STUDY ON TOTAL AND METHYL MERCURY LEVELS IN HUMAN SCALP HAIRS OF LYING-IN WOMEN AND NEWBORNS BY NAA AND OTHER TECHNIQUES

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Abstract

Since the Second Research Co-ordinating Meeting in Malaysia, 24-28 August 1992, our research group has completed the analysis of total and methylmercury in scalp hair samples of 1179 fishermen living at a typical Hg-polluted region in Northeast China and of 27 lying-in women and their newborns in a Beijing hospital by INAA, GC(EC) and other techniques. The longitudinal Hg patterns of the lying-in women show a gradually decreasing tendency during the pregnancy period. Further, the hair Hg contents of the newborn babies are generally above or close to those of their mothers, confirming the mechanism that the methylmercury, an organic species of Hg with high toxicity, is readily able to penetrate the placental barrier and accumulate in the fetus. Thus, the mercury exposure has occurred at the early stage of pregnancy.

1. INTRODUCTION

Mercury is a toxic element to humans. Its specific toxicity lies in the methylated species, *i.e.* methylmercury (MeHg), which is readily able to enter human body via the food chain [1,2] and accumulate through various biological membranes. Recent clinical observations have indicated that the MeHg affects the early stages of fetal development and the later mental ability of children whose mothers were exposed during pregnancy to 3-4 times the tolerable weekly intake set by WHO and FAO [3].

Mercury pollution is still an environmental problem to be solved in some regions of China [4]. In order to study the level of Hg pollution in the Second Songhuajiang River System, a typical Hg-polluted area, we collected hair samples of 1179 fishermen there and determined the total mercury and methylmercury in them by NAA, GC(EC) and other techniques in the framework of the IAEA Co-ordinated Research Project on "Assessment of environmental exposure to mercury in selected human populations as studied by nuclear and other techniques".

It is known that during the prenatal process, the methylated species of Hg is easily transferred from mothers to fetus through placental tissue. In order to study the hereditary toxicity of Hg, the correlation between Hg contents in scalp hairs of lying-in women and

their newborn babies has been investigated in this work. Also, the variation of Hg contents in the hair of pregnant women during their pregnancy was studied by NAA and by synchronous radiation-based XRF.

2. EXPERIMENTAL METHOD

2.1. Sampling

We followed the sampling procedure outlined in the United Nations Environment Programme (UNEP) on "The determination of methylmercury, total mercury and total selenium in human hair", Reference Methods for Marine Pollution Studies No. 46 (draft), October 1987, prepared in co-operation with WHO and IAEA [5]. Head hair samples from 1179 people from the population living at the Second Songhuajiang River System were collected. In addition, 27 sets of hair samples from mothers and their newborn babies were taken, either immediately at or within a few days after delivery in the Beijing Zhong-Guan-Chen Hospital. At the time of hair collection, information, such as, name, age, sex, occupation and nutritional habits was also obtained. All hair samples were taken from the occipital area and as close as possible to the scalp. The length of the samples was at least 10 cm long and about 10 g of hair were obtained from the lying-in women whose hair was without waving or dying in the latest 10 months. Due to limited amount of hair available, the weights of the hair samples from the babies ranged from 0.5 to 1.0 g. The hair washing procedure recommended by IAEA was followed to remove dirty materials from the hair samples, *i.e.* washing by acetone - 3 times bi-distilled water-acetone. The hair was then left to dry in a clean desiccator for later analysis.

2.2. Analysis of total mercury

Neutron activation analysis (NAA), mercurymetry (MM) and atomic fluorescence spectrometry (AFS) were used to determine the total mercury in the hair samples for this work. Here, only the methodology of NAA will be briefly described; detailed descriptions for the determination of total mercury using MM and AFS are given in Refs. 6 and 7.

Hg has two stable nuclides, ^{196}Hg and ^{203}Hg. Both of them are able to be readily determined by NAA. We count the two peaks of 68.8 keV and 77.3 keV from ^{197}Hg produced by ^{196}Hg (n,γ) reaction in a heavy water reactor with neutron flux of 4 - 5 x 10^{13} n·cm^{-2}·sec^{-1} from a 30 min irradiation. The counting was done after 3 d decay using a planar high-pure Ge detector with a better energy resolution in low energy region than normal HPGe detectors. For additional details, please refer to our previous working paper [8].

2.3. Analysis of methylmercury

Our procedure for MeHg analysis of hairs is shown in Figure 1. The detailed experimental conditions are given in our previous report [9]. Two sets of gas chromatography devices are available. One is a Varian Model Vista 6000; the other is Shimadzu Model GC-9A with a C-92A data processor. The chromatographic column is a 10% PEG-20M (ϕ=3.2 mm x 1.1 m). For carrier, 60-80 mesh Chromosorb W is used. The electron capture detector is a 10 mCi source of ^{63}Ni.

2.4. Hg profile analysis of hair

Two independent methods were used to investigate the longitudinal variation of Hg contents from the bottom to the top of hair samples, mainly for pregnant women. One technique was "sectional neutron activation analysis", which means that the long hair sample was cut into 1 cm long portions. The other technique that was used was synchronous radiation-based X-ray fluorescence spectrometry (SRXRF). A Beijing Electron-Positron Collider (BEPC) is available with 2.8 GeV energy and 150 maximum currency intensity. A two-dimensional scanning unit with a size-adjustable slit from 10 x 10 μm to 1 x 1 mm was used. The 9.987 keV L_α line of Hg was employed to calculate the Hg content. One typical SRXRF spectrum of hair is shown in Figure 2.

3. RESULTS AND DISCUSSION

3.1. Total and MeHg contents of 1179 hair samples of fishermen

Our results indicate that most of the hair samples of 1179 fishermen contain low mercury, below 5 mg/kg. Only 18 samples have high Hg contents (see Table I). The No. 5 sample contains the highest Hg content, up to 113 mg/kg. The MeHg contents are also included in Table I. It can be seen that the methylation rates vary from 10% to almost 100%, but the MeHg percentages of most hair samples exceed 50 %. As a comparison, we also determined total and MeHg in hair samples from several tens of workers at a Hg mineral district located in southwest China, which show low MeHg compositions [10]. This fact indicates a different pathway of mercury absorption between fishermen and workers.

3.2. Correlation of hair Hg contents of lying-in women with those of their newborns

The mercury concentrations in hair samples from 27 lying-in women and their newborns determined by INAA are listed in Table II. Figure 3 shows the correlation between them. It can be seen that the hair Hg contents of 22 babies are close to or above those of their respective mothers. Only 5 babies have a slightly lower Hg content. The statistical treatment states that the average Hg value for all babies is 0.66 ± 0.31 mg/kg, while 0.59 ± 0.25 mg/kg for mothers. In addition, there is no significant difference between them ($p>0.05$). Lauwerys, *et al.* [11] reported higher Hg contents of newborns' blood (umbilical cork) than those of mothers' blood (intravenous) by 10-15 % in a non-Hg-polluted area in Belgium. Similar results were also given by Pitkin, *et al.* [12]. Thus, our results agree with those of blood samples. At Hg-polluted districts, the hair Hg contents of babies are likely to be even higher.

3.3. Longitudinal variations of Hg contents in hairs of pregnant women

It is known that the growth rate of human head hair is about 300-400 μm/d, *i.e.* 1 cm per month. Thus, a strand of a 10 cm long hair can cover the time of the whole pregnancy period. INAA was used to determine the Hg contents of hair taken from lying-in women, in portions of 1 cm each. Table III lists the longitudinal variations of hair Hg contents of 3 representative lying-in women obtained by INAA. Our results show that the hair Hg contents of the lying-in women decrease with the increase of pregnancy time. The regression analysis of 3 specimen indicates a significant correlation between them (r_1 =

-0.966, τ_2 = -0.900 and τ_3 = - 0.871, $P<0.001$) (see Fig. 4). Similarly, MeHg also exhibits the same variation tendency (Fig. 5). The SRXRF results are shown in Figure 6.

Our results confirm the mechanism that Hg is gradually transferred from mothers to their fetus during pregnancy period. The animal test claims that the Hg species play a great role in its transfer. The inorganic Hg is basically unlikely to go through placental tissue, while the MeHg, an ester-loving material, readily penetrates it to enter the fetus. It is likely that the fetus is easily able to absorb ester-like materials from the placenta [13]. As the early stage of pregnancy is an important period in which infants develop their cerebrum and nervous system, Hg pollution is more dangerous to fetus than to mothers.

4. PLANS FOR FUTURE WORK

In the final period of this research programme, we plan to:

(1) Improve the available analytical methods by interlaboratory comparison exercise and establish two new methods based only on INAA for MeHg analysis of hair.

(2) Collect additional hair samples from populations living in Hg-polluted regions, especially mother-baby paired hair samples.

(3) Complete the analysis of total and methylmercury contents in all the samples collected during this CRP activity.

(4) Submit a final report and prepare publications of the summarized results of this work.

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TABLE I. TOTAL AND METHYMERCURY LEVELS IN HAIR SAMPLES TKAEN FROM SELECTED FISHERMEN LIVING AT THE SECOND SONG-HUA-JIANG RIVER SYSTEM (mg/kg)

Sample No.	T-Hg (NAA)	T-Hg (MM)	T-Hg (AFS)	MeHg (as Hg) (GC-EC)
1	9.90 ± 0.30	11.9	--	7.92
2	9.82 ± 0.30	10.7	--	8.68
3	11.3 ± 0.3	12.0	--	6.96
4	9.70 ± 0.36	12.0	--	7.22
5	113 ± 10	121	101	60.9
6	10.2 ± 0.2	11.3	10.9	5.35
7	7.86 ± 0.34	10.0	--	6.84
8	9.11 ± 0.27	10.4	--	6.10
9	10.5 ± 0.3	11.6	--	1.50
10	16.7 ± 0.2	15.6	14.9	13.7
11	14.5 ± 0.2	16.8	--	1.90
12	8.45 ± 0.34	13.0	--	4.64
13	16.2 ± 0.1	15.0	--	7.64
14	8.64 ± 0.34	10.1	9.9	3.96
15	13.2 ± 0.1	13.3	--	13.2
16	9.87 ± 0.20	12.7	--	4.57
17	34.6 ± 0.1	54.1	35.5	--
18	13.0 ± 0.1	20.4	15.5	--

TABLE II. Hg CONTENTS OF 27 LYING-IN WOMEN AND THEIR NEWBORNS DETERMINED BY INAA (mg/kg)

Sample No.	Mother	Baby
1	0.83	1.16
2	0.52	0.76
3	0.55	0.66
4	0.42	0.59
5	0.36	0.40
6	0.30	0.39
7	0.92	1.35
8	0.67	0.65
9	0.46	0.45
10	1.01	1.10
11	0.79	0.66
12	0.61	0.82
13	0.76	1.23
14	1.12	0.98
15	0.60	0.46
16	0.40	0.48
17	0.47	0.47
18	0.29	0.42
19	0.95	1.07
20	0.22	0.33
21	0.44	0.43
22	0.41	0.30
23	0.71	0.82
24	0.23	0.29
25	0.80	0.64
26	0.72	0.73
27	0.28	0.30
MEAN ± SD	0.59 ± 0.25	0.66 ± 0.31

TABLE III. VARIATION OF Hg CONTENTS OF LYING-IN WOMEN DURING PREGNANCY (mg/kg)

pregnancy time (month)	Sample No.		
	1	2	3
1	1.17	0.75	1.48
2	1.16	0.64	1.45
3	1.03	0.62	1.03
4	0.90	0.54	0.92
5	0.84	0.49	0.88
6	0.86	0.40	0.75
7	0.61	0.47	0.61
8	0.59	0.47	0.63
9	0.63	0.42	0.69
10(at delivery)	0.55	0.38	0.74

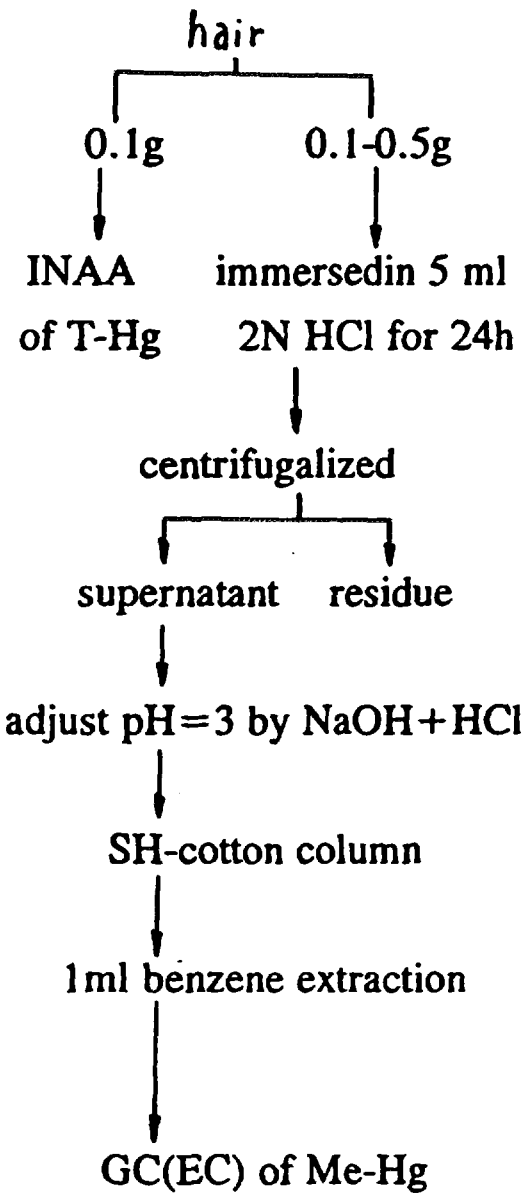

Figure 1. **Experimental procedure for MeHg analysis of hair samples.**

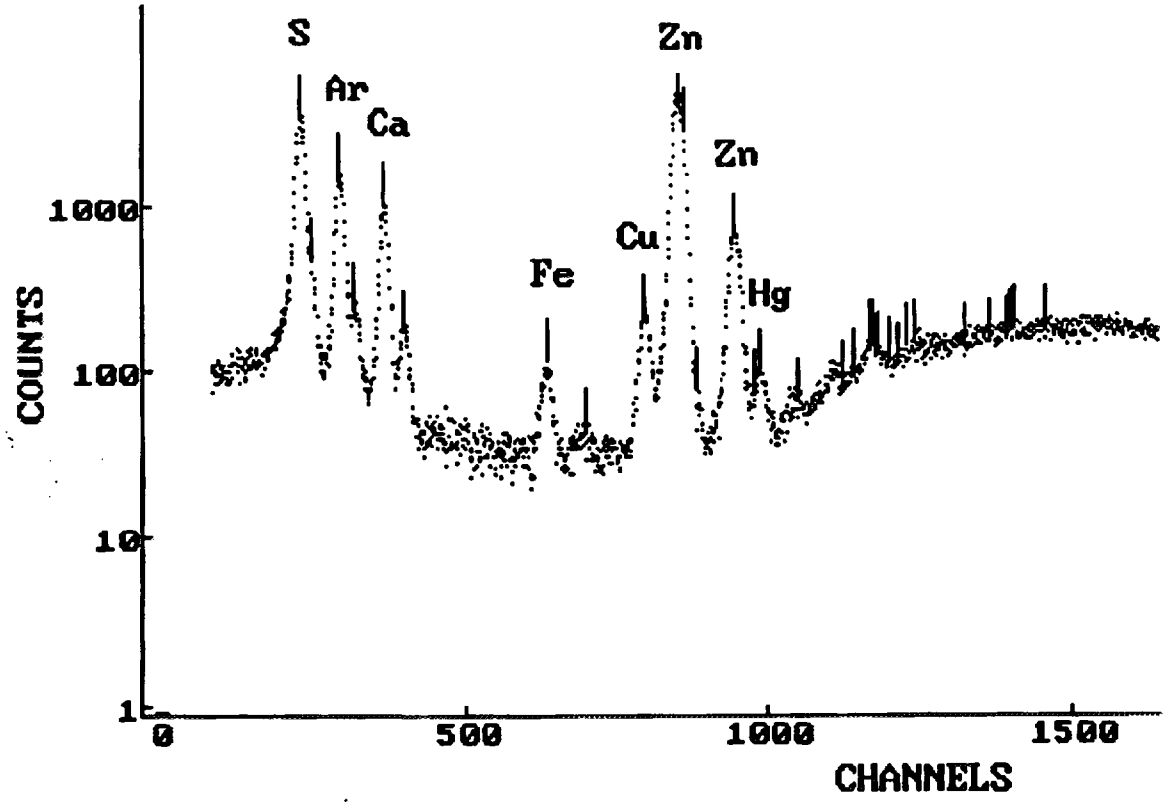

Figure 2. The SRXRF spectrum of a lying-in woman's hair.

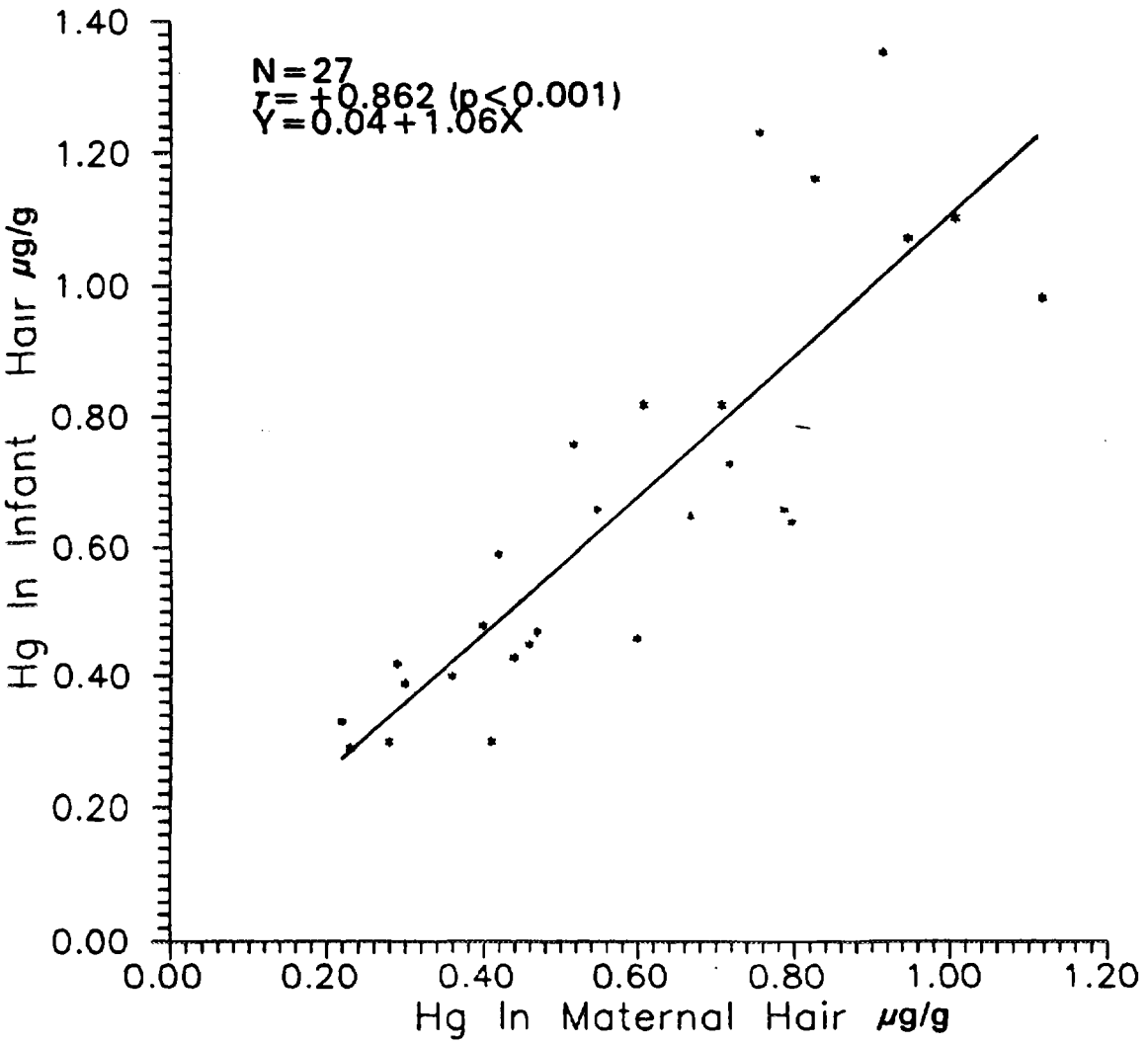

Figure 3. **Correlation between hair Hg contents of lying-in women and their newborns.**

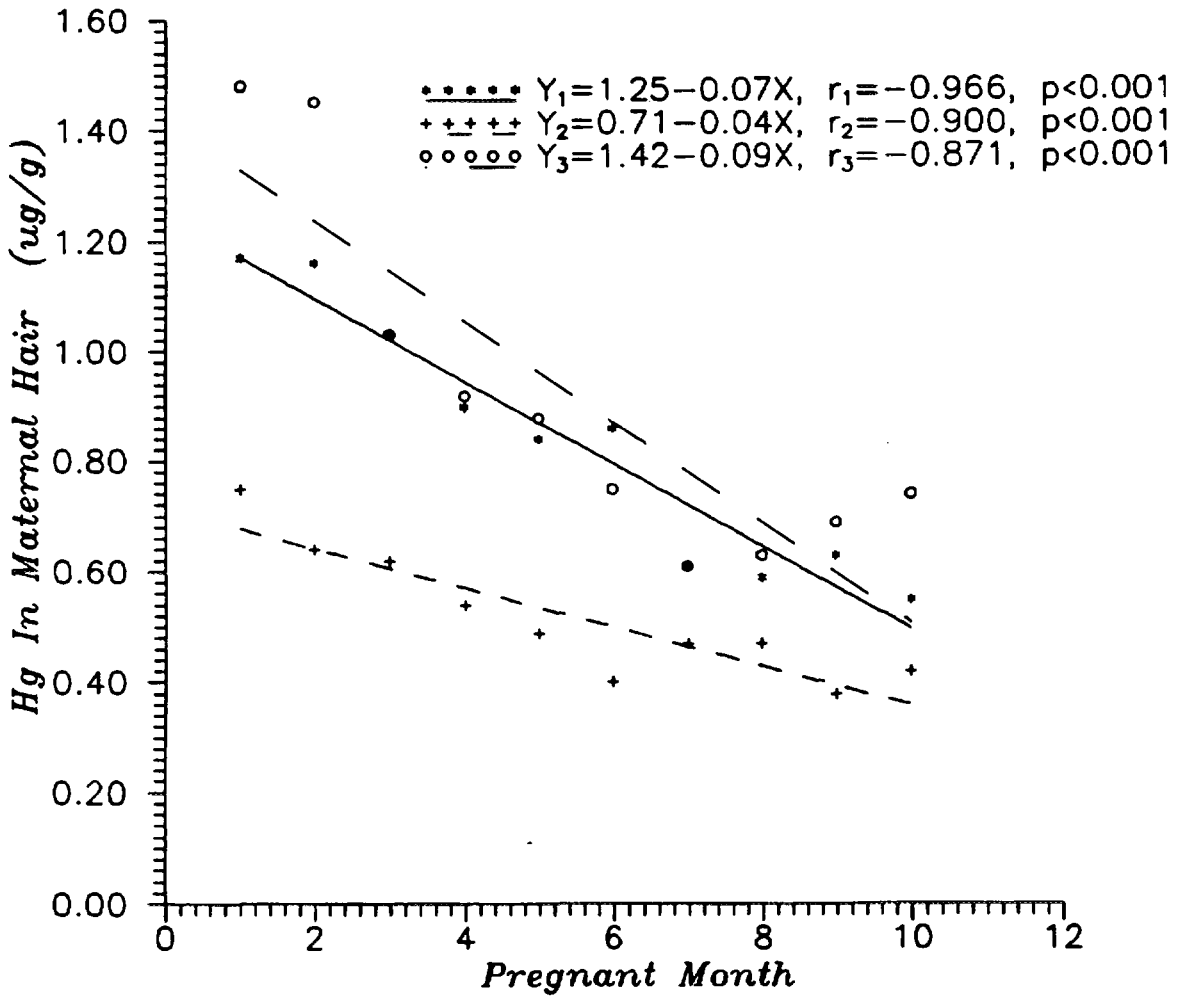

Figure 4. **Variations of hair Hg contents of three pregnant women with time.**

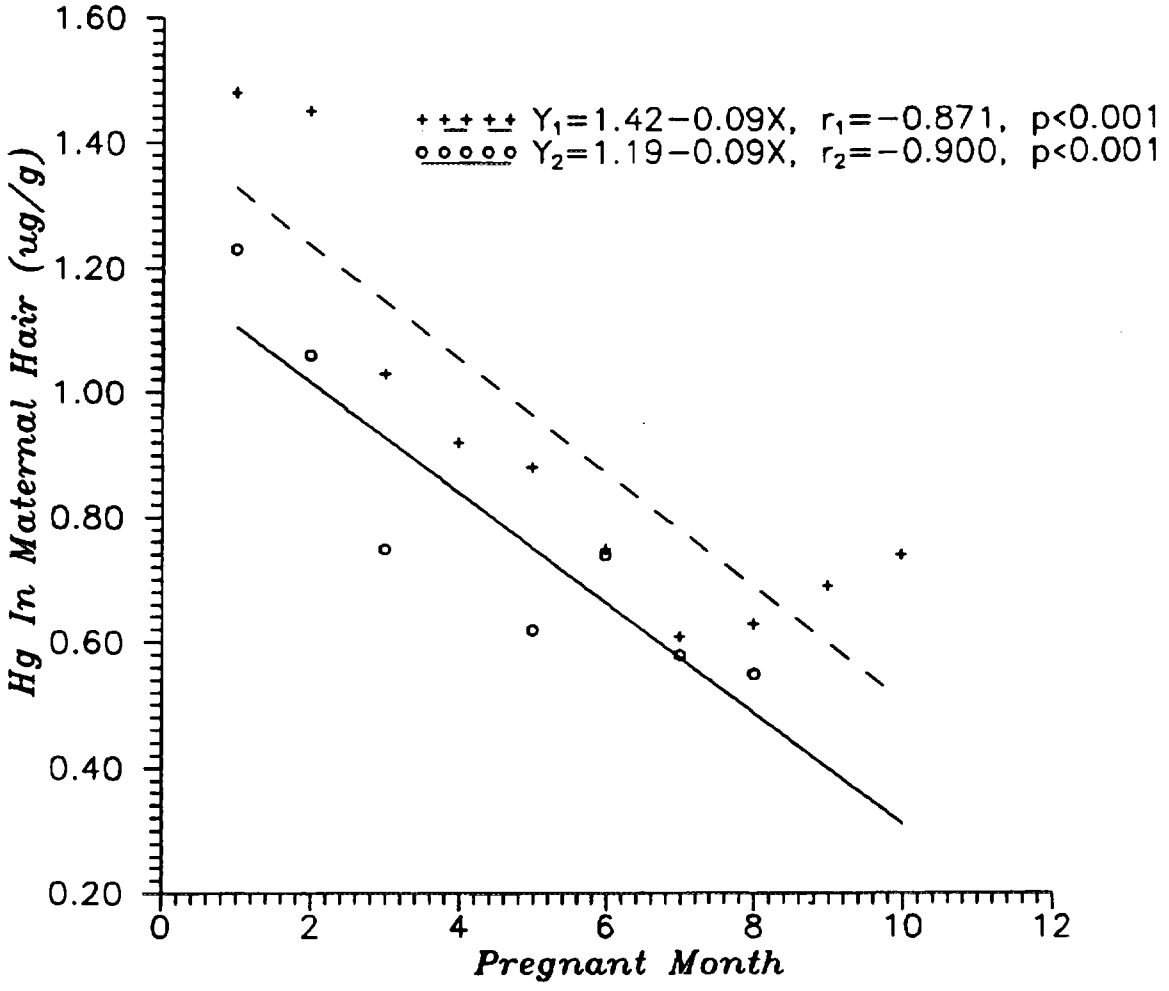

Figure 5. **The changes of Hg and MeHg contents in one pregnant women's hair during her pregnancy determined by sectional INAA and GC(EC).**

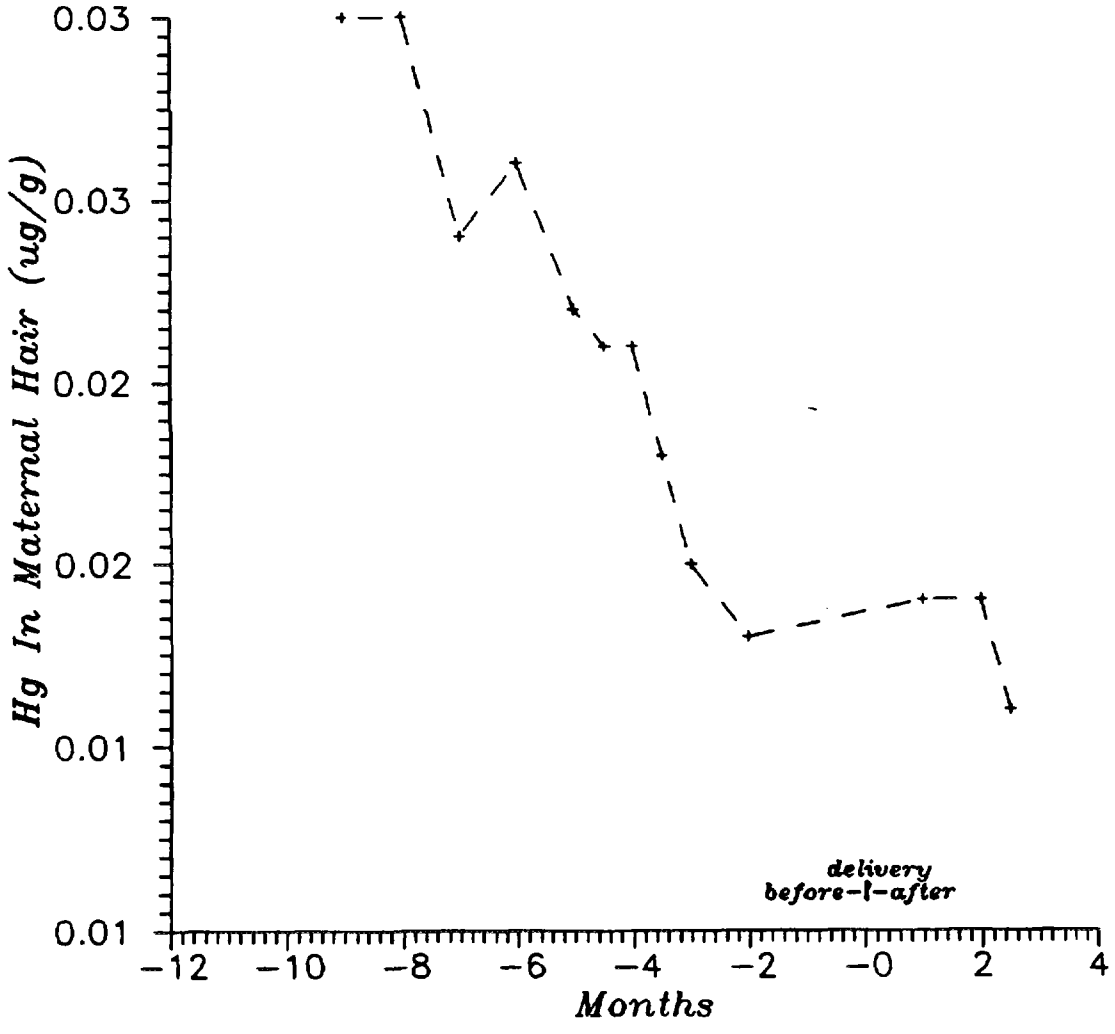

Figure 6. **The variation of Hg contents in one woman's hair during and immediately following pregnancy as determined by SRXRF.**