OT-1 Studies on Mercury Pollution in Amazon, Brazil

(1) Comprehensive Study on the Mechanism of Environmental Mercury Pollution

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Abstract The environmental mercury pollution due to gold mining in the Amazonian region has been become a matter of world-wide concern in recent years. To assess the extent of mercury contamination and its health effects, the collaborative study with Federal University of Rio de Janeiro has been undertaken mainly in the Tapajos river basin where can be considered the oldest and most productive gold mining area in the Amazon. Human hair, blood and urine, as well as fish samples were collected from gold mining areas and fishing villages, and analyzed for total mercury and methylmercury with new methods recently developed in our laboratory.

The results to date showed that the inhabitant of fishing villages near main gold mining area were more exposed to methylmercury than those far from gold mines. While, the levels of methylmercury in hair from people working in the goldfields and goldshop were much low, and it was found that these hair samples were mainly contaminated with mercury in inorganic form. From these data together with fish mercury analysis, the mechanisms of mercury contamination in the study area are discussed.

Key words Mercury pollution, Amazon, Methylmercury, Gold mining, River system

1. Introduction

In the Amazon, a tremendous amount of metallic mercury has been used for recovering fine gold particles from gravel through amalgamation and released into the surrounding environment since early 1980's[1,2]. There are two main pathways of mercury contamination which can affect human populations in the Amazonian region: First occupational exposure of gold miners and goldshop workers to inorganic mercury due to direct inhalation of mercury vapor during the gold recovery processes[3]. Secondly, a part of mercury released into the river system is methylated and ultimately bioaccumulated to a significant level in fish through food chain, and thus people living along rivers and depending on riverine products can be exposed to methylmercury through fish consumption. People living near gold mining areas may be exposed to both inorganic mercury and methylmercury simultaneously from surrounding environment and diets.

Although a growing literature exists dealing with mercury contamination levels in human and environmental materials from the main tributaries of the Amazon region[4-7], it has so far been difficult to predict to what extent these people and biota are exposed to methylmercury that is formed by methylation of inorganic mercury released in the gold mining areas, since the reported date are limited to total mercury analyses.

It is imperative that we need more date concerning mercury contamination in local populations and their environment from detailed mercury speciation studies. This paper is a

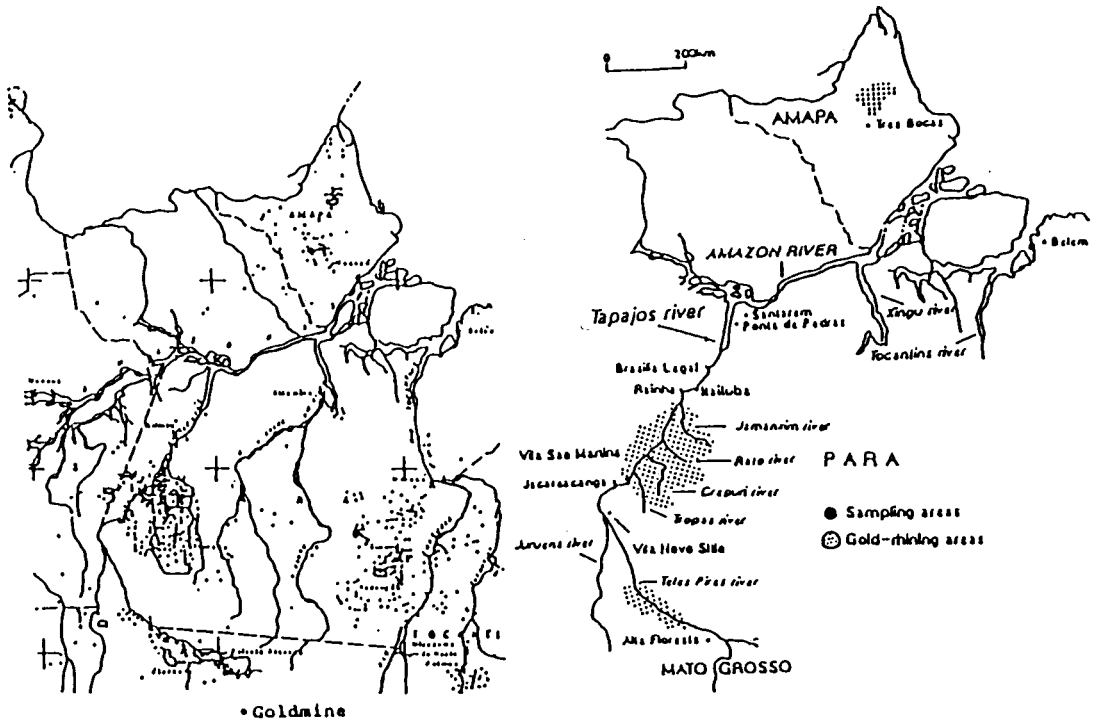

Fig.1. Maps of goldmining spots and study areas

Table 1. Total mercury and methylmercury concentrations in human hair from Tapajos river basin.

Sample origin (Sampling date)	N	T-Hg (ng/mg) Mean±SD (Minn.−Max.)	MeHg (ng/mg) Mean±SD (Minn.−Max.)	%(Mean) (MeHg/T-Hg)
Goldshop workes(1989)	4	15.4 (6.8− 31.3)	2.1 (1.1− 3.8)	13.6
Goldminers(1989)	7	22.2 (0.5−113.1)	1.2 (0.2− 2.5)	5.4
Former goldminers(1989)	13	3.4 (0.8− 9.4)	1.3 (0.6− 3.4)	38.2
Ponta de Pedras(Mar. 1992)	10	10.2 (6.2− 12.6)	9.4 (4.7− 12.0)	92.2
BrasilisbLegal(Mar. 1992)	37	15.8 (3.5− 46.9)	14.1 (0.9− 2.6)	89.2
BrasilisbLegal(Jul. 1992)	19	35.9 (7.2−151.2)	30.5 (6.1−132.6)	85.0
Rainha(Mar. 1992)	11	15.8 (2.4− 31.1)	15.0 (1.9− 29.4)	94.9
Jacareacanga(May. 1992)	48	16.6 (1.4− 46.0)	15.2 (1.1− 43.9)	91.6
Jacareacanga(May. 1993)	29	21.4 (2.9− 69.1)	20.2 (2.5− 68.7)	94.4
Trea Bocas in Amapa State(1992)	11	28.0 (8.4− 53.8)	26.3 (6.1− 50.3)	93.9
Rio de Janeiro				
No regular fish diet	20	1.7 (0.9− 3.1)		
Common fish diet	15	5.4 (1.5− 13.0)		

report on such approach. In particular, one purpose of this study was to evaluate the human and environmental exposure to methylmercury produced as a consequence of mercury methylation in the Amazonian aquatic ecosystems.

2. Research Methods

Tapajos river basin 2,000 km long is one of the main tributaries of the Amazon river system, and the first to be exploited in the gold rush which has taken place since the first discovery of gold in Cuiu-Cuiu in 1956. Gold mining has been extensively carried out in several tributaries of the Tapajos river, mainly in Teres Pires, Tropas, Creperi, Rato, Jamaxim and main channel of the Tapajos river. In order to estimate the actual exposure of local population to methylmercury, human hair and blood samples were collected from the inhabitants of various fishing villages at different distances from the main gold mining areas as shown in Fig.1. In addition, human hair, blood and urine samples were collected from gold miners and goldshop workers in Itaituba and Alta Floresta cities, which are important places as the main gold trading centers in this region.

Fish samples were obtained from Teres Pires river, Rato river, and the main channel of the Tapajos river near Itaituba, Brasilia Legal and Santalem. The human and fish samples were carefully analyzed for total mercury and methylmercury using highly sensitive and reliable methods recently developed and modified in our laboratory[8-10]. The validity and reliability of thelse methods have been repeatedly checked by inter- and intra-laboratory comparisons[11-12].

3. Results and Discussion

(1) Mercury Contamination in Human and Fish

The concentrations of total mercury and methylmercury detected in hair samples taken from goldminers, goldshop workers as well as inhabitants of various fishing villages are summarized in Table1. Total mercury concentrations up to 113.1 ppm were found in the hair samples from gold miners and goldshop workers. However, the concentrations of methylmercury were extremely low and the average proportions of methylmercury to total mercury were only 5.4-13.6% in these groups(Fig.2), suggesting a great contribution of inorganic mercury from air and/or sweat during the gold mining and burning processes. From these results, it is apparent that the measurement of only total mercury in hair samples is not sufficient for evaluating the human exposure to methylmercury in the areas being continuously contaminated with inorganic mercury like gold mining areas.

On the other hand, the results for total mercury and methylmercury concentrations in hair samples from the people living in fishing villages showed abnormally high values ranging from 10 to several 10's ppm on average, with a large variation. At Ponta de Pedras village far downstream of the Tapajos River, relatively low levels were observed, but higher values were obtained in the other fishing villages, indicating more mercury exposure in the upstream Tapajos areas. The highest value of total mercury of 151.2 ppm was observed at Brasilia Legal located around 100 km downstream from Itaituba, the main gold commerce center in the Tapajos river basin. It should be noted that hair methylmercury levels were very closed to the total mercury levels in almost all hair samples taken from the inhabitants in fishing villages as shown in Table.1. Moreover, the levels in the samples from males were significantly higher than those from females in all villages.

The results of total mercury and methylmercury analysis in fish from the Tapajos river are presented in Table2. Total mercury in fish ranged from 0.08 to 3.82 ppm, and most of the fish samples from upstream in the river had relatively high mercury levels exceeding the Brazilian allowable limit of 0.5 ppm. Extremely high levels of mercury were observed in

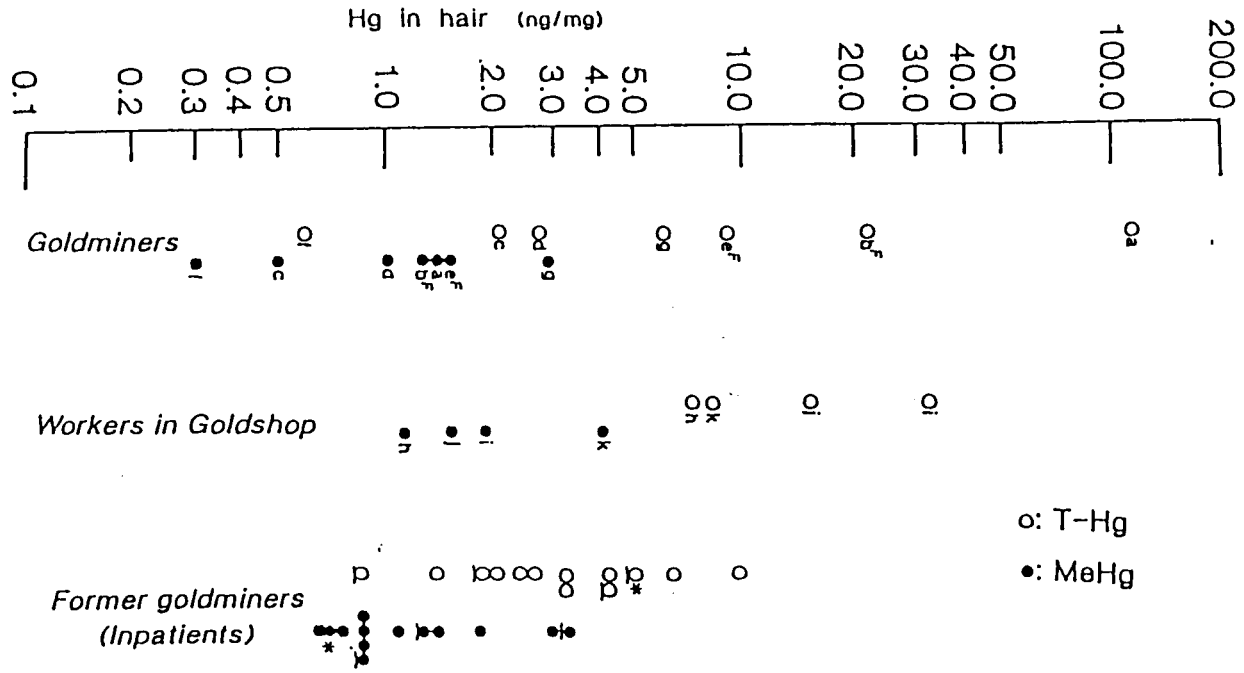

Fig.2. Total mercury and methylmercury concentrations in gold miners, workers in goldshops and former gold miner(inpatients) in Itaituba.

F: Female gold miners, *: Armpit hair.

Table 2. Total mercury and methylmercury in fish samples from the Tapajos river basin.

Origin	Name	Weight (g)	T-Hg (ng/mg)	MeHg (ng/mg)	% (MeHg/T-Hg)
Teles Pires river (near Alta Floresta)	Piranha	400	0.29	0.29	100.0
	Daurada	2700	0.60	0.57	95.0
	Piraiba	22000	3.82	3.29	86.1
	Piraiba	40000	2.85	2.44	85.6
	Jau	23000	0.61	0.58	95.1
	Jau	24000	0.75	0.70	93.3
	Jau	25000	1.03	0.82	79.6
	Jau	32000	0.39	0.36	92.3
Rato river	Peixe-cachorro	100	1.60	1.60	100.0
	Mandube	290	0.53	0.54	101.9
	Aruana	515	0.28	0.24	85.7
	Traira	6000	0.95	0.83	84.4
	Mardube	330	0.56	0.60	107.1
Tapajos river (near Brasilia Legal)	Acara	160	0.17	0.15	88.2
	Tucunare	570	1.16	1.12	96.6
	Pescada	910	0.41	0.36	87.8
	Apapa	1040	0.60	0.52	86.7
	Pacu	1430	0.10	0.09	90.0
Tapajos river (near Itaituba)	Pescada	200	0.56	0.52	92.9
	Apapa	450	0.54	0.46	85.2
	Filhote	4000	1.00	0.95	95.0
Tapajos river (near Santarem)	Apapa	390	0.39	0.37	94.9
	Pirarucu	20000	0.08	0.07	87.5

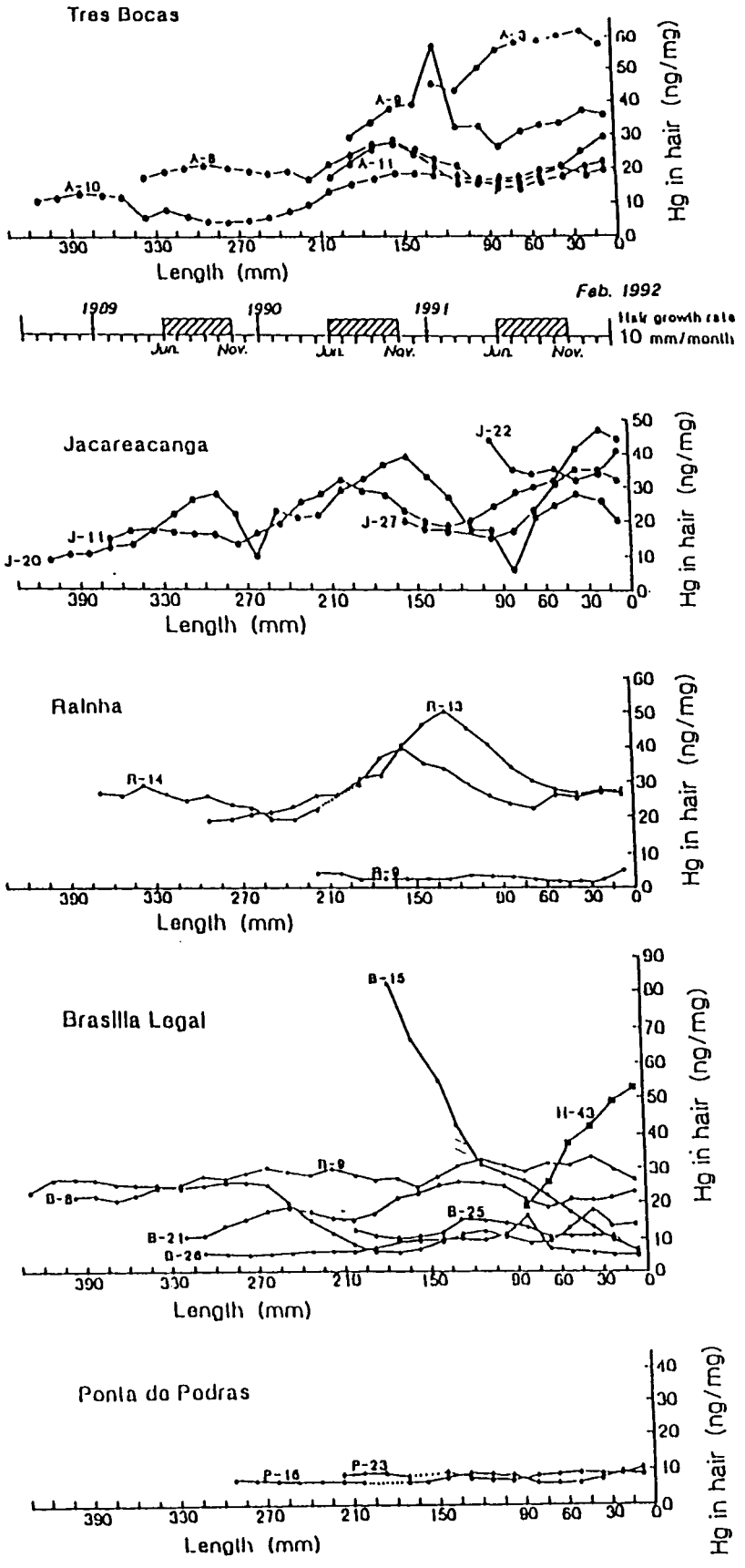

Fig.3. Longitudinal analysies of mercury along the strands of hair.

Teres Pires river near Alta Floresta city far upstream of the Tapajos river system, where the gold mining activities had been growing more and more in recent years. While, far downstream in the Tapajos river, near Santalem the levels were lower even in carnivorous fish. The predominant form of mercury in fish was also found to be methylmercury in all fish analyzed, suggesting high and widespread environmental methylmercury contamination in this region. It seems from these results that regional differences in the levels of methylmercury in each local fish should be reflected in the methylmercury exposure levels of people living in individual areas.

It is known that longitudinal mercury analysis along the strand of hair provides the information on previous exposure levels to methylmercury in individuals. As hair grows at about one centimeter per month, it is possible to monitor methylmercury exposure levels over a period of several months or years depending on the length of hair samples. A number of long hair samples from female individuals at different locations were obtained and analyzed for total mercury after being cut in small pieces(Fig.3).

In the Amazon, June - November is dry season and the other half years is rainy season. Looking over the results in Fig.3, individuals have been continuously exposed to methylmercury at fairly constant levels over at least the last few years up to the present time in all locations with some seasonal variations, significantly so for those who have high levels of methylmercury. In Tres Bocas and Jacareacanga, in particular, it can be seen that there is a trend for increased levels of mercury with time. Sample No. 15 was an exception, showing a drastic decrease in hair mercury with time. The samples was from woman whose hair had been dyed one month before sampling and the mercury in the sample was mostly in inorganic form.

(2) Correlations of Mercury Between Hair, Blood and Urine

As noted earlier, one purpose of this survey was to evaluate more precisely the actual extent of human exposure to mercury due to gold mining activities. For this purpose, we have conducted a field survey in two different types of communities, Jacareacanga, a typical fishing village, and Alta Floresta, an important area as a main gold commerce center in Mato Grosso State. Human hair, blood and urine samples were collected from individuals in each communities. Human hair and blood samples were also collected from two other small and isolated fishing villages, Vila Sao Martins and Vila Novo Sitio, located about 50 and 150 km upstream from Jacareacanga, respectively. Most of the fish consumed in these three fishing villages comes from the Teres Pires river.

The concentrations of total mercury and methylmercury in human hair, blood and urine collected are summarized in Table3, together with the mercury levels in urine collected from the general people living in Minamata, Kumamoto, Japan for comparison. The hair and blood samples from fishing villages contained quite high levels of mercury and again almost all of the mercury in these samples was in the methylated form and the ratio of total mercury to methylmercury was very close to 1. Among 51 hair samples collected, seven samples had levels greater than 50 ppm of methylmercury, the minimum threshold value for methylmercury intoxication established by WHO[13]. The contents of methylmercury in males were about 1.5 times higher than those in females. While, the levels of mercury in the blood samples from goldshop workers were much low and the proportion of methylmercury to total mercury was 72.2% on average, with a large variation ranging from 20 - 100%. High levels of mercury were found in urine samples from goldshop workers with fairly large variation. Almost all of the samples except for one sample contained mercury above the level of 30ng/mg creatinine, at which mild or minor adverse effects might occur among people exposed to mercury vapour[14]. Methylmercury was found also in urine samples, although the

Table 3.Total mercury and methylmercury concentrations in human hair, blood and urine samples from fishing villages and gold mining areas.

Sample origin	sample	N	T-Hg $\bar{X}\pm SD$	MeHg $\bar{X}\pm SD$	%MeHg $\bar{X}\pm SD$
Jacareacanga	Hair(ppm)	27	24.6± 17.8	24.1± 17.8	96.0± 9.8
(JA)	Blood(ppb)	19	90.4± 71.5	90.0± 76.6	97.2± 6.0
Vila Sao Martins	Hair(ppm)	14	37.4± 17.1	36.4± 17.1	96.4± 3.5
(VNM)	Blood(ppb)	8	149.8± 49.5	149.2± 52.5	99.0± 5.1
Vila Novo Sitio	Hair(ppm)	10	28.8± 13.0	27.3± 12.1	95.7± 4.4
(VNS)	Blood(ppb)	7	130.7± 78.4	131.9± 84.2	98.8± 7.4
Alta Floresta	Hair(ppm)	3	4.1± 1.3	3.1± 0.7	85.2± 10.0
(AF)	Blood(ppb)	25	12.2± 8.2	9.0± 6.7	72.2± 25.0
	Urine(μg/gCR)	21	161.8± 95.3	0.4± 0.2	0.4± 0.4
Minamata City	Urine(μg/gCR)	27	22.5± 14.9	0.7± 0.8	3.9± 4.4

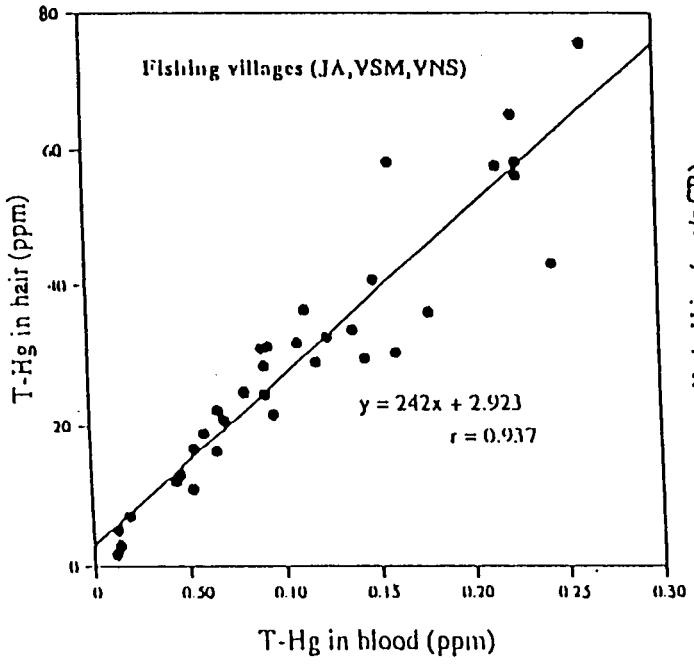

Fig.4. Correlation between blood hair mercury and blood mercury.

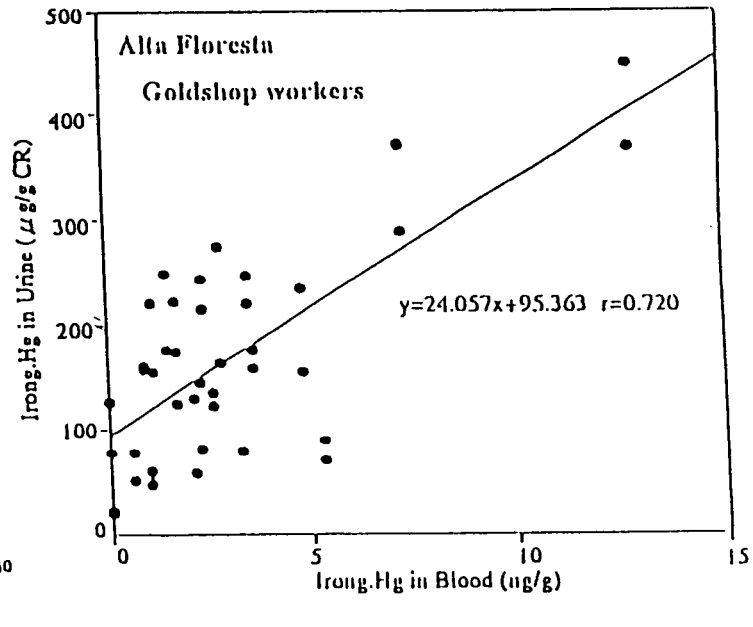

Fig.5. Correlation between blood inorganic mercury and urine inorganic mercury.

levels were extremely low. The proportions of methylmercury to total mercury ranged from 0.04 to 1.7%, with the average value of 0.4%, that was much lower then that of people living in Minamata, due to the greater inorganic mercury contamination. Based on these results, a correlation analysis was conducted.

The correlation between mercury in hair and blood for all in the three fishing villages is shown in Fig.3. As expected from the results of mercury analysis, total mercury or methylmercury in hair was highly correlated with that in blood (correlation coefficient r=0.937). From the regression equation, the overall average ratio of 242 was obtained for hair total mercury versus blood total mercury. This figure was in reasonable accordance with the value of 250, which has been established in various populations exposed to methylmercury at fairly constant levels[13].

No apparent correlation between total mercury in blood and urine was found, but the inorganic mercury in urine was significantly correlated with the inorganic mercury in blood with the correlation coefficient r=0.720 as shown in Fig.4, suggesting the possibility of predicting the levels of inorganic mercury accumulated in blood from the levels of mercury in urine. The scattered distribution of the blood - urine mercury ratios is not surprising taking into account the facts that the exposure levels of mercury vapor vary considerably depending on the frequency of re-burning operations in the goldshop and that the urine samples were collected the day following the collection of blood samples.

4. Conclusions

In order to evaluate the actual extent of human exposure to mercury in the Tapajos river basin affected by extensive alluvial gold mining, human hair, blood and urine as well as fish samples collected from different areas were examined in relation to the exposure to methylmercury produced in the natural environment.

In fishing villages, the inhabitants were found to be exposed to mercury at abnormally high levels mostly in methylated form through the consumption of local fish, with very little confounding exposure to inorganic mercury including mercury vapor in the air. The people living near the main gold mining areas were more exposed to methylmercury than those far downstream from the gold mining sites. It should be noted that quite high levels of methylmercury in hair was found in the fishing village of Tres Bocas near the lake. Moreover, the longitudinal mercury analysis of the long hair samples indicated that the inhabitants in the fishing village were continuously exposed to methylmercury at fairly constant levels at least over the last few years, with even a slightly increasing trend with time.

The human samples from goldminers and goldshop workers contained mercury in both inorganic and methylated forms, though the methylmercury levels were much lower than those in fishing villages. A significant correlation was observed between total mercury or inorganic mercury in urine and inorganic mercury in blood, suggesting the possibility of predicting the levels of inorganic mercury in human blood from the level of inorganic mercury or total mercury in urine. Thus, it would be apparent that chemical speciation of mercury is needed for better understanding the levels of mercury exposure in the populations in the areas where the contamination by mercury in both forms can occur.

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