

Technical report:

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## **SUMMARY**

The present report describes the results of the work achieved during the review of mercury and cyanide in the Artisanal gold Mining.

Ecuador is one of the countries experiencing tremendous development in the gold mining industry and artisanal mining makes up one of its most important sectors. Hence, this report addresses the use of mercury and cyanide in artisanal mining in Ecuador as a case study, by looking at several topics of interest that will advance our understanding of the problem and assist in finding possible routes to improve the situation in the artisanal sector. This report is presented in three different stages: first is an examination of the historical issues surrounding artisanal gold mining in Ecuador; second, an investigation of the current techniques used for gold recovery In artisanal gold mining, looking at its impact both on the ecosystem and on human health; and finally, and most importantly, in an attempt to find solutions, we will examine the issues of participatory development, policy and policy-making, and governance of the artisanal mining industry.

## **The Artisanal Gold Mining: Case study of mercury and cyanide in Ecuador**

### **Introduction**

Due the increasing price of gold, small scale artisanal mining interests have been expanding their activities around the world. However, the growth of mining during the last decade has been accompanied by conflicts among mining operators, companies, communities, and other land users. Mining conflicts have been related to land use, discharges of high suspended solids into rivers, the use of mercury, and, recently, the misuse of cyanide.

This report evaluates the current process of gold recovery in artisanal gold mining in Ecuador and the environmental problems related to the use of cyanide to leach Hg-contaminated tailings. Miners take their gold ore to be ground, concentrated, and amalgamated in one of the 66 Processing Centres in the region of Portovelo-Zaruma. Miners either rent the Centres or pay with the tailings left in the Centre. At one of these centres, the Au-rich tailings are then leached with cyanide. There are 10,000 artisanal, small-scale miners (ASM) in the region using amalgamation and cyanidation to produce around 2 tonnes/ year. Miners concentrate gold using Chilean mills followed by a process involving carpeted sluice boxes. In the process of amalgamating concentrates, miners use either pans (manual) or drums with black sugar to clean the mercury surface. The amalgam typically contains 60% mercury and 40% gold, which is an example of the inefficiency of the squeezing process. The ratio of  $Hg_{lost}:Au$  produced is around 1.5, as artisanal miners do not use retorts to burn the amalgam. All tailings with cyanide and mercury are disposed into the nearby streams. The most evident problems in

artisanal mining areas are the lack of retorts and poor mercury management. Using the LUMEX atomic absorption spectrophotometer, we analyzed the breath of several workers and found that the mercury levels in the air exhaled by the miners increased from 147.3 (sd 6.4) ng/m<sup>3</sup> (before burning) to 1,513 (sd 480.1) ng/m<sup>3</sup> (after). The higher mercury concentration in the surrounding air reached 193, or 800 ng/m<sup>3</sup>.

The interaction of mercury and cyanide is a complex issue and its complexity becomes greater when these substances interact with other elements along the rivers and watersheds. Hence, it is an issue that must be resolved through education, consensus, participation, dialogue, and policy. The approach to these remedies must be tailored to the characteristics of each country, region, and community.

While Mercury has been used since antiquity, mining operations in several countries have made a transition into cyanidation, with the use of cyanide in the leaching process to recover gold. This change in technology has had damaging impact on the social, economical, technical, environmental, and political lives of both the mining and ordinary communities in each country and needs an intervention to reduce the negative effects at both the local and regional levels. Hence, the key to successful mining operations that contribute significantly to job creation and economic advancement is “sustainable development”, which can only be accomplished through a strengthening of social, environmental, and community responsibility for the ecosystem at both the local and large industry level.

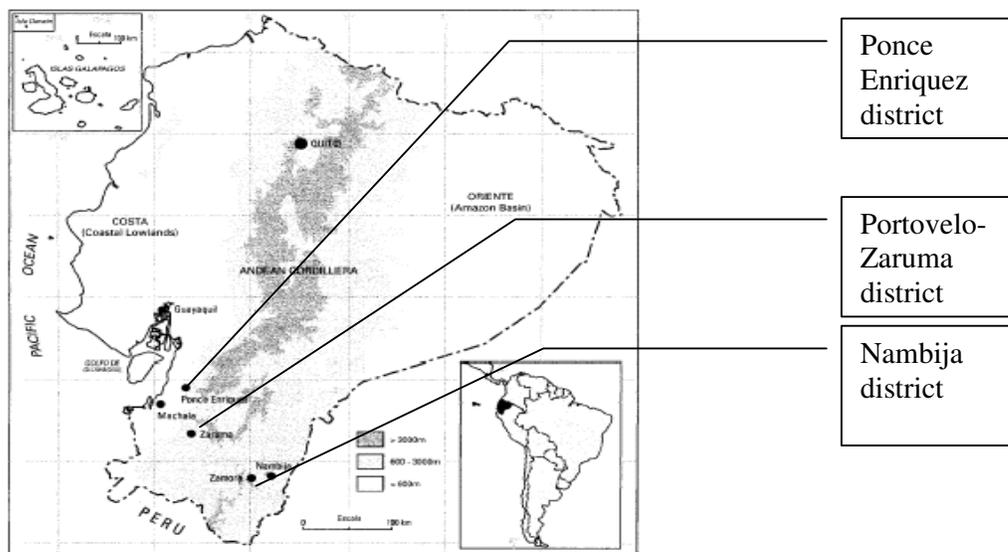
## Historical issues regarding Gold Mining in Ecuador

Ecuador settled on three important scenarios (Fig 1) from which to develop actions to seek generation of improved environmental policy and decision making within the artisanal gold mining context:

**Scenario 1.** Location: *Ponce Enriquez*. This area is located in a coastal basin that hosts four industrial activities of enormous importance for Ecuador: mining, agriculture, aquaculture, and marine fisheries. Pollution from these industrial sectors has had an impact on the river basin of Rio Siete, with Mercury and cyanide as the main pollutants that are creating intense conflicts in the areas of concern.

**Scenario 2.** Location *Zaruma-Portovelo*. This is the main Mining district, which, despite having been studied before, has failed to generate an effective policy for resolving the international conflicts over the heavy metal contamination at the interconnection of the Puyango basin in Ecuador and the Tumbes river basin in Perú. This area continues as the main processing center and its releases of mercury and cyanide are still creating serious environmental problems.

**Scenario 3.** Location: Ecuadorian Amazonia. Gold mining is increasingly disturbing the high diversity of flora and fauna in protected areas of the Amazonia region in Ecuador.



**Fig 1: Geographical location of ASM in Ecuador**

From the point of view of Ecosystem health, community development, economy, diversity, and local production, as well as the management of international conflicts, Ecuador possesses important characteristics for developing studies and related works on: the reduction of emissions, building actions for political and social development, and the replication and transfer of experience and knowledge to neighbouring regions, in the search for options that will promote sustainable development in gold mining.

While each scenario has its own characteristics, due to the historical process of gold mining concessionaries, as well as junior and large scale companies looking to become established in the region, have a special interest in the province of El Oro. Conflicts among the land owners and the small scale miners over the use of land and their rights to exploit the gold have been recently appeared in the area of Portovelo-Zaruma. There are six main districts in which gold mining development is increasing intensively in the province of El Oro. While Zaruma and Portovelo are the

oldest, El Guabo, Atahualpa, Pasaje, and Santa Rosa are more recent developments. The main mining district in this region, Portovelo dates back to the year 1549, when the aboriginal people of Ecuador extracted gold from the Yellow River. Next to Portovelo is the populated centre, St. Anthony's Villa of "*Zaruma's Cerro Rico en Oro*", founded in 1595 by a mining company because of its climate, which was propitious for living in the high zone. The area most recently in development is in the hills surrounding the three cities: Pasaje, Sta Rosa, and Atahualpa.

In 1896, a transnational enterprise of American origin, the South American Development Company – SADCO, initiated its mining operation in the area, which was named Portovelo's Mining Camp. Under nationalistic political pressure, the SADCO shut down its operations in Portovelo in 1950. However, the decline in mining did not last long, as, in the same year, the Mining Associated Industrial Company created the CIMA (with local capital), which kept mining into the 70's.

After the creation of the CIMA Company, artisanal gold mining activity started with the development of processing plants, locally known as "*plantas de beneficio*", where a very rudimentary technology and mercury were used for gold recovery. As the old miners can attest to, they used tonnes of mercury without any consideration of environmental or health impacts. The majority of processing plants are concentrated in Portovelo and Zaruma, with 62 already in operation and 52 in the current legal process of applying to operate. It is here that artisanal and medium scale mining operations have been using mercury and cyanide to extract gold for many years.

The cessation of the CIMA company's operations gave way to a rise in the craft of informal mining, which led to an overall increase in prosperity. This artisan-type skill persists to this day as the principal economic activity of Portovelo, which is considered the First Mining Centre in Ecuador. The colonial epoch's ancient mining camp was consolidated as a city with 700 inhabitants, which, from that time to the present, has increased to 22,000 inhabitants. Out of this population, 80% are involved in different mining activities. The small scale mining outfits sell the gold, both in the city of Portovelo to local customers and to buyers outside Portovelo, especially in Cuenca City, Ecuador.

The city of Portovelo and its immediate surrounds are part of the foothills of "*Cerro Rico en Oro*", an area that still remains the centre of informal mining production for the exploitation of gold. These foothills are flanked by the banks of the Calera River in the west and the Amarillo River in the South, the sources of the main affluent that flows into Río Pindo, which, further downstream, becomes Río Puyango, which flows into the Pacific Ocean in Peruvian territory. Although Portovelo is still an important mining region, most of the material processed comes from surrounding sites, where new mining deposits are intensively worked.

After El Niño wreaked havoc on the coastal plain of Ecuador in the 1980's, the mining town of Ponce Enriquez emerged between the flanks of Azuay and El Oro. In those days, several local investors focused on gold mining as a new opportunity to mitigate the regional disaster both in the bananas plantations and to shrimp farming within the same ecosystem. In fact, the unique characteristics of this region make it no surprise that one local investor has its funds in at least two of three

major industries: banana harvesting, shrimp farming and gold mining. Legal weaknesses, deficient assessments of both risk and environmental impact, and a lack of planning regarding natural resources, have all contributed to the rapid development and exploitation of these resources. At the present time, the government faces three conflicts: a) the conflicts between miners and junior gold mining companies; b) conflicts among gold mining operations and other land users within a watershed structure and, c) international conflicts with Peruvian communities affected by the release of heavy metals in gold mine tailings.

Gold production in the Province is estimated at 4 tons per year, more than 50 % of which comes from small scale mining; however the real quantity of gold produced is unavailable, due to the informality of this activity. Although there is a good technical development, one of the biggest problems in small scale mining is the rudimentary technique employed in gold extraction, in which they use mercury, without any consideration of environmental contamination and its effects on the health of the local population. Most of the rudimentary miners perform this work manually, whilst the more developed sectors of small mining use amalgamated sheets, amalgamation drums (Sandoval F. 2001). One alternative to the use of mercury in gold extraction is cyanidation, which is known to produce better gold recovery; however, since these substances are inappropriately managed, the environmental impact from the complex interaction between mercury and cyanide is controversial. The most severe environmental problem caused by formal and informal mining activities in this region is the contamination of water with high organic loads and heavy metals (Appleton *et al*, 2000, Tarras-Wahlberg and Lane, 2003), but mercury and cyanide will continue to pose the greatest problem until

miners understand the correct ways to use both techniques and the interaction of both compounds.

Unfortunately, mercury and cyanide are currently in use. Although miners have become aware of the mercury poisoning issue—to which they respond by saying that there has been a 90% reduction in mercury use—in an attempt to address the problem of mercury use among small scale miners, we conducted a preliminary assessment study. As a preliminary assessment of the current methods of gold recovery, we studied the social and environmental impacts of this process of gold extraction in Portovelo and Ponce Enriquez. As mercury is still an important instrument for gold recovery, the main objective was to analyse the amount of mercury used and recovered, as well as the levels of mercury in the air. While the population most at risk of over-exposure is that of the informal or small scale miners, themselves—nearby residents are also at risk and,—as yet, there have been no measures taken to mitigate the ambient pollution. However, in spite of recent reductions of mercury, the historic amount of mercury that has already been released into the environment, along with its more recent interaction with cyanide, are two of the major concerns in these ecosystems.

### **Labour structure of Artisanal Miners in Ecuador**

The structure of Artisanal Gold mining in Ecuador is complex and there are different ways to be involved in the process (Fig 2). While these have changed from time to time, as mining develops, so does the need to regulate and control its activities. In the operations involving drums, the miners, named “*chancheros*”, only achieve amalgamation. These miners that use the “*chanchas*”, or drums, are small

miners who lack the resources necessary to build large infrastructures. The majority of this process takes place in Ponce Enriquez, although there are several “*chanchas*” in Portovelo, too. Tailings from this process are sent to Portovelo, where other Miners and Millers currently operate. The owners of the “*chanchas*” take advantage of the tailings with the remaining gold.

Recognized as the most important mining district in Ecuador, Portovelo has several processing plants with large units that, in cooperation with Chilean mills and agitators, recover the gold with zinc or activated charcoal. Most of the owners of these processing plants do not work at the mine and earn their living only through the rental of the equipment and the tailings, which contain enough gold to keep them in business.

This complication not only creates conflict between miners and drum owners but also between miners and millers, as well. The relationship between the miners and the land owners represents another complex situation, in which, on one side you have the landowners, while, on the other side, there are the concessionaires. But there is another group of people recognized as miners who can lend the land for rock extraction and pay the owner with half of the material extracted. While there have been recent discussions between different groups about the rights of local miners in Portovelo with regard to the concessionaires or companies trying to develop large infrastructures for gold recovery, the entire scheme is a complex issue that highlights the need for: the education of mining communities from different sectors, an equitable legal framework for land use in the area, addressing environmental issues, and governmental control of this activity through regulation/legislation.

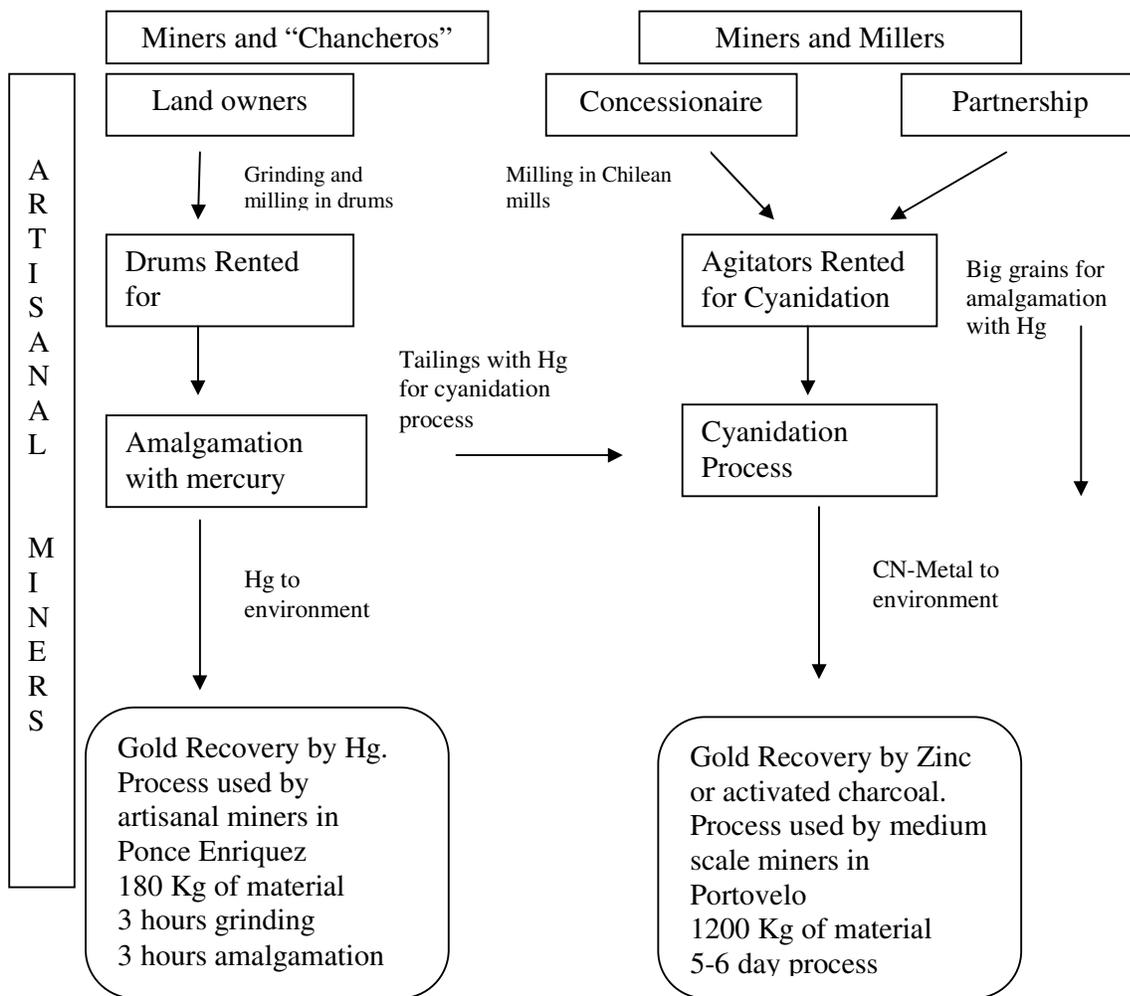


Fig 2. Scheme of the labour structure of Artisanal Gold Mining in Ecuador

Within the scheme of projects developed in Ecuador, in 1995, "Consejo Suizo de Desarrollo"(COSUDE) the Swedish organization for international Cooperation, initiated three-phase development project for improvements in Artisanal gold mining practices in Ecuador.

This program was carried out in the following three phases, developed over 5 years of work:

Phase 1. Use of Retorts

Phase 2. Handling of mining waste

Phase 3. A management plan for the *Puyango-Tumbes* basin regarding contamination of aquatic resources.

Supported by the Swedish government, the COSUDE program focused their actions in Portovelo, Zaruma, and the basin of the River Puyango. Apparently, the final phase of this program, which ran from 1995 to 2001, was unsuccessful because of the strong political barriers put up by important political actors within the gold mining exploration (and exploitation) industries in Ecuador.

Supported by the World Bank, another program, the "*Programa de Desarrollo Minero*", called PRODEMINCA, makes regular evaluations of the contamination of aquatic resources and addresses technical solutions for the pollution problems associated with artisanal gold mining in the south of Ecuador. In particular, they have studied the situation in Portovelo-Zaruma and the *Puyango-Tumbes* river basin, since this became a site of international conflict over contamination. This program has also taken actions in the *Ponce Enriquez* river basin, a new mining district, and is studying the contamination of the basin of *Rio Siete*. Although concerned about the possible effects of mining on the estuarine environment in the coastal area and its ramifications for the important shrimp industry in the region, the project made no technical observations on this matter.

The PRODEMINCA project also paid special attention to the development of *Ponce Enriquez* as a new mining district in *El Oro* Province. Looking to improve mining conditions in Ecuador, the international programs focused mainly on the technological development of the use of mercury in gold mining and, while they implemented some programs for improvement in the mineral extraction, it wasn't until the last stage that they began to pay attention to the environmental impact of gold mining. Based on that project's results, in the year 2001, the government took an important legal step that led to studies regarding the implementation of new regulations and optimum scenarios for the legal disposition of "*Consulta previa*" in mining. This legal action would force companies or miners to take their plans through a community consultation process before implementing any mining operations or viability studies of the mining concessions. However, due to political pressure from interested parties connected with the government at the time, the objective of this legal goal was frustrated and, to this day prior consultation has not been achieved as a formal instrument for the political and social development of gold mining.

### **The Process of Gold recovery**

After extracting the rocks by crushing and grinding the surrounding hills and other places in *El Oro* Province, miners put the material through the amalgamation and cyanidation processes, which are still currently in practice (Fig 3). The extracted material is transported to *El Pache* in *Portovelo*, which boasts the main processing plant of the province. First, the material is crushed and milled in "Chilean mills" with water passing through the conduits and is then picked up in the cloths or "balletas", which are washed in small tanks with water treated with cyanide. The big sand

particles (5-10 % of the total material processed) locally named “las ollas” are placed in barrels or iron plates and panned for amalgamation by mercury. The bigger part of material is treated by cyanide. Another kind of operation takes place in small scale mining, in which miners crush the material using smaller equipment and then mill the material in the barrels or drums, known locally as ‘chanchas’; after that, they pass the material through the carpets or “balletas”, which are used for amalgamation in the same drums or “chanchas”. In this case, the remaining tailing belongs to the owner of the “chanchas” processing centre. Mercury is a problem both in the amalgamation process and also in the tailings that will be used for cyanidation. Thus part of the mercury goes into the local rivers of Ponce Enriquez and surrounding places and another part goes to Portovelo, where the tailings are processed by cyanidation, transferring the problem, both to where the gold is recovered by cyanide and at the new environment.

During the gold processing, the problem is the use of mercury and its presence in the tailings used in the cyanidation process. Mercury contamination in the Gold-Cyanide Process poses serious health and environmental risks (Matlock et.al. 2002). Furthermore, following the heap leaching of gold and silver ores with NaCN solutions, portions of the mercury-cyano complexes often adhere to the activated carbon (AC) used to extract gold

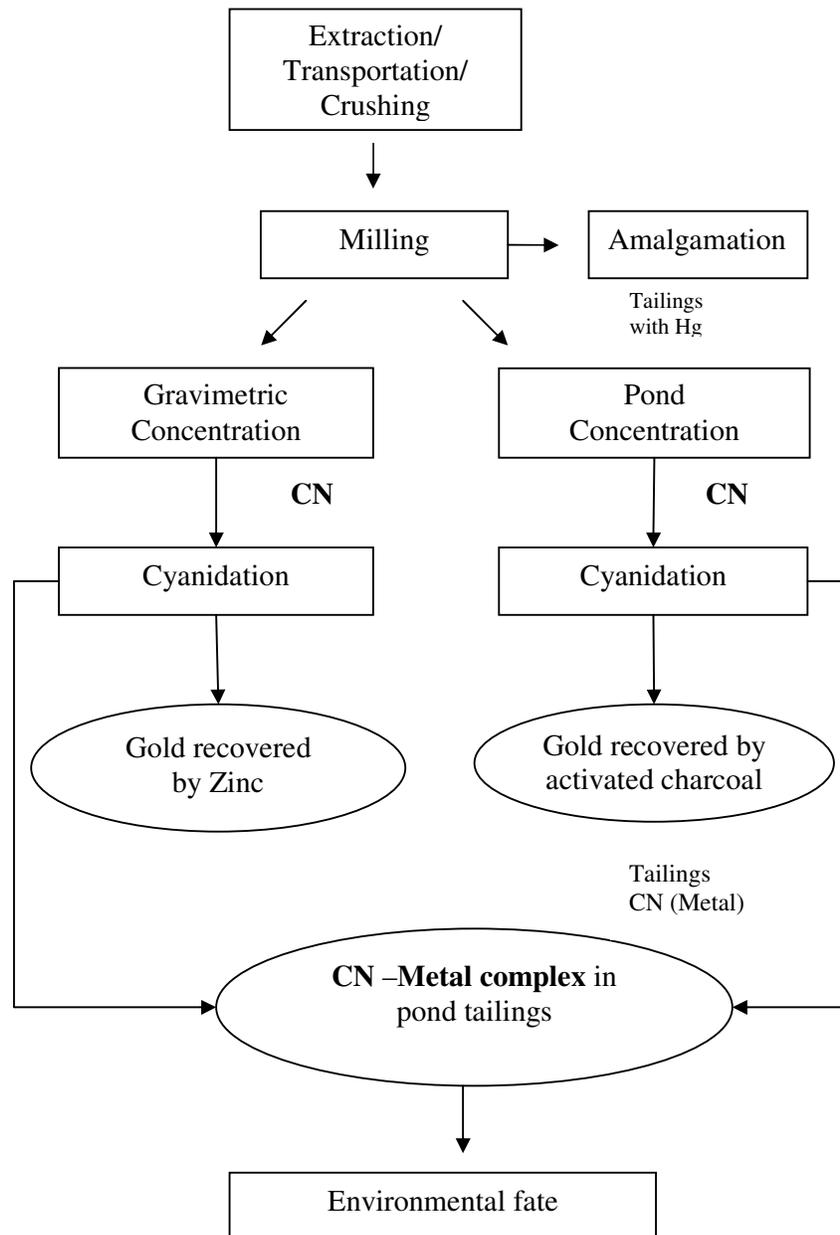


Fig 3. Simplified flowchart of common gold processing by Amalgamation and Cyanidation

## Amalgamation

The process of amalgamation by panning, which takes about 3.5 hours, is done by sprinkling small quantities of mercury on the sand several times until the miner notices that all the gold has been extracted. During this process, small pieces of black sugar are added to clean the amalgam. As a final step of the amalgamation, part of the mercury is recovered by squeezing the amalgam in a piece of leather. Amalgamation occurs in barrels, into which sand, mercury, black sugar and stones are placed and kept in movement for 3 to 6 hours, depending on how long it takes for the amalgam to form. Even though this process of gold extraction has a strong basis in scientific knowledge, the ASM practice it by hand, and although they do it with experience and skill, their methods are rudimentary.

Mercury (Hg) is a liquid metal at ambient temperatures and pressures. It forms salts in two states: mercury (I) and mercury (II). If dissolved in water, these salts are bioavailable and considered toxic. Elemental mercury gives rise to a vapour that is only slightly soluble in water, but is problematic because of easy transport in the atmosphere (Boening 2000). During the gold rush, about 100 t of Hg were released into the atmosphere and aquatic systems in the region of lower Madira in Brazil and the effects of this are still observed (Bastos et al., 2006).

In Ecuador, mercury amalgamation is used as a simple, cheap, and effective method to increase the recovery rate of fine gold. Mercury is used in a variety of methods: a) grinding the whole ore in barrels and spreading it with mercury, b) grinding the ore in Muller mills and using the big ore particles for amalgamation in

barrels. After this process, the tailings with mercury usually go through a cyanidation process. After the amalgam is collected, the excess mercury is squeezed out by a cloth and the remaining amalgam, containing mercury and gold, is decomposed by burning off the mercury with a blowtorch. This is often done in an open pan but sometimes in a retort, which recovers the evaporated mercury and allows miners to recycle it to reuse it in further amalgamation process; however, the mercury is not reactivated. Two cycles are believed to be involved in the environmental transport and distribution of mercury. One involves the atmospheric circulation of elemental mercury vapour. The second cycle is local in scope and depends upon the methylation of inorganic mercury, mainly from anthropogenic sources like the gold mining process (Boening 2000). The stages in this second process remain poorly understood, due to the varying characteristics of the environment, the biological receptors, and the cross interactions with other compounds, such as cyanide, in the mining process.

### **Mercury in Artisanal Mining in Ecuador**

For this study, we performed an assessment of the use of mercury in Artisanal Gold Mining in the Portovelo mining district of Ecuador. Conducted in the small scale mining area of El Pache in the Portovelo district, the intent of this study was to survey the amount of mercury small scale miners were using for gold extraction.

In order to determine the balance of mercury, after the material is crushed and concentrated, we separated three individual artisanal miners, each one with his respective pan and stone in preparation for the amalgamation. In order to find out the total amount of mercury used during this process, we weighed each amount of

mercury at the miners' requests. At the same time, just before the amalgamation process, we measured the mercury levels in the lungs of the three miners. We also measured the mercury levels in the surrounding atmosphere. Finally, we achieved the measurement of mercury concentration, using a LUMEX – portable atomic absorption spectrophotometer (RA915+). A relationship between  $Hg_{lost}$  and  $Au_{produced}$  was posited in order to establish the proportion of mercury that remains during amalgamation. Our study detected mercury both in the air surrounding the miners and in the air they exhaled. The amount of mercury used during this process was measured and the balance of mercury obtained.

For the purpose of this study, we gathered the preliminary relevant data, which were as follows: the miners processed 6000 Kg of rocks by crushing and milling; using gravity concentration, they processed 2000 Kg of sand by panning, the results of which were that, as a whole, they attained 6.3 Kg of ore sand. As there were three miners, we divided this figure by 3 in order to establish the balance of mercury during the amalgamation process.

The total amount of mercury used was 234.3 g. and the amalgam obtained weighed 321.7 g. After the squeezing process, the weight of the amalgam was 226.7g. 94.7 gr. of mercury were recovered, and, after burning, 88.6 gr. of gold were obtained. Of the whole amount of amalgam, 61% was mercury and 39% was gold. The ratio of  $Hg_{lost}$ : Au produced was around 1.5, which suggested that a significant amount of mercury was lost because the miners failed to achieve an efficient recovery of mercury and did not use retorts to burn the amalgam. Some researchers indicate that the optimal mercury-gold ratio is 1:1, revealing an approximate value of

4:1 in Ghana (Babut 2001 et al) and a range of 1.32 (Cursino et al 1999) to 2.0 (Bidone et al 1997) in Brazil. Furthermore, after recovering the mercury, the miners did not activate it for reuse, which not only means an inefficient recycling of mercury, but which, in turn, negatively affects the next amalgamation process because the mercury is less pure. Indeed, not only did the amount of mercury recovered suggest that the miners used more mercury than they needed during the sand mixing process, but also that the percentage of gold obtained showed evidence that the squeezing mechanism was also inefficient. From the amalgam obtained, 97% of the mercury went into the air as elemental mercury and the other 3% of it went into the soil or the nearby streams.

Mercury behaviour in Ecuador has been associated with three pathways: “a) deposition and inwash of mercury mobilized as a vapour during burning amalgams, b) particulate mercury inputs derived from the inwash of contaminated mineral processing tailings, and c) mercury removed from solutions by surface adsorption” (Appleton *et al*, 2001). Mercury was found from the source of pollution to 2 Km away, near the shrimp farming area. Methylation of mercury was associated only to the anoxic sediments in the lower section of the river, but there is no data to confirm such an assumption nor is there any that addresses the possible demethylation effect downstream in a highly productive area. Marine and fresh water fish contaminated by methyl mercury have been found in other countries (Castilhos et al., 2006)

Several studies in different regions in which ASM is practiced and mercury is released, shown that both methylation and bioaccumulation has occurred in river

basins in which fish are contaminated (Table 1). Since fish is the main source of food in several communities in the area, the obvious conclusion is that humans are ingesting this toxic form of mercury through fish consumption.

Studies Area GMP	Av. Concentration in fish ppm (mg/kg)	Sample Size
Brazil <i>Sao Chico</i>	4.16 ± 5,42	7.3
<i>Creporizinho</i>	0,50 ± 0,41	161
Indonesia <i>Galangan</i>	0,21 ± 0,36	264
<i>Talawaan</i>	0,58 ± 0,45	156
Laos <i>Luang Prabang</i>	0,066 ± 0,048	65
Sudan <i>Blue Nile</i>	0,05 ± 0,01	108
Tanzania <i>Rwamagasa</i>	0,12 ± 0,09	258
Zimbabwe <i>Kadoma</i>	0,41	52
Ecuador <i>Yellow River</i>	0.5	----

Table 1. Hg in fish in areas near ASM processing centres

### Cyanidation

The Cyanidation process, which is performed using the remaining amalgamated sand and the unamalgamated tailings, is a dangerous practice because of the presence of mercury in the amalgamated sand. The mill owners take the tailings as a form of payment from the miners and the millers process this material by adding cyanide, in huge open-air piles of crushed sand. Cyanidation tanks can receive around 7 mt of sand. Sufficient lime is added to keep the slurry alkaline, in a pH level of above 10. The solution is separated from the ore by filtration and the gold is precipitated by zinc located in a series of tubes. The gold precipitated is further refined, by smelting, to remove the zinc, and then treated with nitric acid to dissolve the silver. Silver is also obtained in this process. The need for more

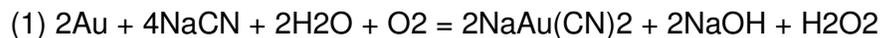
aggressive conditions in the presence of silver can increase the attack on other minerals present in the ore, leading to increased cyanide consumption, decreased selectivity of gold and silver, and higher concentrations of other metals in the solution. Elevated cyanide and metal-cyanide concentrations in the solution can significantly increase the complexity and cost of recovering gold and silver (Mudder et. al. 2001 a). Cyanide is frequently used in a mining technology called cyanide heap leaching, a cheap way to extract gold from its ore. Gold miners spray a cyanide solution (which reacts with gold) on huge open-air piles of crushed ore. They then collect the solution in leach beds and overflow ponds, and extract gold from it by recirculating it a number of times.

The term cyanide refers to a singularly charged anion consisting of one carbon atom and one nitrogen atom joined with a triple bond,  $\text{CN}^-$ . The most toxic form of cyanide is free cyanide, which includes the cyanide anion itself and hydrogen cyanide, HCN, either in a gaseous or aqueous state. At a pH of 9.3 - 9.5,  $\text{CN}^-$  and HCN are in equilibrium, with equal amounts of each present. At a pH of 11, over 99% of the cyanide remains in the solution as  $\text{CN}^-$ , while at pH 7, over 99% of the cyanide will exist as HCN. A problem with this technology is that cyanide is extremely toxic to birds and mammals drawn to cyanide solution collection ponds as a source of water. These ponds also can leak or overflow, posing threats to underground drinking water supplies and wildlife in lakes and streams.

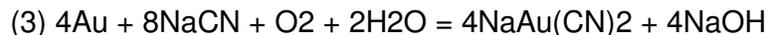
While the chemistry of cyanide solutions is complex, it is this very complexity that is responsible for its ability to dissolve gold and silver. However, the fact that cyanide forms complexes with other metals, such as mercury, zinc, copper, iron, and

nickel, partially accounts for the consumption of cyanide in gold extraction circuits, which generate waters that may be difficult to treat and complicate the analysis of cyanide solutions.

The principal reasons for the prominent place of cyanide in gold ore processing include its wide availability, its efficiency at extracting gold and silver, its relatively rapid extraction kinetics, and the strength and solubility of its gold cyanide complex. Gold dissolution by cyanide (i.e. cyanidation) is believed to be a two-step process, in which hydrogen peroxide is formed as an intermediate compound (Mudder et. al. 2001 a).



The overall reaction known as Elsner's equation is as follows:



Relatively weak cyanide solutions can be used because of the strong complex formed between cyanide and gold. It is believed that in the absence of other metal cyanide complexes, a 100 mg/L solution of NaCN (i.e. about 50 mg/L free cyanide) can provide the maximum rate and extent of gold dissolution (Flying and Mc Gill 1995).

At a pH of 10, approximately 90 % of cyanide is present as  $\text{CN}^-$  ion. Miners increase the alkalinity with lime. The alkalinity ensures that free cyanide ions are not lost as HCN gas. Oxygen and water are also important during the process of cyanidation. At the artisanal gold mining sites, pH has been observed at values below 9, and then there is a loss of CN, which affects both the local environment and the process of gold recovery.

Because cyanide breaks down heavy metals, it can form complexes with other metals or chemicals, which can be as toxic as cyanide itself. Fish and aquatic invertebrates are particularly sensitive to cyanide exposure, as it blocks the absorption of oxygen by cells and causes the species to suffocate. While aquatic life is killed by cyanide concentrations in the microgram per litre (part per billion) range, bird and mammal deaths result from cyanide concentrations in the milligram per litre (part per million) range. Concentrations of free cyanide in the aquatic environment ranging from 5.0 to 7.2 micrograms per litre reduce swimming performance and inhibit reproduction in many species of fish. Other adverse effects include delayed mortality, pathology, susceptibility to predation, disrupted respiration, osmoregulatory disturbances and altered growth patterns. Observations in Ecuador of cyanide levels in tailing ponds were between 400 and 1000 ug/lit of free CN.

Concentrations of 20 to 76 ug/lit free cyanide cause the death of many species, and concentrations in over 200 ug/lit litre are rapidly toxic to most species of fish. Invertebrates experience adverse nonlethal effects at 18 to 43 ug/lit free cyanide, and lethal effects at 30 to 100 ug/lit. Chronic cyanide exposure negatively affects the reproduction, physiology, and levels of activity of many fish species,

which can render the fishery resource non-viable. While the sensitivity of aquatic organisms to cyanide is species specific, it is also affected by water pH, temperature, and oxygen content, as well as the life stage and condition of the organism (Mudder et. al. 2001 a). Algae and macrophytes can tolerate much higher environmental concentrations of free cyanide than fish and invertebrates and do not exhibit adverse effects until concentrations reach 160 ug/lit or more. Aquatic plants are unaffected by cyanide at concentrations that are lethal to most species of freshwater fish and invertebrates. However, since cyanide breaks down naturally with air and sunlight, artisanal miners can treat the cyanide waste with low-cost technology. The main challenge with the emerging technology of cyanidation in the artisanal gold mining is to manage cyanide properly and prevent poisoning and contaminating the environment.

### **Cyanide and Mercury**

Although poisonous, Hg and CN are still used for gold processing. Cyanide leaching still remains the most studied and employed lixiviant system for the extraction of gold and silver on the basis of reagent availability, effectiveness, cost, and environmental compatibility (McNulty 2001).

In Sao Chico, Brazil, studies have revealed high mercury levels in soils and sediments. The studies developed by Global Mercury Project (GMP) have also reported leaching of amalgamation tailings with cyanide. In North Sulawesi, Indonesia, the cyanidation of mercury- contaminated ores is creating dangerous cyanide-mercury complexes that are then lost to the wider environment, resulting in

high mercury levels in local and marine fish. In Zimbabwe, miners crush gold ore primarily with wet stamp mills, creating slurry, which passes over copper plates covered with mercury. After squeezing and burning the amalgam, the mercury contaminated tailings are usually treated with cyanide for additional gold recovery, leading to the creation of additional mercury-cyanide complexes.

Modern gold processing technology is almost exclusively done with cyanide, with activated carbon adsorption. The higher complexes of Hg, which occur at higher free cyanide concentrations, do not absorb as well onto activated carbon. Because cyanide mobilizes mercury, carbon processing can lead to dangerous emissions in the gold room. The presence of mercury retards cyanidation, particularly if it forms a coat of amalgam. Thin layers of cinnabar have also been shown to occur naturally, which inhibit the leaching of gold (Flying and Mc Gill 1995). MacDougall (1984) demonstrated that because  $\text{Hg}(\text{CN})_2$  competes directly with  $\text{Au}(\text{CN})_2$ , it can displace some absorbed aurocyanide.

### **Mercury and Cyanide Exposure in ASM**

While measuring the air mercury concentration directly, we recorded the average concentration. At the same time, we measured breath concentrations in the individual blows of each miner during the amalgamation process.

What we found was that artisanal miners' mercury exposure happens at each of three steps during the amalgamation process: the first is in the panning/amalgamation step; the second is in the squeezing by hand of the amalgam; and the third is the amalgam burning process. Artisanal Miners burn the amalgams

very near to their bodies. Although some miners have retorts, they rarely use them. Retorts are vessels in which the amalgam is heated, allowing the evaporated mercury vapour to condense and flow through to another collection basin. Home retorts have been demonstrated by the Global Mercury Project. Also, because many retorts are not very well designed, they produce direct exposure, both to the bodies of the miners and the surrounding atmosphere. Retorts can be used to capture volatilized mercury and condense it, allowing much of the mercury to be recycled, but miners prefer to burn the amalgam in pans or shovels (Veiga et al 2006). Without retorts, the mercury lost in the amalgamation process is directly released into the environment, either into soil or nearby bodies of water. Although some processing plants had retorts, most of them were either managed inefficiently or poorly constructed, and, therefore, did nothing to prevent the air pollution that was evident. As soon as the amalgam was ready, they burned it, releasing the mercury and leaving an impure gold, with some mercury still attached to the bullion, which was then transported to the jewellers which in fact is the next exposure place. During the first step, namely the amalgamation process, the mercury level in the air jumped from 25 ng/m<sup>3</sup> to 8000 ng/m<sup>3</sup>. In the second step, i.e., the squeezing process, this level increased to 12.500 ng/m<sup>3</sup>. While, at the beginning of the burning, the mercury level fluctuated between 20.000 and 36.000 ng/m<sup>3</sup>, at the end, the mercury reached its highest level, i.e., 193.000 ng/m<sup>3</sup>, making the smoke from the amalgam very dense (Fig 4). Some minutes after the evaporation and burning stopped the levels of mercury in the air decreased until they attained an average of 7500 ng/m<sup>3</sup>. Natural Hg levels in the air from rural areas usually range from 0.001 to 0.004 ng/m<sup>3</sup>, while in urban areas they vary from between 0.01 and 0.17 ng/m<sup>3</sup>. The limit for public exposure is 1.0 ng/m<sup>3</sup>, and the recommended health-based exposure limit for

metallic Hg is 25 ng/m<sup>3</sup> for long-term exposure and 500 ng/m<sup>3</sup> for short-term exposure (Malm et al 1990 and WHO 1991). It also was observed that the air mercury concentration decreases with increasing distance from the mill site (Garcia-Sanchez et al 2006), so it is expected that mercury is being dispersed around the area, contaminating other communities not directly exposed to mining operations.

When we analyzed the mercury concentration in the air exhaled by the three miners who had been exposed to the amalgamation process, we found a level of 147.3 (sd 6.4) ng/m<sup>3</sup> before the process and a level of 1,513.3 (sd 480.1) ng/m<sup>3</sup> of Hg at the end of the process.

Such concerns as mercury retention time, its pathways through the human body, and its cumulative effects, are subjects that require further attention. Although, at the present time, most miners only amalgamate big particles which represent only 5-10 % of the total milled material, which significantly reduces the amounts of mercury used and lost, it should be noted that some miners still amalgamate the whole material in barrels. The normal mercury level in a person's breath depends on the number of amalgam fillings they have and usually ranges from 3 ng/m<sup>3</sup> (no fillings) to 300 ng/m<sup>3</sup>. While this method is rudimentary, it provides a quick assessment of the level of contamination in individuals working with mercury and those living around mines and gold shops. Using this quick assessment method, miners can get immediate information results (faster than with urine analysis) by comparing their breath.

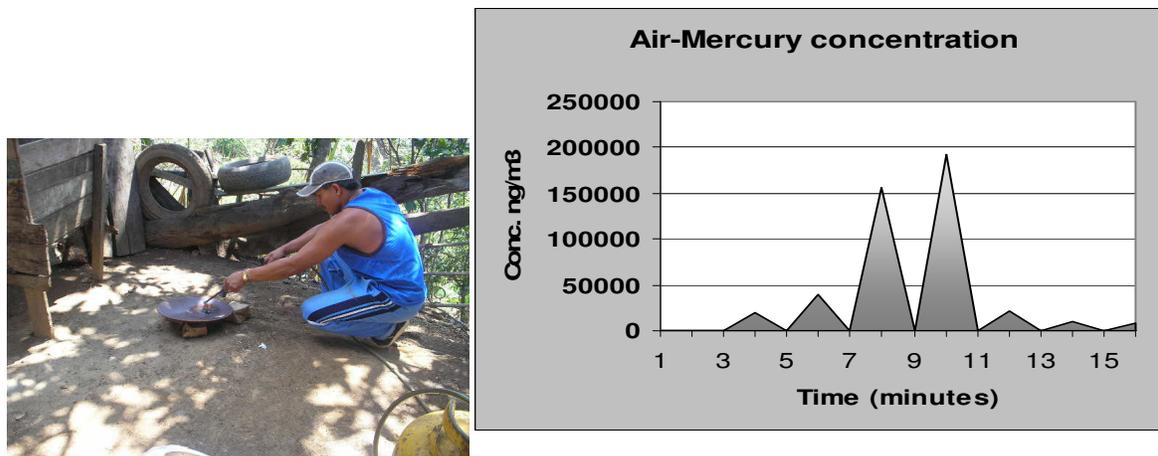


Fig. 4 Air-mercury concentration and human exposure in artisanal gold mining in Ecuador

The concentration of mercury in the surrounding environment in Portovelo has also been assessed and the values have been between 45 ng/m<sup>3</sup> in the lesser exposed places to 1500 ng/m<sup>3</sup> near the gold shops in Portovelo and Ponce Enriquez. Mercury in shopping places has been also monitored with values over 1000 ng/m<sup>3</sup>, revealing that the community is currently exposed to this poisonous element.

A study conducted in Nambija and Portovelo, Ecuador, by Counter *et al* (2002), revealed the presence of mercury intoxication in 114 Andean Saraguro and non-Saraguro (Mestizo) children living in remote gold-mining settlements. Neuro-otological symptoms and abnormalities were observed in Saraguro, non-Saraguro, and Portovelo children. The study concluded that the children of Nambija, particularly the Saraguro "Amer-Indians," exhibited elevated blood-Hg levels from exposure to Hg used in the gold-mining process and were at risk for neurological impairment. The children of Portovelo who reported neuro-otological symptoms but had low Blood-Hg levels (<10 microg/L) may be affected by exposure to sodium cyanide, which is used extensively in the local gold-mining operations.

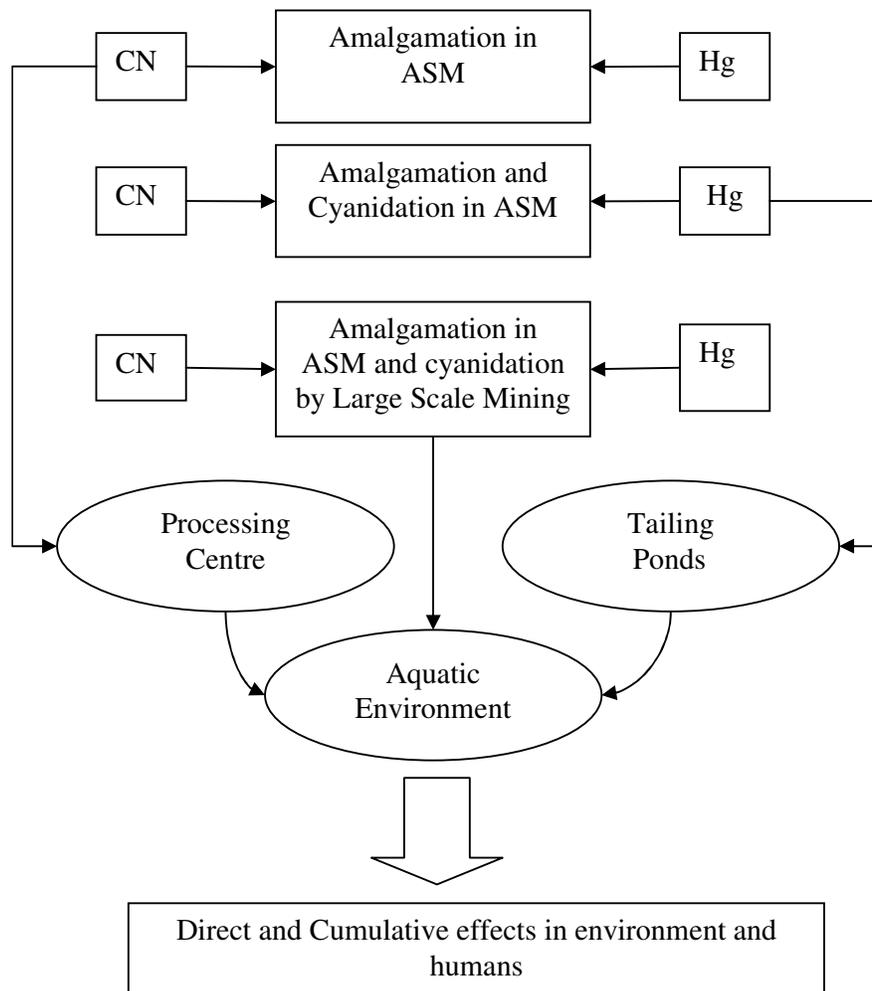
Yet another study on health and the environmental effects of gold mining activities on nearby communities found a frequency of gastrointestinal complaints associated with elevated hair methylmercury levels (Cortes-Maramba et al., 2006). An interesting finding in this study was the increasing incidence of elevated diastolic blood pressure with elevated total mercury levels in hair. Finally, the study also found that mercury storage at home is a risk factor, which also has been observed in Ecuador.

In a comparative study about mercury contamination, Pinheiro et al. (2006) pointed to a lower bioaccumulation and/or the existence of a protection mechanism in babies.

According to our studies Mercury and cyanide can impact the environment in three different ways:

- a) During gold processing, ASMs use Hg for amalgamation and mix it with CN.
- b) During Gold processing by ASM by amalgamation and in the same processing place it is also achieved the cyanidation process.
- c) During Gold process by ASM performing the amalgamation process in one place and in other side ASM or large mining companies make the cyanidation process

This three exposure types (Fig 5) are currently observed in developing countries.



**Fig 5. Exposure pathways of mercury and cyanide in Gold Mining Operations**

There is a need for more studies to understand the behaviour of mercury in the tailings due the expectancy of high methylmercury (MeHg) levels in the tailings, especially in tropical conditions. As it stands, there is a dearth of information on the reaction rates and the oxidation and methylation of metallic Hg in the tailings. Several countries are exposed to the combination of mercury and cyanide during the gold recovery process: Brazil, China, Indonesia, Peru, The Philippines, Zimbabwe

and Ecuador; hence, the misuse of cyanide in the amalgamation process must be considered a global problem.

### **Mercury and Cyanide complexes**

The chemical form of cyanide depends not only on pH exposure to light and air, but also on the presence of chemical forms of metal. The transport of these substances depends on solubility, absorption, materials such as soils and clays, and their interactions with the biomass. Because the cyanide complexes in different metals commonly occur in gold processing wastes and because the chemical properties of the metal cyanide complexes differ greatly, the toxicity of cyanide varies tremendously, depending on the extent to which it is mixed with metals. Reactions involving the cyanide complexes of Hg take place quickly. In solutions of 0,01 M in free CN, typical in precious metal leaching conditions, Hg reacts with cyanide to form  $[\text{Hg}(\text{CN})_4]^{2-}$ . Anionic Hg (II) cyanide complexes are decomposed by soluble acid  $\text{Hg}(\text{CN})_2$ , which is thermodynamically so stable that its decomposition by acid requires the presence of strong ligands, precipitants, or oxidants, e.g., I,  $\text{H}_2\text{S}$  or  $\text{Cl}_2$  (Flying and Mc Gill 1995). The Hg consumes the CN so that it is not available to leach the gold, which results in lower gold recovery

The amount of cyanide used during the cyanidation extraction process differs depending on the type of ore being processed. Consequently, in addition to gold cyanide complexes, a variety of cyanide complexes of accessory elements are present during and after processing. Wastes produced from these operations are discharged in the tailing ponds that come from ores processed in mills.

Sulfides can also control cyanide metal complexation. Soluble sulfides convert all Hg cyanide complexes into insoluble metal sulfides at all pH values, which liberates free  $\text{CN}^-$ / HCN. The reaction between Hg (I) compounds and  $\text{CN}^-$  results in a disproportionate amount of metallic mercury and Hg (II) cyanide complexes (Flying and Mc Gill 1995) .

Because mercury is a metal of environmental concern for a variety of reasons, very low effluent limitations are normally applied. Mercury is bound in a relatively weak complex with cyanide and has a great affinity for sulphide and activated carbon, both of which form the basis of the primary removal processes (Mudder et al 2001 b). The presence of mercury in the cyanide leaching and further carbon treatment also affects the environment, since Hg adsorbs into carbon, preventing gold adsorption.

Regarding the reactions of metal cyanide complexes to decomposition by reagents that are not oxidants, it is known that ethylenediaminetetraacetate (EDTA), one of the strongest known complexing agents, does not display  $\text{CN}^-$  from metal (Hg) cyanide complexes in alkaline solutions. The Hg (CN) is classified as partially weak acid dissociation (WAD) compound. At pH levels below 6, the predominant specie is  $\text{Hg}(\text{CN})_2$  (Flying and Mc Gill 1995). It can be concluded that the process of submitting Hg-contaminated tailings to cyanidation constitutes a dangerous and improper combination of technologies in gold recovery. Furthermore, Hg becomes soluble and bioavailable in this process, which makes it easier to be methylated.

## Cyanide with other metals

In the gold mine industry, the cyanide complex known as Copper(II) forming cyanide ( $\text{Cu}(\text{CN})_4^{3-}$ ) presents the biggest concern in cyanide management because it is much more stable than free cyanide (Sharma, et al 2005).

By other side, the results obtained by Ikingura *et al* (2006b) have shown that the toxicity of cadmium and zinc complexes is higher than that of the corresponding metals, while the toxicity of  $\text{Ni}(\text{CN})_4^{2-}$  is lower than that of the corresponding metals. Furthermore, no differences have been found between the effect of mercury and the corresponding tetracyanide complex. From the data obtained, while it appears that it may not be possible to generalize about the biological effects of complexation within the  $\text{CN}^-$  group, it should be stated that, generally, there are substantial differences between metals and their cyanide complexes, as far as the toxicity in activated sludge is concerned.

In their geological analysis at Ponce Enriquez, Appleton *et al.* (2001) found that because gold is found in arsenopyrite and chalcopyrite hydrothermal veins, extremely high levels of arsenic and copper are expected. Whereas at Zaruma-Portovelo, where base metal rich mesothermal and base metal poor epithermal assemblages are the main characteristics of the deposits, high levels of cadmium and zinc have been found in the river sediments associated to gold processing waste.

One of the results of the Gold Mining process is the release of heavy metals into the air and aquatic environments. Table 2 summarizes the heavy metals found in surface waters in the vicinity of gold mining operations in Ecuador, and these levels are higher than the standard Canadian levels for aquatic environments.

Table 2. Concentration of heavy metals found by Appleton et al. (2001) in aquatic ecosystems connected with Artisanal Gold Mining in Ecuador

Filtered water ug/lit <sup>-1</sup>	Guidelines Canadian	Ponce Enriquez (Near shrimp farm)	Portovelo- Zaruma	Nambija
As	10	470	nd	Nd
Cd	3	9	41	< 4
Cu	2000	7277	437	3.5
Pb	10	Nd	nd	< 40
Hg	6	9.9	0.1	0.1
Ni	70	165	35	< 10
Zn		821	3354	< 5
Suspended Particulate Matter mg/kg <sup>-1</sup>				
As	----	22626	1564	----
Cd	----	18	23	----
Cu	----	6437	2912	----
Pb	----	1061	1997	----
Hg	----	9.61	1.3	----
Zn	----	743	2567	----
Bottom Sediments mg/Kg <sup>-1</sup>	Interim fresh water sediment guidelines			
As	5.9	46049	7494	34
Cd	0.6	24	104	3
Cu	35.7	9134	8750	409
Pb	35.0	666	10524	42
Hg	0.17	13	3.0	34
Zn	123	924	9792	231

The metal cyanide complexation in the gold processing environment is the first kinetic step. The second step is the metal emissions into the environment in complex with cyanide or free metals. Once this bulk material enters the aquatic ecosystem, the availability of metals is controlled by conditions in the local environment. The speciation of cyanide and the concentrations of several metals

have been found to follow diurnal cycles (Johnson *et al*, 2002); hence, cyanide also is controlling the presence of metals in tailings and their transport to the nearby environment.

### **Cyanide in the aquatic environment and the risk of methyl-mercury formation**

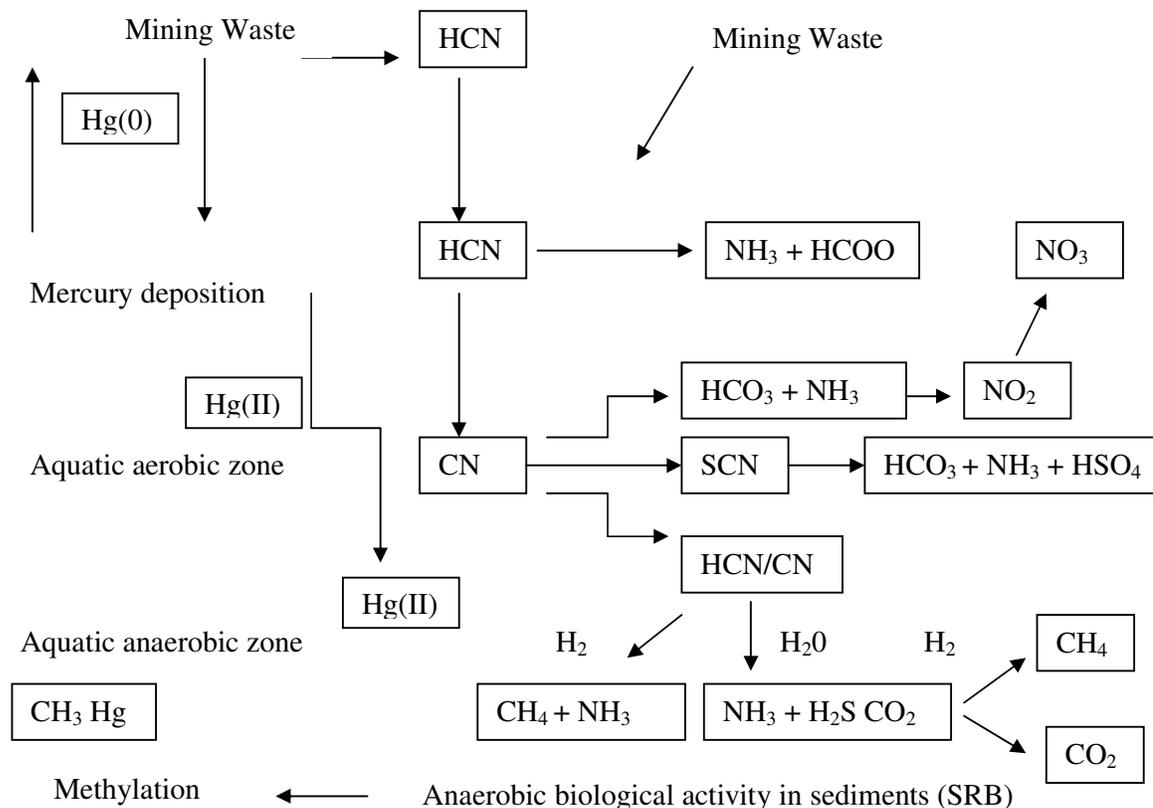
One of the results of cyanidation, after natural attenuation or water treatment, is that a variety of cyanide related compounds are formed in the solution, including thiocyanate, cyanate, ammonia, and nitrate. Related to cyanide, the compound, cyanate, is often found in waters that contain cyanide. Although cyanate originates from the oxidation of cyanide, it exhibits different chemical, analytical, treatment, and toxicity characteristics. Cyanate is the primary by-product of a cyanide treatment in which chemical oxidation processes are employed. The primary approach to the elimination of cyanate is to select water treatment processes that do not form the compound as a by-product. Treatment of solutions for cyanate removal is uncommon, not only because cyanate is much less toxic than cyanide, but also because it is generally present in metallurgical solutions in low concentrations and does not remain in the environment for long periods of time. Thiocyanate is formed through the interaction of cyanide with sulphur-containing compounds, particularly sulphide minerals such as pyrite, pyrrhotite, chalcopyrite, or arsenopyrite, which characterize the gold rock deposits.

Thiocyanate is a potential problem for several reasons, including its consumption of cyanide, its consumption of chemicals in water treatment processes, its toxicity, and its ability to break down to form ammonia. Hence, the removal of

thiocyanate should start in processing of ore, through minimization of its formation. Ammonia is a water quality problem for several reasons, including its own toxicity, its ability to consume oxygen in streams during nitrification, and the toxicity of its breakdown products, nitrite and nitrate. Ammonia is a breakdown product of cyanide and forms through the hydrolysis of cyanate. If cyanate is present in mine waters at an elevated concentration, then often there will be a correspondingly elevated concentration of ammonia. Through a combination of these two sources, the removal of ammonia from mine waters is occasionally required. The concern is with toxicity to aquatic organisms, since ammonia is generally not present in decanted solutions at concentrations that would be toxic to wildlife or watersheds. Nevertheless, while both cyanide and its transformed chemical compound are highly toxic to aquatic life, their toxicity levels would also depend on the quality of the aquatic environment and the physiological conditions of the biota.

Metallic mercury  $Hg^0$  oxidates slowly to form mercury (II), but, when cyanide is present, their reaction will promote the formation of Mercury (II) in a shorter time. Not only is the oxidization of mercury (II) an important step prior to methylation but mercury (II) is more stable in water than mercury  $Hg^0$ , which will evaporate into the atmosphere. Thus, the presence of cyanide and the oxidation of mercury will promote a reaction to methylmercury in the aquatic environment (Fig 6). Further cyanide conversions in the aquatic environment and the physicochemical stage of the receiving aquatic ecosystem are also issues to consider assuming the methylmercury formation.

**Fig 6 Diagram of possible routes of CN and Hg from mining activity into aquatic ecosystems**



A variety of factors, such as temperature, pH, redox potential, and the presence of both organic and inorganic complexing agents, as well as microorganisms activity, are also important in the process of methylmercury formation (Ulrich et al 2001). Methylmercury is a potential neurotoxin that is rapidly accumulated by aquatic biota and can potentially harm human beings through fish consumption.

### **Gold mining waste and ecosystem interconnections in Ecuador**

One of the more relevant impacts of gold mining has been observed at the Ponce Enriquez area, where Gold Mining is interconnected with agricultural and aquacultural areas by a watershed. The mercury waste, which has leached into the river water, is transported downstream to nearby environments, until it reaches the

estuarine region. The fact that the mining waste of Portovelo and Zaruma reaches Peruvian territory has led to an international environmental conflict through the Puyango river. The fact that the Hg-CN and CN, linked with other metals, are transported with water allows them to spread to large areas downstream, contaminating the environment, killing fish, and poisoning drinking water. In the case of Ponce Enriquez and other mining districts in El Oro, a province of Ecuador, the mercury makes its way into agricultural areas, enters soil near schools (Counter, et al 2002), and, further downstream, reaches the large shrimp farming industry, also affecting the estuarine region and mangrove areas, where methylation could be achieved (Appleton, et al 2001). Elevated metal levels in bottom living larvae collected from contaminated sites suggests that sediment bound metals are readily bioavailable (Tarras-Wahlberg *et al*, 2001).

In Ecuador, mercury levels exceeded 0.5 mg/kg in fish from both contaminated and uncontaminated sites in the Yellow River, showing that both methylation and bioaccumulation of mercury are occurring in the Puyango river basin. Appleton *et al* (2006) have also shown that artisanal gold mining has caused agricultural areas in Ecuador to be contaminated with mercury. Other studies (Egler, et al 2006) suggest that Hg uptake probably occurs through stomata by atmospheric mercury deposition.

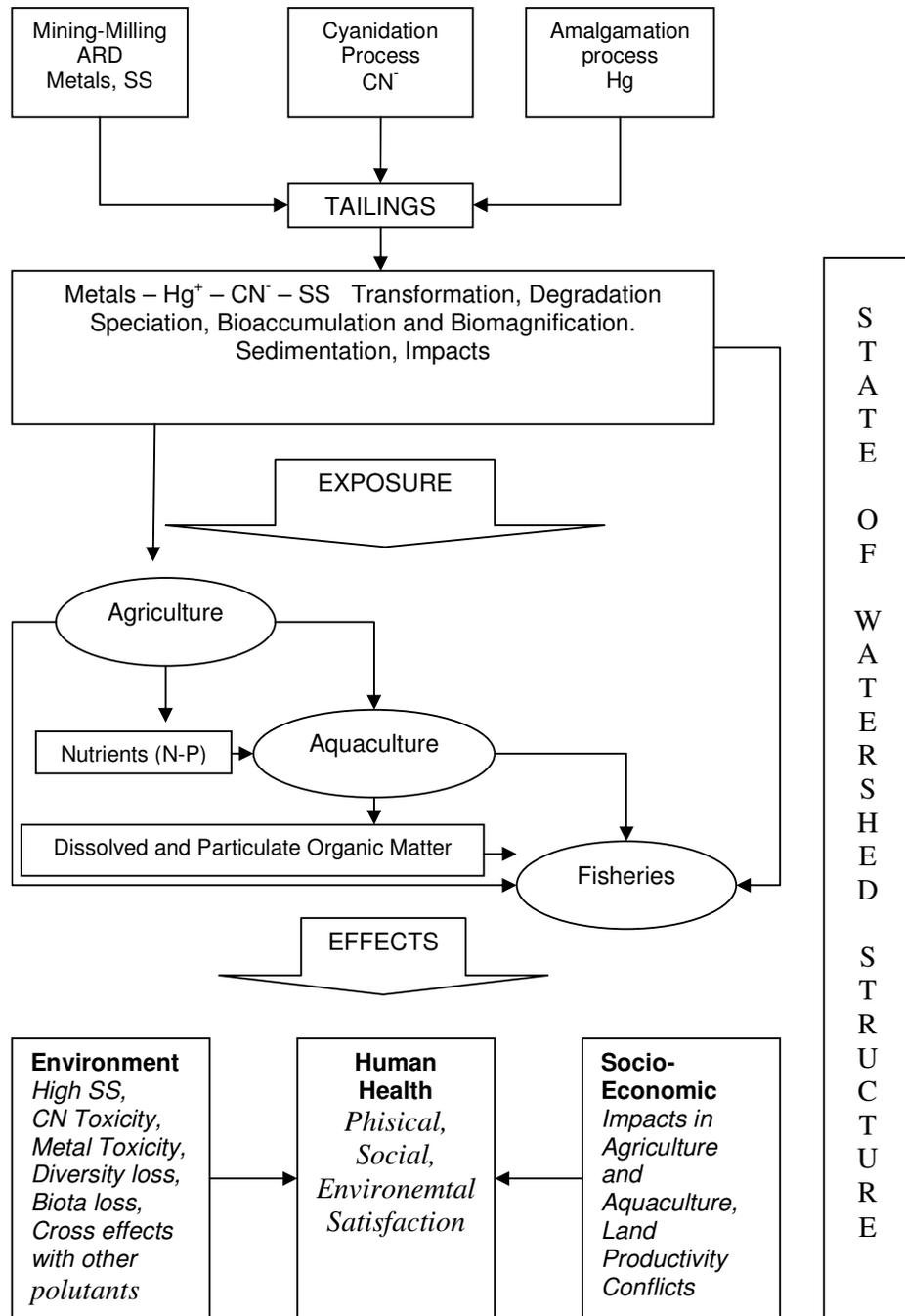
Although fish is a recognized as good indicator, Farias *et al* found no differences in mercury concentrations in fish between two areas, one exposed and one not exposed to gold washing activities (Farias, et al 2005), which suggests that,

although fish can be used as an indicator of mercury contamination, it is only one medium through which to understand the mobility of mercury in contaminated areas.

In examining the Ecuadorian environment, some have noticed that, when the river overflows during the rainy season the mercury reaches the banana plantations and shrimp ponds. While mining waste is composed of mercury, cyanide, suspended solids, and other heavy metals, the main concern is the impact of the complex mix of metal and cyanide, or the effects of the cyanidation process on the environment and human health. The river water transports the tailings and spreads out the waste until it enters the sediments of agricultural and aquacultural areas.

The fact that this cumulative effect has not been studied has made it an issue of great concern in Ecuador. In fact, the socio-economic interaction among mining, agriculture, and aquaculture is a significant issue for the sustainability of this region (Fig 7). According to the local people, the soil contaminated by gold mine tailings is useless for growing any kind of agricultural crop and even local vegetation becomes stunted in such soils. The shrimp-farmers say that when the water from the river enters through the pond-gates, shrimps behave abnormally and then die. Not only does seasonal precipitation play an important role in the transport of mercury and other mining waste, but also the transformations, mobility, and bioavailability of Hg are governed by meteorological conditions (Ikingura, et al 2006a). Studies at the Tapajos River in Brazil have suggested that the mobilization of contaminated sediments from mining lands into the aquatic environment is the main source of pollution (Telmer, et al 2006).

**Fig 7 An ecosystem approach of Artisanal Gold Mining effect in the watershed structure in Ecuador**



In both cases agriculture and aquaculture in Ecuador, the farmers have decided not to use the river for any purpose, neither for agricultural irrigation nor for the re-exchange of water, as is common in shrimp-farming. While some banana and shrimp farms have been abandoned because of this situation, others have started to construct large canals to bring safe or less contaminated water from other areas. The interaction of chemical compounds in the complex mix of mercury and cyanide is a primary issue that needs to be addressed in further studies of the fates and transformations of mining waste, as is water and soil quality in adjoining areas. This environmental problem also bears a relationship to the social and economic fates of small farmers close to the river area. The decimation of the local agriculture and aquaculture farms is having an enormous social and economic impact in the area. In addition, the fact that mining activity in Ecuador is increasing, due to the discovery of new deposits, means that, without further studies, the effects on the social and economic lives of the whole population in the area could be devastating. Studies of the new mining operation sites in Ecuador will help the government and other interested parties address these issues and find cleaner and more efficient alternatives to traditional practices.

The preliminary observations of the small scale mining industry in parts of Ecuador have revealed that it is not only the aquatic and terrestrial ecosystems that are negatively affected by the mercury released through the historic process of amalgamation, but that this poisonous metal is being released into the atmosphere as well. The air is also contaminated with CNH, due to the low pH of cyanidation solutions, as well as emissions of acids and heavy metals into the atmosphere during the gold refining process. As mining activities are increasing, small scale

miners need an intervention that will help them construct clean and efficient techniques of gold recovery. One strategy could be to involve miners, policy-makers, and downstream local communities in a campaign to monitor affected areas. The amalgamation process currently in use needs an intervention for correct management and study of the complex effects of the mercury present in the tailings. The fact that the cumulative social, economic, and health effects of mining waste, especially mercury, are still unknown, constitutes one of Ecuador's biggest problems. Therefore, further research, transfers of technology, and policy changes that will affect communities are issues that require further study. The effects of the ecosystem on methylmercury formation are also an important issue concerning the interaction of mining and aquaculture. In fact, organic loads from aquaculture activity have been found to be a potential resource for methylmercury conversion (Debruin A 2006).

### **Microbial activity and cyanide biodegradation**

In the mid 1980s, the Homestake Gold Mine in the USA commercially demonstrated the destruction of cyanide by microorganisms in the gold mining industry (Mudder & Whitlock 1984). Microbial destruction of cyanide and its related compounds is one of the most important biotechnologies to emerge in the last two decades for treating process and tailings solutions at precious metal mining operations. Adams *et al.* 2001; Akcil *et al.* 2003; Atkinson 1975; Barclay *et al.* 1998; Gurbuz *et al.* 2002; Howe, 1965; Hubb *et al.* 2000; Knowles, 1976; Mihaylov & Hendrix 1994; Nazly & Knowles 1981; Patil & Paknikar 1999; and Raybuck, 1992 have all reported investigations into the microbial destruction of cyanide. Hundreds of plant and microbial species (bacteria, fungi and algae) can detoxify cyanide

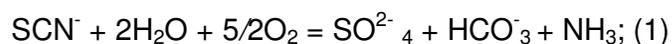
quickly to environmentally acceptable levels and into less harmful by-products. Full-scale bacterial processes have been used effectively for many years in commercial applications in North America (Akcil & Mudder, 2003).

Cyanide contains two of the most important elements necessary for bacterial growth, namely, carbon and nitrogen. Thus cyanide waste can be used for biological purposes. Several species of bacteria can convert cyanide, under both aerobic and anaerobic conditions, using it as a primary source of nitrogen and carbon. It is known that other organisms are capable of oxidizing the cyanide related compounds of thiocyanate and ammonia under varying conditions of pH, temperature, nutrient levels, oxygen, and metal concentrations (Akcil & Mudder, 2003). Iron and sulfide can be microbially oxidized to produce ferric iron and sulfuric acid, and these chemicals convert the insoluble sulfides of metals such as copper, nickel and zinc to soluble metal sulfates that can be readily recovered from a solution. Although gold is inert to microbial action, microbes can be used to recover gold from certain types of minerals because, as they oxidize the ore, they open its structure, thereby allowing gold-solubilizing chemicals such as cyanide to penetrate the mineral (Rawlings, Dew, & du Plessis, 2003).

All water bodies containing cyanide are hazardous to wildlife. Therefore, if cyanide wastes are not properly managed, they can result in tremendous damage to animals, crops, and humans. Accidental spills of cyanide solutions into rivers and streams have produced massive kills of fish and other aquatic biota. Freshwater fish are the most cyanide-sensitive group of aquatic organisms tested, with high mortality rates documented at free cyanide concentrations  $>20$  ug/L and adverse effects on

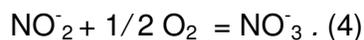
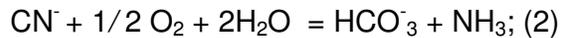
swimming and reproduction at >5 ug/L. Exclusion from cyanide solutions or reductions of cyanide concentrations to nontoxic levels are the only certain methods of protecting terrestrial vertebrate wildlife from cyanide poisoning. If the gold mining industry wants to continue developing, it will have to increase both its knowledge and incorporation of the following remedies: a) effective cyanidation process according to different rock types in order to reduce acid-cyanide emissions during the cyanidation treatment, b) in cyanide waste treatment, a recovery or recirculation system to avoid environmental contamination, c) the use of microbial technologies during the cyanidation process for sand pre-treatment and reduction of cyanide, as well as waste treatment, and d) a new technologically feasible approach to recovering other minerals in the cyanidation process.

In the presence of microorganisms and oxygen, cyanide will undergo degradation through an aerobic biological process. Cyanide also degrades biologically through anaerobic processes, although much more slowly. Biological treatment of cyanide has been shown to be a viable and robust process for destroying cyanide in the mine process water. The classic aerobic biological process involves two separate bacterial oxidation steps to facilitate complete assimilation of the wastewater (Akcil and Mudder 2003).



The first step in this biological treatment process is the oxidative breakdown of cyanides and thiocyanate, and subsequent absorption and precipitation of free

metals into the biofilm. Cyanide and thiocyanate are degraded to a combination of ammonia, carbonate, and sulphate (Mudder *et al.* 1998, Whitlock & Mudder 1998).

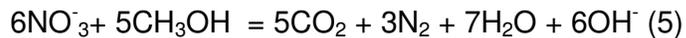


The second step converts ammonia to nitrate through the conventional two-step nitrification process, with nitrite as the intermediate. Various *Pseudomonas* species are responsible for complete assimilation of the wastewater, including oxidation of cyanide, thiocyanate and ammonia. In the destruction process, either chemical or biological reactions are utilized to convert cyanide into less toxic compounds. The aerobic and nutrient rich environment promotes the growth of the microbial population, which is capable of uptake, conversion, sorption, and/or precipitation of thiocyanate, cyanide, ammonia, nitrate, sulfate, and metals (Whitlock and Mudder 1998). Some of the organisms known to oxidize cyanide include species of the genera *Actinomyces*, *Alcaligenes*, *Arthrobacter*, *Bacillus*, *Micrococcus*, *Neisseria*, *Paracoccus*, *Pseudomonas*, and *Thiobacillus* (Given *et al.* 1998). Thiocyanate and cyanide can serve as an organic carbon food sources during their degradation stage, but are toxic to the nitrifying bacteria in elevated levels. At the same time, the breakdown product, ammonia, along with carbonate and bicarbonate alkalinity, serves as a food source for the nitrifying bacteria. An upset in the effectiveness of cyanide degradation will adversely affect the nitrification stage and recovery of the nitrifying bacteria is measurably slower than recovery for cyanide degrading. Thus, the rate-limiting factor incorporated into the treatment plant design is based on the

slower metabolism of the nitrifiers (Akcil and Mudder 2003). Waste water is usually considered a negative issue, but it can also be seen as a positive aspect if its nutrients are used as irrigation for agriculture soil and aquaculture. Nitrogen from cyanide destruction could probably play an interesting role in this respect, either through the incorporation of inorganic nitrogen or enhancing primary productivity in soil and water. The approach of leeching such valuable nutrients into soil and water in areas of high mining activity could be an alternative for integrated management.

Research indicates that micro-organisms convert nearly all of the cyanide carbon to CO<sub>2</sub> and bicarbonate and the majority of nitrogen to ammonia, nitrite, and nitrate (Nesbitt *et al.* 1960). *Because the pseudomonas* species are particularly effective at cyanide degradation, they form the basis of most commercial applications. The enzymatic makeup of the site-specific and patented *Pseudomonas* species can convert cyanide into less toxic compounds through biological reactions, while using thiocyanate and cyanide as the sole nitrogen and carbon sources. Ammonia and carbonate are obtained as breakdown products under appropriate conditions (pH, temperature, population of bacteria, concentration of cyanide etc.).

If treatment is properly managed, cyanide conversion could effectively reduce the risk to wildlife. However, the end result of its degradation is the presence of nitrates, which could enhance not only the eutrophication of the water but could also cause a problem in drinking water, if higher levels of nitrates are found. When cyanide is degraded biologically, in order to avoid nitrates, carbon and nitrogen must be released to enhance the biological metabolism. In this process, methanol is added as an organic substrate and the nitrate is converted biologically to nitrogen gas, as shown in the following equation(Akcil and Mudder 2003):



Oudjehani *et al* (2002) assessed the natural attenuation potential of cyanide via biodegradation and found an absence of biodegradation in old tailings, due to the presence of strong metal-cyanide complexes. In another study, Zagury *et al* (2004) found there was a natural attenuation of cyanide via physicochemical and biological process in old and fresh tailings.

On the other hand, Shehong *et al* (2005) found that the natural degradation of cyanide conforms to a negative exponential equation not only in the tailings impoundment, but also in the second wastewater pond—and even in the receiving streams, if the dilution action from other streams was deducted. Therefore, they suggest that the best way of decreasing the cyanide's impact on the streams is to increase the rate of recycled water, so that the lower the wastewater levels in both the tailing impoundment and the second wastewater pond, the lower the amount of leakage of wastewater into the streams. It has been found that the more reactive cyanide species initially associated with the solid tailings degraded naturally within the mine tailings impoundment area, resulting primarily from volatilization (decrease in pH), leaching, and bacterial degradation Zagury *et al* (2004).

According to Eisler & Wiemeyer (2004), the cyanide extraction of gold through both the milling of high-grade ores and the heap leaching of low-grade ores requires the cycling of millions of litres of alkaline water, containing high concentrations of

potentially toxic sodium cyanide (NaCN), free cyanide, and metal-cyanide complexes.

Hydrogen cyanide is a high volume production chemical that causes severe environmental problems, particularly with regard to agriculture associations. Interestingly, however, it has been found that some vegetables are able to remove cyanide from gold mining wastewaters (Larsen, et al 2004).

Botz and Mudder report on cyanide mining incidents, involving the release of tailings slurry or solution (Botz and Mudder 2002). The major environmental impacts of cyanide have been associated with short-term effects leading to injury and mortality of aquatic life. As with all mining-related environmental incidents throughout the world, the major causes having been related to the water management or engineering aspect of tailings dams. There have also been some cyanide-related deaths that were neither reported in the general literature nor widely publicized. All published accounts of human deaths due to mining related environmental incidents relate to some form of physical inundation with tailings materials. It also appears that the major mining-related environmental incidents have not been concentrated in any geographic location, are likely to occur regardless of the size of the company, and do not occur more frequently with a specific type of mining activity (Cyanide Management Australia 1998). Furthermore, most major incidents have been the result of some sort of dam overtopping, breaching, geotechnical failure, or earthquake. In the context of cyanide treatment and recovery, a number of technologies have been widely demonstrated to reliably control cyanide levels in mining solutions. With proper use of these technologies, cyanide concentrations in

tailings can be maintained at levels protective of wildlife, while reducing the potential for severe environmental incidents (Editorial jclepro 2006). Although cyanide treatments are well known in first world countries, developing countries are still affected by the amalgamation and cyanidation practices of mining operations.

### **Governance, knowledge transfer and participatory development**

According to Akcil (2003), the goal of any Cyanide Management implementation plan should not be to create more regulations but to utilize the operational experience and technical expertise associated with the various cyanide management programs and codes of practice already extant to formulate a single document for global application. In fact, since artisanal small scale miners are turning from amalgamation to the cyanidation process, they should be aware of these implications for management practices. At the same time, adherence to these codes and management plans is not only essential but also requires the acceptance of an alliance and association of the many stakeholders and stockholders involved. This shortcoming notwithstanding, the adoption, acceptance, implementation, and enforcement of existing regulations, standards, codes of practice, and management plans are the keys to minimizing the environmental impact of cyanide use in gold mines (Cyanide Management Australia 1998).

Hilson (2006) addresses the problem of mercury and the need for new policy regarding small scale mining in Ecuador. Based on his observations of the Ecuadorian situation, he states that the mercury pollution problem will not be resolved until governments and donor agencies commit to carrying out research

aimed at improving understanding of the dynamics of small scale gold mining communities. Acquisition of this basic knowledge is the key to designing and implementing appropriate support and abatement measures to address this important issue in the Ecuadorian context. There is valuable traditional knowledge in the Ecuadorian gold mining community that must be studied and incorporated into any local development plans for learning and technology transfer. However, Government Policies that promote foreign investment in the mining sector, in order to establish a large scale, more technologically advanced form of mining in the country, would create conflict with local communities and miners.

Regarding environmental degradation Muezzinoglu (2003) summarizes the basic information known about the environmental impact of the use of mercury and cyanide in gold production, both past and present. He suggests that this activity should be carefully regulated by means of global directives based on an up-to-date knowledge of ecotoxicity principles and modern environmental standards.

Gold mine tailings management is another issue that needs attention. We must consider the technical measures and policy initiatives needed to improve environmental management in the Portovelo-Zaruma mining district of southern Ecuador. In this area, gold is mined by a large number of small-scale and artisanal operators, such as miners, millers, and processors. Discharges of cyanide and metal-laden tailings have had a severe impact on the shared Ecuadorian-Peruvian Puyango river system. Toxic acids are currently emitted into the atmosphere in the local environment. Celik *et al* studied the feasibility of the utilization of the tailings as an additive material cement production in Portland (Celik, Elbeyli, & Piskin, 2006),

while others have considered the use of the water hyacinth *Eichhornia crassipes* as a useful tool in treating cyanide effluents from small scale gold mines (Ebel, et al 2006). Indeed, it's possible that cyanide could even be removed by the water hyacinth because of its high biomass production, wide distribution, and tolerance to cyanide (CN) and metals. It also has been reported that waste rock from mining operations could be directly revegetated, if properly neutralized, fertilized, and amended with organic matter (Sydnor & Redente, 2002). It seems an accepted fact that mining practices will remain for as long as there are minerals available for extraction. If managed sustainably, mining activities can contribute vastly to the world economy, the wealth of individual nations, and the livelihoods of many communities.

The management of tailings in the Artisanal Mining industry in Ecuador could take a communal approach, in which all operators are connected to one central tailings impoundment, which would not only require agreement among a large number of operators but also that miners must move away from rudimentary operations towards bigger, mechanized, and longer-term sustainable operations (Tarras-Wahlberg, 2002). In order to achieve such a scenario, however, some kind of association or cooperative is needed for the small scale mining sector, as well as participatory management of the whole ecosystem, including downstream land users. This would necessitate cooperative environmental management to share control and responsibility of waste management. While the provision of technical solutions in Ecuador is feasible, since the actual technology is quite appropriate, both environmental regulations and environmental impact assessment must also be reviewed and technically analysed. The enforcement of existing regulations must be

improved, which could be achieved by the strengthening of the central authority charged with supervision and control of mining activities. Good governance will require the both local and provincial governments to take responsibly and encourage local public participation in environmental management. Ecuador would need a clearly defined policy for concessions, land rights, and environmental regulations. The reorganization of small operations into a medium-sized units or cooperatives would give the small scale miners the strength they need to sustain rational exploration, while meeting environmental obligations.

Since artisanal scale mining is a complex operation, knowledge transfer, participatory development, and public involvement are important and will play a key role in environmental risk analysis and decision making. Theoretically, while the participation of stakeholders is crucial and seemingly easy to manage in order to achieve a transfer of knowledge, in practice, it would be quite complex and fraught with difficulties, including the intention to connect experts with laypeople and other interested parties. The attempt to reconcile so many different values and positions could lead to a system that is too complex and multidimensional to get anything done. A review of existing reports about risk assessment reveals that, not only are most environmental risk studies concerned only with the technical aspects of Environmental Impact Analysis, but also that, even though such studies are carried out in developing countries, they are usually performed without the participation of the community or the involvement of the stakeholders. Other related articles show not only that expert opinions on a particular issue are often based on minimal information regarding risk analysis, but also most decisions are made without taking into account the needs, views, experience, or traditional knowledge of the local

people who have been connected with the environment for a long time. Although the opinions of both the public and the stakeholders are important, the powers that be often make risky decisions, depending on the geographical, social, political, and economical situations of the stakeholders and the communities. Hence, it is necessary to achieve a rational strategy for public involvement in environmental and/or risk assessment projects and to look at mining issues within a regional framework, in order to achieve sustainability in each region.

The main feature of this approach, in the context artisanal gold mining, is the participation of different stakeholders and integration of data and models to support policy makers. Factors such as power systems, property rights, politics, geographical boundaries, and levels of education in communities, all play a role in the decision-making process and could have very different outcomes for different communities, particularly in developing countries. Furthermore, how information and knowledge are distributed and their target's abilities to understand it are two more major factors that must be considered in the decision-making process. This is an important point because, in reality, we need to develop special strategies for addressing the process of environmental risk management in countries that lack the institutional, political, and technical capacities to overcome the problems the risk analysis is designed to address.

Furthermore, environmental impact or risk analysis research is currently achieved at the source pollution site, i.e., the artisanal gold mining frame. However, beyond that source pollution site, we would point out that, in the developing world, there is a need to scope the problem from a multi-scale point of view, and the

necessity to interconnect different parties with different points of view, in order to achieve a win-win solution. By this I mean that it is not possible to talk about the risks of one source of pollution to the environment without first considering what unique factors are creating the risks to that Area. Most productive systems in the developing world are connected with other systems. For example, many mining operations are situated in geographical positions above agricultural and aquacultural systems, such as fisheries, which are in geographical positions below the agricultural sector. While each industry has its own interests, they are interconnected ecologically. What is needed is a useful analysis of ecosystems on a regional scale (Grajan et al 1991) that allow us to identify the shared values among interested parties, such as in the case of both large and small-scale operators in the mining, agriculture, and aquaculture industries in the same region. This would provide a constructive analysis for regional sustainability and interrelations with others. The issue of crossing boundaries, for example, would have particular relevance for the interrelationship, tolerance, and respect among different groups of people or communities. In the attempt to address such complexity, it appears that a tradeoff analysis is the best option for finding possible common interests among all parties. Only by looking at the impact of the effects of these industries on a large landscape, as well as establishing rational objectives in the form of tradeoffs, can the risks be properly evaluated over time and space. In the context of stakeholder involvement, it is important that we find environmental policies that address the issue of sustainability.

Moreover, we need more information, more efficient public institutions, and well trained personnel in order to evaluate the impact or perform a Risk Assessment.

Finding funding and good people to manage such funds will be also an important step in achieving the transparency necessary for a good process, in both research and development projects. In most cases, these institutions are forced to behave in ways that not only do not benefit the environment or the community but often harm themselves, due to the structure of government institutions. Looking at the issue of stakeholder involvement in the environmental impact assessment and the decision making process in developing countries, is imperative to find new ways to communicate and to build a road that leads to a change of attitudes regarding mining issues and other interconnected or related activities. However, if we fail to address these enormous problems, all these issues will only increase uncertainty at the moment of truth, when the information is being weighed by researchers. Before an impact assessment can be an effective tool, a process is needed establish an essential investment in institutional capabilities throughout the developing world (Antle et al 2002). Even without all this, we could construct alternative ways for connecting interested parties and looking for values of common interest at all levels, with particular attention to the ecosystem as the most valuable resource.

Due to the relevance of involving policy makers, public stakeholders, local communities and scientists, the Tradeoff Analysis process is an appropriate approach. From it, we can extrapolate the need for a three-step research project. We need to: 1) identify the sustainability criteria, 2) formulate a hypothesis regarding potential tradeoffs, and 3) identify disciplines for the research project. In a country like Ecuador, with the conflict between mining resources and other land activities affected, we need the kind of tradeoff analysis that would involve the project's design and implementation, incorporating important goals like: identifying models and data

needs; defining units of analysis; collecting data through intra-disciplinary research; and integrating disciplinary findings and construction of tradeoffs. It is important to note that the situation in developing countries demands an alternative to—or variation on—these established processes of risk perception and tradeoff analysis, which should implement an ongoing learning component for all parties involved, as a way to develop a solid foundation to build on for assessing the impacts of future projects. Not only must we evaluate the impact of said projects by how much is produced in terms of value, but we must begin to take social responsibility and accountability more seriously. Indeed, communities must be seen as partners in the process rather than as research tools.

The use of Tradeoff Analysis and participatory development through a regional or shared process would not only be a better way to achieve the desired goals more realistically, but would also give us more confidence in the process, instead of the uncertainty with which it is now plagued. Not only should the Tradeoff Analysis be based on selective sustainability indicators for one pollution system, but it could actually provide the means of finding indicators for the health of the ecosystem and its consequent effects on human health, with particular emphasis on the complex issues that arise from the interactions of different interested parties in productive systems.

In conclusion, all mining operations, whether artisanal, medium, or large scale, have strong negative impacts in developing countries on a large scale, from soil erosion, sedimentation, dumping contaminants (mercury and cyanide), rock weathering, heavy metals, and acid rock drainage, all of which particularly affect

water quality, which, in turn, affects local and large ecosystems and compromises biota and human health. Hence, there is a pressing need to focus on this complex problem on a broader scale, while instituting the participation of all the various stakeholders and communities in order to achieve responsible, cooperative management of resources that is tailored to both to the specific sites and to the socio-political and economic conditions of each country.

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