Giant Otter (Pteronura brasiliensis) at Risk? Total Mercury and Methylmercury Levels in Fish and Otter Scats, Peru
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Report **Arno Christian Gutleb, Christof Schenck and Elke Staib**

Giant Otter (*Pteronura brasiliensis*) at Risk? Total Mercury and Methylmercury Levels in Fish and Otter Scats, Peru

Mercury and methylmercury levels in fish muscle and scats of the giant otter (*Pteronura brasiliensis*) of Manu National Park, Peru, and in one gold-mining area in the vicinity of its borders were analyzed. In 68% of fish muscles, total mercury levels exceeded the proposed maximum tolerable level of 0.1 mg kg^{-1} fresh weight in fish for the European otter (*Lutra lutra*), and 17.6% exceeded 0.5 mg kg^{-1} fresh weight, the most common standard for human consumption. The ratio of methylmercury to total mercury in fish muscle was from 61.3% up to 96.9%. No methylmercury and only traces of inorganic mercury could be detected in the otter scats. No data for tissue concentrations of the giant otter are available at the moment, but as a high percentage of fish levels exceeded the tolerable level, as given for the European otter, a possible risk of mercury intoxication in the giant otter can be postulated, on the basis of mercury intoxication in free-living otters in Europe and North America described in the past.

Giant otter (*Pteronura brasiliensis*) a highly endangered mammal. Photo: C. Schenck.

INTRODUCTION

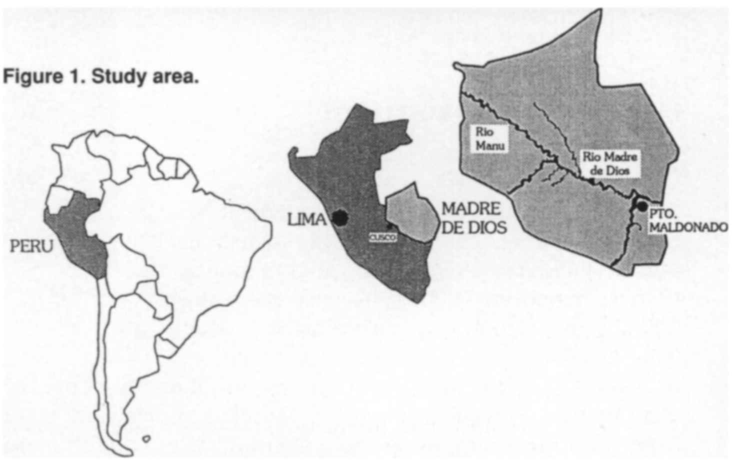
Various environmental contaminants, especially heavy metals and polychlorinated biphenyls (PCBs) are considered to be responsible for the observed decline of the European otter (*Lutra lutra*) in many countries of its former range (1). The giant otter (*Pteronura brasiliensis*) is categorized as almost extinct in two countries of its former distribution, seriously endangered in seven countries, and widespread only in Surinam and Guyana (2). Despite growing concern and research interest in the contamination of otters and their food in Europe and North America (1, 3) very little is known about the levels of hazardous substances like heavy metals, pesticides or PCBs in otter species from other regions.

In 1990, a long-term investigation and conservation project on giant otters was started in Peru by the Frankfurt Zoological Society in cooperation with the Munich Wildlife Society. In the area of Rio Madre de Dios, there are still large areas of natural tropical rainforest and the area is well known for its extraordinary biodiversity (4). However, there is local colonization and gold mining in close vicinity to one of the world's largest National Parks with an area of 18 000 km^2 (Fig. 1).

Mercury (Hg) is known to be responsible for mercury poisoning in otters (*Lutra canadensis*) (5) and in the American mink (*Mustela vison*) (6). The mercury concentrations in the livers of the animals studied were higher than 30 mg kg^{-1}, a value which is proposed to be the critical tissue concentration for otters (7).

Gold mining in the Amazon is a well-known problem (8, 9). A total of 1.2 million people are active in gold-mining activities, covering an area of ca 170 000 km^2 with a total gold production of approximately 200 tonnes (10). Gold occurs as dust in the sediments of many of the rivers. After gravimetrical concentration steps, mercury is used for gold separation through amalgamation. During this process, up to 20% of the mercury used for amalgamation is discharged directly into the river. Then the mixture is heated in retorts, whereby the mercury evaporates and the gold remains. Another 20% of the mercury is lost to the

Figure 1. Study area.



atmosphere in this procedure. In the production of 1 g gold 1–4 g mercury are used (11). The annual amount of mercury lost in these processes in the Amazonian gold-mining areas is estimated to be up to 128 000 kg yr^{-1}, of which 55% enters the atmosphere in the form of Hg°, and 45% enters the rivers as metallic Hg (12). The discharge into rivers leads to an increase of Hg in the sediment, and suspended particles have been demonstrated to be very important for downstream transport of mercury in rivers (13). The importance of atmospheric deposition for mercury pollution of biota has been shown for lakes (14, 15) and for marine mammals (16). The atmospheric dispersion of mercury may enhance mercury levels, especially on a regional scale, as it has been shown that much of the emitted mercury is deposited within 2000 km from point sources (17). High mercury levels have been reported for fish even from remote areas (18). We assume the annual mercury discharge to be between 10 000 to 30 000 kg, in the 85 000 km^2 area of Madre de Dios. These numbers were calculated from data on the annual gold production for the Departement Madre de Dios and the amount of mercury which is necessary for the production of 1 g of gold (11, 19).

Methylmercury is synthesized by methylation of inorganic mercury under anaerobic conditions (20). The environmental conditions in the aquatic ecosystems of the Amazonian area favor high mercury methylation rates. In particular, factors like high bacterial activity under slightly acidic conditions in the presence of high concentrations of dissolved organic carbon (DOC) are very important for methylation (21). In addition, temporal or permanent flooding of vegetation and soil can also increase mercury concentrations in fish (22), a situation which is typical for Amazonian rainforests. Therefore, in the past the analysis of both inorganic mercury and methylmercury in fish from the Amazon was strongly recommended (23).

Mercury and methylmercury are known to biomagnify in aquatic food chains, and the position of a species in a food chain is very important for the accumulated levels of mercury (24). As mercury biomagnifies upward in the food chain, top-level predators such as the giant otter may accumulate mercury up to toxic levels. For otters (*Lutra lutra*) from some European countries tissue concentrations exceeding the proposed critical tissue levels for otters have been reported (25, 26). Furthermore, the specific situation of tropical rainforests, with their efficient recycling of nutrients, increases the probability of methylation and thereafter accumulation in top predators (27). Preliminary results in a small sample of fish gave evidence for mercury pollution and methylation of mercury in the area of the Manu National Park (28).

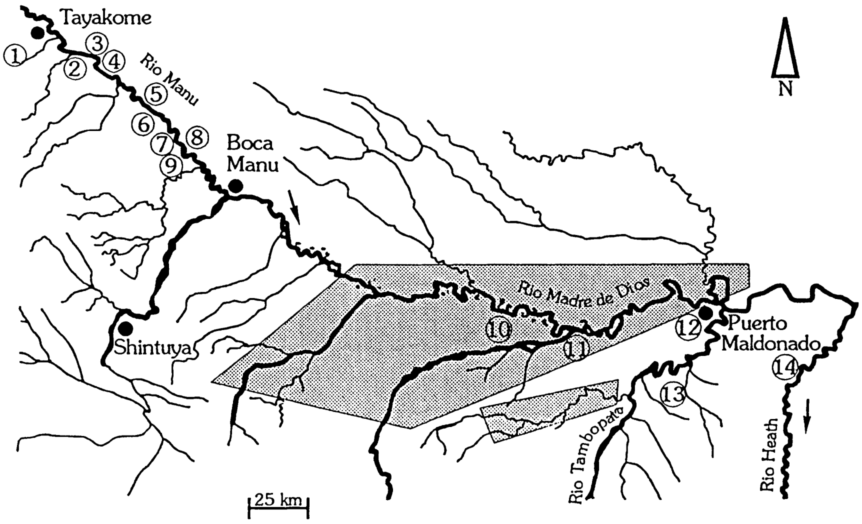


Figure 2. Sampling location (loc.-No.): 1–14 and gold-mining area:

Gold mining area on the Rio Manu, Peru. Photo: C. Schenck.

MATERIALS AND METHODS

Sampling Procedures

All fish were collected in the Departement Madre de Dios (Fig. 2). The sampling of fish and otter scat took place close to the gold-mining activities, but, from 1990–1993, also more than 200 km upstream in undisturbed areas of Manu National Park. Fish were caught in rivers and oxbow lakes by rod and line or gill net. Additionally, some fish were bought on local fishmarkets. Muscle samples were taken from the following fish species: Donsello (*Pseudoplatystoma* sp.), Juaracha (*Potamorhina altamazonica*), Zungaro (*Paulicea* sp.), Piranha amarillo (*Serrasalmus* sp.), Piranha blanca (*Serrasalmus rhombeus*), Corvina (*Plagioscion auratus*), Boca chico (*Prochilodus caudifasciatus*), Chambira (*Cynodon* sp.), Bagre del Rio (*Pimelodus* sp.) and Paco (*Piaractus* sp.). Piranha amarillo, Piranha blanca, Corvina and Chambira are carnivorous fish, whereas Boca chico is a detritus feeder, and Paco is herbivorous. Donsello and Zungaro are top predators, and the fish in our sample had a length of 150 cm and a weight of 10 kg or more. Fish of all other species were in the range of 110 g up to 420 g and had a length of 15 cm up to 32 cm. The two most important commercial fish are Zungaro and Boca chico. At the time of fish sampling, no data on giant otter diet were available. In the meantime, results of scat analyses on the type of fish which constitute the main food source of the giant otter have been published. With the exception of Bujurki (*Satanoperca jurupari*), which accounts for 43.3% of biomass in the otter diet, and is not included in our study, the fish resembles the spectrum of species found in scats (29).

Muscle samples were stored either in formalin (10%) or in absolute ethanol prior to analysis. Scats were collected along the oxbow lakes and were stored in 10 ml plastic containers.

Sample Treatment

Methylmercury was extracted following the method of Bender (30). Up to 3 g of fish muscle were sliced into small pieces and weighed in 40 ml centrifuge vessels. 1 g of NaCl, 1.5 ml of HCl g^{-1} muscle and 5 ml toluene g^{-1} sample were added and the samples were allowed to digest and extract overnight at 20°C. The following day, the samples were stirred on a magnetic-stirrer for 5 minutes. Samples were centrifuged (5 min, 3000 g) and supernatants were pipetted in a second centrifuge vessel. Another 5 ml of toluene were added to the fish sample and the stirring and centrifugation procedures were repeated. The remaining material was transferred into quartz vessels (= Extract I). 3 ml of a 10% cysteine solution (pH = 9) were added to the toluene phase and stirred for 5 min. After centrifugation (5 min, 3000 g) the cysteine phase was pipetted into a quartz vessel. This procedure was repeated (= Extract II). Extract I contains all inorganic mercury and Extract II the methylmercury fraction. To both extracts 3.5 ml of digestion acid (98% H_2SO_4, max. 0.0000005% Hg and 65% HNO_3, max. 0.0000005% Hg; 3:4) were added and the extracts were heated in a microwave sys-

Table 1. Mercury levels in fish (mg kg^{-1} fresh weight)*.

Sampling location	species (n)	inorganic-Hg	methyl-Hg	total-Hg	% methyl-Hg/total-Hg
Rio Cumerjali (1)	*Paulicea* sp. (2)	0.04–0.051	0.181–0.289	0.221–0.34	81.9–85.0
Rio Manu (2)	*Piaractus* sp. (1)	0.01	0.041	0.051	80.4
Rio Manu (3)	*Piaractus* sp. (1)	0.01	0.045	0.055	81.8
Rio Manu (4)	*Pseudoplatystoma* sp. (1)	0.018	0.068	0.086	79.1
	Serrasalmus sp. (2)	0.018–0.024	0.063–0.074	0.087–0.093	72.4–79.6
Rio Manu (5)	*Paulicea* sp. (1)	0.057	0.015	0.072	79.2
Rio Manu (6)	*Paulicea* sp. (7)	0.057	0.0.238	0.280	77.8
		0.01–0.157	0.035–0.909	0.045–0.966	66.2–94.1
	Piaractus sp. (1)	0.05	0.057	0.067	85.1
	Serrasalmus rhombeus (4)	0.038	0.088	0.140	65.4
		0.013–0.058	0.026–0.307	0.039–0.336	61.3–91.3
Rio Madre de Dios (7)	*Pseudoplatystoma* sp. (2)	0.021–0.063	0.66–1.481	0.681–1.544	95.4–96.4
	Potamorhina altamazonica (2)	0.02–0.03	0.064–0.071	0.084–0.102	70.1–76.3
	Plagioscon auratus (1)	0.031	0.424	0.455	93.2
Rio Manu (8)	*Paulicea* sp. (1)	0.015	0.057	0.072	79.2
Rio Manu (9)	*Pimelodus* sp. (1)	0.017	0.034	0.051	66.7
Rio Madre de Dios (11)	*Potamorhina altamazonica* (1)	0.02	0.038	0.058	65.5
Porto Maldonado (12)	*Paulicea* sp. (1)	0.238	0.77	1.008	76.4
	Cynodon sp. (1)	0.041	0.587	0.628	93.4
	Prochilodus caudifasciatus (5)	0.031	0.096	0.125	64.9
		0.02–0.099	0.037–0.14	0.057–0.209	69.5–76.8
Rio de la Torre (13)	*Pseudoplatystoma* sp. (1)	0.101	0.366	0.467	78.3

* mean concentrations and range (min.-max.)

tem A 301 (Prolabo, Paris) for 10 min with 10% efficiency. After addition of 3.5 ml of H_2O_2 the samples were heated again for 10 minutes with 10% efficiency. The digested samples were allowed to cool and were thereafter transferred into 25 ml flasks and stored at room temperature prior to analysis.

Analytical Determination

Mercury was determined with a Z 8100 Zeeman atomic absorption spectrophotometer (Hitachi, Kyoto) using a hydrid formation system HF-2 (Hitachi, Kyoto).

Blanks were always below the quantification limit. Recovery and accuracy of inorganic mercury analysis were checked with a standard sample supplied by the International Atomic Energy Agency (MA-A-2 fish muscle). Recovery and accuracy for methylmercury analysis were checked with a spiked fish muscle sample (0.5 mg kg^{-1}). These standards were analyzed with each set of samples and were always within 10% of the certified and the spiked value, respectively. The detection limit achieved with our method was 0.01 mg kg^{-1}. In the formalin- and ethanol-supernatants used for tissue preservation no mercury could be detected (n = 10).

Assessment of Mercury Contamination for Otters

To assess the potential risk for the European otter, of mercury levels in fish, tolerable levels for total mercury in fish were calculated (31). The level was calculated from mercury levels in fish and otter tissues from the Shetland Islands north of Scotland, where otters still thrive (25). The model also considered the relative frequencies of different prey species in the otter diet. As a result a total mercury concentration of 0.1 mg kg^{-1} fresh weight in fish was proposed as tolerable for otters.

RESULTS

The results for inorganic mercury, methylmercury, and total mercury, levels in the fish muscles as well as the ratio of methylmercury to total mercury are given in Table 1. High levels of total mercury were found in fish species collected from all areas. Two out of seven fish bought on the local market at Puerto Maldonado (sampling location 12) showed levels of 1.01 mg kg^{-1} and 0.63 mg kg^{-1}, respectively, which are higher than the standard of 0.5 mg kg^{-1} set for human consumption in Brazil (32). This is the only regulated value for Amazonian countries known to the authors. The highest mercury level in this study, i.e. 1.54 mg kg^{-1}, was found in a Donsello caught at sampling location 10 in the gold-mining area.

Some fish were collected upwards of the gold mining area (sampling locations 1–9). In the *Paulicea* sp. from the Rio Manu (sampling location 6), five of seven fish exceeded the proposed safe level of total mercury concentrations for *Lutra lutra,* and concentrations in two fish exceeded the maximum level for human consumption of 0.5 mg kg^{-1}. Even in fish caught approximately 200 km upstream from the mining area in the Rio Cumerjali (sampling location 1) a concentration of 0.34 mg kg^{-1} fresh weight was detected, which is well below the maximum tolerable concentration of 0.5 mg kg^{-1} fresh weight for humans, but more than three times higher than what is considered tolerable in the European otter. In 67.6% of the fish samples included in this study, the tolerable level for the European otter of 0.1 mg kg^{-1} was exceeded, and in 17.6% of the samples the tolerable level for human consumption of 0.5 mg kg^{-1} was exceeded.

Fish with levels higher than 0.1 mg kg^{-1} were not caught only in the Rio Manu and its tributaries itself but also in a lot of oxbow lakes. In these oxbow lakes also smaller fish like Piranha blanca, Corvina and Juaracha showed mercury concentrations exceeding the tolerable level for otters.

The percentage of methylmercury, in respect to total mercury level in fish, ranged from 53.5% up to 96.9%.

In seven scats from the Rio Manu (sampling locations 2, 4, 5, 6, 7, 8, 9) and one from Rio Madre de Dios (sampling location 14) no methylmercury was detected. Inorganic mercury was detected in three samples (sampling location 5, 9, 14) with a range from 0.07 mg kg^{-1} up to 0.12 mg kg^{-1}.

DISCUSSION

Total mercury concentrations in Donsello and Zungaro reported here are greater than the maximum tolerable levels (0.5 mg kg^{-1}) for human consumption. The concentrations in 5 of 11 Zungaro exceeded this level. Fish with these high concentrations were not only caught in the gold-mining areas, but also in the National Park itself. Zungaro is one of the most important fish on local fish markets, but no data on the origin of the fish sold on the market in Puerto Maldonado are known to the authors. The high amounts of mercury in fish could lead to mercury intoxication in the local human populations as they depend mainly on fish as a source of dietary protein. The problem of mercurialism in humans living in the Amazonian area is a well known phenomenon (33). Whether the high values of total mercury in these fish are a result of long-range atmospheric transport and/or of seasonal movements of the fish in conjunction with their long lifespan, have not yet been determined (18, 34).

As the composition of the giant otter's diet, with its high proportion of fish, resembles that of the European otter, at least to some extent, the maximum tolerable level is considered to be useful for further discussion. As many as 23 of 34 fish samples (67.6%) exceeded this level up to a total Hg content of 1.54 mg kg^{-1} fresh weight. As the giant otter feeds exclusively on fish, these high concentrations in fish are alarming and could pose a serious threat. The problem might be somewhat less critical in view of the fact that the highest mercury levels were found in large catfish (*Pseudoplatystoma* sp., *Paulicea* sp.) with a weight up to 20 to 50 kg. Nevertheless, at the time of the fieldwork (585 days) otters were observed three times eating these large fish species. Furthermore, no data on mercury concentrations in Bujurki are currently available. At a level of 43.3% of the food source, this species is the dominant prey species of the giant otter.

Oxbow lakes are very important for the giant otters as they are the main forage and breeding areas. In contrast to the large Amazonian rivers, where dilution lowers local mercury concentrations, it is possible that oxbow lakes with their high content of organic material act as a sink for contaminants. Therefore, the fact that amounts of mercury exceeding the tolerable concentrations for otters were also found in smaller fish from oxbow lakes, seems more alarming to us than the high values in the old and large catfish species. Giant otter cubs may be exposed to high mercury levels, and intrauterine mercury accumulation has been demonstrated for *Lutra canadensis* (35). The possible effects of prenatal exposure on otter offspring have not been demonstrated yet.

The ratio of methylmercury to total mercury found in our study confirms previous results for fish from other areas (36, 37). More important than the ratio of methylmercury to total mercury in fish, is the fact that no methylmercury at all could be found in the scats of the giant otter collected along oxbow lakes where fish had mercury levels exceeding the tolerable level. The levels of inorganic mercury in scats were low compared to data for the European otter (26). Methylmercury is considered to be nearly totally absorbed from the intestine due to its high lipophilicity. Until now giant otter tissue has not been available for residue analysis as dead mammals are seldom found under tropical conditions, thus no data are available to corroborate the expected high concentrations in otter tissues.

CONCLUSIONS

The mercury concentrations in the majority of fish in the area of Manu National Park are higher than what is considered tolerable in *Lutra lutra*. These high concentrations may pose a serious threat to humans and wildlife feeding on these fish. Steps to cease mercury release in tropical rainforests are strongly recommended to protect humans and wildlife.

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