AN ABSTRACT OF THE THESIS OF

Nilton Eduardo Deza Arroyo for the degree of Master of Science in Fisheries Science presented on November 8 , 1996.

Title: Mercury Accumulation in Fish from Madre de Dios, a Goldmining Area in the Amazon Basin, Perú

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Abstract approved: ______________________________

Lavern J. Weber

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Wayne K. Seim

In this study mercury contamination from goldmining was measured in tissues of fish from Madre de Dios, Amazonia, Perú. Bioaccumulation, biomagnification, the difference in mercury burden among residential and migratory species, and comparison between fish from Puerto Maldonado (a goldmining area) and Manu (a pristine area) were examined. Samples of dorsal-epaxial muscle of dorado (*Brachyplatystoma flavicans*); fasaco (*Hoplias malabaricus*), both carnivores; boquichico (*Prochilodus nigricans*), a detritivore; mojarita (*Bryconops aff melanurus*), an insectivore; and carachama (*Hypostomus* sp.), an detritivore; were analyzed by using the flameless cold vapor atomic absorption spectrophotometry technique. Dorado, a top predator, displayed the highest values of total mercury (699 ug/Kg ± 296). Six out of ten dorados showed an average higher than safe values of 0.5 ug/g (WHO, 1991). Lower values reported in this study in

the other species suggest that dorado may have gained its mercury burden downstream of Madre de Dios River, in the Madeira River, where goldmining activities are several times greater than that in the Madre de Dios area. Fasaco from Puerto Maldonado displayed higher levels than fasaco from Manu; however, mercury contamination in Puerto Maldonado is lower than values reported for fish from areas with higher quantities of mercury released into the environment. Positive correlation between mercury content and weight of fish for dorado, fasaco and boquichico served to explain bioaccumulation processes in the area of study. Additionally, higher concentrations of total mercury (inorganic + organic) in fasaco, compared with those in mojarita and carachama, suggest biomagnification of mercury occurred.

Mercury Accumulation in Fish from Madre de Dios, a Goldmining Area in the Amazon Basin, Perú

by

Nilton Eduardo Deza Arroyo

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APPROVED:

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Co-Major Professor, representing Fisheries and Wildlife

Redacted for Privacy

Co-Major Professor, representing Fisheries and Wildlife

Redacted for Privacy

Head of the Department of Fisheries and Wildlife

Redacted for Privacy

Dean of the Graduate School

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DEDICATION

To Rebeca, my wife, Yacila and Mara, my children, whom I love the most.

Mercury Accumulation in Fish from Madre de Dios, a Goldmining Area in the Amazon Basin, Perú

INTRODUCTION

Increased world gold price since the early 1970s and poor conditions of life have pushed the people to flood the Amazonia in search of alluvial gold. In Brazil an estimated 650,000 to one million people are working in goldmining (Malm et al., 1990; Nriagu et al., 1992; Greer, 1993); making this country the second largest gold producer in the world. In a relatively small area southeast of Peru in the Madre de Dios River basin (Fig. 1) about 30,000 people work in this activity (GRADE, 1994).

Gold in fine particles is being extracted using mercury by miners in Peru, Brazil and other countries which share the Amazon basin. Gold in the sands is incorporated into metallic (liquid) mercury. The mercury after being separated from the sands by manual pressure is then heated and volatilized leaving the gold behind. Mercury vapor enters the atmosphere to eventually return to the soil in the abundant rainfall. Mercury residues also remain in the discarded sands, giving mercury another pathway into the environment (Fig. 2). Of the total mercury lost in goldmining, 45% is discarded as liquid in soils and streams and 55% enters the atmosphere when the amalgam is heated (Akagi et al., 1995a; Veiga and Meech, 1995). Assessment in Madre de Dios of this kind of mining indicated 90 tons of mercury had been released during 8 years of activity (IMA, 1995). Therefore, the environmental price for goldmining in the Amazonia is the release of significant quantities of mercury into the atmosphere, forests, soils, and eventually waterways.

Naturally occurring mercury is in three oxidative stages (or inorganic mercury): as metallic form Hg^o, in the +1 (mercurous) stage, and the +2 (mercuric) stage. Hg_+ and Hg_{2+} stages form salts of Hg (typical as HgCl, $HgCl_2$, HgO). Among the organic mercury compounds, methyl mercury, belonging to the alkyl mercury group, is the most dangerous (WHO, 1989; Laws, 1993). Metallic mercury is innocuous unless air-breathing organisms are exposed to its vapor. However, salts of Hg, water soluble compounds, are corrosive

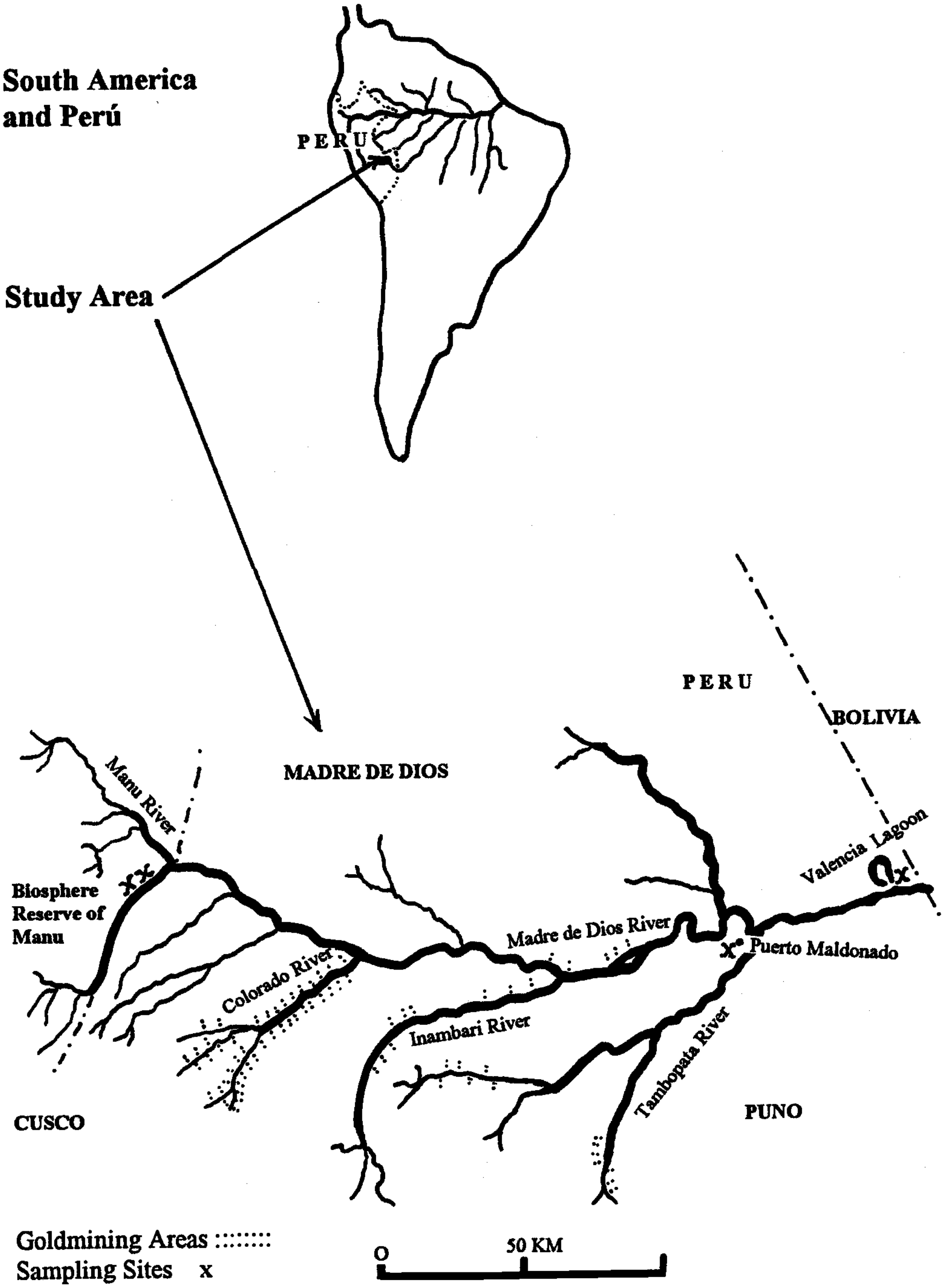

Fig 1 Geographical location of Madre de Dios River, Perú

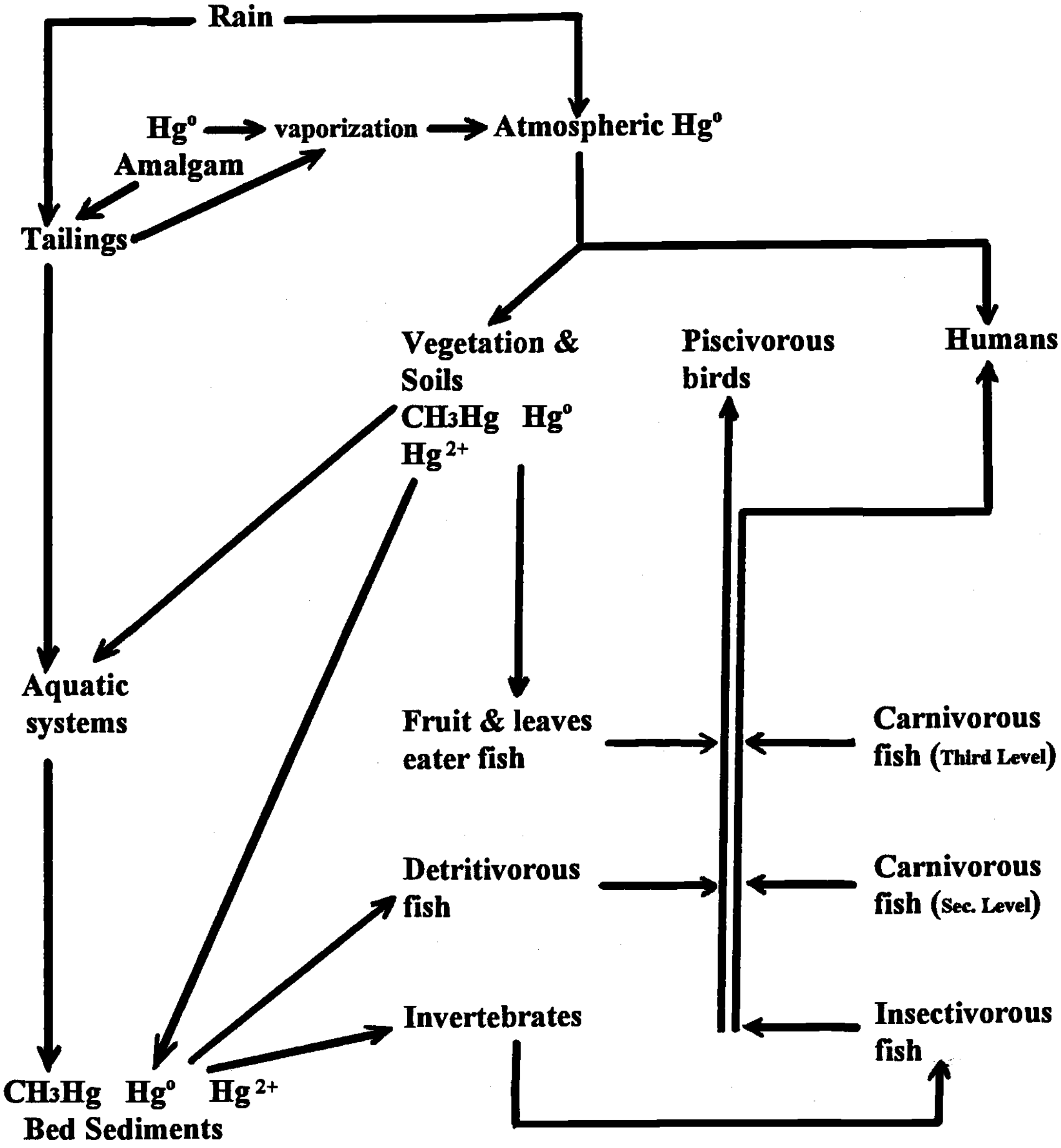

Fig 2 Flow diagram of mercury contamination paths in a tropical rainforest river exposed to goldmining.

to the intestinal tract and damage soft tissues as those in liver and kidneys. When mercury is transformed to organic forms, mostly as methylmercury, it gains properties of high lipid solubility and low water solubility, allowing it to enter in the food web. Jensen and Jernelov (1969) demonstrated that bacteria from bed sediments are able to make this transformation. Other workers found that any microorganism able to synthesize vitamin B_{12} can transform metallic mercury into its methylated form (Grant, 1971). Methylmercury is readily assimilated by aquatic bottom feeders and through biomagnification processes it can be found in large carnivorous fish in high concentrations (Table 3). Methylmercury accounts for >90% of total mercury found in fish muscle (Pfeiffer et al, 1993; Akagi et al, 1995) .

The role played by fish as a source of mercury exposure to human beings is well known. After the events in Minamata, Japan, where the population was poisoned with mercury from seafood, studies in a number of locations around the world indicated this heavy metal present in high levels in waters, bed sediments and biota of exposed areas. Studies in human populations close to the areas of point source mercury pollution with fish in the diet displayed high mercury content (Turner et al., 1980; Jackson, 1988; Guimaraes, 1995; Palheta and Taylor, 1995).

People exposed to mercury vapor in sites where the amalgam had been heated suffer damage in kidneys, liver and intestine. If large amounts of vapor are inhaled, the central nervous system (CNS) is injured. Blindness and mental disorders appear. Methylmercury also damages soft tissue organs and the CNS and interferes with cell formation. Genetic abnormalities may also result (Smith, 1975; Laws, 1993)

In the Brazilian Amazonia, where between 1500 and 3000 tons of mercury have been released into the environment in the last 15 years (Hacon et al., 1995), air, soils, waters, fish and ultimately humans have mercury burdens higher than background values (Tables 3, 4 and 5). Aks et al. (1995) report values of 24.8 ug/Kg of mercury in blood of people exposed to goldmining. Similar findings are corroborated in the Tapajos River with 96 % of the mercury in fish tissue in the methylated form (Akagi et al., 1995). In Tucurui, another mining area, a mean of 65 ug/Kg of mercury was found in the hair of people who consumed at least 14 fish meals per week (Leino & Lodenius, 1995). This level is sufficient to create health disturbances.

The aim of this study was to investigate bioaccumulation of mercury in relation to weight and size of fish, because of both concern for natural processes in the aquatic ecosystem and for the health of human populations who consume mercury contaminated fish. Whatever its position in the food web, each species should demonstrate some pattern of mercury accumulation throughout its life history.

Another objective was to determine levels of total mercury in fish muscle according to their position in the food web. It is assumed that fish, like other living things in aquatic systems, show mercury biomagnification as it passes each trophic level.

The purpose was also to determine the difference between mercury content of fish exposed to mercury contamination from mining sources with fish from a pristine area by comparing data of resident fish from Puerto Maldonado area (with goldmining activities) with those of the same species from the Biosphere Reserve of Manu. Another objective was to contrast the difference between residential and migratory species in Puerto Maldonado and their mercury burden.

MATERIAL AND METHODS

Study Area

Madre de Dios River in the Amazon basin is situated in southeast Peru, in the administrative subregion of Madre de Dios. Downstream, after the confluence of Madre de Dios River with the Manu River, the main stream receives alluvial gold washed out from the oriental slopes of the Andes cordillera. The area is the least populated in the country; even so, goldmining activities have increased steadily since the early 1970s and nowadays involves between 20,000 and 30,000 people (IMA, 1995). Gold production in Puerto Maldonado is shown in Table 2 of appendices.

Initially, most of the mining was done by manual labor, however, in the last decade, heavy machinery and dredging boats have been introduced in the area and recovery of gold has become semi-industrial.

Fish from rivers and lagoons supply local markets and is an important item in the daily diet of Amazonian peoples. Statistics of fish landed in Puerto Maldonado appear in Fig. 10 and 11 of appendices.

Fish samples analyzed in this study were from the areas surrounding Puerto Maldonado, as shown in Fig. 1. Boquichico came from Valencia Lagoon. Fasaco came from a pristine area of the Alto Madre de Dios River in the Biosphere Reserve of Manu (Culture Zone).

Experimental Design

Three residential species of fish from Puerto Maldonado area were selected to test the difference in total mercury content in the food web: carachama (*Hypostomus* sp, Lacepede 1803, Loricariidae), a detritivore; mojarita (*Bryconops aff melanurus*, Bloch

1794, Characidae), an insectivore; and fasaco (*Hoplias malabaricus*, Bloch 1794, Erythrinidae), a carnivore (Deza, 1984; Ortega and Vari, 1986; Chang and Ortega, 1995).

In order to establish the difference in mercury levels between residential and migratory species, the three species mentioned above served as residential species. For migratory species, boquichico (*Prochilodus nigricans*, Agassiz 1821, Prochilodontidae), a detritivore; and dorado (*Brachyplatystoma flavicans*, Castelnau 1855, Pimelodidae), a carnivore, were employed.

Fasaco was used to determine potential differences in mercury content in fish from an area where goldmining is active (Puerto Maldonado) and a pristine area (Manu).

Fish samples were obtained in June and July 1995 and May and June 1996. In total, 136 specimens belonging to the 5 species were sampled: 10 dorados, 42 fasacos (34 in Puerto Maldonado and 8 in Manu), 11 boquichicos, 33 carachamas and 40 mojaritas.

Field Techniques

Sampled fish were bought or obtained in the market of Puerto Maldonado, or caught by net or hook and reel in the study area. Weight (± 0.5 g) and standard length (± 0.1 cm) were taken for each specimen. A five gram sample from the dorsal-epaxial muscle of every fish was stored frozen in zippered plastic bags. In Manu, a dewer (Nitrogen-liquid container) was used to keep the samples frozen. After air transportation of this biological material on ice, it was stored frozen at Oak Creek Laboratory (Oregon State University) until the samples were analyzed in July 1996.

Laboratory Techniques

Analyses for total mercury (inorganic + organic) in fish muscle tissue were performed at the Oak Creek Laboratory by using a cold vapor atomic absorption spectrophotometry method (Magos & Clarkson, 1972; Giovanoli-Jakubczak et al, 1974; and Stoeppler, 1988).

First, a heat alkaline digestion of a muscle sample (around 1 gram wet weight each) was made by adding 2 ml of 10N NaOH heated in a water bath for 10-15 min. To 90 °C and then cooled to room temperature. An aliquot of 1 ml of the digested sample was then placed in a bubbling flask. Three mls of 1% solution of ClNa, 1 ml of 1% L-cysteine, 1 ml 50% $SnCl_2$ + 10% $CdCl_2$ dissolved in 4N HCl, and 4 drops of octanol were added. The mouth of the bubbling flask was then covered with a rubber stopper and 4 ml of 10N NaOH were injected by syringe through the rubber cap. After 30 seconds, pure nitrogen gas was injected at 1.5 l/min. into the flask. Then, the generated mercury vapor passed through a dehydrant column of $Mg(ClO_4)_2$ to the Mercury Analyzer System, model Coleman 50 Perkin-Elmer Co. The recorder operated at 20 mv with a chart speed of 1 cm/min.

To construct the calibration curve, a series of five different mercury standards were used for each species, depending on the total mercury concentration in the corresponding tissue sample. Standard solutions ranged from 0.1 ug/g to 2.5 ug/g for dorado, to 2 ug/Kg to 100 ug/Kg for carachama. Mercury chloride (Sigma 80-2060 with 99.9995 % of purity) served to prepare standard solutions. Reagent blanks were used at the beginning and the end of each series of analyses. In addition, Dorm-2, a reference material of mercury in fish (4.64 ug/g dry weight ± 0.26) served as background to verify the results.

Statistical Analysis

Statistical analyses were performed with Statigraphics Plus, Stat Curve and SAS programs. Results in T-Hg concentration (inorganic + organic) by species were transformed to Log for graphical comparison. Linear regression was used for each species to assess correlation in T-Hg concentration versus length and weight, especially weight. Some of these relationships could also be defined with sigmoid or other curves with higher r-square values than for linear analysis. However, comparison between T-Hg concentration and fish weight for different samples was improved by analysis of linear regression. For testing differences in Hg levels between fasaco from Puerto Maldonado and Manu, the data was analyzed with ANOVA of covariance, with weight as a covariate. The significance of differences in the T-Hg concentration in the three species used to examine biomagnification process was analyzed by comparison of means.

RESULTS

There was a significant difference in total mercury levels among some collected species (ug/Kg wet weight, Fig. 3). Large predatory migratory fish (dorado) presented the highest mercury burden (699 ug/Kg ± 296 SD; range 307 - 1095). Migratory detritivore boquichico (55 ug/Kg ± 35 SD; range 24 - 124) and small resident carnivorous fasaco (44 ug/Kg ± 36 SD; range 13 - 151) were second in order, followed by insectivorous mojarita (29 ug/Kg ± 12 SD; range 12 - 62). Lowest values corresponded to residential carachama (detritivore, 13 ug/Kg ± 7 SD; range 4 - 46). Presented in Table 1 is a summary of all results of the Hg analysis covered by this study. The values in the row "average" serve to illustrate the difference in total mercury concentration by species.

The relationship of total mercury concentration versus fish weight for the five species used in the study was tested through linear regression analysis. The positive correlation between total mercury and weight presented in dorado (a carnivore, r = 0.84), fasaco (a carnivore, r = 0.73), and boquichico (a detritivore, r = 0.72) demonstrated that each of these species accumulates mercury in tissues steadily throughout its life history. The greater the fish weight, the greater was its mercury burden (Fig 4, 5, 6 and 7). These results demonstrated the bioaccumulation process in four out of six groups of fish in the Madre de Dios area. Moreover mojarita and carachama did not exhibit any significant linear correlation between these parameters. Similar findings resulted for regression between standard length and total mercury.

Sixty percent of dorado presented levels of total mercury higher than the allowed limits for human consumption (500 ug/Kg, WHO 1991). The highest value (1095 ug/Kg) in this study was in one dorado weighing 15 Kg. Only this species, out of two species representing migratory fish, showed elevated mercury levels. Boquichicos, sampled in an area with less intense goldmining, had rather low values (55 ug/Kg ± 35 SD). Dorado samples contained concentrations 15.9 times greater than values for fasaco from Puerto Maldonado. Mercury level in boquichico was 1.25 times the values reported in fasaco from the same site.

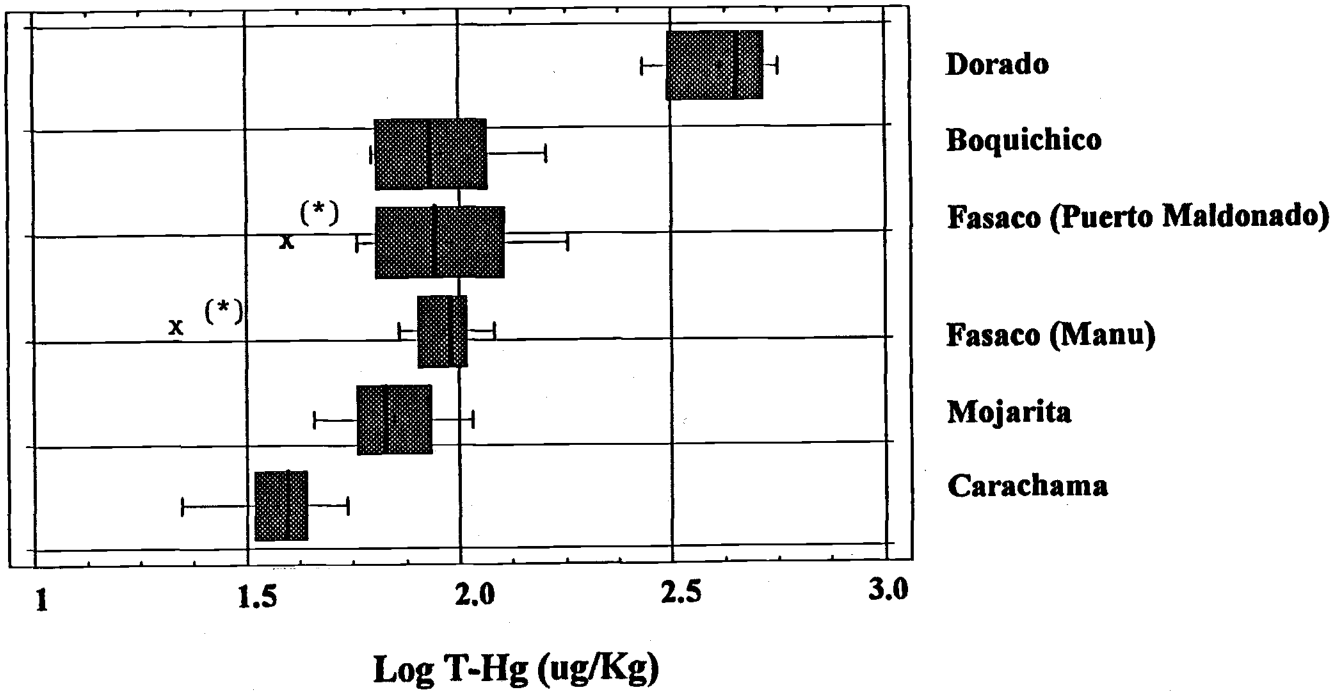

Fig 3. Log of Total Mercury (inorganic + organic) in six different groups of fish from Madre de Dios Area (Not corrected for fish weight). Vertical lines in symbols are means with range indicated.
(*) Weight corrected comparison of fasaco from Puerto Maldonado and Manu.

Table 1 Concentration of total mercury (inorganic + organic) in dorsal-epaxial muscle of fish from Madre de Dios area. Units: ug/Kg wet weight

Fish	Habit	Concentration ug/Kg			Stat. Diff. T-test	N	Fish Weight (g)		
		Average	SD	Range	(95 % CI) (*)		$\bar{X}$	SD	Range
Dorado	carnivorous	699	±296	307-1095	A	10	9750	(±3200)	4000-15000
Fasaco (PM)	carnivorous	44	±36	13-151	(**) B	30	143.34	(±119.41)	34-461.5
Fasaco (M)		50	±15	31-76	(**) B	8	345.38	(±107.66)	161-499
Boquichico	detritivorous	55	±35	24-124	B	10	1060.05	(± 276.28)	713-1616.5
Carachama	detritivorous	13	±7	4-46	C	30	250.25	(± 109.95)	129-611
Mojarita	insectivorous	29	±12	12-62	D	30	11.2	(± 3.5)	6-17.5

PM : Puerto Maldonado (Goldmining area)
M: Manu (Biosphere Reserve)
(*) True for Log transformed data
(**) Values are significantly different when corrected for fish weight.

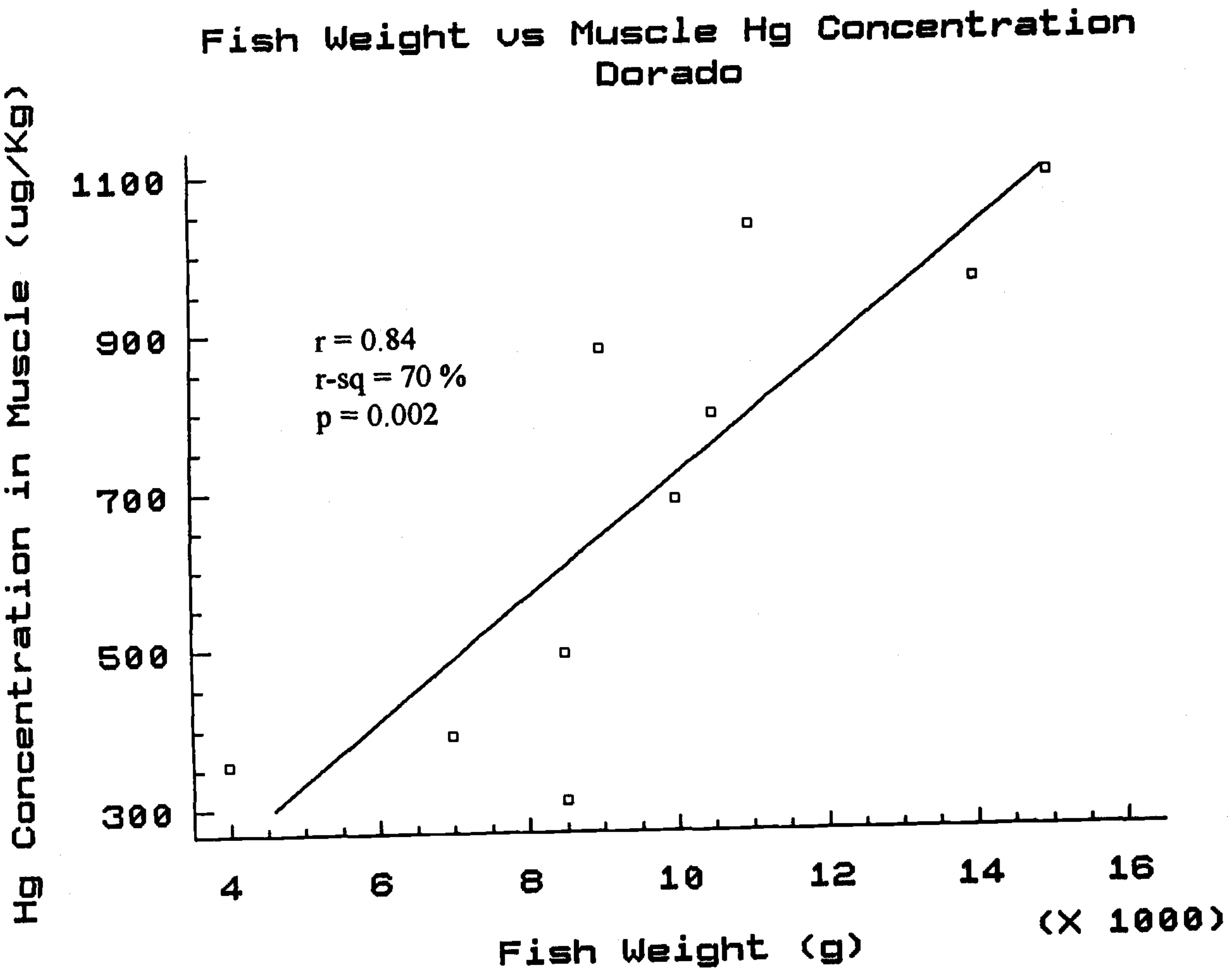

Fig 4. Regression line of weight (g) versus T-Hg (ug/Kg) in dorado.

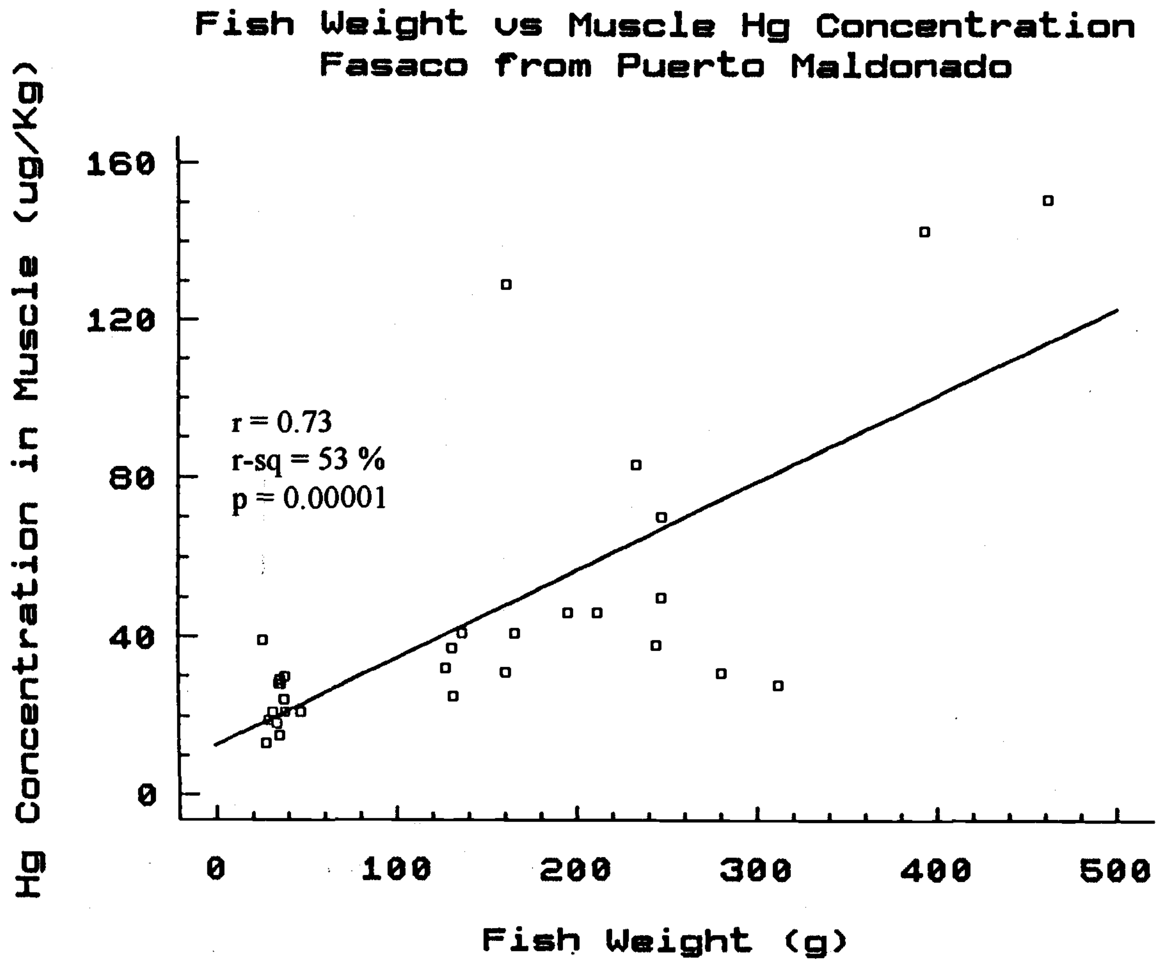

Fig 5. Regression line of weight (g) versus T-Hg (ug/Kg) in fasaco from Puerto Maldonado.

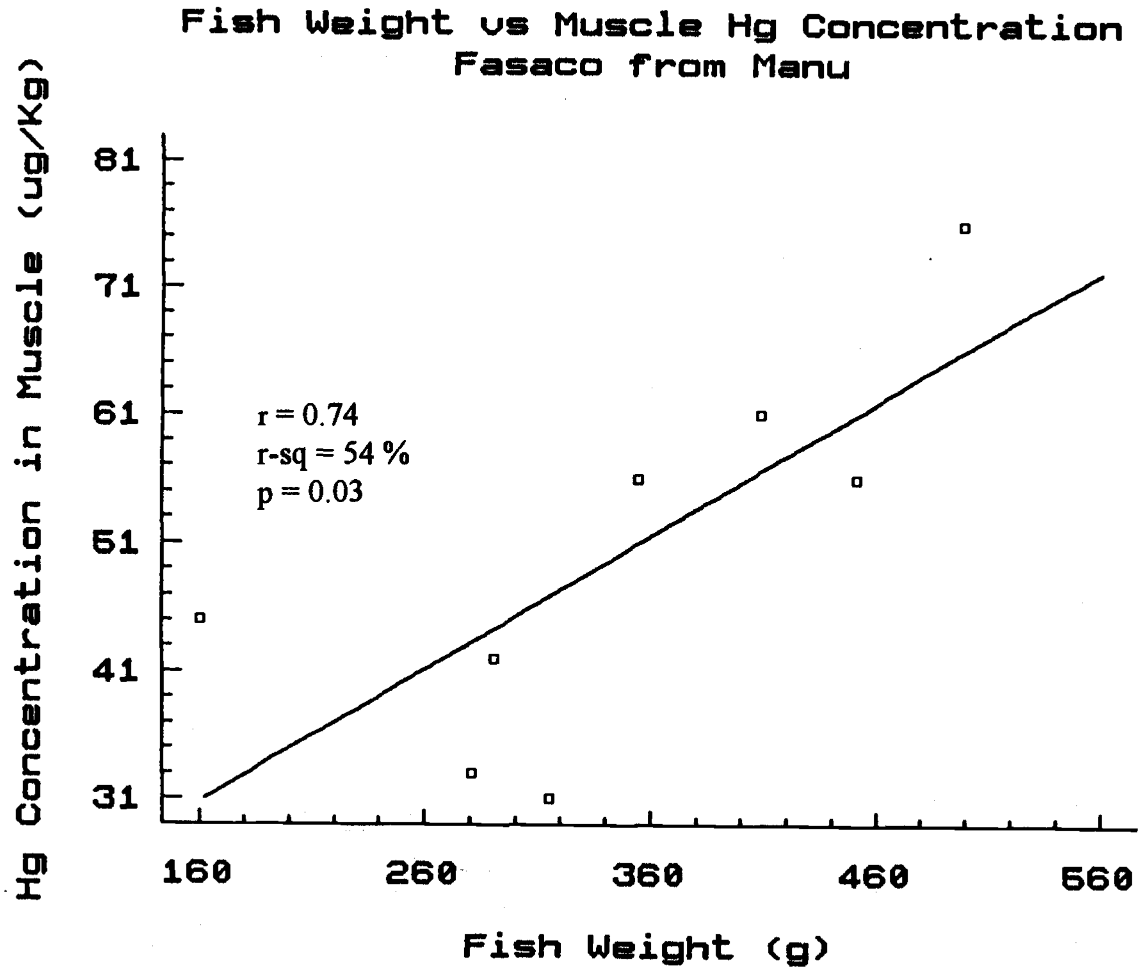

Fig 6. Regression line of weight (g) versus T-Hg (ug/Kg) in fasaco from Manu.

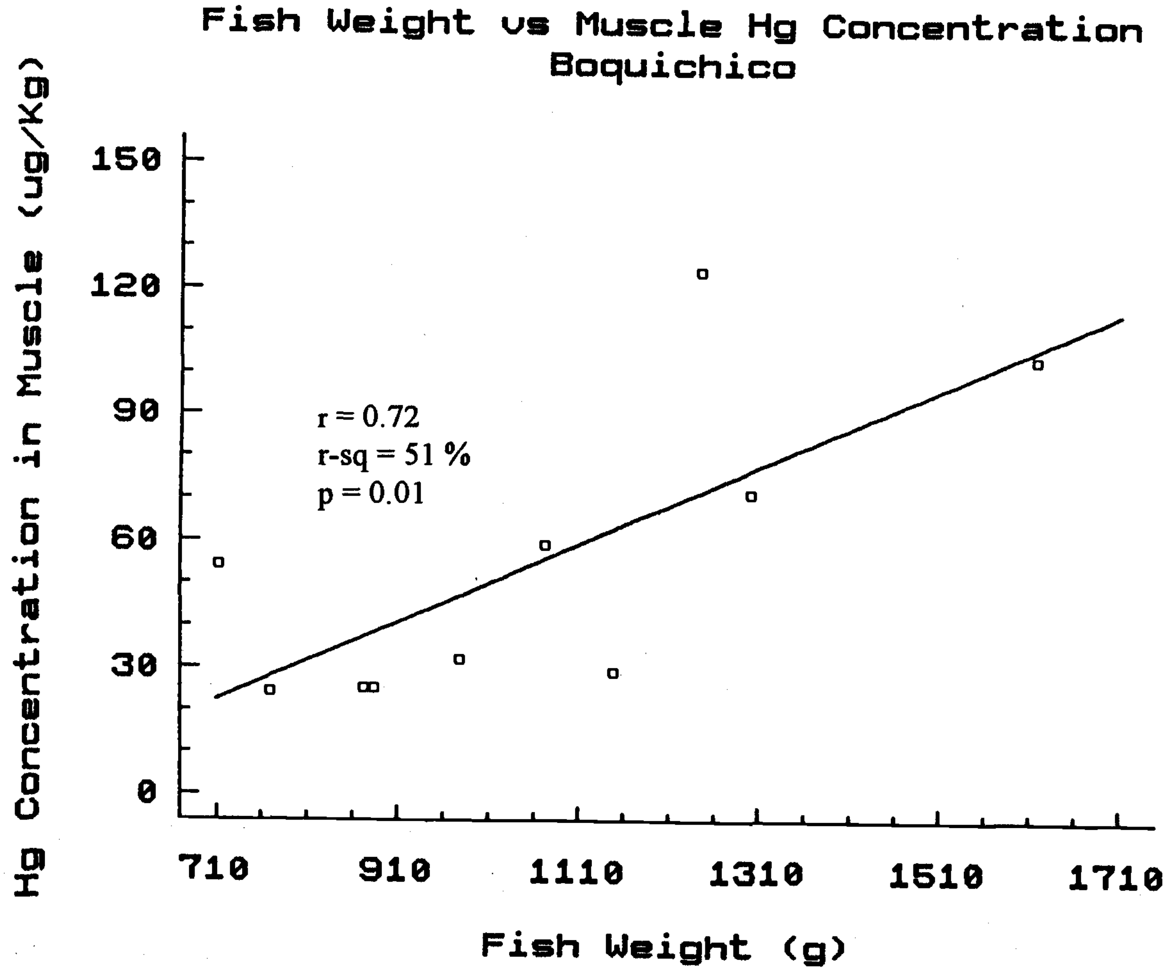

Fig 7. Regression line of weight (g) versus T-Hg (ug/Kg) in boquichico.

An analysis of mercury concentration in resident carachama (detritivore), mojarita (insectivore) and fasaco (piscivore), indicated biomagnification had occurred (Fig. 8). Higher concentrations were evident in fasaco specimens compared with those from mojarita and carachama. Carachama samples contained lower mercury concentration than mojarita. Fasaco had a mercury content 1.25 times greater than that of mojarita, and mojarita was 2.23 times the mercury concentration in carachama. Comparison of difference in means in these three species displayed statistical significance. P-values for t-test analyses between carachama and mojarita (8.61E-7, not assuming equal variances) and between mojarita and fasaco from Puerto Maldonado (0.03, not assuming equal variances) corroborate biomagnification processes in the Madre de Dios area. The results suggest that mojarita, despite its small weight (mean 11.2 g ± 3.5 SD), is able to concentrate mercury more readily than fasaco (greater mercury burden/weight of specimen).

Although mercury contamination was much greater at Puerto Maldonado than at Manu, total mercury in fasaco samples from Manu was higher than in fasaco samples from Puerto Maldonado. This was because of the greater size of the fish sampled at Manu. Since fasaco collected from both sites (Puerto Maldonado and Manu) were different in mean weight (143 g ± 119 SD and 345g ± 108 SD from Puerto Maldonado and Manu, respectively), the comparison of total mercury content in samples from goldmining and pristine areas was made by using ANOVA of covariance, with weight as a covariate. After adjusting standard weight in fish, the result displayed that mercury level in fasaco from Puerto Maldonado was 2.96 times greater than that in fasaco from Manu ($p = 0.0047$). In addition, comparison of slopes in simple regression lines (Fig 9), demonstrates that fasaco from Puerto Maldonado (with active goldmining) show a tendency to accumulate mercury in higher levels than fasaco from Manu (undisturbed area); p-value < 0.01. By testing the hypothesis that fasaco from Puerto Maldonado and fasaco from Manu showed interaction with the same slope, a p-value 0.20 demonstrated no interaction between these two groups.

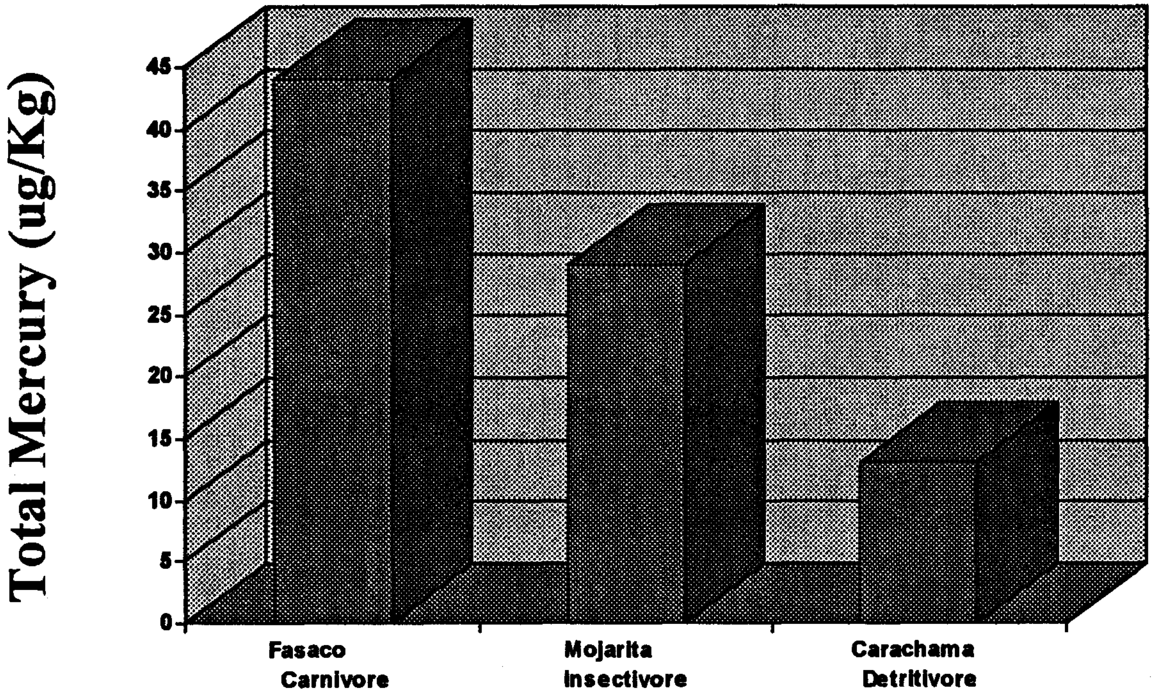

Fig 8. Graphical comparison of total mercury content (ug/Kg) in three species for testing biomagnification.

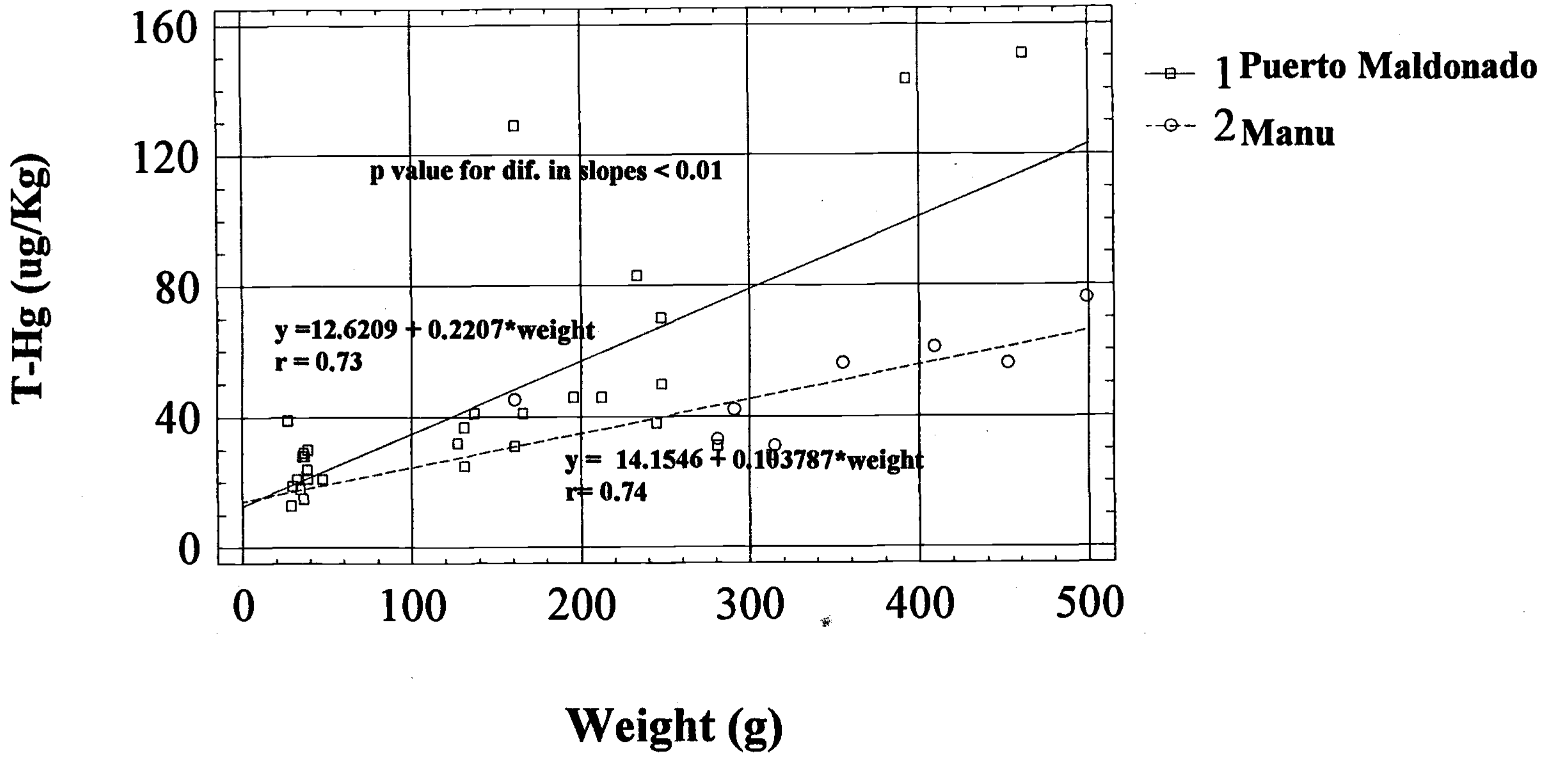

Fig 9. Comparison of regression lines of fasaco from Puerto Maldonado and fasaco from Manu. Total Hg (ug/Kg) vs Weight (g).

DISCUSSION

Residential and Migratory Species

Three residential species (carachama, mojarita and fasaco) and two migratory species (dorado and boquichico) were used to examine the variation of mercury content between these two groups. The former group exhibited low mercury content, (carachama 13 ug/Kg ± 7 SD, mojarita 29 ug/Kg ± 12SD, and fasaco 44 ug/Kg ± 36 SD), even lower than values in fish from areas used as control in studies carried out in Brazil. Freshwater fish not exposed to mercury contamination have levels lower than 200 ug/Kg (Malm et al., 1995). Occasionally, fish from natural waters are reported to have no detectible Hg (trout from Springfield, Montana, Lloyd et al., 1977).

Dorado (*Brachyplatystoma flavicans*), a top predator, displayed the highest values in this study (699 ug/Kg ± 296 SD). Levels as high as 2100 ug/Kg are reported for this species from the Madeira River (Malm et at., 1990, Table 3 of appendices), where goldmining is greater than that in the Madre de Dios area. Because of the low Hg level reported in other groups of fish in this study, it can not be concluded that dorado reached its Hg level in Madre de Dios area. Therefore, it is suspected that dorado arrived at Madre de Dios area with substantial mercury contamination gained downstream in the Madeira River area. Time of exposure to mercury, before dorado migrates upstream, may also account for high Hg values (Westoo, 1973, Boudou and Ribeyre, 1984).

IMA (1995) reports other giant catfish (*Pseudoplatystoma* sp.) in the Madre de Dios River with 790 ug/Kg in its flesh. The concern about high mercury content in the giant catfish (Pimelodidae) from the Amazon basin is because these fish are important items in the daily diet, and therefore a potential hazard to the human populations on the river banks. The carnivores group, which leads the total commercial fish catch in Puerto Maldonado (37%, Fig 10 of appendices), is almost totally composed of giant catfish;

though in the Madeira River, downstream Madre de Dios River, the top predatory group forms only 20% (Malm et al., 1995).

Boquichico (*Prochilodus nigricans*), contributes 100% of the detritivores in the Puerto Maldonado market (22.51%, Fig. 12). Mean T-Hg concentration in boquichico presented in this study is 55 ug/Kg (± 35 SD). This value is very low in comparison to values reported by other workers. Laguna Sandoval, a former meander which eventually became a lagoon where boquichico was sampled for this study, is located 200 Km downstream from the principal goldmining centers. Five specimens from the Madre de Dios River had higher values (mean 125 ug/Kg, Gutleb et al., 1996). Boquichico from Pucurui reservoir showed 70 ug/Kg (Porvari, 1995) and samples from Madeira River fish muscle contained between 100 and 210 ug/Kg (Malm et al., 1990; Pfeiffer et al., 1989; Martinelli et al., 1988). In those areas from Brazil, the quantity of mercury input into the environment is approximately 3 times more than that in Madre de Dios (Lacerda and Salomons, 1991; Voynick, 1992; Hacon et al., 1995; Leino and Lodenius, 1995; IMA, 1995).

Preference for kind of fish and frequency of fish meals has been surveyed in human populations exposed to industry and goldmining as a source of mercury. Since the first case of massive poisoning with a heavy metal in Minamata, Japan, where 750 people died, studies report high mercury content in human populations with a high fish preference in the diet. Svensson et al. (1991), by analyzing a total of 395 subjects in Sweden, found statistically significant associations between fish intake and mercury levels in whole blood. People with 2 fish meals a week had 3.7 times more mercury than people who never had fish. On the coast of Perú (Turner et al., 1980), 82 ug/Kg of Methylmercury (Me-Hg) was found in the blood of those with a high level of fish consumption. These people had an average of 10.1 Kg of fish per family per week. Values of mercury from people in the Amazonia Brazil are displayed in Table 5. Akagi et al. (1995) reported levels up to 149.8 ug Hg/Kg in the blood of people exposed to goldmining in Vila Sao Martins. Safe levels are considered to be 10 ug/Kg (WHO, 1989).

In human populations exposed to mercury contamination from fish, critical factors in ecological risk assessment are both frequency of fish consumption and mercury levels in fish. As an illustration, a total body burden of 25 - 30 mg of mercury (as Me-Hg) is unsafe for an adult of 70 Kg. With a low excretion rate of 1 % of mercury daily an intake of more than 0.03 mg Hg/day would therefore be unsafe (Grant, 1971). Similarly, if dorado in this study had an average T-Hg concentration of 0.7 mg/Kg, a daily intake of more than 43 grams of dorado would be harmful for human consumption if no other source of exposure to mercury existed. Other sources might include exposure to Hg vapor and mercury uptake from other foods. The presence of other likely sources of contamination make any recommendation of safe levels unwarrented without a complete human risk assessment study. Such a study should include analyses of environmental factors, mercury levels in fish, Hg content of human tissues, frequency of fish meals, and clinical studies of the exposed population

Bioaccumulation

Total mercury concentration in fish muscle increased with fish weight (Fig 4, 5, 6, and 7). Regression analyses of total mercury concentration (inorganic + organic) and fish body weight in dorado ($r = 0.84$), fasaco from Puerto Maldonado ($r = 0.73$) and Manu ($r = 0.74$), and boquichico ($r = 0.72$), demonstrate the bioaccumulation of mercury in these species.

Although several studies regarding biological accumulation reported an inclination of fish to accumulate mercury in muscle as it increased in weight and length (Stiefel, 1976; Boudou et al., 1979; Phillips et al., 1980; Allen-Gil et al., 1995), Vostal (1972) declares that the degree of exposure is a more influential factor than age or weight. The efficiency of bioaccumulation is very low. Predatory fish tend to accumulate only 10 % of the methylmercury that occurs in fish used for prey (Jernelov and Lann, 1971; Hildebrand et al., 1980).

Environmental and intraspecific factors have been analyzed by other workers in connection with mercury contamination in aquatic systems. Among the former, mercury concentration in water and bed sediments, organic substrate, pH, potential redox, and temperature are the most influential. Microbial activity in sediments, fish species, age, and trophic level account for biological factors (Tsai et al., 1975; Cember et al., 1978; Veiga and Meech, 1995).

Tropical waters are characterized by high organic matter load and, during the wet season, flooded areas become active aquatic systems. Goulding (1980), estimates that 75% of fish used in human diet originate from these areas in the Amazon watershed. Therefore, mercury deposited by the copious rainfall in flooded areas and that which comes from tailings in the banks of streams is mobilized by organic matter and enters in waterways, ready for biotransformation. Waters like Madeira and Madre de Dios rivers, have pH of about 7 (Lacerda, et al., 1989; Mora, 1995); as a consequence, the methylation process may carried out mostly in small streams with acidic waters (sometimes <5.5, Deza, 1980). This favors biotransformation, as revealed by Lacerda et al. (1989) in the Madeira River area.

Biomagnification

As a result of bioconcentration, mercury is magnified in the food web. A significant difference was found in mercury levels of fish of the species carachama (*Hypostomus* sp), a detritivore; mojarita (*Bryconops aff melanurus*), an insectivore; and fasaco (*Hoplias malabaricus*), a carnivore.

From the ecological point of view, the last step of inorganic mercury in aquatic systems occurs when it reaches bottom sediments. Here mercury is transformed by microorganisms to organic mercurial species (mostly methylmercury) capable of entering the food chain (Berman and Bartha, 1986; Allard and Arsenie, 1991). Invertebrates and detritivorous fish feed on organic matter from bed sediments, accumulating mercury which then passes to higher trophic levels. Ultimately, the biomagnification process, also called food chain concentration, is responsible for high levels of the non-biodegradable methylmercury in top predatory fish, as demonstrated in this study. On the other hand, mercury gained by fish could have another pathway via respired water (Fagerstrom and

Asell, 1973). The food consumption pathway may contribute nine times more mercury than occurs by exposure to water, as determined by Kudo and Mortimer (1979).

Because of the high biodiversity of fish in Amazon systems, it is rather difficult to explain natural biomagnification from the lowest to the top trophic levels in the food web. Currently, there are almost one thousand fish species registered only in the Peruvian Amazonia. For instance, there are no known species that share the same habitats, and which feed exclusively on each other. Equally important is the high complexity and natural richness of the terrestrial and aquatic Amazon ecosystems, which evolved in a more diverse environment than resulted in temperate or boreal ecosystems (Jernelov and Ramel, 1994; Goulding, 1980).

In spite of the small size of mojarita, their muscle tissues contained twice the concentration of mercury found in carachama. Mojarita is an insectivore, and insects may accumulate high mercury concentrations (Jernelov and Lann, 1971; Hildebrand et al. 1980; WHO, 1989; Park, 1996). For example a 1.5 Kg specimen of *Osteoglossum bicirrhosum*, an omnivorous fish with high insect consumption from the Madeira River area, was found by Barbosa et al. (1995) to have accumulated 11200 ug/Kg of mercury. Carachama, lower in the food web than mojarita, feed on fine particulate organic matter (FPOM) (Junk et al., 1989); consequently it showed lower Hg values than mojarita, as reported in this study.

Mercury Due to Goldmining

Fasaco (*Hoplias malabaricus*) from Puerto Maldonado were found to have statistically greater T-Hg concentrations than fasaco from Manu, the control area. ANOVA of covariance indicated that T-Hg concentration in fasaco from Puerto Maldonado was almost three times greater than that in fasaco from Manu ($p = 0.0047$), regardless of the weight of fish which performed as a covariate in the statistical analysis.

Other investigations, however, have measured T-Hg concentration in fish from the goldmining areas of Brazil that are much higher the values found for fish from goldmining area at Puerto Maldonado in this study (Table 3). Apparently, the more extensive level of mining in Brazil resulted in higher levels of mercury contamination in fish than that from affected areas of the Madre de Dios River.

In spite of the higher mercury values in fish from Puerto Maldonado with goldmining activities, compared to mercury burden in fish from the Biosphere Reserve of Manu, fish from more intensive goldmining areas, such as the Brazilian ones, evidence much higher mercury levels (Table 3). Values of T-Hg in muscle of fasaco reported from goldmining areas in Brazil ranged from 160 to 910 ug/Kg (Pfeiffer et al., 1989; Lacerda and Salomons, 1991). Thirty fasacos from Puerto Maldonado showed an average of 44 ug/Kg (± 36 SD) with a range of 13 and 151 ug T-Hg/Kg.

CONCLUSIONS

In this study, analyses of total mercury in muscle tissue of fish with a cold vapor ASS technique was used to demonstrate bioconcentration in three out of five species of fish from Perú. Mercury content found in fish of three different trophic levels suggests biomagnification processes occurred in the area. Fish from Puerto Maldonado, with active goldmining, showed three times greater mercury concentration than for the same species from the Biosphere Reserve of Manu.

The results indicate that fish from the Madre de Dios have been exposed to a measurable level of mercury contamination as a consequence of goldmining activities. Dorado, a top predatory fish, displays sufficiently high values of total mercury in flesh, potentially constituting a hazard for human consumption. The Hg burden in this fish was most likely gained downstream from the Madre de Dios River, in the Madeira River, a more active goldmining area of Brazil.

Public health policy should address potential hazards, especially to children and pregnant women, from consuming fish species shown to contain hazardous concentrations of mercury. A complete human health risk assessment study is recommended.

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APPENDICES

Table 2. Gold production and estimation of mercury inputs into the environment from goldmining in the Madre de Dios area. Comparison is made with mining in the Madeira River. All values are shown in Kg.

Year	Gold produced	Hg input
1987	1560	2028
1988	1976	2608
1989	1272	1680
1990	6500	8580
1991	6500	8580
1992	15215	14800
1993	16525	14900
1994	18999	16000
1979 - 1985(*)	65860	86930

Source: Gold production 1987-1991, WCC/LAO, 95. From 1992 to 1994, Annuary DREM-MD, 1995.
Hg input 1987-1991, estimation of this study. From 1992 to 1994, IMA, 1995.
(*) Lacerda et al, 1989. Data from Madeira River region.

Table 3. Mercury levels in fish from the Amazonia and other regions in the world

Fish/Site	Weight (Kg)	Habit	ug/g T-Hg	Source
Osteoglussum bicirrhosum				
Madeira	1.5	insectivorous	11.5	Barbosa et al., 1995
Prochilodus nigricans				
Tucurui reservoir	-	detritivorous	0.07	Porvari, 1995
Madeira	0.34		.10-.21	Malm et al., 1990
	-		0.21	Pfeiffer at al., 1989
	-		0.10	Martinelli et al., 1988
Puerto Maldonado	1.20		0.027	IMA, 1995
	1.90		0.026	
	0.65		0.019	Mora, 1995
Brachyplatystoma sp.				
Madeira	20	carnivorous	2.10	Malm et al., 1990
Pseudoplatystoma sp.				
Madeira	4.10	carnivorous	0.50	Jernelov & Ramel, 1994
Puerto Maldonado	15		0.26	IMA, 1995
Pseudoplatystoma tigrinum				
Puerto Maldonado	13	carnivorous	0.79	IMA, 1995
Hoplias malabaricus				
Carajas	-	carnivorous	.35-.91	Pfeiffer et al., 1993
Rio Paraiba do Sul	-		.16-.37	Pfeiffer et al., 1989
Amazon Brazil	-		0.61	Palheta, 1995
Oncorhynchus tschawytscha				
NSO	-	carnivorous	0.039	Bloom, 1992
Anoplopoma fimbria				
NSO	-	carnivorous	0.428	
Oncorhynchus mikiss and *Salmo trutta morpha fario*				
Springfield/Montana		carnivorous	0.00	Lloyd et al., 1977.
Big Piney River			0.49	
Perca fluviatilis				
Lake Dubrovskoye	0.027		0.64	Haynes et al., 1992
Lake Tyomnoye	0.154		1.06	

Threshold limit: 0.5 ug/g in Brazil (Lacerda & Salomons, 1991) and USA (Salvato, 1992, WHO, 1991)

NSO: Non Specific Origin

Table 4. Mercury levels in air, soil, water and bed sediments from goldmining areas in the Amazonia.

Site	Air ng/m3	Soil ug/g	Water ug/l	Bed sedim. ug/g	Source
Madre de Dios					
Távara River		0.0013	0.0007		CI, 1994
Malinovski River		0.0012	0.0007		
Inambari River		0.0012	0.0007		
Tambopata River		0.0014	0.0006		
Colorado River			0.0015	0.107	Mora, 1995
M. de Dios River			0.0013	0.358	
Inambari			0.0013	0.264	
Tambopata			0.0008	0.156	
Alta Floresta (Bra.)					
Gold dealers shop	1113-19120				Hacon et al., 1995
Madeira River		.27-.54	ND/9.97	.03-.35	Malm et al., 1990
				.02-.20	Martinelli et al., 1988

Background values: Water: 2 ug/l (WHO : 1 ug/l). Air: 0.01 ng/m3. Sediments: 0.1 ug/g.

Table 5. Mercury content in hair, blood and urine in humans (T-Hg ug/Kg) from different locations

Site	Hair	Blood	Urine	Source
Peru coastal		82 (org)		Turner et al., 1980
Peru inland		9.9 (org)		
Madre de Dios		0.1-12		IMA, 1995
Tapajos River (Bra)		14.6-43.2		Aks et al., 1995
Brasilia Legal	40.4			Akagi et al., 1995a
Para, Brazil		6.2-16.7	11.6-21.9	Aks et al., 1995
Amazon, Brazil	0.2-32	1.0-64.7	0.1-155	Palheta, 1995
Amazon River (Bra)				
Gold shop workers		5.1	61.0	Branches et al., 1993
Gold miners		2.2	35.4	
Others		2.7	9.9	
Vila Sao Martins (Bra.)	37.4	149.8		Akagi et al., 1995
Alta Floresta	4.1	12.2	161.8(*)	
Minamata Bay (Japan)			22.4(*)	
Tucurui				
Main reservoir	65			

Threshold values: Blood : 10 ug/Kg
Hair: 6 ug/g
Urine: 50 ug/l

(*) ug/g CR

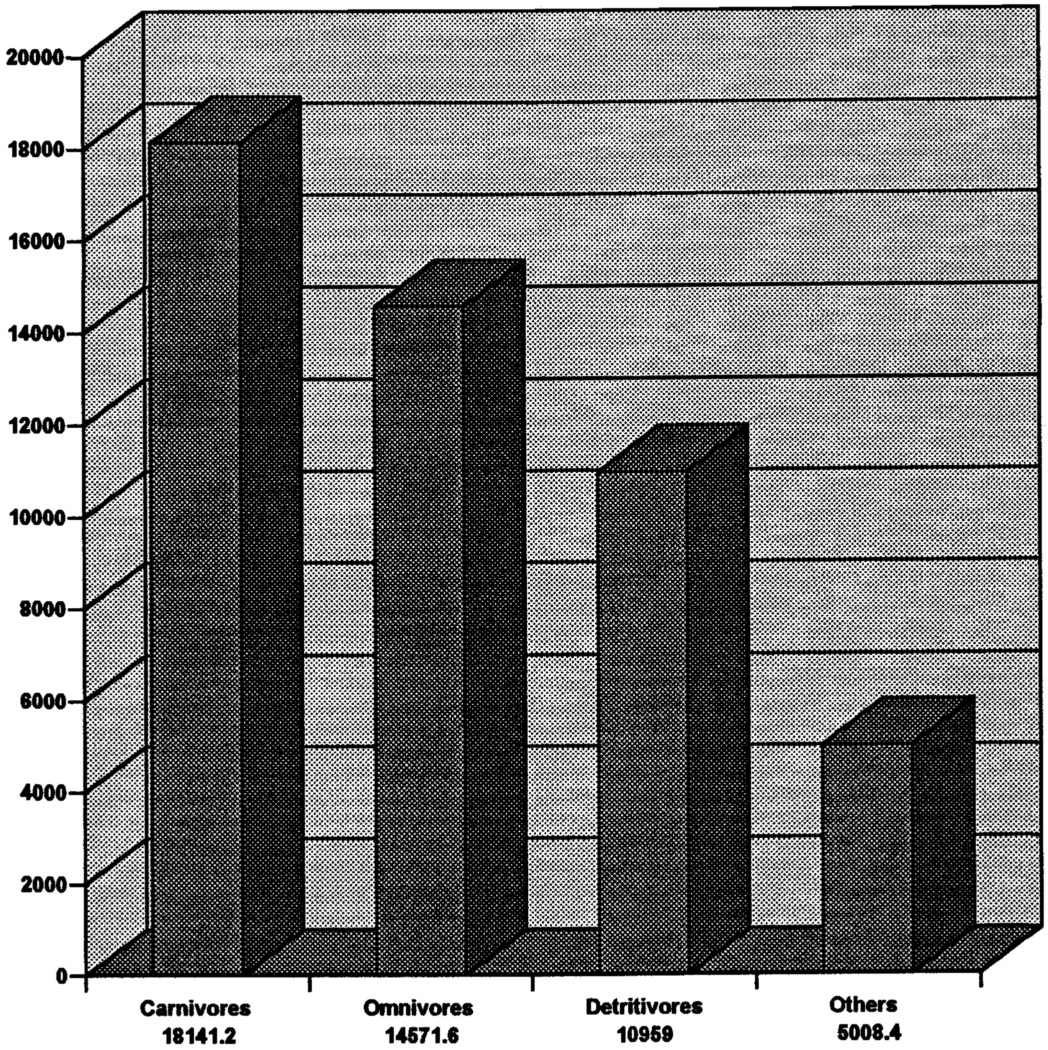

Fig 10. Composition by Kilograms of commercial fish catch in Puerto Maldonado, according to fish feeding habits. July 1995 - May 1996.
Total = 48,680.2 Kg

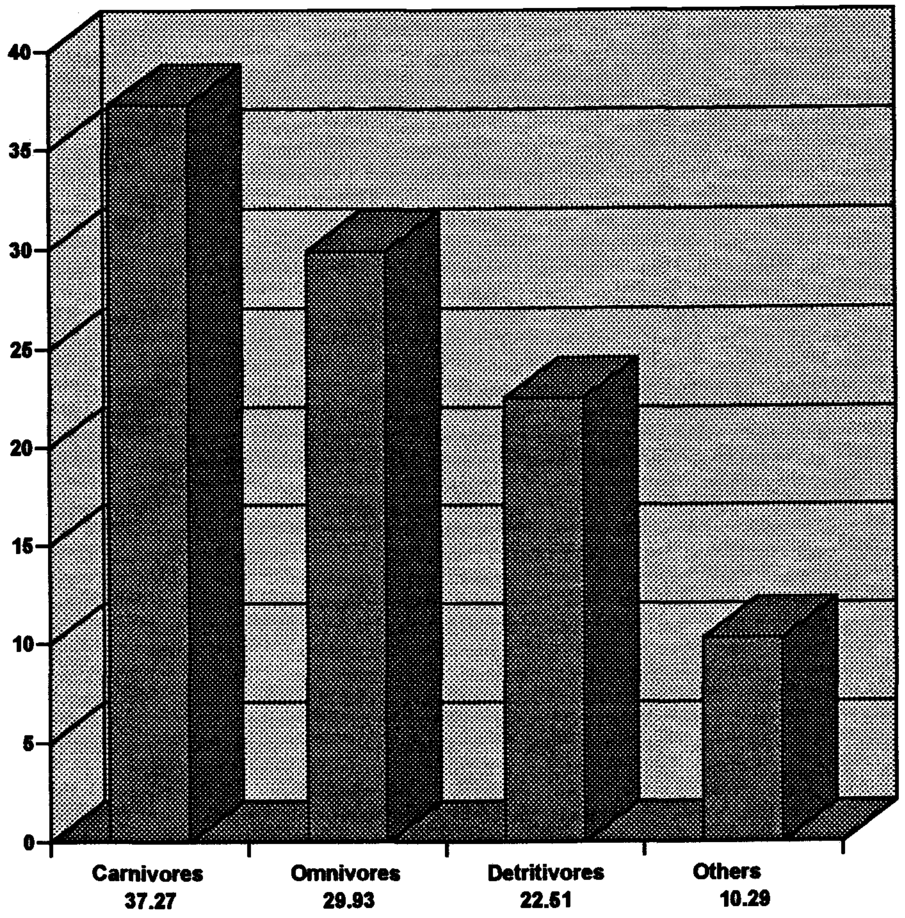

Fig 11. Composition by percentage of commercial fish catch in Puerto Maldonado, according to fish feeding habits. July 1995 - May 1996.