UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

US/GHA/02/006- Assistance in Assessing and Reducing Mercury Pollution Emanating from Alluvial Gold Mining in Ghana - Phase II

Final Report

(December 2003)

Project Manager: Ch. BEINHOFF (PTC/PEM) - UNIDO– Vienna

CONTENT

Three sections constitute this report :

(72 p.)

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

US/GHA/02/006- Assistance in Assessing and Reducing Mercury Pollution Emanating from Alluvial Gold Mining in Ghana - Phase II

General Introduction

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I. INTRODUCTION

In the year 2000, a study of the human and environmental impacts of artisanal gold mining at a pilot site was carried out at Dumasi (Ghana, Western Region) (Rambaud et al., Babut et al., 2001). This pilot site is among others characterised by a typical process, based on solid rocks brought back to the village, then crushed, and afterwards treated by gravity concentration and amalgamation. Therefore, it appeared difficult to extrapolate the conclusions to regions where the typical process is different, in particular when based on alluvium digging. Following the presentation of the findings and conclusions in April 2001, it was thus decided to carry out a second phase study focusing on an alluvial area.

The site of Gyapa (Western Region) was selected on several criteria: year-long exploitation, accessibility, cooperation of the population. It is located about 70 km from Tarkwa, on the road to Dunkwa (figure 1). The village is built on a plateau (alt. 450m) overhanging two different river stretches. The Yaya River is flowing on the northern side of the plateau, while the Akoma Kofi River originates on the eastern side of the village, and flows to the south. Digging sites are located throughout the area, either along the Yaya River or its tributaries such as the Buosim River, or other rivers such as the Subin River (figure 2).

Gold washers dig large pits in the alluvium and/or floodplains along the river. They wash the cobbles and gravels on sluice boxes, where they collect either gold nuggets or powder concentrate gathered on hemp tissues. This concentrate is further processed by amalgamation.

This work will present the human and environmental studies in two parts (Parts I and II respectively). The objectives and general methodology being the base of the project, they will be presented succinctly in the following section. The detailed methodology, results and conclusions are developed in the specific parts.

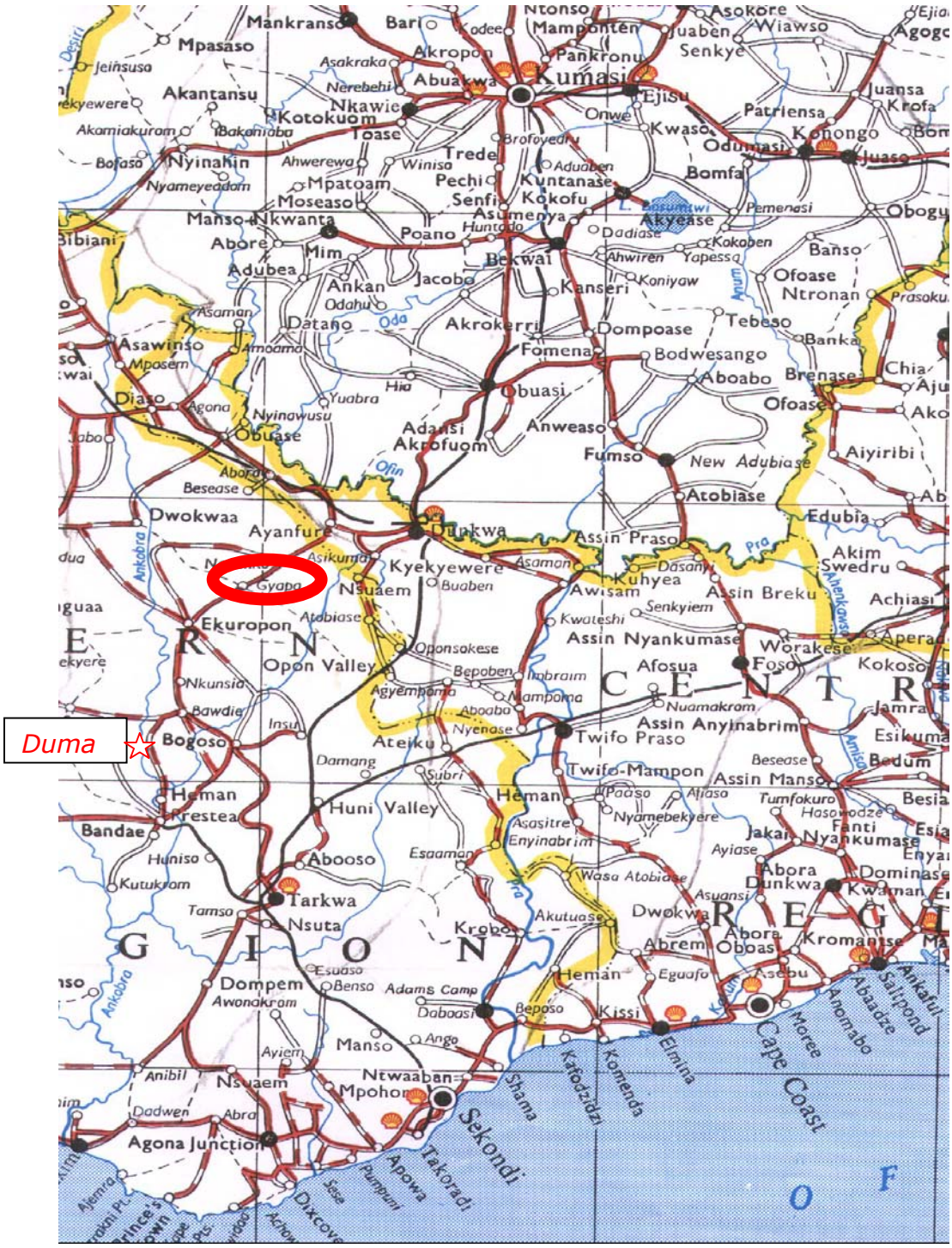

Figure 1 : SELECTED ALLUVIAL MINING AREA: JAPA SITE (phase 2):

Name: Japa or Gyapa (Taboo day = Thursday). Accessibility: Easy, located on Tarkwa to Dunkwa trunk Road. Population: more than 2000 (according to the district electoral officer). Watershed: about 300 Water bodies: One seasonal stream (Yaya) passes through the operational areas. It flows into the Mamire stream which eventually joins the Ankobra River. Operations: Typical alluvial operations with sluice box for concentration and the amalgamation process for gold extraction Japa is a known artisanal mining area, with operations dating back to pre-regularisation period (1989). Japa has most of the desirable characteristics that we are looking for. Although the operations go down considerably during the dry season, most of the operators are said to come from the town and its surrounding villages and can be reached when needed

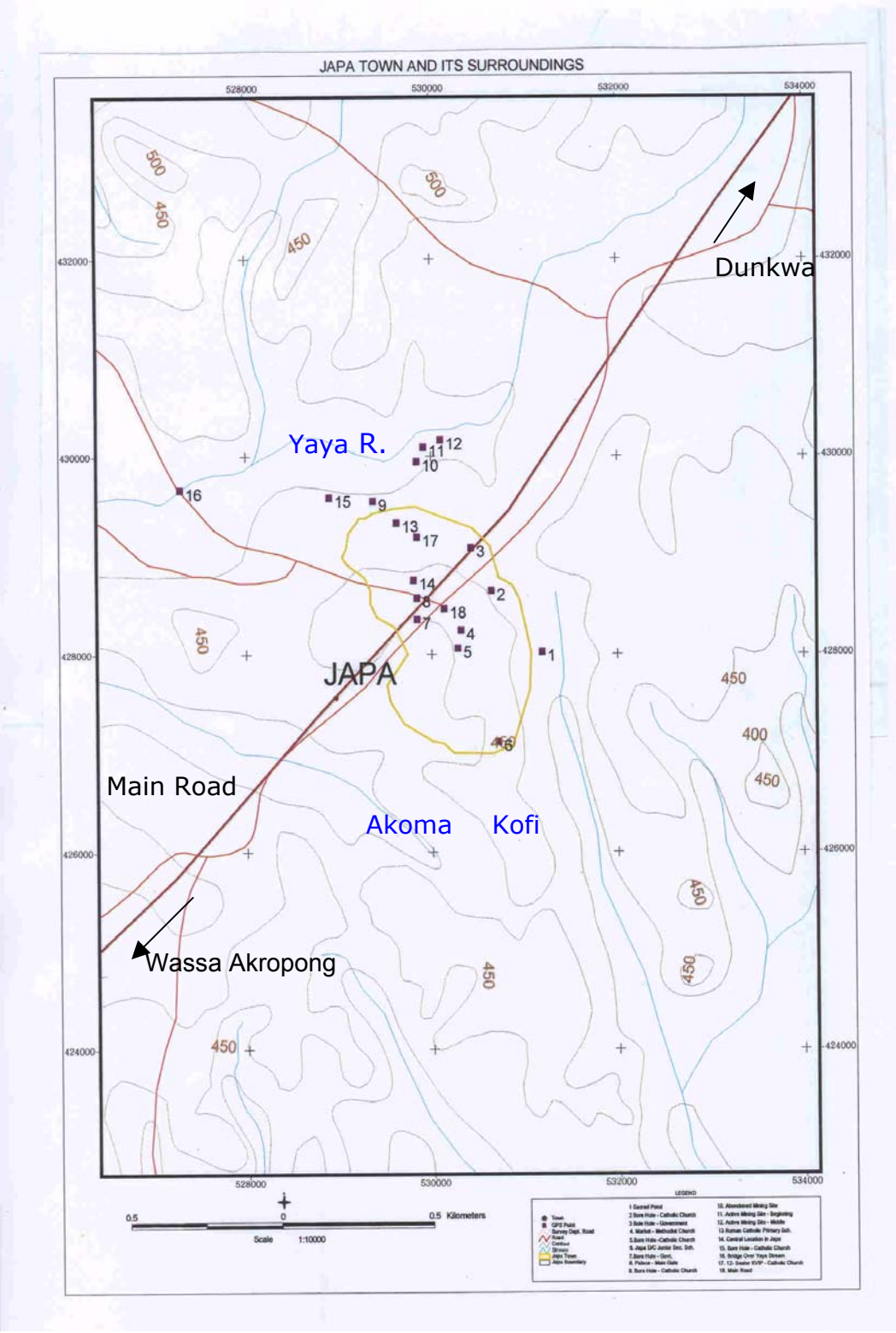

Figure 2 – Map of JAPA town and its surroundings (scale 1/10 000)

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II. OBJECTIVES OF THE STUDY

The study's objectives, as expressed in the terms of reference of the missions, were:

- To meet officials of Government and mining related institutions, discuss present situation of the environment and health in gold mining areas;
- To coordinate field work with Small Scale Mining Unit, EPA, MHO and French Embassy.
- To execute medical and biological sampling programme in cooperation with Government and team members. Take hair, urine and blood samples according to the state of the art in clinical studies.
- To interview population on general health conditions and indication of symptoms of mercury poisoning.
- To cooperate with Ministry of Health and other team members in checking health conditions of directly exposed and non directly exposed members of mining population.
- To perform clinical neurological examination.
- To develop standardised examination protocol with counterparts.
- To investigate situation of the environment around an alluvial gold mining site, and take samples where pollution can be assumed. Specifically, assess the nature and extent of the mercury pollution in a selected river system and adjacent (agricultural) sites.
- To discuss all the issues related to the objective of introducing and setting up a monitoring system for continuous water quality assessment.

Two French-Ghanaian missions were organized in September and October 2003 on the alluvial site of Gyapa. Human and environmental samples (see Back-to-Office-Mission Reports) were transported in France for analysis.

- Mission one (14 – 29 September 2002), concerned human study and was performed by three French experts (Claude CASELLAS, Florence PORTET and André RAMBAUD) and four Ghanaian experts (Samuel O.SACKEY, Nii-Ayi ANKRAH, Collins A. SACKEY).

- Mission two (07-19 October 2002) concerned environmental study and was performed by a French expert (Marc BABUT) and two Ghanaian experts (Ransford SEKYI and Collins SACKEY). Other collaborative inputs by: Moses KPEBU, EPA TARKWA office; William BANNERMAN, Universities of PAU (France) and KUMASI (Ghana); Martine POTIN-GAUTIER, University of PAU.

Human and environmental samples were processed and analysed in the "Laboratoire de Chimie analytique bioinorganique & environnement" (LCABIE) in Pau University (Martine POTIN-GAUTIER, Sylvaine TELLIER, Patrice YVARS, William BANNERMAN) with the participation of David ROSAIN (University Montpellier I - DSESP).

III. ASSESSMENT METHODOLOGY

According to the sociologist study done prior the current assessment (Tsekpo, 2002), the amalgamation process is done in Gyapa either close to the sluice boxes or in the village. In the latter case, the concentrate is brought back to the village with water. This means that two separate contamination pathways can be distinguished and should be accounted for in the sampling strategy: (i) release of mercury in the pits, at the amalgam washing / squeezing and/or burning steps; (ii) diffusion by evaporation and further deposition on soil in the village. Moreover, soils will be washed during the rainy season, and runoff will transport contaminated soil particles. These particles could then contaminate other soils, and return to the river system. These pathways and the kind of samples collected around Gyapa are shown on the diagram at figure 3.

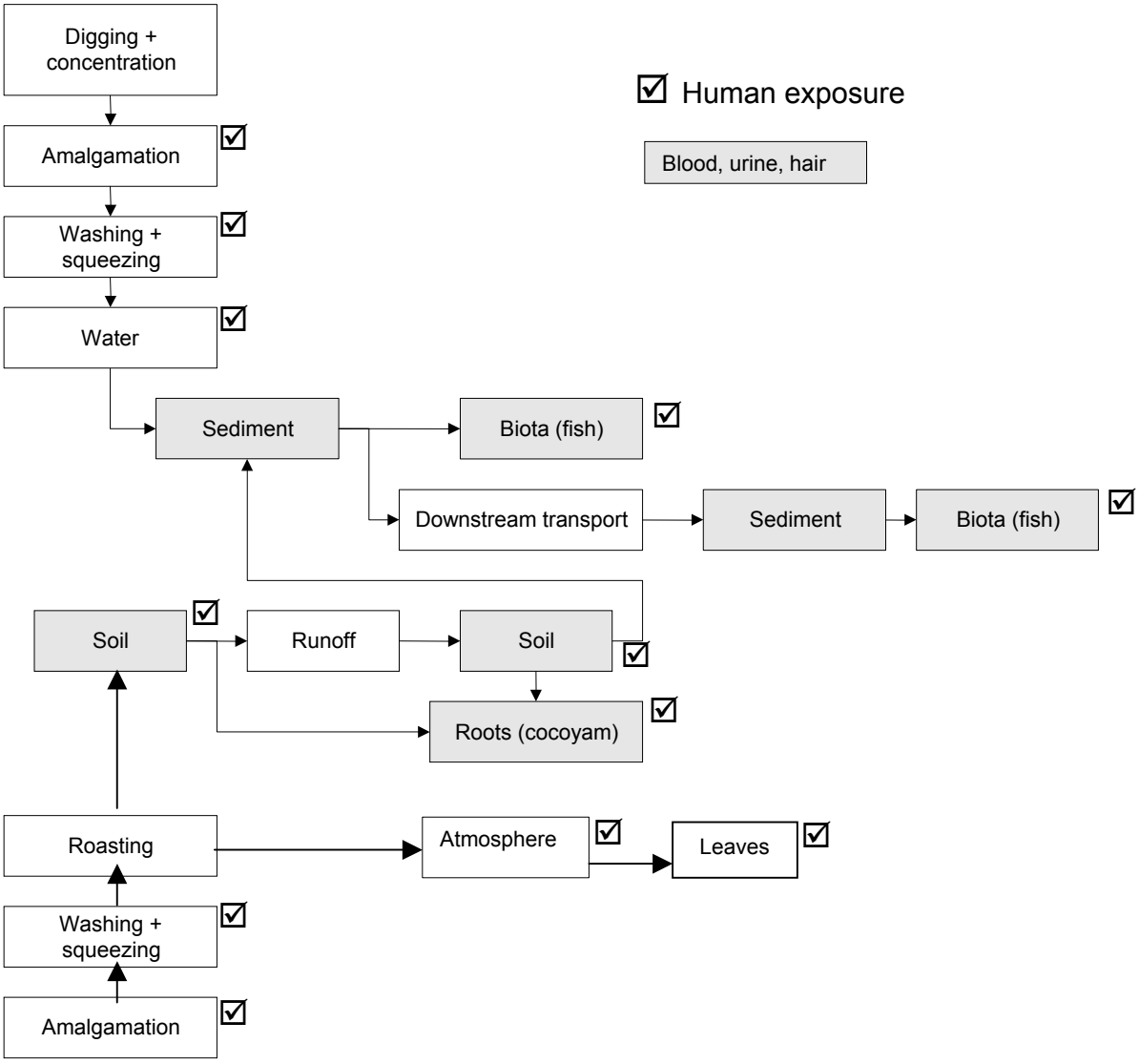

Figure 3 - Mercury diffusion pathways in Gyapa **(Grey boxes designate the types of samples collected at various step of the contamination and diffusion process).**

Therefore, according to our comprehension of the diffusion pathways in Gyapa area (figure 3), the sampling program focussed for humans on blood, urine and hair and for the environment on sediments, fishes, soils and roots of selected vegetables. Sediments should be seen here either as a sink of mercury or as a signature along transport pathways.

IV. REFERENCES

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  - Part II - Conduct of surveys on river systems & overall conclusions (M. BABUT, R.SEKYI, M. POTIN-GAUTIER & S. TELLIER, W.BANNERMAN Claude CASELLAS & A. RAMBAUD)

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Assistance in assessing and reducing Mercury pollution emanating from alluvial gold mining in GHANA – Phase II

US/GHA/02/006

Part I : Health Assessment and Survey Proposals

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Abbreviations

EPA	Environmental Protection Agency
FE-SC	French Embassy (Service of Cultural Affairs)
MoH	Ministry of Health
SMMO	Small Scale Mining Office (Mineral Commission)
PMMC	Precious Minerals Marketing Corporation

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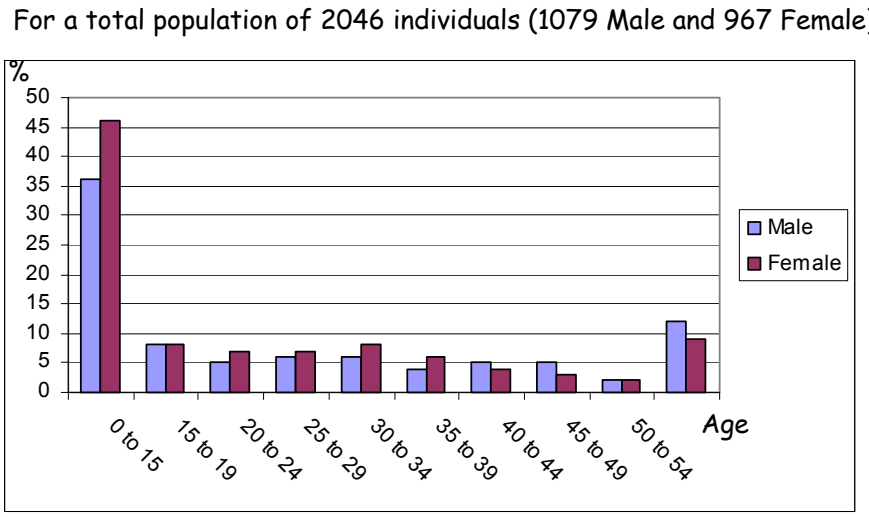
1 DATA COLLECTION

1.1 Social and occupational questionnaire

The questionnaire, and the associated clinical examination procedure, were adapted from a similar study, which was done in Mindanao island (Philippines) under UNIDO auspices. This strategy was deliberately adopted in the previous study (phase I- Dumasi site), to allow a comparison between the different situations. A few modifications were introduced in one hand to take into account the specificity of the Ghanaian context and culture compared to the Philippine context and on the other hand to study the neurological effects of mercury thoroughly compared to the previous study in Ghana. The questionnaire is presented in appendix B.

The questioned people were recruited by the sociologist, and have to explicitly consent to participate in the study. Two hundred and sixty seven volunteers were selected by the sociologist.

The sociological study was performed two months before the human health study by Anthony TSEKPO (2002). It concerned the socio-economic profile of Gyapa. Several important informations are given in this report; we will extract the general age repartition of the population and the households composition (figures 1 and table 1).



Source: 2000 Population and Housing Census, GSS

Figure 1- Age distribution (in percent)

RELATIONSHIP	Total	Male	Female
Total	2,046	1,079	967
Head	401	298	103
Temporary Head	21	5	16
Spouse	196	8	188
Child	809	428	381
Parent/Parent in law	18	3	15
Son/daughter in law	24	5	19
Grandchild	136	60	76
Other relative	415	255	160
Non relative	26	17	9

Source: 2000 Population and Housing Census, GSS

Table 1: Relationship by Sex within Households in Japa

1.2 Cohort recruitment and biological samples collection

The study was performed on 160 individuals recruited among the 267 volunteers (106 individuals did not come) and 20 were recruited during the field study. In the total the study concerned 180 individuals.

Total numbers of samples collected were as follows:

180 samples of blood (1 to 2 replicates of 4ml in EDTA-coated vials).

179 samples of spontaneous urine (1 to 2 tubes of 50 ml).

125 Creatinin determination

193 samples of hair (including 16 children): for three individuals, the quantities were very small, according to the "cranium shaved " fashion of the men.

101 hair samples from health centres in the same region of the studied site.

2 PREPARATION OF SAMPLING MATERIAL

Ultra-clean sampling procedures, handling, and preparations are of utmost important if precise and exact results are required in the analysis of mercury in environmental and biological. The materials and vessels to be used for the sampling were therefore washed and preserved under very strict protocol. Polyethylene gloves are worn at all times during washing and handling. All the washings are done in polyethylene baths reserved only for the purpose and are kept under a fume chamber in a clean room at all times. Washing and washing solutions prepared from Milli-Q de-ionised water.

2.1 Washing Procedures for Bottles and Sampling Materials

New materials are washed as follows

They are placed in 10% solution of RBS detergent for 24 hours

rinsed with tap water and then with Milli-Q water

immersed in a 10% (v/v) HNO_3 bath and heated in an ultrasonic bath for 1 hour (or 24 hours without ultrasonic bath) .

rinsed with Milli-Q water

immersed in a 10% (v/v) HCl bath and heated in an ultrasonic bath for 1 hour (or 24 hours without ultrasonic bath) .

rinsed with Milli-Q water

immersed in Milli-Q water and placed in an ultrasonic bath for 30 minutes

dried at about 70°C in a clean oven specially reserved for the purpose.

After drying all materials are placed individually in double zip-lock bags and kept in a cupboard or in an air-tight container until their use required for use.

With only slight modifications this forms the basis of washing protocol for most laboratory wares used. Washing of used materials begin with washing in hot tap water before immersion into the RBS detergent solution.

2.2 Sample preservation

Only high quality reagents are used (e.g. Ultrapur HCl).

- Urine samples are kept frozen until analysis.
- Blood samples are kept frozen until analysis
- Hair are kept in their secured sachets at ambient temperature until analysis

2.3 Sample transport

All samples, sealed in double zip-lock bags, and sometimes tied together with magnetic tapes are transported in pre-cooled ice-chests filled with frozen ice packs. Suspected highly contaminated samples are kept separately from less contaminated ones

Samples are shipped by air, often accompanied by the investigator, to avoid mishandling by traffic officials. As much as possible overnight flights are used, most samples remain frozen this way.

3 EXPERIMENTAL

3.1 Sample Treatment

3.1.1 Blood

300 µL of blood is transferred into a polypropylene sample tube. 3 mL of aqua regia is added. They are then agitated at 420 rpm until complete dissolution. On dilution the solutions became cloudy and this necessitates centrifuging before CV-AFS analysis of the supernatant liquid.

3.1.2 Urine

When the urine samples are frozen they are no more homogenous solutions when they are de-frozen. Some colloidal solids are collected at the base of the container tubes. Attempts to re-dissolve the solids into solution was impossible if one had to preserve the integrity of the samples.

The urine samples were therefore centrifuged and the solid and liquid portions were separated and treated respectively as follows:

Solid portion: They are dried in an oven at 50°C overnight. 3ml aqua regia were added and agitated on a shaker until complete dissolution. Volumes in the other of 100uL are taken and diluted with the reagent blank for CV-AFS analysis.

- Liquid portion: 1 ml of urine is accurately measured and transferred into 25 ml volumetric flasks and diluted to the mark with 'dilute aqua regia.

3.1.3 Hair

Between 20 mg and 50 mg of the hair samples were weighed in a beaker and then transferred in a polypropylene bottle in order to avoid weight errors introduced by electrostatic forces between the samples and the walls of the polypropylene containers). A 3mL volume of aqua regia is added. The propylene bottle is corked and is placed on a shaker to agitate overnight. Then the solutions was diluted wiith deionised water in a 25 mL volumetric flask.

3.2 Analytical determinations

3.2.1 Atomic Fluorescence Detection

The pre-treatment procedures described earlier ensures that all mercury is present in solution as Hg^{2+}. Total mercury is determined by the cold vapour – atomic fluorescence technique (CV – AFS) using the continuous flow approach. The procedure involves an online reduction of Hg^{2+} to Hg^0 vapour by $SnCl_2$. Typically, the reductant is 5%m/v $SnCl_2$ in 15%HCl. The mercury vapour is swept by argon as carrier gas to the AFS detector (Merlin PSA 10.023).

Various sample matrices are analysed using reagent blanks which are basically in the same chemical media as the analyte in the respective sample solutions. Measurements were controlled by the Touchstone ® control software. Typical gas flow conditions include:

Carrier gas flow (Argon)	0,30 – 0,45 L/minute
Drier gas flow (Argon)	2,5 – 3,0 L/minute
Sheath Flow (Argon)	0,30 – 4,5 L/minute

3.2.2 Creatinine in urine ("Jaffé Method" : Kinetic test without deproteinisation)

Creatinine in an alkaline picrate solution forms a colored orange-red complex. The delta absorbance at fixed times during conversion is proportional to the concentration of Creatinine in the sample.

The reagents and the standard are ready-to-use and stable up to the end of the indicated month of expiry, if contamination is avoided and stored at 2 – 25 °C.

- R1: Sodium Hydroxide 0.16 mol/l
- R2: Pikric acid 4.0 mmol/l
- Standard: 2 mg/dl (177 µmol/l)
- Specimen : dilute urine 1 + 49 with distillated water

Normal range

- Urine: 1000 - 1500 mg/24 h
- Creatinine clearance; Men: 98 – 156 ml/min; Women: 95 – 160 ml/min

3.2.3 QC / QA

Precision and recovery measurements were performed with reference materials (reference materials: Seronorm trace element urine FE1114, Seronorm trace element 404107y whole blood, IAEA 086 hair). Analysis of blanks were done for field variability, digestion/extraction performance and reagents quality. Precision and recovery were evaluated and detections limits were determined.

4 RESULTS & DISCUSSION

4.1 Social and occupational data

180 adults ([1]) were recruited, including 116 men and 64 women. 149 declared to be galamseys (100 men and 49 women). Most of the galamseys are partial time because of the seasonality of the alluvial mining specificity (activity can be performed between May and October). Their alternative activity is shown in the figure 2.

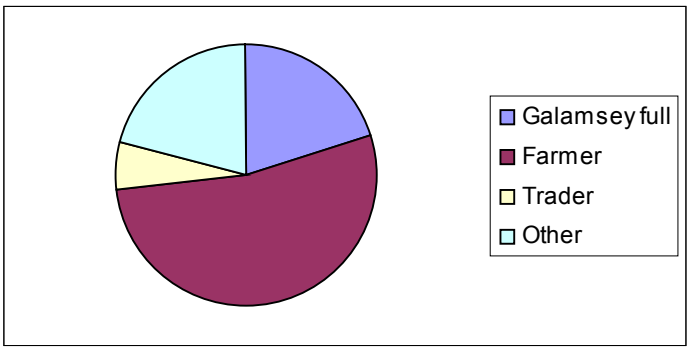


Figure 2: Alternative activity of galamseys

[1] Children (<15 years) were not selected for ethical reasons and difficulties in obtaining parents' consentment

Non-galamsey population was considered as a possible control, and was deliberately limited to 31 individuals. The population is rather young (Figure 3).

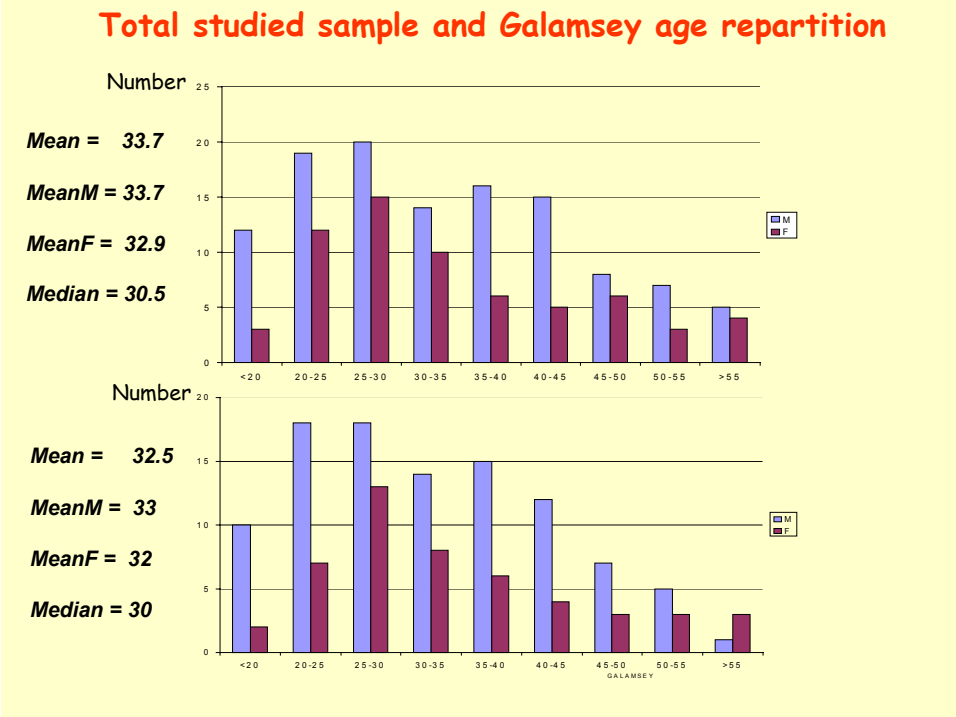


Figure 3- Age distribution in the cohort , F, M

The repartition between migrants and natives shows that half of them are natives (figure 4). In all classes women reprent 1/3rd of the total.

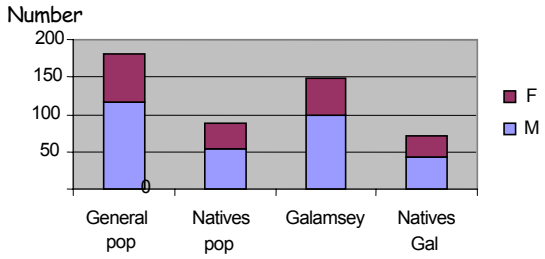


Figure 4: Part of migrants in Gyapa community

The overall population is rather poor, and consumes few tobacco and alcohol. The food is mainly composed of tuber, completed by fish (1 time a day); meat and milk are rarely consumed.

Most of the women are illiterate (Figure 5)

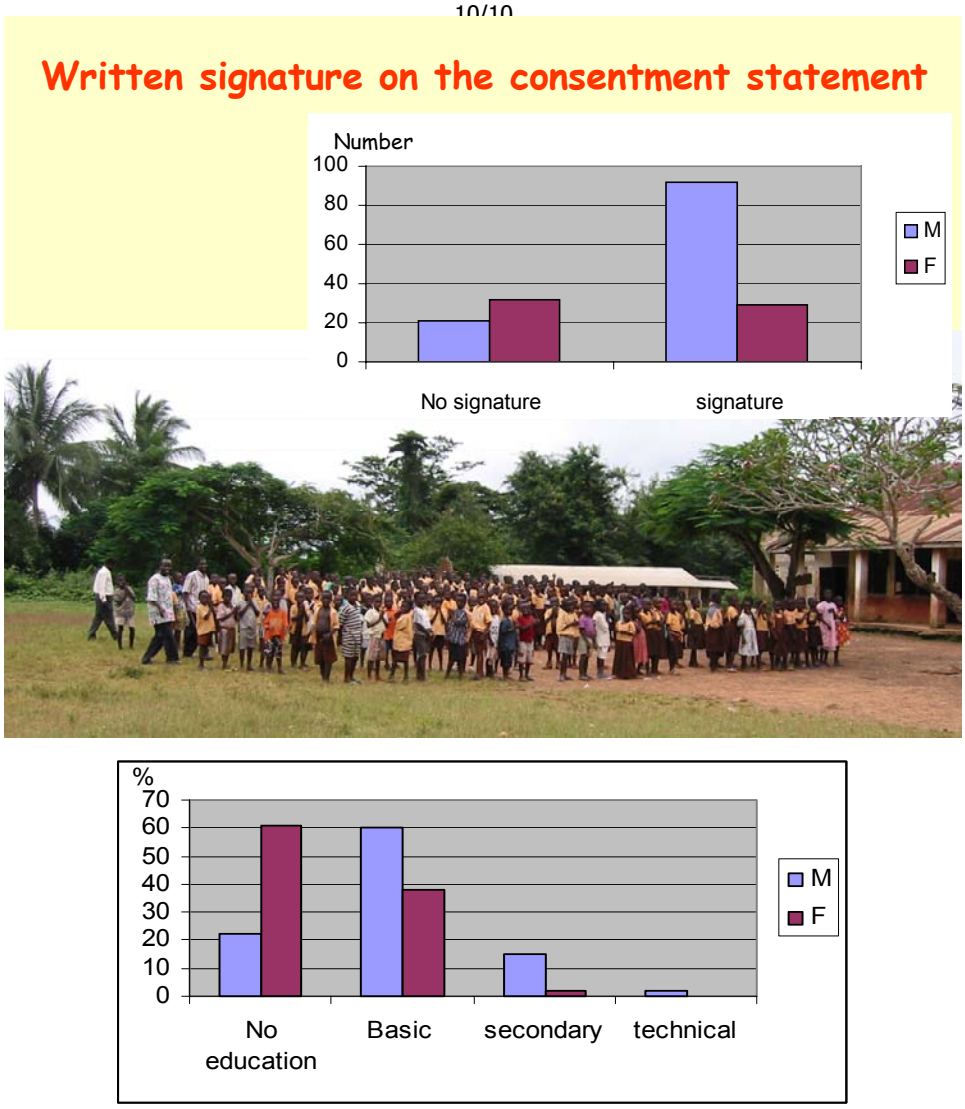
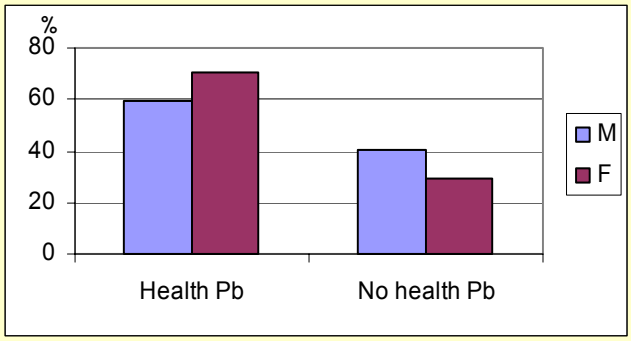


Figure 5 -Written signature on the consentment statement and level of education

4.2 Health perception

40% of male sample – galamseys or not - claimed to have health problems; this ratio was slightly higher in the female sub-group, but in this case galamseys declared more health problems (Figure 6) Most of the declared pathologies were related to the skin area. 90% of the people, being galamsey or not, do not declare or declare slight metallic taste and salivation problems. Nevertheless 20% of the people claimed to have tremors and 65% have sleep disorders.



Main declared problems (Pb) are related to skin, malaria, kidney and repiratory system.

Figure 6 - Percent of persons declaring health problems

4.3 Exposure assessment

4.3.1 Human-biomonitoring (HBM) values for mercury *(Drasch et al.-2001)*

The HBM-values are assessed by toxicological considerations. The HBM I was set to be a 'check value' - this means an elevated mercury concentration in blood or urine, above which the source of the Hg-burden should be sought and, as far as possible, eliminated. However, even when exceeding this HBM I value, the authors claimed that a health risk is not to be expected. In contrast to this, the (higher) HBM II value is an 'intervention value'. For blood or urine levels above HBM II, especially for a longer time, adverse health effects cannot be excluded, therefore interventions are necessary. On the one hand the source should be found and reduced urgently; a medical check for possible symptoms should be performed.

Other toxicologically founded limits are occupational threshold limits. Such limits are established for mercury, e.g. in France and the USA (biological exposure indices BEIs) or Germany (BAT value). For a better comparison with the HBM-values which, to our knowledge, are only established in Germany the German BAT-values for metallic and inorganic mercury are taken for this study. From the definition, these BAT-values are exclusively valid for healthy adult workers under occupational medical control. The occupational burden must be stopped if this threshold is exceeded. These occupational threshold limits are not valid for the total population, especially not for risk groups like children, pregnant women, older or ill persons. Nevertheless, the BAT-values were taken for a further classifying of our high results, too. BAT-values for mercury are established only for blood and urine, but not for hair. Table 2 gives an overview of the HBM-, BAT- and BEI-values :

Table 2 : Mercury threshold values according to Drasch et al.(2001)

	Hg- blood	Hg-urine	
	µg /l	*µg /l*	*µg/g creat.*
HBM I - Human Bio Monitoring	5	7	5
HBM II - Human Bio Monitoring	15	25	20
BEI - Biological Exposure Index	15 a)	-	35 b)
BAT - Biologischer Arbeitsstoff -Toleranzwert (for metallic and inorganic Hg)	25	100	-
	a) after working		b) before working

NB: for hair, the HBM II is 5µg/g (in analogy) and WHO proposes a treshold limit of 7µg/g

4.3.2 Mercury in blood, urine and hair samples

The characteristics of the cohort are given in table 3.

Table 3 - Summary of mercury exposure in the investigated population

Hg content in …	*Blood ($\mu g.l^{-1}$)*	*Urine ($\mu g.l^{-1}$)*	*Hair ($\mu g.g^{-1}$)*	*Hair ($\mu g.g^{-1}$) Children*
Mean-	11.6	18.2	3.0	3.74
Median	10.4	8.4	1.9	2.36
Minimum	< D.L.	0.7	0.2	1.07
Maximum	44.8	206.2	40.8	14.3
Stand.deviation	*6.3*	*30.5*	*4.2*	*3.9*
Number N	*180*	*179*	*177*	*16*

The mean mercury concentrations according to gender, were

- in blood: 12.1 $\mu g.l^{-1}$ for Male and 10.7 $\mu g.l^{-1}$ for Female
- in urine: 23 $\mu g.l^{-1}$ for Male and 9.5 $\mu g.l^{-1}$ for Female
- in hair: 4 $\mu g.g^{-1}$ for Male and 1.2 $\mu g.g^{-1}$ for Female

In the children sample, mercury concentration in hair showed high exposure for two individuals (12.6 and 14.3 $\mu g.g^{-1}$); for 10 of them, the exposure is medium (2-7 $\mu g.g^{-1}$) and only 4 had less than 2 $\mu g.g^{-1}$(e.g. low exposure).

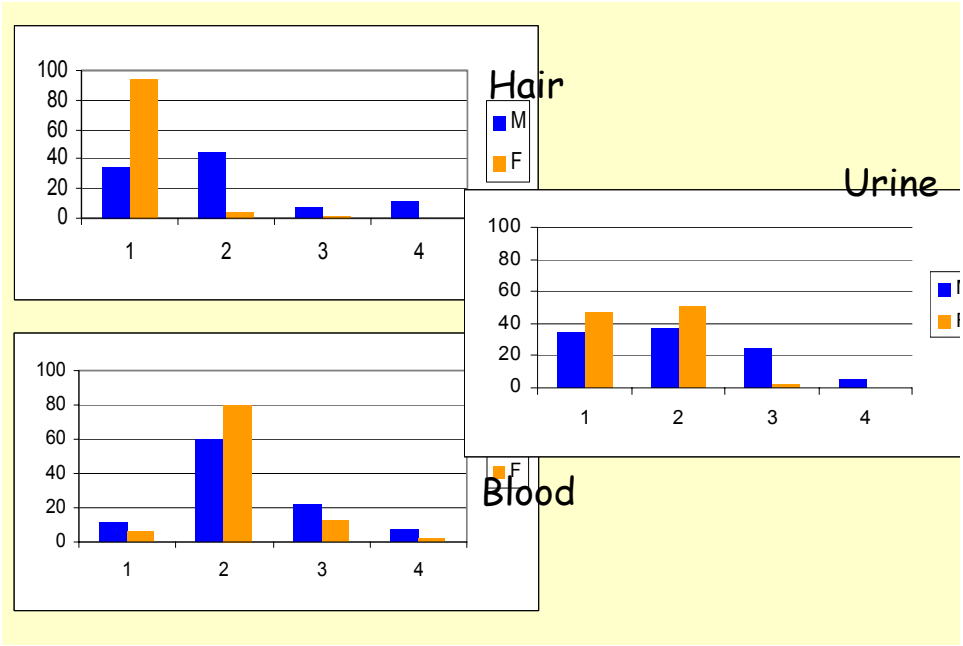
4.3.3 Classification of mercury body burden.

Classes were defined following the HBM, BTA and WHO system as:

Table 4: Classes of mercury body burden.

	HBM 1	HBM2	BTA
BLOOD	5 µg Hg /l	15 µg Hg /l	25 µg Hg /l
URINE	7 µg Hg /l	25 µg Hg /l (BEI)	100 µg Hg /l
HAIR	2 µg Hg /g	5 µg Hg /g	7 µg Hg /g (WHO)
Class	***1*** no exposure	***2*** low exposure	***3*** medium exposure	***4*** high exposure

The distribution of Hg concentration in blood, urine and hair samples is presented in the figure 7.



Figue 7: Mercury body burden classes for galamsey community

In conclusion, among 180 investigated persons, the most exposed ones (class 3 and 4) were 56 individuals in classes 3 and 4 for urine, blood or hair (3 women and 53 men), 8 of them were aged between 18 and 25 years and 15 individuals were aged between 26 and 35 years. 17 individuals were working as galamseys for over 5 years.

4.4 Clinical examination

A special section of the collection of epidemiological data was dedicated to neurological health, as mercury is particularly noxious to the nervous system. The clinical examinations consisted in classical tests related to walking, standing, sitting, lying, to the reflexes, the memory and drawing abilities. In this study, a medical specialist in neurology examined 93 Individuals. It concerned 86 galamseys and 7 non galamseys.

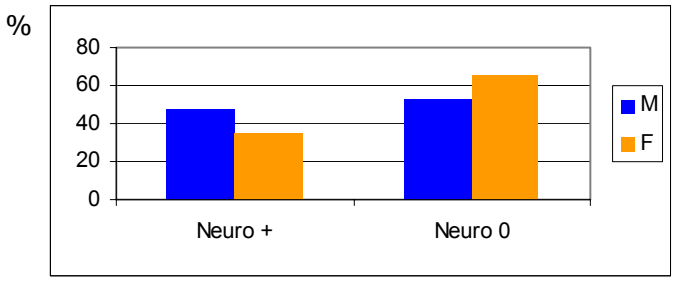


Figure 8 Galamseys overall neurological signs

Figure 8 shows that around 40 percent of individuals have neurological disorders for males and females. This percentage is widely beyond than the one in a normal population. For the seven non galamseys, two had neurological signs, one being wife of galamsey.

Figure 9 shows that neurological disorders are observed in any class of body burdens; class 2 concerns the majority of the sample.

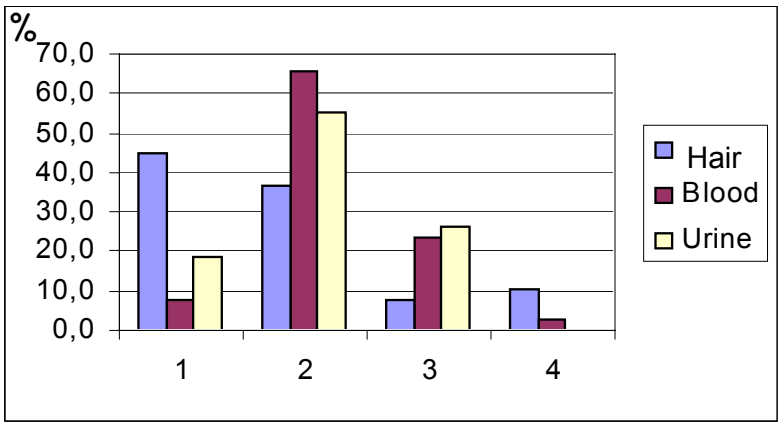


Figure 9 Body burden classes for persons having neurological disorders

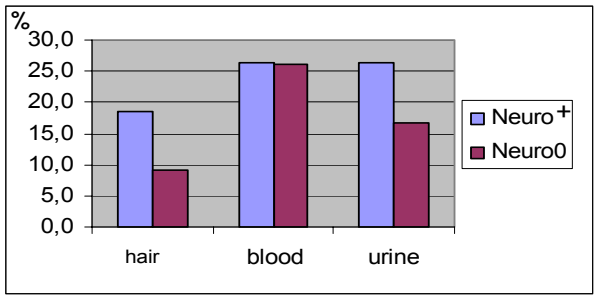


Figure 10: Classes 3 and 4 body burden in the galamsey sample with neurological disorders or without any clinical defects

For classes 3 and 4 of body burden, neurological signs are discriminated by urine and hair. This result would suggest that urine and hair mercury loads are better biomarkers than blood. This is in accordance with the literature that indicates food influence on mercury contents in blood.

In conclusion, 39 individuals had neurological disorders 14 were aged between 18 and 25 years and 11 between 26 and 35 years. 22 were galamseys for over 5 years

5 STRATEGY AND CONCLUSIONS

The first point that should be addressed is that the sociological study is the key for a good epidemiological investigation. In our work, the attempt for a cluster sampling at a family level was difficult to be interpreted because its planification was not programmed. In annex (B 1 and 2) we propose the objectives of a sociological study and a questionnaire for the preparation of a cluster sampling at a family level.

From this study, answers for two main questions could be proposed:

Is the population exposed to mercury?

In the total sample studied (180), 56 individuals are in classes 3 and 4 for urine, blood or hair mercury burden. Our results showed that direct exposure by professional activities (galamseys) increase mainly urine and hair mercury burden. Indirect or direct exposure of children was also observed while spouses and women exposure was lower than men.

Is the population health affected?

The neurological signs in goldwashers group are frequent (40%). The neurological examination (measurement of effects) and the body burden measurement (level of exposure) are done simultaneously. The body burden remains some months while neurological effects appears some years after chronic exposure (maximum levels being 200 µg/l for urine and 40 µg/l for blood). For this reason, the link between body burden and neurological disorders was not always easy to identify.

In perspectives three action levels could be considered:

- At the studied site level

Information on mercury effects and prevention must be done to the whole population.

Considering the most exposed individuals, 33 were selected for a prevention programme with retorts distribution.

- For future human health studies, exposure assessment of mercury by the measurement of mercury in hair in different medical centers of the country would give information on the mean population mercury levels. Planification of a cluster sampling at a household level would indicate the kind of prevention actions that must be proposed.

- At the watershed basin level, the knowledge of the transport and fate of mercury in the river and the estuary would help to identify hot spots. Transport modelling and species measurement would complete the knowledge of mercury fate and would help in identifying populations to be studied.

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APPENDIX

APPENDIX A : ANALYTICAL RESULTS OF HUMAN SAMPLES :

A1 ***- Table 1*** Hg concentration ($\mu g.L^{-1}$ d.w.) in blood samples (*mean of the 2 measurements on 2 different mineralisations excepted for certified seronorm trace element on 8 mineralisations*) - (a) Seronorm spiked with 21 µg methylmercury $.L^{-1}$

A2 ***- Table 2*** Hg concentration ($\mu g.L^{-1}$) in urine samples (*mean of the 2 measurements on 2 different mineralisations excepted for recmmended seronorm trace element on 16 measurements*)

A3 ***- Table 3*** Hg concentration ($\mu g.L^{-1}$) in hair samples (*mean of the 2-3 measurements on 1 mineralisatios excepted for recmmended seronorm trace element on 16 measurements*)

A4 ***- Table 4*** Creatinine concentration ($g.L^{-1}$) in instantaneous urine samples

APPENDIX B : PROPOSALS FOR SOCIOLOGIST STUDY:

B1 - Objectives of the preliminary sociological investigation

B2 - Questionnaire for the sociologist

A1 **- *Table 1*** Hg concentration (µg.L^{-1} d.w.) in blood samples (*mean of the 2 measurements on 2 different mineralisations excepted for certified seronorm trace element on 8 mineralisations*) - (a) Seronorm spiked with 21 µg methylmercury .L^{-1}

Id. N°	Mean	St.Er.Mean	Id. N°	Mean	St.Er.Mean	Id. N°	Mean	St.Er.Mean	Id. N°	Mean	St.Er.Mean	Id. N°	Mean	St.Er.Mean
0	11,1	0,40	73	9,1	0,72	122	9,3	0,23	190	7,7	0,86	266	8,5	0,42
1	14,1	1,70	74	16,8	1,13	123	11,8	0,54	196	8,2	2,09	267	19,1	1,30
2	13,3	0,49	76	8,7	1,38	126	9,4	0,99	198	9,7	1,30	268	9,5	1,18
3	14,5	0,62	77	19,6	1,10	127	9,7	2,78	200	7,2	0,94	269	15,8	1,21
8	9,4	0,53	79	11,5	2,44	128	13,2	2,28	201	12,4	2,21	270	4,2	0,79
11	17,7	1,58	80	6,7	0,18	130	6,4	2,17	206	21,6	2,82	271	9,3	1,55
15	7,9	1,14	81	7,2	1,66	134	7,6	0,21	207	7,4	0,55	272	8,0	1,00
16	2,9	1,13	84	3,9	2,28	135	11,0	1,07	208	12,5	0,99	273	8,8	1,96
17	12,3	2,79	85	13,9	1,33	138	10,7	1,12	209	26,2	2,60	274	<l.d.	
18	10,9	0,34	86	14,7	0,50	139	5,0	0,57	212	10,1	0,33	275	6,6	1,06
19	10,8	0,47	87	12,4	0,87	141	8,4	0,24	215	11,7	0,66	276	2,9	0,21
20	10,4	0,51	88	8,5	0,62	144	24,6	2,36	216	7,1	0,90	277	8,6	1,11
21	12,7	0,74	89a	11,5	2,50	147	8,2	0,18	218	5,1	0,18	278	10,9	1,50
23	11,2	1,95	89b	11,2	0,60	149	8,9	2,23	219	17,4	1,47	279	7,5	0,41
25	18,2	2,38	90	15,1	1,48	150	12,4	2,14	220	16,3	0,90	280	5,2	0,17
27	9,6	0,48	92	13,5	0,52	151	16,5	1,66	223	4,1	0,26	281	2,8	0,50
28	5,8	0,84	93	17,6	1,54	152	9,8	0,72	224	4,8	0,92	282	8,9	1,79
30	9,6	1,43	94	28,2	2,37	153	10,1	0,41	228	11,1	0,49	283	2,6	0,59
31	3,9	0,30	96	19,2	2,99	154	15,6	0,91	229	7,3	1,53	284	9,3	1,54
33	13,0	1,00	98	33,0	0,99	155	16,8	0,71	230	16,3	0,66	285	10,4	0,40
34	5,9	0,57	99	33,0	2,18	157	9,6	1,29	231	14,5	1,72	Ref a	**20,8**	2,4
35	30,7	1,52	100	20,4	1,72	158	10,1	0,54	232	10,3	0,97			
39	2,7	0,37	101	12,1	1,39	159	6,9	0,51	234	15,9	2,10			
40	6,2	0,21	101 w	12,5	0,74	160	8,3	0,65	236	17,1	1,77			
41	44,8	2,84	102	8,6	0,53	161	6,2	0,30	237	13,9	0,66			
43	3,1	0,78	103	26,0	1,23	162	6,3	1,38	238	28,4	0,90			
44	10,6	2,00	105	13,4	0,31	163	11,5	1,02	238b	5,8	0,86			
45	12,3	1,87	106	5,6	0,65	164	10,7	0,57	239	8,8	0,77			
49	9,4	2,26	107	4,3	0,79	165 w	20,7	1,69	240	8,9	0,29			
50	11,4	2,03	109	12,4	1,11	166	12,7	0,66	244	5,7	1,48			
52	10,7	0,71	110	8,9	0,25	167	5,6	1,48	246	15,1	0,68			
55	12,0	1,87	111	17,2	2,01	169	6,7	0,66	247	11,2	0,57			
57	10,8	1,78	112	3,6	0,26	171	19,9	1,23	250	10,3	0,57			
58	17,2	1,89	114	8,8	0,64	172	5,8	2,30	254	5,8	0,37			
60	10,5	0,29	115	8,4	0,47	175	7,2	0,80	255	14,3	1,54			
61	8,6	1,64	116	13,4	0,60	179	15,0	1,42	258	14,0	2,09			
63	2,4	0,44	117	4,6	1,14	180	21,0	1,02	259	17,2	1,37			
65	15,5	1,63	118	15,8	0,65	181	8,3	1,86	260	6,1	0,15			
68	24,8	0,67	120	14,3	0,60	182	18,2	1,21	261	10,9	2,80			
70	13,2	1,00	121	13,1	2,13	189	3,5	0,30	262	6,8	0,29			

A2 **- *Table 2*** Hg concentration (µg.L^{-1}) in urine samples (*mean of the 2 measurements on 2 different mineralisations excepted for recommended seronorm trace element on 16 measurements*)

Id. N°	Mean	St.Er.Mean	Id. N°	Mean	St.Er.Mean	Id. N°	Mean	St.Er.Mean	Id. N°	Mean	St.Er.Mean	Id. N°	Mean	St.Er.Mean
0	11,0	0,32	74	38,0	1,18	123	23,3	0,51	190	6,6	0,27	262	4,8	0,24
1	15,8	0,55	76	20,3	1,14	126	3,8	0,19	196	6,5	0,22	266	5,9	0,35
2	6,1	0,56	77	31,8	1,32	127	6,6	0,35	198	16,8	1,39	267	65,8	3,00
3	11,8	0,36	79	9,3	0,33	128	12,1	0,39	200	11,5	0,53	268	2,9	0,36
8	8,8	0,22	80	4,0	0,20	130	6,9	0,51	201	3,4	0,15	269	26,7	0,95
11	44,0	0,80	81	8,5	0,44	131	5,9	0,74	203	66,3	3,04	270	5,2	0,51
15	11,9	0,77	84	4,9	0,40	134	21,8	0,54	206	34,5	1,32	271	5,0	0,26
16	5,7	0,18	85	13,2	0,75	135	7,3	0,15	207	31,0	1,24	272	5,5	0,67
17	10,9	0,25	86	4,5	0,27	138	4,9	0,11	208	33,2	1,11	273	30,7	1,20
19	11,6	0,78	87	2,6	0,09	139	13,8	0,41	209	57,8	2,95	274	2,5	0,20
20	5,5	0,26	88	4,2	0,46	141	9,7	1,33	212	3,1	0,27	275	3,8	0,22
21	8,5	0,48	89	10,9	0,34	144	206,2	10,13	215	3,8	0,14	276	3,6	0.40
23	4,6	0,13	89b	8,5	0,83	147	9,9	0,51	216	5,1	0,23	277	11,5	0,30
25	33,4	0,77	90	6,2	0,46	149	5,9	0,33	218	8,4	0,89	278	46,7	0,26
27	7,9	0,38	92	60,2	3,96	150	11,8	0,27	219	11,8	0,63	280	0,7	1,81
28	7,5	0,20	93	9,3	0,51	151	8,2	0,29	220	14,9	0,91	281	4,4	0,40
30	52,0	1,75	94	130,2	7,84	152	7,6	0,19	223	4,7	0,20	282	11,7	0,16
31	7,3	0,98	96	6,8	0,36	153	6,7	0,12	224	4,9	0,56	283	4,9	0,57
33	30,6	1,03	98	198,6	8,95	154	9,5	0,40	228	10,5	0,39	284	11,4	0,35
34	12,1	0,69	99	105,4	4,86	155	93,6	1,22	229	9,0	0,77	285	29,8	0,64
35	199,6	3,51	100	6,6	0,28	157	6,1	0,32	230	24,3	0,91	Reference	50,1	2,20
39	4,8	0,56	101	6,7	0,40	158	5,2	0,24	231	28,5	1,23			
40	32,0	0,76	101w	9,3	1,03	159	20,4	1,01	232	11,6	0,71			
41	52,8	2,40	102	7,5	0,19	160	9,5	1,09	234	10,2	0,30			
43	12,6	0,35	103	25,4	2,45	161	6,8	0,16	236	6,8	0,28			
44	5,0	0,62	105	7,3	0,32	162	5,2	0,10	237	6,9	0,36			
45	6,5	0,18	106	9,0	0,69	163	8,0	1,00	238	11,6	0,53			
49	3,8	0,23	107	4,2	0,32	164	6,3	0,33	238b	24,3	0,42			
50	9,1	0,82	109	9,1	0,83	165w	8,1	0,36	239	4,0	0,36			
52	16,4	1,85	110	17,2	0,90	166	4,6	0,48	240	8,5	0,56			
55	19,7	0,62	111	6,4	0,11	167	5,4	0,21	244	5,8	0,16			
57	5,5	0,27	112	2,6	0,20	169	4,9	2,02	246	7,2	0,64			
58	24,7	1,93	114	6,9	0,12	171	6,6	0,37	247	5,1	0,59			
60	18,8	0,72	115	5,5	0,12	172	6,9	0,38	250	2,4	0,16			
61	11,2	0,51	116	47,7	1,16	175	7,2	0,47	254	4,5	1,04			
63	12,1	0,73	117	5,0	0,25	179	3,6	0,21	255	7,4	0,20			
65	10,5	0,40	118	7,0	0,27	180	83,8	2,73	258	6,3	0,27			
68	70,6	2,18	120	3,0	0,45	181	10,1	0,61	259	7,6	0,27			
70	2,6	0,13	121	22,0	0,55	182	14,0	1,20	260	13,6	0,54			
73	9,3	0,41	122	6,4	0,26	189	3,2	0,26	261	14,4	0,63			

A3 **- *Table 3*** Hg concentration (µg.L^{-1}) in hair samples (*mean of the 2-3 measurements on 1 mineralisatios excepted for recmmended seronorm trace element on 16 measurements*)

Id N°	Mean	St.Er.mean	Id N°	Mean	St.Er.mean	Id N°	Mean	St.Er.mean	Id N°	Mean	St.Er.mean	Id N°	Mean	St.Er.mean	Id N°	Mean	St.Er.mean
0	2,8	0,14	61	1,6	0,07	109	0,4	0,11	159	0,2	0,09	220	4,8	0,03	273	2,1	0,05
1	2,9	0,37	63	1,7	0,04	110	2,1	0,07	160	1,0	0,03	223	0,7	0,13	274	1,0	0,35
2	0,6	0,12	65	6,6	0,48	111	3,2	0,20	161	1,1	0,07	224	0,9	0,03	275	1,5	0,12
3	2,2	0,21	68	11,7	0,31	112	1,5	0,05	162	0,6	0,09	228	1,7	0,07	276	1,6	0,07
8	1,2	0,09	70	2,4	0,30	114	1,5	0,08	163	1,4	0,04	229	2,1	0,05	277	2,8	0,11
15	2,1	0,45	73	0,2	0,14	115	1,5	0,16	164	2,0	0,09	230	3,9	0,28	278	2,6	0,05
16	0,6	0,04	76	2,3	0,25	116	4,5	0,17	165w	1,9	0,08	231	2,7	0,25	279	1,6	0,08
17	1,6	0,08	77	15,7	1,6	117	2,3	0,38	166	2,7	0,10	232	1,9	0,76	280	1,8	0,11
19	1,6	0,05	79	1,9	0,30	118	4,2	0,16	167	0,5	0,21	234	2,1	0,06	281	1,8	0,10
20	1,8	0,17	80	1,3	0,08	120	1,6	0,10	169	0,9	0,08	236	3,0	0,19	282	1,7	0,15
21	1,3	0,09	81	2,9	0,17	121	4,4	0,35	171	0,8	0,01	237	0,4	0,13	283	1,7	0,12
23	2,5	0,33	84	1,8	0,11	122	3,1	0,68	172	0,8	0,00	238	1,5	0,07	284	2,5	0,09
25	6,7	0,34	85	1,4	0,14	123	2,6	0,22	175	1,2	0,12	238 b	3,3	0,09	285	4,1	0,11
27	0,7	0,07	86	2,3	0,60	126	2,4	0,06	179	3,1	0,59	239	1,4	0,17	Children		
28	1,6	0,35	87	4,4	0,10	127	1,7	0,28	180	5,8	0,15	240	0,7	0,02	3\2	2,7	0,33
30	14,1	2,1	88	2,6	0,41	128	2,5	0,48	181	1,7	0,05	244	0,9	0,06	19\1	1,1	0,04
31	0,8	0,02	89	1,7	0,03	130	1,8	0,18	182	0,3	0,02	246	2,7	0,50	55/2	1,5	0,06
33	5,7	0,34	89b	5,7	0,23	134	1,6	0,20	189	0,7	0,03	247	2,0	0,12	63/1	2,3	0,10
34	2,2	0,22	90	0,6	0,10	135	2,6	0,26	190	1,3	0,16	250	0,8	0,03	92-2	2,6	0,47
35	13,3	0,55	92	7,3	1,07	138	8,0	0,26	196	2,5	0,03	254	0,6	0,10	96/2	2,4	0,28
39	0,8	0,22	93	3,0	0,31	139	1,9	0,09	198	2,0	0,07	255	2,6	0,09	101/2	12,6	0,36
40	3,2	0,12	94	9,5	0,24	141	1,6	0,10	200	1,4	0,13	258	1,8	0,14	131/2	2,1	0,07
41	5,0	0,24	96	0,8	0,11	144	40,8	0,98	201	0,6	0,04	259	1,0	0,13	150/1	14,3	1,9
43	0,5	0,23	98	6,1	0,18	147	3,5	0,00	203	8,4	0,34	260	0,9	0,05	153/2	5,1	0,64
44	1,2	0,06	99	4,3	0,17	149	1,2	0,37	206	6,6	0,16	261	2,0	0,08	160/1	1,1	0,07
45	1,5	0,15	100	2,2	0,33	150	1,8	0,02	207	3,2	0,31	262	0,6	0,12	163/1	2,0	0,08
49	1,4	0,06	101	5,9	0,28	151	4,7	0,51	208	6,8	0,58	266	0,4	0,08	165/2	3,1	0,11
50	1,9	0,19	101w	1,6	0,04	152	1,7	0,07	209	0,4	0,03	267	12,3	0,50	182/1	1,9	0,32
52	3,2	0,17	102	1,9	0,21	153	1,0	0,09	212	1,1	0,24	268	0,3	0,09	238/1	2,2	0,37
55	1,9	0,08	103	19,9	1,62	154	2,0	0,17	215	1,9	0,08	269	11,3	1,58	267/1	3,0	0,13
57	3,6	0,29	105	1,3	0,11	155	2,1	0,09	216	15,0	5,25	270	1,1	0,08			
58	5,0	0,53	106	2,0	0,31	157	0,5	0,10	218	0,2	0,05	271	2,4	0,07			
60	0,7	0,14	107	1,3	0,05	158	0,5	0,16	219	2,5	0,24	272	2,2	0,06			

A4 - ***Table 4*** Creatinine concentration ($g.L^{-1}$) in instantaneous urine samples

Id.N°	g,L^{-1}	Id.N°	g,L^{-1}	Id.N°	g,L^{-1}	Id.N°	g,L^{-1}	Id.N°	g,L^{-1}
11	1,37	68	2,18	117	1,64	167	1,73	239	0,93
15	1,28	73	0,90	118	2,39	172	1,94	240	0,90
16	0,54	74	1,79	120	1,61	175	2,03	244	1,43
19	1,07	76	1,76	121	1,64	181	1,34	247	1,52
23	1,91	77	0,99	122	1,76	182	1,79	258	2,09
25	0,90	79	1,61	123	2,21	196	1,76	259	1,34
27	1,04	80	0,54	126	1,52	200	0,99	260	1,52
28	1,46	81	1,67	127	1,01	201	0,93	261	1,88
30	0,84	84	1,37	128	1,49	206	0,81	267	1,46
31	1,19	86	1,25	130	1,91	207	2,18	270	0,48
33	1,76	89	1,52	131	1,37	208	0,39	271	0,81
34	1,16	92	2,87	134	2,33	209	2,00	272	0,87
39	0,75	96	1,58	139	2,66	218	2,27	273	2,45
40	1,73	98	1,61	141	1,58	219	1,46	274	1,22
41	0,90	99	1,64	147	1,34	220	1,01	275	1,37
43	1,85	101	1,13	144	1,91	223	1,55	276	0,87
45	3,01	103	0,81	151	1,88	224	0,87	277	0,75
52	0,39	105	1,04	153	1,97	227	1,16	278	1,10
55	1,10	106	1,01	154	2,48	231	1,13	280	1,85
57	0,99	107	1,22	159	2,03	232	1,40	281	1,31
58	1,37	107	0,69	160	1,49	234	1,10	282	1,91
60	2,57	110	1,91	161	1,91	236	2,18	283	2,00
61	3,76	112	0,36	162	0,99	237	1,16	284	1,19
63	1,46	115	1,19	163	0,75	238	1,31	285	0,87
65	1,04	116	0,84	165	0,90	238	1,31		

B1 - OBJECTIVES OF THE PRELIMINARY SOCIOLOGICAL INVESTIGATION

The objectives to be waited through the preliminary sociological investigation gather in 2 categories:

- Knowledge of the overall population sociology;
- Informations concerning individuals.

1 - Knowledge of the overall population sociology;

The location of the site using precise maps and, if it is possible, satellite pictures would be appreciated .

- THE VILLAGE AND ITS POPULATION :

- overview of the population : number of males, females , children; distribution of ages

- Description of the type of habitat:

How many households? How many people by household (mean)?

- Ethnic diversity

- Education: local school(s) ? levels ? number of pupils

- Infrastructure: sources of drinking water and of other water uses, hygiene and sanitation (toilets…), health facilities, sources of energy, market …..

- Political Authority: chief(s), assembly …..

-Types of activity: mining, farming (importance of agriculture and animal rearing in this area. Is there pesticides use in agriculture. Describe the proximity of rice fields.), trading,……

- ARTISANAL GOLD MINERS (AGM) COMMUNITY

- General description of this community: number, sex, age, other occupational activities, where do they live.

- Detailed description of the overall process of gold production; what is the role of each AGM operator in this process. Where does mercury amalgamation, burning, occur: in the field? In the household? or other? Is it a seasonal activity (dry and wet season), local organisation of gold and mercury market. Is there child labor.

Amount of mercury yearly used in the village, ratio gold/mercury for gold production in the different seasons.

- DIET HABITS

Type of food consumed. Fish consumption: Name the fish they consume regularly. List from the most consumed species to the least (try to obtain a % of each species consumed in each season).

2 - Informations concerning individuals.

See the individual questionnaire. This questionnaire must be filled for 150 to 200 individuals in the AGM site and 50 approximately in the control site.

B2 - QUESTIONNAIRE FOR THE SOCIOLOGIST

Name of interviewer:

Questionnaire for the sociologist

Small-scale gold mining and mineral processing

Introduction and Informed Consent
(Introduce yourself, explain the purpose of the interview and request consent to be interviewed)

Personal Data **ID Number:**

Surname of the particpant

First Name

Date of Birth **Age:**.....

Sex: ☐ Male ☐ Female

Status ☐ Living alone ☐ Married ☐ Number of wives??

Education level (to be defined by sociologist: (none, basic, primary, secondary?))

Number of children and dependants living in the house: …….

Chlidren or dependants name						
Sex						
Age						
Education level						

Address:……. *To be defined by the sociologist after 4 to 5 zones identification in the* ***village***

How long do you live in this area? **_____ year(s)**

Work Exposure

Detailed description of the job

____ Miner (in an industrial plant)
____ Artisanal gold miner (AGM)
____ Gold smelter (gold buyer)
____ Mercury seller
____ Farmer
____ Trader
____ Office Job
____ Driver
____ Other job.....

How long do you work as an artisanal gold miner (AGM)
Years

Who is working as an AGM

 yourself Spouse

Number of children: ….. Number of other dependants: …..

For how long do you work as an AGM (Years)

Yourself: ….. Spouse: …..

Child 1 : ….. Dependant 1: ….
Child 2: ….. Dependant 2: ….

Number of months per year of activity as an AGM

Yourself: ….. Spouse: …..

Child 1 : ….. Dependant 1: ….
Child 2: ….. Dependant 2: ….

2.6Occupation (Detailed description of the job)

- **Washing**
- **Sieving**
- **amalgamation**
- **Burning**

comments:.....

1.7 Do you handle mercury?

 Yes No Uncertain

1.8 Where do you get mercury for amalgamation and other inputs?

a) Gold Dealers
b) Spouse
c) Relative
d) Others (specify)

1.9 Are you aware of any health or environmental hazards that may be caused by mercury use in gold mining?

☐ Yes
☐ No

If yes, what are the hazards?

3 Diet Issues

How many times per week do you eat each of the following foods:

a) Meat
b) Fish
c) Chicken
d) Eggs
e) Milk
f) Rice
g) Vegetables
h) Fruits
i) Other (specify).....

4 Training

4.1 Have you received any training regarding your mining activities?

☐Yes ☐ No

Where……. What type of training ……..
Who facilitated the training? ……..
Has the training helped in your activities: ☐Yes ☐ No
How? ……

(The interviewer should read a short description of the improved mining technology and explain it if necessary)

4.2 What are your comments in case of the introduction of proposed improved mining and processing technology?

……
…
.....

4.3 Would you be willing to learn this technology?

☐Yes ☐ No

You will be questioned about your living circumstances and health problems related to mercury. you will be medically examined including neurological examination. Blood, urine and a small amount of hair nail will be taken.would you participate? ***Yes*** ***No***

Thanks for your cooperation, do you have any questions?

SUMMARY of the questionnaire

Name	
ID Number	

Sex of Respondent

Location (zone in the village)

Age of Respondent

Level of Education of Respondent

Residential Status (native/migrant)

Status (married…)

Number of children

Other Economic Activities Outside AGM

How long working as AGM

Persons working AGM in your house

Respondent Mercury Use Status

No. of times Respondent burns amalgam

Knowledge of hazards associated with exposure to Mercury

First source of Food

Second source of Food

Third source of food

Participation: Readiness to take Medical Exams

5-Jan-2004
Original: English

Assistance in assessing and reducing Mercury pollution emanating from artisanal gold mining in GHANA – Phase II

US/GHA/02/006

Part II - Assessment of mercury releases to the environment and proposal for monitoring these releases

Prepared by Mr Marc BABUT and Mr Ransford SEKYI

On the basis of the analytical work done by the LCABIE (Laboratoire de Chimie Analytique Bio-inorganique & Environnement), University of Pau (Pr Martine POTIN-GAUTIER, Ms Sylvaine TELLIER & Dr William BANNERMAN (University of Kumasi, University of Pau), and the technical help of the University of Montpellier I

Project Manager: Christian BEINHOFF (PTC/PEM)

United Nations Industrial Development Organisation Vienna

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Appendix

Sampling points locations in and around Gyapa (map + table)

Abstract

This study is part of the second phase of a project aiming at assessing human health and environmental impacts of mercury pollution due to artisanal gold mining in Ghana. While the first phase occurred in a typical village (Dumasi) where gold is extracted from hard rock, the second was realised in an area (Gyapa) where gold is obtained from alluvium. Sediment and fish samples were collected in several extracting sites around Gyapa; soil and vegetables (cocoyam roots) were sampled within and around the village. A few sediment and fish samples were also gathered at the Ankobra estuary. Analyses of mercury were done in Pau (basically total-Hg by CV-AFS; methyl-Hg was looked for in a few soil and sediment samples, and in all the cocoyam roots).

Sediments in the river system display variable mercury concentrations, from high to moderate levels. The sediments sampled in exploited pits are polluted, whilst mercury concentrations tend to decrease almost rapidly in abandoned pits. Soil contamination is more pronounced around amalgam distillation places. However, gold extraction related activities are not the only source of mercury in the area: some types of tropical soils may be naturally enriched; moreover, vegetation fires would increase the mercury content of topsoil, and its mobility through erosion accordingly. Food items (fish and vegetables) are also contaminated by mercury. Cocoyam roots mercury contents remain low, as compared to the soil concentrations. Although mercury concentrations in fish are most often less than safety limits fixed by WHO or US-FDA, the acceptable weekly (and daily) intake could be exceeded for certain species. There is also an evidence of large scale transport, leading to an accumulation of mercury in mangrove sediments in the Ankobra estuary. The contamination pattern appears more diffuse than in the hard rock gold mining site investigated during the first phase study. Thus sediments and fishes display lower mercury levels in Gyapa (phase II) than in Dumasi (phase I). This statement can be extrapolated with caution to other sites using the same processes.

Gold extraction in alluvium leads to major physical damages; when it is done in the river bed and the associated floodplain, it strongly disturbs the flow regime, and destroy habitats for invertebrates, fish and plants for quite a long time. Pits may also be dug directly in cultivated parcels. Therefore, gold extraction from alluvium affects also directly the food resources availability.

A monitoring program allowing to assess the mercury pollution due to artisanal gold mining is proposed for the whole auriferous region. This program should use sediment and fish as sampled matrices; the sampling campaigns would occur at the end of the dry season. Some preliminary studies should accompany the program, in order to determine mercury background concentrations and to select the fish species to sample.

The introduction of appropriate technology such as retorts would contribute to decrease mercury releases to the environment, but would not eliminate them. Other approaches, e.g. education, or fish farming, could also help to decrease the environmental impacts of artisanal gold mining.

INTRODUCTION

In the year 2000, a study of the environmental impacts of artisanal gold mining at a pilot site was carried out in Dumasi (Ghana, Western Region) (Babut *et al.*, 2001). This pilot site is among others characterised by a typical process, based on solid rocks brought back to the village, then crushed, and afterwards treated by gravity concentration and amalgamation. Therefore, it appeared difficult to extrapolate the conclusions to regions where the typical process used is different, in particular when based on alluvium digging. Following the presentation of the findings and conclusions in April 2001, it was thus decided to carry out a second phase study focusing on an alluvial area.

The site of Gyapa (Western Region) was selected on several criteria: year-long exploitation, accessibility, cooperation of the population. It is located about 70 km from Tarkwa, on the road to Dunkwa (Figure 1). The village is built on a plateau (alt. 450m) overhanging two different river stretches. The Yaya river is flowing on the northern side of the plateau, while the Akoma Kofi river originates on the eastern side of the village, and flows to the south. Digging sites are located throughout the area, either along the Yaya river or its tributaries such as the Buosim river, or other rivers such as the Subin river (see map in annex).

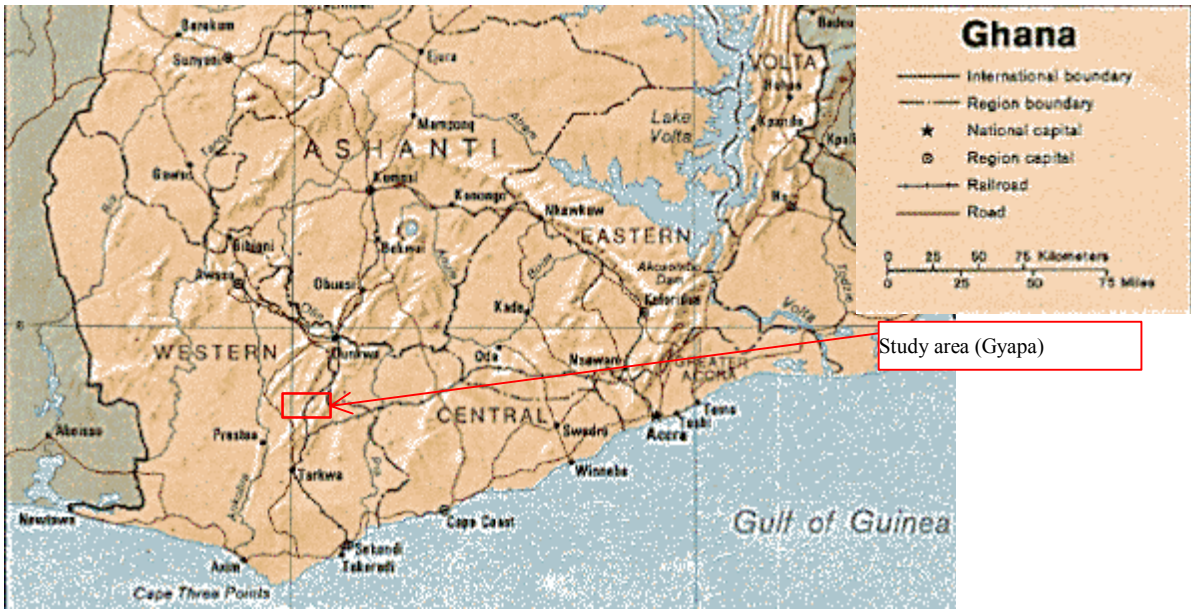

Figure 1 – Map of South-Western Ghana including the study area

Gold washers dig large pits in the alluvium and/or floodplains along the river. They wash the cobbles and gravels on sluice boxes, where they collect either gold nuggets or powder concentrate gathered on hemp tissues. This concentrate is further processed by amalgamation.

I.A Objectives of the study

The study's objectives, as expressed in the terms of reference of the mission, were twofold:

(a) Investigate situation of the environment around an alluvial gold mining site, take samples where pollution can be assumed. Specifically, assess the nature and extent of the mercury pollution in a selected river system and adjacent (agricultural) sites.

(b) Discuss all the issues related to the objective of introducing and setting up a monitoring system for continuous water quality assessment.

II ASSESSMENT METHODOLOGY

II.A Strategy

According to the sociologist study done prior the current assessment (Tsekpo, 2002), the amalgamation process is done in Gyapa either close to the sluice boxes or in the village. In the latter case, the concentrate is brought back to the village with water. This means that two separate contamination pathways can be distinguished and should be accounted for in the sampling strategy: (i) release of mercury in the pits, at the amalgam washing / squeezing and/or burning steps; (ii) diffusion by evaporation and further deposition on soil in the village. Moreover, soils will be washed during the rainy season, and runoff will transport contaminated soil particles. These particles could then contaminate other soils, and return to the river system. As the first phase study had shown a rather high concentration of mercury in one sample of cocoyam root (Babut *et al.*, 2001), this kind of vegetable should also be collected where soils would be sampled. These pathways and the kind of samples collected around Gyapa are shown on the diagram at Figure 2.

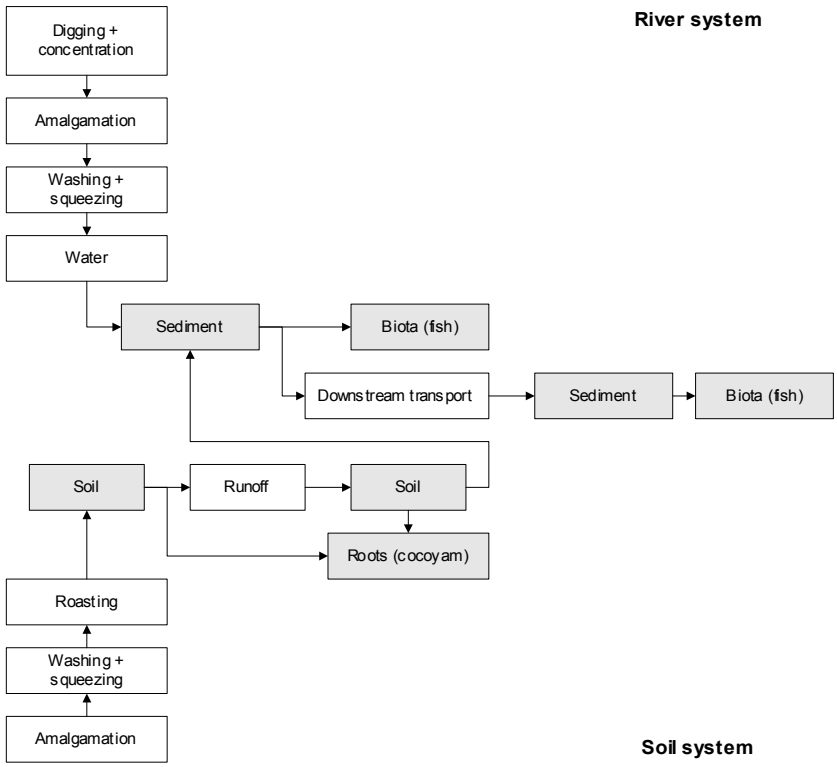

Figure 2 - Mercury diffusion pathways in Gyapa

Grey boxes designate the types of samples collected at various step of the contamination and diffusion process.

The atmospheric pathway could also be important. Further deposits on leaves is possible, followed by absorption into the shoots (Boening, 2000; Melieres *et al.*, 2003). Thus human (or wildlife) exposure to mercury could occur through leaves consumption[1]. However, leaves samples would be difficult to keep in appropriate condition before their analysis. Therefore, it was decided not to sample leaves. The issue of the extent of mercury atmospheric transport in the surroundings of *galamseys* sites remains pending and should probably be addressed through a research approach, rather than through a survey such as the study described herein.

Therefore, according to our comprehension of the diffusion pathways in Gyapa area (Figure 2), the sampling program focussed on sediments, fishes, soils and roots of selected vegetables. Sediments should be seen here either as a sink of mercury or as a signature along transport pathways. For all samples, the sampling program has to include a few reference (upstream) samples, and on-site and downstream samples accordingly.

[1] Leaves of specific vegetables are used in some local recipes

A few samples (mainly sediments) were also collected out of the study area; they were collected quite far downstream. Their number is obviously not sufficient to give an overview of mercury contamination in the whole catchment, but will provide an insight on long range transport. The sampling program is summarised in Table 1; the locations figure on the map in Appendix.

River	*Site name*	*fish (fillet)*	*sediment*	*soil*	*vegetable(root)*
Akoma kofi	old pits Gyapa	1	2		
	soil Gyapa (reference ?)			1	
Ankobra	estuary, left bank		1		
	estuary, right bank	2	1		
Buosim	river		1		1
	river, pits	1	1		
Esheri	bridge - tarred road		1		
Subin	old pit,		1		
	pit, down the main road,		1		
	pit,		1		
	pit/river	1	1		
	bridge	1			
	upstream mining site		1		
Yaya	downstream Yaya river	1	2		
	field - Gyapa	1	2		2
	Gyapa village			5	3
	pits Gyapa		1		
	pits upstream pits	1	1		
	upstream reference site		1	1	1
Total		*9*	*20*	*7*	*7*

Table 1 - Summary of the sampling program

II.B Sampling protocol

The geographic coordinates were taken at each sampling site with a GPS device (GPS76, GARMIN, Olathe, Kansas, USA).

II.B.1 Sediments

At each site, fine grain sediments (≈ 5 cm thick) were collected in several places with a shovel and put in a bucket. Vegetal debris and cobbles were removed and the sediment was gently homogenised. Then about 250 ml were taken in a plastic bottle with a double cap and frozen.

II.B.2 Fishes

Fishes were captured by various methods, depending of environmental (physical and hydrological) conditions. In alluvial mining surroundings, fishes are supposed to live in the ponds formed in the pits. So in that case the water in the pits was pumped almost

completely, and the fishes caught by hand or with a wicker basket. When the fishes were to be captured in less disturbed river courses, wicker traps were placed 1 or 2 days in advance in the river bed. The few fishes collected in the Ankobra estuary were caught with nets by local fishermen.

Fishes were dissected within a few hours after capture, and a few grams of dorsal muscle was sampled and kept in plastic bags (suitable for food conservation) and frozen.

II.B.3 Soils

The first 1-2 cm of top soils were grasped in several places of each site; cobbles, small rocks and plant debris were removed, and the soil carefully mixed until the heap became homogenous. Then it was divided in 4 parts. 3 of them were discarded; the remaining part was again divided, in 2 to 4 part depending of the available quantity. Again 1 part was taken, packed in a plastic bag and frozen.

II.B.4 Vegetables

According to the conclusions of the Dumasi's study (Babut *et al.*, 2001) and to further analyses on a range of plants in the Ankobra catchment (Bannerman, 2003), the sampling focused on cocoyam tubers. They were gathered at various places in the village and close to the mining area, in order to reflect possible pathways of mercury; as far as possible, they were collected close to soil sampling sites. Then the roots were washed with tap water followed by de-ionised water and frozen in plastic bags.

II.C Analytical methods

All samples were processed and analysed at LCABIE (Analytical Bioinorganic & Environmental Chemistry Laboratory) in Pau University (France).

II.C.1 Samples preparation

II.C.1.1 Soils

Masses between 50-100g of samples were freeze – dried, hand ground in porcelain mortar with pestle and preserved in clean water-tight screw-capped polypropylene containers (POLY LABO sterilised). About 0.5 g of the dried sample was weighed into the sample holder of a microwave digester (PROLABO 301) and digested according to the following six-step automated digestion programme using concentrated HNO_3, HCl and HF (MERCK Suprapur):

STEP	1	2	3	4	5	6
REAGENT	HNO_3	HCl	HF		HCl	WATER
SPEED 1/10	10	10	8		10	10
VOLUME ml	6	5	15		3	40
POWER %	10	20	20	85	15	35
TIME mn.	5	5	5	20	10	10

Table 2 - Soil sample pre-treatment protocol

The digested solutions were diluted to 100ml with deionised water (Milli-Q). Further dilutions were made with reagent blank prior to the Cold Vapor-Atomic Fluorescence Spectrometric (CV-AFS) analysis.

II.C.1.2 Sediments

The samples were freeze - dried, hand ground and preserved in clean water-tight screw-capped polypropylene containers (POLY LABO sterilised). About 0.25 g of the dried sample was weighed into the sample holder of a microwave digester (PROLABO 301) and digested according to an automated digestion programme summarised in Table 3.

STEP	1	2
REAGENT	HNO_3	H_2O_2
VOLUME ml	8	2
POWER %	10	10
TIME min.	5	5

Table 3 - Sediments pre-treatment protocol

The digests were diluted to 50ml with Milli-Q water. Further dilutions were made with reagent blank prior to the Cold Vapour-Atomic Fluorescence Spectrometric (CV-AFS) analysis.

II.C.1.3 Fishes

About 100 mg of the homogenised dry fish is weighed into an extraction tube and digested in an open focused 200W microwave system (MICRODIGEST 301 PROLABO) using the three – step programme described in Table 4. Excess KMnO4 may be removed after the digestion by addition of a few drops of hydroxylamine chloride. The obtained digest is diluted with Milli-Q water in a 25 ml volumetric flask.

STEP	I	II	III
REAGENT	*Aqua regia*	H_2O	5% $KMnO_4$
VOLUME (ml)	3	5	2
POWER (W)	40	0	40
TIME (min.)	5	0	5

Table 4- Pre-treatment of fish samples

II.C.1.4 Vegetables

Vegetable samples were peeled (when necessary) on the field, washed successively with tap water and then with Milli-Q water, chopped with plastic knives, placed in double zip-lock bags and kept frozen. They were then freeze-dried, ground in suitable clean mortars and kept refrigerated in polypropylene air-tight bottles until analysis.

Between 100 mg and 200 mg dried homogenised vegetable sample is weighed into a microwave sample tube and digested according to the program summarised in Table 5. Then ultra-pure water to 25 ml is added up to the necessary volume in a volumetric flask.

STEP	1	2	3
REAGENT	HNO_3	-	H_2O_2
QUANTITY (ml)	5	-	3
POWER (%)	40	0	40
TIME (min)	5	5	5

Table 5 – Vegetables pre-treatment protocol

II.C.2 Total mercury analysis

The pre-treatment procedures described earlier ensures that all mercury is present in solution as Hg^{2+}. Total mercury is determined by the cold vapour – atomic fluorescence technique (CV – AFS) using the continuous flow approach. The procedure involves an online reduction of Hg^{2+} to Hg^0 vapour by $SnCl_2$. Typically, the reductant is 5%m/v $SnCl_2$ in 15%HCl. The mercury vapour is swept by argon as carrier gas to the AFS detector (Merlin PSA 10.023).

Various sample matrices are analysed using reagent blanks which are basically in the same chemical media as the analyte in the respective sample solutions. Measurements were controlled by the Touchstone ® control software.

The analytical performances of the procedures employed were assessed for linearity, limits of detection and accuracy and precision of the analytical measurements. The analyses were done in dust-free rooms meant for trace metals. The reference materials used for the accuracy assessment include NIST SRM 2709 San Jaoquin Soil, NIST SRM

2710 Montana Soil and BCR RM 320 River sediment. Recoveries were higher than 95%. For other types of samples, the reference materials were GBW 08508 rice and BCR 464 fish. Recoveries were also satisfactory.

II.C.3 Methyl-mercury analysis

In most fishes, 90% or more of the total Hg is methyl-mercury (USEPA, 1999); therefore, in the context of this study it is useless to analyse this species in fish muscles. As little is known on methyl-mercury content in vegetables[2], it seems preferable to focus on root and soil samples, in order to get an estimation of possible pathways and transfer rates.

A few sediment samples were also analysed for methyl-mercury (Me-Hg), although there is no simple direct relationship between the sediment content and fish contamination in general.

The first step of the analysis of Me-Hg in sediments involves the extraction of that species and Hg^{2+} from the sediment by an open microwave method. Approximately 1 g of homogenised dried material is weighed in the vessel; 10 ml of nitric acid (6M) is then added and exposed to microwave irradiation at 60 W for 3 mn. The obtained solution is cooled to room temperature, transferred to a 15 ml tube and centrifuged at 5000 RPM for 5 mn. The supernatant is kept refrigerated in a Pyrex ® with a Teflon cap till analysis. The analysis itself is done following the ethylation- cryogenic trapping - gas chromatography - atomic fluorescence spectrometry (ET-CT-GC-AFS) procedure. In this procedure, the first step consists of a derivatization of the mercury species with sodium borate tetraethyl. The gas chromatography step yields 3 peaks, namely Hg^0 (blank), ethyl-Me-Hg corresponding to the former Me-Hg, and ethyl-Hg from the initial Hg^{2+}.

A very similar procedure was used for vegetables; operational details are given in W. Bannerman's thesis (Bannerman, 2003).

[2] a quick search on Science Direct provided 0 response.

III RESULTS

III.A Sediments and soils

Sample	*River*	*Site name*	*Total Hg*
SE1	Yaya	field - Gyapa	55.0
SE2	Yaya	pits Gyapa	106.0
SE3	Yaya	pits Gyapa	583.5
SE4	Akoma Kofi	old pits Gyapa	24.0
SE5	Akoma Kofi	old pits Gyapa	<5
SE6	Subin	upstream Subin	<5
SE7	Subin	pit, Subin	40.5
SE8	Subin	pit/river Subin	183.5
SE9	Subin	pit, down the main road, Subin	166
SE10	Subin	old pit, Subin	18.0
SE11	Esheri	bridge - tarred road	88.0
SE12	Yaya	downstream Gyapa	1102
SE13	Yaya	downstream Gyapa	569
SE14	Buosim	Buosim river	<5
SE15	Buosim	Buosim river, pits	18.0
SE16	Yaya	pits Yaya (upstream pits)	3021
SE17	Yaya	Yaya upstream reference site	780.5
SE18	Ankobra	Ankobra estuary, right bank	1578.5
SE19	Ankobra	Ankobra estuary, left bank	1691.5

Table 6 - Mercury concentrations in sediment samples (µg.kg^{-1} dry weight)

The recoveries of both soil and sediment certified samples were higher than 95%; measured values were in accordance with the target values.

Mercury concentrations in sediments appear quite variable in the field; the contaminant can not be detected in several abandoned pits along the Akoma Kofi river. There is evidence of downstream transport throughout the catchment (cf. Esheri, Ankobra estuary); the sample collected in the Esheri river could not be taken in a deposition area, and contained some clay from the bank, so the concentration may be underestimated.

Surprisingly, the mercury concentration in the sediment collected upstream the Yaya river seems rather high.

Index	*Site*	*Total Hg*
SO1	Gyapa village	1932.0
SO2	Gyapa village	2697.5
SO3	Gyapa village	1397.5
SO4	Gyapa village (10 meters away from SO3)	22935.5
SO5	Gyapa village	9301.0
SO6	Gyapa (supposed reference)	837.0
SO7	Yaya upstream reference site	1303.5

Table 7 - Mercury concentrations in soil samples (µg.kg^{-1} dry weight)

Mercury concentrations in soils appear quite variable, at a meter scale: SO3 and SO4 samples were collected in two yards distant of 10 meters from each other. The two samples supposed to be reference soils, i.e. away from amalgam burning, display Hg concentrations between 800 and 1300 µg.kg^{-1}.

Five sediment samples (SE4, SE8, SE13, SE18 and SE19) were analysed for methyl-mercury (MeHg); they ranged between 3 and 5 ng.g^{-1} (dry weight). Moreover, MeHg was measured in three soil samples (SO2, SO5 and SO7). The concentrations were 5, 4 and 4 ng.g^{-1} respectively.

In both cases, there was seemingly no relationship between MeHg and total Hg concentrations.

III.B Fish

Code	*Common name*	*Local common name*	*Length (cm)*	*Hg total (dw)*	*std dev*	*Moisture %*	*Hg total (ww)*	*std dev*
F1/1	mudfish	adwen	16.0	1.233	0.08	81.1	0.23	0.02
F1/2	mudfish	adwen	17.5	0.626	0.05	80.2	0.12	0.01
F2/0	mudfish	adwen	31.0	2.758	0.20	80.3	0.54	0.04
F3/1	mudfish	adwen	12.5	1.831	0.07	82.6	0.32	0.01
F3/2	mudfish	adwen	14.5	1.675	0.03	80.6	0.32	0.01
F4/0	mudfish	adwen	49.5	1.931	0.10	78.5	0.42	0.02
F5/0		kwafon	18.7	2.413	0.09	81.2	0.45	0.02
F6/1	mudfish - black	adwen	17.5	1.935	0.10	76.4	0.46	0.02
F6/2		kwafon	14.5	4.441	0.16	83.1	0.75	0.03
F7		kwafon	nm[3]	2.860	0.11	80.6	0.55	0.02
F7/1		kwafon	18.0	2.629	0.14	80.4	0.52	0.03
F7/2	mudfish	adwen	17.0	2.024	0.09	83.1	0.34	0.02
F8/0		nsumpu	21.2	0.960	0.05	78.3	0.21	0.01
F9/2	grey mullet	msamba	13.0	0.223	0.01	78.1	0.05	0.00
F9/1	grey mullet	msamba	17.0	0.182	0.04	77.4	0.04	0.01

Table 8 - Mercury concentrations in fish samples (µg.g^{-1})

Except the 3 specimen caught in Ankobra estuary, contamination of fish muscle is comprised between 0.12 and 0.75 µg.g^{-1}. There is no obvious relationship with fish size (data not shown).

Mean concentrations in *kwafon* are higher than in *adwen.* Nevertheless, according to a Student test, total mercury mean concentrations in both species are not significantly different at p = 0.01.

[3] Not measured

III.C Vegetables

Code	*Site name*	*Hg dw*	*SD*	*Moisture (%)*	*Hg ww*	*SD*
RV7	Yaya upstream reference site	19	1.00	71	5.51	0.29
RV1	field - Gyapa	112	18.00	93	7.84	1.26
RV3	Gyapa village	27	2.00	68	8.64	0.64
RV4	Gyapa village	127	7.00	94	7.62	0.42
RV5	Gyapa village	111	9.00	82	19.98	1.62
RV2	field - Gyapa	19	1.00	58	7.98	0.42
RV6	Buosim river	30	2.00	89	3.30	0.22

Table 9 – Total mercury concentrations in cocoyam roots (µg.kg^{-1})

Although about 1000 times lower than concentrations in sediments and fish, total Hg concentrations in cocoyam roots are non negligible, and show evidence of transfer from the soils to these vegetables.

MeHg was measured in the seven cocoyam roots samples. It was lower than the detection limit in all of them.

IV DISCUSSION

IV.A Alluvial mining, an ecological disaster

Alluvial mining strongly disturbs the physical characteristics of the environment. Miners do not care about water discharge; they are just looking for a place to dig, and manage the flow according to their own needs – not too much water in the pit, just enough for washing the gravels – (Figure 3, part a). At a wider scale (Figure 3, part b), the discharge becomes thus completely erratic. Accordingly, habitats for fish and invertebrates are strongly disturbed: as a consequence of the excavations, which modify the depth and the slope of the banks; as a consequence of the flow regime disturbance; and because of the deposition of fine clay particles instead of organic matter-rich sediments. Food availability is also reduced, because excavations destroy the vegetation cover and aquatic macrophytes, reducing the amount of organic matter (plant detritus etc.) available for invertebrates and omnivorous fishes. Carnivorous fishes would also be affected indirectly.

Not surprisingly, it was quite difficult to get some fishes in that system. All the specimens we got were from the same species, and they seem quite rare.

a) active pit

b) alluvial field North Gyapa

Pictures by A. Rambaud

Figure 3 - View of a digging zone close to Gyapa

It was out of the scope of our mandate to assess this kind of ecological effects, and the means involved were not appropriate for assessing them either qualitatively or quantitatively. Nevertheless, impacts are obvious, and are certainly also of concern for villagers, as rivers are an important food source for them. Moreover, the durability of these physical impacts would certainly be interesting to study: pits remain visible quite a long time after being abandoned, and the flow regime also remains disturbed.

Aside ecological impacts due to mercury releases, there is therefore a dramatic impact of artisanal mining, which affects both the biodiversity and the biomass in the aquatic ecosystems all over the area.

IV.B Mercury impacts in Gyapa area

IV.B.1 Bed sediments

The picture of sediment mercury contamination in Gyapa area appears somewhat confused. When comparing the results (Table 6) to either the tentative background concentration (100 $\mu g.kg^{-1}$) or the "threshold effect concentration" (180 $\mu g.kg^{-1}$) used in the Dumasi study (see Babut *et al.*, 2001) for details), it appears that some sediments are contaminated or highly contaminated, while others, sometimes sampled close to the previous ones, are not. Moreover, the supposed reference site in the Yaya river catchment belongs to the contaminated subset. Thus, the contamination gradient along the Yaya river is less than obvious (Figure 4-a), while it is more apparent in the case of the Subin river (Figure 4-b). The latter samples however were collected in pits rather than in the river, which was no more distinguishable at the time of sampling.

a) Yaya river **b) Subin river**

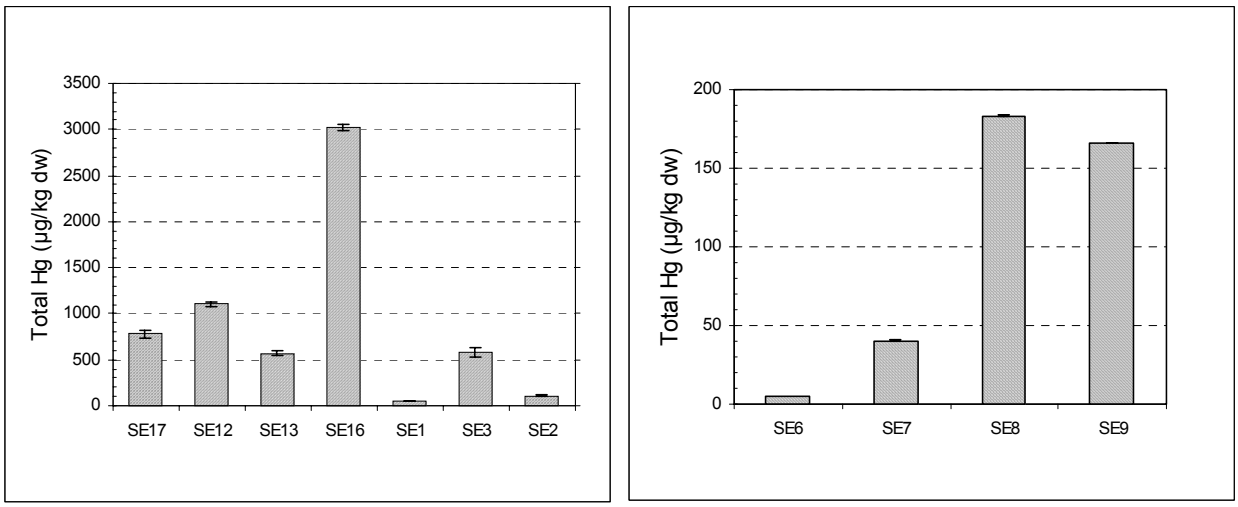

Figure 4 - Total Hg in river and pit sediments

SE17, SE12, and SE13 were taken in the Yaya river itself (up- to downstream order from left to right); SE16, SE1, SE2 and SE3 were collected in pits. Note that on graphs (a) and (b) Y axis scales are very different.

Sampling in pits was also done in order to assess the durability of mercury contamination in these environments. Figure 5 clearly shows two subsets: all abandoned pits (on the left side of the figure) display low mercury concentrations, while pits still in activity (right side) display variable but rather higher concentrations. This suggest that mercury concentrations decrease rapidly when the pits are no more exploited. It can probably be assumed that most of the mercury initially lost in the pits is transported downstream associated to fine particles. Most of this transport may even occur during the exploitation phase itself, whilst the connection to the river is not systematic when the pits are abandoned.

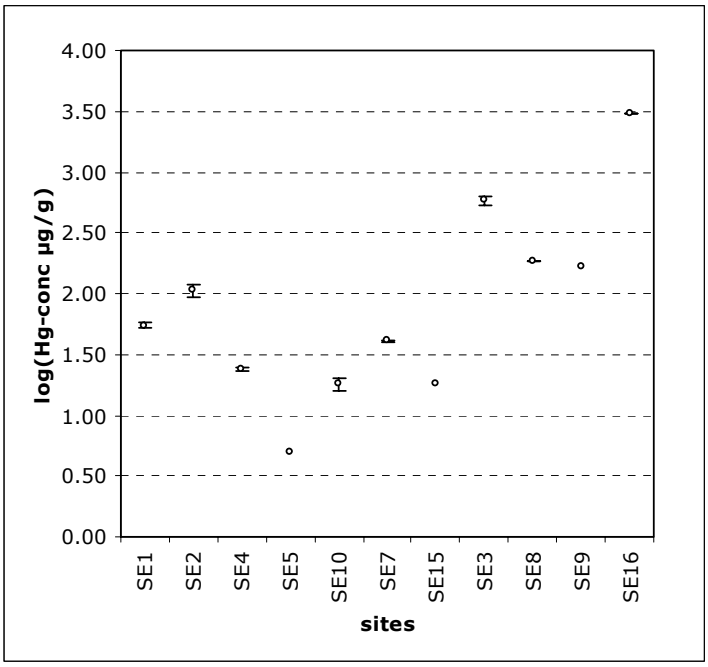

Figure 5 - Total Hg in pits

Error bars correspond to the standard deviation of measurements.

IV.B.2 Fishes

There is seemingly no relationship between fish tissue and sediment mercury concentrations from the data collected in this study. Fishes are exposed to mercury either in their habitats (fish living at the bottom of the river) or through food (species feeding on sediment, or on invertebrates, other fish species etc). Thus, depending on their way of life, fish species will be more or less directly exposed to mercury from sediment. Furthermore, the food exposure pathway is of more concern than the exposure within the habitat, at least for fishes. It is usually assumed that the most contaminated species are carnivorous species (Bidone *et al.*, 1997; Castihos *et al.*, 1998; Fréry *et al.*, 1999).

Two different species were caught in Gyapa area: *adwen* (local name for a kind of mudfish) and *kwafon* (Muggilidae). Both are omnivorous, the former feeding more on shellfishes and fin-fishes and the latter, a pelagic fish, on insects and other invertebrates in the water column (Water Research Institute in Accra, personal communication). Therefore, it could be expected that *adwen* fishes would be more exposed than *kwafon*; our data do not confirm this hypothesis (III.B), but the number of samples is indeed too small for testing it.

IV.B.3 Soils

Soils in the village and its surroundings are extensively contaminated. Unlike sediments, none of the samples displayed non measurable mercury (Table 7). The less contaminated soil (0.837 $mg.kg^{-1}$) was collected in the village itself, on the plateau's edge upstream the Akoma Kofi river. This value cannot be considered as a reference value, because it may be influenced by atmospheric deposition of mercury following amalgam distillation in the village. Conversely, many tropical soils naturally contain high levels of mercury (Roulet *et al.*, 1999). So apart the samples collected in the vicinity of burning places it may be difficult to interpret the mercury concentrations in soils without a thorough knowledge of the typical mercury concentrations in different types of soils. This knowledge is not currently available for Ghanaian soils.

The concentration measured at the remote site upstream the Yaya river seems surprisingly high; it is as high as those in samples collected around burning places. There is however no clear-cut indication that such a high concentration (also observed in sediment and vegetable samples collected nearby) is due to mercury issued from gold extraction. Forest fires in tropical environments are a known source of mercury enrichment (Meech *et al.*, 1997); so the seemingly high concentration observed at that point might also be linked to fires lighted by farmers in order to clean land prior to seeding a field; indeed, the place where this sample (SO7) was collected had been burnt recently.

Contamination of soils near places where amalgam is distilled range between 1.4 and 22 $mg.kg^{-1}$. These values compare well with published data on soils affected by gold extraction (e.g. (Pestana et Formoso, 2003; Ramirez Requelme *et al.*, 2003), and are clearly above mercury concentrations in non-affected tropical soils (0.23 – 0.40 $mg.kg^{-1}$ in Amazonian soils, (Lechler *et al.*, 2000).

The contaminated soil particles may be transported away from amalgam distillation sites either as dust by the wind, or by runoff in case of rain. One sediment sample (SE3) was collected at the lower end of a runoff pathway; according to the mercury concentration measured in that sample, it belongs to the group of contaminated sediments. Although this concentrations is lower than those of soil samples collected around the upper end of the same pathway (Figure 6), it can be assumed that mercury is exported from the soils in the village to the adjacent river system, confirming our initial hypothesis (II.A; Figure 2).

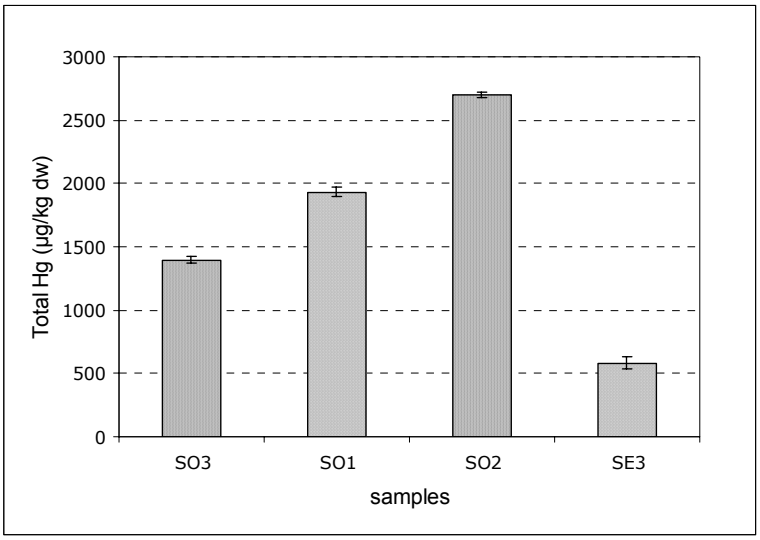

Figure 6 - Total Hg in a soil-sediment system at Gyapa

IV.B.4 Vegetables

At four different sites throughout the village, soil and cocoyam roots were collected close to one another (see Table 1; SO1/RV3, SO2/RV4, SO5/RV5, SO7/RV7). As it can be seen on Figure 7, there is an obvious relationship between Hg contents in vegetables and in soils. However, the corresponding uptake is rather low, as the concentrations in the roots are about 400 times smaller than those in the corresponding soils.

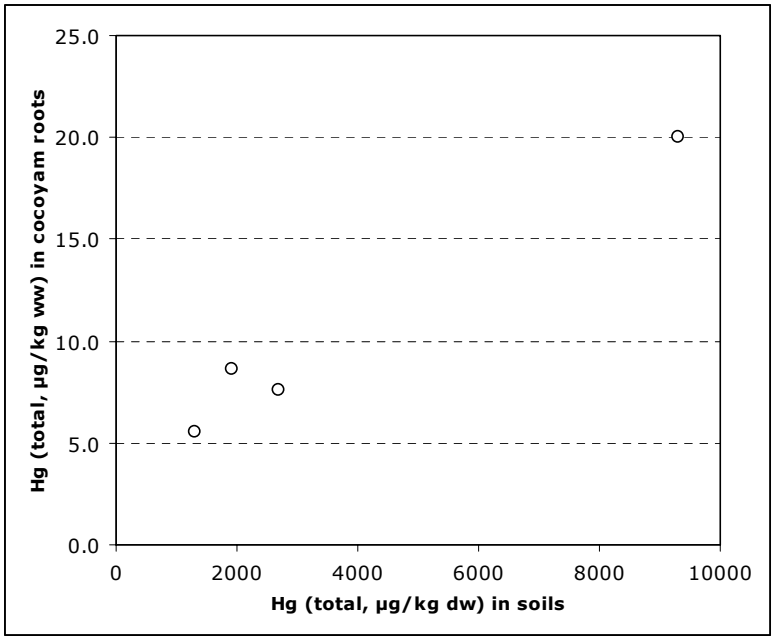

Figure 7 – Relationship between soil and cocoyam roots samples

IV.C Mercury downstream transport throughout the Ankobra catchment

The two samples (*SE18*, 1578.5 mg.kg^{-1}; *SE19*, 1691.5 mg.kg^{-1}) collected in the estuary (upstream the section subject to tidal influence) are among the most contaminated sampled during this study. In the meantime, the only sample obtained in a reach downstream the study area (SE11, Esheri river) did not show any evidence of contamination, as the total mercury content of this sample is below the supposed background concentration. However, the place where this latter sample was taken is not a depositional area, and some clay from the river bank was probably present in the sample, diluting the sediment and lowering the mercury concentration.

Nevertheless, our measurements in the estuarine sediments fit quite well with W. Bannerman's findings (Bannerman, 2003). According to his results, most of mercury inputs upstream Prestea originate from artisanal gold mining, whereas both artisanal and former industrial mines are responsible for the observed contamination downstream Prestea till the estuary.

The mercury concentrations measured in the two estuarian sediments are indeed among the highest in our dataset; this does not necessarily means that these sediments cause a hazard to the estuarian environment as the mangrove can be seen as a trap or a physical and biogeochemical barrier to metal contaminant transport (Machado *et al.*, 2002). However, there no certainty that these sediments would remain in place in case of high flow.

Only two fishes could be sampled in the mangrove, and they did not display worrying mercury concentrations. However, this is insufficient to conclude about the transfer of mercury from sediments into food webs, mainly because of the sample size.

In summary, there is indeed a concern and a need for further researches with the very high level of mercury in these estuarine sediments. The potential impact on shellfishes, and more generally on food webs (including humans) should be assessed in the area, and the fluxes to the coastal system as well.

IV.D Human exposure through the diet

According to the World Health Organization (WHO), concentrations higher than 0.5 µg.g^{-1} may be dangerous, in particular for pregnant women or children (FAO and WHO, 1999). This safety limit was exceeded by three fish samples (F6/2, 7/0 and 7/1) only. Moreover, none exceeded the Food and Drug Administration (FDA) action level of 1.0 µg.g^{-1}. Interestingly, all the specimens which exceeded the WHO limit were of the same species (*kwafon*); they were caught in the Buosim river (F6/2) and close to the most upstream pits in the Yaya river (F7). The concentrations of mercury observed in Buosim sediments were rather low, but the number of samples (whatever the kind) remains low. So it

seems very difficult to relate the observed concentrations in fish either to sediment contamination or to the local geography of gold extraction. Indeed, the pits are dug until people do not find any more gold, then rapidly abandoned; therefore, the use of mercury in any pit is rather transient, and spread over quite large areas. This pattern is very different of that observed in Dumasi, where gold extraction was occurring in relatively limited areas, even though the "sluice boxes" were not permanent installations.

The typical food ration is unknown to us neither for Gyapa population, nor in Ghana; so, instead of assessing the risk associated to food, we only calculated the quantity of each type of food necessary to obtain the ADI of about 43 $\mu g.d^{-1}$ recalculated from a weekly intake of 300 µg of total mercury, according to WHO (WHO, 1989). According to our results, this amount is obtained on average[4] either with about 75 g to 125 g of fish per day, depending of the species. It would need 4.9 kg of cocoyam daily to reach this value.

IV.E Comparison with the phase I study (Dumasi)

The comparison with the contamination pattern in Dumasi (Babut *et al.*, 2001) is obviously needed, as an important conclusion of this previous study was that probably the contamination was different in an alluvial area. Due to the respective numbers of samples available, the comparison is only possible for sediment and fish.

IV.E.1 Sediment contamination patterns in the two study sites

Prior to that comparison, the supposed reference sites were removed from the datasets. Although the comparison of variances prohibits any statistical comparison between the two subsets, it appears obvious that the Dumasi sediments are much more contaminated than those from Gyapa (respective means 15.97 and 0.399 $\mu g.g^{-1}$).

At the end of the first phase study (Dumasi), it was recommended to study an alluvial site, where it was expected a higher consumption of mercury and higher concentrations in sediments accordingly. The underlying assumption was that Dumasi miners allocated a large amount of their time to crush the ore, while alluvial miners would wash the gravels directly and spend more time on amalgamation. Although this assumption is probably true, the fact that at Gyapa an undetermined part of the gold is present in alluvium as nuggets probably incline miners to use less mercury.

The reduced contamination in Gyapa as compared to Dumasi may also be related to the fact that sluice boxes are very mobile in Gyapa, being moved as pits are displaced along, while in Dumasi the sluice boxes are moved in a narrow area along the river. Therefore

[4] The calculation was made on the basis on mean concentrations, rather than maximum values. The latter would have been a worst case estimate, whilst using the mean accounts for the fact that people pick up their food all over the area, and thus are exposed to a range of concentrations.

the mercury emission pattern is rather diffuse in Gyapa, while it is closer to a point source in Dumasi.

IV.E.2 Fish contamination patterns in the two study sites

According to a Student t test, fishes from the first phase study (Dumasi) are significantly more contaminated than those of the second phase ($p=0.01$). Again this suggests a different contamination pattern between the two sites, and accordingly a higher fish exposure in Dumasi. Fish feeding habits may also contribute to the observed difference. As a consequence, the population will be more exposed to mercury through their diet in Dumasi than in Gyapa.

Can these findings be extrapolated to other villages in Ghana? In other words, would it be possible (i) to infer that mercury contamination of the environment is more pronounced in hard rock processing sites than in alluvial ones, and (ii) to consider that in general populations from villages where gold is obtained from hard rock would be more exposed to mercury from their environment than populations from places where gold is extracted from alluvium?

(i) Because the design of the sampling program focused on the transport pathways, it can be estimated that mercury pollution from alluvial processing sites is more diffuse than from hard rock processing sites, leading to lower average concentrations.

(ii) If one considers that these villages are typical of these kinds of processes, the response should be yes. But we would also like to warn against any misunderstanding of this statement, for at least two reasons. First, if gold washing is applied in hard rock processing sites on more extended areas than in Dumasi, the exposure through the environment would probably decrease to a certain extent. Second, some fractions of the populations in alluvial processing sites may be as exposed as populations from hard rock processing sites. Thus, it should not be inferred that alluvial mining is safer than hard rock mining from the viewpoint of exposure from the environment.

IV.F Summary of findings

- There are several lines of evidence of mercury pollution related to alluvial mining around Gyapa:
  - Sediments in the river system display variable mercury concentrations, from high to moderate levels. The sediments sampled in exploited pits are polluted, whilst mercury concentrations tend to decrease almost rapidly in abandoned pits.
  - Soil contamination is more pronounced around distillation places. However, gold extraction related activities are not the only source of mercury in the area: some types of tropical soils may be naturally enriched; moreover, vegetation fire would increase the mercury content of topsoil, and its mobility through erosion

accordingly.

- There are two pathways involved in environmental contamination in that village, i.e. release of mercury directly in pits and on soils; in that case, runoff brings a part of mercury back to the river system.

- Food items (fish and vegetables) are also contaminated by mercury. Cocoyam roots mercury contents remain low, as compared to the soil concentrations. Although mercury concentrations in fish are most often less than safety limits fixed by WHO or US-FDA, the acceptable daily intake could be exceeded for certain species.
- There is also an evidence of large scale transport, leading to an accumulation of mercury in mangrove sediments in the Ankobra estuary.
- Provided Gyapa can be considered as a typical alluvial gold mining site, the contamination pattern appears more diffuse than in the hard rock gold mining site investigated during the first phase study. Thus sediments and fishes display lower mercury levels in Gyapa (phase II) than in Dumasi (phase I). This statement can be extrapolated with caution to other sites using the same processes.
- Gold extraction in alluvium leads to major physical damages; when it is done in the river bed and the associated floodplain, it strongly disturbs the flow regime, and destroy habitats for invertebrates, fish and plants for quite a long time. Pits may also be dug directly in cultivated parcels. Therefore, gold extraction from alluvium affects also directly the food resources availability.

V A PROPOSED FRAMEWORK FOR MONITORING THE MERCURY POLLUTION IN THE CONCERNED CATCHMENTS

According to the available international experience (UN-ECE, 1996), monitoring should be viewed as a cycle starting from the information needs (Figure 8). The different steps of this cycle are briefly reviewed in the following paragraphs.

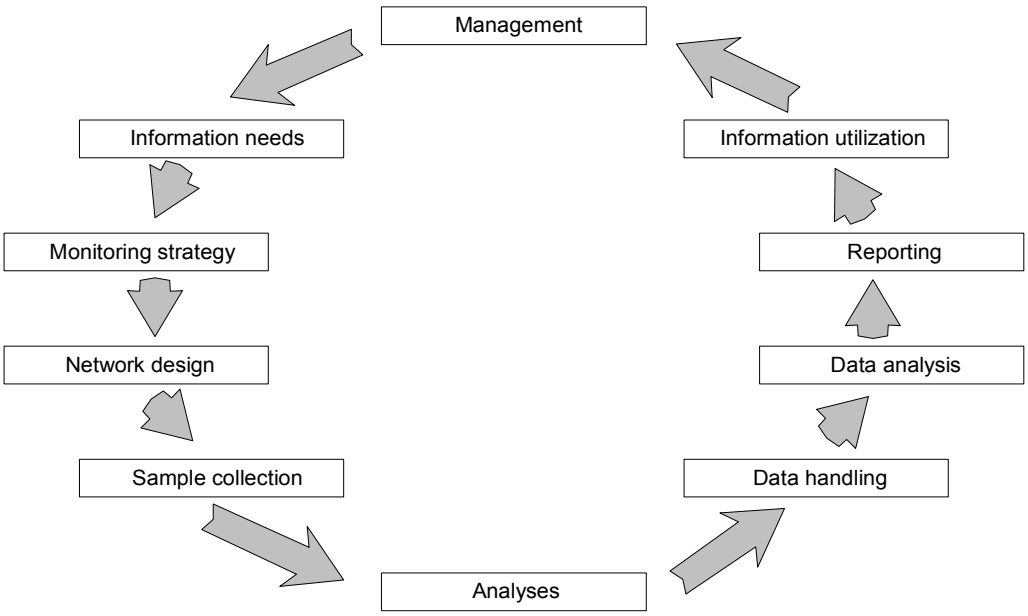

Figure 8 - Representation of the monitoring cycle

V.A Objectives

The proposed objectives are currently deduced from information needs of the "problem owners", i.e. in the case of artisanal gold mining in Ghana the Minerals Commission and the Environment Protection Agency, on behalf of their respective Ministries. They are merely the same as those proposed at the end of the phase I study (Babut *et al.*, 2001):

1. Extend the current evaluation to the whole auriferous area, in order to understand the contamination pattern, and to provide data allowing to assess the risks to human health and the environment.
2. Detect trends.

V.B Strategy

V.B.1 Type of materials

As exposed in the phase I report (Babut *et al.*, 2001), the best compromise choice for the materials to be sampled and analysed are sediments and fishes. Contaminant concentrations in sediments reflect the water contamination, as mercury like other metals tends to adsorb on settling particles (Gray *et al.*, 2000; Lawson *et al.*, 2001 ; Lindstrom, 2001); moreover, they are much less variable than water concentrations, thus allowing to assess the contamination level with a lower effort than a strategy focussing on water. Contaminant levels in fish also reflect the overall contamination of the system, and account for various exposure pathways. Both kinds of materials however present specific pros and cons (Table 10), which should not be ignored, as they may hamper the interpretation of data and the overall efficiency of the monitoring system.

Criteria	Sediment	Fish
Sample collection	**Relatively easy to difficult**: depends of accessibility, river depth and width, current speed etc.	**Uneasy and uncertain** (fishes are mobile, and must be caught by fishermen)
Handling, processing	**Relatively easy** (conservation at 4°C or frozen)	**Difficult**: ideally, samples should be processed and frozen in the field.
Analysis	**Difficult** (due to mercury volatility)	**Very difficult** (basically same process as for sediments, but some steps are more tricky)
Relevance (a) according to the current knowledge, interpretation criteria …	**Good**	**High**
(b) sensitivity to possible policies	**Uncertain**, depends of the age of the deposit collected, currently not measurable; also influenced by downstream transport processes	**Relatively good** (if fishes are analysed separately, and juveniles can be distinguished from older specimens)

Table 10 - Sediment and fish pros and cons as sampling materials

According to these elements, it appears clearly that sediment sampling, handling and analysis would be easier, more efficient, in the sense that it would be less uncertain to collect sediments, and probably less expensive. However, the relevance of this approach is somewhat limited: depending of the flow regime in the period preceding the sampling, the collected sediments may not reflect current contamination trends. Another difficulty is related to the lack of background values for Ghanaian watercourses, which would hamper the interpretation of measurements.

The former difficulty could be bypassed by sampling the upper layer sediments once a year, at the end of the dry season. Thus the top layer of bed sediments would be generally constituted of recent deposits; this approach would permit to assess contamination trends.

The second remark (lack of background values) should lead to a specific study aiming at assessing background levels, preferably for an array of metallic cations, in different sub-catchments of Ghanaian waterbodies[5].

It seems also reasonable to complete sediment measurements by a limited number of fish analyses, caught in some particularly interesting areas.

[5] These sub-catchments would be selected to represent the various geological substrata

V.B.2 Measurements

Considering the array of mining related pollution sources, for sediments the measurements should include grain size, organic carbon, total mercury and if possible other metals (Cadmium, Chromium, Copper, Lead, Nickel and Zinc) and Arsenic.

For fish, they should include species identification, length, weight, lipid content, moisture and total mercury. A preliminary study should address the issue of species selection: one possibility could be to avoid species selection, but interpretation rules would be difficult to design and would probably not be applicable immediately (discrimination according to feeding habits; comparison among groups having the same behaviour; need to develop as many background values as the number of collected species). Conversely, selecting a limited number of species, e.g. 3, could lead to make difficult to collect fishes in some reaches (no a priori evidence that any species is able to live either up- and downstream).

V.B.3 Frequency

According to the results of recent research in the Ankobra basin, two main periods can be distinguished in the yearly contamination pattern, i.e. the dry season (November to March approximately) and the rainy season (April to October) (Bannerman, 2003). During the rainy season, flows are rather high, erode bed sediments, and tend to dilute the mercury loads. Moreover, high flows may hamper gold extraction activities in some parts of the basins. Conversely in the dry season, flows are low, mercury concentrations are higher and mercury contaminated particles tend to settle down.

Therefore the most appropriate period for sediment sampling should be at the end of the dry season. Depending of the number of sampling locations, it could perhaps be interesting to split the program into different packages on a geographical basis, and to apply it through several years (1 or 2 packages per year). Thus cost and technical issues would be kept at a manageable level.

V.B.4 Sampling points selection

Either for sediments or for fishes, the program should include reference points (upstream), where no pollution can be assumed. These reference points would permit to determine background levels; they would also account for atmospheric deposition following long range transport. For sediments, other sampling should be located on main streams and certain important tributaries, close to confluences, in order to determine contamination pattern in sub-catchments. An appropriate selection of the sub-catchments would also allow to monitor various geological and land cover contexts. For fishes, sampling points should be located in areas where pollution is suspected.

V.B.5 Application

It is suggested to set up the monitoring program with 30 sampling points for sediments and 10 for fishes. A larger program would be difficult to implement and fund, and there are a lot of technical issues to solve first, which would use a lot of efforts and resources: samples handling and storage, quality insurance of the analyses, data handling etc. Therefore it seems more reasonable to set up a program limited in size, but manageable and allowing building capacities in the country.

It seems also necessary to get support from cooperation agencies or programs for different aspects of this program: development of analytical capacities, quality insurance, data management (GIS-based databases).

V.C Monitoring program summary

- Appropriate objectives for a monitoring program gold extraction environmental impacts could be:
    1. Extend the current evaluation to the whole auriferous area, in order to understand the contamination pattern, and to provide data allowing to assess the risks to human health and the environment.
    2. Detect trends.
- The best compromise in terms of sampled matrices appears to be a combination of sediments (basis of the program) and fishes.
- Aside a set of metals (Cadmium, Chromium, Copper, Lead, Mercury, Nickel and Zinc) and Arsenic analysed as total concentrations, sediment measurements should include grain size and total organic carbon. In fish, length, weight, lipid content, moisture and total mercury should be measured, and the species determined.
- Specific studies are needed at the beginning of the program, for determining mercury and other metals background concentrations in sediments, and refine the strategy for fishes (species selection).
- Sediments should be sampled at the end of the dry season. It is suggested to apply this strategy to 30 sediment sampling points and 10 fish sampling points. Sampled locations should include reference points and locations close to confluences of tributaries. If more points were selected, the program could be planned on several years.
- It seems necessary that cooperation agencies afford appropriate support for developing further the analytical capacities, quality insurance and data management.

RECOMMENDATIONS

- Considering the mercury pathways to the environment (see summary pp 22-23), a better organisation of the gold production process along with the introduction of appropriate equipment needs to be developed. For example, in Gyapa case, doing the amalgamation and the distillation out of the village, in places un-connected to the river, and using retorts at the distillation step would normally decrease the transfer of mercury to rivers and soils.
- Fish contamination seems a bigger issue in regions where artisanal gold mining relies upon hard rock processing. In these regions, it should be recommended to the populations not to eat fishes caught downstream the process sites. Developing alternative fish sources (for example aquaculture in ponds) could be a way to decrease human exposure to mercury from the diet.
- Side-effects of alluvial mining such as physical damages to the floodplains or to cultivated land should also be accounted for. That is, alluvial miners should restore the dug locations when they leave, at least by filling the pits. Obviously, this recommendation is rather naïve; however, Ghanaian authorities – and populations – should be aware that these physical damages hamper their own resources, perhaps as much as industrial mines do. But while industrial mines are now involved in operations aiming at limiting the environmental impacts of their activities, artisanal miners do not.
- Environmental impacts of artisanal gold mining should be monitored throughout the auriferous region; in order to develop this program, some complementary studies are needed, to determine background concentrations in sediments and select the appropriate fish species.
- Because there is evidence of long range transport of mercury throughout the Ankobra basin till the estuary, it is important to determine whether mercury is then brought to the sea and contaminates fishes and shellfishes along the coast. A study of the functioning of the mangrove and the estuary is therefore highly desirable.

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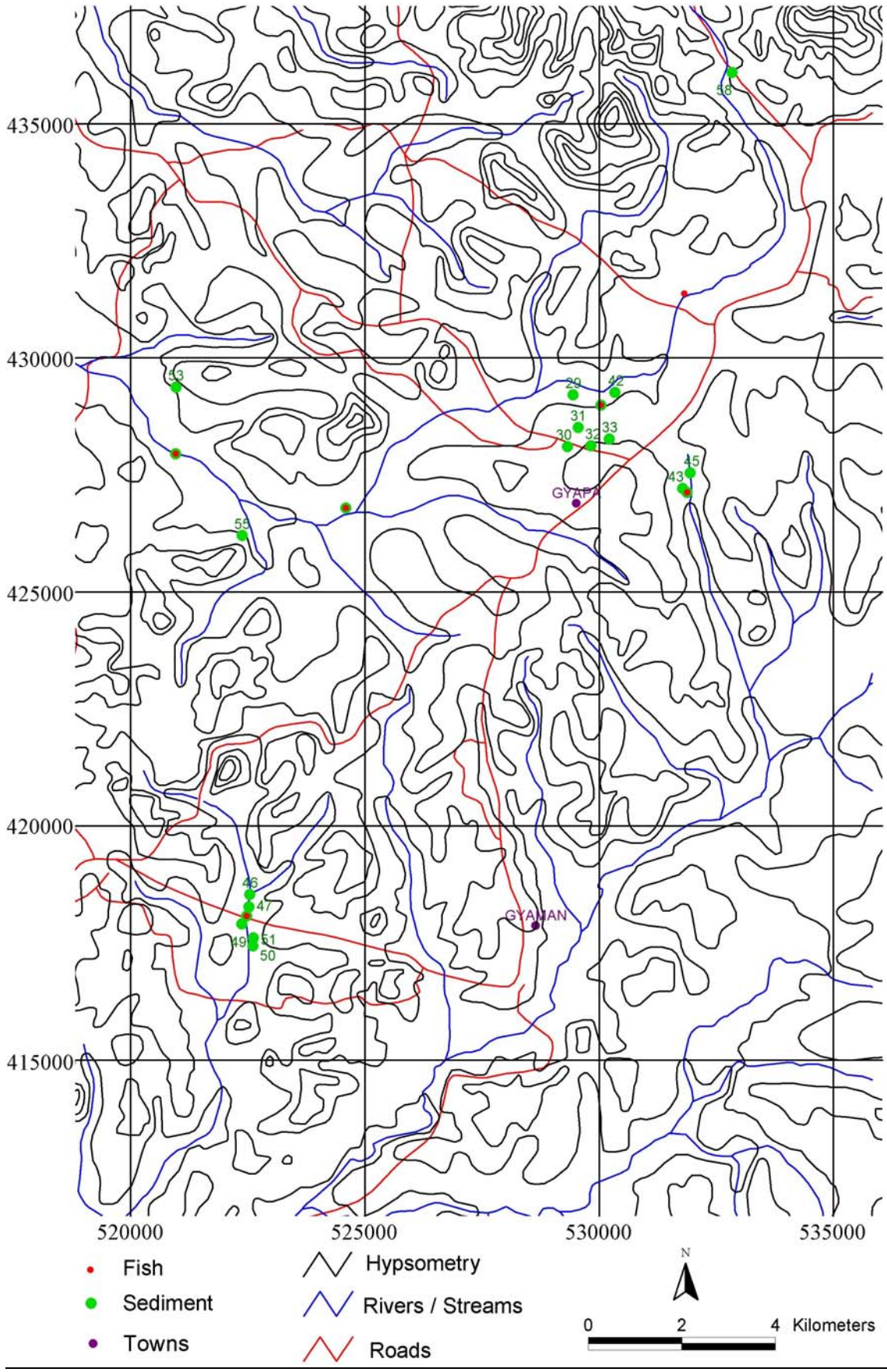
Appendix – Sampling points locations in and around Gyapa



Site	Ref	Sample Code	Sample
Yaya	28	RV1	Cocoyam
		SE1	Sediment
		F3/1 & /2	Fishes
	29	RV2	Cocoyam
		SE3	Sediment
	42	SE2	Sediment
	57	SE16	Sediment
		F7	Fish
	53	SE12	Sediment
	54	SE13	Sediment
		F5	Fish
	58	SE17	Sediment
		RV7	Cocoyam
		SO7	Soil
Gyapa (village)	30	RV3	Cocoyam
		SO1	Soil
	31	RV4	Cocoyam
		SO2	Soil
	32	SO3	Soil
		SO4	Soil
	33	RV5	Cocoyam
		SO5	Soil
Akoma Kofi	43	SE4	Sediment
	44	SE5	Sediment
		F4/0	Fish
	45	SO6	Soil
Subin (pits)	46	SE6	Sediment
	47	SE7	Sediment
	48	SE8	Sediment
		F1/1 & /2	Fish
	49	SE9	Sediment
	50	SE10	Sediment
	51	F2/0	Fish
Buosim	55	SE14	Sediment
		RV6	Cocoyam
	56	SE15	Sediment
		F6	Fish