Mercury Exposure of Workers and Health Problems Related with Small-scale Gold Panning and Extraction

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Summary: This study was conducted to investigate mercury (Hg) exposure and health problems related to small-scale gold panning and extraction (GPE) in the northern Pakistan. Urine and blood samples of occupational and non-occupational persons were analyzed for total Hg, while blood's fractions including red blood cells and plasma were analyzed for total Hg and its inorganic and organic species. The concentrations of Hg in urine and blood samples were significantly (P<0.01) higher in occupational persons as compared to non-occupational and exceeded the permissible limits set by World Health Organization (WHO) and United State Environmental Protection Agency (US-EPA). Furthermore, the data indicated that numerous health problems were present in occupational persons involved in GPE.

Keywords: Amalgamation; gold panning; gold extraction; health problems; mercury; occupational exposures, blood.

Introduction

Being a highly mobile heavy metal, mercury (Hg) is considered as a global environmental pollutant and leads to contamination of atmosphere, lithosphere and hydrosphere. Hg contamination mostly occurs from anthropogenic sources including agrochemicals, urban discharges, mining, coal and biofuel combustion, battery and fluorescent lamp production, cement production and industrial waste discharges [1,2]. Moreover, gold mining and extraction (GME) process is also well known for indiscriminate use of Hg which contaminates the environment with Hg. During 1980s, the GME boom using Hg for amalgamation has dispersed about 2000 t of Hg only in the Amazon [3]. Similarly, in many countries of the world such as America, Africa, Brazil, China, Columbia, Mongolia, Russia, Peru, Spain, Philippines etc, Hg is used in extraction of gold in both large and small scale gold mining [1]. It has been estimated that for the recovery of 1 kg of gold, approximately 1.32 kg of Hg is lost to the environment, out of which 40% Hg (in liquid form) is released to river, lake, stream or sediments, while 60% Hg (vapors) is released directly to the atmosphere [4]. Nevertheless, according to Straaten [5] (2000) about 70-80% Hg is directly released to the atmosphere. The inorganic Hg (inorg-Hg) species released to environment, undergoes several reactions to form organic Hg (org-Hg) such as methyl Hg, which accumulates in the food chain [6-8]. Methyl Hg is recognized as highly toxic fraction of Hg and both occupational and non-occupational people are exposed to it through the consumption of Hg contaminated food. The major fraction of Hg directly enters into air as vapors of inorg-Hg and occupational people mostly expose to it through inhalation and direct skin contact. It means that consumption of contaminated water and food items [9], inhalation, ingestion of soil and dermal contact are the major human exposure pathways [10].

Characteristically, Hg exposure has potential risks to the human health [11, 12] and generally cause a wide range diseases such as neurological abnormalities (cerebeller dysfunction and altered mental status), bronchiolitis and pneumonitis, pulmonary edema, proliferation of air way lining cells, neuropsychiatric symptoms, occurrence of tremors and weight and appetite loss [1].

In the past, numerous studies have been conducted on the health risks associated with Hg exposure from GME; nevertheless, no published data is available from Pakistan regarding Hg contamination of the environment and human health risks. In northern Pakistan, including Gilgit and Chitral, Hg is generally used during small-scale gold panning and extraction (GPE) along Gilgit, Hunza and Indus rivers. The aim of this study was to investigate the level of Hg exposure and its health risks among the workers involved in GPE. For this purpose, urine and blood samples were collected from occupational persons and non-occupational

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persons (control group) and analyzed for total Hg and its organic and inorganic species. A questionnaire survey was also conducted to collect information regarding demography, socio-economic and dietary status and health problems of the persons involved in the study.

Results and Discussion

Hg Concentrations in Urine

Table-1 summarizes the mean concentrations of total Hg in the samples of urine for both occupational and non-occupational persons including adults and children. Total Hg concentrations ranged from 41.7-129.9 µg/L in occupational adult (18-50 years) with mean concentration of 57.1 µg/L in male and 68.5 µg/L in female. The data indicated that nearly 98% urine samples have exceeded the WHO [13] limits (50 µg/L) set for urine. The data also suggested that total Hg concentration was significantly (P<0.01) higher in occupational persons as compared to non-occupational persons. Among the occupational persons, the female workers have shown higher concentrations of total Hg as compared to male workers. Total Hg concentrations ranged from 2.5-30.6 µg/L in urine samples of occupational children (8-15 years) with mean concentration of 8.3 µg/L in male and 6.5 µg/L in female children. These concentrations were significantly (P<0.01) higher in occupational than non-occupational children.

Table-1: Mean concentrations (µg/L) of total Hg in the samples of urine, RBC and plasma (n=50).

Individuals	Gender	Urine	RBC	Plasma
Occupational group				
Adults	Male	57.1 (24.2)	38.0 (23.4)	74.6 (63.1)
	Female	68.5 (28.7)	47.4 (35.0)	81.3 (25.6)
Children	Male	24.5 (8.3)	37.8 (7.6)	28.4 (5.2)
	Female	13.6 (6.5)	26.7 (23.2)	19.1 (3.8)
Non-occupational group				
Adults	Male	2.8 (1.2)	1.2 (1.1)	3.9 (1.2)
	Female	2.6 (1.5)	2.9 (1.6)	2.4 (0.9)
Children	Male	1.7 (1.2)	2.1 (1.7)	2.2 (1.4)
	Female	2.9 (1.3)	3.4 (2.2)	2.1 (1.3)

Numbers in parentheses indicate standard deviation

Hg Concentrations in Blood

The mean concentrations of total Hg in the samples of RBCs and plasma for both occupational and non-occupational persons including adults and children are given in Table-1. The mean concentrations of total Hg in the RBC samples of male and female children were 37.8 µg/L and 28.4 µg/L, respectively, while in plasma samples were 26.7 µg/L and 19.1 µg/L, respectively. The data indicated that total Hg concentration was significantly (P<0.01) higher in occupational persons as compared to non-occupational. In occupational adult persons, total Hg concentrations ranged from 16.2-85.7 µg/L in the samples of RBCs, while ranged from 9.8-167.6 µg/L in the samples of plasma. The mean concentrations of total Hg in the RBCs and plasma samples of male adults were 38.0 µg/L and 74.6 µg/L, respectively, while for female adults were 47.4 µg/L and 81.3 µg/L, respectively. The data of RBCs and plasma samples revealed that Hg concentration was higher in female workers compared to male. In the blood samples, Hg concentrations increased with the increase of age of the persons involved in GPE occupation. Similarly, total Hg concentrations ranged from 8.5-50.3 µg/L in of RBC samples and from 5.8-41.7 µg/L in plasma samples of occupational children.

The mean concentrations of inorg-Hg in RBCs and plasma samples of both groups considered for this study are given in Table-2. The inorg-Hg concentrations ranged from 2.5-63.3 µg/L in the samples of RBCs, with the mean concentration of 19.1 µg/L in occupational male adults and 21.6 µg/L in occupational female adults. In the plasma samples, this concentration ranged from 8.5-163.5 µg/L, with the mean concentrations of 76.8 µg/L in the occupational male adults and 75.4 µg/L in occupational female adults. In occupational children, inorg-Hg concentrations ranged from 0.8-24.6 µg/L in the samples of RBCs and from 1.2-30.2 µg/L in the samples of plasma, which were significantly (P<0.01) higher in occupational children as compared to non-occupational children. The mean concentrations of inorg-Hg for children are given in Table-2. In occupational adults, org-Hg concentrations ranged from 5.0-35.2 µg/L in RBC-samples, while ranged from 3.9-22.3 µg/L in plasma samples. Similarly, in occupational children, org-Hg concentrations ranged from 1.7-28.5 µg/L in the samples of RBCs and from 0.7-12.6 µg/L in the samples of plasma. The data clearly indicate that inorg-Hg concentrations were significantly (P<0.01) higher in occupational persons as compared to non-occupational persons.

Table-2: Mean concentrations (µg/L) of Hg species in RBC and plasma samples (n=45).

Individuals	Gender	RBC		Plasma	
		Inorg-Hg	Org-Hg	Inorg-Hg	Org-Hg
Occupational group					
Adults	Male	19.1 (19.8)	19.8 (8.4)	76.8 (62.9)	3.8 (3.3)
	Female	21.6 (12.7)	26.2 (13.9)	75.4 (27.5)	6.6 (4.5)
Children	Male	17.5 (3.7)	21.2 (6.3)	21.2 (3.2)	8.1 (2.6)
	Female	13.0 (8.3)	14.2 (9.4)	14.7 (2.6)	4.3 (1.5)
Non-occupational group					
Adults	Male	0.9 (0.4)	1.1 (0.7)	1.5 (0.5)	2.8 (0.9)
	Female	1.5 (0.6)	1.8 (1.2)	1.6 (0.8)	1.2 (0.5)
Children	Male	1.0 (0.6)	1.6 (0.5)	1.9 (1.2)	0.9 (0.3)
	Female	1.1 (0.5)	2.1 (1.3)	1.3 (0.9)	1.0 (0.7)

Numbers in parentheses indicate standard deviation

Mercury and its species concentrations in the blood of the occupational and non-occupational persons are shown in Fig. 1. The data indicate that the concentrations of Hg and its types were significantly (*P*<0.01) higher in workers as compared to non-workers. The mean concentrations of total Hg in male and female workers were 114 µg/L and 120 µg/L, respectively, while org-Hg concentrations were 24.5 µg/L and 33.2 µg/L, respectively. In case of inorg-Hg concentrations, there was no significant difference between male and female workers.

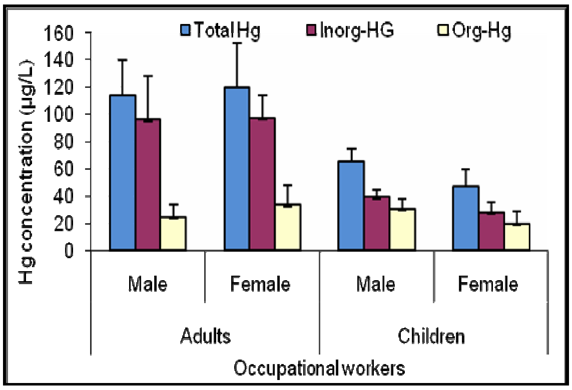

Fig. 1: Total, inorg-Hg and Org-Hg concentrations (µg/L) in the blood; error bars indicate standard deviation.

Linear Regression and Hg Species Ratio

Linear regression analyses were performed to identify the relationships between the total Hg and inorg-Hg species concentrations in RBCs, plasma and urine samples (Fig. 2). The relationship between total Hg and org-Hg species was very weak (R^2 ranged from 0.194-0.562), while strong relationship was observed between total Hg and Inorg-Hg species (R^2 ranged from 0.910-0.999). Furthermore, inorg-Hg and org-Hg ratios ranged from 0.52-0.96 for the samples of RBCs and ranged from 0.8-20.2 for the samples of plasma (data not shown).

Health Problems

A summary of the prevailing health problems in the occupational and non-occupational persons is given Table-3. A total of 80 persons were interviewed and examined, out of them 23-67% individuals (both male and females workers) complained of tiredness and headache, 30-56% kidney diseases, 20-45% cognitive impairment, 38-48% skin rashes, 28-31% sensory problems, 57-67% chest pain, 9-16% tremor, 7-12% loss of memory, 22-31% cough and sputum, 2-9% night blindness, 21-28% palpitation, 8-10% limb extremity pains, 4-6% hyporeflexia and hyperrefkexia, 12-16% disturbance in smell and taste and 7-8% neurasthenia. Similarly, slow growth was observed in 67-71% children of the occupational families.

Table-3: Major health problems (%) in the GPE occupational group (*n*=180)

Health Problems	Occupational		Non-occupational	
	Male	Female	Male	Female
Kidney diseases	56	30	2	1
Skin rashes	38	48	NR[a]	NR
Tiredness and headache	67	23	5	7
Cognitive impairment	45	20	NR	NR
Sensory problems	31	28	3	2
Chest pain	53	67	7	4
Tremor	16	9	NR	NR
Slow growth in Children	67	71	5	11
Loss of memory	12	7	1	NR
Cough and sputum	31	22	7	13
Palpitation	21	28	2	4
Limb extremity pains	10	8	1	2
Hyporeflexia and hyperrefkexia	6	4	NR	NR
Disturbance in smell and taste	16	12	NR	NR
Night blindness	9	2	1	1
Neurasthenia	7	8	NR	NR

[a] not reported

To authors' knowledge, this is the first study on investigation of Hg and its speciation in the samples of blood, RBCs and plasma fractions, and urine of the GPE workers and related health problems in Pakistan. During gold extraction process, a large amount of Hg released to environment particularly, to atmosphere during amalgamation and roasting of amalgamated gold. The determination of Hg in urine samples is considered to be the method of choice to evaluate a long-term exposure to inorg-Hg species [1]. In this study, the concentrations of total Hg in urine samples have revealed high health risks, as it was exceeding human biological monitoring value (20 µg/L) set by the German Commission on Human Biological Monitoring [14]. Total Hg concentrations were very high in urine samples of those workers, whose were involved in amalgamation and amalgam roasting processes, and the highest urinary Hg concentration was detected in a person who has been adopted this profession far last 25 years. These findings are consistent with the previous research [5]. However, urinary total Hg concentrations were lower than those reported by Li et al. [15] in the exposed workers of Hg mines in Guizhou, China. In the study areas, the GPE workers are spending nomadic life and are living in huts on the banks of rivers. They had no proper ventilation system for pushing out the fumes of Hg produced during amalgam roasting and the whole family spent much of the time in sitting around the fireplace to get warm during winter and also used it for cooking purposes. This traditional practice is very dangerous and nearly all the family members were frequently exposed to Hg vapors. This study clearly shows the high exposure risks in the workers involved in Hg amalgamation and roasting process. It is well noticed during the present study that the correlation between the total Hg concentrations and inorg-Hg species concentrations was very high as compared to that of the org-Hg concentrations (Fig. 2). Furthermore, no correlation was found between smoking habits and Hg concentrations in urine samples. As mentioned earlier, Hg in urine is a better indicator for exposure to inorg-Hg. However, different other kinds of samples including blood, milk and hair specimens have also been used by various researchers to investigate the human exposure to organic and inorganic Hg [16].

It is necessary to determine both inorg-Hg and org-Hg species in both RBCs and plasma because humans are usually exposed to both Hg species simultaneously. The Hg speciation is providing direct and accurate information regarding uptake sources including inhalation, skin contacts and dietary Hg intake. The findings of this study indicated that total Hg concentrations in RBCs and plasma were significantly (P<0.01) higher in occupational persons as compared to that of non-occupational persons and exceeded the corresponding Hg concentration (5.8 µg/L) in blood [17]. Similarly, the inorg-Hg contents were significantly higher (P<0.01) in occupational persons than non-occupational persons, indicating the direct and frequent exposure of the workers to inorg-Hg (vapors). Inorg-Hg concentrations were higher in plasma samples as compared to RBC samples. In addition, org-Hg concentrations were higher in the samples of RBCs than the samples of plasma (Table-2). These observations are consistent with the findings of Halbach et al. [16]. Previously, numerous studies have been conducted on interaction of inorg-Hg and org-Hg species in blood and kinetics of Hg in human's RBCs [16, 18], and suggested that there is intracellular redistribution and extrusion of Hg and stoichiometric replacement of inorg-Hg by org-Hg. In this study, the relationships between the total Hg concentrations and inorg-Hg species concentrations for both RBCs and plasma were strong (Fig. 2) as compared to total Hg concentrations and org-Hg species concentrations. Furthermore, difference in the ratios for inorg-Hg and org-Hg species was less for RBCs than plasma samples. These findings are inconsistent with those reported by Halbach et al. [16] in the RBCs and plasma samples collected from amalgam patients.

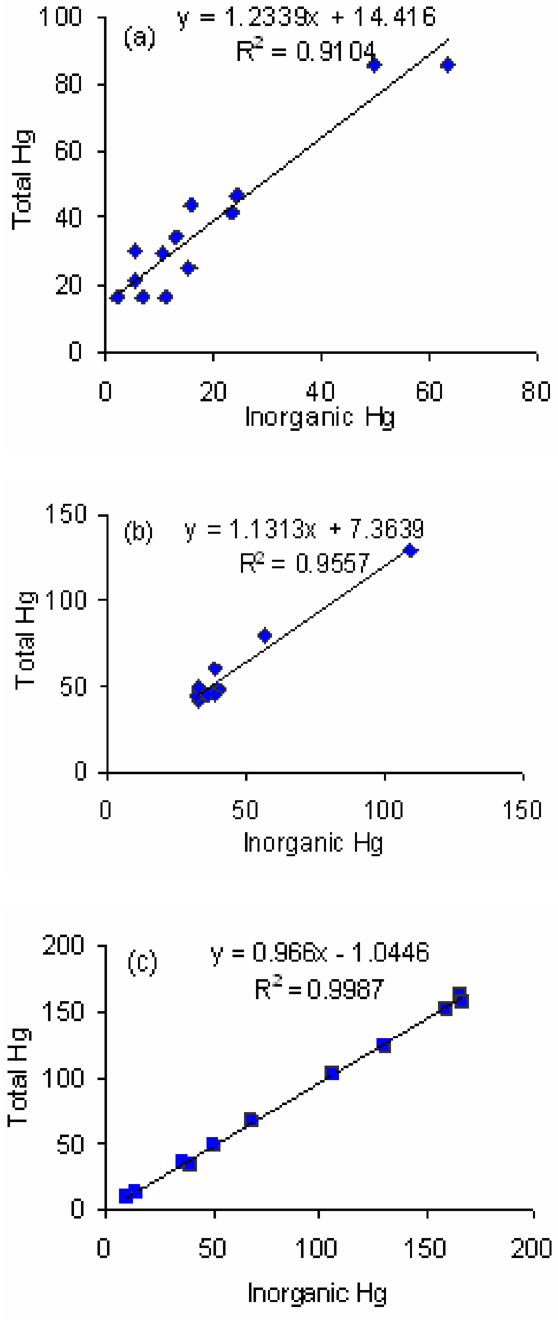

Fig. 2: Linear regression relationships between total and inorg-Hg concentrations; (a) RBC, (b) plasma and (c) urine samples.

In the present study, Hg concentrations detected in the urine samples collected from non-occupational group indicated that though the concentration was not exceeded the WHO limit but still their environment may be contaminated with Hg, as they belong to urban area. Similarly, the minor fractions of inorg-Hg and org-Hg species concentrations in their blood samples also indicated that their food or/and drinking water may be contaminated with Hg. The higher concentration of org-Hg species was detected in blood samples of those persons who on average ingested 2-3 times fish in a week as compared to those who ingested 2-3 times in a month. Passos et al. [19] have also reported a positive relation between fish consumption and inorg-Hg in both blood and urine which may result from absorption of inorg-Hg from fish or from demethylation of methyl-Hg.

As mentioned earlier, inhalation is the major exposure pathway of inorg-Hg emitting from GPE processes. The high amount of inhaled inorg-Hg vapors are absorbed through alveoli member and reached to lungs [1], which may have caused various health problems in occupational group as mentioned earlier (Table-3). According to Mountinbo et al. [20] the inhaled-Hg can cause capillary damage, pulmonary edema, tremors, weight and appetite loss and neuropsychiatric diseases. In this study, almost all investigated health problems were restricted to occupational group because of high Hg exposure. These subjective and objective symptoms indicated that the health problems were higher in occupational group than non-occupational group. Similar health problems were also reported in the previous literature [4]. This study further suggests that the Hg level in urine, blood and health problems were closely related with the age and duration of this occupied job.

Experimental

Study Area Description

The study area is located in Gilgilt, northern Pakistan, as shown in Fig. 3. Gilgit has an area of 38021 km^2 and has great potentials of glaciers, water, wildlife, various minerals and other natural resources. In the study area, miners were local people and belong to the same population and their lifestyle, habits and other social behaviors were also the same. The GPE areas are located along the banks of Gilgit, Hunza and Indus rivers. The human population for this study was divided into two groups; occupational people (involved in small-scale GPE) and control people (not involved in GPE) but can be exposed to org-Hg through food chain sources. Different sampling sites were selected including Shimshal and Jutal from River Hunza, Ishkumen, Gupis, Gulmiti, Khari, Dainyor, and Jalalabad from River Gilgit, and Haramosh, Jaglot and Astor from River Indus (Fig. 3).

Small-Scale GPE

In the study area, the GPE activities are highest in winter (November to February) because the river flow decreases due to low melting of glaciers. From mid June to the end of August, these activities are completely stopped due to high flow in rivers. In winter when the flow of river is at low level, the gold washers collect panned concentrates from around big boulders and dry sites along the banks of rivers and river beds for gold extraction. The heavy panned concentrates are collected by traditional washing and panning methods. In amalgamation process, the Hg is added to the panned concentrates and mixed by hand without using any kind of gloves. Then they wash the concentrates using water to get amalgamated gold at the bottom of the pan. In the next step, the gold is recovered in their huts using Hg evaporation/roasting process. The raw gold is further refined by gold-dealers and goldsmiths in shops and refinement places. This small-scale GPE process is similar in all selected sites of the study area.

Samplings and Laboratory Analyses

Urine and blood samples were collected from both occupational and non-occupational (control) persons including male, female and children. Urine samples were collected in clean sterile polyethylene bottle treated with 10% nitric acid to avoid volatilization of Hg. After collection, urine samples were kept frozen until analysis. At the same time, venous blood samples were also collected in 10 ml disposable syringes and treated with EDTA in plastic tubes. Blood samples were centrifuged to separate red blood cells (RBCs) from plasma and stored at 4°C for analysis. Hg was determined in the samples of urine, RBCs and plasma using the method adopted by Halbach et al. [16] with some modification. Briefly, sodium tetrahydrobromate ($NaBH_4$) was used as reductant with dilute HCl and KOH for total Hg and org-Hg analysis, respectively using mercury hydride system (MHS-15) with Perkin Elmer-700 atomic absorption spectrophotometer. From the last two decades, atomic absorption spectrophotometer technique is used to determine Hg [21]. The concentration of inorg-Hg was calculated as the difference between the total and org-Hg.

For quality control, the blank and matrix spiked with Hg were used in triplicate. After every 9 samples, standard was run as unknown to check accuracy of the instrument. However, the spike recoveries for total Hg and org-Hg were 96±7% and 94±10%, respectively.

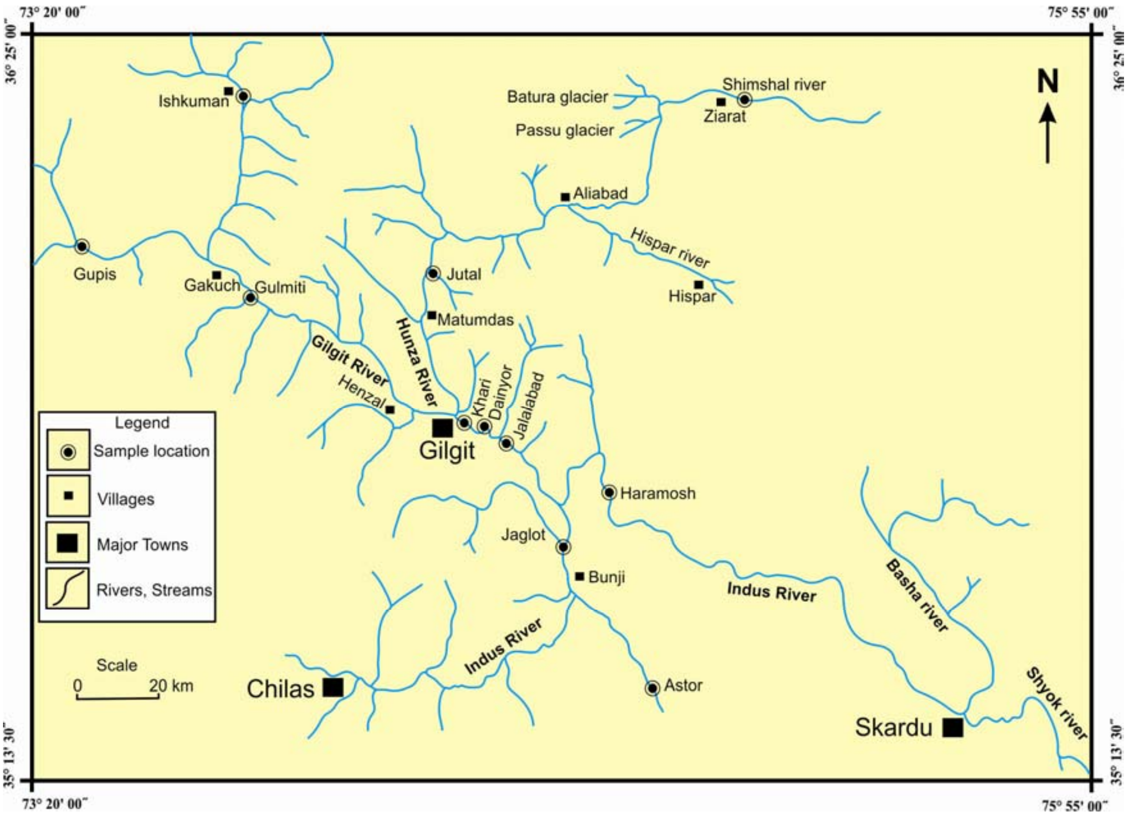

Fig. 3: Location map of study area showing sampling sites.

Questionnaire Survey

A questionnaire survey was also conducted to collect general information such as age, education, body weight, monthly income, smoking or non-smoking habits, occupational exposure and duration, type of food and fish consumption, diseases, general body problems and other health related problems. All these questions were asked from both occupational and non-occupational persons of the study area.

Statistical Analysis

All analyses were carried out in triplicate and means, standard deviation and variance (ANOVA) were determined using SPSS 11.5 package. The means were compared using Pair-Samples T-Test, with a significance level of $P<0.01$.

Conclusions

It was concluded that the small-scale GPE workers and their children were highly exposed to Hg and were, therefore, at high health risks. Total Hg in urine and inorg-Hg species in the samples of RBCs and plasma collected from occupational group indicated that the investigated Hg was contributed by Hg vapors present in air contaminated through amalgam roasting. Furthermore, the inhalation of these vapors induced numerous health problems in the workers involved GPE process. Further research work is needed to investigate environmental contamination with Hg and design an appropriate roasting process for amalgamated gold to recycle the Hg and also prevent the workers from Hg exposure.

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