A HEURISTIC SYSTEM FOR ENVIRONMENTAL RISK ASSESSMENT OF MERCURY FROM GOLD MINING OPERATIONS

by

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ABSTRACT

Mercury pollution in the Amazon region represents today one of the most serious environmental issues faced by mankind. Quantities from 70 to 170 tonnes of mercury are discharged into the Amazonian environment annually from gold mining operations conducted by so-called "garimpeiros" or informal miners. The transformations of mercury in the environment are not well understood by non-technical people and neither are methods to alleviate dangerous situations.

As the issue is fraught with complex and vague concepts, Expert Systems can play an important role in transferring heuristic knowledge to non-technical people interacting directly with miners. A synergy is obtained if these people are also made aware of the toxic effects of mercury, methods to minimize emissions and of methods to diagnose critical situations. This work shows how an Expert System, HgEx, was developed to assist non-expert people to obtain a preliminary Hg bioaccumulation risk assessment without conducting a complex monitoring program. Fuzzy Logic techniques and a new weighted inference method allow program users to input imprecise field observations and still obtain conclusions about pollution extent and bioaccumulation possibilities. Because of its simplicity and ability to combine complex technical issues together with heuristic operational observations, the technology of an Expert System can play an important role in providing a rapid risk assessment for non-technical people. An initial picture of the contamination potential of a region or mining site together with measures to minimize mercury emissions and remedy critical situations are the main results presented to users who might include health workers, environmental and mining inspectors, engineers, biologists, etc.

This work also stresses the importance of organic-rich environments in Hg-complex formation and points out the importance of vegetation fires as an additional source of Hg not previously considered in the Amazon. The tutorial part of the system can give guidelines for mercury-monitoring field work as well as an overview on the mercury biogeochemical cycle.

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DEDICATION

... this work is dedicated to the true "garimpeiro",
victim of the disorganized Brazilian Society;
and to my loving family,
victims of my own disorganization

1. Introduction

"A gold mine is a hole in the ground with a liar on top."
Mark Twain

1.1 - Statement of the Problem

Informal mining operations, or "garimpos" expanded in Brazil, especially in the Amazon during the 1970s as a consequence of poorly conducted policies about agricultural projects, together with increased inflation and unemployment rates. Informal miners use mercury to amalgamate fine gold and their lack of knowledge about adequate technical procedures and toxicology have caused considerable occupational hazards and contamination not only where mining takes place, but also in other communities. Brazilian and international researchers started monitoring programs in 1984 when the first signs of methylation and bioaccumulation were observed and these studies have demonstrated considerable ambiguity regarding the extent of the problem.

Fish is the main diet of most Amazonian communities and people living distant from mining activities have shown higher levels of mercury in blood than workers exposed to mercury vapour. This and other facts have confused many environmentalists who have two main deficiencies that hinder an efficient approach to this issue :

- lack of knowledge about the Hg biogeochemical cycle in tropical regions,
- lack of knowledge about teaching informal miners how to improve and work more safely.

Mercury pollution from gold mining activities has received attention from the Brazilian government and the technical support of researchers from other countries, such as UK, Germany, Japan, Sweden, the Netherlands and Canada. A limited amount of work has been done with monitoring programs but remedial procedures have not yet been considered. The interdisciplinary nature of environmental science causes frequent misunderstanding by people involved in such research programs. This represents loss of money and time as well as inconclusive results.

Armed force has proven ineffective to stop these squads of almost one million people. Environmental studies often "flame" the "garimpeiros" into violent resistance and shock the population into fear. An alternate approach is needed. Recently, educational approaches have been tried by a few groups as an effective and durable measure to alleviate this problem, but the process has to start by training the educators. An Expert System may lend itself to this operation and provide assistance to the knowledge-transfer process.

1.2 - Outline of this Work

This work describes the essential parts of an Expert System developed to assess risk situations of mercury bioaccumulation. The Expert System (HgEx) uses methods that accommodate vague data to accumulate certainty in conclusions based on field observations and expertise about the environmental behaviour of mercury. It must be stressed that provision of knowledge to health workers, engineers, environmentalists, inspectors and miners about mercury behaviour in the environment can be an important contribution to solving this potentially devastating problem.

The reasoning adopted to conduct a risk assessment is based on a balance of synergistic and antagonistic factors that contribute to bioaccumulation. In other words, the intensity of a specific mercury emission must be combined with factors that enhance methylation and those which decrease bioavailability to establish the risk level for organisms and man. Heuristic models have been developed using Fuzzy Logic techniques and Weighted Inference Equations to combine pieces of evidence in rules that conclude about potential risk. The system predicts the bioaccumulation risk and gives suggestions for monitoring programs, reduction of mercury emission and remedial procedures. This rationalizes the need to sample biota and human subjects which always involves expensive and complex procedures.

This work also provides a review of mercury pollution caused by gold mining operations in the Amazon and other parts of the world. Natural variables which must be used to diagnose risk situations are discussed and case studies are listed to support the system conclusions.

1.3 - Proposed Solutions

The justification to build this heuristic system is based on a lack of experts in the subject as well as the fact that the problem is assuming epidemic proportions in the Amazon, and possibly in other tropical regions around the world. Computers, as a multimedia vehicle, have never been used in this field. So it is considered that the technology known as Expert Systems can play an important role. An Expert System is an effective way to transform heuristic and dispersed knowledge into an interactive process to help diagnose critical situations.

Such systems provide unique access to knowledge to give assistance and advice on related topics.

1.4 - Organization

This thesis is presented in 10 distinct sections.

The first three chapters essentially summarize the Tutorial part of HgEx which is also the technical basis used to build the knowledge base for the Diagnostic part. Most information in these chapters was obtained in field observations by the author or described by the few published articles in this field, or from unpublished technical reports many of which were issued with the author's participation. It is important to highlight that many of these reports were used not only as an information source but included personal interpretation of the data.

Chapter 2 gives an overview of the methods and history of amalgamation as a gold recovery process in order to understand why and how gold miners use mercury.

Chapter 3 discusses how Hg enters the environment - its reactivity with organic and inorganic species and the important factors which influence its transformation. This section details an original experimental study of the reaction between metallic Hg and natural organic acids.

Chapter 4 presents evidence of Hg bioaccumulation in the Amazon and the way in which metallic Hg and methylmercury affect the human body.

The next three chapters describe the Diagnostic part of HgEx and how pieces of evidence are accumulated to conclude about bioaccumulation risk.

Chapter 5 provides an overview of the field of Expert Systems and the process by which one builds, tests and evaluates a system.

Chapter 6 gives the structure of the Diagnostic part of HgEx detailing the heuristic approach to data management and the incorporation of uncertainty principles within the framework of the knowledge base.

Chapter 7 demonstrates the effectiveness of the system to diagnose 4 regions contaminated with Hg in order to prove that the system provides accurate conclusions.

Chapter 8 reports on a "subjective" evaluation of HgEx conducted by a number of Experts and potential users.

Final conclusions are given in chapter 9 while chapter 10 lists the claims to original research that derived from the building of this system.

Finally the thesis ends with a number of suggestions for future work in chapter 11. These suggestions were prioritized to provide new technical knowledge to continue developing an understanding about Hg bioaccumulation and new methods to remedy the problems.

2. Gold and Amalgamation

"Far away a word was whispered, oft a tale by many told
Born of greed, it soon echoed with the cry of Gold! Gold! Gold!"
Irene Edwards

2.1 - Garimpos and Garimpeiros

"Garimpo" is a mining site where the "garimpeiros" or informal miners, work. "Garimpo" is a migratory activity which occurs due to lack of jobs or lack of gold. Over 85% of "garimpeiros" in the Amazon are originally from other regions (Alves and Sabrosa, 1993). Since 1940 the Brazilian mining codes have shown preference to organized mining work over "garimpos". In the Constitution of 1967 the law determined that all "garimpo" activity must be stopped when a legal lease is conceded. Which activities should be considered "garimpo" and which are organized mining, has never been made clear, leading to misinterpretation. Classification of the types of minerals allowed to be mined by "garimpeiros" is only one source of misinterpretation (CETEM, 1989; Barreto, 1991).

The conflicts between mining companies and "garimpeiros" were not solved with the Code of 1978 in which areas reserved for mining by "garimpeiros" were established. As the ore is not always located totally within these reserves, the limits imposed by law have not been respected. Illegal operations were flagrant across the country and ecologically sensitive areas received large squads of miners. Company leases were not respected either.

In the law 7805/89, the classification of "garimpo" is still attached to the type of ore deposit. The geological characteristic, by laws, delimits the type of work, or workers, applied to each kind of deposit. As placer deposits imply a high risk for companies, the laws have tried to leave the risk with adventure-seekers. The transitory nature of this type of mining has always been the focus of Brazilian laws, however this is unrealistic. "Garimpeiros" have developed their own technology; they formed unions; they imported equipment to continue their work in the areas they occupied. This equipment varies from primitive riffled sluices to sophisticated centrifuges.

Disorganization and pollution are results of the absence of technical support for these miners. The scorn of the dominant society, which in fact spawned these economic and social distortions, has also contributed to distance these people from an organized company. Likewise in any society, there are different types of people hidden behind professional categories. Some of them are trying to evolve, but some just think about immediate benefits regardless of the hazards to themselves and the environment because of their activities. The evolution of "garimpos" into organized companies happened in North America and the history is unlikely different in developing countries, unless society and government refuse to participate in this evolution.

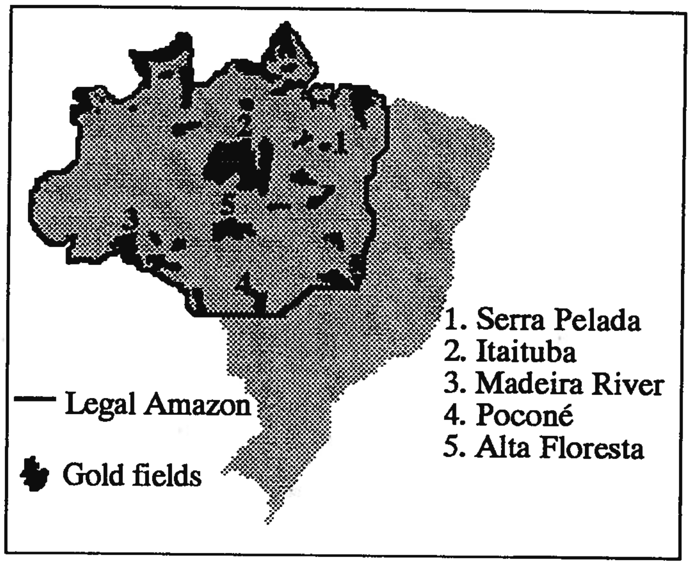

Fig. 2.1 - Main gold fields worked by garimpeiros in the Amazon
Source: Feijão and Pinto (1992)

Serra Pelada (Fig. 2.1), which opened in the early 80s, started the modern gold rush in the Amazon. Almost 80,000 miners operated numerous small plots to extract more than 40 kg per day at the peak era in 1981, while today less than 5 g per day is typical. Much like Serra Pelada, in excess of 2000 "garimpo" mining prospects are being worked today in the Legal Amazon Region. The human contingent, involved directly and indirectly with this economic activity, numbers more than 4.5 million. They are responsible for the highest steel consumption per capita in South America as well as diesel oil, carpets (for gold sluices) and other goods. More than 25,000 units of mining equipment, 20 helicopters, 750 airplanes and 10,000 boats (some as large as ships) are used to produce an average of 100 tons of gold annually from the region (Feijão and Pinto, 1992). The environmental costs of this production are only now being measured.

2.2 - Brief History of Amalgamation Practices

Mercury is the 7th metal of antiquity and has been known and used for more than 3500 years. Samples of mercury were discovered in ancient Egyptian tombs that date to 1500 or 1600 BC. The first reference to metal extraction in written records is attributed to Aristotle in the 4th century BC. Romans used cinnabar (HgS) for writing their books and as a pigment to decorate tombs, statues and walls. They also used elemental Hg as an amalgam to separate gold from other materials and as an amalgam to coat gold onto copper (Nriagu, 1979; D'Itri, 1972).

The chemical symbol of mercury, Hg, comes from the Greek name Hydrargyrum (liquid silver) and the name Mercury was given by medieval alchemists after the fleet-footed Greek god. In 1533, Paracelsus wrote a book about occupational diseases in which he described in detail Hg poisoning of miners. Although Paracelsus was intrigued with Hg, he considered it a metal that was deficient in its coagulation ability. He believed that all metals were liquid Hg up to the midpoint of the coagulation process. Consequently, he expended much unsuccessful effort trying to coagulate Hg to convert it into gold (D'Itri,1972).

Inorganic Hg compounds have been used extensively as antiseptic, disinfectant, purgative, and counterirritants in human and veterinary medicine. Various Hg compounds were developed to aid in the control of bacteria, fungi and other pests. Paracelsus introduced probably the most unusual medicinal use for Hg. He dissolved Hg in oil of vitriol (sulphuric acid) and distilled the mixture with Spiritus vini (alcohol) as a cure for syphilis. This use of Hg persisted until the 1930's (D'Itri, 1972, op.cit.). Many of these applications are gradually being replaced by other compounds.

The extraction of gold by amalgamation was widespread until the end of the first millennium. In the Americas, mercury was introduced in the 16th century to amalgamate Mexican gold and silver. The import of Spanish mercury to Bolivian and Peruvian goldfields lasted from 1560 to 1860 (Nriagu, 1989; CETEM, 1989). The Spanish authorities encouraged mercury ore prospecting in order to supply the Californian mines. In 1849, during the American gold rush, small mercury deposits were exploited. At this time, mercury was widely used by American miners (prospectors) in their pans, sluices, etc. Mercurialism became a common illness among the cinnabar miners and gold panners (D'Itri and D'Itri, 1977).

In Quebec, old gold mines in Val d'Or used amalgamation throughout much of the 20th century. Today most abandoned sites show high Hg content in sediments (up to 6 ppm) and in fish. As a result of chemical analysis of fish muscle, it was observed that bioaccumulation is related to food web and fish age. A total of 31 specimens of pike showed an average level of 2.6 mg/kg (ppm) - more than 5 times above the guideline level. All fish collected upstream of tailing ponds along the rivers Colombière and Bourlamaque contain more Hg than do the fish collected downstream. These are darkwater rivers and explanations for these phenomena are still being researched (Poirier, 1993, Louvicourt Project - personal communication).

Lane et al. (1989) studying plants as a mercury indicator in old gold tailings in Nova Scotia, found Hg in leaves ranging from 0.18 to 0.55 ppm; although roots showed values up to 6.1 ppm. Such high levels in roots suggest that a process of bioaccumulation is occurring.

In South America, Africa and Oceania, news about Hg use in gold operations is told by native engineers and geologists, but little is reported in the literature. In Peru, a current gold rush was triggered in Madre de Dios Department where about 10,000 "chichiqueros" (informal miners) have worked since 1990. About 130 kg of gold/month are recovered by similar methods used by Brazilian "garimpeiros" and Hg is extensively used and burnt (Bliss and Olson, 1992).

Amalgamation and cyanidation are practiced by informal miners in Ecuador in the cities of Zaruma and Portovelo. There are 68 plants in operation with a capacity to process 14,000 tonnes of ore/month. The ore is exploited through shafts to be crushed and ground in different mills (balls, rods, etc.). Concentration is carried out in sluices lined with carpets. Gravity concentrates are amalgamated in a sort of "Muller" pan for 2 to 4 hours. Amalgam is usually burnt in pans, sometimes wrapped in aluminum foil. The gold production is estimated at 1.4 tonnes/year with recovery around 50 percent (Vaca, 1992).

In Brazil, the first gold cycle started in 1695 with discovery of gold close to Vila Rica (today Ouro Preto city), although there are reports of gold prospecting works dating back to 1552. This gold cycle was marked by the pioneers (so called "bandeirantes") who grubbed the western lands seeking and mining alluvial and lateritic gold (rich in nuggets) with rudimentary methods. There is no evidence of mercury use during this time. Amalgamation processes seem to be applied in the beginning of 19th century when British technology was imported to Brazil.

A second gold cycle is marked in Brazil and in other developing countries, at the end of 60s, by the end of the 1944 Breton-Woods agreements, which had held the price of a troy-ounce (31.1g) of gold at US$ 35 for a very long time. The price of gold gradually rose during the 70s, leading to the reworking of ores hitherto considered low grade.

2.3 - "Garimpos" in Western North America

The Pacific Northwest is situated in one of the major mercuriferous belts of the earth. Mercury was mined in the past in some parts of California and in Pinchi Lake, British Columbia. High levels of Hg in soils are related to organic matter. Background levels around 0.5 ppm in sediments collected at depths greater than 15 cm are reported in Washington State (Bothner and Piper, 1973). As mercury was used in the 1850s in gold mining operations, some authors have doubts about the origin of Hg in water, sediments and fish samples from Northwestern America. Buhler et al. (1973) make reference to 7 - 30 g of Hg discharged in the waste water per tonne of gold ore processed by miners in the 1860s in southern Oregon and Idaho.

Analyses of surface horizons of peaty-muck soils and those predominated by vegetative litter in British Columbia indicate an average of 165 ppb Hg and as much as 740 ppb Hg in non-mineralized areas. In the vicinity of Pinchi Lake (1km) surface soils show lower values (750 ppb) than deeper horizon (25 cm = 2320 ppb Hg), although most sites not directly related with mercury ore deposits show 1/4 the concentration of those in surface litter, such as samples from the Fraser Valley (John et al., 1975). No correlation was found between Hg and organic matter analyzed in these soils, but surface soil was identified as the main Hg source. Sometimes statistical correlation between only two natural variables is not enough to explain an association. In this case, soils containing up to 70% of organic matter obviously play an important role in Hg adsorption although other variables such as microbial activity, mineral composition, pH, salinity, etc. also influence the relationship between two specific variables such as Hg and organic levels.

Garrett et al. (1980) also reported high Hg concentration in many areas in the Yukon Territory and in British Columbia. Levels up to 5.2 ppb Hg in surface waters were analyzed. The source of these high levels is not well understood.

The amalgamation process was widely used by Canadian miners in the 1860s until 1890s as observed in the reports of the Minister of Mines. Nuggets had a better price ($ 16.5/oz) than fine gold (MMBC, 1881) and mercury became a solution to extract fine gold from benches of the Fraser river extending from Hope to Lillooet. The text below extracted from MMBC (1875) shows clearly this fact: *"... On the bars near the mouths of rivers, it is found in a fine impalpable dust, known as flour gold, and can only be collected by the aid of quicksilver."*

Mercury was used in sluice boxes or in copper plates. It is reported that native indians and Chinese were the best gold savers at that time. These latter were usually hired by the "white men" and then began their own operations later (MMBC, 1881).

In Yellowknife, NWT, the impact of the use of Hg in gold amalgamation from 1950 to 1969 in the Discovery Mine site, is mirrored today by high Hg levels in fish of Giauque Lake. About 2.5 tonnes of Hg were discharged together with tailings. Due to the extent of Hg contamination, Giauque Lake has been closed to sport and domestic fishing for several years and has been described as a contaminated site under the Environment Canada National Contaminated Site Program (Baker et al, 1992).

Mudrock et al. (1992) investigated the effect of heavy metals in biota of a past gold mining activity in the Cariboo region. In Jack of Clubs Lake, Wells, B.C., an old operation used amalgamation from 1933 to 1966. The Hg concentration in trout has been shown to exceed the 0.5 ppm Hg guideline for human consumption. The authors concluded that limited information is available on the effects of the abandoned gold mine tailings on the Fraser River Basin ecosystem.

In order to evaluate mercury contamination at an old mining site in Western Canada, a quick geochemical survey was conducted at Port Douglas in 1991. Port Douglas was a small village founded in the late 1850s at the tip of Harrison Lake, British Columbia to serve as the transit jump-off point to Cariboo goldfields. In 1859 more than 30,000 miners passed through the town. Primitive panning methods and sluice boxes were used to extract gold from the Lillooet River Delta by these pioneers but the Cariboo discoveries in the late 1860s meant the death knell for Port Douglas (Edwards, 1977; Basque, 1993). Some spot endeavours lasted up to 1920 but little information about gold output from this region is available.

The Lillooet River placer deposit is situated in the Canadian Cordillera Coast belt tectonic division where the gold is associated in quartz lodes emplaced in fissures and shear zones. The host environment contains altered Upper Paleozoic to Upper Jurassic eugeosynclinal or arc-type and volcanic rocks adjacent to plutonic complexes of varying size and composition. The placer gold is in part a product of aggradation of lode deposits, but precipitation of gold and mercury from hot springs may be a feasible process as well. (Steiner, 1983; Whitten and Brooks, 1988).

Soil and creek sediment samples collected around Port Douglas (today a camp of a gold exploration company) were analyzed. Some samples, a mixture of bottom sediments, were wet screened (no new water added) on a nylon 200 mesh (0.074 mm) screen in the lab. The -200 mesh fractions were filtered through a coarse filter paper then followed by a 0.45 µm Millipore® filter. Water and solids, dried at 60°C, were analyzed by flameless atomic absorption spectrometer (AAS). Gold in solution was determined by induction plasma spectrometer and in solids by aqua-regia attack + MIBK extraction and AAS readings (analyses performed at Quanta Trace Lab, Burnaby, Canada - liquids and solids and CETEM - Centre of Mineral Technology - Brazil's National Research Council, Rio de Janeiro, Brazil - some solid samples).

The presence of Hg droplets can be seen in sands from the Lillooet River. During gravity concentration in a shaking table, small mercury beads are frequently observed in the concentrates. Natural amalgam in this placer occurs in the form of platy particles, with a paste consistency, very often stuck to gravel surfaces as observed under the optical microscope. Hot springs might be the main source of gold and mercury in the region and organic matter may have played a role in transporting Au and Hg in solution or as fine suspended particles.

Nugget formation from organic complexes has been observed in other placer deposits, such as Goodnews Bay, Alaska (Mardock and Baker, 1991). According to these researchers, humic acids transport gold and mercury, and amalgamation in the environment can account for subsequent accretion of gold.

The results of the geochemical survey in Port Douglas may suggest an anthropogenic influence in several sites possibly exploited by the pioneers (Table 2.1), however samples collected distant from Port Douglas, in sites unlikely worked in the past, also showed high Hg values (Table 2.2). The majority of the samples are characterized by high organics (dark brown colour), 3.8 to 18.4% total carbon content, sometimes with the strong smell of hydrogen sulphide.

Table 2.1 - Samples from Port Douglas with possible influence of old miners

Sample	Water (<0.45 •m)		Solids	
	Hg (ppb)	Au (ppb)	Hg (ppm)	Au (ppm)
M4 (-200#) - creek in Port Douglas	<0.2	<1	4.37	0.02
M4 (+200#)	na	na	3.62	0.005
M7 (-200#) - creek near the	<0.2	3	15.6	0.3
M7 (+200#) - Little Harrison Lake	na	na	0.72	0.01
M8 (-200#) - creek 3km from P.Douglas	<0.2	5	2.53	0.03
M8 (+200#)	na	na	0.73	0.005
M15 (+200#) - sand Sloquet creek	na	na	2.28	<0.05
M19 (-200#) - creek 500 m from P.D.	2.6	15	29.5	3.92
M19 (+200#) - in front of an old hut	na	na	0.58	0.02
M20 (-200#) - same creek	na	na	3.0	<0.05
M20 (+200#) - surface sample	na	na	1.54	0.09
M21 (+200#) - soil in P.Douglas	na	na	0.57	0.01
M22 (+200#) - Little Harrison Lake	na	na	0.49	0.005
M23 (+200#) - Little Harrison Lake	na	na	0.49	0.01

na - not analyzed

The sample from the Lillooet River delta (M17) showed an outstanding enrichment of Hg and Au. The black waters reached values around 2 ppb Hg and 20 ppb Au in solution or in colloids finer than 0.45 µm. These numbers are respectively 200 and 2000 times higher than the expected background for these elements in freshwater (Förstner and Wittmann, 1979). When samples rich in organics were subjected to extraction with caustic soda (5M NaOH), at 80°C for 2 hours, 30% of the Au and 50% of the Hg were extracted, indicating a strong association of these metals with organic matter, in spite of a weak correlation between total carbon and Hg content in the samples.

Table 2 2 - Samples from Port Douglas with unlikely influence of the old miners

Sample	Water (<0.45 μm)		Solids	
	Hg (ppb)	Au (ppb)	Hg (ppm)	Au (ppm)
M1 (+200#) - black sand Douglas creek	na	na	0.77	0.1
M3 (+200#) - organic matter-mountains	na	na	2.89	<0.05
M10 - soil 0 - 1 m - 50 km from P.D.	na	na	3.55	<0.05
M10 - placer - 1 - 3 m	na	na	4.81	<0.05
M10 - placer - 3 - 5 m	na	na	0.85	<0.05
M11 (+200#) - soil 28 km from P.D.	na	na	3.19	0.01
M12 - water from hot spring	<0.2	2	na	na
M13 - drinking water from mountains	<0.2	2	na	na
M14 - water 10 km from P.D.	1.5	3	na	na
M16 - bog water - Lillooet delta	<0.2	2	na	na
M17 - bog water - Lillooet delta	1.9	24.0	57.2	2.80
M18 (+200#) - sand Lillooet delta	na	na	0.85	0.005

na - not analyzed

2.4 - Current Amalgamation Practices in the Amazon

Although Hg is not allowed to be used in "garimpos", in fact amalgamation is the main process used. Cleary (1990) reported only one "garimpeiro" who did not use Hg and he was regarded as eccentric by his peers. More than 90% of the gold present in gravity concentrates can be trapped in amalgam according to field observations at some operations. Price is not an impediment for reducing use. Even at 5 times the international price, Hg is still a cheap reagent for extracting gold, with a cost equivalent to 0.012 g of gold per tonne processed. (Veiga and Fernandes, 1990). The mining and amalgamation methods used in "garimpos" are variable which together with the fate of contaminated tailings and Au-Hg separation procedures define the extent of Hg losses.

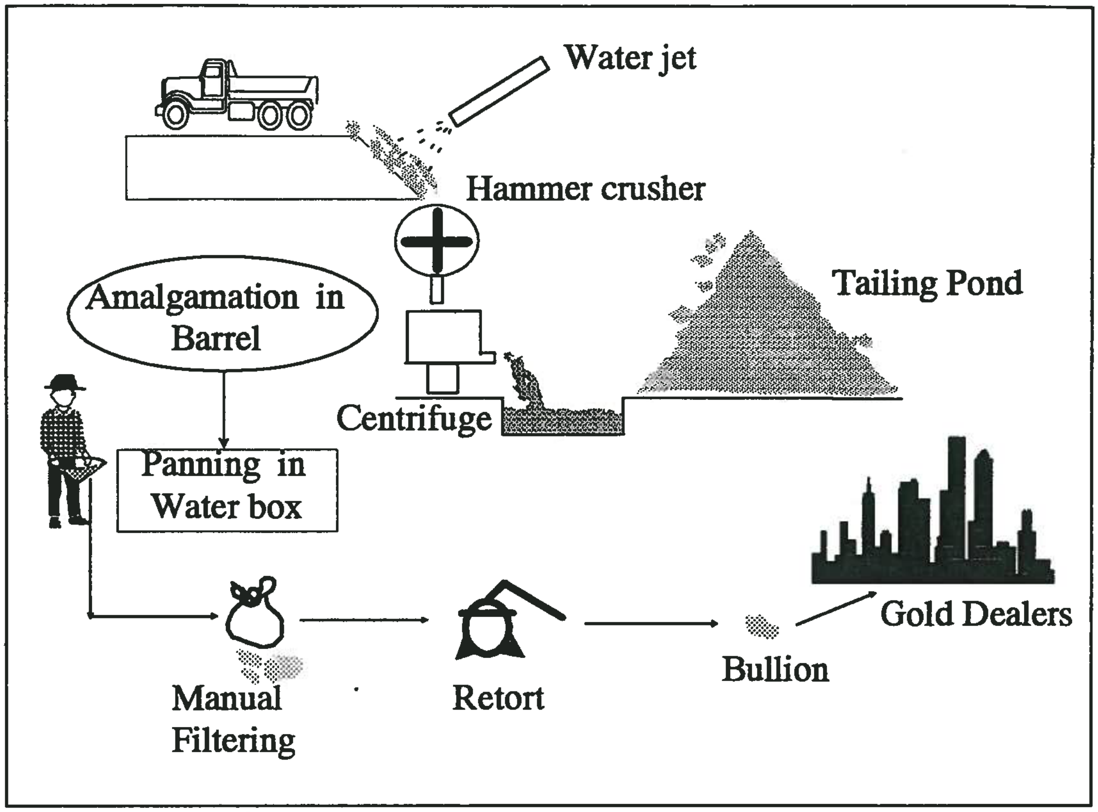

Fig. 2.2 - Flowsheet of a typical “garimpo” in Poconé, MT, Brazil

Farid et al. (1991) evaluated a type of "garimpo" which used a grinding operation (hammer crusher) and gravity concentration (sluice or centrifuge). Figure 2.2 shows a simplified flowsheet of the operations involved in this type of garimpo, while an Hg-balance is provided in Figure 2.3. These operations are conducted on a lode ore and its weathered part. Erosion of the quartz vein hosted by ferruginous and carbonaceous phyllites spread out gold into the weathered layer. The gold grade is poorer than in quartz veins but easier to mine. Large production can be achieved, such as 3 million tonnes of run of mine/year, but gold recovery in the gravity circuit is usually lower than 50% due to poor liberation.

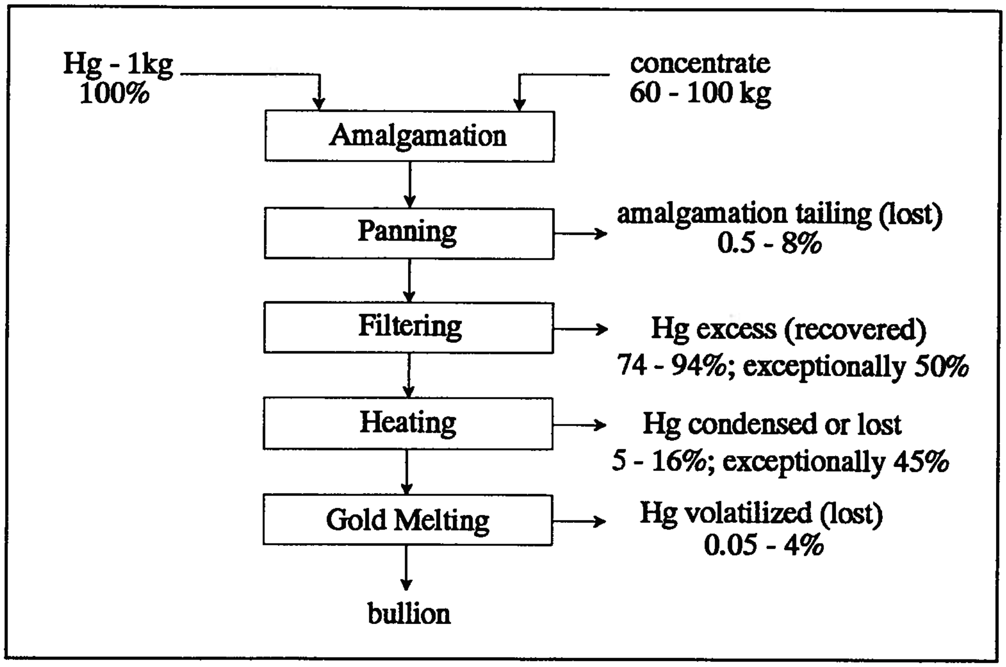

Fig. 2.3 - Balance of mercury in the amalgamation steps
(adapted from Farid et al, 1991)

Concentrates are usually amalgamated in barrels or pans and the mineral portion is separated from amalgam by panning. This operation takes place either in waterboxes or in pools excavated in the ground. The method used to remove the excess mercury from amalgams is filtration using a piece of fabric to squeeze by hand. The amalgam obtained, usually with 60% gold content is retorted or simply burnt in pans. The bullion still contains 5% residual mercury which is released during melting operations in gold shops. Mercury entering the atmosphere can represent as much as 50% of that introduced into the amalgamation process when retorts are not used (Fig. 2.3).

Pfeiffer and Lacerda (1988) reported that Hg losses due to dredge mining range from 30 to 45% of the Hg introduced in the process. When retorts are not used, the losses include 45% released into rivers and 55% into atmosphere.

Brazil is not a mercury producer and imports around 340 tonnes annually. From 1972 to 1984, Mexico was the main Hg supplier to Brazil. Since 1984 this picture has changed and non Hg-producing countries (the Netherlands, Germany and England) are responsible for almost 80% of the Hg entering Brazil. Mercury imports are allowed only for registered industrial uses, however the declared uses (electronic industries, chlorine plants, paints, dental, etc.) are declining. The updated Brazilian laws (Norm 434 - Aug.9/89 and Norm 14 - Jan.15/90) intend to exert more control on Hg imports. In 1989 this represented about 22% of the total 340 t of mercury. The remainder was imported for re-sale to industries, but it is estimated that over 170 t were illegally diverted to "garimpos" (Ferreira and Appel, 1991).

As a rough estimate, if we assume losses of 40% of 170 tonnes Hg, 68 tonnes/year are calculated as losses due to poorly conducted amalgamation practice. This is similar to the range of 50 to 70 tonnes Hg/year reported by Pfeiffer and Lacerda (1988). The ratio $Hg_{consumed}$: $Au_{produced}$ is sometimes used to calculate Hg losses. This seems to be an inaccurate approach since gold output from these mining activities is not well established and is difficult to estimate, ranging from 34 (official production by DNPM, 1989) to 220 (Fernandes and Portela, 1991) tonnes/year. In addition, stockpiling is not taken into account by this ratio and this may actually be a preferred practice by "garimpeiros" because of the "illegal" nature of this commodity.

The Hg:Au ratio provides a picture of mercury consumption on a large scale. For instance in the Amazon region this ratio ranges from 0.6 to 1.3. A distribution of mercury losses can be done as follows (CETEM, 1989) :

- 70% by volatilization during amalgam distillation (when retorts are not used),
- 20% dragged with the amalgamation tailings and
- 10% volatilized in the gold shops when gold is melted.

3. Mercury in the Environment

"The garimpeiro is a thorn in the foot of the formal Economy."
Marceonílio M. Neto - garimpeiro leader

3.1 - Contamination Pathways

The form in which mercury is released into the environment determines its reactivity and transformation rate. In "garimpos", two pathways are recognized:

- Hg entering the atmosphere due to amalgam burning in frying pans and gold melting,
- Hg dragged with amalgamation tailings.

Lindqvist et al. (1991) pointed out that mercury can remain in the atmosphere for 6 to 24 months in a dry climate. However the reactions that occur in clouds result in a shorter residence time as mercury returns to the earth through rainfall.

At present, it is widely accepted that Hg° vapour constitutes by far the largest component of the total gaseous Hg concentration in the atmosphere with perhaps some minor amount of divalent Hg (II) and Me-Hg (Iverfeldt,1991). Owing to its high vapour pressure (0.246 Pa or 1.85×10^{-3} Torr at 25 °C) mercury in ambient air is predominantly in the gaseous phase (as individual Hg atoms) rather than associated with particulate matter as with other transition metals (e.g. Cd, Zn, Cu, Ni, Pb). Mercury bound to particulate solids represents less than 2% of the total Hg level in air, according to observations in Nordic countries (Schroeder et al, 1991; Brosset and Lord, 1991; Lindqvist et al, 1991; Bloom and Fitzgerald, 1988).

The process in which Hg^{o} vapour oxidizes in the atmosphere is not well understood. Oxidation is certainly accelerated in clouds in the presence of ozone (O_3) and chlorine (Cl_2) but reduction of Hg(II) to Hg^{o} is also a feasible process (Schroeder, 1991).

The extent of metallic mercury dispersion due to amalgam burning in pans is not quantified. Neither air analysis nor soil samples up to 500 m from gold shops show significant mercury concentration (CETEM, 1991a, 1991b, 1993). According to Marins et al. (1991), the majority of Hg is deposited near the emission source (i.e. with 1 km).

Precipitated mercury or that which is dumped with amalgamation tailing enters the aquatic system predominantly in metallic form. How this mercury is transformed into soluble compounds depends mainly on sediment (soil) composition and physico-chemical characteristics.

3.2 - Mercury Reactivity in Natural Aquatic Systems

3.2.1 - Inorganic Species

If we assume that metallic mercury is in equilibrium in a simple aquatic system, the predominant mercury species in solution would be undissociated mercury, Hg^o (aq.). Data from Balej (1985): $\Delta G^o(Hg^o_{aq}) = 37200$ Joules, $RT = 5706$ Joules

$$Hg^o\,(l) = Hg^o\,(aq) \qquad (3.1)$$

$$\log K = \frac{-\Delta G^o}{RT} \quad \therefore \quad K = 10^{-6.5} \qquad (3.2)$$

Mercury has to be oxidized to become more soluble, i.e. to form Hg(II) species or complexes which are far more reactive. Mechanisms of methylmercury formation are faster when Hg (II) compounds exist (Bisogni and Lawrence, 1975; Imura et al., 1971). The dominance of each Hg (II) species is controlled basically by pH, Eh, chloride concentration, sulphide concentration and the presence of other soluble substances, such as organic matter (Björnberg at al., 1988).

The stability of mercury compounds can be studied using Eh-pH diagrams. The Eh-pH diagram presented in Fig. 3.1 was built with the CSIRO THERMODATA program with the assistance of Dr. Ernest Peters (Metals & Materials Eng., UBC). The system was simplified by assuming concentrations of [Hg]= 2ppb (or 10^{-8} M), [Cl]= 3.5ppm and [S]= 3.2ppm (or 10^{-4} M for each) as used by Hem (1970). Hg^o (aq) with a nearly constant solubility of 63 ppb (eq. 3.2), is predominant but other species also exist in aerated waters. Surface waters (aerated) and terrestrial soils can exhibit Eh > 0.4 V favouring stability of other Hg species that are more soluble and reactive than Hg^o (aq.), such as $Hg(OH)_2$ and $HgCl_2$. (Gavis and Ferguson, 1972; Schuster, 1991). In an oxidizing condition, if Hg(II) is present, $HgCl_2$ (aq) or $Hg(OH)_2$ should be the predominant inorganic species in solution depending on chloride concentration.

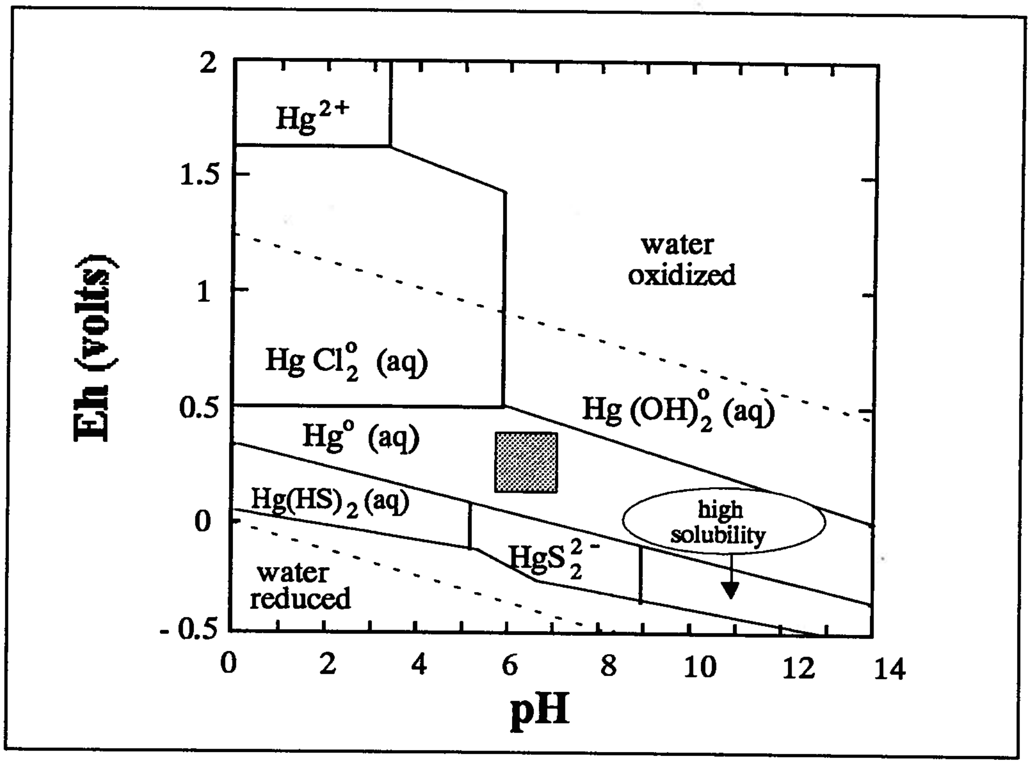

Fig. 3.1 - Eh (redox potential) versus pH for the main inorganic Hg species.
▒ : results from Poconé after Silva et al. (1991)

It seems that the information obtained from Eh-pH diagrams with respect to natural systems, must be used carefully. The theoretical values are applied to a system in equilibrium. In natural waters, it is common to find non-equilibrium conditions, as transformation rates to more stable compounds can be very slow (Baeyens et al., 1979). The most toxic form of mercury, methylmercury is an example. It is thermodynamically less stable than inorganic species. So equilibrium of inorganic and organic mercury species at high organic concentrations is not possible (Hem, 1970; Stumm and Morgan, 1981). In addition methylmercury is mainly produced in sediments and afterwards released into the water column to be accumulated rapidly by biota.

The thermodynamic analysis based on Eh-pH diagrams (Fig. 3.1) suggests that metallic mercury dumped in an aquatic environment with a sediment redox potential (Eh) below 0.4 V should be stable. However, the presence of soluble organic acids in the sediments changes this conclusion.

3.2.2 - The Influence of Organic Matter

When dissolved organic matter (say fulvic acid) is present at concentrations higher than 1 mg/l (ppm), the complex formed (Hg-FA) is more stable and predominant than any of the inorganic species (Duinker, 1980; Xu and Allard, 1991) (Fig. 3.2). The presence of fulvic acids (FA), is an important parameter that enhances solubility of organic matter and associated mercury. The more FA present in the aquatic system, the more the metal becomes water-soluble as a complex. When the ratio FA:Hg > 2, formation of water soluble complexes is favoured. Solubility of such complexes increases with pH and they are more stable than inorganic Hg complexes, preventing Hg compounds from precipitating. Schnitzer and Kerndorff (1981) have shown that over a large range of pH (4 to 9), when more than 20 ppm of FA is added to solution, Hg becomes very soluble. The authors pointed out that Hg interacts with fulvic acid in partly hydrolyzed forms.

It is known that Hg-organic complexes are formed from reaction of mercuric compound solutions with organics (Lövgren and Sjöberg, 1989; Ramamoorthy and Rust, 1976). However, no information is found in the literature to predict the complex formation when metallic mercury is brought into contact with organic-rich solutions, as occurs when Hg is condensed from vapour or amalgamation tailing is dumped into Amazon creeks that bear sediments with high organic levels. Since natural organic acids have extremely variable chemical composition, thermodynamic data on metallic-complexes are difficult to estimate.

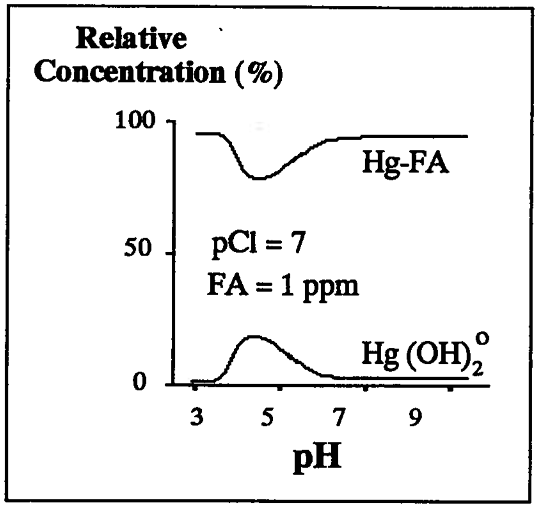

Fig. 3.2 - Relative predominance of the complex Hg-fulvic acid in relation to $Hg(OH)_2$ (Source: Xu and Allard, 1991)

Lövgren and Sjöberg (op.cit.) evaluated experimentally the formation of complexes from reacting a mixture of organic compounds found in bog waters with $HgCl_2$. The ligand is represented as a diprotic acid H_2L. Two complexes are formed, HgL and $Hg(H_1\,L)^-$ according to the reactions:

$$HgCl_2 + H_2L = 2H^+ + 2Cl^- + HgL \text{ .... } \beta = \frac{[H^+]^2[Cl^-]^2[HgL]}{[HgCl_2][H_2L]} = 10^{-10.84} \text{...............(3.3)}$$

$$HgCl_2 + H_2L = 3H^+ + 2Cl^- + Hg(H_{-1}L)^- \text{.. } \beta = \frac{[H^+]^3[Cl^-]^2[Hg(H_{-1}L)^-]}{[HgCl_2][H_2L]} = 10^{-15.24} \text{ ......(3.4)}$$

Using the solubility constants that the authors calculated for $HgCl_2°$ (aq) and H_2L equilibrium, we calculated the potential for the Hg°(aq)/complex equilibria. The Nernst Equations become:

$$E_{HgL/Hg^o_{aq}} = 0.591 + 0.0296 \log \frac{[HgL]}{[Hg^o_{aq}][H_2L]} - 0.0591\,pH \text{ .... (3.5)}$$

$$E_{Hg(H_{-1}L)^-/Hg^o_{aq}} = 0.721 + 0.0296 \log \frac{[Hg(H_{-1}L)^-]}{[Hg^o_{aq}][H_2L]} - 0.0887\,pH \text{ .... (3.6)}$$

(See Appendix XII for all steps used to derive eq. 3.5 and 3.6)

Equations 3.5 and 3.6 are plotted in Figure 3.3. The upper line represents equilibrium between complexes and Hg° (aq) in common Amazonian darkwaters, in which the dissolved organic concentration is around 10^{-4} M (Walker, 1990). In this situation, the redox potential of acidic waters (pH 4 to 5.5) must be above 0.4 V to favour Hg-organic complex formation. The higher the pH, the lower the redox potential necessary to form Hg-complexes.

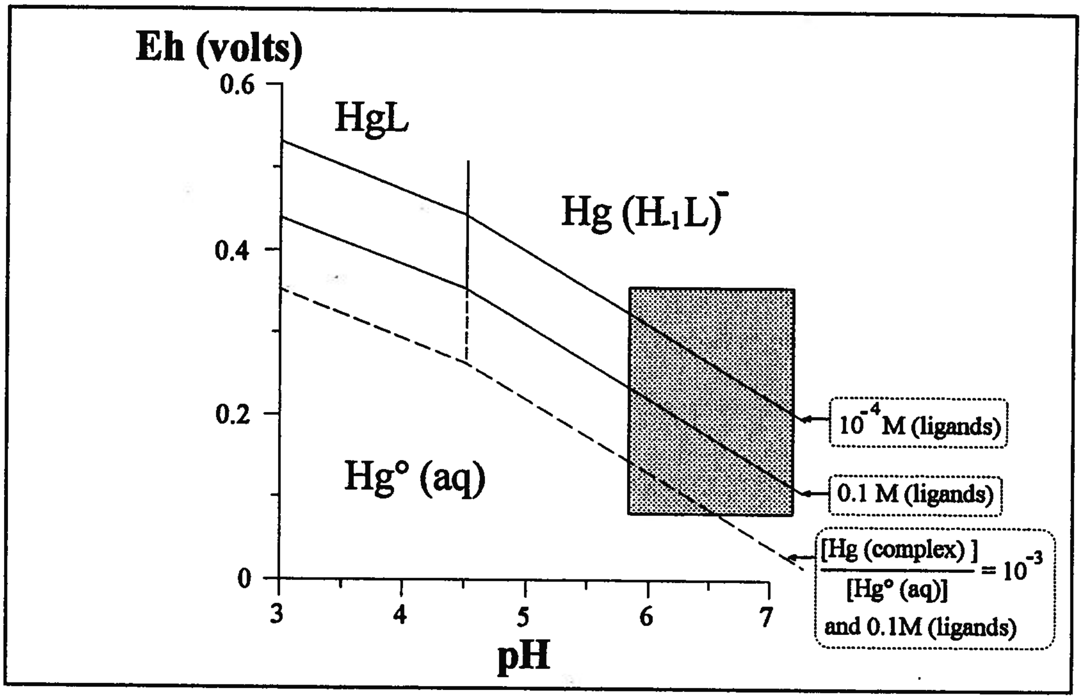

Fig. 3.3 - Equilibrium boundaries of Hg°(aq) and Hg-organic complexes.
▒ : results from Poconé after Silva et al. (1991)

Organic-rich solutions, such as interstitial waters, when in contact with metallic mercury, can form soluble complexes at lower Eh levels than those observed in the Eh-pH diagram for inorganic species (Fig. 3.1). As we do not know the chemical composition of the organic acid which provides the ligand that complexes with mercury, we assumed that the molecular weight is 1000 g and there is 100 g/l (or 0.1 M) of this ligand in the contaminated sediment. This is a reasonable assumption for interstitial waters of organic sediments according to Dr. L. Lowe (Dept. Soil Science, UBC, personal comm.). This condition is represented in Fig. 3.3 as the second full line.

The dotted lines in Fig. 3.3 represent a situation in which the concentration of the Hg complex in the interstitial water is 1000 times lower than the Hg^o(aq) concentration. If we consider a Hg^o (aq) concentration of 63 ppb, then in this situation, Hg-complex concentration would be 0.063 ppb. This level is close to background for natural waters (Fitzgerald, 1979). It can be reasonably assumed that under these conditions, there is no likelihood of Hg bioaccumulation or danger since no significant complex concentration exists in solution.

Fresh water, even with low concentrations of ligand in contact with metallic mercury, at equilibrium with Hg^o (aq) at the metal surface, might favour the stability of Hg complexes at low levels of redox potential. The Eh-pH conditions measured in bottom sediments of Poconé from June 1990 (dry season) until January 1991 showed that Eh ranges from 0.07 to 0.38 V and pH from 5.8 to 7.6. The highest measurements were obtained in the rainy season (Silva et al. 1991). Fig. 3.3 shows that Hg complex formation is possible in most investigated environments.

How these organic complexes transform into methylmercury is unclear. Bioaccumulation of these complexes likely is feasible through biotic and abiotic processes (Mannio et al., 1986; Verta et al., 1986) since fulvic acids are methyl group donors.

Humic substances, such as fulvic acids can also adsorb Me-Hg produced in the sediments (Hintelmann et al., 1994). This mechanism facilitates Me-Hg transport, and increases residence time of the toxic substance in water (Watras et al., 1994). The toxicity of Me-Hg bound to fulvic acid (a soluble complex) is considered lower than free Me-Hg but is still very high (H. Hintelmann, Trent Univ., Peterborough, Ontario - personal communication).

3.2.3 - Reactivity of Metallic Mercury with Organic Acids

In order to investigate the possibility of Hg-complex formation, I contacted metallic mercury with solutions of active components of organic soils, such as tannic acid, fulvic acid and a solution extracted from Canadian red cedar wood. Other tests were done with tea and an organic soil (from UBC) as a source of organic acids (see procedures in Appendix I). The Eh, pH and Hg concentration were analyzed in the solution at the beginning of the test and at 7, 21, 44, 77 and 100 days of contact (30 ml of solution in contact with Hg - area of contact 7 cm^2). All solutions were analyzed by flameless atomic absorption spectrometry after being centrifuged for 30 minutes at 4000 rpm.

Table 3.1 - Organics and Hg contact - Hg(mg/l) in solution.

organic compound	hours of contact						
	None	0.5	168	504	1056	1848	2400
tannic acid	0.02	0.02	0.70	7.9	9.4	-	10
cedar extract	0.03	0.33	6.5	12	60	-	94
fulvic acid	0.003	-	6.4	-	-	-	12
tea	0.02	0.02	-	31	-	174	-
soil extract	-	0.022	-	0.05	-	0.52	-

As observed in Table 3.1, the Hg concentration increased substantially reaching a level as high as 174 ppm (mg/l) Hg in the case of the tea solution. The concentration increase was accompanied by a significant change in solution Eh (Table 3.2).

The potential difference between Hg and the calomel electrode was measured and converted to Hg with respect to hydrogen by adding 0.24 V to the readings. The Eh measured is actually the result of a mixed potential of complex formation and organic oxidation. As oxygen is likely the main electron donor in the complex formation reaction, Hg oxidation is controlled by oxygen diffusion in water. So, we can conclude that the worst situation for Hg complexation with organics is when "hot spots" exist in shallow creeks with considerable dissolved oxygen available. For deep sediments, the available oxygen is likely to be extremely low and non-replenished.

Table 3.2 - Organics and Hg contact -Redox potential (volts).

organic compound	hours of contact					
	0.5	**168**	**504**	**1056**	**1848**	**2400**
tannic acid	0.360	0.390	0.483	0.490	-	0.490
cedar extract	0.300	0.310	0.425	0.424	-	0.450
fulvic acid	0.365	0.385	-	-	-	0.385
tea	0.358	-	0.394	-	0.428	-
soil extract	0.330	-	0.310	-	0.336	-

It can be seen from Tables 3.2 and 3.3 that the high levels of Hg in solution confirm the complex formation indicated by the Eh-pH diagram depicted in Fig. 3.3.

As the test proceeded, the pH of the cedar solution increased substantially (Table 3.3) and a fine dark precipitate was observed on the mercury surface. This deposit was removed by centrifugation prior to sending the solutions to the analytical laboratory (ASL - Analytical Service Laboratories Ltd.).

Table 3.3 - Organics and Hg contact - initial and final pH.

Solution	**initial pH**	**final pH**
tannic acid	3.2	2.8
cedar extract	3.9	6.1
fulvic acid	2.5	4.0
tea	4.8	4.4
soil extract	4.5	4.2

Data suggest that different complexes result for each organic material examined. With cedar extract, the Eh and pH both increased significantly suggesting that oxidation of the organic solution accompanied the complexation of Hg. With tannic acid and tea however, the pH dropped while the Eh increased suggesting formation of a different complex. Surprisingly, the Hg levels are extremely high for tea. As the Hg levels in solution were extremely high, a bacteria mediated reaction is unlikely since Hg is a bactericide. Tea should contain other organic compounds besides tannic acid which may contribute to complex formation. We did not identify such compounds.

These points are important in order to build the part of the knowledge base concerned with interaction of metallic Hg with sediments (soils) to predict bioaccumulation risk of an affected area. As methylation occur mainly in sediments, the presence of organic matter increases the risk of metallic mercury transformation (i.e. complexation) and subsequent methylation.

3.3 - Methylation

Mercury methylation is the transformation of inorganic mercury (mercuric species) into the most toxic forms of mercury: monomethylmercury (Me-Hg) and dimethylmercury. Methylation is related to the Hg(II) activity, and the presence of hydrosulphide species in solution (H_2S or HS^-), even at very low concentrations, can precipitate HgS, reducing mercury availability to the methylating agents (Björnberg et al., 1988).

Me-Hg poisoning was first identified in the early 50s by an infamous incident at Minamata Bay, Japan in which a plastic factory was discharging Me-Hg chloride into the river and bay. Up to 1992, a total of 2940 victims have been compensated and 1200 deaths were recognized. The number of victims slightly affected by Minamata disease is estimated at 10,000 (Malm, 1993).

In the 1950s, Swedish researchers observed reductions in some bird populations: first the seedeaters and later, birds that preyed on them. The use of seeds treated with organomercurial fungicides, since World War II, was the main reason for bird contamination (Putman, 1972).

In 1969, public attention was focused on mercury pollution in Canadian waterways when the Dept. of Fisheries embargoed commercial fishing catches from lakes located in Manitoba and Saskatchewan. In 1970, Fimreite, a graduate student from University of Western Ontario showed the highest[1] levels of Hg yet reported for freshwater fish anywhere in the American continent and possibly the world. Fish from the Wabigoon-English-River system were polluted with Hg from the waste of a pulp and paper factory and from a chloroalkali plant. Ojibway Indians who had fish as their main diet, exhibited symptoms of mercurialism (D'Itri and D'Itri, 1977).

In 1972, fish from old reservoirs in Manitoba showed high Hg levels. No man-made source of Hg could be precisely identified. The high Hg background associated with recent impoundments stimulated biomethylation and subsequent incorporation of Me-Hg in the aquatic biota. Forest fires were also suggested as an additional source of mercury emission (Williamson, 1986).

The most tragic episode took place in Iraq in the early 70s, when farmers ate Hg-treated seed instead of planting them. The official numbers of fatal cases were 459, but numbers as high as 100,000 people permanently disabled have been suggested by Förstner and Wittman (1979).

Although most of these episodes happened with organo-mercurial compounds, in 1967 a group of Swedish scientists proved that microbes living in bottom sediments could transform some inorganic species of mercury into methyl forms. Later on, knowledge about methylation processes increased, but some key steps about the chemical and biological mechanisms are still not well understood. Although methylation occurs in the intestine of some organisms, very high Me-Hg levels found in fish are probably due to absorption from outside rather than from internal methylation (Kersten, 1988).

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[1] Analyzing 510 fish, Fimreite found 28 ppm Hg in a northern pike, 20 ppm in walleye, 10 ppm in bass and 25 ppm in burbot. At Minamata the record was 24.1 ppm analyzed in a disabled fish that floated on the surface and 39.0 ppm in shellfish from the bay.

Many different processes of mercury methylation are presented in the literature. Basically they can be divided into: BIOTIC and ABIOTIC.

Me-Hg can be produced by most bacteria aerobically (e.g. as a misdirected synthesis of methionine) and anaerobically (e.g. during synthesis of vitamin B12). Because these pathways are shared by a large number of bacterial species, the capacity to methylate is not restricted to one or a few types of microorganisms but seems to be a widespread process associated with many bacteria (Hecky et al., 1987).

Jensen and Jernelov (1969) provided the first indication of the biological formation of Me-Hg when they spiked sediments with $HgCl_2$. Significant quantities of methylcobalamin may be available in the sediments because it is a common coenzyme in both aerobic and anaerobic bacteria. Cobalt is the active part of the methylcobalamin molecule to which the methyl group is attached. In the presence of Hg(II), cobalt is reduced to the 2+ oxidation state and methylation of mercury occurs. Any microorganism capable of synthesizing methylcobalamin is a potential methylmercury producer (Gavis and Ferguson, 1972; Wood,1971).

Kelly et al. (1994) studying Canadian reservoirs concluded that concentrations of total Hg in sediments is not a good predictor of Me-Hg and that certain environments enhance rates of Me-Hg production relative to total Hg concentration. The rate of biological methylation is determined primarily by the concentration and form of available Hg in the aquatic system as well as the methylating capacity of the microbes. The physicochemical and biological characteristics of aquatic systems also contribute to the rate of methylation and its subsequent bioaccumulation in fish. Mercury biomethylation occurs mainly in sediments and its extent depends on their characteristics. In any aquatic environment (sediments) only a small portion of the total Hg exists as Me-Hg, ranging from 0.1% to 1.4%.

Methylation seems to occur primarily in the top 1 to 2 cm of the sediments where most microbes are located. Mercury can be methylated by microbes in many aquatic matrices. Methylation has been observed in mucus and intestines of fish, rats and humans; in sewage sludge, in surface slimes and, as demonstrated by Westöö (1967), in chicken livers. Other biological mechanisms, not involving methylcobalamin, can transform mercuric compounds into Me-Hg (Wood, 1971; Fageström and Jernelöv, 1972; Mitra, 1986; D'Itri, 1990).

Sediment characteristics are important features for mercury methylation. The presence of organic matter (OM) for instance, creates a propitious environment for methylation by providing nutrients for microbes. Sometimes the role of OM in the mercury biogeochemical cycle is contradictory: it favours microorganism proliferation, promoting methylation of Hg bound to organic acids (Verta et al., 1986), but it may also act as a reducing agent for Hg(II) species, decreasing toxicity and availability (Allard and Arsenie, 1991; Alberts et al., 1974)

Some microorganisms are capable of promoting mercury demethylation, i.e. transforming Me-Hg into metallic mercury. Because Me-Hg production in sediments results from a reversible process, the actual Me-Hg production may be governed by how quickly the Me-Hg is removed from the sediments into overlying waters (Parks et al., 1984). As methylation is mainly controlled by microbial activity in the sediments, the OM type is an important variable (Gavis and Ferguson, 1972; Lindqvist et al., 1991). Nevertheless OM is a significant substrate for supplying the components for microbial growth.

An experiment carried out by Rogers (1977) introduced the possibility of abiotic methylation. The importance of abiotic methylation mechanisms for natural aquatic systems are not well understood, and probably have minor importance when compared with biological methylation. These mechanisms probably account for less than one-tenth of the Me-Hg formed in sediments according to Kersten (1988). However, Finnish researchers stress the possibility of abiotic methylation based on Hg bound to organic matter (Verta et al., 1986).

Rogers (1977) carried out his experiments using 3 soils from Nevada, USA, with organic carbon ranging from 0.5 to 3.4%. Extracting the organic matter with 0.5N of sodium hydroxide, he autoclaved the caustic solution to eliminate the possibility of bacteria presence, and amended this solution with 500 ppm of Hg as mercury nitrate. The methylating agent was not identified, but the process was considered chemical, not biological, mediated by some low molecular weight material from the fulvic acid fraction.

Lee et al. (1985) produced Me-Hg through a reaction between fulvic acid and inorganic Hg salts. The catalytic effect of Fe^{+2} and Fe^{+3} in Me-Hg production was remarkable within the pH range studied (3 to 6.5). They concluded that the mechanism of Me-Hg production from fulvic acid is not yet known but methylation increases when the fulvic acid is coordinated to other metals.

The availability of mercury species to aquatic organisms can be controlled by adsorption or precipitation mechanisms where hydrous Fe/Mn oxides and sulphides play a major role. However, Me-Hg does not bind as tightly with organic matter in sediments as does the inorganic Hg compounds. Consequently Me-Hg readily remobilizes from the stable and less reactive sediments into the overlying water. The rate of Me-Hg remobilization influences bioaccumulation in aquatic organisms, although the amount of Me-Hg can be small (<1%) relative to the total mercury concentration in the sediments (D'Itri, 1990).

Fish and other aquatic organisms assimilate methylated compounds via respiration and/or food intake. Whatever the route of bioaccumulation, uptake of Me-Hg is much more efficient than inorganic Hg. The balance between Hg accumulation and excretion depends on the type of organism. Most Hg found in fish is in methylated form so it is easily transferred to man since the intestinal absorption of Me-Hg is extremely high.

3.4 - Factors Influencing Bioaccumulation

Methylmercury, CH_3Hg^+, is mainly produced in sediments and can be incorporated into aquatic organisms via gills and/or food intake. From 70 to more than 90% of the Hg in fish is in the form of CH_3Hg^+ (Huckabee et al., 1979). The other forms of Hg found in fish are predominantly inorganic compounds. Dimethylmercury or other organic forms have not been reported in processes of accumulation in biota. Once inside the cell Me-Hg has a strong affinity for proteins. It binds to, and affects the configuration of nucleic acids, inhibiting a large number of enzymes by blocking sulphydryl groups. The combination of the lipophilic properties and affinity for the sulphydryl groups of amino acid compounds results in rapid accumulation in the muscles and fat tissues until Me-Hg is metabolized and excreted. As Me-Hg is more slowly metabolized and eliminated than inorganic compounds, the overall result is a net bioconcentration in the organism over time (D'Itri, 1990; Armstrong, 1979).

Pollutants in solution cross the gills reaching the tissues by blood flow. Assimilation of inorganic Hg across the gills is between 10 to 100 times slower than Me-Hg. In contrast, invertebrates (crayfish) show no difference between Me-Hg and $HgCl_2$ uptake by gills (Wright et al., 1991). The diffusion rate of Me-Hg across cell membranes is very fast, around 10^{-8} sec. Organisms accumulate Me-Hg so fast that the concentration of Hg analyzed in water is very low (D'Itri, 1990), or often, undetected by analytical methods.

Because Me-Hg is assimilated rapidly and is eliminated slowly, its synthesis in sediments does not have to be rapid to promote bioaccumulation. The mechanisms and rates of accumulation and elimination are unclear, but appear to depend on the specific biological characteristics of each species of fish as well as the properties of the aquatic systems. A comparison of animals differing in species, size and feeding habits confirms that the food intake of Hg is far more important than direct uptake from water. So the Hg levels in the top predators are always higher than in their food (D'Itri, 1990; D'Itri, 1972; Lindqvist et al., 1991; Connel, 1990).

Many studies on bioaccumulation attempted to find correlations between environmental variables and Hg in fish (Håkanson et al., 1988; Lindqvist et al., 1991). In fact, the search for parameters to predict bioaccumulation has always focused on finding a simple way to monitor and control Hg bioaccumulation. Unfortunately exact equations are not obtained, in spite of the effect of each separate variable on Hg bioaccumulation being relatively well established. This suggests that there are too many "unknowns" to produce satisfactory models.

To build the HgEx Expert System, we used those variables in which the influence on the process of bioaccumulation is well recognized. These variables are as follows :

3.4.1 - Water Colour

The role played by dissolved organic substances to form complexes with mercury was discussed in section 3.2. Water colour (brown) is well correlated with the organic matter content in waters. In fact, fish caught in dark waters of the Amazon region almost always show more Hg than those living in white water rivers (CETEM, 1991b; GEDEBAM, 1992). So, the presence or absence of dark waters is a good indicator of high organic loads and enhanced bioaccumulation.

3.4.2 - Water Conductivity

Low water conductivity has been correlated with high Hg content in fish. (Björnberg et al., 1988; Håkanson et al., 1988). As conductivity is related to calcium content in water, the influence of calcium is suggested. Low calcium waters increase the permeability of biological membranes (such as gills). So, in low conductivity waters, Hg species are more easily incorporated into fish via respiration than in high conductivity waters (Spry and Wiener, 1991).

3.4.3 - Sediment pH

The effect of pH on Hg bioaccumulation is complex. Field observations have shown more Hg accumulated into fish living in acidic waters (Lindqvist et al., 1991; Verta, 1986;). In aquarium studies, rainbow trout after 56 days of exposure to Me-Hg incorporated twice as much Hg at pH

5.8 than at neutral pH (Ponce and Bloom, 1991). The effect is unclear in some studies, as no correlation was obtained when pH and Hg concentration in fish are plotted. The Me-Hg production in sediments is not influenced by pH as demonstrated by a Canadian study (Miller and Akagi, 1979). However, a decrease in pH of one or two units doubled the amount of Me-Hg released from sediment into the overlying water, i.e. the pH affects the partitioning of Me-Hg between water and sediment but not the actual methylation process itself.

A review of the effect of pH on bioaccumulation was done by Richman et al. (1988). They listed 6 proposed mechanisms by which pH can influence Hg uptake:

1. Hg may enter the aquatic system with acid deposition, i.e. acid rain polluted with Hg;
2. Acidification of water can mobilize Hg from soil in the surrounding watershed;
3. Lower pH may favour production of Me-Hg over dimethyl-Hg;
4. pH conditions may alter the rate of Hg methylation and/or demethylation;
5. Acidic lakes are less bioproductive than neutral systems;
6. Biota in acidic systems are more efficient bioaccumulators than in more neutral conditions.

These factors appear to play a significant role in increasing Hg in fish in acidic systems and they can be divided into a) factors influencing bacterial processes; b) factors influencing geochemical processes. In either case, pH is a significant factor.

3.4.4 - Sediment Eh

The redox conditions of interstitial water are considered important to determine the stability of Hg° over Hg-organic complexes (as discussed in section 3.2). Depending on the sediment (soil) characteristics (high or low in organics) the Eh-pH diagram to be employed is switched between Figure 3.1 (only inorganic species considered) and Figure 3.3 (organic complexes considered).

3.4.5 - Biomass

Fish in more productive systems have been found to contain lesser amounts of Hg than in low productivity waters. This effect can be explained by a dilution effect. When more biomass is available to incorporate Me-Hg, the pollutant is shared among more individuals resulting in a lower Hg content per unit mass. In addition, fish in eutrophic (productive) waters show a higher growth rate which also increases the dilution effect. Analyses of phosphorous and nitrogen in waters do not show the real capacity of productivity of an environment. Dystrophic (low productive) waters can have P and N bound to humic substances in such a way they will not be available for primary biological production (D'Itri, 1990; Mannio et al., 1986; Björnberg, 1988). So estimates of biomass levels must be directly provided to be useful diagnostic features.

3.4.6 - Presence of "Hot Spots"

As Hg in gold mining activities is released into the environment through amalgamation tailings and by amalgam burning, two different behaviours are predicted. With amalgamation tailings, the formation of hot spots are typical. No dispersion halo has ever been observed, i.e. Hg levels analyzed in soils surrounding an old amalgamation site have not shown a gradual transition between high values (contaminated sites) and background (natural values). However, with mercury released to the atmosphere (e.g. by gold dealers), surface soil contamination can be followed by high Hg in soils in the vicinity of gold shops (Fig. 3.4).

The relatively low mobility of metallic mercury in natural watercourses creates points with very high concentrations of mercury. Even when amalgamation is conducted on dredging barges, some miners dump tailings into the river forming high mercury concentration spots. Malm et al. (1990) have reported numbers around 160 g/tonne Hg analyzed in bottom sediments from Madeira River in the Amazon region. In Poconé, Mato Grosso, old amalgamation areas could be identified by a field survey analyzing mercury by panning. Those spots could be identified either at the bottom of creeks or close to their margins, which were old amalgamation pools.

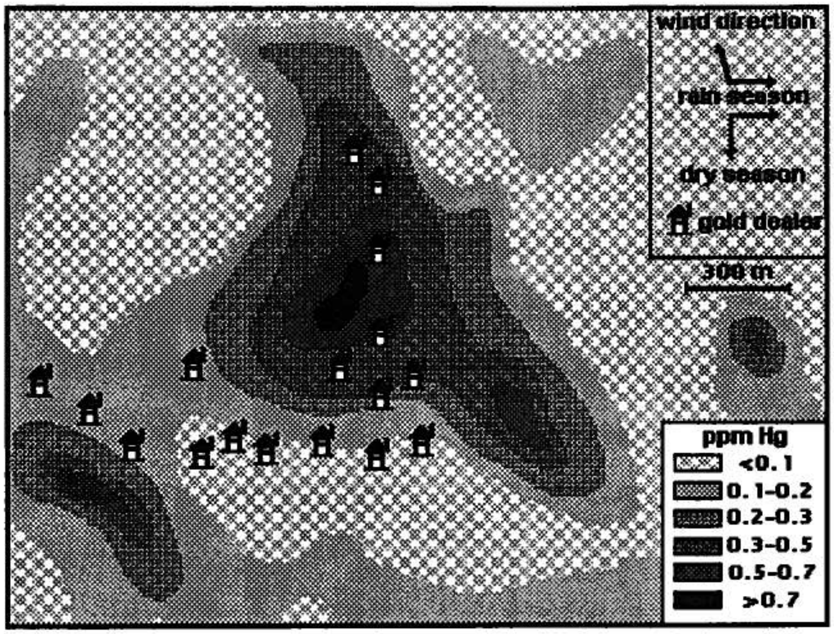

Fig. 3.4 - Hg distribution in soils around gold shops of Alta Floresta (Source: CETEM, 1991b)

In field work in Poconé, I observed that when mercury was visible after concentration by panning, the sediment (hot spot) had Hg levels higher than 3 ppm.

Clearly the presence of these hot spots in an aquatic system increases the possibility of Hg complexation and bioaccumulation.

3.4.7 - Desorption

Desorption studies are important to understanding the nature of mercury-sediment binding as well as to predict whether mercury compounds can be released from the sediment in contact with salty waters. Reimers and Krenkel (1974), in lab studies, found the desorption of inorganic Hg compounds to be negligible for almost all of the clays, organics and sands investigated. The exception to this rule occurred at high chloride concentration and pH>7. The same conclusions were found by Ramamoorthy and Rust (1976). Even when high concentrations of fulvic acid are present (10 ppm FA), less than 1% of the sediment-bound (organic-rich) mercury was removed.

3.4.8 - Contamination Factor (Hg in sediment/Hg background)

Mercury is classified geochemically as a chalcophilic element, i.e. it is mostly associated with sulphide phases. A concentration of 0.077 ppm is suggested by Saukov (1946) as the average content in igneous rocks. Jonasson and Boyle (1979) showed a wide range of Hg concentration in igneous rocks but the average is 0.028 ppm for basic and 0.062 ppm for acid rocks. The same authors showed a wide range of Hg concentration in sediments ranging from 0.010 to 3 ppm. The average of 0.071 ppm Hg is suggested by Andren and Nriagu (1979) for soils. A mean of 0.080 ppm of mercury is reported by Taylor (1964) as the earth's crust background.

The background level in rocks and sediments is divided by some authors, into two types: a) pre-industrial and b) present. They maintain that Hg background levels in surface environments throughout the world are increasing with global industrial activities (Lindqvist et al., 1984).

When we consider that the background is the natural content of a certain heavy metal in a soil or sediment, some sites, for instance, can be considered "naturally contaminated". For example in a mineralized area, rich in sulphides, Hg is higher than in ordinary areas. The pollution effect for human beings is as hazardous as from one caused by mercury discharge by gold mines. In both cases, natural variables will act to control or promote methylation.

In order to recognize anthropogenic sources of mercury in the environment, the background should be established. Soils and aquatic sediments are the best evidence to assess mercury contamination caused by local or global sources.

The Hg content usually changes with depth in the majority of soils. In general, the shallower the sampling depth, the higher the Hg content. This surface enrichment can be attributed to:

- external Hg as atmospheric fallout,
- small quantities released by chemical weathering of minerals,

- small amounts of Hg taken up by plants and returned to the soil surface by decaying plant residues (litter),
- small amounts of Hg transpired or carried by capillary action towards the surface from ground water or deeper soil layers. Hg° (gaseous) may also be transferred towar s the surface horizon and be trapped by organic matter or hydrous ferric oxides.

In the Amazon, the surface material can be influenced by two effects: a) anthropogenic mercury deposited from local or regional sources; b) lithogenic mercury transported from deep to top layers as the water flows toward the surface during the dry season. In any case, as suggested by Lindqvist et al. (1991), it seems that the best material to sample for background determination is from the soil's B horizon or deeper where the influence of anthropogenic emissions is slight.

In lateritic soils and bottom sediments from Poconé and Alta Floresta ("garimpo" regions), values ranging from 0.1 to 0.3 ppm Hg are accepted as background levels for the -200 mesh (<0.074 mm) fraction of these iron oxide-rich materials (CETEM, 1989, 1991b). Lacerda et al. (1990) have analyzed bottom sediments of non-impacted Amazonian river. They found values ranging from 0.05 to 1.2 ppm of Hg for size fractions <0.063 mm. The higher values are related to more organic matter associated with the sediment, whereas intermediate numbers were observed for sediments rich in hydrous ferric oxides (HFO).

The presence of organic matter promotes higher Hg levels in sediments. Grain size can also influence Hg content. Fine fractions concentrate Hg more than coarse ones because of their higher specific surface area. Gravels represent coarse sediments composed of limestone, sandstone, or any igneous or metamorphic rocks (e.g. granite, gneiss, diorite, gabbro, etc.) which are rocks usually low in Hg content. The colour of the sediment can also be used to infer Hg background. White sediments are frequently related with parent rock poor in Hg. The presence of HFO (yellow-red) as products of weathering of mafic minerals or the presence of organic matter (grey-black) will increase the Hg background since these components are strong adsorbents of minute amounts of mercury from water.

Mercury can also be dispersed in the sediments as a result of amalgam burning. Fine fractions usually have more mercury than coarse ones. Mercury in the +200 mesh (0.074 mm) fraction frequently occurs as droplets while in the finer fraction, usually it is adsorbed onto the mineral surface (e.g. hydrous ferric oxides). The Hg analyzed in the -200 mesh has the anthropogenic and lithogenic contribution. So, the background must be established in order to discount the lithogenic portion (CETEM, 1989). When samples are analyzed without screening, high amounts of coarse quartz reduce the Hg assay. In addition, more homogeneity is obtained with -200 mesh samples (CETEM, 1991b).

When chemical analysis of a sediment is available, it should be compared with the background concentration to establish the contamination level of a site or region. The Index of Geoaccumulation (I_{geo}) first proposed by G. Müller and described by Förstner et al. (1990) as a quantitative measure of metal pollution in aquatic sediments, uses the relationship between concentration (C) of the element in the sediment (fraction <2 μm) and the background in fossil argillaceous sediment - average shale (B):

$$I_{geo} = \frac{\log_2 C}{1.5 \cdot B} \quad \text{(3.7)}$$

Rodrigues (1994) applied this index to evaluate the -200 mesh fraction of sediments from "garimpo" areas in Poconé and Alta Floresta and used the Hg concentration of the -200 mesh fraction of non-impacted creek sediments as the background level. Most sediments in Poconé showed I_{geo} between 0 and 2. An average index of 5 was observed in turbid rivers of Alta Floresta which mirrors the capacity of the fine (ferruginous) sediment to transport adsorbed Hg.

Håkanson (1980) introduced the concept of risk in the sediment analysis. He proposed an "ecological risk index" which takes into consideration a contamination factor, the toxicity of the metal, its abundance, etc. This is a complex index to calculate, but the contamination factor (C_f) is calculated by dividing the mean content of Hg from at least 5 samples by the pre-industrial reference value (0.25 ppm for Hg). This pre-industrial factor was calculated based on an average Hg content in sediments mostly from Swedish lakes. It seems that this factor could be replaced with the background level to be applied in other regions.

The process of describing the contamination factor in linguistic terms is the most attractive point of this work. The terms adopted by Håkanson (1980) to characterize his contamination factor are shown in Table 3.4.

Table 3.4 - Description of the Contamination Factor (C_f)
(Håkanson, 1980)

C_f	**Characteristic**
< 1	low
1 to 3	moderate
3 to 6	considerable
> 6	very high

In the HgEx System, the Hg concentration in a sediment (-200 mesh fraction), when available, is divided by the background level (analyzed or inferred) to determine the contamination factor and this variable is mapped into Fuzzy sets to obtain the Degree of Belief (DoB) in each of the following linguistic terms : "low", "moderate", "considerable" and "very high" (Fig. 3.5).

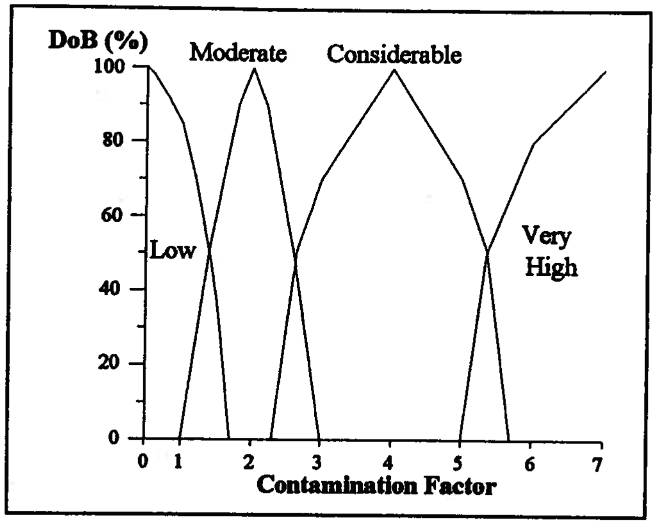

Fig. 3.5 - Fuzzy Sets to define the Contamination Factor

When the contamination factor is 1.2, there is 70% of belief in the concept "low" and 30% in "moderate". These linguistic terms are used in the heuristic model described in the Chapter 6.

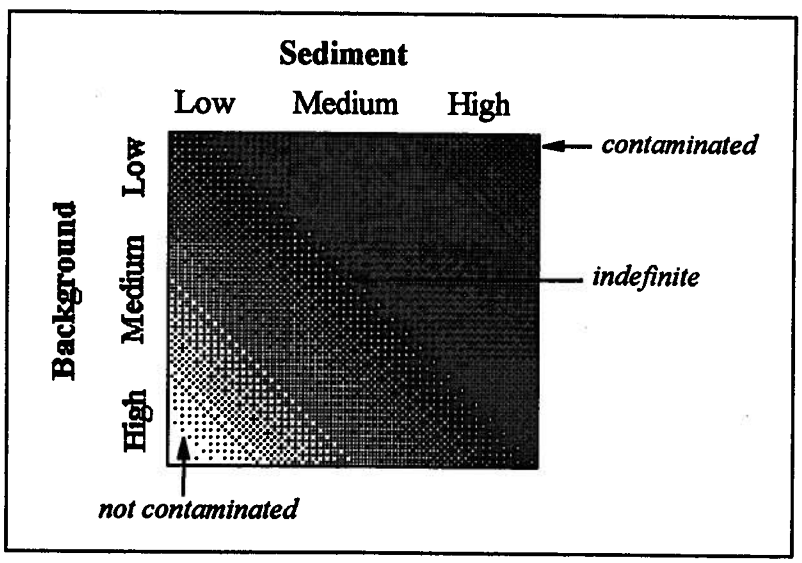

Fig. 3.6 - Contaminated or not-contaminated sediment: a fuzzy concept

Classification of contamination level is a fuzzy concept since the contamination factor is in a continuum gradient derived from comparison between background levels and Hg concentration in sediments (Fig. 3.6). A reasonable definition of pollutant is "*a substance present in greater than natural concentration as a result of human activity and having a net detrimental effect upon its environment or upon something of value in that environment*". Contaminants, which are not classified as pollutants unless they have some detrimental effect, cause deviation from the normal composition of an environment. (Manahan, 1991). Since pollution implies a toxic situation, the contamination factor is insufficient on its own to characterize a bioaccumulation risk.

3.4.9 - Other Factors

There are other factors which enhance methylation and bioaccumulation, such as temperature, and sulphate levels. As there are controversies about the influence of these variables on the biota, they were not taken into account in our heuristic model.

Temperature can increase the microbial production of Me-Hg as well as the metabolic rates of fish and Hg uptake. However it was observed that the biological half-life of Hg in fish decreases with increasing temperature. Therefore, fish from watercourses in which the temperature reaches 20°C can be expected to eliminate Hg approximately twice as fast as fish in water of about 10°C. (Spry and Wiener, 1991; D'Itri, 1990).

Sulphate levels in water can stimulate bacteria growth. Although laboratory tests indicated that the methylation rate is not sensitive to the concentration of sulphate in waters (Kerry et al., 1991), a very strong relationship between Me-Hg and sulphate has been observed by Parks et al. (1984) studying Canadian lakes. If we introduce sulphate as an important variable (it does not appear to be) we would introduce an additional difficult data input into the system. The same logic applies to dissolved oxygen and sulphide concentration in water, both variables of which have contradictory cause and effect studies.

3.5 - Factors Controlling Bioaccumulation

Adsorption is the main mechanism to control availability of soluble mercury to the biota. The mechanisms of adsorption depend on sediment grain size, composition and the aquatic system variables. In fact, resuspension of non-mercury polluted sediments has been suggested as a method to reduce bioavailability of mercury in the water column and to reduce concentration of mercury in the surface sediments of Wabigoon-English River system (TCOSC, 1983).

Most natural adsorption processes that occur with heavy metals such as copper, zinc and lead are related to single ions, i.e. Cu^{2+}, Zn^{2+}, Pb^{2+}. However, since the dominant species of Hg in solution are uncharged complexes, the adsorption mechanism is not ion exchange but rather formation of compounds. This is known as specific adsorption (Schuster, 1991). Inorganic Hg compounds are not adsorbed by soils and sediments better than are methylmercury and other organic compounds (Adriano, 1986; D'Itri, 1990).

Amorphous and poorly crystalline hydrous ferric and manganese oxides (HFMO) have an enormous capacity for fixation of heavy metal ions from solution as demonstrated by many authors (Chao and Theobald, 1976; Hem, 1974). Studies of ferruginous sediments from Poconé showed an outstanding capacity for mercury adsorption. This phenomenon was also responsible for almost no incorporation of mercury in test organisms caged for 3 months in contact with heavily polluted sediments (CETEM, 1991a). A correlation between Fe and Hg ($r = 0.72$) was found in the impacted sediments showing that the HFO are the main Hg bearing phase in Poconé (Rodrigues, 1994).

Irreversible adsorption of some elements suggests formation of compounds on the surface (Veiga et al., 1991). Recent studies of adsorption of $HgCl_2$ (Silva et al., 1991) onto synthetic hydrous ferric oxides (HFO) showed 98% of mercury was adsorbed in less than 15 minutes. This experiment showed the coprecipitation of mercury and HFO as the most effective process of metal adsorption as demonstrated by Krauskopf (1956) in earlier work.

Lockwood and Chen (1974), studying adsorption of Hg(II) salts onto synthetic HFO, found that adsorption is not affected by pH in the range from 4 to 10, but dropped off sharply between pH 4 and 3. The same fact was reported for HFO-rich sediments of Poconé (CETEM, 1991a). These

American researchers have also observed that the magnitude of adsorption of Hg(II) on manganese oxides, is far greater than on HFO. The large adsorption capacity, up to 10% of Hg by weight, may make MnO_2 useful in water treatment.

Studies with ferruginous and slightly organic sediments from Poconé have shown an outstanding capacity for mercury adsorption. Two water boxes lined with epoxy paint received 280 litres of water each, 100 kg of each soil and enough mercury chloride to give 10 ppm of Hg in solution. The boxes remained undisturbed for 17 days with frequent analyses of Hg content in solution. Around 80% and 96% of the mercury added was adsorbed by the end of the experiment onto the ferruginous and carbonaceous sediments respectively (CETEM, 1991a).

Breteler and Saska (1985) have shown that organic sediments are good scavengers of mercury but they did not retain this metal very well. Mercury desorption was highest in the period immediately following the adsorption study.

Clay minerals are also active components to adsorb Hg from solution. The adsorption capacity of these minerals is very high but the binding strength is usually weak and dependent on aquatic system variables such as: pH, type of species in solution, Eh, etc. In the case of Hg adsorption, the stable soluble species are not charged and little effect of pH was observed on $HgCl_2$ adsorption by clay minerals (Reimers and Krenkel, 1974). Clays may show an indirect effect in heavy metal adsorption due to the ability to act as nucleation centres for Fe/Mn oxides or organic matter. These materials are more effective for metal adsorption (Duinker, 1980).

The inhibition of Hg adsorption is remarkable when high chloride levels are present in solutions containing HFO or MnO_2 (Lockwood and Chen, 1973), clay minerals (Reimers and Krenkel, 1974) and organic matter (Lodenius et al., 1983).

Partial or selective heavy metal extraction is the usual methodology to study the metal association with sediment components (Adriano, 1986). Mercury associated with each sediment component is determined by applying selective extractants which are capable of dissolving a specific component (small attack on others) allowing the associated mercury to go into solution. After each attack, the sediments are filtered and washed recovering the solids for the next attack. The solutions obtained in each extraction are analyzed.

Silva et al. (1993) applied a sequential extraction method to two samples of a ferruginous (17% Fe_2O_3) and a carbonaceous (1% of total carbon) sediment from Poconé, Brazil. The Fe-rich sediment was collected in a "hot spot", i.e. an abandoned amalgamation pool, and the -200 mesh (0.074mm) fraction analyzed 1 ppm Hg. The clay fraction (0.002 mm) had approximately 20 times more mercury than the total sample. The -200 mesh fraction of the carbonaceous sample, collected distant from "garimpo" influence, analyzed 0.02 ppm Hg and its clay fraction 0.21 ppm. As observed in Table 3.5, the procedure revealed that most mercury is associated with the hydrous ferric oxides (77.5%) and with organic matter (64 %) in the Fe-rich and carbonaceous sediments respectively.

At UBC, the Hg mobilization from an amalgamation tailing from Poconé was studied. This tailing is the result of gravity separation by centrifuging and is composed mostly of heavy ferruginous minerals. Two samples of 150 g of amalgamation tailing with 27 ppm Hg were mixed with 200 ml distilled water in separate dark vials. In one vial, tannic acid was added to reach 0.01 M concentration. After resting for 21 days, the solutions were siphoned, centrifuged and analyzed. About 0.05 ppm of Hg was analyzed in both solutions, indicating either that the tannic acid solution was not sufficient to complex metallic Hg or ferruginous components of the tailing adsorbed any Hg complex formed.

Table 3.5 - Sequential extraction of Hg from different components of sediments from Poconé. Source: Silva et al. (1993).

	% Hg extracted	
Hg-associated phase	Fe-rich	carbonaceous
Exchangeable(1)	3.0	14.0
Organic matter + metallic Hg(2)	2.0	64.0
Hydrous ferric oxides(3)	77.5	13.0
Residual Hg(4)	17.5	9.0
TOTAL	100	100

NOTE:

(1) This is the Hg weakly adsorbed onto the sediments, usually on clay minerals, which can be exchanged by ammonium acetate (1M).

(2) This step was not capable of distinguishing between Hg associated with organic matter and eventual metallic Hg : 20 ml of oxygenated water (30% vol.) + 0.02 M nitric acid in the proportion of 5 H_2O_2 : 3 HNO_3; five hours shaking following two hours at sand bath (60°C). Afterwards 10 ml of ammonium acetate (3.5 M) is added and a further one hour of constant agitation at room temperature is needed.

(3) Mercury associated with hydrous ferric oxides (mainly amorphous) was evaluated by attack with 50 ml HCl 0.5 M for 8 hours of agitation at room temperature.

(4) This is the residual mercury, i.e. that which is very tightly bound to the sediment, including the original lithogenic mercury. A strong triacid mixture: $HF+HClO_4+HNO_3$ (5ml+5ml+5ml) was used at 60 °C in order to dissolve all solids.

(5) All solutions were analyzed by flameless atomic absorption spectrometry.

The following points about mercury adsorption by natural components of sediments are outlined based on the contribution of several authors (Schuster, 1991; Schnitzer and Kerndorff, 1981; Xu and Allard, 1991; Duinker, 1980; CETEM, 1989; Silva et al., 1993; Andersson, 1979) :

- in freshwater conditions, no charged species of Hg are adsorbed;
- the intensity of adsorption of HFO is higher than clay minerals;
- chloride decreases mercury adsorption in any sediment component;
- at neutral pH, hydrous Fe oxides are effective adsorbents;
- organic matter has the ability to adsorb and form soluble compounds with mercury;
- how mercury bound to soluble or insoluble organic matter transforms biotically or abiotically into Me-Hg is not well-understood;
- hydrous ferric and manganese oxides are effective in reducing the mercury bioavailability.

4. Mercury and Man

"The garimpeiros' forest is radically different from the ecologists' forest ... which is the true forest: the profane or the sacred one ?"
Lívia Barbosa

4.1 - Signs of Bioaccumulation in "Garimpos" : Blood, Sweat & Tears

The first evidence of mercury bioaccumulation in Amazon fish was reported in 1984 by the Jacques Cousteau Society as a result of an expedition of the scientist to Serra Pelada in 1982 (Hacon, 1990). A limited number of monitoring expeditions took place in the following years.

Many environmentalists did not have clear knowledge about mercury toxicity and its transformations in the environment, and so not infrequently they were surprised by theatrical performances of "garimpeiros" with the intent to embarrass ecologists. In 1987, José Altino Machado, a "garimpeiro" leader, ingested metallic mercury in front of TV cameras to show that mercury is inoffensive. In a further interview he declared (Barbosa, 1992):

"*... the mercury we employ is inert: it is the same as that in teeth, the same that old people used to cure constipation; it goes in and goes out of the organism. There is no relation with the mercury in Japan* (Minamata)*... It does not contaminate. Even "garimpeiros" who inhale mercury vapours, they are not poisoned... We will measure mercury levels in the waterways. I challenge someone to show me a person, just a person, contaminated by mercury in the Amazon... The point is, as they* (ecologists and government) *cannot do anything against a citizen pursuing a better way of living, they make up this story of river pollution and shut down all "garimpos". These ecologist "boys" do not realize they are being used as political instruments.*"

Mercury became an interesting weapon to attack "garimpos" although little knowledge about its effect was understood by the accusers. One example is an interview of a renowned ecologist and anthropologist Maria Manuela C. Cunha to an important Brazilian journal, "Ciência Hoje, v.11, n.64, p. 68-72", in 1990, about the recent invasion of Yanomami land by "garimpeiros". The anthropologist declared:

"... all preserved areas in the Amazon belong to natives. I have seen satellite images and it is possible to distinguish between native areas and mining areas. In the Yanomami land occupied by "garimpeiros", the colour of the creeks calls attention; this is caused by mercury contamination of the water..."

Despite her obvious "limited" knowledge on how to interpret satellite images, this anthropologist did state one useful and important fact in her interview : people in the capital of the Roraima State, Boa Vista city, were no longer drinking tap water and were afraid to eat fish.

The frightening term "methylation" changed the image about mercury. How methylation happens and how it is measured was another mystery and a taboo to be addressed and discussed only by a selected elite. In some cities, fish consumption declined and mineral water started to be a good business. The media was creating panic instead of alerting and providing solutions for affected communities.

Concern for the environment began to enter into the speech of the "garimpeiros" in the 90s as a way to address the harsh criticisms. In 1991, Ivo Lubrina, president of the Amazonian Union of "Garimpeiros" - USAGAL declared in a interview (Lobato and Barbosa, 1992):

"Thanks to radio and TV, "garimpeiros" are concerned now about mercury, but they don't know exactly why. As there is no orientation from government or technical people, everything continues as before. I would say that the transfer of news among "garimpeiros" is happening like a rotten onion: it is going from one hand to another".

The natural background in fish has been estimated to be between 0.05 to 0.3 ppm and may be less than 0.01 ppm in short-lived herbivorous species (Suckcharoen et al., 1978). However, the tolerance[2] limit level of Hg in fish is a variable value adopted by many countries to control Hg

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[2] This level is established for an average ingestion of 400 g fish weekly. For a person ingesting 200 g of fish daily, as observed in the Amazon, this level should be lower (see ADI on page 60).

content in edible parts: 0.5 ppm (μg/g wet weight) is used by USA, Canada, Brazil; 0.7 ppm by Italy; 1 ppm by Finland, Sweden and Japan (Johansson et al, 1991; Hacon, 1990).

Many studies have established the extent of concentration in fish in the Amazon region. Levels higher than 0.5 ppm Hg are mainly related with carnivorous species. Martinelli et al. (1988) analyzed eight samples of fish showing Hg levels ranging from 0.04 to 2.24 ppm Hg and 3.8 ppm was measured in a sample of "acari-bobo" eggs. A series of studies in Madeira River Basin, have confirmed the high levels of Hg in fish, but few correlations between these values and natural variables are reported (Malm et al., 1990; Pfeiffer et al., 1989; Pfeiffer et al., 1991).

Fernandes et al. (1990) analyzed 46 samples of fish in Carajás, PA, where small "garimpos" were operating. Herbivorous species contained Hg ranging from 0.04 to 0.42 ppm whereas carnivorous varieties had 0.05 to 0.91 ppm Hg. These authors measured Hg in hair from people living in these regions and the average was 4.8 ppm. The normal level of Hg in hair is 2 ppm, but fish-eating people usually have 6 ppm as normal background.

No contamination was observed when 236 samples of different species of fish (average 0.1 ppm) and 100 snails (average 0.23 ppm) from Poconé, MT, were examined. In spite of the existence of highly polluted areas, the highest Hg level measured in fish was 0.38 ppm in "acará" (*Geophagus sp.*) and 0.9 ppm in snail (*Pomacea caniculata*). It seems that the abundance of iron oxides in this area restricts the bioavailability of Hg. (CETEM, 1989; CETEM, 1991a).

In 1991-92, an international team comprising Brazilian and British scientists analyzed 52 fish from three areas of "garimpo" in the Amazon region showing values ranging from 0.01 to 2.6 ppm Hg. About 30% of fish samples exceeded the guideline of 0.5 ppm Hg established by the Brazilian Government as the safe limit for fish consumption. Higher levels were observed in fish from the village of Jacareacanga where "garimpo" and other activities with gold (i.e. gold melting) had been discontinued several months before fish sampling (GEDEBAM, 1992).

In Alta Floresta, MT, samples of mollusc *Hemisinus tuberculatus* showed more Hg in guts (up to 1.1 ppm) than in muscles (up to 0.63), indicating an uptake via the food web. No correlation was observed between size and Hg content. Almost 100 samples of fish from different rivers of Alta Floresta showed Hg ranging from 0.02 to 0.43 ppm, and 0.05 to 0.71 ppm in muscles and livers respectively. The exception was a "jaú" (*Paulicea sp.*) of 4 kg fished in a remote region, from a black water river, where no gold mining operation has ever existed. This carnivorous fish showed values of 0.9 and 1.1 ppm Hg in muscles and liver respectively (CETEM, 1991b).

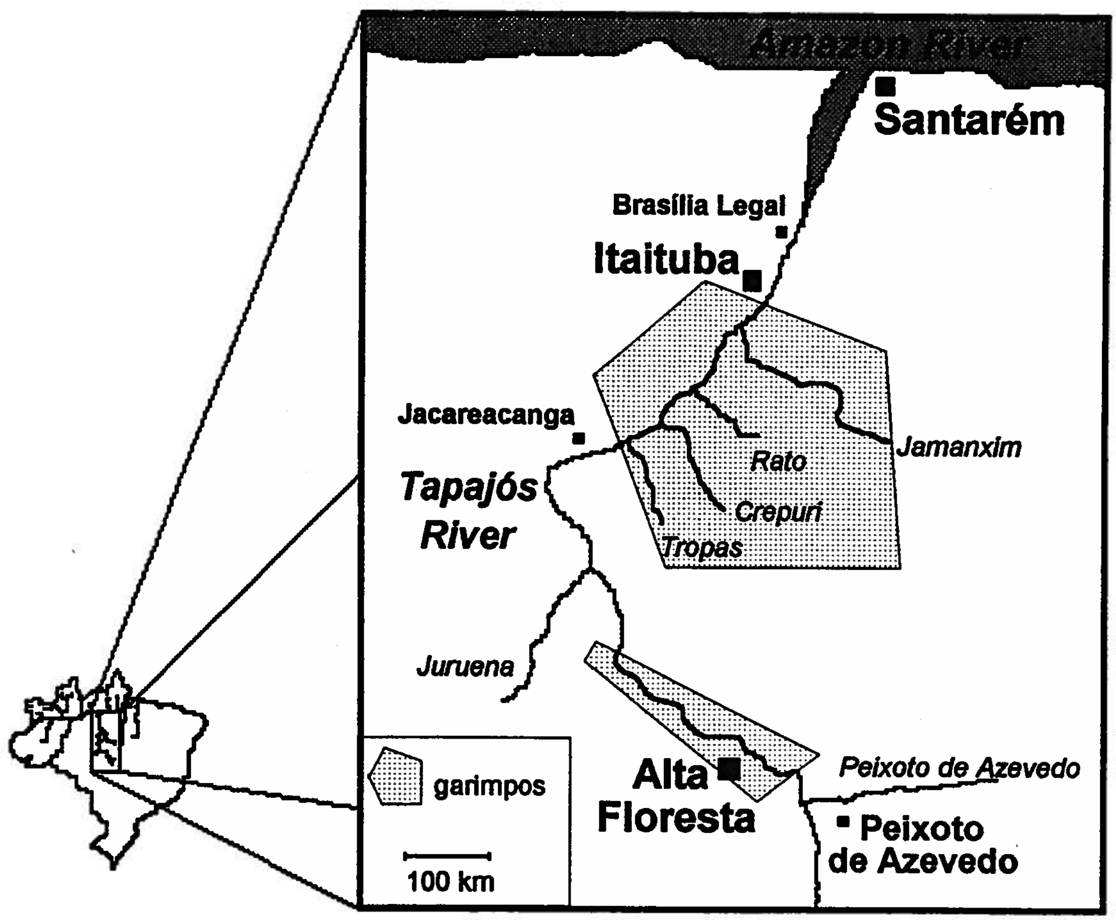

Fig. 4.1 - "Garimpos" in the Tapajós River region

In the Rato River, region of Itaituba, State of Pará, Brazil (Fig. 4.1), 13 samples of carnivorous fish showed an average of 0.69 ppm Hg (0.31 to 1.40 ppm), while omnivorous and detritivorous fish analyzed an average of 0.03 and 0.01 ppm Hg respectively. Methylmercury represented more than 84% of the total Hg in the carnivorous fish (CETEM, 1993).

In a large monitoring program, the Secretary of Mining of Pará State (SEICOM) obtained an average of 0.5 ppm Hg in 20 carnivorous fish collected in Itaituba in 1991. In other surveys in 1992, the average was 0.41 ppm for 47 carnivorous fish. No significant difference was observed between fish sampled in dry and rainy seasons (Silva et al., 1994 and Alberto Rogério B. Silva, SEICOM - personal comm.). The surveys conducting by SEICOM in 1991 and 1992 have shown that fish in Itaituba are more contaminated than those sampled in Jacareacanga (250 km) and Santarém (500 km) (Table 4.1). In Jacareacanga, tucunaré (*Cichla ocellaris*), one of the most edible species in the Amazon (Boischio, 1992), showed an average of 0.43 ppm, while in Santarém this average drops to 0.12 ppm. In spite of high levels of Hg in large (80 to 100 cm) filhote samples (*Brachyplatystoma filamentosum*), low levels of Hg were detected in 122 carnivorous samples fished in Tapajós River near Santarém.

It is difficult to compare Hg levels in fish from the 3 sites due to different migration habits of species. Piranhas in general do not make long migrations and live mostly in quiet waters. Piranha mafurá has low Hg levels because this specie, in spite of being carnivorous, has a preference for seeds. In contrast, black piranha has 80% of its diet based on fish (Goulding, 1980). It seems that this species is the best indicator of Hg contamination of a site.

Barbosa et al. (1994) showed that 22% of the piscivorous fish from Madeira River have Hg levels higher than 0.5 ppm. In other work, Boischio and Barbosa (1994) showed that ingestion of herbivorous fish should be encouraged among riverine communities. As depicted in Table 4.2, the average Hg content in carnivorous fish is 10 times higher than in herbivorous ones.

Table 4.1 - Hg in carnivorous fish (adapted from unpublished data from SEICOM)

Fish	Hg (ppm)	n	Range (ppm)
Itaituba			
Pescada (*Plagioscion squamosissimus*)	0.43	33	0.072 - 1.23
Piramutaba (*Brachyplatystoma sp*)	0.43	7	0.18 - 0.67
Tucunaré (*Cichla ocellaris*)	0.42	23	0.18 - 0.96
Jacareacanga			
Peixe-cachorro (*Rhaphiodon vulpinus*)	0.69	5	0.52 - 0.91
Jacundá (*Batrachops sp*)	0.47	3	0.46 - 0.48
Surubim (*Pseudoplatystoma fasciatum*)	0.46	2	0.42 - 0.51
Tucunaré (*Cichla ocellaris*)	0.43	10	0.21 - 0.93
Mandi (*Pimelodus sp*)	0.28	6	0.24 - 0.38
Piranha-mafurá (*Serrasalmus cf. striolatus*)	0.10	6	0.051 - 0.17
Santarém			
Filhote (*Brachyplatystoma filamentosum*)	0.45	10	0.11 - 0.92
Surubim (*Pseudoplatystoma fasciatum*)	0.30	19	0.13 - 0.54
Dourada (*Brachyplatystoma flavicans*)	0.29	28	0.13 - 0.54
Pescada (*Plagioscion squamosissimus*)	0.22	29	0.05 - 0.46
Black Piranha (*Serrasalmus rhombeus*)	0.21	8	0.078 - 0.39
Tucunaré (*Cichla ocellaris*)	0.12	28	0.014 - 0.26

n = number of samples analyzed

Table 4.2 - Hg in fish from Madeira River
Source: Boischio and Barbosa (1994)

Trophic level	Mean (ppm Hg)	Range (ppm Hg)	number of samples
carnivorous	0.74	0.076 - 2.21	116
omnivorous	0.35	nd - 0.15	88
detritivorous	0.16	0.03 - 0.96	58
herbivorous	0.074	nd - 0.5	56

nd = not detected (<0.02 ppm)

4.2 - Mercury and Human Health

Mercury accumulation in humans has two main pathways in the Amazon:

1. occupational exposure to vapours,
2. methylmercury transferred by fish.

4.2.1 - Hg Vapour Exposure

Inhalation of Hg vapour is more significant for "garimpeiros" and gold shop workers. Once in the lungs, Hg is oxidized forming Hg (II) complexes which are soluble in many body fluids. The ultimate effect of Hg and related compounds is the inhibition of enzyme action (Jones,1971). Cases of occupational mercury exposure are reported in a variety of workplaces. Some high values of Hg in air are listed in Table 4.3.

Oxidized mercury can easily diffuse across the blood-brain barrier which is a series of multiple systems which regulate the exchange of metabolic material between brain and blood. The impairment of the blood-brain barrier, together with the possible inhibition by Hg of certain associated enzymes will certainly affect the metabolism of the nervous system (Chang, 1979).

Table 4.3 - Cases of occupational exposure to Hg vapours

Hg ($\mu g/m^3$)	Workplace	Reference
60,000	amalgam burning in a "garimpo"	Malm, 1991
12,000	dentist office (amalgam restorations)	Stopford, 1979
6,000	underground cinnabar mining	Stopford, 1979
3,000	police office - finger printing powder	Stopford, 1979
1,000	filling operation of fluorescent lamps	Stopford, 1979
300	gold dealer shop in Rondonia, Brazil	Malm et al., 1990
100	chloroalkali plant & thermometer factory	Stopford, 1979
30	lighthouse in British Columbia	van Netten and Teschke, 1988

NOTE: background in cities Hg is 0.01 $\mu g/m^3$ (Matheson, 1979)
limit for public exposure is 1.0 $\mu g/m^3$ (Malm et al., 1990)
limit for industrial exposure 50 $\mu g/m^3$ (BC-MEMPR, 1992)

Hg vapour is completely absorbed through the alveolar membrane and is oxidized in the blood and tissues before reacting with biologically important sites (Mitra, 1986). The biological half-life of Hg in blood absorbed as vapour is about 3 days (Hacon, 1990) when it is excreted through urine and feces. The time interval between passage of elemental Hg through the alveolar membrane and complete oxidation is long enough to produce accumulation in the central nervous system (Mitra, 1986).

The kidneys are the affected organs in exposures of moderate duration to considerable levels while the brain is the dominant receptor in long-term exposure to moderate levels (Suzuki, 1979). Total mercury elimination can take several years. The half-life of mercury in the brain is longer than in the kidney, thus urine levels would not be expected to correlate with neurological findings once exposure has stopped A short-term exposure to high levels causes clinical symptoms which mainly involve the respiratory tract. Mercury levels in the urine of new workers should be lower than those of workers with a longer duration of exposure (Suzuki, 1979; Stopford, 1979).

Cook and Yates (1969) reported an incident of fatal mercury intoxication in a 42-year-old dental surgery assistant with at least 20 years of mercury handling. She died as a consequence of a fatal nephrotic syndrome. Over 520 ppm of mercury in her kidneys were measured. This is almost 100 times higher than in a normal kidney.

The symptoms usually associated with undue Hg vapour exposure are erethism (exaggerated emotional response), gingivitis and muscular tremors. This latter is a symptom associated with long-term exposure to high levels of Hg vapour. The common manifestation of chronic exposure to excessive levels of Hg vapour is metallic taste and gum diseases, such as gingivitis, ulcers and formation of a blue line at gum margins (Stopford, 1979). A person suffering from a mild case of Hg poisoning can be unaware because the symptoms are psycho-pathological. These ambiguous symptoms may result in an incorrect diagnosis (Cassidy and Furr, 1978).

Typical symptoms of long-term Hg-vapour poisoning were patterned by the Mad Hatter in Lewis Carroll's *Alice's Adventures in Wonderland.* Back in the 19th century, workers in the felt-hat industry dipped furs into vats of mercury nitrate solution to make them pliable for shaping. In the process they absorbed the compound through their skin and inhaled mercury vapour. The result was tremors, loss of teeth, difficulty in walking, and mental disability (Putman, 1972).

Since inorganic Hg poisoning affects liver and kidneys, high Hg levels in the urine can indicate undue exposure to Hg vapour. Experiments with animals indicate continuous exposure to Hg above 0.3 $\mu g/m^3$ of air may present a health hazard. Acute Hg poisoning, which can be fatal or can cause permanent damage to the nervous system, has resulted from inhalation of 1,200 to 8,500 $\mu g/m^3$ of Hg (Jones, 1971).

A level of 60,000 $\mu g/m^3$ was measured by Malm (1991) in the air when amalgam is burnt in pans. This number reduces to as low as 10 μg Hg/m^3 when retorts are used. This is still high, but lower than the limit of 50 μg Hg/m^3 for industrial exposure - TWA[3] (BC-MEMPR, 1992). Inside the gold shops, Malm (op. cit.) measured 83 μg Hg/m^3 as a mean concentration for 2 hours of sampling when gold was not being melted.

GEDEBAM (1992) investigated the effect of mercury in the "garimpeiros" who have burnt amalgam in pans. Samples of urine have shown Hg levels >20 μg.l^{-1} for workers burning amalgam daily (Fig. 4.2) whereas levels lower than 10 are considered normal (OECD, 1974). Some of these "garimpeiros" should show signs of mercurialism, however the diagnosis is not easy as symptoms are often confused with fever, alcoholism, malaria or other tropical diseases.

Despite the fact that blood analysis gives a combined picture of both metallic and organic Hg contamination, studies by GEDEBAM (1992) show that blood is a better indicator of undue vapour exposure than urine samples for "garimpeiros" who burnt amalgams occasionally. According to A. Boischio (Univ. Indiana, personal comm.), an expert in Hg toxicology, urine analysis is a complex task and at low Hg concentrations, sampling and analytical problems are usual, with considerable random variations.

Farid et al. (1992) analyzed urine of employees in gold shops at Alta Floresta, Mato Grosso, Brazil. The city has 32 gold shops where 1 tonne of gold is bought and melted per month in fume hoods with no filters. Gold bullion has between 1 and 5% Hg (Farid et al., 1991). The five most important shops were chosen and 17 workers were sampled. About 200 ml of the first urine of the day were collected. The results showed an occupational intoxication of at least 13 individuals (>20 μg.l^{-1} Hg). Symptoms such as irritability, decreased memory and metallic taste were detected among the workers during interviews. Regretfully, information about the period of exposure or the levels of Hg levels in the workplace is not available in this study.

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[3] TWA = Time Weighed Average means the time weighed average concentration for a normal 8 hour day and 40 hour workweek, to which nearly all workers can be repeatedly exposed without adverse effect.

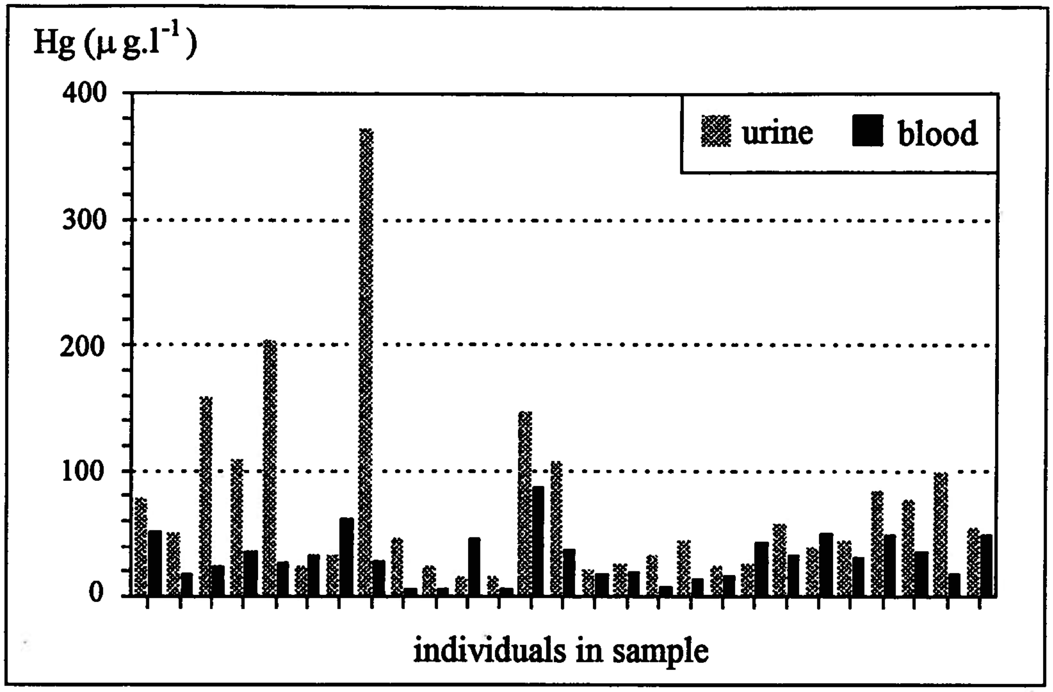

Fig. 4.2 - Hg in blood and urine of workers burning amalgam daily.
(Adapted from GEDEBAM, 1992)

The use of adequate fume hoods (Veiga and Fernandes, 1990) could minimize this occupational intoxication as well as contamination of people in the city.

4.2.2 - Methylmercury Exposure

When contaminated fish is consumed, methylmercury is the main form to be transferred to human beings. Organomercurials are more available for intestinal absorption (> 90% in mice). These pass into the blood stream and are distributed throughout the tissues. Kidney accumulation is lower than with inorganic Hg compounds, but the brain is affected significantly. According to Dr. Akagi from Minamata Institute (personal communication), Me-Hg poisoning, or "Minamata disease" has five classical symptoms :

1. visual constriction
2. numbness of the extremities
3. impairment of hearing
4. impairment of speech
5. impairment of gait

The first two symptoms are strongly indicative of the beginning of the illness. Muscular atrophy and mental disturbance are prominent in acute intoxication. Some cases of long-term effects of mercury are reported. Forty-nine cases of people who lived in the Minamata area around 1956, but departed afterward, are reported by Harada (1978). They had eaten contaminated fish for limited periods and the symptoms appeared many years after ingestion had been suspended. Studies on Iraqi and Japanese patients revealed the delayed appearance of neurological symptoms after a lapse of one year in persons who had elevated Hg levels in hair but not confirmed neurological symptoms at the first examination (Suzuki, 1979).

The effect of Me-Hg on the human body in terms of the degree of contamination is thought to be as follows: when Me-Hg enters the body in large doses[4], there are symptoms of acute brain damage such as aberrations of consciousness, convulsions, and paralysis, followed by death. When the Me-Hg intake is lower, mild, atypical or incomplete symptoms may appear or another disease may be manifested. Previously, it was thought that the harmful effects of Me-Hg were confined to the nervous system, however it has become apparent that effects on other organs must also be considered (Harada, op.cit.).

Me-Hg can penetrate into the placental barrier transferring mercury to the fetus. It has been observed that when a female's intake of the poison is large and she becomes ill, sterility occurs. When the dosage is smaller, pregnancy can take place but the fetus may be aborted spontaneously or is stillborn. An even smaller dose permits conception and live birth, but the baby will have severe neurological symptoms. A dosage too small to cause noticeable neurological symptoms in the child may cause congenital mental deficiency. But in any of these cases, the mother's symptoms are relatively mild. It was observed in Iraq that maternal milk contained 5 to 6% of the organic mercury concentration analyzed in the mother's blood (Harada, 1978; Bakir et al., 1973).

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[4] Accumulation of 30 mg of Me-Hg in a 70 kg adult (0.43 μg/g of body) causes sensory disturbance and 100 mg (1.4 μg/g of body) causes all typical poisoning symptoms (Harada, 1984). Laboratory studies in cat and mice have shown that 30 μg of Me-Hg per gram of brain is likely the threshold level to manifest neurological symptoms followed by death (Nelson et al., 1971)

Mercury in hair from the scalp is a good indicator of Me-Hg exposure. Hair grows about 1cm per month and accumulates Me-Hg during its formation showing correlation with Hg blood levels. Although hair analysis is affected by external factors, such as use of dyes and exposure of Hg° vapour, the simplicity of the sampling procedure and analysis indicate hair for toxicological assessment. The normal Hg level in hair is less than 6 ppm and signs of Me-Hg intoxication can be observed with 50 ppm. Hazardous effects to the fetus are possible when 20 ppm is analyzed in the hair of pregnant women (Krenkel, 1971; Padberg, 1990; Malm, 1991). Levels of 10 ppm must be considered as the upper limit guideline for pregnant women (Skerfving, 1973).

Although Me-Hg concentrates in the hair and epidermis, these tissues have small excretory roles in relation to the body burden. Variation in metabolism, detoxification, and excretion of the different types of mercurials is considerable. Data on excretion of Me-Hg compiled by Nelson et al. (1971) show fecal excretion of about 4% in the first few days and then 1% per day thereafter. Only about 0.1% per day is lost in urine. In contrast, inorganic compounds are very poorly absorbed by the gastrointestinal tract, i.e. the majority is flushed out of the organism. However, Rowland et al (1977) showed that Hg(II) ingested as a chloride can be methylated in less than 20 hours by intestinal bacteria. They estimated that the total methylmercury synthesized from ingested inorganic mercury in man is approximately 0.4 μg/day.

The biologic half-life of Me-Hg determined by total body burden of birds is 70-84 days (Fimreite, 1979). Measurements of blood levels of mercury and levels of intake of fish containing Me-Hg suggest that a direct relationship exists in man. Clarkson (1973) compiling results from other authors showed that, for a 70 kg individual, Hg in blood (ppb) = 0.95 x Hg (μg) daily intake from fish. Swedish individuals who are considered to have reached the equilibrium between dietary intake and body burden of mercury, show a simple direct relationship between Hg in blood and hair. Hair values are about 300 times higher than blood but this depends on which part of the hair is sampled (Nelson et al., 1971). In this case a correlation between Hg in the hair in ppm (H), mass of fish consumed daily in grams (W_f) and Hg concentration in fish in ppm (F) is approximately obtained:

$$H = 0.285 \times W_f \times F \quad (4.1)$$

So, a person consuming 200 g of fish containing 0.5 ppm Hg daily, as observed in some regions of the Amazon (Barbosa et al,. 1994), would be expected to show around 30 ppm of Hg in hair samples. This is clearly an approximation since many site specific variables must be taken into account. The time following fish consumption also plays an important role in Hg blood levels.

Hair from the scalp of people with no direct contact with "garimpos" was collected in different sites along Tapajós River (Malm et al., 1993). The study concluded that riverine communities are the most affected. From 85 to 90% of Hg analyzed in hair was in methylated form and a correlation with large carnivorous fish ingestion was suggested. Despite high levels of Hg in hair (M = 25 ppm), no case of classical Minamata disease symptom has been recognized, yet!

Barbosa et al. (1994) showed that the Indians from Madeira River region, Rondônia, Brazil, have more Hg in blood (32 ppb) than "garimpeiros" (17 ppb) due to a higher fish consumption habit. The concentration of total Hg in the hair of fish-eating people is 250 times higher than their blood levels. About 3% of the fish-eating people showed Me-Hg concentration in hair ranging from 50 to 300 ppm. According to the authors, this corresponds to between 200 to 1200 μg Hg as the daily intake dose. Considering the Canadian limit of 13 μg/day as the Allowable Daily Intake[5] - ADI of any kind of Hg form (CWQG, 1987) , 60 g of a fish with 0.2 ppm Hg are sufficient to reach the limit. Considering that the riverine people consume 200 g of fish daily, the ADI would be observed if only herbivorous fish are ingested.

Malm (1991) also has shown a correlation between fish ingestion and mercury in the hair of people from Madeira river. Typically, "garimpeiros" show a low mercury level in hair due to low

[5] The ADI was established based on the lowest whole-blood concentration for toxic symptoms using a safety factor of 10 (Nelson et al., 1971; CWQG, 1987). ADI is calculated for a body weight of 70 kg.

fish consumption. The author stressed that fortunately carnivorous fish represent only 20% of the fish market in large cities in the Madeira region.

The impact of the high Hg levels in fish (0.009 to 2.75 mg/kg) can be seen from the high blood Hg levels for residents of Jacareacanga (10 to 206 μg $Hg.l^{-1}$) (Fig. 4.3). Fish is the main diet of this community 250 km upstream of the Tapajós River from "garimpo" activities in Itaituba region (Fig. 4.1). So considering normal Hg blood levels range from 6 to 12 $\mu g.l^{-1}$ (Krenkel, 1971), the gravity of the situation is apparent. Symptoms of sub-clinical intoxication are indicated according to Dr. Kazantzis, a renowned toxicologist from Imperial College, U.K. (D. Cleary, Univ. Cambridge - personal comm.).

Fish contamination is also a problem for another city 250 km downstream from "garimpos" of Itaituba. Brasilia Legal (Fig. 4.1) is also a fishing village of 1000 people and an average of 34 ppm Hg in hair was analyzed in this community (Malm et al, 1993). As the direct influence of mercury released from "garimpos" is not clearly proven, this raises the possibility of forest and pasture fires as an additional Hg emission source (Veiga et al., 1994) (see Appendix II).

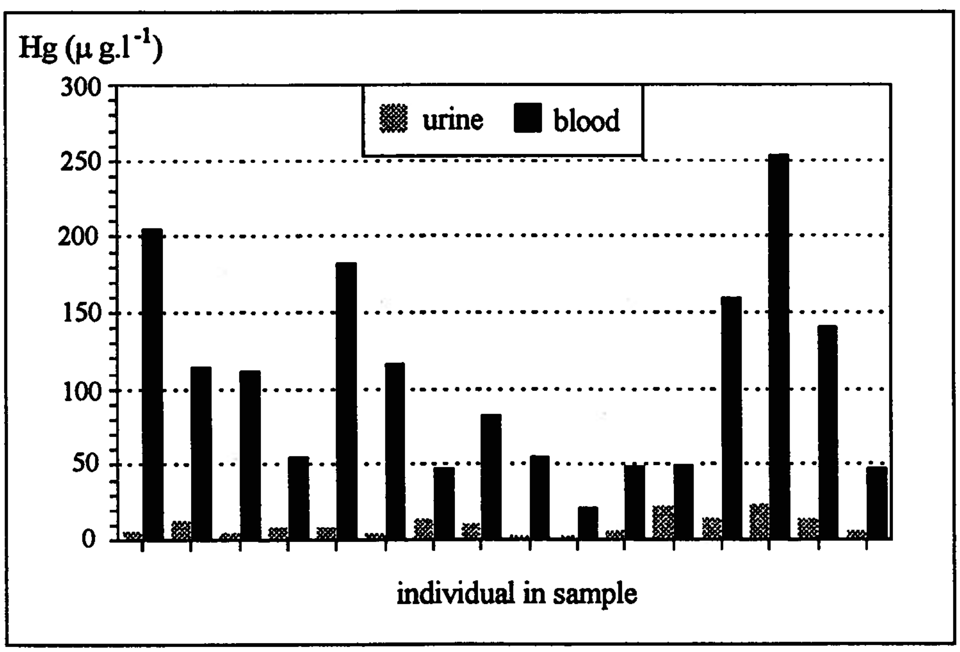


Fig. 4.3 - Hg in blood and urine of fish-eating people from Jacareacanga.
(Adapted from GEDEBAM, 1992)

5. Heuristic Approach to the Problem

"Judgment is the end result of the search inference process we call thinking"
J.V. Parkin

5.1 - How to Approach the Problem ?

Different approaches have been applied to the Hg pollution problem in the Amazon, but with low effectiveness. The following approaches can be identified :

- Armed
- Legal
- Ecological
- Educational

The use of armed force by the Brazilian Army has been applied in many episodes where "garimpos" threatened indian cultures (e.g. invasion of Yanomami reserve by 45,000 garimpeiros in 1989), or ecological parks (e.g. Poconé in 1988 and 1993), or companies' leases (e.g. Carajás in 1985). These measures have shown temporary effects but "garimpos" are dispersed over 250,000 km^2. So, they have always returned to their illegal activities.

The legal approach has been tried by administrators and legislators, but the Brazilian Constitution always attached the "garimpo" activity to the type of mineral deposit, type of work and workers. It also established cooperatives as the only legal form of informal mining activity. Little improvement has been observed, but formation of unions is an important step in organizing this activity. Legal control is also hindered by depletion of easily exploitable gold in a site with subsequent movement of miners to other areas. The lack of trained inspectors is another difficulty to implement effective control of mercury usage in "garimpos".

The ecological approach comprise the alerts and denunciations made by environmentalists and research groups. They investigate the level of Hg pollution in the environment to sound alarms. It is an important measure, but few suggestions to stop emissions and to mitigate highly polluted areas have actually been generated. In addition, the decision-making people do not have access to or understanding of the technical results of academic researchers.

A few educational measures have been applied to the problem. In 1985, the Secretary of Mining of Goiás State, started a promotion among "garimpeiros" to use mercury properly. Mr. N. Bittar, produced a brochure with pictures about mercurialism effects. Impotence was stressed as one of the first symptoms. Despite being criticized by a lack of precise information about mercurialism, this was the first attempt by technical people to alert the miners and provide options for handling mercury. In the following years several meetings with "garimpeiros", other brochures, video tapes and TV shows were produced. The amount of budget and effort spent in this method were certainly lower than those of other approaches.

One of the greatest difficulties in reducing mercury emission and recognizing dangerous sites is the scarcity of experts capable of transferring knowledge to people who have frequent contact with "garimpeiros". A multi-disciplinary approach is needed; one which can deal with field observations as a preliminary step for rapid evaluation of the pollution extent.

Computers, as a multimedia vehicle to educate and assess risk situations have never been used in this field. When an issue has many components with little quantifiable interconnections, the experience of professionals and case studies can help bring together information to establish a standard of behaviour. Expert Systems are adequate tools to deal with situations fraught with vagueness, theory not well established and lack of experts (Pivello, 1991).

Expert Systems are not a solution to the pollution problem, but rather they can bring additional information to help diagnose dangerous situations and support rapid decisions.

5.2 - Expert Systems: Brief Overview

An Expert System (ES) is a computer program which uses human expertise contained within it to make "real world" decisions. The technology of ES is a subfield of Artificial Intelligence (AI), which advances the capabilities of the computer beyond traditional use by allowing us to utilize decision-making logic in addition to interpreting large amounts of data. These systems are capable of explaining and justifying their behaviour (Harris and Meech, 1987).

Some differences between Conventional Programs (CP) and Expert Systems (ES) are listed below (Meech and Kumar, 1993):

- CP do not make mistakes; ES make mistakes just as experts do.
- Changing knowledge in CP is not easy; it is easy in ES.
- CP have to be complete to be operational; ES can function on incomplete knowledge and without all stages of the process completed.
- CP cannot function with incomplete or uncertain data; ES thrive with vague data.
- CP effectively manipulate large data bases; ES handles large knowledge bases.
- With CP efficiency is a major goal; with ES effectiveness is a major goal.
- CP usually deal with only quantitative information; ES can handle both quantitative and qualitative information.
- In CP, the syntax of expression is important; in ES, the semantics of expression is important. They deal with the meaning of an expression rather than the way it is written.
- Execution of CP is algorithmic (step by step); execution of ES uses heuristics and logic.

In the structure of an ES, there are 3 main components :

1. Knowledge Base
2. Inference Engine
3. User Interface

A *Knowledge base* is a collection of data, rules, inferences and procedures organized into frames, blackboards, semantic networks, scripts, rules, and other formats. It contains everything necessary for understanding, formulating and solving the problem. It includes facts, theory, experience and rules that direct the use of knowledge to solve problems. The information which comprises the knowledge base is usually based on pieces of evidence identified by an expert or group of experts. This experiential knowledge sometimes is not directly supported by theory or empirical data, but by the informal judgmental knowledge of a recognized Expert in an application area. This is called heuristic knowledge (Meech and Kumar, 1993).

The term "heuristics" comes from the Greek word for discovery. Heuristics are decision rules which contain information on problem solving. They may involve designed experimentation or rules of thumb based on trial-and-error processes. Heuristic programming involves step-by-step procedures that are executed until a reasonable, satisfactory solution is obtained. The key issue is that the selection of items to test is based on current information. As the current "instance" of the knowledge base is updated, new facts become instantiated, requiring a new selection of sets of rules or other facts to be selected. The process continues until a goal is reached or is proven to be correct (Nilsson, 1980). Heuristic thinking involves searching the problem domain, learning about facts, judging information/decisions, and then repeating this process while solving a problem.

Humanity has learned to deal with complexity by using heuristics. Although such heuristics have served us well, they have also left us with many biased concepts, i.e. we stereotype situations on the basis of little information. In unfamiliar situations, ordinary human beings use heuristics to simplify choice and this may produce bias. However, when experts are performing familiar tasks, these deep processes will be overlain by a patterning that can utilize large blocks of previously learned information to produce split-second judgments (Parkin, 1994).

Reverend Bayes almost 200 years ago devised a statistical approach which takes into account a "pre-conceived" judgment about a situation. The essence of this approach rests on the belief that for everything, no matter how unlikely it is, there is a prior probability that it could be true (Savage, 1961). The establishment of the prior probability is empirical (based on previous data) or heuristic (based on experience), which usually involves an expert opinion. Bayesian Statistics was applied in the now-famous Prospector Expert System developed by the Stanford Research Institute, to help geologists assess the mineral potential of a site (Duda et al., 1979).

Finding an optimum solution to complex problems usually involves time and money, but these expenditures do not guarantee that a solution is found. In such situations, satisfactory decisions can be arrived at more quickly and perhaps, less expensively by applying heuristics. Heuristics are primarily used for ill-structured problems, but they can also provide reasonable solutions to complex, well-structured problems quicker and cheaper than algorithms.

Rowe (1988) has discussed the methodology of heuristic programming. The heuristic procedure identifies rules that help solve intermediate problems; sets up problems for final solution by establishing the most promising paths to search; and also discovers means to retrieve and interpret information acquired during the analysis. Heuristic reasoning must not be regarded as final and strict, instead it is provisional and plausible; the main aim is to find an approach that can lead to a general solution (Turban, 1990).

The *inference engine* is the "brain" or the thinking part of an expert system. It is a computer program which processes the knowledge contained in the knowledge base and drives the conversation with the user, establishing connections between questions and answers. It contains a methodology to reason with the information in the knowledge base and arrive at conclusions. The inference engine provides the following facilities:

- statement analysis
- degree of belief assignment
- rule examination
- strategy application

- explanation and justification of questions and answers
- communication with users and external programs

In this work Comdale/X, developed by the Canadian company Comdale Technologies Inc., was used as the development tool for the Expert System. The main advantages of this software over other commercial ones are :

- programming is done in English;
- formulating rules and procedures is easy (Windows Environment);
- Fuzzy Logic programming is available;
- Hypertext facilities are part of the User Interface;
- dealing with uncertain data input is a main feature of the tool.

The *user interface* is the facility which accommodates communication between the user and the computer. In some cases, communication may be by line command or through menus. The user interface allows a user to query the actions of the systems. The user may need explanation for a question or more details about a subject. A friendly interface is fundamental to keep the attention of the user as well as to transfer the knowledge effectively. Comdale's Hypertext facility was used as the interface. This contains hotkeys, which are words, sentences or diagrams that provide additional explanation or execute commands and functions such as jumping pages, displaying pictures, making animations or consulting the knowledge base to make a decision.

5.3 - Knowledge Acquisition

Knowledge Acquisition is the transfer and transformation of problem-solving expertise from knowledge sources to a computer program (Hayes-Roth et al., 1983). The construction process consists of various stages that include problem definition, acquiring knowledge about the domain, development of the expert system, and evaluation, testing and refining (Buchanan et al., 1983).

The knowledge acquisition process to establish a knowledge base on environmental impact assessment is a complex and laborious multi-disciplinary task involving the identification, estimation and comparison of a wide variety of aspects. Most assessments require prediction of the future conditions of environmental elements over time and space. These predictions are often obtained with mathematical models based on conceptual representations of the processes (deterministic simulation) or probabilistic descriptions based on data of past events (stochastic simulation). In the absence of adequate mathematical models or sufficient quantitative information, assessment can be done based on experience and judgment of an expert evaluator about the magnitude of the impact (Julien et al.,1992).

In the case of mercury pollution, the processes of bioaccumulation have been studied for almost three decades by researchers all over the world. The knowledge accumulated in this field still has many uncertainties and a number of controversies about the effect of some natural variables have been raised (Richman et al., 1988; Verta et al., 1986, D'Itri, 1990) but the influence on bioaccumulation of pH, humosity, conductivity, biomass, solids in suspension and Hg in sediments seems to be applicable to most environments (see Chapter 3).

Swedish researchers have attempted to formulate mathematical models to predict bioaccumulation based on environmental variables measured in Swedish lakes. A tendency for increased mercury in fish over the years has been recorded. Correlations between date and mercury in fish (FHg) was established by Håkanson et al. (1988) based on very scattered data from 1386 lakes (Fig. 5.1). Geographical, physical and chemical variables as well as Hg in fish were reduced to 57 lakes to generate an empirical equation which was statistically significant at the 99.5% level with an r^2 of 0.78 between predicted and observed Hg levels. But in fact, even with this heuristically-filtered approach, the equation had a error range of about 50%. So application of statistical analysis to masses of data requires significant data reduction that generates empirical results that must be used with extreme caution. Why not apply the heuristics directly to generate logical conclusions which can be explained in terms of a knowledge base search pattern?

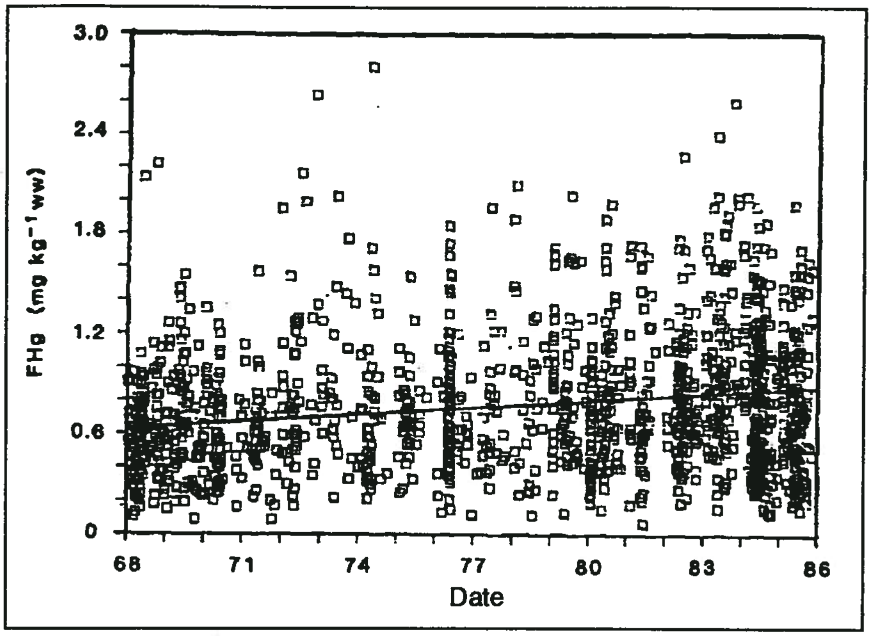


Fig. 5.1 - Hg in fish (FHg ppm) in 1386 Swedish lakes
Håkanson et al. (1988) show in this trend analysis that bioaccumulation is increasing over time.

International experiences in mercury pollution have been used in the Amazon to investigate the bioaccumulation risk. Over ten years of studies, about 100 researchers have been found in Brazil working on different segments of the problem. Many reports and publications have been issued about the effect of natural variables on mercury transformations in the Amazon as well as describing the monitoring program results. However, an overall view is needed. The experience of each research group, reported in publications or by personal communications has been extremely important to build the knowledge base of this ES. The heuristic approach was used based on field observations and experience of different professionals in the field. Monitoring programmes continue in Brazil and they will provide more information to update and improve the knowledge base in the future. A classical mathematical model based on a huge collection of data seems to retard decisions, implies high cost and does not transfer knowledge effectively to many novice researchers and non-technical people directly involved with the issue.

The knowledge acquisition process to build the knowledge base was achieved by the author's experience in the field and through an extensive literature review to establish which natural variables are related with bioaccumulation. Those variables in which the bioaccumulation effect is controversial (e.g. temperature) were not considered in the heuristic model.

5.4 - How Good is a Model ?

The complexity of environmental systems and the degree of non linearity usually have limited the use of quantitative approaches in natural sciences. Although models have been developed to predict site specific problems, they need to be tested to guarantee accuracy or reliability when applied to the real world.

The process of an Expert System (ES) evaluation is usually divided into validation and verification (Parsaye and Chignell, 1988). Validation has been defined as : "a comparison of a model's predictions with the real world to determine whether the model is suitable for its intended purpose" (McKinion and Baker, 1982). Verification is the part of an evaluation which checks if the knowledge base was constructed properly (Turban, 1990).

The terms validation and verification are frequently confused by many authors. There are so many different definitions for these terms in the literature that it seems there is a fuzzy boundary between both concepts. Actually, Marcot (1987) listed 17 criteria to evaluate a knowledge base going beyond the simple differentiation between validation and verification. Some of these criteria are listed below :

- Accuracy - how the system reflects reality.
- Adaptability - possibilities for future changes.
- Appeal - how well the knowledge base matches intuition and practicality.
- Breadth - how well the domain is covered.
- Depth - degree of detail.
- Credibility - how acceptable is the knowledge.
- Generality - capability of knowledge to be used with a broad range of similar problems.

- Precision - consistency of advice.
- Robustness - sensitivity of conclusions to model structure.
- Sensitivity - impact of changes in the knowledge base on quality of outputs.
- Turing test - ability to identify if a conclusion is made by an ES or by a real expert.
- Usefulness - how adequate the knowledge is for solving correctly.
- Validity - knowledge base's capability of producing empirically correct predictions.

Mayer and Butler (1993) noted that there is a lack of criteria for model validation. In many cases the choice of technique is restricted by potential uses and testing requirements of the model, the type of data that the model generates or the availability of real-world data. These authors grouped validation techniques into 4 main categories :

- Subjective Assessment : involves evaluation by a number of expert in the field;
- Visual Techniques : graphical displays of the simulated data and the observed data;
- Deviance measures : a numerical error is calculated using simulated and observed data;
- Statistical Tests : t-test, regression analysis or non-parametric sign test are used.

The use of subjectivity implies something that is not good, particularly in the scientific field. But actually, all belief systems are based on subjective assessment even those that employ statistical analysis. The "real" truth lies somewhere inside subjective assessment - where it exactly resides perhaps, is determined by "expert intuition" rather than a "guess".

Usually, Expert Systems are evaluated (and validated) by experts in the field (Harris and Meech, 1987; McClure, 1992). The term "subjective assessment" used above seems rather broad to mirror methods performed by experts, otherwise why would we call them "Experts"? There is also a great misunderstanding about the relationship between subjective (strongly influenced by personal opinions - Colbuild, 1989) assessment and methods that are based on deterministic techniques. It seems that an evaluation of a model by somebody who is an accepted expert, is an intuitive process. The assessment is based on something perceived immediately by the mind (Webster, 1974) without necessarily applying analytical knowledge (Ferreira, 1986). Deterministic or statistical procedures usually look for correlations to explain relationships between data but sometimes there is no theory to explain a lack of interaction between variables. The only interaction, when available, is a logical chain between observations (Casti, 1990).

Einstein was also concerned with verification (or validation ?) of a scientific theory which can be developed preferentially by intuition or by observation. He gave special status to those that are intuitively obvious. An intuitive principle is one that can be derived either from ordinary experience or from a thought experiment. An observable principle is just a special case of an intuitive one, but in contrast with a purely theoretical principle that cannot be derived from a thought experiment (Brown, 1991). So, a heuristic system is, in some respects simply a thought experiment in which fundamental principles are applied to generate hypotheses about cause and effect relationships without necessarily formulating an exact model.

Leaving aside the semantic discussion about the difference between validation and verification, we can say that evaluation of a model based on field observation can be either an observable or an intuitive process. This depends on the skill of the evaluator. Is it necessary that an evaluator has experience in "garimpos" to perceive the mercury emission level of a poor amalgamation practice? We think that the intuitive process is as important as observed experience and the outcome of a evaluation process can improve and refine the heuristic model.

The relationship between variables affecting bioaccumulation is likely more complex. An enormous amount of research has been carried out around the world to establish linkages between variables and bioaccumulation levels. The "formal" statistical treatment has been unable to establish useful mathematical models. So, knowledge has been based on observable effects of these variables in the environment. Specialists have background to judge these variables but a user can also provide a reliable verdict of whether the model is valid over time. This is what Turban

(1990) defined as *evaluation for performance.* He suggested the following sequence to evaluate an ES prototype :

- testing with case studies
- evaluation by experts and users
- analysis of results
- improvements and refinements

We believe that evaluation is a step performed by users and experts to check usefulness, acceptability and effectiveness of the system. The perception of these qualities in an ES varies with the type of evaluator. So, selection of different types of evaluators gives us a more comfortable profile of system qualities and user needs than a traditional validation by 2 or 3 experts in the field.

A system can be valid but not acceptable, useful or effective. There are examples of many valid models and systems that sit on the shelf. The following causes identify situations in which Expert System are rejected or no longer used by users :

- user interface is unfriendly (difficult to operate);
- questions asked by the system are unclear, irrelevant and insufficient
- text and explanations are unclear
- final report is unclear and too direct
- the conclusions are full of absurdities
  (some due to poor knowledge acquisition, some to errors in representation)
- no justification is provided for the conclusions
- lack of maintenance; system becomes obsolete very quickly
- lack of commitment
- political problems
- the system transferred knowledge to the user successfully

This last point is interesting to be found listed with problematic facts, but when a consultative (off-line) ES has accomplished its role to train novices, the users no longer need further consultations.

Most problems are related to the friendliness of the user interface and the reliability of the knowledge base. Maintenance is important to follow up system performance as well as to update the knowledge base, as new facts become available.

Lack of user commitment is a major cause of system rejection. Users should believe that ES technology is useful and can bring additional knowledge. There are often thoughtless postures taken against AI techniques : "*I didn't try it because I didn't like it*". One example of failure caused by lack of commitment is described in the Polaris system by Harris and Kosick (1988).

The Polaris Expert was the first example of an Expert System for real-time control applied in the Mining Industry in 1988. Located near the North Pole, the Polaris mine appeared to be a perfect place to introduce this technology to standardize operating practices, stabilize circuit operation, provide a training environment for inexperienced operators (turn-over was high at Polaris), give on-line support and guidance to process operators. The system was developed in concert with the operators over a one year period. The claim is made that it performed well but the system needed to be maintained. Failure occurred because the "Champion" of the idea quit the company and the commitment of others in the organization to keep the system functioning was insufficient. The ES performed well as long as a "Baby-Sitter" was available. It seems strange that a company would spend large sums of money on a project and then let the project die because no one was available to keep it going. Initial commitment to this project was clearly poor (Meech and Kumar, 1993).

Political problems are also sources of failures. Sometimes, Union personnel do not understand that consultative ES are useful for training novices and are not aimed at worker replacement. This creates a very uncomfortable situation and an ES user can be seen as a traitor by his peers. When a knowledge base is captured from operator experience, any suspicious attitude can destroy the trustworthy level of communication that must exist between the operators and knowledge engineer, who builds the knowledge base.

The advisory system developed at Highland Valley Copper mine, BC, for flotation control is an example of reluctance of older operators to share their expertise with knowledge engineers. Some of them had little faith in the ES technology for training younger operators. When the knowledge was finally obtained and the ES implemented, the relief-operators responded positively to the new ideas and actions provided by the system (Poirier et al., 1993).

An ES is frequently seen by Experts as a competitor. In environmental sciences this is also true. Environmental evaluation involves different elements such as physical, chemical, biological and anthropological knowledge (Julien et al., 1992). Environmental evaluation is a fuzzy concept which involves many segments of a Society. In the last decade, concern about environment quality increased substantially and nowadays everyone has an individual opinion about pollution. This makes environmental science an interdisciplinary realm in which technical factors are only a part. Some people think this is the main part of environmental science and use technical arguments to hinder access to discussions with non-technical individuals. It is our belief, that ES can actually fill this gap and give non-technical people access to the information in a form they can understand. In this regard, Expert Systems are competitors with some technical "gurus".

The following chapter shows the structure of the HgEx - Expert System and details how the heuristic model was built and evaluated.

6. HgEx Structure

"When the only tool you have is a hammer
All your problems look like nails"
Lotfi Zadeh

6.1 - System Division

The Expert System HgEx is divided into three main parts :

1. Tutorial part
2. Diagnostic part
3. Remedial procedures

The *Tutorial* part has an encyclopedic aspect and can be read as a book. The main goal is to bring together dispersed information about mercury pollution in different parts of the planet but focused on the Amazon region. The Hypertext environment provides the user with a comfortable and objective way to read due to direct interaction with the hotkeys and the use of unsophisticated language. Comments on biogeochemical cycle, Hg chemistry, amalgamation methods, emission balance in "garimpos", adsorption and desorption phenomena, methylation processes, aquatic geochemistry, toxicity, guidelines, mercury pollution episodes in the world, etc. are included in about 1000 topics (electronic pages) distributed in the following chapters :

- Physical & Chemical Properties of Mercury
- Sources and Uses of Mercury : World and Brazil
- Mercury Emissions : Natural and Man-Made
- Mercury Background Levels: Soils, Sediments and Waters
- Mercury in Gold Mining Operations
- Mercury in Aquatic Systems
- Bioaccumulation
- Mercury Mobility
- Toxicity
- Biogeochemical Cycle
- Remedial Procedures

- Guidelines for Mercury Levels: Fish, Water, Soil and Air.

The *Diagnostic* part provides for data entry on a site or region and generates a report evaluating the following :

- Presence and level of Hg emission from "garimpos"
- Potential risk of Hg bioaccumulation,
- Possibility of human poisoning

The system uses Fuzzy Logic techniques which allow vague data input and still provide useful output. The process of knowledge accumulation uses a Weighted Inference Method that will be discussed in detail ahead.

The *Remedial Procedures* part gives advice on clean-up techniques for polluted areas as well as measures to reduce Hg emission. As only a few remedial procedures described in the system have been tested in the Amazon region (Farid et al., 1991; Souza et al., 1991), the system uses the expertise of other authors in different parts of the globe to provide advice (Parks and Baker, 1969; Jones, 1971; Bonger and Khattar, 1972; Feick et al., 1972; McKaveney et al., 1972; Tratnyek, 1972; Jernelov and Lann, 1973; Logsdon and Symons, 1973; Masri and Friedman, 1973; Beszedits, 1979, Pandey and Chaudhuri, 1981; EPA, 1982; Asai et al., 1986; Eutrotech, 1991; Paulsson and Lindbergh, 1991; Lindqvist et al. 1991). Due to the nature of emission, mercury can be dispersed in sediments (atmospheric emission) or concentrated in "hot spots" (when amalgamation tailing is dumped). The treatments contemplated for these situations are somewhat different as delineated in Fig. 6.1.

Procedures to minimize bioaccumulation have been applied in Canada and Sweden (e.g. selenium dispersion, liming) where Hg sources are industrial emissions such as coal combustion, pulp and paper or chlor-alkali effluents which dispersed Hg into the environment. Sometimes the pollution source is unknown. The system lists these techniques in about 50 electronic pages and suggests tests that must be done to adapt these measures to the polluted areas in the Amazon.

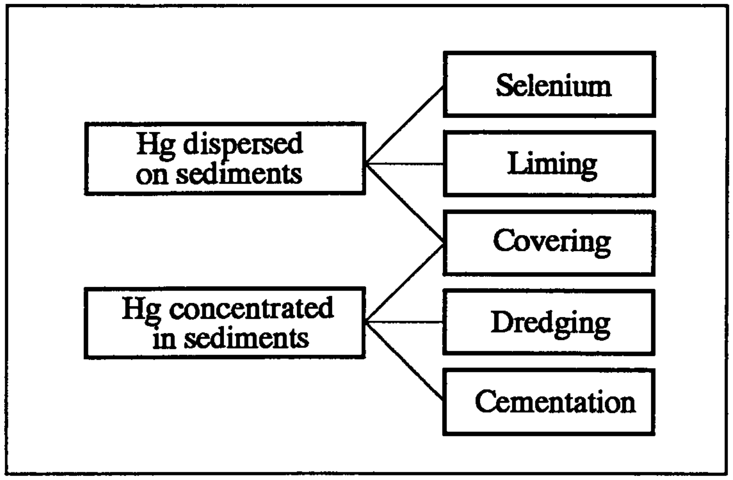


Fig. 6.1 - Description of remedial procedures for mercury polluted sites.

The report generated in the Diagnostic part suggests measures for controlling mercury bioaccumulation. Dredging and covering a "hot spot" with laterite or pyrite are highlighted as feasible and affordable processes to be tested. Methods to treat dredged spoil are also described. Experiments performed on Poconé dredged sediments containing 7 to 113 ppm Hg illustrate how clean-up procedures can remove 70 to 80% of Hg by gravity separation and as high as 99 % by an electrolytic method for generating hypochlorite from NaCl added to a pulp of contaminated material (CETEM, 1989).

The Remedial Procedures part also includes processes to reduce mercury emission from amalgam burning. In the Amazon, only 10% of the miners use retorts to condense mercury vapour (DNPM, 1993). With retorts, mercury condensation is usually higher than 95%. When Hg is distilled in a reducing atmosphere, 99% recovery is possible (EPA, 1972). There are a large variety of retorts on the Brazilian market. Some of them are made with stainless steel while others use inexpensive cast iron. Even a home-made retort devised by Dr. Raphael Hypolito of Universidade de São Paulo is a practical solution for this problem. This retort is made with water pipes (used for plumbing) and the distillation chamber is made by connecting an end plug into which the amalgam is placed (Anonymous, 1990a; Anonymous, 1990b). Unfortunately simple solutions are not widely promoted among "garimpeiros" due to lack of information on the people who are in contact with the miners.

Air filters for gold shops are also described as an effective procedure to reduce emissions drastically during gold melting. The use of activated charcoal impregnated with iodine increases the efficiency of vapour absorption. A prototype fume hood evaluated in Poconé, showed a reduction of 99% of Hg emitted by one gold shop (Veiga and Fernandes, 1990).

6.2 - General Overview of the Diagnostic Part

The Diagnostic part of the Expert System integrates biological, geochemical, engineering, medical and social data to conclude about emission levels, bioaccumulation risk and the possibility of Hg poisoning through a heuristic model which uses Weighted Inference Equations (basic Neural Equations) to obtain the Degree of Belief in a conclusion.

The system is able to deal with different types of data input. When available, the user can input measurements obtained during a field trip, which are converted into linguistic expressions with respective Degrees of Belief (DoB) in a concept used by the heuristic model to make inferences. Lack of measurements can also be accommodated in some cases, with questions applied to convert field observations into a DoB through inference equations or IF-THEN rules (Fig. 6.2).

The structure of HgEx is based on the simple concept that risk of bioaccumulation is a function of the level of mercury emission and the degree of transformation in the environment. Mercury abatement by adsorption on fine ferruginous sediments is the only way in which the risk can decrease. The potential risk is compared with analyzed biota samples, when available, and conclusions about the current and future bioaccumulation are provided. For example, when the system indicates that there is a high potential for bioaccumulation but the biota does not show high Hg levels, the system suggests frequent monitoring programmes and remedial procedures to avoid future problems (Fig. 6.3).

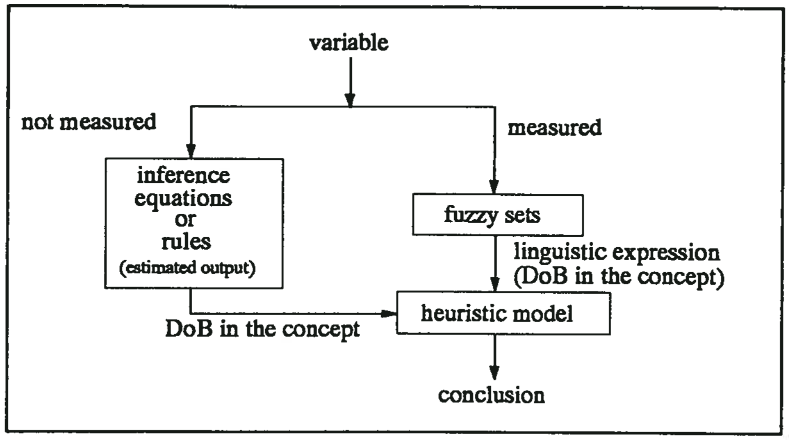


Fig. 6.2 - Process in which HgEx deals with data input

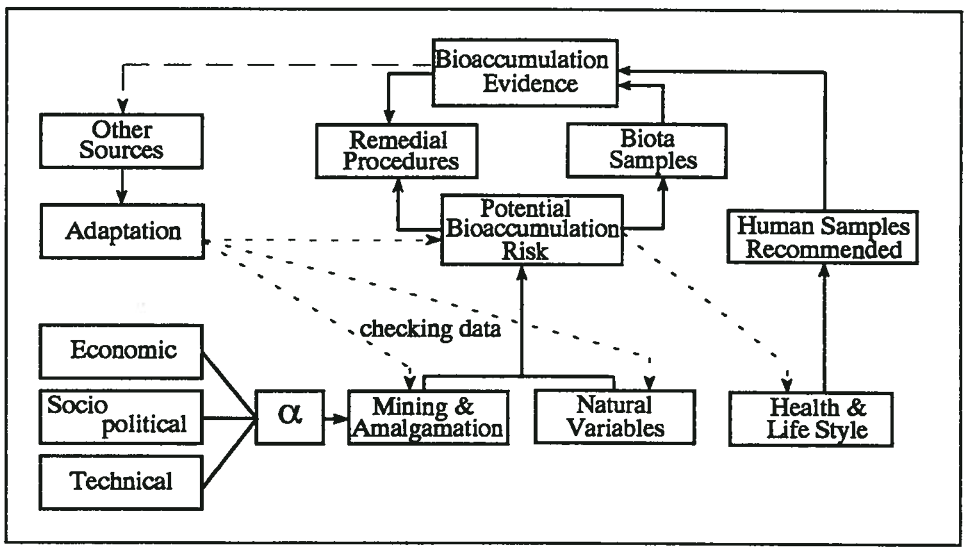


Fig. 6.3 - Structure of the Diagnostic part of HgEx

Biological samples (fish, snail or human) can provide evidence of bioaccumulation based on chemical results. The Hg concentration in these samples, when available, is input by the user and transformed by Fuzzy Sets into linguistic expressions such as "high", "medium" and "low". These concepts are compared with the potential bioaccumulation risk predicted by the heuristic model to check for a conflict. If the bioaccumulation evidence is higher than the risk predicted by the system, conflict sources are checked and eventually adaptation of the diagnosis is performed.

6.3 - Weighted Inference Method

Rules are usually employed in ES to combine pieces of evidence. However when the numbers of variables and premises are large, the number of combinations necessary to describe all situations becomes enormous and unfeasible. We examined four methods to combine pieces of evidence:

- Minimum Degree of Belief
- MYCIN
- Bayes' Theorem
- Weighted Inference Equations

The Minimum Degree of Belief method is the simplest and most often used in rule-based systems. Unfortunately the method does not transfer smoothly changes in the Degree of Belief (DoB) values from the premises to conclusion. In addition, a large number of rules and possibilities must be established to represent the expertise precisely.

The MYCIN method accumulates evidence using a unique rule for each step (Forsyth, 1984). Shown below is the process used in MYCIN to combine four premises:

$DoB_{Rule\ 1} = CF_{Rule\ 1}\ (DoB_1\ /100)$

$DoB_{Rule\ 1,\ 2} = DoB_{Rule\ 1} + CF_{Rule\ 2}\ (DoB_2\ /100)\ (100 - DoB_{Rule\ 1})/100$

$DoB_{Rule\ 1,\ 2,3} = DoB_{Rule\ 1,\ 2} + CF_{Rule\ 3}\ (DoB_3\ /100)\ (100 - DoB_{Rule\ 1,\ 2})\ /100$

$DoB_{Rule\ 1,\ 2,\ 3,4} = DoB_{Rule\ 1,\ 2,\ 3} + CF_{Rule\ 4}\ (DoB_4\ /100)\ (100 - DoB_{Rule\ 1,\ 2,\ 3})\ /100$

The Certainty Factor (CF) associated with each rule must be formulated by the Expert and represents a weight associated with each input event. The method associates information in a very synergistic fashion and although convergence to full belief is approached when all the evidence is known, significant uncertainty can still exist with much accumulated evidence. The method distributes the relationship across the knowledge base as separate rules that are slower to activate than a single equation. It is more difficult to provide satisfactory explanations and justification. A single equation can be formulated for this technique but the number of terms in such an equation increases in a combinatorial fashion with the number of variables.

Bayesian Logic requires establishing a prior probability for each conclusion option (50% can be chosen for convenience). The likelihood of the conclusion being observed in the presence and absence of each event must also be determined. So, twice as many relationship factors must be considered for each input, the levels of each probability having significant impact on the final outcome. In my experience, Experts generally balk at establishing the relationships in this way, however there are other successful Expert Systems that are based on this approach.

The method used in this work is adapted from the basic neural equation which propagates weighted evidence to a conclusion. The model is based on the now famous Perceptron network developed by Rosenblatt in 1957 (Minsky and Papert, 1969). All inputs to a node in the network are summed after multiplying by a "suitable" weighting value between 0 and 1. In Rosenblatt's original network, the summation output is passed through a "hard" threshold limit which causes the node output to be either true or false.

The Weighted Inference Method derives the DoB in a conclusion combining the importance of each evidence (W_i) with the Degree of Belief (DoB_i) of the user that the evidence is occurring:

$$DoB_{conclusion} = \sum_{i=1}^{n} W_i \cdot DoB_i \qquad (6.1)$$

This approach is akin to the Fuzzy Neural Rules proposed by Meech and Kumar (1992) and Khan (1993) and the Neural-Fuzzy Expert Systems (Kosko, 1992). The Comdale/X software used to build this system allowed us to experiment in the rule base design with the myriad of options presented above. The MYCIN and Bayesian methods can be made to work as well as the Weighted Inference Method but we believe their drawbacks are significant.

In HgEx, output emerges from a single node as a Degree of Belief ($DoB_{conclusion}$) ranging from 0 to 100 in the concept. The actual output displayed to the user is filtered through a function which involves *linguistic defuzzification* of the $DoB_{conclusion}$ into terminology which characterizes the spectrum in which the concept ranges (e.g. from non-existent to extremely high).

The main advantages of this method are:

- Dependent variability can be handled.
- A single output node can represent multiple output values.
- Outputs are easily adjusted for other situations.
- It is easy to explain the knowledge accumulation process.
- A User can input uncertainties and multiple choices per step or leave a step unknown.
- The output calculation can be done at any time using one simple equation.

The system has four main blocks which include heuristic models based on Weighted Inference Equations. They can be observed in the lower part of Fig. 6.3 which is detailed in Fig. 6.4.

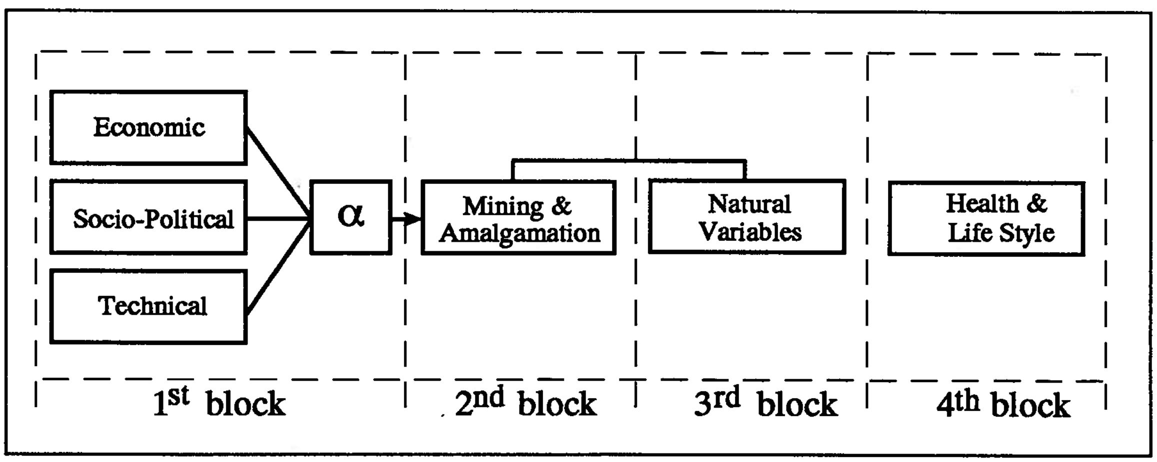
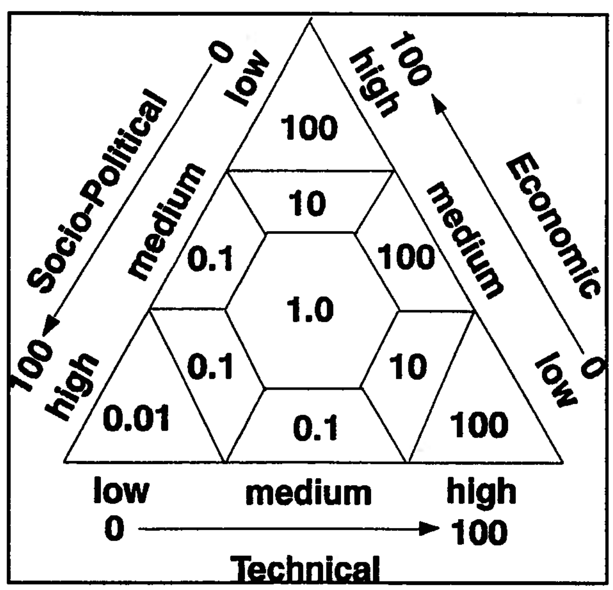


Fig. 6.4 - Four blocks which contains the heuristic models (see Fig. 6.3 for full structure)
NOTE :
1st block - calculates alpha factor, which adapts the diagnostic on Hg emission to other societies;
2nd block - estimates the mercury emission level based on mining and amalgamation practices;
3rd block - estimates the risk of methylation and bioaccumulation based on natural variables;
4th block - estimates the possibility of human contamination;

6.3.1 - First Block - Alpha Factor

The alpha factor was devised to accommodate differences in the perception of the intensity of man-made mercury emissions. It is observed that the behaviour of workers depends on society incentives and reactions. As a result, the development level of a society will change our definition of high and low levels of mercury emissions. To map these differences, an alpha factor is calculated based on Socio-Political, Technical and Economic aspects of a society which relate to the acceptance or rejection of mercury use in gold mining operations (Fig. 6.5).

A high alpha factor indicates the acceptance of amalgamation practice and a low control of Hg emission enforced by a society, which can be a country or a region. For the Amazon situation, alpha is 1.0. For Canada, where mercury is practically banned and well-monitored by authorities, alpha factor is much lower (0.1 or 0.01). For Canada 150 years ago, when the hazardous effects of Hg were unknown and thousand of miners were colonizing the West, alpha would be much higher (about 100). The factors used to calculated alpha are related to Economic, Technical and Socio-Political aspects which vary for each society. Based on the DoB in each factor, a heuristic model (Weighted Inference Equations) combines pieces of evidence to calculate the alpha factor.



NOTE: 0 = rejection 100 = acceptance

Fig. 6.5 - Rule structure to calculate alpha-factor

The system asks nine questions to identify the economic situation of a Society in which mining has been seen as an alternative for employment and surviving (see Appendix III for details). Questions are related to:

- Relative Significance of Mining on the Economy
- Operating & Capital Costs
- General Economic Conditions

Ten questions evaluate technical situations related to use of amalgamation as an option. If the miners develop their own technology because they do not have technical support or access to alternative technologies it seems clear that they will continue using amalgamation. When no technical support is available and alternatives are not easily applicable, the technical factors tend to promote amalgamation and consequently, alpha factor increases in this society. The questions are split into two categories:

- Technical Incentives for Mining and Amalgamation.
- Technical Support & Alternatives.

Nine questions investigate socio-political aspects in a society which drive its citizens into informal mining operations. These questions are related to:

- Legal & Political Aspects.
- Culture & Education.
- Public Awareness.

The existence of laws and regulations are not sufficient to control Hg misuse. In the case of the Amazon region, Hg is not allowed to be used for mining, however laws are difficult to enforce when a squad of almost 1 million people is dispersed and struggling to survive. The society, through its representatives, is the main resistance point for Hg use and must establish mechanisms of controlling misuses and abuses.

The heuristic model works by determining the socio-political, economic and technical situations which increase the resistance or acceptance for amalgamation use. Each situation asked of the user has a respective weight (W_i) which will be multiplied by the Degree of Belief (DoB_i) in each answer to reach a conclusion about resistance and acceptance (eq. 6.1). For example, the socio-political situations which promote acceptance of mercury use are :

1. mystique that gold mining is an easy way to become rich ($W_1 = 0.2$);
2. it is easy to evade laws which control Hg usage ($W_2 = 0.4$);
3. incentive (political importance of a region) for "garimpos" ($W_3 = 0.2$);
4. mining is a traditional occupation ($W_4 = 0.2$).

The social characteristics of a society which increase resistance to mercury use are:

5. high education level ($W_5 = 0.3$);
6. frequent interaction of miners with other educated people ($W_6 = 0.1$);
7. political power of the groups affected by Hg pollution ($W_7 = 0.2$);
8. reliable media ($W_8 = 0.2$);
9. active ecological groups ($W_9 = 0.2$).

A DoB_{social} in socio-political situations is generated by the difference between the Degree of Belief in situations which encourage the use of Hg ($DoB_{acceptance}$) and situations that resist the use ($DoB_{resistance}$). Similar questions are asked to determine the economic and technical factors. A numerical variable is obtained for each factor according to the equations 6.2, 6.3 and 6.4:

$$S(\%) = \frac{DoB_{social}}{DoB_{social} + DoB_{economic} + DoB_{technical}} \cdot 100 \qquad (6.2)$$

$$E(\%) = \frac{DoB_{economic}}{DoB_{social} + DoB_{economic} + DoB_{technical}} \cdot 100 \qquad (6.3)$$

$$T(\%) = \frac{DoB_{technical}}{DoB_{social} + DoB_{economic} + DoB_{technical}} \cdot 100 \qquad (6.4)$$

These factors can now be mapped into Fig. 6.5. The three factors add to 100%. Once the position of each factor in Fig. 6.5 has been obtained, the alpha-factor is calculated using Fuzzy sets and ten rules, one for each field of Fig. 6.5. One example of a rule is:

IF Economic.Factor.High .... DoB_1

AND Technical.Factor.Low .... DoB_2

AND Social.Factor.Low .... DoB_3

THEN (alpha.factor.very_high)$_r$ is TRUE .... $DoB_r = MIN(DoB_1, DoB_2, DoB_3)$

THEN α_r = Defuzzification (alpha.factor.very_high)$_r$

The last line in the rule transforms the rule Degree of Belief (DoB_r) into a crisp number α_r by consulting a Fuzzy Set that represents the concept very high. In the example, if DoB_r is 85%, then $\alpha_r = 5$ (Fig. 6.6). Ten Fuzzy Sets exist to transform DoB_r of each rule into crisp numbers (see all rules and Fuzzy sets in Appendix III).

All ten rules represented in Fig. 6.5 are fired and ten potential alpha-factor (α_r) values are obtained from their respective Fuzzy set. The final alpha-factor is calculated through a defuzzification process expressed by equation 6.5:

$$\alpha = \frac{\sum_{r=1}^{10} DoB_r \cdot \alpha_r}{\sum_{r=1}^{10} DoB_r} \qquad (6.5)$$

This defuzzification method is akin of the Weighted Average method but instead of multiplying the DoB of each Fuzzy Set by the supremum[6] position of the set (Smith and Takagi, 1994), we

[6] The supremum of a Fuzzy Set is the discrete value of the Fuzzy Set associated with the highest belief level. In Fig. 6.6 this would be 100 (which has DoB = 100%).

multiply by the actual value (alpha-factor) extracted from each Fuzzy Set. This provides considerable adaptability and allows for characterization of very non-linear functions.

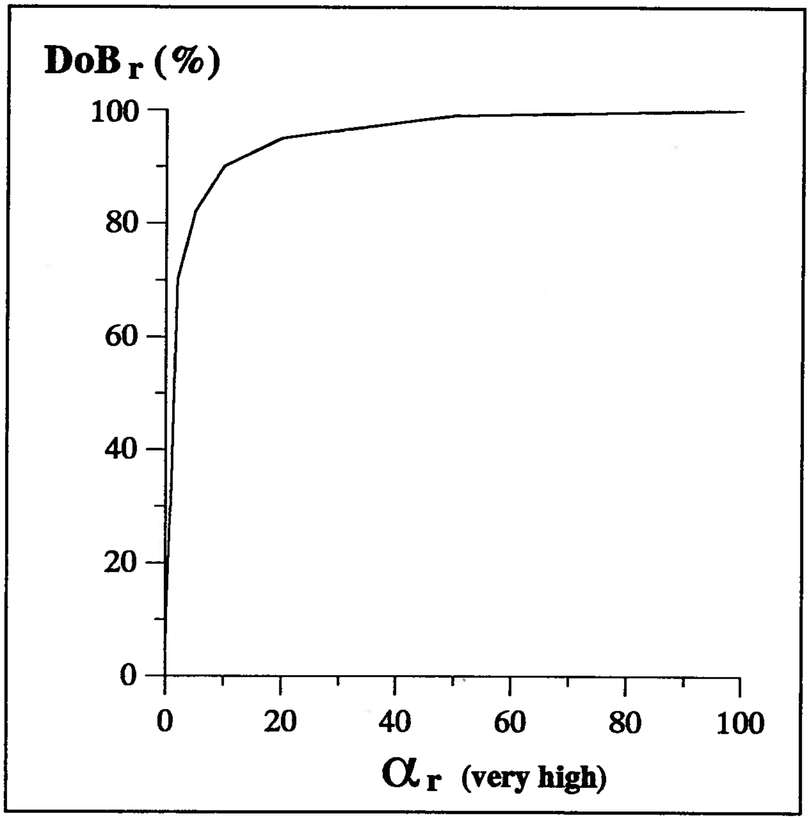


Fig. 6.6 - Fuzzy Set to define very high alpha factor

The Fuzzy sets have been designed to reflect exponential relationships to ensure that the change in α from 1.0 occurs if the situation approaches an extremity position in the diagram of Fig. 6.5.

6.3.2 - Second Block - Mining and Amalgamation Practice

To predict the extent of Hg emission, a number of events involved with mining and amalgamation has been examined (Fig. 6.7), derived from observations at different Amazon operations.

If all events of the Fig. 6.7 are combined in rules to predict the degree of mercury emissions in a region or a single site, there are about 70,000 combinations (rules).

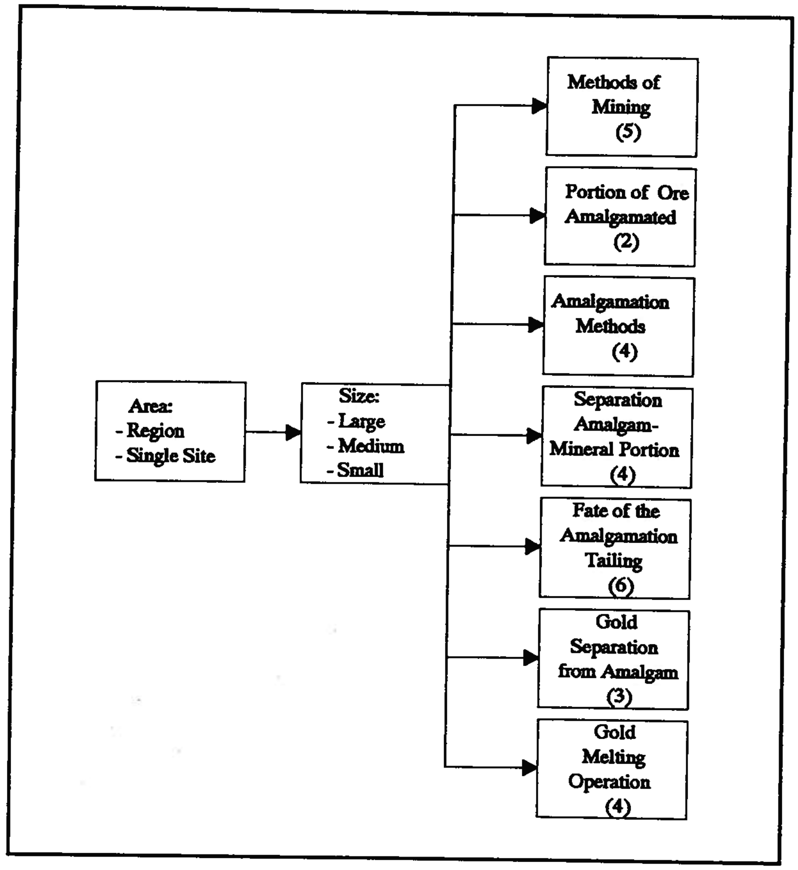


Fig. 6.7 - Steps involved in mining and amalgamation practices.
(In parentheses is the number of possible alternative events in each step)

A term called "High Emission Factor" or HEF has been coined to represent the collection of events involved in mining and amalgamation operations that derives belief in a high emission level. The following Weighted Inference Equation provides the combined Degree of Belief (DoB_{HEF}) in the existence of high emission factors when the degree of belief that event *i* occurs (DoB_i) and importance of each event *i* (W_i) are considered.

$$DoB_{HEF} = MIN(100, \sum_{i=1}^{n} W_i \cdot DoB_i) \quad \text{.......................................} \quad (6.6)$$

The higher the DoB_{HEF}, the higher our belief that a high Hg emission is occurring. DoB_{HEF} is shown to the user in the form of linguistic expressions such as: "high", "low", "very low", etc. to characterize the level of Hg emission from a mining operation. We know, however, that these expressions are context sensitive. What is "low" for some can be considered "very high" for others. This depends on the concerns and reactions of a society to the socio-political, technical and economic factors which promote gold mining activities. So, the DoB_{HEF} is raised to an exponent value (alpha factor) which shifts the linguistic expression definition (Fig. 6.8):

$$DoB_{HEF} = 100 \cdot [MIN(100, \sum_{i=1}^{n} W_i \cdot DoB_i) / 100]^{\alpha_{HEF}} \quad \text{.............................(6.7)}$$

where: α_{HEF} = α-factor - determined from external parameters

Eight real cases of mining operations were used to formulate the weight (W_i) of each event in concluding about DoB_{HEF} (Table 6.1) (see Appendix VI). These cases represent most of the "garimpeiros" behaviour and mining activity in the Amazon. While exceptions may exist, it is considered that the Inference Model used in this work will be able to cope with any unusual cases.

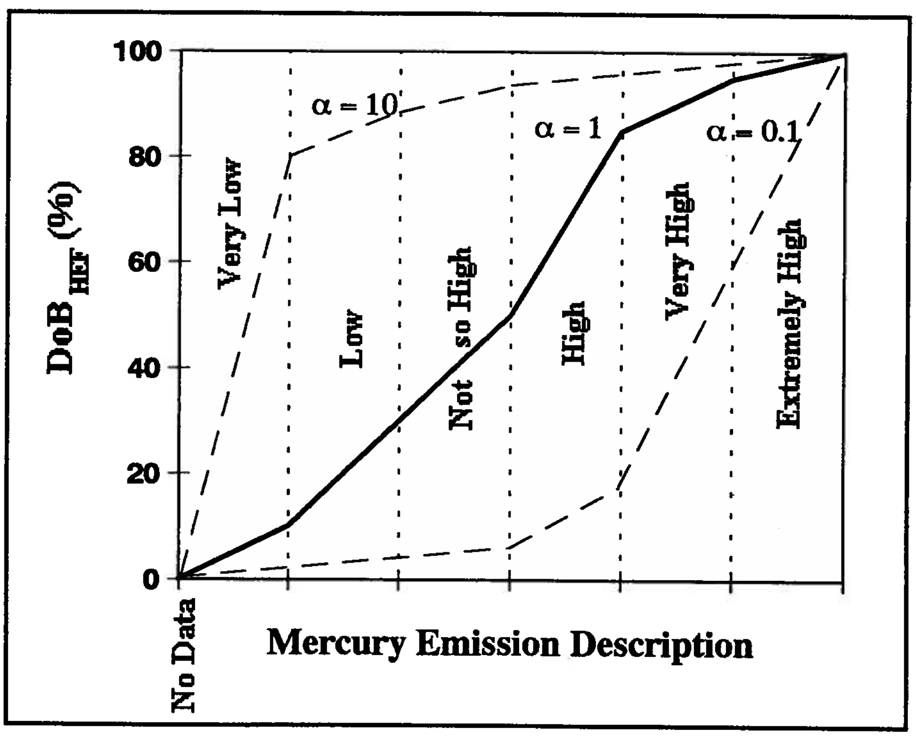


Fig. 6.8 - Linguistic output of DoB in High Emission Factor

Table 6.1 - Correlation of the model output with observations at mining sites

Case	DoB_{HEF}	Hg emission	Reference
Madeira River - dredges	100	extremely high	Pfeiffer et al., 1991
Madeira River - rafts	100	extremely high	Pfeiffer et al., 1989
Rato River - hydraulic mining	100	extremely high	CETEM, 1993
Poconé - mill	65	high	author's visit (1994)
Poconé - mill	40	not so high	CETEM, 1989
Teles Pires - rafts	100	extremely high	CETEM, 1991b
Serra Pelada - mill	40	not so high	author's visit (1985)
Roraima - manual	100	extremely high	Feijão and Pinto (1992)

From Table 6.1, we can observe that amalgamation operations on board vessels are the main source of Hg emission to the environment. Substantial reduction could be achieved by using retorts and by reprocessing amalgamation tailing separately in a plant. Most "garimpeiros" conduct amalgamation and separate amalgam-heavy minerals in a water box on board. When the box is full, they dump the contaminated tailing into the river. This author has tried in the past to work with a "garimpeiro" leader (José Alves da Silva) from Madeira River to set up a process to collect contaminated water boxes with tailing before being discharged. The logistic of this operation is not easy since thousands of barges and rafts (5000 in 1990) are dispersed along the river. The high investment in a plant as well as the uncertainty associated with the tailing supply to the plant have not encouraged Brazilian investors to go ahead with this idea.

The weights used in equation 6.7 range from 0.3 to 0, i.e. from "very-high" to "low" (Appendix IV). An example of correlation between importance and weight can be seen as follows :

Importance	Weight	Example of Event
very high	0.3	amalgam is burnt in pans
high	0.2	making amalgamation at the creek margin.
medium-high	0.15	amalgamation tailing is recycled to primary gravity circuit
medium	0.1	amalgamation uses pots or copper plates
medium-low	0.05	dredges or rafts are used; blenders are used in amalgamation
low	0	miners use retorts

Only two events were ranked "very high" :

- burning amalgam in pan
- dumping contaminated tailing into watercourse

The weight of 0.3 for these situations was chosen to ensure that at least 4 pieces of evidence are known in order for HEF to be 100% certain. Three of the 8 items shown in Fig. 6.7 are critical to evaluating Hg emission and must be answered by the user otherwise the DoB_{HEF} is not calculated:

- Size of the region or mining operation
- Fate of amalgamation tailing
- Gold separation from amalgam

When considering a region or a single mining operation (Appendix V), the system asks its question in different ways. A region usually contains many single operations. It is also better for the user to organize data files by site rather than by region, with each region being a separate sub-directory. The data files store information about mining and amalgamation practice which can be followed up by the user over time. An example was a visit of the author in 1989 to Fazenda Salina, Poconé. At that time, this large "garimpo" was beginning to operate in a well-organized way. The DoB_{HEF} calculated then was 40%, which means that Hg emissions were "not so high". In June 1994, the author returned to the site and observed that amalgamation tailing was left in pools as well as being recycled to the primary gravity circuit. Contaminated tailing is likely reaching watercourses. The updated DoB_{HEF} increased to 65%, i.e. high emission was occurring. This emission level was also noticed by Rodrigues (1994).

There is a clear logic associated with the process of establishing weights for events that are directly or indirectly related with the amalgamation operation itself. The size of the mining operation for example is relevant. If an amalgamation procedure uses poor methods, this could derive a high DoB_{HEF}. However, it is obvious that the smaller the operation, the lower the emission. Then large mining operations using amalgamation have a weight of 0.2 while a small one has 0.05. Certainly we might find elsewhere, a large operation working properly with mercury. If all steps are showing low emission, the DoB_{HEF} would be 20% or low for the Amazon region but high in a Canadian context. This seems acceptable and is reflective of the fact that there are no large gold mining operations in North America using amalgamation.

The weight of some events are associated with a "pre-conceived" judgment of the operation itself. For example, as it is observed that most dredges and rafts are the main emitters, we must increase the HEF factor by using a weight of 0.05 just for the fact that a dredge is in operation. This weight mirrors the fact that frequently mercury is spilled on board and amalgamation is carried out less carefully than on land. The same thought process is applied when blenders are used in amalgamation. We know that mercury is more dispersed in the tailing when high speed blenders are used to mix mercury with gravity concentrates. So a weight of 0.05 is also applied to mirror the fact that this tailing carries more Hg than tailing generated by manual panning but not more than tailing from continuous amalgamation processes, such as pots, plates or sluices. These latter methods have higher weights ($W_i = 0.1$).

It is conceivable that Neural Network learning algorithms could have been used to automatically generate the weights of the Weighted Inference Equations. This would be an interesting exercise to establish how close an automated technique would be to the expert heuristic evaluation but this is beyond the scope of the current work.

6.3.3 - Third Block - Natural Variables

Methylation and bioaccumulation are controlled by a number of environmental factors. The effect of some of these variables was discussed in Chapter 3. Those variables which contribute to enhanced methylation and bioaccumulation are defined as Dangerous Environmental Factors, or DEF while variables capable of reducing mercury availability to methylation and bioaccumulation agents are defined as Mercury Adsorption Factors, or MAF. A methodology similar to that used for DoB_{HEF} (eq. 6.7), is applied to determine DoB_{DEF} and DoB_{MAF}. To conclude about the effect of Dangerous Factors, the following variables are evaluated :

- water colour,
- water conductivity,
- sediment pH,
- sediment Eh,
- biomass,
- presence of "hot spots",
- contamination factor.

As observed in Appendix VII, which lists all natural variables considered, the importance of each variable ranges from "very high" to "low" which corresponds to weights from 0.3 to 0. The weights rank how dangerous one variable is in relation to others. The following list shows the relationship between importance and weight for several variables:

Importance	Weight	Example of Variable
very high	0.3	sediment contamination factor is high
high	0.2	water colour is dark
medium-high	0.15	water conductivity is low; Hg cross gills easily
medium	0.1	biomass in a creek is moderate; medium dilution effect
medium-low	0.05	hot spot is located and has at least medium-low Hg
low	0	sediment pH is neutral

When field measurements are available, Fuzzy Sets or inference equations are used to determine the DoB in each concept used in the heuristic model. For example, when pH and Eh of the contaminated sediments are measured, the system recognizes the importance of organic matter (based on a colour scale) and determines the Degree of Belief in metallic mercury oxidation (complexation) based on equations obtained from Eh-pH diagrams described in Chapter 3 (see Appendix VIII for details).

The following variables are used to conclude about the importance of Mercury Adsorption Factors. The influence of these variables was discussed in Chapter 3 :

- presence of hydrous ferric oxides - quantified by sediment colour,
- presence of clayey sediments,
- solids in suspension.

In Appendix IX the variables used to calculated DoB_{MAF} are listed with their importance and weights; which vary from "extremely high" to "low" or from 0.5 to 0 respectively. Fine ferruginous sediments are the best adsorbents for Hg compounds in the water column as observed in the following example of the use of these variables in DoB_{MAF} :

Importance	Weight	Example of Variable
extremely high	0.5	sediment is rich in hydrous ferric oxides (HFO)
very high	0.3	sediment is rich in clay fraction (< 0.002 mm)
high	0.2	sediment has medium HFO
medium	0.1	medium solids in suspension
low	0	water is clear; low adsorption of Hg from solution

Although adsorption by organic matter could minimize methylation mechanisms by reducing Hg(II) to metallic Hg (Allard and Arsenie, 1991; Alberts et al., 1974) or can promote more methylation by reactions between Hg and organics (Rogers, 1977; Verta, 1986), the HgEx

System adopts a conservative approach and the presence of organic matter in the polluted environment does not reduce bioavailability.

In order to establish the pollution effect, the Potential Bioaccumulation Risk or PBR is calculated:

$$DoB_{PBR} = DoB_{HEF} + DoB_{DEF} - DoB_{MAF} \qquad (6.8)$$

The risk of bioaccumulation is a function of the level of mercury emission and the degree of transformation in the environment. Mercury abatement and adsorption by fine ferruginous sediments are the only ways to decrease the risk of biota contamination.

Conclusions based on DoB_{PBR} are formatted to be presented in the form of warnings, such as: "*This condition is highly favourable for bioaccumulation. Check the fish. We suggest remedial procedures*". The DoB behind this conclusion, for example 89.97%, is just a mathematical result of the Inference Model. As the statistical significance of this number is questionable, the linguistic expressions allow us to accommodate multivalued concepts, which mimic the human reasoning approach, as described by Zadeh (1973). This technique can be considered as Linguistic Defuzzification.

6.3.4 - Fourth Block - Health and Life Style

Based on the environmental picture established by belief in a Potential Bioaccumulation Risk, a questionnaire is available in the program to indicate if an individual is subjected to mercury poisoning. The conclusions do not yield a definitive clinical diagnosis but rather provide advice on situations in which hair, urine or blood samples should be collected. If analyses of such samples are available, the system will compare them with normal ranges and based on the symptoms observed will suggest whether an individual is subject to mercurialism or not.

When human samples are taken indiscriminately without prior environmental evaluation, confusion and suspicion can spread among affected communities, since the analytical results and treatment methods for Hg intoxication are rarely given to the sample donors. In addition, the cost involved in collecting and transporting chilled samples to laboratories is high. Rationalization and optimization of this operation must be applied to ensure reliable data.

The questionnaire investigates undue occupational exposure of workers and possible indirect intoxication of ordinary people. The user inputs information from interviews with individuals affected directly (workers) or indirectly (non-workers) by mercury pollution. Questions are concerned with the following factors :

- Diet Habits : questions are related to the habit of eating fish, how many times per week and which kind of fish. If the individual has carnivorous fish from darkwater as his/her main diet, we assume that he/she has a high possibility of more Hg in the blood than an individual who eats fish infrequently or eats other species. This derives $DoB_{diet\ habits}$.

- Symptoms : questions related to symptoms of mercurialism are asked. These symptoms are divided in symptoms related to Hg vapour (derives $DoB_{symptoms\ Hg}$) and Me-Hg poisoning ($DoB_{symptoms\ Me\text{-}Hg}$). Symptoms can be masked by other diseases or habits such as malaria, congenital mental problems, drinking and gasoline handling. In contrast some habits can increase mercury exposure. For example, an individual who handles mercury and smokes, frequently brings his/her dirty hands close to the nose increasing the Hg vapour exposure.

- Occupational Exposure : questions aim to know how the worker handles mercury. We have considered workers who burn amalgam, those who melt gold and those who share the same contaminated workplaces. This derives $DoB_{occupational\ exposure}$.

- Life Style : questions are more relevant for non-workers than for workers. If a worker handles Hg frequently in a workplace and keeps contaminated clothes at home, then there is a possibility that members of the family are also inhaling Hg vapours. As a life style factor, we have also included the place where the individual lives. If this is near a contamination source such as a mining activity or a gold dealer, then this individual is probably inhaling more Hg. This derives $DoB_{life\ style}$ which is the DoB that life style factors contributed to Hg poisoning.

Each factor derives a specific DoB based on a Weighted Inference Equation which can be seen in Appendix X. The relative importance of each event was derived from the literature and from experts in the field. The Degree of Belief in mercurialism is 80% when high Hg blood, hair or urine are provided. This means that without chemical analysis of biological samples, mercurialism cannot be definitely identified. However, biological samples are recommended based on the factors listed above. When inorganic Hg poisoning is likely, the system recommends urine samples. Blood analysis gives a combined picture of inorganic and organic contamination but can be more indicative of a recent or occasional undue vapour exposure (A.A.P. Boischio - Univ. Indiana - personal comm.). When the evidence is not very strong about exposure, blood samples are more indicative than urine. Urine samples are recommended when evidence in vapour exposure poisoning is strong (DoB >75%).When Me-Hg poisoning is suspected, hair analysis is suggested. Urine or blood analysis is recommended based on the following equation :

for workers: $$0.3\ DoB_{symptoms\ Hg} + 0.6\ DoB_{occupational\ exposure} + 0.1\ DoB_{life\ style} \quad (6.9)$$

for non-workers : $$0.5\ DoB_{symptoms\ Hg} + 0.5\ DoB_{life\ style} \quad (6.10)$$

$DoB_{urine\ or\ blood}$ derived from the equations above is transformed into the following expressions :

DoB	Output expression
100 - 75	Urine samples are recommended.
40 - 74.9	Blood samples are recommended.
25 - 39.9	Evidence is not strong to recommend blood analysis, but if this facility is available, analysis may be useful.
0 - 24.9	Evidence is insufficient to recommend blood analysis.

In the case of workers, occupational exposure has higher weights than other facts. Non-workers can be indirectly exposed to Hg vapours. The main events to be investigated are related to symptoms and life style.

Hair analysis for workers and non-workers is suggested based on :

$$0.4\ DoB_{symptoms\ Me\text{-}Hg} + 0.3\ DoB_{diet\ habits} + 0.3\ MAX\ (DoB_{PBR}, DoB_{BE}) \ldots\ldots\ (6.11)$$

Equation 6.11 highlights methylmercury poisoning symptoms as the main factor to suggest sampling. However, many fish-eating individuals in the Amazon are not showing symptoms of "Minamata disease" with Hg concentrations as high as 100 ppm in hair (Malm et al., 1994). This leads us to give high importance (combined weight = 0.6) to diet habits and bioaccumulation evidence. This latter, shown at the end of the equation 6.11, emphasizes the concept that prior evaluation of the bioaccumulation potential of a region must be done before collecting human samples. When high Hg is analyzed in fish and/or other biota samples, bioaccumulation evidence is provided, otherwise the predicted bioaccumulation risk (DoB_{PBR}) is used in equation 6.11.

As before, linguistic defuzzification is used to provide conclusions such as: "*Urine samples are recommended.*", "*Blood samples are strongly recommended.*", "*Hair samples can be helpful*", "*Evidence is insufficient to recommend blood or hair analysis.*", etc.

6.3.5 - Fifth Block - Biaccumulation Prediction versus Evidence

The potential bioaccumulation risk obtained by the heuristic model in blocks 2 & 3, is compared with analyzed biota samples, when available, and conclusions about current and future bioaccumulation are provided (Fig. 6.9). When the system indicates a high potential for bioaccumulation but the biota does not show high Hg levels, the system suggests frequent monitoring programmes and remedial procedures to look for problems to develop in the future.

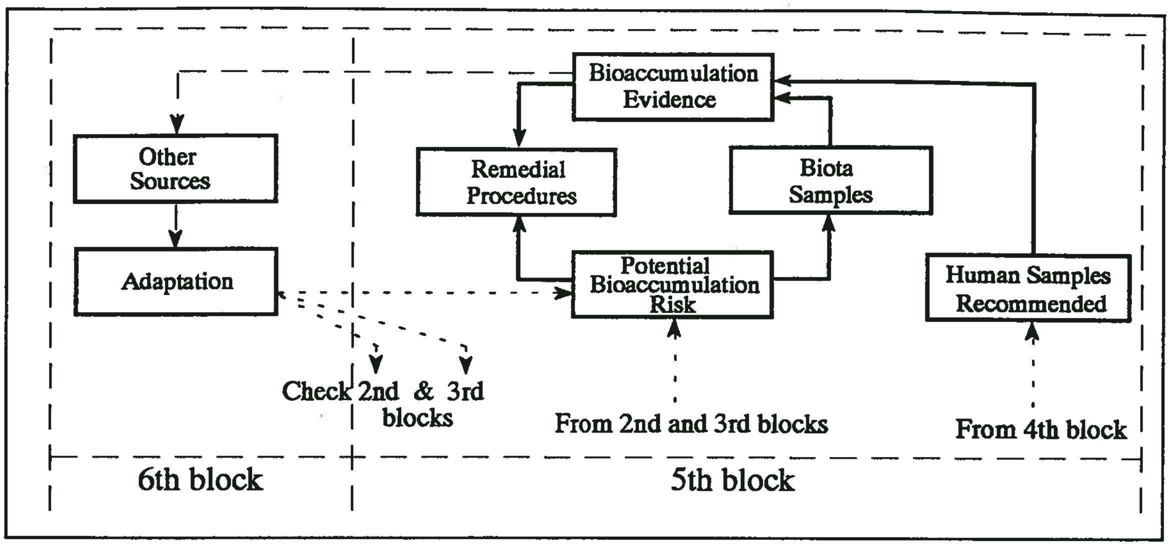


Fig. 6.9 - The two upper blocks of the system structure (see Fig. 6.3 for full structure).

The Degree of Belief in Bioaccumulation Evidence (DoB_{BE}) results from :

- DoB in fish analysis is high ($DoB_{Hg\ in\ fish\ is\ high}$) or
- DoB in snail analysis is high ($DoB_{Hg\ in\ snail\ is\ high}$) or
- DoB in high number of individuals with medium or high levels of Hg in hair ($DoB_{high\ number\ of\ individuals\ with\ high\ or\ medium\ Hg\ in\ hair}$).

Fuzzy sets transform analytical results of biological samples into a Degree of Belief in high. DoB_{BE} is finally calculated by the following expression :

$$DoB_{BE} = MAX\,(DoB_{Hg\ in\ fish\ is\ high} \cdot DoB_{number\ of\ biota\ samples\ is\ sufficient} / 100,$$
$$DoB_{Hg\ in\ snail\ is\ high} \cdot DoB_{number\ of\ biota\ samples\ is\ sufficient} / 100,$$
$$DoB_{high\ number\ of\ individuals\ with\ high\ or\ medium\ Hg\ in\ hair})$$

A Fuzzy set defines how many biota samples are required to provide reliable results. This Fuzzy set is a linear relationship in which 30 samples are considered sufficient (DoB = 100%).

The DoB in a high number of individuals with medium or high levels of Hg in hair is defined by two separate Fuzzy sets (Fig. 6.10). It is observed that 8 individuals with high Hg analyzed in hair samples or 16 individuals with medium Hg level are end members of the respective Fuzzy sets, i.e. high number of individuals poisoned with Me-Hg were identified in the study area.

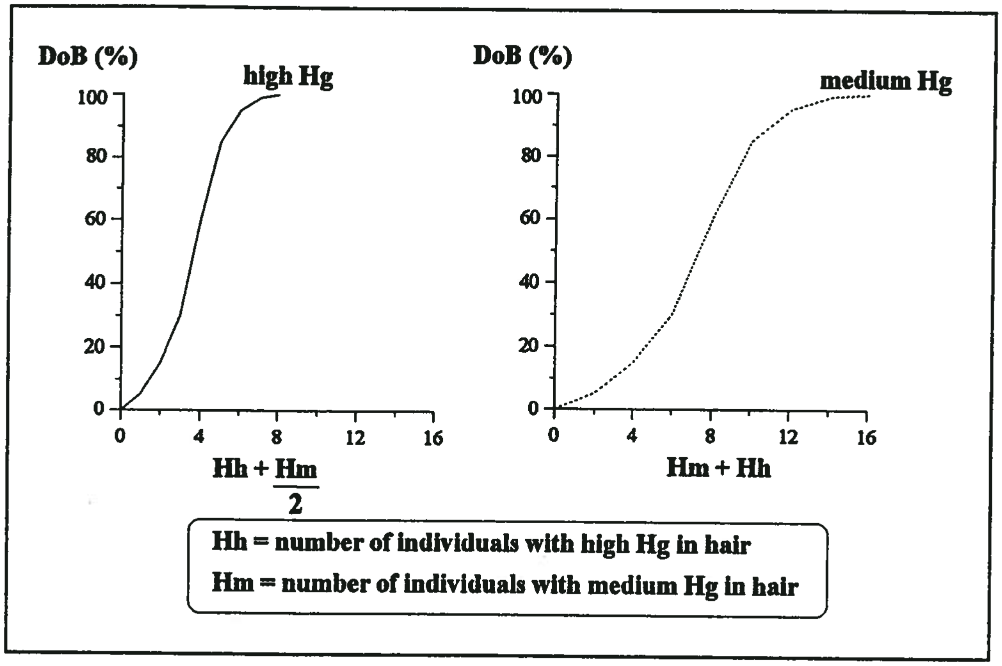


Fig. 6.10 - Fuzzy sets to define high number of hair samples with Hg

Remedial procedures for polluted sites are recommended together with measures to reduce mercury emission. Different suggestions are reported depending on the situation described by the user. Examples of these recommendations can be seen in Chapter 7.

Biological samples (fish, snail or human) can provide evidence of bioaccumulation based on chemical results. The procedures to obtain chemical results usually involve specialists to choose the biological subjects, to sample, transport and analyze them. The Hg concentration in these samples, when available, is input by the user and transformed by Fuzzy sets into concepts "high", "medium" and "low" to characterize the bioaccumulation level. The Bioaccumulation Evidence (DoB_{BE}) increases when more samples are input. When more than 30 biological samples are input, the system considers that sufficient numbers of samples are available. DoB_{BE} is compared with the predicted bioaccumulation risk (DoB_{PBR}) to check any conflict.

6.3.6 - Sixth Block: Adaptation

Occasionally, the system may predict a low bioaccumulation risk at a time when reliable biological samples provide evidence of a mercury accumulation process. The system will check the user inputs, searching for imprecise data. If conflicts exist between chemical results and bioaccumulation prediction - DoB_{PBR}, the system will check the number of samples collected and the reliability of the chemical analyses.

After a hierarchical process of checking (Fig. 6.11), if the conflict persists, the system uses the consultation data to adapt its diagnosis for the case study. The predicted risk, DoB_{PBR} is raised to an exponent (α_{PBR}) to match the diagnosis with the bioaccumulation evidence (DoB_{BE}). The predicted bioaccumulation risk which is calculated by a heuristic model, (based on eq. 6.8 : $DoB_{PBR} = DoB_{HEF} + DoB_{DEF} - DoB_{MAF}$), applying the exponent (α_{PBR}) as follows :

$$(DoB_{PBR})_{new} = (DoB_{PBR})_{old}^{\alpha_{PBR}} \quad \text{...} (6.12)$$

The new Degree of Belief in Potential Bioaccumulation Risk is modified after adapting α_{PBR} which represents the existence of other Hg emission sources known to the user. The α_{PBR} is calculated to increase the DoB_{PBR} to half of the difference between the predicted and evidenced DoB in bioaccumulation.

$$\alpha_{PBR} = \frac{\log(DoB_{PBR} + (DoB_{BE} - DoB_{PBR})/2)}{\log DoB_{PBR}} \quad \text{...........................} (6.13)$$

The system could be designed either to accept DoB_{BE} based on biological samples or to reject the evidence and use the predicted DoB_{PBR}. As it is not possible for the system to check the quality of the analytical results of the biological samples input by user, a conservative approach has been adopted in which DoB_{PBR} is increased by one half of the difference between the evidenced and predicted bioaccumulation beliefs.

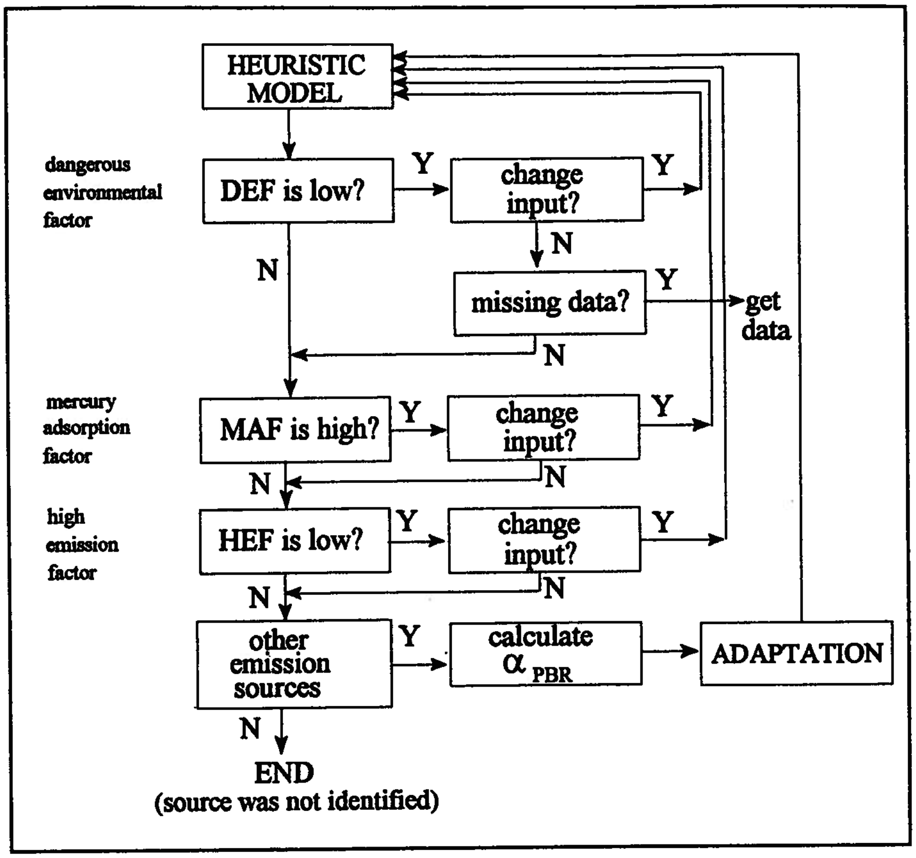


Fig. 6.11 - Hierarchical structure to adapt the Potential Bioaccumulation Risk

Other sources of emission are considered the main reason for discrepancies between the predicted and evidenced bioaccumulation level. The system provides suggestions to look for these other sources such as:

- Biological Degassing : Nriagu (1989) has established that 40% of the global Hg emissions come from natural sources, which means an average of 2,500 tonnes/year of Hg (range: 100 to 4900). Biologically-mediated volatilization accounts for about 30 to 50% of this estimate. Non-methane hydrocarbon compounds, such as isoprene and terpenes from plants may form strong complexes with Hg and other trace metals and thus play a part in the transfer of metals to the atmosphere. Particulate organic carbon, which is the dominant component of atmospheric aerosols is another Hg bearing phase. This source is difficult to measure, i.e. involves a large monitoring programme to establish its importance in the Amazon.

- Recent Impoundments : high Hg in fish is observed when large areas are flooded for building hydroelectric plants. Hg content in soil and vegetation is leached out when reservoirs are being flooded which transfers to fish. Verdon et al. (1991) estimated that between 20 to 30 years are needed to return Hg in fish to the preimpoundment levels. In Brazil, a recent study conducted by Finnish researchers observed that predatory fish caught near Tucuruí port, in which the forest was cleared before flooding, showed significantly lower Hg levels than those sampled in other parts of the reservoir (Boonstra, 1993). The results of this study show the extreme sensitivity of Hg uptake to this environmental change.

- Other Industrial Sources: most early studies of man-made emissions into the global atmosphere estimated numbers from 7,500 to 38,000 tonnes Hg/year. A detailed study carried out by Nriagu and Pacyna (1988) estimate a range from 910 to 6,200 tonnes Hg/year in which coal combustion is responsible for about 50% worldwide. The user must check the existence of other industrial activity locally.

- Forest Fires : we have calculated that the amount of Hg emitted by deforestation in the Amazon is at the same magnitude or even higher than Hg emitted by "garimpos". Considering that pastures are also burnt to control pests, Hg emissions from vegetation fires can be twice that emitted by "garimpos". In Appendix II, these conclusions are detailed. So, if significant fires are occurring in a region, this can affect Hg background levels significantly. Prior to this work, no one else has recognized the importance of this source.

The system asks the user if he/she believes that other Hg emissions can be the source of conflict between high Hg levels encountered in biota samples and the prediction of low bioaccumulation risk. If the user accepts one of these sources, the system calculates the new DoB_{PBR}, otherwise no adaptation is done since the discrepancy is unknown.

6.4 - Linguistic Defuzzification

The structure of an Expert System can allow for input of different types of data. When linguistic variables are used, the system can become easy to use and more accessible for non-technical people. The Fuzzy Logic technique devised by Zadeh (1965) employs human analysis to provide an approximate and yet effective means to describe behaviour of situations which are too complex or ill-defined to allow precise mathematical analysis. According to Zadeh (1992), the strength of human reasoning lies in the ability to grasp inexact concepts directly rather than formulating exact ones. This technique is extensively used in HgEx as a way to manage complex issues. It allows a diagnosis even when vague data are input by the user.

Linguistic concepts are characterized by a membership value of each fact in a particular concept. When we characterize a variable in the form of linguistic expressions such as "high", "low", "acidic", "medium", "dark", etc. we have to define the meaning of these expressions. Each expression has a membership grade derived from a discrete value. This grade is called Degree of Belief (DoB). Variables, when available, such as conductivity, water transparency, Hg concentration, number of gold shops, Eh, pH, etc., are requested from the user to be transformed into expressions with respective DoB to be handled in the heuristic model.

For example, how acidic is pH=5 ? We have built Fuzzy Sets to define the DoB in the concept "acidic". Our belief that pH 5 is acidic is around 80% (Fig. 6.12). This is less acidic than pH 2 which has a DoB of 99. Fuzzy Sets glide smoothly across a continuum which goes from TRUE to FALSE or DoB = 100 and 0 respectively for each concept.

The shape of each fuzzy set is the result of pH-range definitions for soils and sediments (Dragun, 1988) together with the experience of the author with respect to the domain of this work.

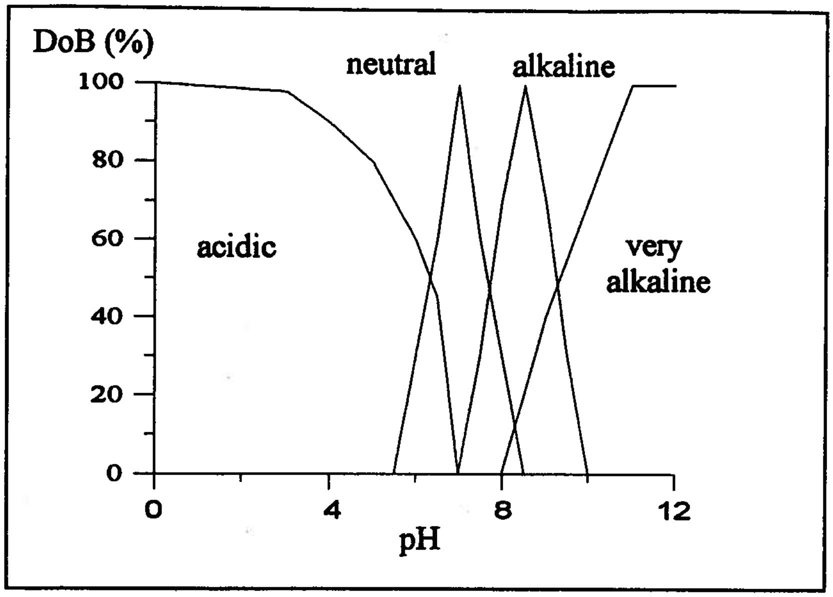


Fig. 6.12 - Fuzzy Set definitions for pH of soils and sediments

All input data are transformed into linguistic expressions with their respective Degree of Belief. For example if the pH measured in a watercourse is 7.5, then the Degree of Belief in "alkaline" is only 30%, and 60% in "neutral" according to Fig. 6.12. "Very slightly alkaline" would likely be the fuzzy set having full membership at this pH level or 100% DoB. If we narrow the pH range to accommodate more linguistic expressions, we would have a large number of fuzzy sets to describe "precisely" our view point but in this case the linguistic expressions would cope with a semantic problem. How would we describe a fuzzy set in which pH 7.2 would be the member with 100% of DoB ? "Just a little bit alkaline"? "Almost neutral" ? We believe that four fuzzy sets can express reasonably the level of acidity or alkalinity of a sediment.

Linguistic defuzzification is also achieved for output variables such as High Emission Factor. In this case, the term used to describe the range in DoB is elastic with respect to outside influences such as technical, socio-political and economic issues. A description of this adaptable, context-sensitive method was given in section 6.3.1.

Each concept has a grade (DoB) that is used in the heuristic model to conclude about the bioaccumulation risk. Weighted Inference Equations can deal with these variables using the importance of each fact (weight) on the conclusion that the environment shows dangerous conditions for methylation and/or bioaccumulation.(DoB_{DEF} - Degree of Belief in Dangerous Environmental Factors).

6.5 - Defuzzification to Discrete Values

The heuristic model deals with DoB in concepts. We have seen above that Fuzzy Sets convert measured variables into DoBs. However, frequently the user may not have analyzed a certain variable. A DoB must be inferred, if this variable is needed. In many cases an exclusive set of questions is displayed to define the variable level. This is the case of water transparency evaluation. The user has to make a choice if the watercourse is "clear", "a bit cloudy", or "muddy" if Secchi disk readings are not available. This exclusive set method creates a crisp boundary between each concept, but allows an alternative field observation input.

Fuzzy Logic can also be used to transform qualitative data into inferred numbers. The contamination factor is the ratio between Hg analyzed in a sediment and the background level. If the background was not established in field work, the system may infer a number making use of Fuzzy rules and inference equations.

High mercury contents result from Fe/Mn-rich minerals, sulphides and rocks or sediments rich in organic matter. So, the sediment colour can also be used to infer Hg background. White sediments are frequently related to parent rocks poor in Hg while hydrous ferric oxides (HFO) or organic matter will tint sediments to a maroon or black colour respectively. Despite the large diversity of sediment types, when considered with respect to mercury content alone, we can formulate three types which commonly have low, medium and high mercury respectively:

- Type 1: comprises gravels, white or light grey clay or sand, limestones, sandstones;
- Type 2: comprises any reddish clayey or sand sediment;
- Type 3: comprises organic-rich sediments.

Rules can be built that correlate user belief in a sediment type with a conclusion about the Hg level. One rule could be:

RULE 1

IF sediment is classified as Type 1	DoB = 80 (user input)
THEN Hg level is low	CF = 100

If we consider that the $DoB_{low} = DoB_{type\ 1} \cdot CF/100$, the DoB of this conclusion is 80%. The significance of 80% DoB_{low} can be transformed (or defuzzified) into a discrete value. According to the fuzzy sets established from the detailed literature review (see Chapter 3), we can say from this DoB that this sediment should have a value around 0.06 ppm Hg, as obtained from the fuzzy set shown in Fig. 6.13. This is a rather low value for even Type 1 sediments. Most have contents above 0.07 ppm although values as low as 0.003 have been infrequently measured. So with this uncertainty, we would prefer to have a much higher Hg level chosen. As will be seen, an exponential Inferencing Equation can be used to achieve this performance.

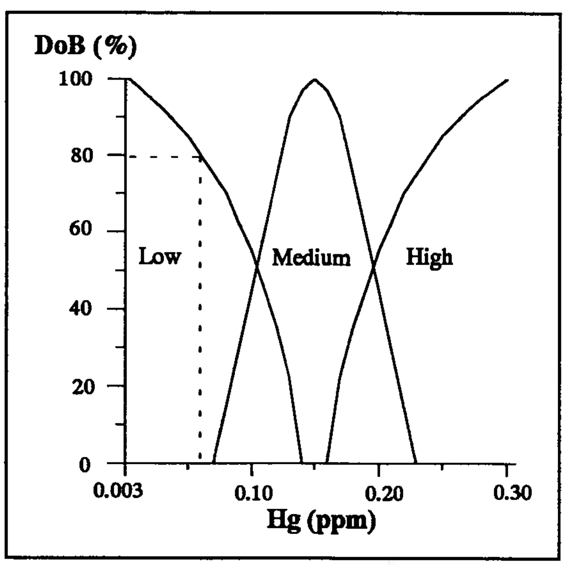


Fig. 6.13 - Fuzzy Sets for Hg levels in sediments.

As well when other components with high mercury concentration are present in the sediment, but the user still believes that Type 1 best describes the case, the rule becomes more complex:

RULE 2

IF sediment is classified as Type 1	DoB = 80 (User input)
AND hydrous ferric oxides are present	DoB = 100
AND sulphide mineral is present	DoB = 100
AND organic matter is present	DoB = 100
THEN Hg level is low	CF = 0

In this case, the Certainty Factor is zero, i.e. the user may believe that this sediment is better classified as Type 1, but the system will not believe in a low Hg level since the presence of other components most certainly increases the natural Hg concentration. Regardless of the method used to combine the DoBs of the premises, we know that the Degree of Belief of this conclusion (low Hg level) is zero provided the DoBs of all premise parts exceed the confidence level. Otherwise the firing of this rule will be unsuccessful.

So, the DoB of the conclusion must accommodate all cases between False and True. An Inference Equation can play this role, i.e. an equation established to correlate $DoB_{type\ 1}$ and DoB_{low} together with the DoB values associated with Hg-containing minerals. Sometimes, a synergetic effect between premises is desired. An empirical equation has been derived from the two extremes cases shown above that is capable of accumulating all ranges of belief in the various sediment species:

$$DoB_{low} = \exp\left(0.046 \cdot \left(DoB_{type1} - \frac{DoB_{Fe\ oxide} + DoB_{sulphides} + DoB_{organics}}{3}\right)\right) \quad \ldots\ldots (6.14)$$

where: $DoB_{Fe\ oxide}$, $DoB_{sulphides}$ and $DoB_{organics}$ are the degrees of belief input by the user about the presence of each of these sediment components.

Equation 6.14 is the mathematical result of heuristic reasoning which correlates Hg levels with sediment components as shown in Fig. 6.14. The desired exponential decay relationship between $DoB_{type\,1}$ and DoB_{low} is apparent. Only a single rule is necessary to obtain this relationship.

Equations to relate Type 2 and Type 3 with the concepts of medium and high Hg levels, respectively, were also heuristically developed :

$$DoB_{medium} = \exp\left(0.046 \cdot \left(DoB_{type2} - \frac{DoB_{sulphides} + DoB_{organics}}{2}\right)\right) \quad (6.15)$$

$$DoB_{high} = DoB_{sulphides} + DoB_{type3} \cdot (DoB_{organics} / 100) \quad (6.16)$$

The $DoB_{organics}$ is obtained by a colour scale from white to black or from 0 (false) to 100 (true). When the user selects a tint of grey, the system takes the associated $DoB_{organics}$ with the colour.

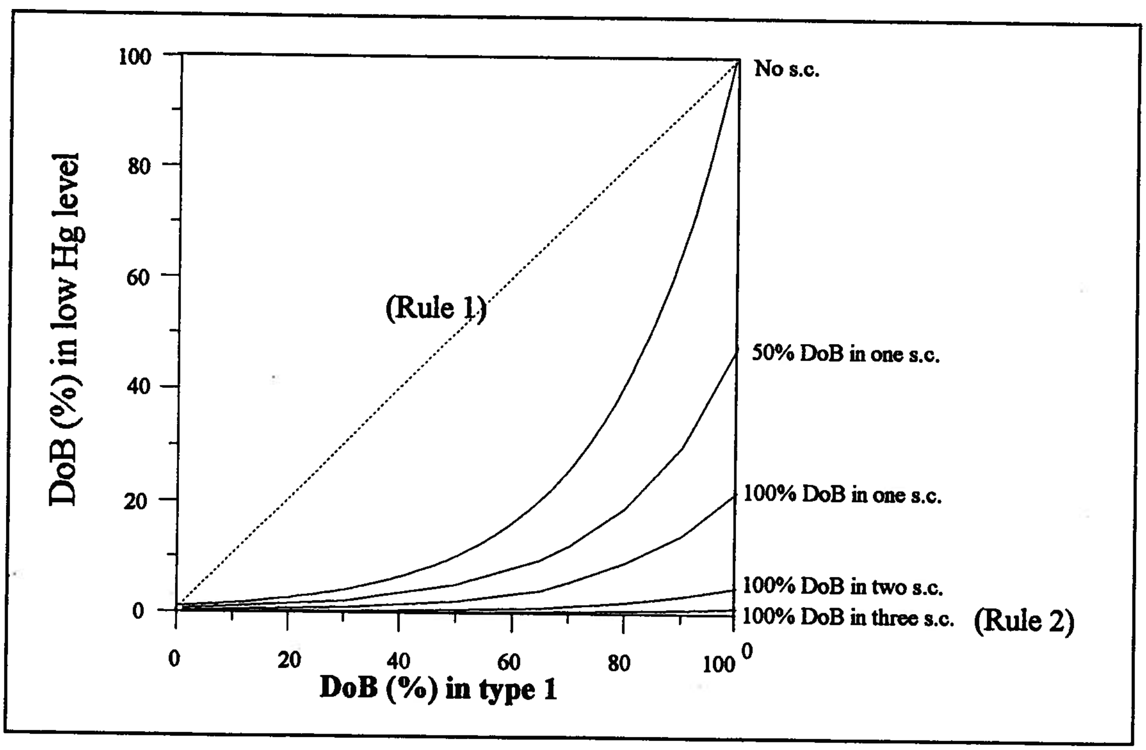


Fig. 6.14 - Relationship between degrees of belief in low and sediment type.
s.c. = sediment components with high mercury content

Subsequent defuzzification obtains a discrete value from the respective Fuzzy Sets (Fig.6.13). Defuzzification can follow one of 80 different reasoning methods, any of which under different circumstances can provide the "best" result (Smith and Takagi, 1994). For the purposes of this work, it was decided to use an adaptation of the Weighted Average Method (shown in eq. 6.5) combining the DoB in each concept: low, medium and high. This technique is useful to provide an analysis even when the background level was not established in a field survey. In this way, the contamination factor can be inferred from direct observations about the sediment.

6.6 - System Characteristics

HgEx was developed using the Comdale-X Development Tool, v. 5.13. All information is stored in the form of logical, string or numerical keyword triplets which comprise object, attribute, value and Degree of Belief.

Objects are physical entities in the real world such as sediment, water, bioaccumulation, etc. Attributes describe object properties or characteristics such as "colour", "conductivity", "evidence", etc. A value is attached to the object-attribute pair to classify them (e.g. "dark", "moderate", "high"). All keyword triplets carry a Degree of Belief ranging from 0 to 100, to determine whether the keyword triplet is significant of not.

When the information about a keyword triplet is needed but the DoB is "not known", the system is forced to search through rules in the knowledge base. Keyword triplets together with DoBs form the fundamental basis for representing knowledge as well as providing a driving force for the system in its search for knowledge during execution (Kumar, 1991).

The User Interface is a Hypertext facility which is part of the Comdale-X tool. This interface comprises 9 separate documents created to facilitate the programming job. The Knowledge Base is consulted when a decision is required, i.e. a hot key (word or bitmap) executes commands which link Hypertext with a specific rule in the knowledge base to instantiate (obtain DoB) a keyword triplet. Programming in Hypertext might be considered an unusual process. However the flexibility of the Comdale/X tool to accumulate a dynamically-changing User Interface gives HgEx a much improved interface despite the increased programming time required.

In spite of the easy environment provided by the Development Tool (programming in English), about 4,000 hours were required to build HgEx. The main causes for this long programming time were:

- programmer did not have prior practice with ES technology or Windows Environment;
- all figures are bitmaps; most of them were manually drawn;
- all hot bitmaps (including buttons) were set up in pieces;
- hypertext editor (ASCII) is time-demanding to fit sentences in a page space;
- the uncertainty input facility in hypertext was developed;
- knowledge base was modified based on new pieces of evidence;
- the size of the domain is very large.

The main features of the prototype version of the system are shown in Table 6.2. The system requires an IBM compatible computer with processor higher than 386 and at least 4 Mbytes of RAM memory to have a comfortable consultation section. The system, mainly the Diagnostic part, becomes extremely slow on hardware with configuration worse than 386/40 MHz.

The use of a commercial development tool which allows input of uncertain data and Fuzzy Logic operations was fundamental to obtain a user-friendly system. The lack of a Hypertext editor with drawing facilities (to create buttons automatically for example) is the main criticism about the Comdale/X tool.

In conclusion, it is emphasized that the structure of HgEx allows a user to obtain conclusions with justification of all inference steps. As well, the system gives wide flexibility to the user to switch between sections in the consultation and to answer the questions following different orders of data input. The Weighted Inference Equations mean that uncritical questions do not need to be answered to obtain conclusions. The quality of the diagnostic provided by the system is shown in four examples which comprise the next Chapter.

Table 6.2 - HgEx system characteristics

Characteristic	**Number**
Program Size	9.97 Mbytes
Files	734 (546 bitmaps)
Rules in the Knowledge Base	305
Keyword triplets	810
Objects	156
Characters in the Knowledge Base	300,000
Procedures in the Knowledge Base	113
Fuzzy Sets	94
Documents in Hypertext	9
Documents in Tutorial part	4
Documents in Diagnostic part	3
Documents in Help	2
Characters in the documents	905,000
Electronic Topics in Hypertext	1,500
Man-hours of Programming	4,000
Man-hours to draw bitmaps	800
Man-hours in Tutorial part	800
Man-hours in Diagnostic part	2,400

7. Case Studies

"It is not everything that can be proved,
otherwise the chain of proof would be endless"
Aristotle

7.1 - Introduction

Potential bioaccumulation risk predicted by the system is compared with analyzed biota samples, when available, and conclusions about current and future bioaccumulation are provided. Biological sample analysis requires special attention in sampling, muscle removal, freezing, transportation, dissolution and analytical techniques. Usually experts are called to do this job which involves high costs. The HgEx reduces the need for extensive biological monitoring programs of a mining site and provides a preliminary diagnosis about bioaccumulation risk from an Expert's point of view (Veiga and Meech, 1992; Veiga and Meech, 1994).

Four cases were selected to be tested by the system. In three cases, biological samples were available and the predicted bioaccumulation risk was compared with the bioaccumulation evidence. In the last case, the system predicts that bioaccumulation risk exists and biological samples are not available. The following four cases are shown below :

- Poconé
- Alta Floresta
- Itaituba
- Port Douglas (a site in British Columbia, Canada)

Poconé, Alta Floresta and Itaituba regions represent three important mining regions in Brazil. The majority of "garimpo" behaviours can be seen in these areas. Different mining processes and amalgamation methods are used in these regions. Data input were obtained from the author's visits as well as published data and discussion with the following professionals in 1994 :

- Alberto Rogério B. da Silva (geologist, Director of Mining of the Secretary of Industry, Commerce and Mining of Pará State; expert in "garimpos" and gold geology - data published in GEDEBAM, 1992; Silva et al., 1994).
- Alexandre Pessoa da Silva (chemical eng., MSc., technical supervisor of Poconé and Itaituba Projects; consultant of Pan-American Health Organization - data published in CETEM (1989, 1991a, 1993; Silva et al., 1991; Silva and Veiga, 1992, Silva et al., 1993).
- Ana Amélia P. Boischio (biologist, MSc, PhD candidate at Univ. Indiana, Bloomington,; prof. in Univ. of Rondônia, Brazil, specialist in Hg toxicology - data published in Barbosa et al., 1994; Boischio and Barbosa, 1994).
- Augusto Kishida (geologist, MSc, PhD, specialist in gold geology and "garimpos"; director of Madison do Brasil, a subsidiary of Consolidated Madison Holdings Ltd., a Canadian Mining Co. investing in acquisition and reclamation of Brazilian "garimpo" areas).
- Saulo Rodrigues (geologist, MSc, head of the geochemistry group of the Poconé and Alta Floresta Projects - Hg monitoring programs in Brazil - data published in CETEM, 1989, 1991a, 1991b, Farid et al., 1992; Rodrigues, 1994).

Port Douglas, an old mining site in B.C., located at the tip of Harrison Lake, was used to check the system performance when applied to diagnose bioaccumulation in another country.

The report generated for each case gives the following Degrees of Belief (DoB)

- High Emission Factor (DoB_{HEF})
- Dangerous Environmental Factor (DoB_{DEF})
- Mercury Adsorption Factor (DoB_{MAF})
- Potential Bioaccumulation Risk (DoB_{PBR})
- Bioaccumulation Evidence (when biological samples are available) (DoB_{BE}).

7.2 - Poconé Region

The presence of lateritic gold in the western-central part of Brazil was reported at the beginning of the 18th century. The "bandeirantes", Brazilian pioneers, developed the Beripoconé mines in 1777 which were the embryos for Poconé city. The economy of the municipality until 1982 was based on cattle and agriculture, when gold suddenly became the main economic source of the city. Around 4500 miners have been working excavating weathered layers of eroded quartz veins hosted by sericite and graphite phyllites from the Proterozoic (800 to 600 My) Era (Rodrigues, 1994). The high production causes fast exhaustion of the weathered material. The quartz veins are also mined manually. Gravity circuits usually use copies of the Knelson centrifuge with a capacity of 32 tonnes/h of solids. The proximity of an important Ecological Park in South America ("Pantanal") makes this region the target of environmentalists and constant monitoring programs for Hg (Veiga and Fernandes, 1990). Data input for bioaccumulation assessment were as follows :

1) Size of the Mining Activity: *small region*

2) Method of Mining: *mill (predominantly)*

3) Portion of Ore Amalgamated: *concentrates*

4) Amalgamation Method: *barrels and manual panning*

5) Separation Amalgam-Mineral Portion: *panning in water boxes, pools and at creek margins*

6) Fate of Amalgamation Tailing: *discharged to watercourses, recycled to plants, left in pools, safely stored*

7) Gold Separation from Amalgam: *retorts and burnt in pans (DoB=60%).*

8) Gold Melting Operation: *less than 10 gold dealers without any special fume hood*

DoB_{HEF} for the region = 100%

9) Sediment Background : *inferred based on ferruginous phyllite = 0.15 ppm*

10) Water Colour : *Bento Gomes River = 50% dark water*

11) Biomass : *Bento Gomes River = high*

12) Water Conductivity : *Bento Gomes River = 60 μS/cm = moderate*

13) Hot Spots : *identified visually in many creeks of the region; >3 ppm Hg (inferred)*

14) Contaminated Sediment Type : *rich in clay, red-maroon (max 20% Fe_2O_3)*

15) Contaminated Sediment Hg Concentration : *0.1 ppm Hg (40 samples)*

16) Contaminated Sediment Highest Redox Potential : *0.390 V (with pH = 6.3)*

17) Water Transparency in the Main Stream : *a bit cloudy*

DoB_{DEF} = 55 % (relatively dangerous)

DoB_{MAF} = 100 % (definitely possible)

DoB_{PBR} = 55% (moderate-high)

18) Biota Samples : *average of 20 carnivorous fish = 0.1 ppm Hg*

average of 100 snails (Pomacea canaliculata) = 0.23 ppm Hg

DoB_{BE} = 30% (moderate)

7.3 - Alta Floresta

Gold in the Tapajós river has been known since 1750, but mining operations only began in 1958. Mechanized "garimpos" were introduced from 1976 onwards. Tapajós river is one of the major alluvial gold deposits in the world. It comprises an area of 100,000 km^2 along the river where 140,000 miners have worked in 460 mining sites (Cleary, 1990). The river is 2000 km long with a flow rate of about 12,400 m^3/s and water velocity around 0.4 m/s. The gold province extends from the southern border of the Amazon Basin where Alta Floresta is located, to the northern part, where Itaituba is the main "garimpo" region (Feijão and Pinto, 1992).

Dredges and rafts produce about 1 tonne Au monthly and hydraulic mining 0.3 tonne in Alta Floresta (Farid et al., 1992). Mining activities are carried out on Teles Pires river (a Tapajós tributary) and its tributaries, such as Peixoto de Azevedo river. Bottom sediment comprises a hard iron oxide crust over an auriferous gravel. Auriferous quartz veins are hosted in shear zones by granites (1860-1100 My) covered by recent colluvial material which is usually mined by hydraulic monitors (CETEM, 1991b).

Alta Floresta, a city of 20,000 km^2, is located in the Mato Grosso State almost at the border of Para state, in the southern part of the Amazon region. It was founded in 1976 by a colonization project and became a municipality in 1979. At this time, gold was discovered in the Teles Pires River attracting prospectors. With 140,000 people, the city has a strong social and economic component based on agriculture (58,000 ha of crops and 85000 tonnes/y of grains produced) and mining. The official gold production is 1 tonne of gold per month. Around 5% of the population enter the hospital annually with malaria. (CETEM, 1991b). Amalgamation is done by mixing gravity concentrates from sluices (with carpets) and Hg in tanks or buckets with blenders. The amalgam-concentrate separation is done by panning. Retorts are not often used and the gold dealers working downtown, do not have any mercury filter in their fume hoods to retain volatilised mercury evolved during gold melting. Data input are listed below :

1) Size of the Mining Activity: *large region*

2) Method of Mining: *dredge, rafts and hydraulic monitor*

3) Portion of Ore Amalgamated: *both concentrate and whole ore*

4) Amalgamation Method: *blenders, barrels and manual panning*

5) Separation Amalgam-Mineral Portion: *panning in water boxes, pools and at creek margins*

6) Fate of Amalgamation Tailing: *discharged to watercourses, left in pools*

7) Gold Separation from Amalgam: *both retorts and burnt in pans*

8) Gold Melting Operation: *more than 30 gold dealers without any special fume hood*

DoB_{HEF} for the region = 100% (extremely high)

9) Sediment Background : *analyzed = 0.1 ppm*

10) Water Colour : *Cristalino River = dark water*

11) Biomass : *Cristalino River = high*

12) Water Conductivity : *Cristalino River = 22 µS/cm = low*

13) Hot Spots : *identified in Teles Pires River (main river) = 2 ppm Hg = high*

14) Contaminated Sediment Type : *rich in clay, yellow-orange (max 10%* Fe_2O_3*)*

15) Contaminated Sediment Hg Concentration : *1.06 ppm Hg (44 samples)*

16) Contaminated Sediment Highest Redox Potential : *0.273 V (with pH = 6.9)*

17) Water Transparency in the Main Stream : *Secchi disk = 0.35 m = cloudy*

DoB_{DEF} = 50 % (relatively dangerous)

DoB_{MAF} = 61 % (moderately possible)

DoB_{PBR} = 89% (high)

18) Biota Samples : *average of 15 carnivorous fish = 0.23 ppm Hg*

average of 204 snails (Hemisinus tuberculatus) = 0.25 ppm Hg

DoB_{BE} = 50% (moderate)

7.4 - Itaituba Region

In the 18th century, gold occurrence in the region was reported by the Jesuit priests who encouraged the natives to exploit it. In 1958, news of the discovery of a rich alluvium attracted some "garimpeiros" to the region. Until 1960, there are no records of gold production. In 1971, the Minister of Mines used the region for political and economic promotion which lured many gold seekers. In 1980, the Tapajós "Garimpo" Reserve was created by the government with an area of about 40,000 km^2, expecting to organize the activity (DNPM, 1992).

Itaituba was the main municipality (17 million ha) of the Tapajós region until 1992 when it was split into 3 cities: Novo Progresso, Jacareacanga and Trairão. Mining activities in Itaituba transformed this triad into the main gold-trading centre in Brazil with a gold production around 320 tonnes between 1980 and 1989. It is estimated that about 520 tonnes of Hg was discharged to the watercourses in the same period (Silva et al., 1994). The primary gold deposit is associated with volcanic sequences of the Xingu Complex (Archean >2.5 By) while the secondary deposits are Pleistocenic (13,000 to 35,000 y) (DNPM, 1992).

Hydraulic monitors are the main mining method in the region. This method consists of a strong water jet produced by a group of water pumps, which is able to dislodge weathered ore. The hoses (10-15 cm) are operated by 4 to 6 men. The released material flows as a pulp to small pools where some manual classification takes place (some boulders are rejected) and then pumped to the concentration unit (sluices or centrifuges). The pulp density is visually controlled by a man who adjusts the pumping rate in order to send 50% of solids to the sluices. Water is not recycled and a production of 25 tonnes of solids per hour is usual. Very often tailings reach the watercourses. Numbers around 4000 mg/l of total solids in suspension (TSS) have been reported in drainages closely impacted by this type of mining operation. Mercury is sprinkled at the top of sluices or mixed with concentrates in pans. Sometimes "garimpeiros" introduce mercury in the pool which receives the ore pulp (Feijão and Pinto, 1992).

About 100,000 people are involved in "garimpo" activities in the Itaituba region and today there are about 250 airstrips in use and disused in the south of Itaituba (GEDEBAM, 1992). As the alluvial material is becoming exhausted, a few "garimpeiros" are now investing in the primary ore.

The HgEx system gives a bioaccumulation diagnosis based on the following data input extracted from (Farid et al., 1992, CETEM, 1993, GEDEBAM, 1992, DNPM, 1992) :

1) Size of the Mining Activity: *large region*

2) Method of Mining: *hydraulic monitor (predominantly) and raft.*

3) Portion of Ore Amalgamated: *both concentrate and whole ore*

4) Amalgamation Method: *blenders and manual panning*

5) Separation Amalgam-Mineral Portion: *panning in water boxes, pools and at creek margins*

6) Fate of Amalgamation Tailing: *discharged to watercourses, left in pools*

7) Gold Separation from Amalgam: *both retorts and burnt in pans*

8) Gold Melting Operation: *more than 30 gold dealers without any special fume hood*

DoB_{HEF} for the region = 100% (extremely high)

9) Sediment Background : *analyzed = 0.12 ppm*

10) Water Colour : *Rato River = dark water*

11) Biomass : *Rato River = moderate*

12) Water Conductivity : *Rato River = 10 µS/cm = low*

13) Hot Spots : *identified in Igarapé Fé em Deus(tributary of Rato River) = 2.5 ppm Hg = high*

14) Contaminated Sediment Type : *sand-silt, medium in organics, medium iron oxides*

15) Contaminated Sediment Hg Concentration : *0.2 ppm Hg (30 samples)*

16) Contaminated Sediment Highest Redox Potential : *0.24 V (with pH = 5.8)*

17) Water Transparency in the Main Stream : *muddy*

DoB_{DEF} = 94 % (very dangerous)

DoB_{MAF} = 20 % (slightly possible)

DoB_{PBR} = 100% (high)

18) Biota Samples : *average of 65 carnivorous fish = 0.44 ppm Hg*

DoB_{BE} = 76% (high)

7.5 - Port Douglas Site

The heuristic model was applied to a much different site located in British Columbia. A small R&D company located in Port Douglas, B.C., Canada was using a pilot plant to evaluate several placer gold deposits in the Lillooet River Delta. The operation began in 1990 with screening of gravels (2 mm) and amalgamation of the undersize material using a processing unit called an *Electrostatic Amalgamator*, marketed by an American company named Action Mining Services Ltd. This is a sophisticated amalgamation pot with an electrode in the Hg which *supposedly* improves fine gold particle attraction. All material is soaked in a proprietary solution containing potassium permanganate to reduce Hg surface tension. In the next step, the material passes through a 15 cm mercury layer and is discharged. Mercury oxidation definitely occurs in this apparatus and mercury droplets are dragged to the tailing as well.

This operation did not aim for profitable gold production but rather were conducting a deposit evaluation. It is my belief that these dangerous practices were done out of ignorance of the dangers of mercury rather than a careless attitude about the environment.

The High Emission Factor was adapted to the Canadian context giving an alpha-factor = 0.003, which means that small emission derives a high DoB_{HEF}. The events involved in the mining and amalgamation steps are listed below as well as the environmental variables analyzed in field trips to the site in 1991, 1992 and 1993.

1) Size of the Mining Activity: *small*

2) Method of Mining: *mill (in this case, screening)*

3) Portion of Ore Amalgamated: *whole (pre-screening of the ore is not strictly a concentrating method; only 30% mass was rejected)*

4) Amalgamation Method: *pots (Electrostatic Amalgamator)*

5) Separation Amalgam-Mineral Portion: *other concentrator (mechanical spirals)*

6) Fate of Amalgamation Tailing: *safely stored (in plastic barrels)*

7) Gold Separation from Amalgam: *acid (solution of* HNO_3 *30%, at 70°C, overnight)*

8) Gold Melting Operation: *question is not applicable because little gold was produced*

$$DoB_{HEF}\ (\text{pre-}\alpha_{HEF}) = 55\%\ (\text{high})$$

$$DoB_{HEF}\ (\text{post-}\alpha_{HEF}) = 100\%\ (\text{extremely high})$$

9) Sediment Background : *analyzed = 0.7 ppm*

10) Water Colour : *small creeks = dark water*

11) Biomass : *small creeks and Lillooet River = low*

12) Water Conductivity : *7 µS/cm = low*

13) Hot Spots : *identified in Port Douglas and Lillooet Delta, 5 ppm = high concentration*

14) Contaminated Sediment Type : *sand, rich in organics*

15) Contaminated Sediment Hg Concentration : *3 ppm Hg (15 samples)*

16) Contaminated Sediment Highest Redox Potential : *0.2 V (with pH = 7)*

17) Water Transparency in the Main Stream : *clear*

$$DoB_{DEF} = 94\ \%\ (\text{very dangerous})$$

$$DoB_{MAF} = 20\ \%\ (\text{slightly possible})$$

$$DoB_{PBR} = 100\%\ (\text{high})$$

18) Biota Samples : *not available*

$$DoB_{BE} = \text{not available}$$

7.6 - Discussion

7.6.1 - Emission Level

The resulting DoB_{HEF} for each of the three Amazon regions analyzed above, mirror the poor amalgamation practice conducted by most miners. When a region is analyzed, a variety of mining and amalgamation methods are considered. All these events combine to produce a prediction of "extremely high" emission for almost all of the mining regions in the Amazon. This is to be expected since the total emission rate in the Amazon is about 70 tonnes Hg/year. The DoB_{HEF} becomes more sensitive for site-specific analysis where the behaviour of a particular operation can be evaluated in detail and followed over time.

In Port Douglas, the DoB_{HEF} calculated for the site was 55% which means "*High*" for an Amazon situation. However when the DoB_{HEF} is raised to an alpha factor of 0.003 (calculated for British Columbia - see section 6.3.1) this changes the DoB_{HEF} to 100%, i.e. "*Extremely High*" emission, which is more appropriate. In spite of the experimental character of this operation, fortunately it was discontinued after one month of operation when the potential risk was pointed out to the owners. Other examples likely exist today considering the fact that there are a number of popular books, magazines and companies promoting mercury usage in North America for the small-time prospector. The "Gold Panner's Manual" (Basque, 1991) sold in Canada and the US, actually suggests a simple way of separating gold and mercury by "baking" amalgam in the cavity of a scooped potato. It is obvious that isolated examples exist but I believe they are not significant enough to consider that Hg pollution is rampant in North America... at least I hope not!

The sentences in the report are formed according to the Degree of Belief in events input by the user which generates different linguistic outputs. For example, if the user inputs a DoB in the observation that amalgam separation is or was performed at creek margins, then the following range of terms are used in the report :

DoB (user input)	Linguistic Output
90, 100	Amalgam separation is performed at creek margins.
50, 89.9	Amalgam separation is possibly performed at creek margins.
30, 49.9	Amalgam separation is suspected to be performed at creek margins.
10, 29.9	Amalgam separation at creek margins is inferred.
0, 9.9	Amalgam separation is not performed at creek margins.

The system does not use fixed pages to generate output. Instead, dynamic strings are obtained from rules depending on the amalgamation practice. The sentences in the report are composed to give information on how to improve amalgamation and consequently reduce emission. For example the following paragraph is found in the Poconé report:

"... Barrels are efficient for promoting mercury-gold contact in 1 or 2 hours. Gold recovery is higher than 90% when gold particles are exposed. Unliberated gold particles are not amalgamated. Mercury flouring can occur with amalgamation periods above 2 hours. The recommended Hg-concentrate ratio is about 1:100. Less than 1 kg of soda/tonne of concentrate cleans gold surfaces effectively and improves mercury contact... Manual amalgamation is ineffective for gold recovery. Mercury needs time to contact gold particles. Very fine gold particles usually are not amalgamated..."

Other paragraphs are composed dynamically to explain the environmental impact caused by poor amalgamation practices. In the Poconé report, the following alarms are generated :

"Amalgam separation performed at creek margins leads to hot spot formation. Separation in waterboxes is a relatively safe method to separate mercury and amalgam from the mineral portion of the ore. Operators who come into direct contact with mercury must use masks. ATTENTION: masks must be discarded daily! Amalgamation tailing is dumped in watercourse. Formation of hot spots is expected. A careful investigation must be carried out to locate these sites along the watercourses. When amalgamation tailing is recycled to gravity circuit, a portion of mercury is retained in gravity concentrators, but another portion is carried out to the tailing ponds being dispersed. Amalgamation tailing still contains gold values, a separate circuit to process tailing is recommended. Amalgamation tailing is left in pools. When miners leave a site,

these pools become hot spots. Plastic-lined pools are recommended. Clean-up procedures should be applied. This procedure means future field surveys do not have to search for these spots... It is possible (the DoB input by the user was 60%) that amalgam is burnt in pans. When Hg vapour is not condensed properly it can accumulate in the miner's blood. Levels of Hg in urine indicate the intoxication levels. Hg (vapour) can also be transported to other areas..."

Diagnostic about the presence of hot spots is also generated from strings obtained in rules. In the case of Poconé, no chemical analysis was done to identify hot spots. Instead a panning survey discovered many sites were highly polluted. The system gives the following paragraph :

"... Hg was identified visually in sediments from hot spots. We would expect Hg concentrations higher than 3 ppm... So, a remedial procedure has to be found. As a preliminary step, you should evaluate the size of each hot spot. By collecting and analyzing more samples, you will probably also find other highly contaminated sites...By analyzing local biota (e.g. snails) living close to these polluted sediments, a good picture about Hg bioavailability can be obtained... Among a number of factors, mercury incorporation in biota is a function of sediment and water characteristics... A small bioassay program is useful to establish which remedial procedure must be adopted or whether natural adsorption can control biota contamination..."

If hot spots were not identified, the system would indicate that there is a high possibility of their existence due to amalgam separation being conducted at creek margins or in pools.

"... Hot spots have not been observed but there are indications, that they should exist (e.g. the method by which amalgam is separated from the mineral portion of the ore)... There is a high possibility of hot spots because of the method of amalgam separation in use... Abandoned amalgamation sites can be identified by asking an old miner and by performing a quick field-survey using a pan. Mercury droplets will be concentrated and are visually observed in the pan.... Sediments with less than 1 ppm Hg are difficult to identify after panning. Sometimes a dash of soda in the pan will agglomerate Hg droplets facilitating visual identification ..."

7.6.2 - Bioaccumulation

The moderately-high risk of bioaccumulation in the Poconé environment shows that relatively dangerous conditions for methylation and bioaccumulation in Poconé have been controlled by the high capacity of the Hg adsorption of the ferruginous sediments. This fact matches with the bioaccumulation evidence, i.e. the biota is moderately contaminated. Monitoring programs are recommended by the system to follow this situation over time.

In contrast, the nature of the environment found in the Tapajós region (Alta Floresta and Itaituba) indicates that bioaccumulation is highly possible. Biota samples from Alta Floresta are not showing high Hg content yet. Only one carnivorous fish in 15 samples and 5 snails in 204 samples showed a Hg concentration higher than 0.5 ppm (Farid et al., 1992) (DoB_{BE} based on these data is considered moderate) and so the system strongly recommends monitoring programs and additional carnivorous fish analysis because DoB_{PBR} is high.

In Itaituba, the results of 65 samples of carnivorous fish based on data of CETEM (1993) and Silva et al. (1994) resulted in high DoB_{BE} which matches with the predicted bioaccumulation risk. The system explains why this conclusion is achieved and provides justification for each fact.

The conclusion of the system is generated with linguistic outputs based on DoB of each factor (HEF, DEF, MAF) used to calculate DoB_{PBR}. An example is seen below from the Poconé report :

"Mining activities are emitting extremely high mercury levels into the aquatic environment in
(DoB_{HEF} = 100%)
which natural conditions are relatively dangerous for methylation and bioaccumulation.
(DoB_{DEF} = 55%)
Mercury adsorption by sediments is definitely possible to control bioavailability. This situation
(DoB_{MAF} = 100%)
leads us to believe that the risk of increasing mercury levels in the biota is moderately high."
(DoB_{PBR} = 55%)

In the case of Port Douglas, the high DoB_{PBR} obtained is not only attributed to the pilot plant operation. The most important point found in the diagnostic is the relatively dangerous conditions for methylation and bioaccumulation. High Hg level in sediments, low conductivity, organic-rich environment, darkwaters, low biomass and the possibility of Hg-organic complex formation are strong pieces of evidence to believe that bioaccumulation is highly possible. The Hg left by pioneers in the 1860s is an additional reason to believe that not just Port Douglas should be monitored, but all of the region. Unfortunately, the B.C. and Canada authorities do not think in the same way. There could be potential "hot spot" problems for local First-Nation groups.

7.6.3 Remedial Procedures

The system recognized for the four areas studied above that mercury is both dispersed and concentrated in the sediments (hot spots). Dispersion is caused by one of the following facts:

- amalgam is burnt in pan
- the whole ore is amalgamated
- amalgamation tailing is dumped in watercourses (from rafts)
- amalgamation tailing is dumped in the tailing pond
- amalgamation tailing is recycled to primary gravity circuit
- amalgamation is performed in a continuous process

Remedial procedures are recommended for the areas analyzed. The paragraphs are formed dynamically based on information that gives evidence that Hg is being dispersed to the environment (e.g. burning amalgam in pans) or is forming "hot spots" (e.g. amalgamation tailing is left in pools) The following text is extracted from the reports :

"... Remedial procedures must deal primarily with the source of Hg dispersal. We suggest :
- retorts
- air filters for gold melting operations
Measures to minimize bioaccumulation of dispersed Hg must attempt to reduce the transport of Hg from the catchment area, to change the nutrient web, to increase the biomass (productivity) in order to obtain a dilution effect or to reduce the biological availability. Liming and selenium addition are the most promising methods, but are expensive and must be tested in a pilot area... Covering sediments with laterite crusts or sulphides are inexpensive procedures that should be tested in this case... Hot spots were identified and remedial procedures must deal with two decisions:

- Dredging or

- Covering

Removal operations are costly and the gold extracted from the hot spots can reduce these costs. A gold and mercury recovery plant must be planned to treat dredged spoil. In contrast, covering procedures involve low operational cost and little investment. In both cases monitoring programmes must be set up to follow up the pollution level after the remedial measure... Dredging operations are a definitive measure for highly polluted spots. Dredging has 3 main problems regarding environmental impact :

a) dispersal of Hg into the streams

b) covering of the dredged site

c) disposal of contaminated spoil

Treatment of dredge spoil is an essential procedure... "

A dredging operation is an expensive procedure and is recommended only when the gold content in the spoil can return part of the costs. Recently (June 1994) two samples of amalgamation tailing from Poconé were collected before being dumped in the watercourse. Chemical analyses showed 38 and 28 ppm Au and 27 and 3.5 ppm Hg respectively. This illustrate that it is common to find hot spots with high gold content. A separate processing plant to extract gold and mercury from tailing as well as from dredging material is an opportunity to be promoted among the "garimpeiros". As the extraction processes involves high technology by "garimpeiro" standards, organized companies can play an important role in this field.

In the Poconé report, an average of 7 ppm of Au was analyzed in hot spots (Farid et al. 1991) and mercury was inferred as 3 ppm (CETEM, 1989). The following string is seen in the report :

"... The gold content appears to be high in the hot spots. A removal operation followed by a gold and mercury extraction procedure seems to be an interesting alternative. Check the investment for a plant and determine the volume of gold rich material in the hot spots ..."

Evaluation of the material characteristics is important to decide which dredging procedure should be applied, since dispersion of the pollutant can occur during removal operation.

The principle of covering is based on the fact that Hg-polluted sediments are stable at the bottom of the aquatic system and eventual Hg oxidation can be controlled by adsorption which hinders the action of methylation agents. This process was used in Minamata Bay to control Me-Hg production in sediments (H.Akagi, Minamata Inst. - personal comm.). Laterite crust is suggested as a covering material due to its high content of iron oxides and abundance in the Amazon region.

A series of covering procedures for polluted sediments is suggested in the reports. Explanations about the process principles as well as references are provided. It is advised that all covering materials should be tested in the Amazon environment before being widely adopted. Some of these materials are seen below :

- Laterite crusts : natural and cheap raw materials.
- Sulphides : natural materials capable of precipitating Hg compounds.
- Scrap Iron (e.g. automobile bodies) : application is restricted to specific sites.
- Rubber scraps (e.g. old tires) : it is also restricted. The tires must be shredded.
- Fibers (e.g. old carpets) : this application must be reserved to dry hot spots.

7.7 - Toxicological Observations

As commented in Chapter 6, interviews with individuals may rationalize the need for biological sample analysis. An example of an interview with a miner is described as follows. This interview occurred in June 1994, in Poconé. Fish is an important part of diet of this 45 year old individual. This is an unusual situation for a "garimpeiro". This individual is also aware of the Hg side-effects and uses retorts constantly. The following data were input into the HgEx system :

1) Fish Consumption : *3 times per week*

2) Types of Fish Consumed Most :
- tambaqui (Colossoma macropomum - herbivorous)
- traira (Hoplias malabaricus - carnivorous)
- piranha (Serrasalmus sp - carnivorous)
- tucunaré (Cichla ocellaris - carnivorous)
- pacu (Mylossoma spp - herbivorous)

3) Fish Origin : *darkwaters*

4) Burning Mercury in Pans : *never*

5) Melt Gold in Cheap Fume Hoods : *never*

6) Handling Mercury : *daily*

7) Spillage or Accident with Mercury : *never*

8) Open Flask Storage : *never*

9) Smoking : *no*

10) Health Problems :

- *Depression*
- *Numbness of the extremities*
- *Visual Constriction*
- *Impairment of Hearing*

11) Health Problems Worsened since Exposure to Mercury : *yes*

12) Malaria : *no*

13) Alcohol Consumption : *rarely*

14) Mental Problem : *no*

15) Gasoline Handling : *infrequently*

16) Workclothes : *kept at home*

17) Place of Living : *in the mining site*

No biological samples (blood, urine and hair) were available at the time of the interview. The system diagnosis was as follows :

"... Inorganic Hg poisoning is unlikely (DoB = 33%). Evidence is not strong to recommend blood analysis, but if this facility is available, analysis may be useful .
... Methylmercury poisoning is possible (DoB = 67%). Hair samples are recommended."

All conclusions generated by the system are justified. The recommendations are based on events combination explained in section 6.3.4.

The inference equation (eq. 6.9) used to conclude about the need for blood or urine samples was :

$$DoB_{blood,\ urine} = 0.3\ DoB_{symptoms\ Hg} + 0.6\ DoB_{occupational\ exposure} + 0.1\ DoB_{life\ style}$$

The system concluded that *"... health problems related with exposure to metallic Hg vapours are unlikely ($DoB_{symptoms\ Hg}$ =13%)"*, because only depression was selected as a symptom.

As this individual handled Hg daily for 5 years, but never had spillages and never burnt amalgam in pans, then the system concluded :*"... the combination of these facts derives the conclusion that occupational exposure is possibly an issue in this case ($DoB_{occup.\ exposure}$ = 45%)."*

The life style factors are more important for non-workers. In this case the $DoB_{life\ style}$ of 20% was calculated based on fact that *"... the worker keeps workclothes at home and lives near garimpo derives the conclusion that indirect vapour sources are unlikely to be relevant."*

Hair analysis was suggested based on equation 6.11 :

$$DoB_{hair} = 0.4\ DoB_{symptoms\ Me\text{-}Hg} + 0.3\ DoB_{diet\ habits} + 0.3\ MAX\ (DoB_{PBR}, DoB_{BE})$$

As three typical symptoms of methylmercury poisoning were selected: numbness of the extremities, impairment of hearing and visual constriction, this generated a $DoB_{symptoms\ Me\text{-}Hg}$ of 80%, i.e. *"... symptoms related to Me-Hg poisoning are very likely."*

The $DoB_{diet\ habits}$ of 62% was calculated based on fact that this individual is *"... a high consumer of carnivorous fish from darkwaters..."*.

The DoB_{PBR} of 55% (which is higher than the DoB_{BE} = 30%) (see section 7.2) was used to generate the DoB_{hair} of 67% in the conclusion that hair analysis are recommended.

Unfortunately we do not know if this individual looked for a physician based on the system advice and certainly a physician in Poconé does not yet have the HgEx system to assist him to recommend hair analysis for this individual !

7.8 - Conclusion

The bioaccumulation levels predicted by the system for the three Amazon regions match with the bioaccumulation evidence provided by biota samples. Although biota samples only show moderate levels of Hg in Alta Floresta, the system predicts a high potential risk for biota contamination in this region (Table 7.1).

Table 7.1 - Predicted and evidenced bioaccumulation results

	Poconé	**Alta Floresta**	**Itaituba**	**Port Douglas**
DoB_{PBR}	moderate-high	high	high	high
DoB_{BE}	moderate	moderate	high	n.a.

The concept that mercury is a time-bomb in the Amazon (Lacerda and Salomons, 1991) must be confirmed and monitored. As the predicted bioaccumulation risk is strongly influenced by the high emission levels observed in the Amazon regions, information about active mining activities must be updated. The conservative approach adopted by the system (the DoB in potential bioaccumulation risk is higher than DoB bioaccumulation evidence) is important to alert users that constant monitoring programs are fundamental to follow critical situations as well as to accommodate diagnostics where mining activity has stopped and the amalgamation process is not well known.

8. System Evaluation

"The truth varies according to whether we deal with a fact of experience, a mathematical proposition, or a scientific theory"
Albert Einstein

8.1 - Evaluators' Profile

More than 30 copies of the HgEx system prototype were distributed to experts and potential users together with an evaluation questionnaire (Appendix XI). Only 15 questionnaires were received back and they comprise the evaluation shown as follows.

To indicate the background of the evaluators, they have been classified into the following categories :

by Expertise :

- 9 Potential Users
- 5 Experts in Hg pollution
- 1 Specialist in Expert Systems

by Main Field of Work/Study :

- 6 in Environmental Sciences
- 4 in Applied Science (Engineering)
- 2 in Medicine
- 1 in Gold Geology
- 1 in Animal Science (fishery)
- 1 in Education

by Education Level :

- 9 Ph.D. (4 students)
- 2 M.Sc. (1 student)
- 2 University Degree (1 student)
- 2 High School (1 student)

<u>by Workplace (Institution) :</u>

- 9 in Universities or Research Institutes
- 5 in Companies or Private Business
- 1 in High School (student)

<u>by Nationality :</u>

- 10 Brazilians
- 2 Canadians
- 1 German
- 1 Serbian
- 1 Mexican

<u>by Knowledge about Garimpos/Amalgamation</u>

- 8 have never been in "garimpo" but are aware about the process and Hg side-effects
- 4 have been in "garimpos" many times
- 2 have been in "garimpos" a few times
- 1 had no idea about the problem

8.2 - Answers about the Tutorial Part of the System

We investigated the Operation, Content and Clarity of the Tutorial part of the HgEx system. Many statements were shown to the evaluators (Appendix XI) and the answers were requested based on the following criteria :

(1) Disagree

(2) Mildly disagree

(3) Neutral

(4) Mildly agree

(5) Agree

Seven statements were used to evaluate the topic Operation, while Content and Clarity had eight and six statements respectively. The average of each topic was obtained from each questionnaire and the average of all evaluators is shown in Table 8.1 The questions were set up in such a way that the higher the score, the higher the acceptability of the Tutorial part by the evaluator. Further comments and suggestions were also provided.

Table 8.1 - Evaluation result of the Tutorial part of HgEx

Tutorial	Average	Range
Ease of Operation	4.7	4.1 - 5
Quality of the Content	4.4	3.4 - 5
Clarity of the Chapters	4.6	3.2 - 5

In General, the Tutorial part was well accepted by the evaluators who considered it a significant review about Hg problems and an important source of information and training for inexperienced people directly or indirectly involved with the problem. The lack of a quick way to access keywords was a point criticized that certainly will be considered.

The most appreciated parts of the Tutorial were:

- Sources and Use of Hg
- Hg Emissions
- Hg Bioaccumulation
- Hg Biogeochemical Cycle

The main criticisms of the Operation of the Tutorial were :

- connections between the General Index and Sub-indexes are not clear;
- more yellow key words (jump page) should be provided to improve flexibility;
- the way of starting the program is not clear (missing a big button).

One evaluator, a foreign specialist in Hg pollution disagreed, that the existing information in the Tutorial *is not easily available in common publications.* However, most Brazilians (experts and non-experts) agreed that specific information about mercury pollution from gold mining activities is usually dispersed and not easily available in Brazilian libraries.

The main criticisms received about Content were:

- number of topics should be expanded;
- information must be updated annually.

About the Clarity of the Tutorial part, in general, the evaluators agreed that the Tutorial is presented in a clear and understandable way. The main criticisms were :

- other versions of the ES in different languages (Portuguese, Spanish) would be useful;
- the terminology in some parts is not easy to understand;
- there are grammatical errors.

8.3 - Answers about the Diagnostic Part of the System

The process of evaluating the Diagnostic part was based on the same process used for the Tutorial. Three topics were rated: Operation (7 statements), Questions Asked by the System (6 statements) and Report (9 statements). All statements were also rated from 1 to 5 to express disagreement or agreement respectively. Averages for each topic were obtained and the general result derived from all questionnaires is shown in Table 8.2.

Table 8.2 - Evaluation result of the Diagnostic part of HgEx

Diagnostic	Average	Range
Ease of Operation	4.2	2.9 - 4.7
Relevance of the Questions Asked by the System	3.9	2.2 - 5
Usefulness of the Report	4.2	3.1 - 5

The Tutorial part was ranked higher than the Diagnostic part. The main criticisms about Operation of the Diagnostic part were :

- unskilled people need some training to operate the system;
- Uncertainty (how to input information) should be stressed.

In the question "*a monitoring program can be planned based on the structure of the Diagnostic section* ", one evaluator stressed "*this Expert System does not replace experts' observations to plan a monitoring program*". Lack of planning is a common practice in monitoring programs in Amazon, even ones performed by experts. This was a reason that we built this system; we believe an ES can help to build a plan, not to execute it !

About the Questions Asked by the System the main criticisms were :

- technical questions are not adequate for both technical and non-technical people;
- more questions about natural variables (e.g. microbiological aspects) should exist;
- the concept of alpha-factor should be highlighted.

One expert strongly criticized the alpha-factor concept, i.e. the adaptability of Hg emission levels based on reactions of a Society. According to this individual, "*pollution is not a relative problem that can be minimized or accepted by different Societies*". This is absolutely right. In theory, hazardous situations affect people indiscriminately, but History shows that unprivileged groups of a Society have suffered the effects of a low environmental concern of industrial activity more than the dominant class. Incidents with mercury in Minamata (1960s), Canada (1970s), Iraq (1956, 1960, 1972), Pakistan (1961), Guatemala (1963), USA (1969) (Malm, 1993) as well as from other pollutants in India, Russia and Latin American countries have shown that ignorance together with low political power of the affected people intensifies the extent of the tragedies. Brazil has excellent environmental laws but they are not enforced or even realized by the affected people. This work wishes to contribute to increase the knowledge of communities affected by Hg pollution in such a way that they may take the right posture against polluters. As well, the degree of pollution is variable from site to site when a problem is as widespread as Hg use by "garimpos". It is important to stop high pollution sources first and then address the low ones later. In North America, no Hg emissions of this kind are tolerated and so system adaptation is a necessity.

Another expert in Amazon commented on the alpha-factor usefulness as follows : "*I agree that Brazil has high tolerance for pollution and this mainly stems from lack of education about the subject. This is of course precisely why this system is urgently needed*".

About the Report generated by the system, the main criticisms were :

- output format could be improved;
- the report is more sensitive for single sites than for regions.

The Report was appreciated more by non-experts than by experts. One expert criticized that "*most Remedial Procedures suggested by the system are not feasible in the Amazon*". The main suggestions in the Report are based on use of simple retorts and air filters to reduce vapour emissions and the use of laterite or sulphides to cover "hot spots". Promotion of retorts for "garimpeiros" possibly is not an easy task for scientists, but likely is feasible for a non-expert in daily contact with these miners. The covering procedures have never been tested before in Amazon. As these are the main measures used in other countries, I believe that they should be tested in highly affected areas.

8.4 - Evaluation Conclusion

As the program was primarily designed for non-experts, it was expected that a better evaluation would be obtained from this group. However, no relationship between knowledge that the evaluators have about Hg pollution and "garimpos" and their evaluation was observed in both Tutorial and Diagnostic parts (Fig. 8.1). Other correlations were tried using education level, work/study field, nationality, age, etc., but no relationship with evaluation was found either.

As discussed in section 5.4, we believe that evaluation is a step performed by users and experts to check usefulness, acceptability and effectiveness of the system. The perception of these qualities in an ES varies with the type of evaluator and is clearly a subjective matter. The system was well accepted by both experts and non-experts. Most evaluators understood the targeted user as well as the objective of the system. All criticisms were (or will be) used to improve the system to reach its objectives.

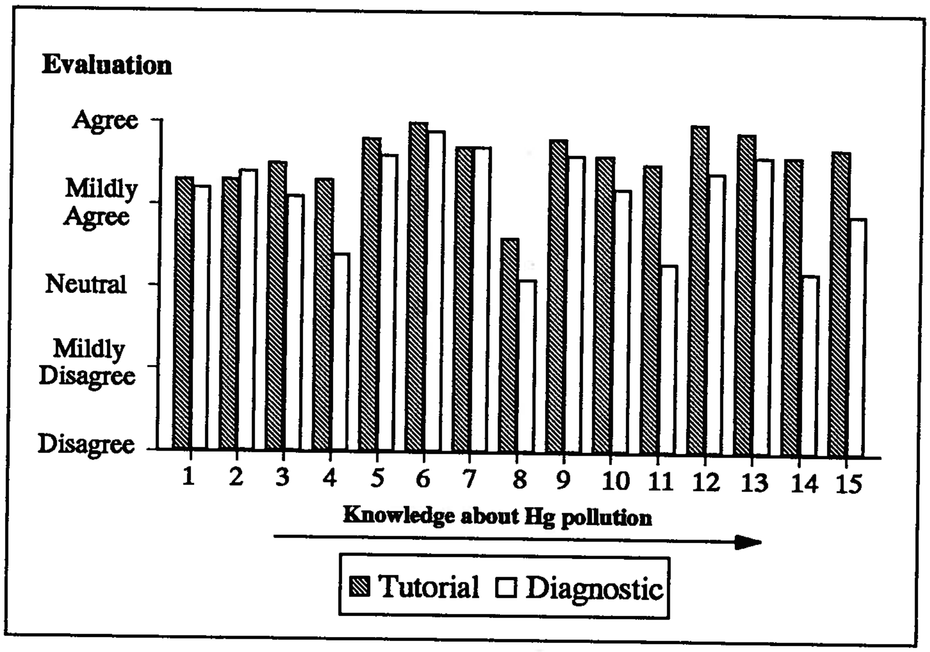


Fig. 8.1 - Evaluation result

The fact that most evaluators were known by the author and vice-versa can bring some bias to the evaluation. Only 3 evaluators (1 expert and 2 users) were unknown by the author. Their evaluations were positive about the system as seen in Fig. 8.1 (numbers 2, 6 and 15).

The evaluators ranked the potential users in the following way :

1. Health workers in mining regions
2. Environmental inspectors
3. Mining inspectors
4. Inexperienced technical people involved in environmental research

5. Experienced technical people involved in environmental research
6. Students
7. People from Environmental Groups
8. Engineers from mining companies
9. Skilled miners
10. Union Personnel
11. Social Assistance workers
12. Politicians (Mayor, Aldermen, etc.)

This list shows that most evaluators understood that the potential users are those directly involved with "garimpeiros", namely health workers and inspectors, who need training to carry out a preliminary risk assessment. A surprise in the list above is that experienced technical people ranked in 5th place. This suggests that there is something useful in the program even for experts. It is also clear for the list above that the evaluators think some skill is necessary to operate and understand the utility of the system.

In general the acceptability and usefulness of the program as a source of information for experienced and inexperienced people was the consensus. The Diagnostic part was recognized by most evaluators as a preliminary risk assessment tool as well as a way to document and follow emission levels from mining sites. The main benefits of the system listed by the evaluators are :

1. rapid and preliminary diagnosis of impacted area and toxicology;
2. rapid knowledge transfer;
3. quick and easy access to a comprehensive, interactive system dealing with Hg pollution;
4. portability and ease of updating information.

In spite of the program being developed in an intermediate technical language, the need for different versions for different user levels was stressed by many evaluators. The main point criticized was the fact that some training is required to operate the system. This is an important point but it is strange that this criticism came primarily from evaluators highly familiar with computers. Versions in other languages seem to be useful but not critical, since the main potential users indicated by evaluators have University level and can read English.

The physicians consulted agreed that the questions on "Toxicological Observation" are sufficient and relevant to provide a preliminary analysis of Hg poisoning and suggest biological samples to be taken. Initially the system mixed together symptoms of undue exposure to Hg vapours and methylmercury poisoning. Toxicologists and biologists such as Dr. H. Akagi (Institute of Minamata), Dr. O. Malm (Int. Biophysics of Rio de Janeiro) and Ms. A.A.P. Boischio (Univ. Indiana) suggested to break the symptoms into separate groups. The system was modified and now there is no connection between both types of symptoms.

Several suggestions to promote the system were listed by the evaluators :

- advertisements in technical journals, Conferences and newspapers;
- direct contact with Environmental Agencies and Groups;
- presentations in schools;
- use of computer media (e-mail)

Because the system is based on heuristic equations, maintenance and adaptability is very easy. Changes in inference approach are easy to do but need the presence of the knowledge base builder. Correction of grammatical errors and adding/deleting information are not difficult tasks to be performed by other individuals.

The edition of the system in other languages has been considered and discussed with environmental agencies in Brazil and international organizations to sponsor the job.

9. Conclusion

"The most important problem does not lie in understanding the laws of the objective world and thus being able to explain it, but in applying the knowledge of these laws actively to change the world"
Mao Tse-Tung

The main conclusions of this work are as follows :

1. Education is the focus of this work as one of the most important measures to help minimize mercury emission from gold mining operations in developing countries, particularly in Amazon. Any solution, preventive or remedial, should be aimed at providing better knowledge about mercury behaviour in the environment. As the issue is fraught with complex and vague concepts, this Expert System, HgEx, can play an important role in transferring heuristic knowledge to non-technical people interacting directly with miners. A multiplying effect is expected if these people become aware of the toxic effects of mercury, how to minimize emissions and how to diagnose potential bioaccumulation risk without the need for biological sample analysis.

2. The system can also assist health workers to decide if biological samples are necessary to yield a definitive clinical diagnosis about mercury poisoning caused by either undue vapour exposure or contaminated fish ingestion.

3. Weighted Inference Equations are a suitable technique to deal with heuristic knowledge to mimic Expert reasoning, conferring elasticity to the Degree of Belief calculated for conclusions. Weighted Inference Equations are easy to understand, adapt and reduce the need for large numbers of rules to represent all possible situations as well as allow the user to input vague data or uncertain field observations.

4. Fuzzy Logic is a useful technique to infer and transform field variables into Degrees of Belief in concepts to be handled in heuristic models which use linguistic terms that are more understandable by non-technical people than complex mathematical models. Rapid risk assessment can bring rapid decisions.

5. Hg emission levels are influenced by the power of a Society to react against polluters. This power stems from socio-political, economic and technical factors. HgEx can be used in different Societies and the linguistic output about mercury emission will be adapted to diagnose the social reality of a Society.

6. Case studies have shown that the system provides accurate predictions about bioaccumulation which match evidence provided by biota samples. The system advised constant monitoring programs and remedial procedures for the three regions studied in which the predicted risk had a Degree of Belief higher than that evidenced by biota samples.

7. The high values of Hg analyzed in organic sediments and bog waters from the Lillooet River Delta region, BC, together with other natural variables and the historical use of Hg in amalgamation practices of old miners suggests that the potential bioaccumulation in this region is high. In spite of the lack of biota sample analysis, monitoring programs were strongly recommended by the system.

8. Deforestation and cerrado (pasture) vegetation burnings in the Amazon have not been previously considered as an important source of Hg emission. About 75 tonnes of Hg were likely emitted to the atmosphere in 1988 due to burning of 50,000 km^2 of forest to create cattle pastures. Today, it is estimated that only 10% of the biomass burnt is due to deforestation and 90% is pasture burning to control pests and to restore nutrient levels in the

soil. This lead us to believe that about 70 tonnes of Hg is emitted annually from vegetation fires.

9. The system was well accepted by both Hg experts and non-experts. The Tutorial part was ranked higher than the Diagnostic part. A wide spectrum of potential users was indicated by evaluators: health workers, environmental and mining inspectors, inexperienced and experienced technical people involved in environmental research, students and people from environmental groups.

10. Experiments with metallic mercury and organic compounds have shown the possibility of Hg-complex formation under Eh-pH conditions commonly found in Amazon sediments. A new Eh-pH diagram was conceived to indicate Hg-complex formation in organic-rich environments. In spite of the variety of organic compounds found in nature, this diagram introduces a fuzzy concept that derives Degree of Belief in the possibility of complex formation when organic matter is an important component of the contaminated sediment. This brings an additional parameter to be used in monitoring programs to identify dangerous conditions for mercury transformations.

10. Claims to Original Research

"... Paul Bunyan picked up a handful of mud and threw it into the St. Lawrence River ... and thus was created the Thousand Islands"
from Canadian Folklore

I claim that the following contributions of this work are original :

1. A Heuristic System has been developed to assist many different people in their work with studying and alleviating the significant Hg pollution occurring in the Amazon today. This is the first comprehensive electronic document with information about mercury use and its consequences in gold mining activities and the first use of computer media to assist non-technical people to diagnose risk situations caused by mercury pollution.

2. This work contains an original approach to adapt the diagnosis of Hg emission levels based on socio-political, economic and technical factors predominant in a particular Society.

3. This is the first time that vegetation fires in the Amazon have been identified as a significant source of Hg emissions in amounts equal to or greater than that derived from "garimpeiro" activities.

4. This work contains the first data on Hg-organic complex formation derived from reaction of metallic mercury with natural organic acids.

11. Suggestions for Future Work

"Dibidi, dibidi, dibidi, dibidi, dibidi ... that's all folks !"
Porky Pig

The knowledge acquisition procedure to build this Expert System has involved a wide (sometimes dramatic) brainstorming process. Throughout this process, the author was exposed to different opinions and approaches which showed points in the knowledge base that could be improved with more knowledge.

This chapter lists suggestions for future work in the knowledge base of mercury pollution caused by gold mining activities as well as indicating procedures to improve the HgEx system.

The following points highlight suggestions for future research related to mercury emissions and transformations in the environment. These points can be useful to understand the future behaviour of Hg discharged by recent Brazilian and old Canadian "garimpos":

1. A better knowledge about the extent of Hg emitted by fires must be established distinguishing this source from "garimpo" contribution. Much of this Hg likely cycles around the systems, but a significant quantity must be moving into dangerous environments.

2. Many monitoring programs have indicated that Hg released from amalgam burning in open pans does not reach long distances. It is important to "quantify" which portion of Hg goes long distances. In this respect, CETEM (1993) has started to use bioindicators (a plant which absorbs atmospheric Hg), but laboratory and/or theoretical simulations probably can also give indications of the level dispersed to remote areas. Other obscure points which deserve further investigation are the oxidation rate of Hg vapour, effect of catalysts (e.g. fly ash) and thermodynamic conditions for oxidation of metallic Hg (the literature makes reference to Hg emitted from sources other than gold amalgams).

3. The study of metallic mercury complexation with organic acids should be expanded. Equilibrium constants can be obtained from reactions with acids of known chemical composition. Other components can be introduced in the laboratory experiments, for example iron in solution, sulphides, chloride, etc. Studies can be extrapolated to test the action of these organic acids on dental amalgams and the influence of diet on the transformation of Hg.

4. It is known that Hg is transported in aquatic systems by adsorption onto suspended particles. Desorption studies can bring more understanding about the stability of adsorbed Hg under different water conditions (e.g. pH changes, dissolved organic substances, salinity, other pollutants).

5. Covering procedures using laterite, sulphides or other absorbent materials must be tested in laboratory and field experiments.

The following points are suggested for investigation in future research related to Expert Systems, in particular HgEx :

1. A Neural Network structure could be used to adjust the weights in the weighted inference equations used in HgEx. The output could be compared with expert opinions.

2. Introduction of different user levels in the HgEx system which can determine user types by pollution knowledge or by different language understanding.

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APPENDIX I - Reactivity of Organic Acids with Metallic Mercury

TANNIC ACID

Purified reagent, $C_{14}H_{10}O_9$, Molecular Weight = 322 g. A 0.1 M solution was prepared with distilled water and distributed in 5 different transparent plastic vials with 30 ml of solution. Every vial received 5 ml of metallic mercury. The contact surface of metallic mercury with tannic solution was 7 cm^2. The solutions were agitated manually once per week to crudely simulate the natural conditions to which dumped Hg might be subjected. At the indicated date, an Eh reading was conducted using a calomel electrode attached to a salt bridge to avoid solution contamination during measurements. This operation lasted 3 min. and the solution was immediately siphoned, centrifuged and frozen for Hg analysis by ASL Ltd., Vancouver.

CEDAR

A piece of red cedar was obtained from the Wood Science Dept. - UBC (Dr. Simon Ellis). This timber had been logged one year prior to receipt. The timber was sawed and 3.5 grams of the powder generated was heated (60°C) for 30 min. with 200 ml of distilled water. The yellow solution was filtered and cooled before contact with 5 ml of Hg as described above.

FULVIC ACID

Purified fulvic acid was obtained from the Soil Science Dept. (Dr. Lawrence Lowe). He obtained this acid by extracting from an organic British soil using 0.2 M NaOH followed by acidification with HCl to pH 2 (this precipitates humic acid and leaves in solution the fulvic fraction). The solution was contacted with AMBERLITE XAD-8 resin to retain only fulvic acid. The elution was made with NaOH and frozen evaporation was conducted to obtain the fulvic acid in powder form. A solution was prepared with concentration of 10 g/l or 0.01 M assuming the Molecular Weight = 1000 g. The contact with Hg was similar to the tannic acid test.

TEA

A regular English tea (No Name brand) was prepared by dipping a single bag for 5 min. in about 150 ml of hot distilled water (85 °C). After cooling down, 30 ml of solution were contacted with 5 ml of Hg in different vials as described above.

SOIL

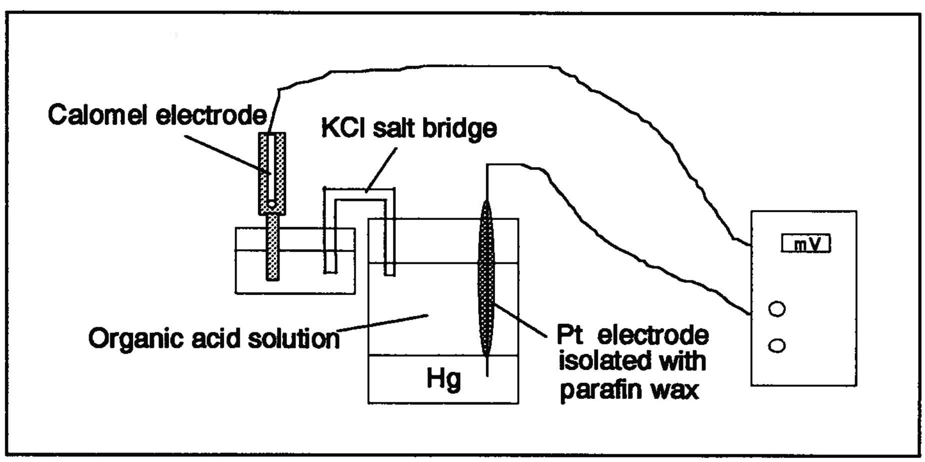
The organic soil was collected in the Acadia Park's forest (UBC campus) and 20 g was mixed with 70 ml of distilled water and heated for 2 hours. 35 ml of the pulp were contacted with 5 ml of Hg in different vials as described above.

Hg ANALYSIS (according to ASL) - Flameless Atomic Absorption Spectrometry.
Solution samples were oxidized with sulphuric acid, potassium permanganate and potassium persulphate in a hot water bath or microwave oven. Excess potassium permanganate was removed by addition of hydroxylamine hydrochloride. Hg^{2+} in solution was converted to elemental mercury by adding stannous chloride (reducing agent) :

$$Hg^{2+} + Sn^{2+} = Hg^{o} + Sn^{4+}$$

The elemental Hg vaporizes and is passed through a 30 cm gas cell via argon. A light beam with wavelength of 253.7 nm crosses the cell and mercury atoms absorb light. The absorbance is measured in a photocell and is transformed into concentration units.

DIAGRAM of the EXPERIMENTS



APPENDIX II - Hg Emission from Vegetation Fires

Forest fires may be expected to mobilize Hg contained in biomass and redistribute it into the atmosphere either as vapour or attached to particulates.

Fish from reservoirs in northern Manitoba showed high Hg levels. No man-made source of Hg could be precisely identified. The high Hg background of organic soils associated with impoundments stimulates biomethylation and subsequent incorporation of Me-Hg in the aquatic biota. Natural forest fires were also attributed as an additional source of mercury emission. The amount released annually to the atmosphere from natural fires in the boreal forest region of Manitoba was calculated at 20 g Hg/ha representing only 0.02% of the provincial annual emissions from natural sources which creates high short-term emissions in the form of a pulse. The evaluation assumed 0.4 ppm as the Hg concentration in timber, but about 0.08 ppm was considered lost during fires (Williamson, 1986).

Worldwide, wild forest fires are estimated as responsible for releasing 20 tonnes of Hg to the atmosphere, which comprise less than 1% of natural emissions (Nriagu, 1989). However, intentional wood combustion represents 60 to 300 tonnes of Hg (about 5% of all man-made emissions in 1983) (Nriagu and Pacyna, 1988). This estimate was based on a range of 0.1 to 0.5 ppm Hg in wood. Today with the very high rate of deforestation by fires in the Amazon, Hg emissions derived from wood combustion must be a more important source. Between 35,000 (1987) and 50,000 (1988) km^2 of the Amazon are estimated to be deforested per year becoming mostly cattle pasture, although other expansion reasons are also apparent (Fearnside, 1989; Terborgh, 1992).

Natural Hg levels in plants range from 0.001 to 0.1 ppm (dry weight). In forest ecosystems, this increases to 0.01 to 0.3 ppm (Pendias and Pendias, 1992), while crops grown in soils containing less than 0.04 ppm Hg vary from 0.004 to 0.09 ppm (Gracey and Stewart, 1974). Little is known about Hg distribution in the Amazon flora. Samples of macrophyte (*Potenderia lanceolata*) from uncontaminated areas around Brazilian "garimpos" show Hg levels of 0.10 ppm (Lacerda, 1991). Other aquatic macrophytes, *Victoria amazonica* and *Eichornia crassipes* collected at polluted sites in Madeira River "garimpos" show levels up to 1 ppm Hg (Martinelli et al., 1988).

A wide range of temperatures can be encountered in vegetation fires; between 650 and 1100°C are reported (Raison et al, 1985). At 200 - 300°C destructive distillation of up to 85% of organic substances occurs (Benscoter and Neuenschwander, 1989). Losses of trace metals during fires occurs through bonding with particulate matter (M. Feller, Dept. Forestry, UBC, personal comm.). Most mercury compounds are volatile at temperatures between 25 - 450°C, in which organic mercurials usually have lower boiling points than inorganic compounds. Mercury emission from fossil fuels is partly or fully in vapour form. In a coal fired power plant, it was observed that 92% of Hg was released in vapour form, 7% in particulate form and 1% was retained in the ash. When coal is burnt, loss of 90 - 99% of Hg is reported (Mukherjee, 1991; Kaiser and Tolg, 1980). In combustion plants 50% of mercury emitted is elemental and 50% in divalent form. This latter can be in gaseous form or bound to particles (Hall et al., 1991). When chloride is present in a combustion process, such as in waste incinerators, $HgCl_2$ is reported to be the predominant form emitted (Pacyna and Münch, 1991). This compound is stable at high temperatures, but HgO decomposes above 500 °C. In a combustion process HgO can be formed from gaseous mercury at temperatures between 300 and 500 °C, during the cooling process (Hall et al., 1990). HgO formation was observed by Hall et al. (1991) only in the presence of a catalyst (activated carbon). Obviously soot or ash particles could assist in this process.

Kaufman et al. (1992) estimated that the combustion efficiency average 91% and 97% in tropical deforestation and cerrado fires respectively. These authors analyzed about 1,000 ppm Hg in smoke particles smaller than 2.5 μm but the source of this metal was not identified. The use of Hg by "garimpos" was inferred by the authors as a possible source.

Considering that most mercury is present in wood in organic form, it seems reasonable to assume that about 90% of Hg is lost from above ground biomass (M. Feller - Dept. Forestry, UBC, personal comm.). It is also reasonable that, similar to other metals, the remaining portion of Hg becomes weakly bound to the ash after burning and is easily leached by runoff water.

Table A1 - Estimated Hg emissions from deforestation

Biomass	Average (t/ha)	Hg (ppm)	Hg release efficiency (%)	Hg released (g/ha)
Above ground wood	260	0.05	90	11.7
Above ground leaves	9	0.05	90	0.4
Above ground roots	20	0.05	90	0.9
Below ground roots	35	0.05	20	0.4
Fallen trunks	16	0.05	90	0.7
Humus	11	0.1	20	0.2
Soil organic matter	47	0.1	20	0.9
Total	398	0.06	67	15.2

We have calculated the amount of Hg emitted by deforestation from estimates of biomass distribution in the Amazon (Jordan, 1989). We assumed that the majority of the Hg compounds will be released from above ground biomass even without complete combustion, while only a minor amount is volatilised from organics in the soil surface. Our evaluation of the efficiency of

Hg release is shown in the Table A1. Using an estimate of Hg levels in plants and organic matter of 0.05 and 0.1 ppm respectively, about 15 g/ha (1.5 kg/km^2) of Hg are being emitted. Considering that 50,000 km^2 were burnt in 1988, 75 tonnes of Hg likely were emitted to the atmosphere that year.

The total area of forest lost until 1991 is estimated at 404,000 km^2 (Abril, 1993). So over 610 tonnes of Hg have been emitted into the atmosphere from this source. Applying a range of 0.1 to 0.5 ppm Hg in wood as claimed by Nriagu and Pacyna (1988), the Hg emitted from above ground wood alone would range from 950 to 4750 tonnes up to 1991.

Following deforestation of an area, the land is generally used for pasture. On a cycle between 2 to 7 years, the pastures are reburned in order to control pests and to restore adequate nutrient levels in the soil. Cerrado vegetation (mainly grasses and bush) takes up mercury from soil and deposition by rain. Today, it is estimated that only 10% of the biomass burnt is from deforestation (A. Seltzer, Brazil's National Inst. Space Research, personal comm.) and 90% is from cerrado burning. This mercury is also released upon burning and although the amount of biomass is much lower than the forest, the extent of burning is considerably higher. The above ground biomass of cerrado estimated by Setzer and Pereira (1991) is 43 tonnes/ha. Using the same relationship between above ground and below ground biomass in the Table A1, we calculated the cerrado biomass and Hg released by cerrado burning (Table A2).

Table A2 - Estimated Hg emissions from cerrado burning

Biomass	Average (t/ha)	Hg (ppm)	Hg release efficiency (%)	Hg released (g/ha)
Above ground vegetation	43	0.05	90	1.94
Roots	5	0.05	50	0.13
Humus	2	0.1	20	0.04
Soil organic matter	7	0.1	20	0.14
Total	57	0.06	68	2.25

Mercury is also released from soil organics and humus material following a forest fire because of organic decay. Release occurs in two ways - by volatilization and by surface water leaching. Rate of removal is considerably slower than from the initial release by burning. The rate of organic decay depends on many factors - climate, type of original soil, geology of the underlying rock, land use, weather, etc. The exact model is thus extremely uncertain and site-dependent.

Setzer and Pereira (1991) estimated that 200,000 km^2 were burnt in the Amazon (40% deforestation, 60% cerrado) in 1987. Using these numbers, we calculated the Hg released by deforestation (200,000 x 0.4 x 1.5 kg Hg/km^2 = 120 tonnes Hg) and Hg emitted by cerrado burning (200,000 x 0.6 x 0.225 kg Hg/km^2 = 27 tonnes Hg). This shows that Hg released by fires is substantially higher than Hg emitted by "garimpos" (about 70 to 100 tonnes/y).

Pacyna and Münch (1991) showed that more than 50% of Hg released from coal-fired boilers is in a water soluble form. No information was found about the Hg form in wood combustion gases but we assume that part of this mercury is in the elemental form and oxidized mercuric species may be formed during cooling. This represents an imminent danger since these forms of Hg can be easily transformed into methylated compounds in the waterways. Deforestation and cerrado burning has not been considered in monitoring programs in the Amazon, although some studies are examining transport of mercury by fly ash from forest burning in mining areas (Hacon, 1993). Mercury emissions from any source must be stopped and remedied but all significant villains must be recognized.

APPENDIX III - Alpha Factor Calculation

The alpha factor (or acceptance factor) is defined based on Economic, Technical and Socio-political factors which provide the driving forces in a Society to use or reject a potential polluting process. The Economic situations which promote "garimpos" and consequent amalgamation practice are :

1. recent examples of spectacular gold discoveries (or rushes) ($W_1 = 0.1$);
2. mining activity is important for the regional economy ($W_2 = 0.2$);
3. the region is experiencing difficult economic times and mining is seen as a feasible economic alternative ($W_3 = 0.2$);
4. minimum wage is low ($W_4 = 0.3$);
5. agriculture represents the main activity in the region, and the quest of land leads individuals to see mining as an alternative ($W_5 = 0.2$).

The Economic situations which increase resistance for gold mining and amalgamation are :

6. mercury price is high compared with the international market (U$ 8 to 10/kg/) ($W_6 = 0.3$);
7. mercury represents a high cost in the mining operation ($W_7 = 0.2$);
8. mining operations require expensive equipment ($W_8 = 0.2$);
9. inflation is low ($W_9 = 0.3$).

The Technical situations which promote "garimpos" and amalgamation are :

1. amalgamation is the first option considered by miners ($W_1 = 0.3$);
2. mercury is easily available for miners ($W_2 = 0.2$);
3. miners work gold placers, colluvium, laterite deposits and abandoned tailings which are usually neglected by companies due to low grade ($W_3 = 0.3$);
4. miners make frequent improvements in the amalgamation process to increase gold recovery and reduce mercury emission ($W_4 = 0.2$).

The Technical situations which increase resistance to gold mining and amalgamation are :

5. it is easy to introduce new gold extraction technologies ($W_5 = 0.1$);
6. miners are aware of side-effects of Hg ($W_6 = 0.2$);
7. miners have access to specialized technical support ($W_7 = 0.2$);
8. miners work ores in which gold recovery is low when amalgamation is used ($W_8 = 0.1$);
9. alternatives or solutions for Hg use have been investigated ($W_9 = 0.2$);
10. monitoring programs to survey the extent of Hg pollution are easy to set up ($W_{10} = 0.2$).

The Socio-political situations which promote acceptance of mercury use are :

1. mystique that gold mining is an easy way to become rich ($W_1 = 0.2$);
2. it is easy to evade laws which control Hg usage ($W_2 = 0.4$);
3. incentive (political importance of a region) for "garimpos" ($W_3 = 0.2$);
4. mining is a traditional occupation ($W_4 = 0.2$).

The Social characteristics of a society which increase resistance to mercury use are:

5. high education level ($W_5 = 0.3$);
6. frequent interaction of miners with other educated people ($W_6 = 0.1$);
7. political power of the groups affected by Hg pollution ($W_7 = 0.2$);
8. reliable media ($W_8 = 0.2$);
9. active ecological groups ($W_9 = 0.2$).

Economic, Technical and Socio-political factors are calculated by subtracting the resistance components from the acceptance ones. Fuzzy sets establish the level of these factors, i.e. the DoB in "low", "medium-low", "medium", "medium-high" and "high" (Fig. A1). Now these factors are combined in rules.

Ten rules are fired (Table A3), ten conclusions are obtained (DoB_r) and ten potential alpha-factor (α_r) values are obtained from their respective Fuzzy set (Fig. A1, A2, A3, A4, A5 and A6). The final alpha-factor is calculated through a defuzzification process expressed by the equation :

$$\alpha = \frac{\sum_{r=1}^{10} DoB_r \cdot \alpha_r}{\sum_{r=1}^{10} DoB_r}$$

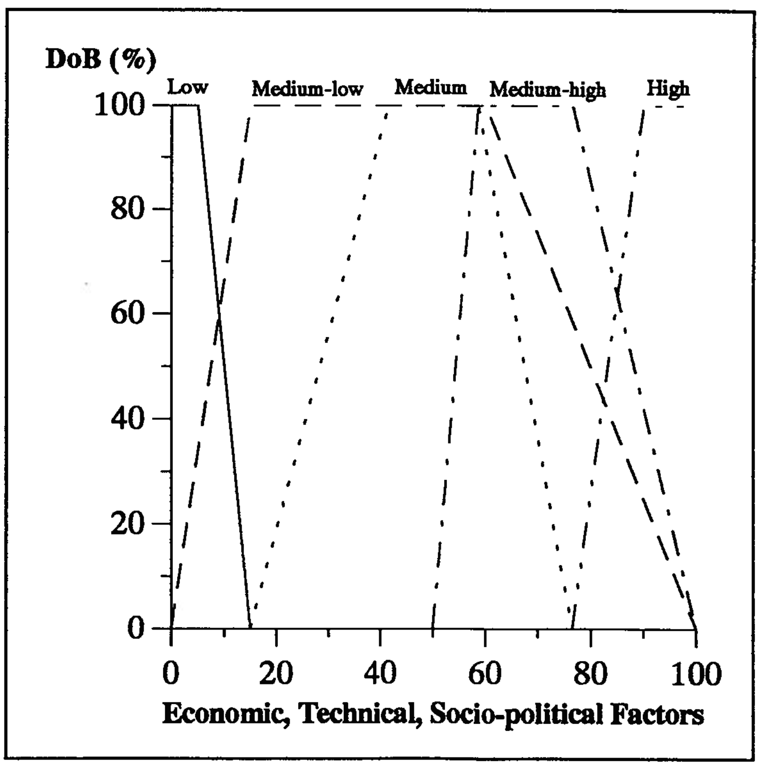


Fig. A1 - Definition of the level of Economic, Technical and Socio-political factors

Table A3 - Fuzzy rules to define alpha factor level

α	Economic	Technical	Socio-political
very low	low	low	high
low	medium	low	medium
low	low	medium	medium
low	low	low	medium-high
medium	medium-low	medium-low	medium-low
high	medium-high	low	low
high	low	medium-high	low
very high	medium	medium	low
very high	low	high	low
very high	high	low	low

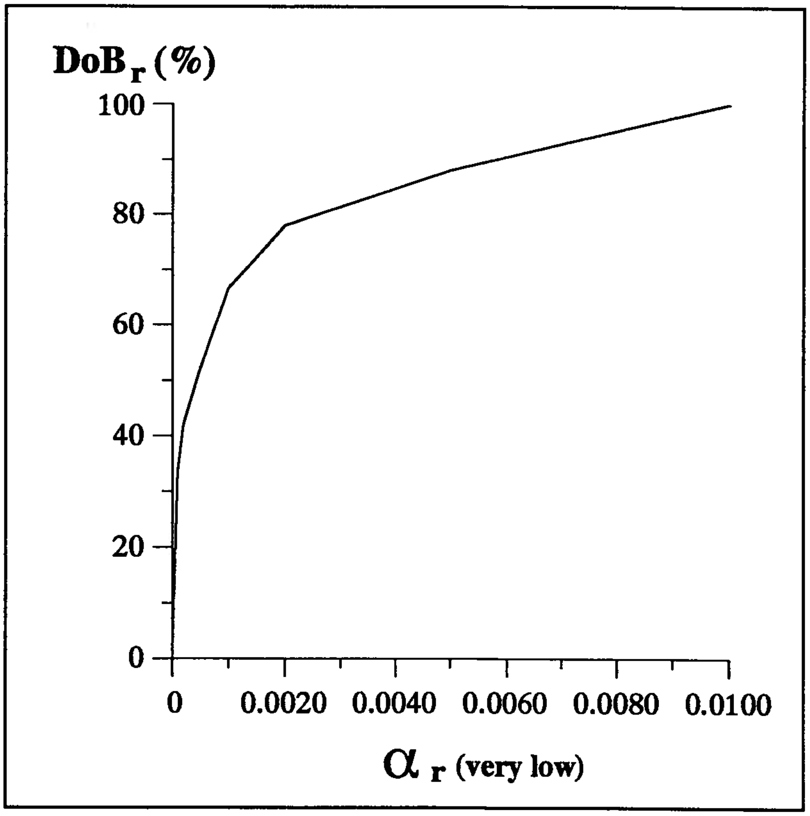


Fig. A2 - Fuzzy Set to define very low alpha factor

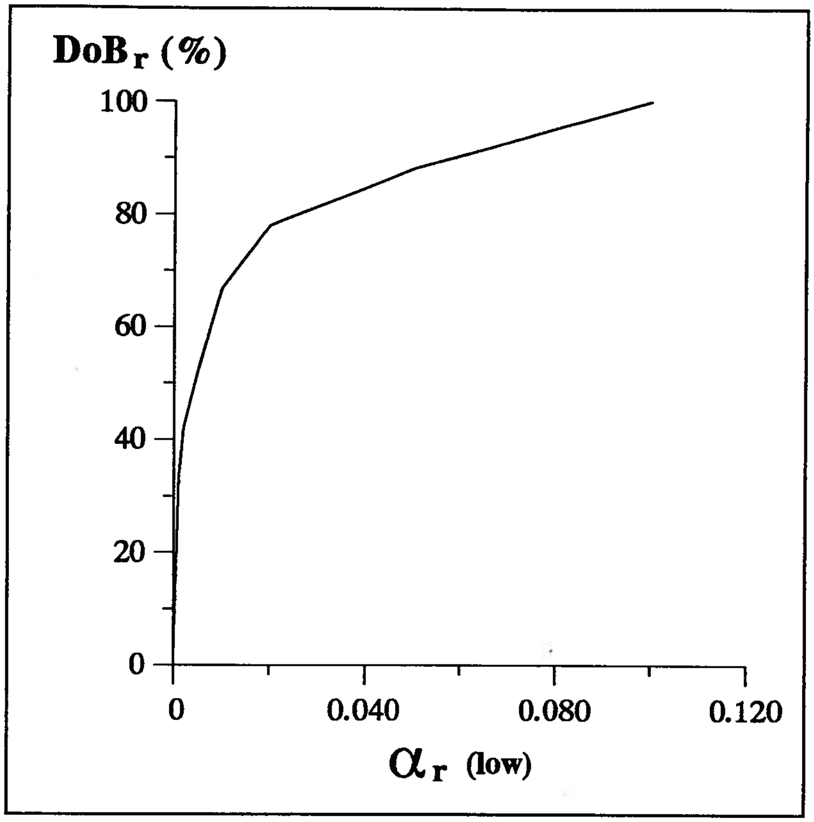


Fig. A3 - Fuzzy Set to define low alpha factor

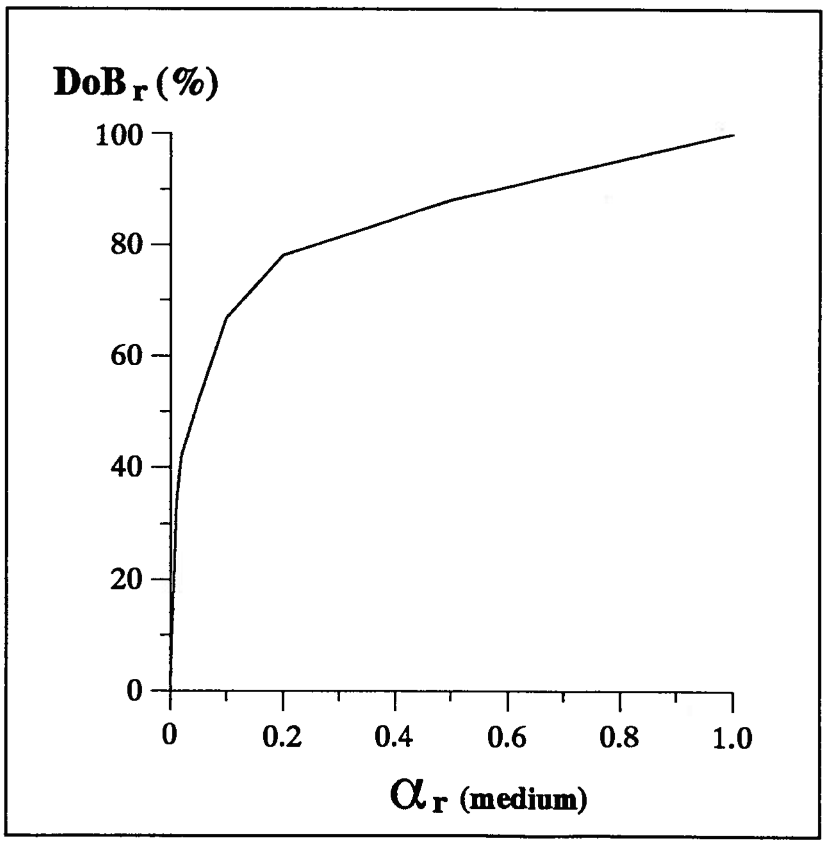


Fig. A4 - Fuzzy Set to define medium alpha factor

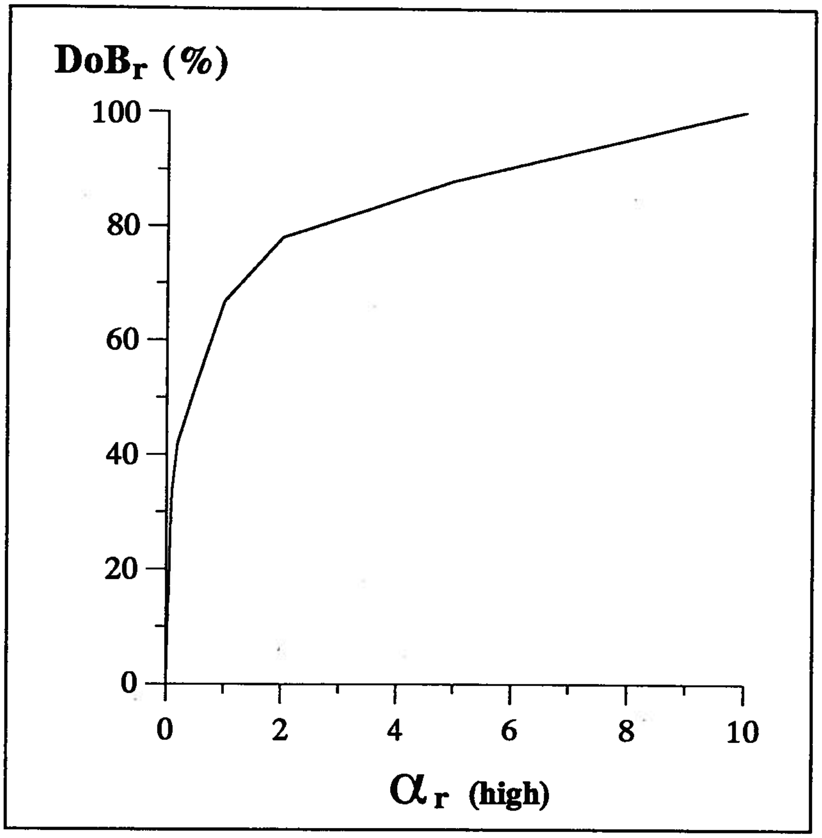


Fig. A5 - Fuzzy Set to define high alpha factor

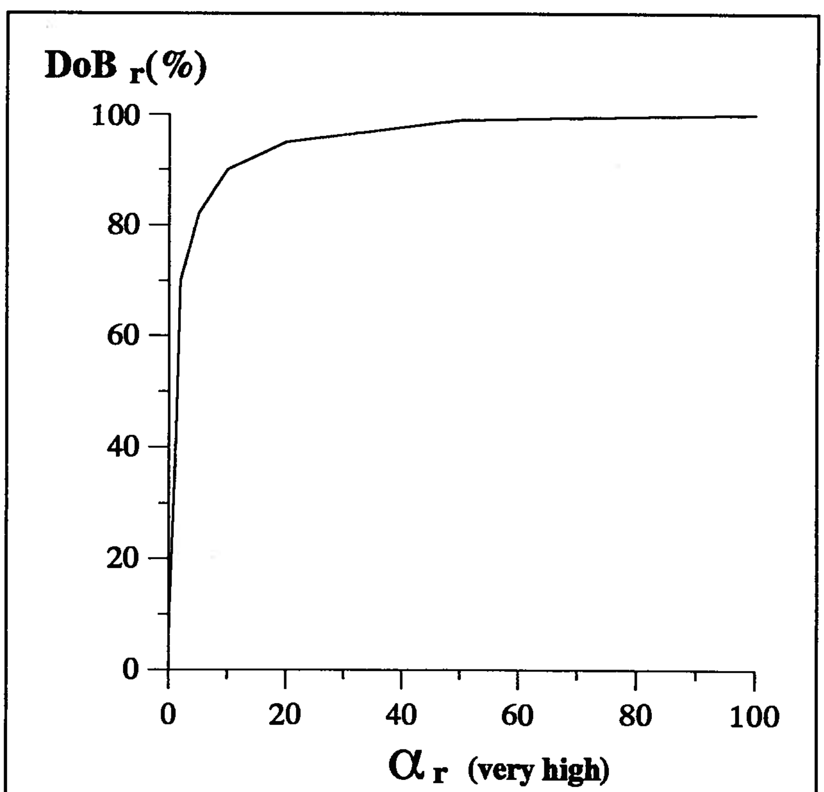


Fig. A6 - Fuzzy Set to define very high alpha factor

APPENDIX IV - Events influencing DoB in High Emission Factor.

$$DoB_{HEF} = MIN\ (100, \sum_{i=1}^{n} W_i . DoB_i)$$

Step	Event	Importance	Weight (W_i)
Mining size	Small	Medium-Low	0.05
	Medium	Medium	0.1
	Large	High	0.2
Method of mining	Mining with Dredge	Medium-Low	0.05
	Mining with Raft	Medium-Low	0.05
	Manual mining	Medium-Low	0.05
	Hydraulic mining	Medium	0.1
	Milling	Low	0
Portion of ore amalgamated	Concentrates	Low	0
	Whole ore	Medium-High	0.15
Method of amalgamation	Barrels or Mechanical Pans	Low	0
	Manual Panning	Low	0
	Pots, plates or sluices	Medium	0.1
	Blenders	Medium-Low	0.05
Separation Amalgam-Mineral Portion	Panning in water boxes	Low	0
	Panning in pools	Medium-Low	0.05
	Panning at creek margins	Medium-High	0.15
	Elutriator or other concentrator	Low	0
Fate of the Amalgamation Tailing	Discharged to tailing pond	High	0.2
	Discharged to watercourses	Very High	0.3
	Recycled to the plant	Medium-high	0.15
	Left in pools	Medium	0.1
	Safely stored	Low	0
	Sold for reprocessing	Low	0
Hg-Au Separation	Burnt in pans	Very High	0.3
	Burnt in retort	Low	0
	Dissolved in acid	High	0.2
Gold Melting Characteristics	Use of special air filter	Low	0
	No filter and small shop	Medium-Low	0.05
	No filter and medium shop	Medium	0.1
	No filter and large shop	Medium-High	0.15

APPENDIX V - Definition of Size of a Mining Activity:

- **Mining Region**

A mining region or province, as designated by Feijão and Pinto (1992), is a large area (km•) characterized by a gold deposit, with local geological characteristics and working conditions differing from other region. Serra Pelada, Itaituba, Poconé, Alta Floresta, are examples of mining regions. There are at least around 20 mining regions identified in the Amazon Region. Each region has many mining sites (e.g. in Gurupi region, 25 mining sites are identified) with different operations. A small gold mining region has a gold production lower than 200 kg/month, and a large mining region produces more than 500 kg/month as reported by USAGAL, a Union of Garimpeiros in the Amazon. The number of miners associated with these regions is variable and an average of 9 to 10 g gold/miner/month is observed. So, based on these numbers, a small region should have less than 20,000 miners and a large region more than 50,000. The gold production is a better parameter for defining the size of a mining region than the number of miners.

- **Single Mining Site or Operation**

In the Amazon region, 2,000 mining sites (or "garimpo" sites) are identified, according to Feijão and Pinto (1992). These sites are characterized as an agglomeration of miners working at the same ore deposit or mining operation, like a mining lease. They are usually known by funny names, such as "Garimpo do Molha Bêbado" (Wet Drunk "garimpo") or by the name of the owner, such as "Garimpo do Zé Bigode", "Garimpo do Marcinho", or still by the name of the site, e.g. "Garimpo da Cascalheira". In 13 mining regions reported by Feijão and Pinto (op.cit.), the number of miners divided by the number of mining sites result in a range from 200 to 1700 miners/point. Certainly some sites are bigger than others, but based on these numbers, it can be assumed that the average is around 1000 miners/point. This was used to define the threshold between a small and a medium mining operation (point). We defined a large operation as one with more than 3,000 workers. Gold production lower than 10 kg/month was defined as small and more than 30 kg of gold/month characterizes large operations. The user can also define a single site by the activities which use the same mining operation method in a region, such as raft, manual mining, hydraulic mining, mill, etc.

AREA	SIZE	Au Production (kg gold/month)	NUMBER of WORKERS
Region*	Small	<200	<20,000
	Medium	200 to 500	20,000 to 50,000
	Large	>500	>50,000
Single Site**	Small	<10	<1,000
	Medium	10 to 30	1,000 to 3,000
	Large	>30	>3,000

NOTE: * when more than one single operation is being evaluated.

** when only a single operation is considered.

APPENDIX VI - Case studies for DoB_{HEF} calculation

a) Madeira River region

This is located in the southwestern part of the Amazon region, in Rondonia State, close to the Bolivian border. It is an important Amazon River tributary and its watershed covers about 100 km•, all in Brazilian territory. Since 1975, miners ("garimpeiros") have exploited gold from the bottom sediments using dredges (nowadays around 2000) to produce between 1 and 1.5 tonnes/month of gold. Dredges pump the sediments to a riffled sluice box where the concentration takes place. Sometimes mercury is placed in the riffles or amalgamation is done in a separate water box. Many miners dump the content of these water boxes (amalgamation tailings) into the river. Amalgams are burned with or without retorts on board large dredges or rafts. Evaluation of the 1988 situation based on Malm, (1990); Pfeiffer and Lacerda, (1988).

1) Size of the Mining Activity: *large region*
2) Method of Mining: *dredges, rafts and hydraulic mining*
3) Portion of Ore Amalgamated: *both concentrate and whole ore*
4) Amalgamation Method: *manual panning, Hg in sluices and blenders*
5) Separation Amalgam-Mineral Portion: *panning in water boxes*
6) Fate of Amalgamation Tailing: *discharged to watercourses*
7) Gold Separation from Amalgam: *both retorts and burnt in pans*
8) Gold Melting Operation: *more than 30 gold dealers without any special fume hood*

DoB_{HEF} for the region = 100%

b) Madeira River - raft operations

Evaluation of an operation using rafts. Scuba-divers use suction dredges to exploit sandy and clayey sediments. The concentrate obtained in sluices or other equipment is amalgamated. Sometimes Hg is sprinkled on the top of sluices. Evaluation based on interview with José Alves da Silva ("garimpeiro" leader) in 1989 and data from Pfeiffer et al. (1989).

1) Size of the Mining Activity: *large single site mining (> 30kg Au/month)*
2) Method of Mining: *rafts*
3) Portion of Ore Amalgamated: *concentrates and whole ore*
4) Amalgamation Method: *manual panning, Hg in sluices and blenders*
5) Separation Amalgam-Mineral Portion: *panning in water boxes*
6) Fate of Amalgamation Tailing: *discharged to watercourses*
7) Gold Separation from Amalgam: *retorts and burnt in pans*
8) Gold Melting Operation: *not applicable (gold is sold in to dealers)*

DoB_{HEF} for the operation type = 100%

c) Rato River - hydraulic mining operations

Rato River is a tributary of the Tapajós River. The number of "garimpeiros" is estimated around 1500. Hydraulic mining is the main mining process at the site. Data from CETEM (1993).

1) Size of the Mining Activity: *medium site*

2) Method of Mining: *monitors (predominantly)*

3) Portion of Ore Amalgamated: *concentrates and whole ore*

4) Amalgamation Method: *manual panning*

5) Separation Amalgam-Mineral Portion: *panning in pools and at creek margins*

6) Fate of Amalgamation Tailing: *discharged to watercourses, left in pools*

7) Gold Separation from Amalgam: *burnt in pans*

8) Gold Melting Operation: *not applicable (gold is sold to dealers)*

DoB_{HEF} for the operation type = 100%

d) Poconé - Fazenda Salinas operation - single site

This is a well organized operation working since 1988 with 12 centrifuges (32 tonnes/h each) and the concentrates are amalgamated in a sort of trommel. Visited in 1991 and 1994, this evaluation based on field visit in 1994.

1) Size of the Mining Activity: *large single site*

2) Method of Mining: *mill*

3) Portion of Ore Amalgamated: *concentrates*

4) Amalgamation Method: *barrels*

5) Separation Amalgam-Mineral Portion: *panning in pools*

6) Fate of Amalgamation Tailing: *left in pools, recycling to mill*

7) Gold Separation from Amalgam: *retorts*

8) Gold Melting Operation: *melted at the mining site (large amount) as well as sold to dealers*

DoB_{HEF} for the single site = 65%

e) Poconé - J.Pinheiro operation

This is another typical operation in Poconé. The main difference between this operation and the one above is the mining size. This is a small operation and emissions could be reduced if tailing was not recycled. Data obtained from author's visit in 1989 and CETEM (1989).

1) Size of the Mining Activity: *small single site*

2) Method of Mining: *mill*

3) Portion of Ore Amalgamated: *concentrates*

4) Amalgamation Method: *barrels*

5) Separation Amalgam-Mineral Portion: *panning in water box and in pools*

6) Fate of Amalgamation Tailing: *tailing is recycled*

7) Gold Separation from Amalgam: *retorts*

8) Gold Melting Operation: *melted at mining site (small) or sold to dealers in Poconé.*

DoB_{HEF} for the single site = 40%

f) Teles Pires River - raft operations

Teles Pires is a Tapajós tributary in the State of Mato Grosso. About 1 kg of gold is monthly produced by about 1000 miners working on rafts. Evaluation is based on the situation in 1991 published by CETEM (1991b) and Farid et al. (1992).

1) Size of the Mining Activity: *small operation*

2) Method of Mining: *rafts*

3) Portion of Ore Amalgamated: *both concentrate and whole ore*

4) Amalgamation Method: *Hg in sluices and blenders*

5) Separation Amalgam-Mineral Portion: *panning in water boxes*

6) Fate of Amalgamation Tailing: *discharged to watercourses*

7) Gold Separation from Amalgam: *both retorts and burnt in pans*

8) Gold Melting Operation: *not applicable (gold is sold to dealers)*

DoB_{HEF} for the operation type = 100%

g) Serra Pelada - single site

Serra Pelada is located between Xingu and Tocantins rivers. High grade material was exploited from 1980-90 and conveyed manually to the treatment plants. Nuggets are a common feature of this deposit, but Hg is employed to recover fine gold. The water in the big open pit bottom hinders further ore exploitation but around 1 t of gold/year has been produced since 1988 from the gravity tailings, worked by 15,000 men. Serra Pelada experienced different type of miners and amalgamation methods. A single mining operation, visited in 1985 was evaluated as follows:

1) Size of the Mining Activity: *medium single site*

2) Method of Mining: *mill*

3) Portion of Ore Amalgamated: *concentrates*

4) Amalgamation Method: *manual panning*

5) Separation Amalgam-Mineral Portion: *panning in water boxes*

6) Fate of Amalgamation Tailing: *safely stored in water boxes*

7) Gold Separation from Amalgam: *both retorts and burnt in pans*

8) Gold Melting Operation: *melting in the mining site (large operation without special fume hood)*

DoB_{HEF} for the single site = 40%

h) Roraima - manual mining operation

"Garimpos" located in the western part of Roraima State have existed since 1940. Invasion of 25,000 "garimpeiros" to the Yanomami lands in 1988 called attention of the international institutions to the problem. In spite of the existence of some operations using hydraulic monitors, manual mining using pickaxes, shovels, sluices, pans and other rudimentary tools is the main method employed in this region. The data input in the system are based on Feijão and Pinto (1992) and related only to the manual operation in the region. Most "garimpeiros" were expelled from Yanomami territory in 1991. Recently, there are rumors that "garimpeiros" are returning to the First Nation territories. This evaluation is related to the 1991 situation.

1) Size of the Mining Activity: *large*

2) Method of Mining: *manual*

3) Portion of Ore Amalgamated: *both concentrates and whole ore*

4) Amalgamation Method: *manual panning*

5) Separation Amalgam-Mineral Portion: *panning in water boxes, pools and at creek margins*

6) Fate of Amalgamation Tailing: *discharged to watercourses and left in pools*

7) Gold Separation from Amalgam: *burnt in pans*

8) Gold Melting Operation: *not applicable (gold is sold to dealers)*

DoB_{HEF} for the operation type = 100%

APPENDIX VII - Events influencing DoB in Dangerous Environmental Factors

$$DoB_{DEF} = MIN\ (100, \sum_{i=1}^{n} W_i . DoB_i)$$

Variable	Level	Danger	Effect	Weight
Water Colour	Dark*	High	More Hg observed in fish	0.2
	Clear	Low	No effect observed	0
Water Conductivity	High	Low	Difficult to cross gills (Me-Hg)	0
	Medium	Medium	Medium difficult to cross gills	0.1
	Low	Medium-High	Easy to cross gills	0.15
Sediment pH	Acidic	High	More bioaccumulation	0.2
	Neutral	Low	No effect	0
	Alkaline	Low	Formation of dimethyl (volatile)	0
	Very alkaline	Very Low	Formation of dimethyl (volatile)	0
Redox Potential	Complexation	High	Hg organics complex formation	0.2
	Complexation	Medium-High	Hg inorganic complex formation	0.15
	Complexation Inferred	Medium	Hg-organic complex formation is inferred based on sediment colour	0.1
Biomass	High	Low	High dilution effect	0
	Medium	Medium	Medium dilution effect	0.1
	Low	High	Low dilution effect	0.2
Hg in Hot Spots	High or visible	High	More Hg to be methylated	0.2
	Medium	Medium	Medium Hg to be methylated	0.1
	Low	Medium-Low	Medium-low Hg to be methylated	0.05
Sediment Contamination Factor (C/B)	Very High	Very High	Extremely contaminated	0.3
	High	High	Highly contaminated	0.2
	Moderate	Medium	Moderately contaminated	0.1
	Low	Low	Slightly contaminated	0
Hg Desorption	Likely**	High	Hg can be released from sediment	0.2
	Unlikely	Low	Hg is attached to sediment	0

NOTE: * The DoB in water colour is input by the user, creating a gradation between the higher and lower level
** Determined by proximity of seawater

APPENDIX VIII - Calculation of DoB in Hg-complex formation

The boundary lines of the Eh-pH diagrams (Fig 3.2 and 3.3) represent equilibrium between two mercury species - Hg^{o} (aq) and Hg-complex. This situation indicates a DoB of 100% that complex formation is relevant. We have considered that complex concentration is not relevant when the concentration of the Hg complex is 1000 times lower than the Hg°(aq) concentration (see Fig. 3.3). Based on equations 3.5 and 3.6, the DoB in importance of complexation is obtained from the following equation :

When organics are considered (based on contaminated sediment colour) :
MAX (MIN (100, 1.1 Eh + 99.84 pH - 738.7), MIN (100, 1.099 Eh + 60.44 pH - 564.83))

When the user enters the Eh and pH of contaminated sediments, this situation in the Eh-pH diagram is recognized by the equations above and a linguistic term is generated. For example in Port Douglas the highest Eh of contaminated organic-rich sediments was 200 mV with a corresponding pH of 7. This gives a DoB in complexation = 100%. The output generated by the system is the following linguistic expression :
"The Eh and pH conditions favour the stability of Hg in solution as organic complexes."

When organics are considered in the sediments and Eh and pH are known, the following rule is fired to give the linguistic output seen above:
IF pH and redox potential are known (user input pH and Eh values)
AND organic matter is relevant in sediments (user indicated that sediment colour is dark grey)
AND complexation is relevant (DoB determined by equation above > 50)
THEN linguistic term is "*The Eh and pH conditions favour the stability of Hg in solution as organic complexes.*"

When organic matter is not an important component of the sediment the DoB in Hg oxidation is established by the following equation:
MAX (MIN (100, 1.25 Eh - 525), MIN (100, 3.33 Eh + 196.66 pH - 2703.314))

As most freshwater environments in the Amazon have chloride concentrations between 2 and 3 ppm (pCl around 4) (Furch, 1984), $Hg(OH)_2$ and $HgCl_2$ are the predominant inorganic species depending on the pH. The full lines of Fig. A7 represent the equilibrium of Hg° (aq) and $HgCl_2^{\circ}$ (aq) and $Hg(OH)_2^{\circ}$ (aq) respectively. The dotted lines in Fig. A7 represent conditions in which concentration of uncharged species ($HgCl_2^{\circ}$ or $Hg(OH)_2^{\circ}$) are 1000 times lower than the Hg^{o} (aq) concentration, i.e. in this case the importance of these complexes in the formation of Me-Hg is considered insignificant.

A similar rule as above is consulted to obtain linguistic output when organics are not relevant components in the sediment. In this case the system recognizes that if a high redox potential and a pH below 6 are measured in interstitial waters, this should favour $HgCl_2$ (aq) formation and at pH above 6, $Hg(OH)_2$ (aq) would be the predominant soluble specie.

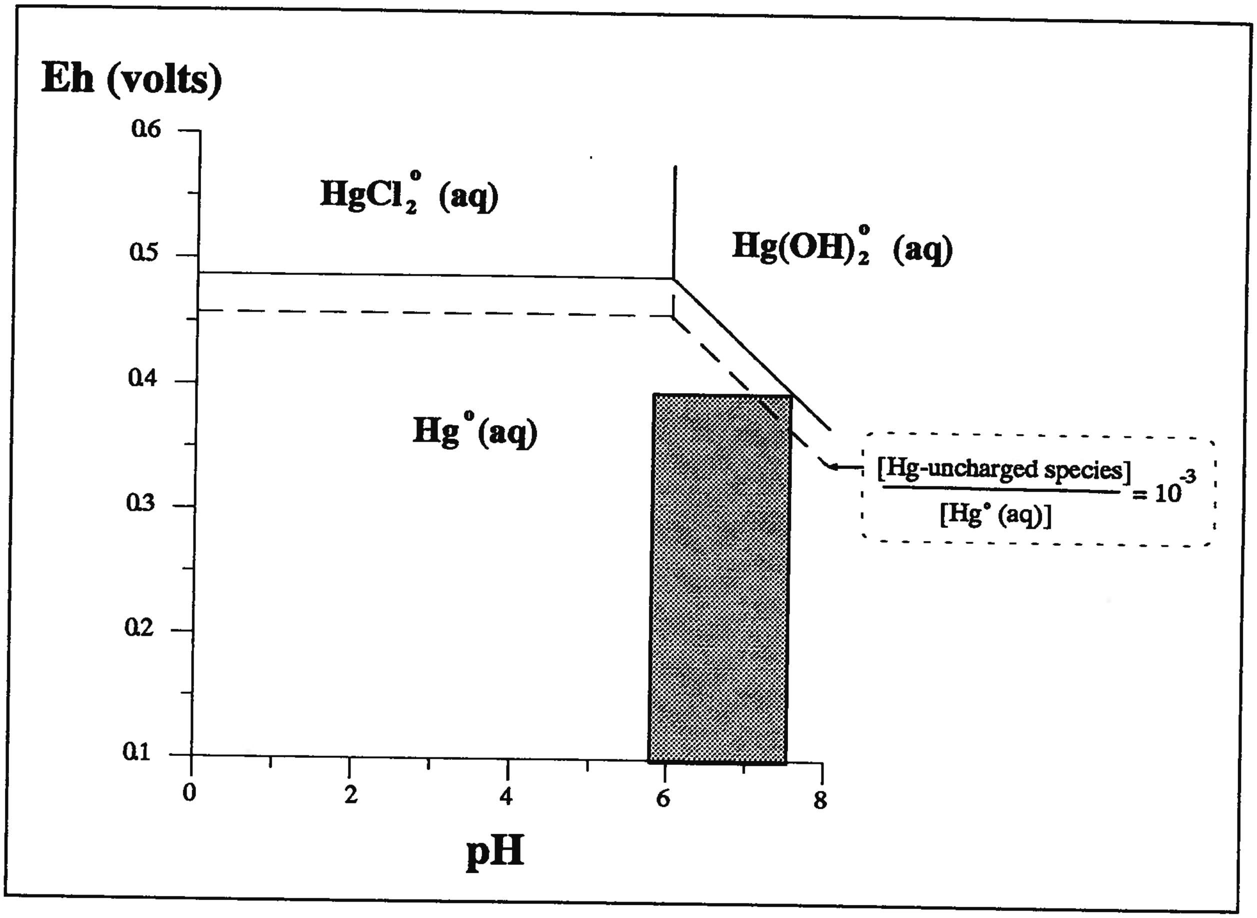


Fig. A7 - Equilibrium boundaries of Hg°(aq) and Hg-inorganic complexes
▒ : results from Poconé after Silva et al. (1991)

APPENDIX IX - Events influencing DoB in Mercury Adsorption Factors

$$DoB_{MAF} = MIN\ (100, \sum_{i=1}^{n} W_i . DoB_i)$$

Variable	Level	Benefit	Effect	Weight
Hydrous Ferric Oxides	Maroon	Extremely High	Strong adsorption	0.5
	Orange	High	Fair adsorption	0.2
	Yellow	Low	Weak adsorption	0
Sediment Grain Size	Clay	Very High	Fair adsorption	0.3
	Silt	Medium	Medium adsorption	0.1
	Sand	Low	Low adsorption	0
	Gravel	None	No adsorption	0
Water Transparency	Muddy	High	High adsorption	0.2
	Cloudy	Medium	Medium adsorption	0.1
	Clear	Low	No adsorption	0

APPENDIX X - Events influencing DoB in Health Factors

Events Influencing Diet Issues

Events	Level	Importance	Weights
Fish Consumption	Daily	Very High	0.3
	2 to 3 times/week	High	0.2
	Once a week	Medium	0.1
	Occasionally	Medium-Low	0.05
	Rarely	Low	0
Fish Type	Carnivorous	High	0.2
	Omnivorous	Medium	0.1
	Detritivorous	Medium-low	0.05
	Herbivorous	Low	0
Fish Origin	Dark water*	High	0.2
	Clear water	Low	0
Hg in fish	High**	High	0.2
	Low	Low	0

NOTE: * The DoB in water colour is input by the user, creating a gradation between the higher and lower level
** Determined by chemical analysis and a Fuzzy set.

Events Influencing the Degree of Belief in Inorganic Hg Poisoning Symptoms

Symptoms	Importance	Weights
Muscular tremors	Extremely High	0.5
Gingivitis	High	0.2
Excessive salivation	High	0.2
Metallic taste	High	0.2
Irritability	Medium-High	0.15
Depression	Medium	0.1
Kidney problem	Medium	0.1

Events Influencing the Degree of Belief in Me-Hg Poisoning Symptoms

Symptoms	Importance	Weights
Visual Constriction	Very High	0.3
Numbness	Very High	0.3
Impairment of Gait	Very High	0.3
Impairment of Speech	High	0.2
Impairment of Hearing	High	0.2

Events Influencing the Degree of Belief in Poisoning Symptoms Masking Factors
(These factors reduce the DoB in symptoms related to mercurialism)

Event	Level	Importance	Weight
Recent Malaria	Yes	Very High	0.3
	No	No effect	0
Alcohol	Daily	Very High	0.3
	Sometimes	Medium	0.1
	Rarely or none	No-effect	0
Mental Problem	Yes	Extremely High	0.5
	No	No effect	0
Handling Kerosene or Gasoline	Daily	High	0.2
	Occasionally	Medium	0.1
	Rarely or Never	No effect	0

Events Influencing the Degree of Belief in Occupational Exposure

Event	Level	Danger	Weight
Burning Amalgam in Pans	Daily	Extremely High	0.7
	2 or 3 days/week	Extremely High	0.5
	Occasionally	Very High	0.3
	Rarely	High	0.2
	Never	No effect	0
Melting Gold*	Daily	Extremely High	0.5
	2 or 3 days/week	Very High	0.3
	Occasionally	High	0.2
	Rarely	Medium	0.1
	Never	No effect	0
Years in this Activity	Many	High	0.3
	Some	Medium-High	0.15
	Few	Medium-Low	0.05
	Never	No effect	0
Hg Handling (Pouring)	Daily	Medium-high	0.15
	2 or 3 days/week	Medium	0.1
	Occasionally	Medium-Low	0.05
	None	No effect	0
Accident with Hg	Yes	Medium-High	0.15
	No	No effect	0
Storage in Open Flask	Yes	Medium High	0.15
	No	No effect	0
Smoking	Lots	Medium	0.1
	Moderate	Medium-Low	0.05
	Rarely or none	No effect	0

NOTE : * The DoB is multiplied by DoB in use of inadequate fume hood

Factors Influencing the Degree of Belief in Life Style

Event	Level	Importance	Weight
Work Clothes in Home *	If the worker burns amalgam in pans	Extremely High to Medium	0.4 to 0.1
	If the worker melts gold in cheap hoods	Very High to Medium	0.3 to 0.1
Hg Accident at Home	Yes	Extremely High	0.3
	No	No effect	0
Storage in Open Flask at Home	Yes	Extremely High	0.3
	No	No Effect	0
Place of Living	Near gold shop	Very High	0.3
	Near garimpo	High	0.2

NOTE : * The DoB depends on how frequently the worker burns amalgam in pans or melts gold

APPENDIX XI - Expert System Evaluation Questionnaire

INDIVIDUAL DATA

- Name: ....
- Institution: ....

- Your main field of work/study is:
 ( ) biology; ( ) geochemistry; ( ) mining; ( ) health; ( ) environmental science
 ( ) others ....

- Your highest education level is:
 ( ) Ph.D.; ( ) M.Sc.; ( ) University degree; ( ) Technical; ( ) High School; ( ) Elementary

- Have you ever visited a gold mining operation employing amalgamation ?
 ( ) Yes, many times.; ( ) Yes, a few times.; ( ) No, but I'm aware about the process and the side-effects of mercury .; ( ) No, I have no idea at all.

- Please list your computer characteristics:
( ) 286, ( ) 386, 25 MHz, ( ) 386, 33 MHz, ( ) 486, 25 MHz or better,
Memory RAM : .... MBytes

- Did you encounter any system instability problem ? (It failed/ crashed?)

- Do you feel that the system ran slowly on your machine ?

- The following questions should be rated according to the following range :
 (1) Disagree
 (2) Mildly disagree
 (3) Neutral
 (4) Mildly agree
 (5) Agree

TUTORIAL

Operation

1. It is easy and convenient to operate in the Hypertext environment.
2. The Instructions to operate the Hypertext are satisfactory.
3. It is easy to follow the connections/linkages available in the Tutorial
4. The number of connections (yellow key words) are adequate in linking topics as well as providing flexibility while reading.
5. The General Index and sub-indexes are easy to understand.
6. The white key-words are sufficient to provide definitions and further explanations.
7. The green keys work satisfactorily and are useful to display Tables and Figures.

Content

1. The number of topics are sufficient.
2. Information discussed in the Tutorial is objective and not biased.
3. Most significant issues related to Hg Problems in Gold Mining Operations were discussed.
4. The information provided in the Tutorial is not easily available in common publications.
5. Reviewing information on Hg-pollution and presenting it in a user friendly way is a major contribution of this tool.
6. There are several topics that were a useful learning experience for me.
7. It would be useful to update the information in the Tutorial annually.
8. The Tutorial will serve as an important source of information and training for inexperienced people directly or indirectly involved with the problem.

Clarity

1. The terminology is easy to understand.
2. Chapters' division is clear.
3. Size and colour of letters in the text as well as tables and diagrams are satisfactory.
4. In spite of the vagaries of the issue, the subject is presented in a clear way. No ambiguity was observed.
5. The language is easy to follow.
6. It would be useful to have versions of this Expert System in different languages.

Comments and Suggestions:

DIAGNOSIS

Operation

1. It is easy to answer the questions.
2. The Help buttons provide a useful explanation on why certain data are requested.
3. It is easy to understand how Users can input UNCERTAINTY for each answer.
4. A monitoring programme (to be followed in the field) can be planned based on the structure of the Diagnostic section.
5. Links between pages are easy to achieve and follow.
6. Links between Report and Questions are clear and easy to check and/or recheck your Inputs.
7. Unskilled people can operate the system without any special training.

Questions asked by the System

1. Data requested by the MINING & AMALGAMATION CHARACTERISTICS questions are sufficient and relevant to identify mercury emission level.
2. Data requested by the AQUATIC SYSTEM VARIABLES questions are sufficient and relevant to identify a potential risk for mercury bioaccumulation.
3. Question related to ALPHA FACTOR are sufficient and relevant to identify the "tolerance" level for pollution in a given Society.
4. The meaning of ALPHA FACTOR is easy to comprehend
5. The technical level of the questions is adequate for both technical and non-technical people.
6. The Questions on TOXICOLOGICAL OBSERVATION are sufficient and relevant to provide a preliminary analysis of Hg poisoning and suggest biological samples to be taken.

Report

1. The output format of the Report is satisfactory
2. The Report provides a satisfactory diagnosis of Mercury Emission levels.
3. In spite of the vagaries about the relationship between Aquatic Variables and Bioaccumulation, the Report provides a satisfactory first analysis of critical situations.
4. The Report gives a satisfactory picture of the various ways by which mercury poisoning may have occurred.
5. Suggestions about which biological samples should be collected are relevant.
6. The Degree of Belief for each Conclusion is a heuristic factor (subjective) but is useful to elucidate the Expert's opinion.
7. The REMEDIAL PROCEDURES recommended in the Report are clear and feasible.
8. The Report may be used for monitoring purposes, to follow up in mining regions and operations.
9. No conflict was observed in the logic used to report the recommendations.

Suggestions and Criticisms :

USERS & BENEFITS

- Who do you think are the potential users of this system ? (Please use numbers to rank users)

( ) Environmental inspectors
( ) Mining inspectors
( ) Health workers in mining regions
( ) Experienced technical people involved in environmental research
( ) Inexperienced technical people involved in environmental research
( ) Social Assistance workers
( ) Skilled miners
( ) Union Personnel
( ) Politicians (Mayor, Aldermen, etc.)
( ) People from Environmental Groups
( ) Students
( ) Engineers from mining companies
( ) Others, please describe these :

- What are the main benefits of using this system ? Please list them.

- If you feel that the performance or capability of the system could be enhanced by including some additional features, please mention them :

- Do you think this expert system is a useful product for training individuals/groups who frequently encounter mercury-related problems ? If yes, what would be your approach to promote this system such that it could be widely used ?

APPENDIX XII - Steps to calculate Hg°(aq)/organic complexes equilibrium

Based on the work of Lövgren and Sjöberg (1989), the reaction of mercuric chloride with organics (bog waters) $HgCl_2 + H_2L = 2H^+ + 2Cl^- + HgL$, derives equation A1 (same as eq. 3.3):

$$\beta_1 = \frac{[H^+]^2[Cl^-]^2[HgL]}{[HgCl_2][H_2L]} = 10^{-10.84} \text{ ......(A1)}$$

The free energy (ΔG_1^o) of this equation is calculated by:

$$\Delta G_1^o = 2G^o_{Cl^-} + G^o_{HgL} + 2G^o_{H^+} - G^o_{HgCl_2} - G^o_{H_2L} = -RT\ln\beta_1 \text{ ......(A2)}$$

and $G^o_{H^+} = 0$, at 25 °C

Consequently:

$$G^o_{HgL} - G^o_{H_2L} = G^o_{HgCl_2} - 2G^o_{Cl^-} - RT\ln\beta_1 \text{ ......(A3)}$$

Considering the equilibrium Hg°(aq)/HgL, the following reaction applies:

$$HgL + 2H^+ + 2e^- = Hg^o_{(aq)} + H_2L$$

The free energy is calculated for this reaction:

$$\Delta G_2^o = G^o_{H_2L} - G^o_{HgL} + G^o_{Hg(aq)} + 2G^o_{H^+} \text{ ......(A4)}$$

Substituting A3 into A4, $\Delta G_2^o = -11.396 \times 10^4$ J

So, the standard redox potential is calculated as:

$$E_2^o = -\frac{\Delta G_2^o}{2F} = \frac{11.396 \times 10^4}{2 \times 96{,}500} = +0.591\text{V} \text{ ......(A5)}$$

Now the Nernst Equation can be obtained (same as eq. 3.5):

$$E_{HgL/Hg^o_{aq}} = 0.591 + 0.0296\log\frac{[HgL]}{[Hg^o_{aq}][H_2L]} - 0.0591\,\text{pH} \text{ ......(A6)}$$

The other reaction considered by Lövgren and Sjöberg (1989) assumed a second mercuric organic complex: $HgCl_2 + H_2L = 3H^+ + 2Cl^- + Hg(H_{-1}L)^-$. The equation A7 (same as eq. 3.4) is derived:

$$\beta_2 = \frac{[H^+]^3[Cl^-]^2[Hg(H_{-1}L)^-]}{[HgCl_2][H_2L]} = 10^{-15.24} \text{ ......(A7)}$$

The free energy (ΔG_3^o) of this equation is calculated by:

$$\Delta G_3^o = 2G^o_{Cl^-} + G^o_{Hg(H_{-1}L)^-} + 3G^o_{H^+} - G^o_{HgCl_2} - G^o_{H_2L} = -RT\ln\beta_2 \text{ ......(A8)}$$

Considering the equilibrium $Hg^o(aq)/Hg(H_{-1}L)^-$, the following reaction is derived:

$$Hg(H_{-1}L)^- + 3H^+ + 2e^- = Hg^o_{(aq)} + H_2L$$

The free energy calculated for this reaction is:

$$\Delta G^o_4 = G^o_{H_2L} - G^o_{Hg(H_{-1}L)^-} + G^o_{Hg(aq)} \text{ ....(A9)}$$

Substituting A8 into A9, ΔG^o_4 = - 13.907 x 10^4 J and $E^o_4 = +0.721V$

The Nernst Equation is then as follows (same as eq. 3.6):

$$E_{Hg(H_{-1}L)^-/Hg^o_{aq}} = 0.721 + 0.0296 \log \frac{[Hg(H_{-1}L)^-]}{[Hg^o_{aq}][H_2L]} - 0.0887\ pH \text{ .... (A10)}$$

The vertical lines separating the regions in the Eh/pH diagram (Fig. 3.3) correspond to the reaction: $HgL = Hg(H_{-1}L)^- + H^+$ which derives equation A11:

$$\beta_3 = \frac{[H^+][Hg(H_{-1}L)^-]}{[HgL]} = 10^{-4.4} \text{ ....(A11)}$$

when $[HgL] = [Hg(H_{-1}L)^-]$, then $[H^+] = \beta_3$, i.e. at pH >4.4, $[Hg(H_{-1}L)^-]$ is the dominant species.

All equations used to derive the Eh-pH diagram (Fig. 3.3) for Hg-organic complexes assumed the reaction of organic acids with aqueous Hg^o, i.e. a Hg species in solution. This implies that mercury droplets dumped with amalgamation tailing and mercury vapour precipitated from fumes emitted when amalgam is burning in pans go into solution as $Hg^o(aq)$ which then reacts with organic acids and oxygen in the water column. However, we can also considered that metallic mercury may react directly with organic acids. In this case the following reaction takes place:

$$HgL + 2H^+ + 2e^- = Hg^o(l) + H_2L$$

The Nernst equation derived for this reaction is:

$$E_{HgL/Hg^o_{(l)}} = 0.783 + 0.0296 \log \frac{[HgL]}{[H_2L]} - 0.0591\ pH \text{ ....(A12)}$$

Regarding the experiments using organic acids described in Appendix I, when 0.1M tannic acid solution contacted metallic Hg for 2400 hours, 10 ppm of Hg was analyzed in the solution (Table

3.1). Considering that all mercury in solution is in a complex form ([HgL]=[Hg in solution]), so 10 ppm represents a concentration of $5x10^{-5}M$, when $[H_2L]=0.1M$. Substituting these values into equation A12, the redox potential obtained for the equilibrium HgL/Hg°(l) is 0.519 V at pH=2.8. The value analyzed (Table 3.2) was 0.49 V, which is in good agreement with the theoretical value.

A similar calculation for the fulvic acid data show 0.385 V measured (at pH 4) versus 0.42 V calculate which is also in good agreement.

Considering that we are dealing with many different oraganic species, it is indeed remarkable that such close correlation between experimental results and thermodynamic theory has been obtained.