawners (Vaux et al., 1988). Other fish that are caught by net or by hand-line in Lake Titicaca include the carachi (a native killifish, belonging to the genus *Orestias*), and two species of indigenous benthic catfish (belonging to the genus *Trichomycterus*) known locally as mauri and suche. The carachi is a small, bony fish which is mainly eaten by locals in soup or stew. The most abundant killifish species are *O. mulleri* and *O. ispi*, the former being more abundant in benthic or littoral environments and the latter primarily pelagic. Carachi and other *Orestias* species are found throughout the high altitude lakes of Peru, Chile and Bolivia (Parenti, 1984; Lüssen et al., 2003), and are also present in tributary streams, such as the Río Ramis below Azangaro. Although native to Lake Titicaca, the *Trichomycterus* catfish are very rare, and are reportedly close to extinction: therefore, they do not constitute a major portion of the local diet.

2. Methods

2.1. Sampling sites and dates

A suite of samples was collected at La Rinconada in 2001 to determine the concentrations of Hg in water, soil, and sediment immediately downstream of the areas of primary processing activity. Three gold processing plants are located in Fig. 2. Sample 4 was a composite sample of tailings that were dumped immediately downstream of Lake Lunar del Oro, which is a small lake downstream of the majority of the gold processing activities. Samples 7 and 8 were taken upwind and downwind, respectively, of an abandoned processing plant that released airborne mercury. Although large rainbow trout reportedly inhabit Lago Rinconada (near the La Rinconada mining camp), we were unable to obtain specimens during our 2002 visit. After documentation of extensive Hg pollution associated with mining and processing of gold ore at La Rinconada (Young et al., 2002), our group made a second visit during July 7–10 of 2002 to determine if contamination from mining in the headwaters of the Río Ramis could be traced to Lake Titicaca. During this second field campaign we re-visited the Rinconada mine and traveled down the length of the Ramis, sampling at a number of localities on the main stem, as well as several tributary streams (Fig. 1).

Specimens of fish from Lake Titicaca were sampled in three successive years for analysis of Hg in muscle tissue. In January of 2001, 10 specimens of pejerrey were bought from a fishing boat at a bridge near the mouth of the Río Ramis, in the village of Yanaoco (Site M of Fig. 1, located upstream of the confluence of the Ramis and Huancane Rivers). These fish were reportedly caught "in the middle of the lake." In July of 2002, 15 additional pejerrey specimens were collected at the same location, along with 4 specimens of carachi (most likely *O. mulleri*, based on the size of the fish; the closely related species *O. ispi* is somewhat smaller) and 8 specimens of mauri and suche (*T. dispar, T. rivulatus*), all identified according to ecological studies by Vaux et al. (1988). Also in July of 2002, 5 freshly caught pejerrey were purchased in the Puno fish market, at the west end of Lake Titicaca. Additional specimens of pejerrey and carachi *(O. mulleri)* were obtained from the Yanaoco and Puno markets in July-2003. Photographs of each fish type sampled in this study are shown in Fig. 3.

2.2. Field methods

Environmental parameters such as pH, specific conductivity (SC), alkalinity, and temperature were collected at each station along the Río Ramis, as well as samples of filtered (0.45 μm) and unfiltered water. Water samples were collected and transported in acid-washed HDPE bottles. Non-filtered (raw) water samples collected in 2001 were acidified in the field to 10% v/v HNO_3 (Trace Metal grade); filtered and raw water samples collected in 2002 were acidified in the field to 1% v/v HNO_3 (Fisher Optima grade). Streamflow was measured at several sites in 2002 using a velocity meter and measuring tape, although this was not feasible at all stations. At locations where discharge exceeded roughly 500 l s^{-1}, a width- and depth- integrated water sample was collected for chemical analysis by wading across the stream, or by repeated sampling from a bridge with a glass pitcher suspended from a nylon rope.

Each fish sampled from Lake Titicaca was first weighed and the length measured. A small skin-on fillet section approximately 3 × 5 cm was dissected between the head and dorsal fin, and above the lateral line. Internal examination indicated that some of the pejerrey were eating minnows, confirming their predatory eating habits. Each fillet section was placed in an individual zip-lock bag with all air removed, and the samples were packed with blocks of ice in an insulated "6-pack"

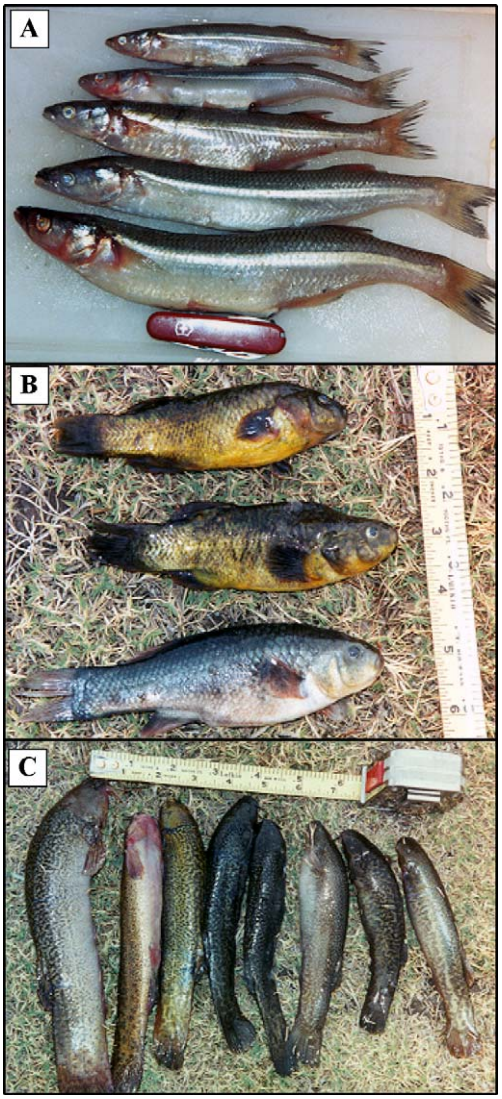

Fig. 3. Photographs of fish sampled in this study: A) pejerrey; B) carachi; C) mauri and suche (the latter is the large specimen on the left).

cooler. The small cooler was placed inside a larger Styrofoam cooler, again packed with ice blocks. Samples from the 2001 and 2002 campaigns arrived at the Univ. of California-Davis laboratory within four days of collection and were in excellent condition, with solid ice still present in the container. Samples from the 2003 campaign arrived in a partially decomposed state, but nonetheless were salvaged. Sub-samples for mercury analysis and moisture percentage were dissected from the centers of each sample piece. Moisture percentage was determined on all samples as a measure of sample condition and was found to be in the normal range for fresh fish muscle tissue (approximately 77–82% in these samples).

2.3. Analytical methods

Mercury contents of soil, sediment and water samples collected near the Rinconada Mine in 2001 were analyzed at Montana Tech by cold-vapor atomic absorption spectrometry (CVAAS) using glassware dedicated to mercury analysis. Prior to analysis, the sediment samples were digested in nitric acid and diluted to levels that could be analyzed by the equipment. The raw-acidified water samples were filtered immediately prior to CVAAS analysis. Acidified water samples collected in 2002 from the Río Ramis and headwater streams were analyzed for metals by inductively coupled plasma atomic emission spectroscopy (ICP-AES) at the Murdock Laboratory of the University of Montana (Missoula, MT). Non-acidified samples were analyzed for anions by ion chromatography (IC). After ICP-AES analysis and within 3 weeks of field sampling, the raw-acidified samples were submitted to a commercial laboratory in Butte, MT, for analysis of Hg via CVAAS. The analytical detection limit for Hg for the latter batch of samples was 34 ng l^{-1}.

Extensive quality assurance checks were run for all CVAAS and ICP-AES analyses, including blanks, standards, and lab duplicates every 10 samples, as well as field duplicates and field blanks. The field blanks (raw-acidified and filtered-acidified) were both very low for all elements of concern, and field duplicate samples showed excellent agreement for all solutes reported here. To calculate the concentration of bicarbonate ion the field pH, temperature, and alkalinity of each sample were put into the geochemical modeling program MINTEQ (Allison et al., 1991). All samples speciated in this way had very good charge balances (most <5% imbalance).

Preparation and analysis of fish samples was performed at the Univ. of California-Davis. Fish samples were digested in a mixture of concentrated, trace metal grade sulfuric and nitric acids. Total mercury was analyzed using CVAAS. Extensive, research level QA/QC accompanied the analyses, with all results well above standard acceptance criteria. The level of detection for analysis of Hg in fish tissue was 0.005 μg g^{-1}.

3. Results and discussion

3.1. La Rinconada mine complex

Mercury concentrations of soil, sediment, and unfiltered water samples collected in 2001 from the vicinity of La Rinconada are given in Table 1. The samples had varying but locally very high levels of mercury, with

Table 1
Hg concentrations of water and sediment samples collected near La Rinconada Mine Complex (n.a.=not analyzed)

Sample identification and description	Total Hg conc. in water, μg l^{-1}	Total Hg conc. in sediment, μg g^{-1}
1—Mine drainage	0.77	45
2—Amalgamation drainage	0.92	11
3—Amalgamation effluent (unfiltered)	3.5	n.a.
4—Tailings composite	n.a.	2460
5—Downstream discharge	5.8	228
6—Mill discharge	244	227
7—Incinerator soil (upwind)	n.a.	5.8
8—Incinerator waste (downwind)	n.a.	110
9—Amalgamation effluent	207	n.a.
11—Ditch from La Rinconada to Ananea	58	n.a.
12—Stream sediment in Pampa Molino	n.a.	232
13—Inlet to Laguna Rinconada	5.2	205
17— Laguna Rinconada	n.a.	1.8
19—Ananea Mine discharge	1.1	1.0
20—Inlet from placer deposit	0.62	0.94
21—Floodplain soil – 1.5 m depth (from Pampa Molino)	n.a.	1.7

maximum values of 2460 μg g^{-1} in mine tailings, 232 μg g^{-1} in sediment (diversion ditch from Lunar del Oro to Ananea), and 244 μg l^{-1} in water (mill discharge). The latter value is well above US EPA aquatic life criteria for chronic or acute exposure to Hg (0.77 and 1.4 μg l^{-1}, respectively). Although a more detailed and systematic sampling would be needed to understand the details of how mercury is partitioned between liquid, solid and gaseous media, it is clear from these preliminary results that significant Hg contamination exists at the mine complex. Given the fact that miners and their families are handling Hg with little concern as to its adverse health effects, there is a high probability that many individuals in the mining camp are placing themselves at risk of Hg exposure.

3.2. Río Ramis

Selected water quality parameters and metal concentrations from the July-2002 sampling campaign are given in Tables 2 and 3. The outlet to Lake Lunar del Oro (Site B of Fig. 2), in the midst of La Rinconada mining complex, is one of the headwaters of the Río Ramis. Despite the fact that water entering and exiting L. Lunar del Oro was acidic (pH<4), the concentrations of most common heavy metals (e.g., Cu, Pb, Zn) were relatively low. The acid pH was due to oxidation of sulfide minerals exposed by mining operations. Based on hand samples and polished sections, typical gold ore at La Rinconada is rich in the acid-generating sulfide minerals pyrrhotite (FeS), pyrite (FeS_2), and arsenopyrite (FeAsS), and contains relatively low quantities of other common base metal sulfides, including sphalerite (ZnS), galena (PbS), and chalcopyrite ($CuFeS_2$). The low base metal content helps to explain the low concentrations of Zn, Cu and Pb in the acid drainage, as compared to the Río Cecilia (see below).

The level of total recoverable Hg in water exiting L. Lunar del Oro was notably high (260 ng l^{-1}), although the streamflow was only 34 l s^{-1}. A nearby mine adit (Site C) was discharging ~14 l s^{-1} of acidic water

Table 2
Selected water quality data for river samples collected from the Ramis watershed in July 2002

Site	Description	Temp °C	Flow l s^{-1}	pH	Cl	NO_3 as N	SO_4	HCO_3	Ca	K	Mg	Na	Si
A	Inlet to L. Lunar del Oro	10.2	n.a.	3.80	n.a.	n.a.	265	n.a.	63.5	1.1	13.6	9.6	8.4
B	Outlet to L. Lunar del Oro	1.4	34	3.55	3.65	0.46	259	n.a.	44.1	2.2	12.8	6.2	9.2
C	Adit discharge	13.3	14	3.53	n.a.	n.a.	290	n.a.	53.8	1.6	18.7	7.4	10.6
D	Outlet to L. Rinconada	7.1	100	6.17	n.a.	n.a.	101	8.5	22.6	2.9	10.3	4.2	5.5
E	R. Grande at Saycotocha	n.a.	n.a.	6.63	n.a.	n.a.	28	n.a.	13.1	1.7	5.9	3.2	4.8
F	R. Cecilia at mouth	11.1	57	5.09	13.5	0.20	812	n.a.	169	4.4	37.2	16.9	5.2
F-d	Field duplicate of F	–	–	–	n.a.	n.a.	803	–	165	4.5	36.8	17.7	5.1
G	R. Crucero below Cecilia	8.2	n.a.	6.72	n.a.	n.a.	93	29.3	35.3	2.0	9.3	4.8	5.2
H	R. Crucero at C. Gutierrez	9.1	1300	8.00	2.14	0.21	84	90.3	71.8	1.6	12.9	5.2	4.5
I	R. Crucero near Totorani	16.0	n.a.	8.10	n.a.	n.a.	84	79.9	75.0	1.8	14.5	4.9	4.4
J	R.Crucero near San Anton	11.7	1200	7.88	1.73	0.21	69	75.6	59.6	1.7	12.4	4.1	3.5
K	R. Azangaro near M. Chico	9.4	6100	8.27	34.9	0.00	226	77.5	111	4.9	17.1	41.4	5.1
L	R. Ramis at Saman	8.5	34000	8.24	59.9	0.07	164	79.9	90.6	4.5	14.9	49.3	6.3
M	R. Ramis at Yanaoco	n.a.	n.a.	8.60	61.5	0.05	168	86.0	91.3	4.6	15.4	51.6	6.4
	Trip blank	–	–	–	0.04	0.00	0.1	–	.007	<.005	<.006	0.009	0.05

All results in mg l^{-1}.
n.a.=not analyzed.

Table 3
Trace metal concentrations of river water

Site	Type	Al	As	B	Cd	Cu	Fe	Hg	Mn	Ni	P	Pb	Sr	Zn
A	RA	2900	<3	<2	<1.5	16	533	0.118	895	84	8	<3	595	342
B	RA	7280	8	<2	3.7	40	16,300	0.259	1830	324	<6	17	303	919
B	FA	7210	10	<2	3.6	39	16,000	n.a.	1830	318	9	16	304	912
C	RA	567	27	<2	<1.5	<2	22,100	0.081	2570	25	25	<3	438	204
D	RA	762	81	<2	<1.5	41	12,300	0.045	1379	60	930	22	186	177
D	FA	8	4	4	<1.5	<2	2	n.a	937	31	9	<3	151	15
E	FA	10	<3	11	<1.5	<2	6	n.a	55	<2	59	13	73	4
F	FA	758	6	2560	265	5	29,600	n.a	21,000	67	<6	9	656	104,000
F	RA	322	27	2610	266	11	46,000	0.375	20,500	63	180	96	643	101,000
F-DUP	FA	793	<3	2580	261	6	29,000	n.a	20,400	60	<6	9	638	91,000
F-DUP	RA	3180	27	2650	268	11	45,700	0.086	21,100	69	190	103	662	102,000
G	RA	10,400	75	248	9.9	34	15,100	0.06	1480	27	570	18	268	4060
G	FA	9	<3	256	2.5	<2	3	n.a	796	2.9	17	<3	225	919
H	RA	138	<3	103	<1.5	<2	198	<0.034	22	<2	10	<3	632	33
H	FA	14	<3	94	<1.5	<2	4	n.a	16	<2	<6	<3	593	15
I	RA	106	<3	99	<1.5	2	147	<0.034	10	<2	10	<3	523	17
I	FA	18	<3	99	<1.5	<2	3	n.a	5	<2	8	<3	554	7
J	RA	54	<3	89	<1.5	<2	65	<0.034	8	<2	7	<3	485	11
J	FA	11	<3	79	<1.5	<2	3	n.a	5	<2	8	<3	432	6
K	RA	39	<3	508	<1.5	2	73	<0.034	61	<2	14	<3	1020	5
K	FA	20	<3	501	<1.5	<2	27	n.a	57	<2	7	<3	1050	7
L	RA	45	9	719	<1.5	<2	82	0.036	28	<2	19	<3	953	5
L	FA	17	13	727	<1.5	<2	12	n.a	22	<2	18	<3	944	5
M	RA	47	10	733	<1.5	<2	85	<0.034	13	<2	20	<3	954	5
M	FA	17	9	745	<1.5	2	9	n.a	6	<2	14	<3	906	6
blank	RA	<3	<3	5	<1.5	<2	2	<0.034	<1	<2	<6	<3	<1	2
blank	FA	<3	<3	4	<1.5	<2	<1.4	<0.034	<1	<2	<6	<3	<1	2

All concentrations in μg l^{-1}.
DUP=field duplicate sample; FA=filtered-acidified; RA=raw-acidified; n.a.=not analyzed.

containing 81 ng l^{-1} Hg. The combined load from these two sources amounts to approximately 1 g Hg per day. Roughly 10 km downstream, at the outlet to Lago Rinconada (Site D), the Hg concentration decreased to 45 ng l^{-1} while the flow increased to 100 l s^{-1}, for a computed load of 0.39 g Hg d^{-1}. Some of the apparent decrease in Hg load could be explained by the exportation of surface water via the diversion ditch from Lunar del Oro to Ananea (Fig. 2). Substantially greater Hg loads in these headwater streams are to be expected during high flow conditions.

Concentrations of mercury in the Río Ramis downstream of Ananea were generally near or below the analytical detection limit of 34 ng l^{-1}. The exception was a sample taken directly below the confluence with the Río Cecilia, a small iron-stained tributary that flows north to join the Río Crucero (upper Río Ramis) near the village of Crucero. The Cecilia (Sample F) had a relatively small streamflow (57 l s^{-1}) but contained very high levels of metals, including Pb (up to 103 μg l^{-1}), Cd (up to 268 μg l^{-1}), Mn (up to 21 mg l^{-1}), Fe (up to 46 mg l^{-1}), and Zn (up to 104 mg l^{-1}). The extremely high Zn concentrations are notable, and equate to a Zn load of ~500 kg d^{-1}! For reference, the levels of dissolved Zn in this stream were approximately 800 times and 14 times higher than the US EPA standards for aquatic life (120 μg l^{-1} at 100 mg l^{-1} hardness) and human health (7.4 mg l^{-1}), respectively (US EPA, 2005). Concentrations of Pb and Cd also greatly exceeded US EPA standards. This stream also had the highest concentration of Hg (375 ng l^{-1}) in our July-2002 study. Most of this contamination apparently stems from the Cecilia zinc mine, higher in the tributary drainage.

A comparison of filtered vs. unfiltered samples from R. Cecilia (Table 3) shows that a significant percentage of the total metal load was in particulate form for Al, As, Cu, Fe, P, and Pb, whereas B, Cd, Mn, Ni, and Zn were transported mainly in dissolved form. Cobbles and boulders in the Cecilia creek bed were covered with a thick coating of orange-red Fe-hydroxide, which – like the suspended sediment – is probably rich in heavy metals. It is likely that much of the sediment on the stream bed becomes suspended during high discharge periods, with subsequent down-gradient transport of adsorbed metals. Even under dry season baseflow con-

ditions, the Río Crucero below the confluence of the Río Cecilia (Site G) showed significant contamination with both Zn and Hg from the polluted tributary.

If a conservative dilution model is used, the maximum concentration of Hg in the Río Ramis at Site L (near Juliaca) in July-2002 that could be attributed to the combined discharge from the Rinconada and Cecilia mines is slightly less than 1 ng l^{-1} (1 part per trillion), given that the estimated flow at this location was 34,000 l s^{-1}. Following the same reasoning, the calculated Zn concentration for the Río Ramis at Saman based on loadings from the Río Cecilia is 310 μg l^{-1}. By contrast, the measured Zn concentration at Saman was only 5 μg l^{-1}. This indicates that >98% of Zn inputs to the Ramis watershed from Río Cecilia were attenuated before reaching Lake Titicaca during the period of our July-2002 visit. Possible metal attenuation mechanisms include adsorption onto clays or other solid surfaces, mineral precipitation or co-precipitation, and biological uptake. Much of this attenuated metal load can be expected to be transported downstream during high flow events.

3.3. Lake Titicaca fish

The results of Hg analyses of fish muscle tissues are summarized in Table 4 and Figs. 4 and 5. The data are reported in units of fresh/wet wt μg Hg/g (equivalent to ppm). The Hg content of pejerrey – the most popular food fish of Lake Titicaca – generally increased with fish length (Fig. 4A) and mass (not shown). This general positive relationship between Hg concentration and fish size is typical of lakes and reservoirs throughout the globe (e.g., Ikingura and Akagi, 2003; Weis, 2004; Mirlean et al., 2005), and is symptomatic of bioaccumulation. Eleven of the larger specimens (27% of the total sample population) exceeded the US EPA (2001) fish tissue-based water quality criterion level of 0.30 μg g^{-1}, and four fish (9.8% of total population) had a Hg content at or above the regulatory limit of 0.50 μg g^{-1}

Table 4
Concentrations of Hg (μg g^{-1} wet weight) in fish muscle from Lake Titicaca

Site	Date sampled	Species	Mass (g)	Length (mm)	Hg (μg g^{-1})	Site	Date sampled	Species	Mass (g)	Length (mm)	Hg (μg g^{-1})
Y	12-Jan-01	Pej	60	210	0.14	Y	23-Jul-03	Pej	460	413	0.26
Y	"	Pej	90	230	0.10	Y	"	Pej	880	440	0.50
Y	"	Pej	175	280	0.10	P	"	Pej	150	283	0.24
Y	"	Pej	180	285	0.06	P	"	Pej	335	375	0.19
Y	"	Pej	200	275	0.27	P	"	Pej	665	420	0.44
Y	"	Pej	250	315	0.10	P	"	Pej	150	280	0.23
Y	"	Pej	300	340	0.26	P	"	Pej	250	350	0.36
Y	"	Pej	300	335	0.42	P	"	Pej	600	475	0.52
Y	"	Pej	650	450	0.35	P	"	Pej	750	475	0.88
Y	"	Pej	740	440	0.46						
P	11-Jul-02	Pej	113	323	0.21	Y	11-Jul-02	Car	28	146	0.40
P	"	Pej	57	299	0.26	Y	"	Car	57	158	0.19
P	"	Pej	57	259	0.18	Y	"	Car	28	134	0.31
P	"	Pej	28	223	0.26	Y	"	Car	28	128	0.19
P	"	Pej	14	183	0.28	P	23-Jul-03	Car	25	105	0.30
Y	11-Jul-02	Pej	610	427	0.38	P	"	Car	35	125	0.41
Y	"	Pej	397	381	0.31	P	"	Car	60	158	0.48
Y	"	Pej	340	366	0.63	P	"	Car	65	160	0.36
Y	"	Pej	284	335	0.12	P	"	Car	50	127	0.30
Y	"	Pej	198	320	0.20	P	"	Car	50	140	0.10
Y	"	Pej	170	320	0.14	P	"	Car	85	177	0.41
Y	"	Pej	113	305	0.25	P	"	Car	95	195	1.18
Y	"	Pej	113	320	0.20						
Y	"	Pej	85	274	0.21	Y	11-Jul-02	Mauri	57	186	0.23
Y	"	Pej	85	280	0.18	Y	"	Mauri	28	180	0.14
Y	"	Pej	85	274	0.18	Y	"	Mauri	57	174	0.40
Y	"	Pej	57	250	0.17	Y	"	Mauri	28	152	0.22
Y	"	Pej	28	235	0.10	Y	"	Mauri	28	162	0.13
Y	"	Pej	28	229	0.16	Y	"	Mauri	57	192	0.52
Y	"	Pej	28	213	0.12	Y	"	Mauri	57	192	0.14
Y	23-Jul-03	Pej	100	153	0.15						
Y	"	Pej	160	290	0.18	Y	11-Jul-02	Suche	142	250	0.21

Sites: Y=Río Ramis Bridge, village of Yanaoco, at north end of Lake Titicaca; P=Puno fish market. Species: Pej=pejerrey; Car=carachi.

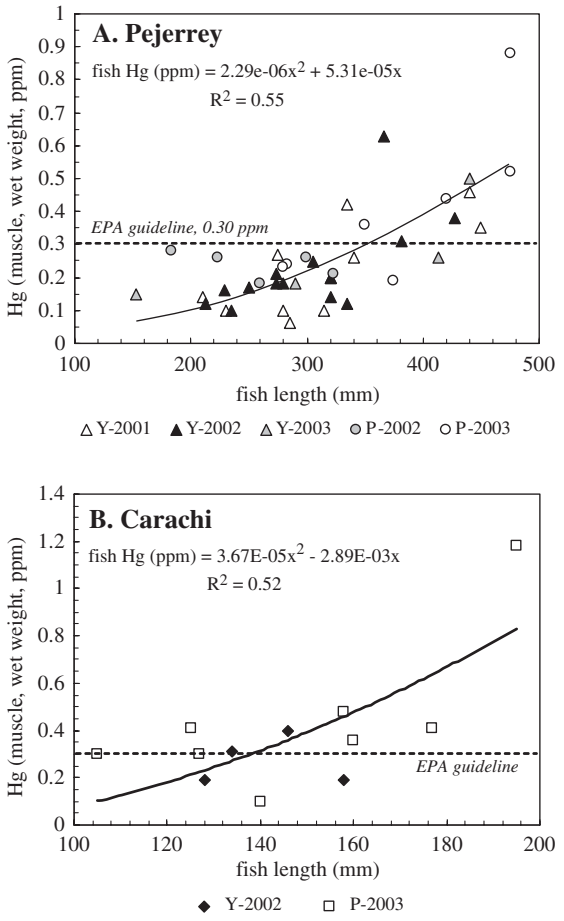

Fig. 4. Relationship between Hg concentration and fish length for pejerrey and carachi. Separate populations are shown for fish obtained at the Yanaoco (Y) and Puno (P) markets.

adopted by most countries (excluding the U.S.) for human consumption. No clear differences were noted between sub-samples of pejerrey collected from different parts of the lake (e.g., Yanaoco vs. Puno), or on different years. Based on these results, it is concluded that pejerrey in Lake Titicaca that exceed 0.5 kg or 350 mm in length may have Hg concentrations that are a potential concern to human health.

Despite their smaller size, 9 of 12 carachi (75%) had Hg levels that exceeded the 0.30 μg g^{-1} EPA criterion (Table 4, Fig. 4B). The largest carachi specimen had an anomalously high value of 1.18 μg g^{-1}. After pejerrey, the carachi is the second most popular food fish in the local markets. Unlike the pejerrey, for which small fish form a major portion of their diet for specimens >200 mm in length (Vaux et al., 1988), the carachi are reported to be non-piscivorous, instead mainly subsisting on a diet of zooplankton and benthic crustaceans, such as copepods and cladocerans (Vaux et al., 1988). The relatively elevated Hg levels found for carachi in this study suggest that the food habits and age structure of this species may warrant additional study. In any case, based on the results of our study, it appears that substantial consumption of carachi could lead to unhealthy levels of Hg exposure. Similarly elevated Hg concentrations were observed for the mauri catfish (Fig. 5), although the single larger suche catfish was not proportionally enriched in Hg. Because mauri and suche are rare species in the lake, it is unlikely that these fish pose a significant health hazard to the local population. Any other fish species of higher trophic status in Lake Titicaca (for example, large fish-eating trout) can be assumed to contain significantly greater mercury levels at a given size then the fish sampled in this investigation.

The concentrations of Hg in muscle tissue of fish from Lake Titicaca are much higher than levels that are considered typical of uncontaminated environments. For example, Downs et al. (1998) suggested a value of 0.035 μg g^{-1} for minimum Hg concentrations in fresh water fish from pristine rivers and lakes. In a recent field study of lakes in southern Brazil, Mirlean et al. (2005) found average Hg concentrations of 0.041, 0.093, and 0.117 μg g^{-1} in natural, suburban, and industrial settings, respectively. The vast majority of fish in Lake Titicaca have Hg concentrations well above these values (Table 4). Mirlean et al. (2005) also compiled information on Hg analyses of fish from other published studies of South American rivers and lakes. Based on these data, the range of Hg concentration in fish from reference waters (unpolluted rivers or lakes) is 0.0001 to 0.0064 μg g^{-1}, whereas the majority of fish from waters with suspected point source or non-point source contamination had Hg concentrations in the range of 0.1 to 1.0 μg g^{-1}, with the

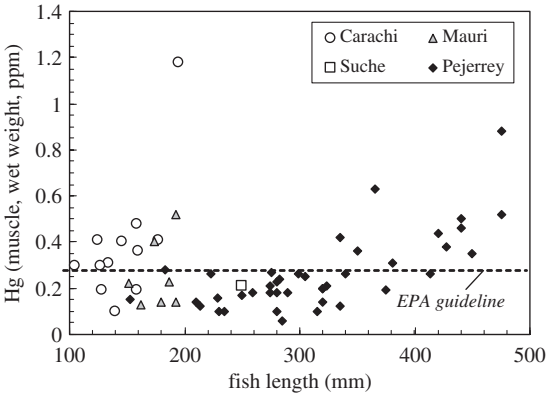

Fig. 5. Relationship between Hg concentration and fish length for all species investigated in this study.

highest values invariably from piscivorous species. The Hg content of *all* fish species (both fish-eating and non fish-eating) in Titicaca fall within the range of reported values from contaminated South American fresh waters. The source of this "contamination" is presently unknown, although a brief discussion follows.

3.4. Sources of mercury in the Titicaca basin

The fact that total Hg concentrations in the Río Ramis watershed decreased quickly with distance downstream from the mining centers is strong evidence that Hg in the headwater streams was sourced from mining activities, and not from background geologic or atmospheric sources. However, the same cannot be said for the elevated levels of Hg in fish from Lake Titicaca. In many large lakes – even in remote areas of the Southern Hemisphere – the largest input of mercury is in the form of atmospheric deposition (Meili et al., 2003; Mirlean et al., 2005). Lacerda et al. (2002) estimated a background Hg concentration of 0.24 ng l^{-1} for rain in a remote location in Brazil, far from any industrial or municipal Hg sources. Mirlean et al. (2005) measured Hg contents of rain in more populous regions of Brazil that were at least 10 times higher. If we take the lower value of 0.24 ng l^{-1} as a conservative estimate of Hg concentrations in average rainfall in the Peruvian Altiplano and assume an average annual rainfall of 710 mm for the Lake Titicaca basin (Guyot et al., 1990) and a lake surface area of 8559 km^2, this corresponds to an atmospheric flux from direct precipitation of roughly 1.5 kg y^{-1} of mercury. If we consider the entire Lake Titicaca drainage basin (area = 57,100 km^2, Guyot et al., 1990), this figure increases to nearly 10 kg of Hg per year. This compares with a combined flux from the two mining-impacted headwater streams (upper R. Grande and R. Cecilia) measured in this study of roughly 1 kg Hg y^{-1}. Johannesson et al. (1981) estimated a total biomass of fish in Lake Titicaca based on echo-sounding of roughly 100,000 metric tonnes. Assuming that the majority of these fish are carachi and pejerrey, and assuming an average Hg concentration of 0.28 μg g^{-1} (average of all fish specimens analyzed in this study), then this suggests that as much as 28 kg of Hg may be stored in living fish tissue. The fact that this figure is considerably higher than the two estimated annual fluxes of Hg into the lake from mining and atmospheric deposition underscores the long residence time of Hg in the food web, and its propensity for bio-concentration into species of higher trophic status.

The above mass balance comparisons are over-simplistic, and suffer from several major problems: 1) Hg concentrations of precipitation in the Titicaca basin may be quite different from those estimated for southern Brazil; 2) our estimate of mining-sourced Hg loads does not include inputs from other mine sites in the Ramis watershed, nor other major river basins that drain into Lake Titicaca; and 3) it is likely that the total Hg flux from the mining centers is much greater during periods of high flow, when metal-rich stream sediment and organic matter in headwater streams are re-suspended. To further complicate matters, the concentrations of Hg released to the watershed from natural weathering of soil and bedrock are not known, nor are the possible inputs of Hg from industry in the major cities in the basin (such as Puno and Juliaca). For all of these reasons, further work is needed to understand the sources, transport mechanisms, and bio-concentration of mercury in the Titicaca basin, and to better address the question of whether or not Hg inputs to Lake Titicaca from past and present artisinal mining are significant in comparison to other sources.

4. Conclusions

This study has documented the existence of elevated Hg concentrations in muscle tissues of several species of food fish from Lake Titicaca. We have also documented mercury contamination of surface water, soils, and stream sediment near the La Rinconada Mine Complex at the headwaters of the Ramis River, as well as heavy metal and Hg contamination in a tributary stream (the Río Cecilia). It is probable that similar loadings of Hg and heavy metals exist in other watersheds that drain into Lake Titicaca. Once in the lake, the concentrations of toxic substances will increase due to evaporation if the solutes behave conservatively. Alternatively, the contaminants may be sequestered by clays and other mineral surfaces, or may be bio-accumulated, as is often the case for mercury. Because of the high nutrient loading from agriculture and population centers ringing the lake, it is likely that the bottom water in portions of Lake Titicaca is anoxic, which would favor methylation and subsequent bioaccumulation of Hg into fish (Mason et al., 1993; Slotton et al., 1995a,b; Boudou et al., 2005). These fish – primarily the pejerrey and carachi – are an important food for local residents.

From this study it is not known whether the moderately elevated Hg concentrations in fish from Lake Titicaca are attributable to mining or to other causes. Based on our sampling of July-2002, the amount of Hg

entering Lake Titicaca that can be directly traced to mining activities in the Río Ramis watershed was below the quantifiable limit. However, before discounting the impacts of mining on Hg pollution in Lake Titicaca, it is necessary to collect samples of river water and suspended sediment during a high-flow period. It is likely that most of the down-gradient transport of Hg and heavy metals from the mining centers takes place via suspended solids during episodes of rapid snowmelt or storm flow. During our July-2002 visit, the rivers were near their 12-month discharge minima. A more systematic sampling of fish and aquatic macro-invertebrates in the rivers could also be used to trace the downstream migration of Hg and other contaminants from the mining centers to the lake. Biological assays of this type may help to answer the question of whether the elevated Hg levels in Lake Titicaca fish are due to Hg from mining activities or to other sources.

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