— Minireview —

Human Exposure to Mercury and the Accumulation of Methylmercury that is Associated with Gold Mining in the Amazon Basin, Brazil

Hirokatsu Akagi[*,a] **and Akira Naganuma**[b]

[a]*National Institute of Minamata Disease, Hama, Minamata 867–0008, Japan and* [b]*Laboratory of Molecular and Biochemical Toxicology, Graduate School of Pharmaceutical Sciences, Tohoku University, Aoba-ku, Sendai 980–8578, Japan*

(Received July 7, 2000)

In order to evaluate the extent of human exposure to mercury in the Amazon, in particular, in the Tapajos River basin, which is a site of extensive alluvial gold mining, we analyzed samples of human hair, blood and urine, as well as fish, collected from different areas for total levels of mercury and methylmercury. In fishing villages, the inhabitants were found to have accumulated mercury, mostly in the form of methylmercury, at abnormally high levels as the apparent result of 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 had accumulated higher levels of methylmercury than people living far downstream from the gold-mining sites. Quite high levels of methylmercury were found in samples of hair from inhabitants of the fishing villages.

Key words —— mercury pollution, gold mining, human exposure, Amazon, methylmercury

INTRODUCTION

Gold mining using mercury amalgamation has markedly increased in many developing countries during recent years. In the Brazilian Amazon, it has been estimated that more than 650000 gold miners are currently working at more than 2000 mining sites.[1–3] Huge amounts of metallic inorganic mercury (Hg^0) have been used for the recovery of fine gold deposits from gravel by amalgamation and have been released into the environment in this region since the early 1980's.[4,5] The metallic mercury released into the river system may be reduced to Hg^{2+}. Some of the environmental Hg^{2+} has been shown to be methylated and converted to methylmercury (CH_3Hg^+) by various mechanisms.[6,7] Methylmercury is known to accumulate in the aquatic food chain, reaching the highest concentrations in predatory fish.[8] Therefore, today, evaluation of the exposure of people who live along gold-mining rivers to methylmercury through the consumption of local fish is a major concern.

*To whom correspondence should be addressed: National Institute of Minamata Disease, Hama, Minamata 867–0008, Japan. Tel.: +81-966-63-3111; Fax: +81-966-68-2011; E-mail: hiroakagi

Accumulation of Methylmercury in Fish and Human Hair

In the Amazon, extensive gold mining has been carried out along several tributaries of the Tapajos River, mainly in Teles Pires, Tropas, Creperi, Rato, Jamaxim and the main channel of the Tapajos River itself. In order to estimate the exposure of local populations to methylmercury, we collected samples of human hair and blood from the inhabitants of various fishing villages located at different distances from the main gold-mining areas, as shown in Fig. 1. In addition, samples of human hair, blood and urine were collected from gold miners and workers in gold shops in the cities of Itaituba and Alta Floresta, which are the main gold-trading centers in this region. Samples of fish were obtained from the Teles Pires River, the Rato River, and the main channel of the Tapajos River near Itaituba, Brasilia Legal and Santarem. The various samples were analyzed for total mercury and methylmercury by the highly sensitive and reliable methods that were recently developed and modified in our laboratories.[9–11] The validity and reliability of these methods have been repeatedly checked by inter- and intra-laboratory comparisons.[12,13]

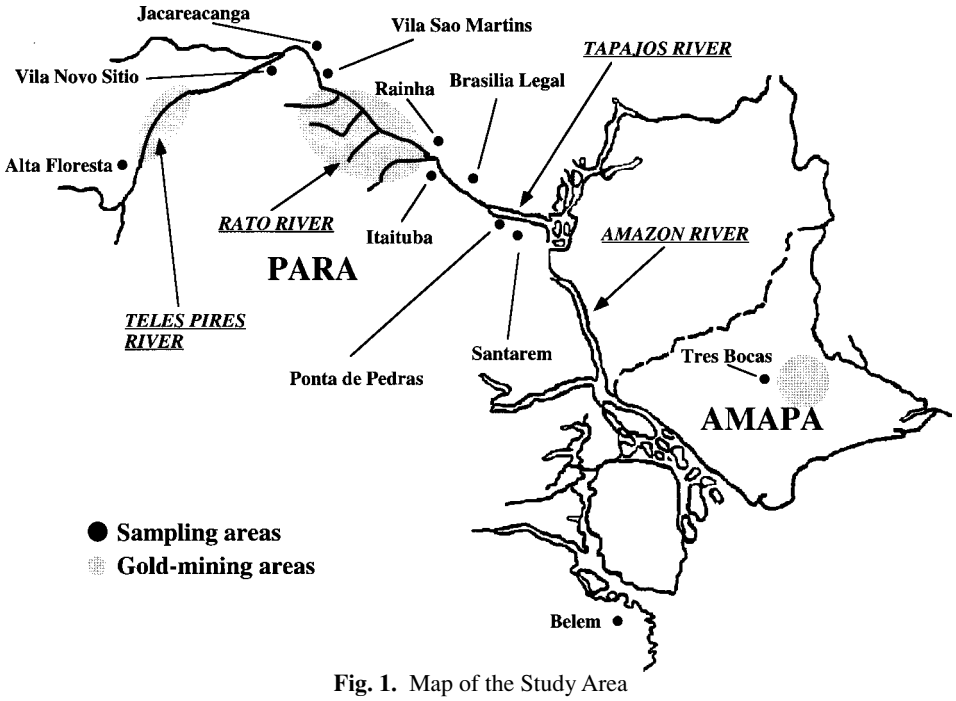

Fig. 1. Map of the Study Area

Table 1. Concentrations of Methylmercury (Me–Hg) and Total Mercury in Hair Samples from of Inhabitants of the Tapajos River Basin

		Me–Hg (ng/mg)		Total Hg (ng/mg)		Me–Hg/Total Hg
Origin (sampling date)	*n*	Mean ± S.D.	(min.–max.)	Mean ± SD	(min.–max.)	(%)
Gold-shop workers (1989)	4	2.1 ± 31.3	(0.1– 3.8)	15.4 ± 11.3	(6.8– 31.3)	13.6
Gold miners (1989)	7	1.2 ± 0.7	(0.2– 2.5)	22.2 ± 40.7	(0.5–113.1)	5.4
Former gold miners (1989)	13	1.3 ± 0.9	(0.6– 3.4)	3.4 ± 2.3	(0.8– 9.4)	38.2
Ponta de Pedras (March, 1992)	10	9.4 ± 2.5	(4.7– 12.0)	10.2 ± 2.2	(6.1– 12.6)	91.1
Brasilia Legal (March, 1992)	37	15.8 ± 10.3	(0.9– 42.6)	17.5 ± 10.3	(0.8– 42.6)	90.3
Brasilia Legal (July, 1992)	19	30.5 ± 31.5	(6.1–132.6)	35.9 ± 36.8	(7.2–151.2)	84.9
Jacarecanga (March, 1992)	48	15.2 ± 10.5	(1.1– 43.9)	16.6 ± 10.5	(1.4– 46.0)	88.4
Rainha (March, 1992)	11	15.0 ± 8.5	(1.9– 29.4)	15.8 ± 8.9	(2.4– 31.1)	94.1
Tres Bocas (July, 1992)	11	26.3 ± 13.0	(6.1– 50.3)	28.0 ± 13.3	(8.4– 53.8)	92.0
Rio de Janeiro						
Not regular fish-eaters	20			1.7 ± 0.6	(0.9– 3.1)	
Frequent fish-eaters	15			5.4 ± 3.0	(1.5– 13.0)	

It is generally recognized that the general population is primarily exposed to methylmercury through consumption of fish, and that analysis of head hair is the most appropriate method for monitoring the intake of methylmercury in persons at risk.[13,14] The concentrations of total mercury and methylmercury detected in samples of hair from gold miners, gold-shop workers and the inhabitants of various fishing villages are summarized in Table 1. Total mercury concentrations of up to 113.1 ppm were found in the samples of hair from gold miners and gold-shop workers. However, the concentrations of methylmercury were extremely low and the average levels of methylmercury relative to that of total mercury were only 5.4–13.6% in the various groups. These observations suggested a large contribution by inorganic mercury attached to the outside of these hair samples since it is known that little bodily inorganic mercury is accumulated in head hair. From these results, it is apparent that measurements only of total mercury in hair samples are not sufficient for evaluation of the human exposure to methylmercury in those areas, such as gold-mining areas, that are continuously being contaminated with

Table 2. Concentrations of Methylmercury (Me–Hg) and Total Mercury in Fish Collected at Various Locations in the Tapajos River Basin

Origin	Type of fish	Weight (g)	Me–Hg (ng/mg)	Total-Hg (ng/mg)	Me–Hg/ Total-Hg (%)
Rato River	Peixe-cachorro	100	1.60	1.60	100.0
	Mandube	290	0.54	0.53	101.9
	Mandube	515	0.24	0.28	85.7
	Aruana	6000	0.83	0.95	84.4
	Traira	330	0.60	0.56	107.1
Teles Pires River	Piranha	400	0.29	0.29	100.0
(near Alta Floresta)	Piranha	22000	3.29	3.82	86.1
	Piranha	40000	2.44	2.85	85.6
	Daurada	2700	0.57	0.60	95.0
	Jau	23000	0.58	0.61	95.1
	Jau	24000	0.70	0.75	93.3
	Jau	25000	0.82	1.03	79.6
	Jau	32000	0.36	0.39	92.3
Tapajos River	Tucunare	320	0.35	0.36	97.2
(near Jacareacanga)	Surubim	215	1.00	1.01	99.0
	Surubim	430	1.06	1.03	102.9
	Pintado	1600	0.62	0.62	100.0
	Pintado	270	0.33	0.33	100.0
	Aruana	1250	0.41	0.41	100.0
	Traira	340	0.53	0.53	100.0
	Traira	360	0.92	0.97	94.8
Tapajos River	Pescada	200	0.52	0.56	92.9
(near Itaituba)	Apapa	450	0.46	0.54	85.2
	Filhote	4000	0.95	1.00	95.0
Tapajos River	Acara	160	0.15	0.17	88.2
(near Brasilia Legal)	Tucunare	570	1.12	1.16	96.6
	Pescada	910	0.36	0.41	87.8
	Apapa	1040	0.52	0.60	86.7
	Pacu	1430	0.09	0.10	90.0
Tapajos River	Apapa	390	0.37	0.39	94.9
(near Santarem)	Pirarucu	20000	0.07	0.08	87.5

inorganic mercury. However, the concentrations of total mercury and methylmercury in samples of hair from people living in fishing villages revealed abnormally high total mercury levels, which ranged from 10.2 to 35.9 ppm on average, with large variations. At the village of Ponta de Pedras, which is far downstream on the Tapajos River, we detected relatively low levels of mercury in hair, but higher levels were detected in hair from people who lived in the other fishing villages, indicating greater exposure to mercury in the upstream region of the Tapajos River. The highest level of total mercury, 151.2 ppm, was found in hair from people who lived in Brasilia Legal, which is located about 100 km downstream from Itaituba, the main gold-trading center in the Tapajos River basin. It should be noted that levels of methylmercury in human hair were very close to the levels of total mercury in almost all samples collected from the inhabitants of fishing villages, as shown in Table 1. Moreover, the levels of methylmercury in samples from males were significantly higher than those from females in all villages. The

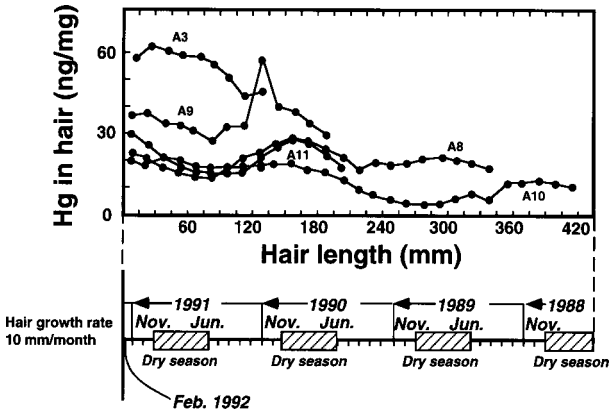

Fig. 2. Longitudinal Analysis of Concentrations of Mercury along Strands of Hair

Hair samples were obtained in February, 1992, from women with long hair who lived in Tres Bocas.

high levels of methylmercury in the hair from the inhabitants of the village of Tres Bocas village was noteworthy. These high levels might have been due to the elevated levels of methylmercury in fish in the lake that resulted from the longer retention time of methylmercury in the lake, as compared with river systems.

The results of analysis of levels of total mercury and methylmercury in fish from the Tapajos River are presented in Table 2. Total mercury levels in fish ranged from 0.08 to 3.82 ppm. Most of the fish sampled from the upper part of the river had relatively high levels of mercury that exceeded the Brazilian permitted limit of 0.5 ppm. Extremely high levels of mercury were detected in fish from the Teles Pires River near the city of Alta Floresta, in the far upstream region of the Tapajos River system, where gold-mining activities had increased until 1994. However, in far downstream regions of the Tapajos River, near Santarem, levels were lower, even in carnivorous fish. The predominant form of mercury in all fish analyzed was methylmercury, suggesting widespread and high-level environmental contamination by methylmercury in this region. It seems, from these results, that regional differences in levels of methylmercury in fish are reflected in the exposure to methylmercury of people living in these regions.

The longitudinal analysis of mercury along a strand of hair provides information about the timing of the exposure of individuals to methylmercury.[15] Hair grows at a rate of about one cm per month. Thus, it is possible to monitor exposure to methylmercury over a period of several months or years, depending on the length of a hair sample. We obtained a number of samples of long hair from women who lived in Tres Bocas and analyzed segments for total mercury after cutting the hair into short pieces (Fig. 2). In the Amazon, the dry season extends from June to November and the rainy season extends from December to May. The results in Fig. 2 indicate that the various women had been exposed to methylmercury continuously at fairly constant levels over at least the past few years at all locations, with some seasonal variations. In particular, we noted a trend towards increases in the levels of methylmercury in hair samples with time.

Concentrations of Methylmercury in Human Blood and the Correlation with Levels of Mercury in Hair

Samples of hair, blood and urine were collected from individuals in Jacareacanga, a typical fishing village, and in Alta Floresta, the main gold-trading center in Mato Grosso State. Samples of human hair and blood were also collected in two other small, isolated fishing villages, Vila Sao Martins and Vila Novo Sitio, which are located about 50 and 150 km upstream of Jacareacanga, respectively. Most of the fish consumed in these three fishing villages comes from the Teles Pires River. The concentrations of total mercury and methylmercury in the samples of human hair, blood and urine are summarized in Table 3, together with the levels of mercury in urine collected from members of the general population in Minamata, Japan, for comparison. The samples of hair and blood from inhabitants of the fishing villages contained quite high levels of mercury and, again, almost all of the mercury in these samples was in the methylated form. The amount of methylmercury was very close to 100% of the total mercury. Among 51 hair samples, seven had levels of methylmercury greater than 50 ppm, which is the minimum threshold value for methylmercury intoxication established by the World Health Organization.[16] The levels of methylmercury in hair from males were about 1.5 times higher than those in hair from females. However, the levels of mercury in the samples of blood from gold-shop workers were quite low and the level of methylmercury relative to that of total mercury was 72% on average, ranging from 20–100%. High levels of total mercury were found in urine from gold-shop workers but variations in levels were large. All of the urine samples, with one exception, contained total mercury at levels of that exceeded a level 30 ng/mg creatinine. Mild or minor adverse effects of mercury exposure are expected to occur at such levels.[17] Methylmercury was also detected in the urine samples, but the

Table 3. Concentrations of Methylmercury (Me–Hg) and Total Mercury in Samples of Hair, Blood and Urine from Inhabitants of the Tapajos River Basin

			Me–Hg (ng/mg)		Total Hg (ng/mg)		Me–Hg/Total Hg
Origin	Sample	*n*	Mean ± S.D.	(min.–max.)	Mean ± S.D.	(min.–max.)	(%)
Jacareacanga	Hair (ppm)	27	24.1 ± 17.8	(2.7– 69.0)	24.6 ± 17.8	(2.9– 69.0)	96.0
	Blood (ppb)	19	90.0 ± 76.6	(11.9–274.9)	90.4 ± 71.5	(12.3–261.3)	97.2
Vila Sao Martins	Hair (ppm)	14	36.4 ± 17.1	(7.6– 65.8)	37.4 ± 17.1	(8.6– 68.2)	96.4
	Blood (ppb)	8	149.2 ± 52.5	(89.0–226.7)	149.8 ± 49.5	(90.3–226.6)	99.0
Vila Novo Sitio	Hair (ppm)	10	27.3 ± 12.1	(1.6– 39.2)	28.8 ± 13.0	(1.6– 43.3)	95.7
	Blood (ppb)	7	131.9 ± 84.2	(11.3–257.7)	130.7 ± 78.4	(11.4–244.3)	98.8
Alta Floresta	Hair (ppm)	4	4.2 ± 2.3	(2.3– 7.6)	5.2 ± 2.5	(2.5– 8.6)	86.0
	Blood (ppb)	25	9.0 ± 6.7	(1.7– 23.3)	12.2 ± 8.2	(2.3– 39.7)	72.2
	Urine (ng/mg Cr*)	41	0.4 ± 0.2	(0.0– 1.1)	165.7 ± 96.5	(20.8–449.5)	0.3
Minamata (Japan)	Urine (ng/mg Cr*)	27	0.7 ± 0.8	(0.0– 3.4)	22.5 ± 14.9	(2.6– 80.3)	3.9

*Cr, Creatinine

levels were extremely low. The level in urine of methylmercury relative to that of total mercury ranged from 0.04 to 1.7%, with an average value of 0.4%. This value was much lower than that in urine samples from people living in Minamata, as a result of the greater contamination of urine by inorganic mercury. These results were subjected to correlation analysis. As expected from the analysis, levels of total mercury or methylmercury in hair were strongly correlated with those in blood (correlation coefficient $r = 0.937$). From the regression equation, an overall average ratio of 1 : 242 was obtained for the ratio of the total mercury levels in hair to that in blood. This figure is in good agreement with the value of 250, which was established in a study of various populations exposed to methylmercury at fairly constant levels.[16] We found no apparent correlation between total mercury levels in blood and urine, but the level of inorganic mercury in urine was significantly correlated with the level of inorganic mercury in blood (correlation coefficient $r = 0.720$). There are several previous reports on the relationship between levels of mercury in urine and blood in populations exposed to mercury vapor, but the results vary considerably.[18–20] In the present study, we also found a slightly positive but statistically insignificant correlation between the levels of total mercury in urine and blood. These results are reasonable in view of the fact that, on average, 72% of the total mercury in the blood samples tested was in the form of methylmercury and was not associated with exposure to mercury vapor. Therefore, levels of individual species of mercury in blood should be measured if we are to characterize the relationship between levels of mercury in urine and blood in populations exposed to mercury vapor, in particular at low levels. In fact, we have found a significant positive correlation between levels of inorganic mercury in blood and urine when confounding effects of methylmercury are eliminated, a result that suggests the possibility of predicting levels of inorganic mercury accumulated in blood, as a consequence of exposure to metallic mercury, from levels of mercury in urine. The scattered distribution of the ratios of levels of mercury in the blood and urine, observed in the samples from the gold-shop workers, is not surprising given that the levels of exposure to mercury vapor vary considerably, depending on the frequency of re-burning operations in the gold shop and, moreover, that the urine samples were collected one day after the collection of blood samples.

In conclusion, in fishing villages of the Tapajos River basin, the inhabitants have been exposed to methylmercury at abnormally high levels as a result of the consumption of local fish. Confounding exposure to inorganic mercury, including mercury vapor in the air, seems to have been very limited. The people living near the main gold-mining areas have been exposed to more methylmercury than those living far downstream from the gold-mining sites. The concentrations of methylmercury in the hair of some inhabitants are above the threshold value defined for methylmercury intoxication. Therefore, immediate plans should be ready to prevent further increases in the environmental accumulation of methylmercury, which is derived from the inorganic mercury that is used in mining for gold.

REFERENCES

1) Mallas J., Benedicto N., *Ambio*, **15**, 248–249 (1986).
2) Clearly D., "Anatomy of the Amazon Gold Rush," MacMillan, Oxford, p. 245, 1990.
3) Jernelov A., Ramel C., *Ambio*, **23**, 166 (1994).
4) Pfeiffer W.C., Lacerda L.D., *Environ. Technol. Lett.*, **9**, 325–330 (1988).
5) Lacerda L.D., Pfeiffer W.C., Ott A.T., Silveira E.G., *Biotropica*, **21**, 91–93 (1988).
6) Akagi H., Mortimer D.C., Miller D.R., *Bull. Environ. Contam. Toxicol.*, **23**, 372–376 (1979).
7) Imura N., Sukegawa E., Pan S.K., Nagao K., Kim J.Y., Kwan T., Ukita T., *Science*, **172**, 1248–1249 (1971).
8) Clarkson T.W., *Crit. Rev. Clin. Lab. Sci.*, **34**, 369–403 (1997).
9) Akagi H., Nishimura H., "Advances in Mercury Toxicology," Suzuki T., Imura N., Clarkson T.W., (eds.), Prenum Press, New York, pp. 53–76, 1990.
10) Akagi H., Malm O., Branches F.J.P., Kinjo Y., Kashima Y., Guimaraes J.R.D., Oliveira R.B., Haraguchi K., Pfeiffer W.C., Kato H., *Water Air Soil Pollut.*, **80**, 85–94 (1995).
11) Akagi H., Malm O., Kinjo Y., Harada M., Branches F.J.P., Pfeiffer W.C., Kato H., *Total Environ.*, **175**, 85–95 (1995).
12) Matsuo N., Suzuki T., Akagi H., *Arch. Environ. Health*, **44**, 298–303 (1989).
13) Suzuki T., Hongo T., Yoshinaga J., Imai H., Nakagawa M., Matsuo N., Akagi H., *Arch. Environ. Health*, **48**, 221–229 (1993).
14) Abe T., Ohtsuka R., Hongo T., Suzuki T., Tohyama C., Nakano A., Akagi H., Akimichi T., *Arch. Environ. Health*, **50**, 367–373 (1995).
15) Suzuki T., Hongo T., Yamamoto R., *J. Appl. Toxicol.*, **4**, 101–104 (1984).
16) WHO, "IPCS, Environmental Health Criteria 101: Methylmercury", pp. 76–99, 1990.
17) WHO, "IPCS, Environmental Health Criteria 118: Inorganic mercury", pp. 84–114, 1991.
18) Smith R.J., Vorwald A.J., Patil L.S., Mooney T.F.J., *Am. Lnd. Hyg. Assoc. J.*, **31**, 687–700 (1970).
19) Lindstedt G., Gottberg I., Homgren B., Jonsson T., Karsson G., *Scand. J. Work Environ. Health*, **5**, 59–69 (1979).
20) Roels H., Abderladim S., Ceulemans E., Lauwerys R., *Ann. Occup. Hyg.*, **31**, 135–145 (1987).