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Levels of Mercury in Scalp Hair of Fishermen and Their Families from Camara de Lobos–Madeira (Portugal): A Preliminary Study

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Mercury is probably one of the most investigated natural and anthropogenic contaminants, especially in aquatic environments. It occurs in nature in a wide variety of physical and chemical states and the fate and behavior of the different forms are related mainly to their physico-chemical and partition properties. Among the inorganic forms, elemental mercury (Hg°) presents a marked tendency to reach the air as vapor, and in terrestrial systems to bioaccumulate in plant biomass (Gaggi et al. 1991; Bacci et al. 1994), whereas other inorganic compounds (e.g., mercury sulphide) are characterized by low mobility and bioavailability. These last compounds once in water (and especially at the water-sediment interface) can undergo a process of methylation. Methylmercury (MeHg) is readily bioaccumulated by aquatic organisms and leads to a phenomenon of enrichment from lower to higher trophic level.

The extensive literature on MeHg and human health shows that the consumption of fish and/or shellfish is the main source of exposure, the contribution from air and water being negligible and mainly related to inorganic forms. A human population consuming large amounts of seafood with high MeHg levels can be considered at risk when consumption exceeds a certain amount. This level has been set by the WHO (1976; 1990) and other agencies, at 300 µg/week of total mercury (totHg) of which there should be no more than 200 µg as MeHg.

The nervous system is the principal target of the effects of MeHg in humans. The most common functions affected are the sensory, visual and auditory functions, together with those of the cerebellum, which is concerned with coordination. As far as prenatal exposure is concerned, the developing central nervous system of humans and animals has been found to be more sensitive to damage from MeHg than the adult nervous system (Marsh et al. 1980).

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The degree of hazard for consumers of large amounts of seafood is totally dependent on time of exposure, and the general health of the exposed groups. A long-term daily ingestion of 200-500 µg of MeHg can lead to a blood concentration of approximately 200-500 µg/L and a hair concentration of 50-125 µg/g (Renzoni 1992). Humans with hair levels of over 50 µg/g may be considered at risk (Skerfving 1974).

The aim of this preliminary study was to obtain such information on a group of fishermen and their families living in the fishing village of Camara de Lobos (Madeira, Portugal). This population is potentially at risk because of the high frequency of seafood in their normal diet.

MATERIALS AND METHODS

Although some human subjects were reluctant to give hair for analysis, 80 samples of hair were obtained from 22 women and 58 men, mostly fishermen, fishermen's wives and children. As variations have been observed in the concentration of mercury in hair from the different parts of the head (Airey 1983), hair was sampled from the occipital region by cutting them with scissors (1-2 cm of hair close to the skin). To avoid accidental contamination each sample was stored in a plastic tube with a hermetic cap until analysis.

The diet of the group included three or more meals of fish per week. Fishing was constant throughout the year and the consumption of seafood by the studied population did not undergo significant variations.The population can therefore be regarded as chronically exposed.

For the evaluation of TotHg, hair samples (0.05-0.1 g) were decomposed with concentrated HNO_3 (2.5 mL) under pressure (3000 kPa) in teflon vessels at 130 °C, according to the method of Stoeppler and Backhaus (1978). TotHg was detected by atomic absorption spectrophotometry (Perkin-Elmer 2280), after direct reduction to Hg° with an aqueous solution of $SnCl_2$ (10%) $NH_2OH \cdot HCl$ (6%) NaCl (6%) and H_2SO_4 (1 N) and air current stripping.

For the evaluation of MeHg, homogeneous samples (0.1-0.2 g) were hydrolyzed with the addition of aqueous solution of KBr (4 M) and H_2SO_4 (2 M): MeHg was extracted into toluol, purified by the addition of cysteine solution, re-extracted into toluol and then measured by gas chromatography, according to Horvat et al. (1990). A Carlo Erba Vega 6000 gas chromatograph with ECD and a 1m x 2mm (i.d.) borosilicate glass-column packed with 5% Carbowax 20 M on 100/120 Supelcoport was used. The carrier gas was argon-methane 95/5%; flows 90 and 40 (as scavenger) mL/min; injector, oven and detector temperatures were 190, 180 and 280 °C, respectively.

Homogeneous sub-samples were used to measure water content (24 hr, 105 °C) and the results of the analysis were then normalized on a dry weight basis. Pure reference standard solutions for calibration, recovery evaluation, and quantification were used. The method of additions before pretreatment was used for the calibration procedure. The instrumental detection limits were 10 and 20 ng/g for TotHg and MeHg, respectively. The precision of TotHg and MeHg analytical methods, evaluated on 6 homogeneous replicates of the same sample, was 9.2 and 13.6%, respectively, as coefficient of variation. The accuracy was tested by analyzing standard reference materials from the U.S. National Bureau of Standards and by intercalibration exercises organized by the International Atomic Energy Agency. The values given for the standard reference materials was within the interval of our mean±standard deviation.

RESULTS AND DISCUSSION

TotHg and MeHg determinations were made in all 80 samples collected (Table 1). Comparison of the results (Fig. 1) indicates that most of the metal was in the organic form. The intercept of the equation obtained (-0.876 µg/g) is not significant and its value appears to be due to analytical error. The slope of the curve in Figure 1 indicates that for an increase of one µg/g of TotHg, the level of MeHg increases by almost the same amount. From our observations it appears that hair sample analysis was a good method for evaluating MeHg levels in humans and, then, a good method of risk evaluation. The ratio MeHg/TotHg is, on average, about 0.9 for both men and women.

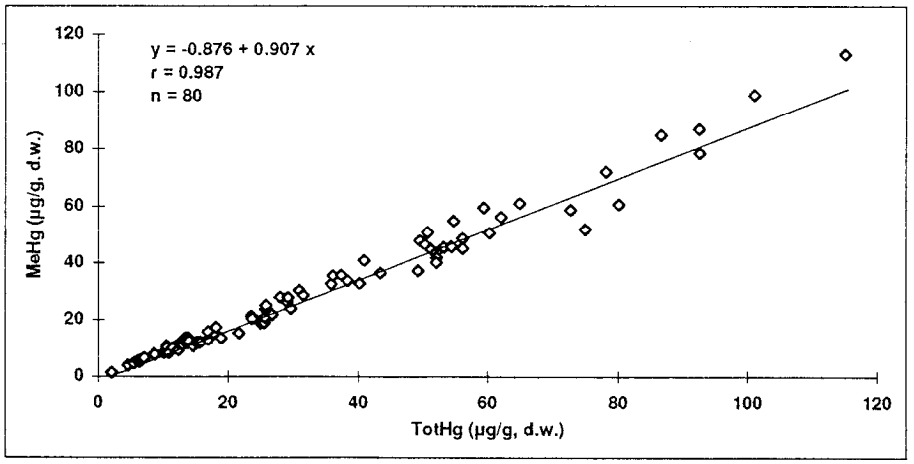

Figure 1. Correlation between methylmercury (MeHg) and total mercury (TotHg) in hair samples of fishermen and their families from Madeira, Portugal.

Table 1. Total Hg and MeHg concentrations (µg/g) in hair samples of fishermen and their families from the Island of Madeira, Portugal; $\bar{x}$ = mean, S.D. = standard deviation, n = number of samples.

		$\bar{x}$	S.D.	range	n
TotHg	men	39.76	30.31	3.70 -146	58
	women	16.22	14.31	2.50-56.1	22
MeHg	men	36.25	24.74	3.94-113	58
	women	15.50	10.88	5.2-45.0	22

Table 2. Total Hg concentrations (µg/g) in hair samples of fishermen and their wives; $\bar{x}$ = mean, S.D. = standard deviation, n = number of samples.

		$\bar{x}$	S.D.	range	n
Tuscan Archipelago (northern Tyrrhenian Sea, Italy) (Renzoni 1992)	men	36.38	21.62	6.44 - 62.8	39
	women	6.81	2.34	2.07-9.74	7
Eolian Archipelago (southern Tyrrhenian Sea, Italy) (Renzoni 1992)	men	5.64	3.73	0.99 - 13.3	37
	women	-	-	-	-
Maldives Islands (Renzoni 1992)	men	10.69	1.81	5.61-19.4	26
	women	7.56	1.99	4.43-12.7	40
Seychelles (Matthews 1982)	men	26.29	14.51	5.50 - 68.2	40
	women	12.25	6.60	4.08 - 38.5	36
Vada (northern Tyrrhenian Sea, Italy) (Bacci et al. 1976)	men	27.11	29.30	4.00 - 109	27
	women	7.52	8.79	0.75 - 23.2	6

The average concentration of TotHg in hair of Maderian fishermen and their families was higher than the other populations consuming large amount of seafood reported in Table 2; this is evidently due to the higher content of methylmercury in the most common fish (*Aphanopus carbo* Lowe) caught and eaten by the Madeiran population (Renzoni, in preparation). Comparing the values for TotHg reported in Tables 1

and 2, the higher content of mercury in male hair with regards to women agrees with the available data in the literature (Renzoni 1992). The large difference may be related to the frequency of seafood meals. Information obtained during sampling confirmed that Madeiran fishermen eat seafood while at sea fishing and at home, whereas wives eat seafood in the evening and only occasionally at lunch time.

Various reports suggest that the risk of neurological damage to adults with a high consumption of seafood is only 5% when hair MeHg exceeds 50 µg/g. From our results, levels of over 50 µg/g of MeHg have been found in 36% of fishermen. Maximum values in men is 113 µg/g, with several intermediate values between 50 µg/g and the highest value. The highest concentration detected in women is 45 µg/g. The risk for adults, especially men, seems therefore real.

Recent studies on children exposed to MeHg *in utero* have shown that a significant increase in neurological problems (in comparison to controls) may occur in children with a maternal maximum monthly hair mercury level of 10 µg/g (Marsh et al. 1980; Berlin 1986). Another recent study in New Zealand on children aged 4 (Kjellström et al. 1986) showed that "the children of mothers with pregnancy mean hair mercury levels above 6 µg/g have deficiencies in their development, as tested by the Denver Developmental Screening Test, more than twice as common as in a matched control group with lower hair mercury levels". Comparable results were obtained in another population of children at age 6 (Kjellström et al. 1989) similarly exposed *in utero* to mercury. Although the minimum level of total mercury found in the 22 women tested in Madeira was 5.2 µg/g, 87% of them showed concentrations of MeHg higher than 6 µg/g and, therefore, any children they may bear will be at risk.

An additional study (Renzoni et al., in preparation) has therefore been undertaken to evaluate:

1. mercury levels in blood and hair samples of a large number of women from the Madeira fishing village during the first months of pregnancy (early stages of nervous system development in the fetus);
2. the incidence of psychomotor retardation and neurological signs, particularly visual and brainstem auditory evoked potentials, electrocardiographic R-R interval variability and postural balance test, in children of the same fishing village (age 6-7).

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