



# RATE OF UPTAKE AND DISTRIBUTION OF Hg IN DISSOLVED ORGANIC CARBON COMPOUNDS IN DARKWATER ECOSYSTEMS BY ICP-MS AND ENRICHED STABLE ISOTOPE SPIKING

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## **Abstract:**

*The role of natural organic acids on mercury binding, transportation, net uptake rates and possibly net methylation rates will be evaluated by tracing these processes with isotope enriched mercury and ICP-MS technology. The correlation between dissolved organic matter and Hg in waters is well documented. It appears that organic acids can react with mercury residing in or emitted from different sources such as soils (particularly hydromorphic soils), laterites, natural degassing, forest fires, fuel combustion, gold mining activities, etc. to form soluble Hg-organo-complexes. The formation of these complexes is believed to greatly enhance Hg transport and be an important preliminary step in the formation of Methyl-Hg and biological uptake. The rates of these reactions and the key organic compounds involved in mercury binding will be determined by reacting isotopically-enriched Hg with samples containing a variety of concentrations and types of organic acids and subsequently analysing both reactants and organisms exposed to the reactants (bioassays) for Hg isotopes by ICP-MS. The Hg spike will allow the precise determination of rates of uptake and the most active agents of uptake. Initially, the method will be used to examine total Hg uptake and distribution but if technological limitations are overcome, this same approach can be used to determine net rates of methylation and net MeHg uptake.*

*After the method is validated the experimental design can be altered to test the relative effects of such things as the addition of CO<sub>2</sub> (pH change), or adding a substrate such as Fe-Mn oxyhydroxides. The addition of synthetic materials such as mulched automobile tires, can also be tested with the goal developing a pragmatic remedial method for Hg containment. Ultimately, this research should contribute to an understanding of mercury mobilization, transport and bio-concentration mechanisms, and provide a basis for developing management and treatment strategies. Emphasis will be on the mercury bioaccumulation processes occurring in abandoned and active gold mining areas, where mercury has been misused to amalgamate gold but will also investigate pristine dark water ecosystems which have recently been shown to play the major role in the natural Amazonian Hg cycle.*

## **1. SCIENTIFIC BACKGROUND**

### **1.1. Artisanal Mining**

Mercury has been used in gold and silver mining since Roman times. With the invention of the 'patio' process in Spanish colonial America, silver and gold were produced in relatively large volumes, mostly in Americas but also in Australia, Southeast Asia and even in England. Mercury released to the environment from this process is estimated to be on the order of over 260,000 t from 1550 to 1930, at which time silver reserves in Spanish colonial

America were essentially exhausted and the Hg amalgamation process was replaced by the more efficient cyanidation process. Huge increases in gold prices and worsening socio-economic conditions in the developing world during the 60's and 70's, galvanized a new gold rush in the southern hemisphere, involving an estimated 10 million people. Presently, Hg amalgamation is the preferred method used in gold production in the South, particularly in the Amazon basin, China, Southeast Asia and in some African countries since it is simple, effective and cheap. Artisanal mining represents a significant livelihood for many rural communities in 40 countries in which 30 different substances are exploited. Worldwide, gold is the main mineral exploited by almost 6 million workers (Veiga, 1995). In Latin America, over 1 million people are producing somewhere between 115 and 190 tonnes/year of gold and emitting at least an equivalent amount of mercury due to poor amalgamation practices. Mercury inputs to the environment from this activity are estimated to reach up to 460 tonnes/y and account for approximately 10% of global anthropogenic Hg emissions by Lacerda (1997). This figure is still disputed but certainly is the correct order of magnitude.

### *1.1.1. Mercury in Brazil*

The Tapajós River Basin in Brazil has been mined for placer gold by garimpeiros (farmers turned gold miners) since the 1950s. Activity increased in the 1960s in the tributary Marupa which ultimately prompted the gold rush of the 1970s when an estimated 100,000 garimpeiros worked the gold rich alluvium in the Tapajós Basin. During those high times, rumours abounded of extraction rates by single workers of up to 2 kg gold/day. One particularly fortunate garimpeiro is said to have owned 16 aircraft. Gold mining activity peaked around 1978 when gold was trading near \$800US/ounce. During this era the infamous Sera Pelada (naked hill) deposit was exploited in the Carajós region of Pará. Social turmoil prompted the government to attempt to establish a system of regulation but this failed primarily because garimpos (the small scale gold mines) were still constitutionally illegal. The antiquated constitution gave farmers ownership of the land surface only while the subsurface remained the exclusive property of the government. For example a farmer could not sell water from a spring on his land without governmental permission, which could be arbitrarily denied. As rich deposits were exhausted, garimpeiros migrated to new and more remote areas leading to the establishment of over 300 airstrips in the Tapajós basin. Under such conditions the government agency responsible for regulating mining activity DNPM (Departamento Nacional de Produção Mineral) realised that existing regulation systems were futile let alone unfair and so in an attempt to bring the garimpeiros back into contact with the government, legal status for garimpos was considered. In 1988 a constitutional change allowed the introduction of the PLG (permissão lavra garimpeira) which allowed garimpeiros to establish and operate garimpos legally for the first time and the Reserva Garimpeira was established to protect the land holdings of garimpeiros in the Tapajós Basin. Within this special area, mining companies cannot stake claims without negotiating with the affected garimpeiros as was formerly allowed. This has stabilized both the society of the garimpeiros and their relationship with the Brazilian government sufficiently to allow collaboration on addressing the environmental problems associated with garimpo style mining, namely, river siltation and toxic mercury pollution.

Mercury (Hg) based extraction techniques are very commonly used by garimpeiros to extract the very fine gold particles found in the paleo-river sediments and consequently, the potential of toxic Hg pollution and accumulation in the food chain has become a concern. Mercury escapes to the environment during two distinct phases of the gold (Au) extraction: (1)

sediment is aspirated from river bottoms or washed from laterite deposits to form a sluice to which Hg is added to amalgamate the Au. The amalgam is then collected by a variety of separation techniques (hand squeeing, centrifuge, Hg plated copper...). Some of this Hg inevitably escapes with the effluent. Estimates range from 5-40% (Malm et al., 1990; Malm et al., 1995; Nriagu Jerome O et al., 1992; Martinelli et al., 1988) but it certainly less now than it was during the early period of the boom when garimpeiros put Hg directly in the sluice boxes; (2) The collected amalgam is heated to evaporate the Hg leaving a precious metal residue. Depending on the technology used, some or all of the evaporated Hg escapes to the atmosphere. The Hg:Au ratio used in Au extraction ranges from a minimum of 1.3:1 to a maximum of 10:1 (Martinelli et al., 1988; Pfeiffer et al., 1991) and so a poorly constrained estimate of the amount of Hg used in gold mining can be estimated from total Au production (Brazil produces roughly 50 tonnes of Au/year, mainly from the Amazon basin). Emissions of Hg to the atmosphere in Brazil have been recently estimated by Lacerda (1997). He estimates that total emissions reach approximately 116 tonnes/y. Of this, chlor-alkali production, represents 10.1%, the paint and dye industry, electronics manufacturers, and energy production from biomass and fossil fuel burning, account for less than 0.5%; smelting of Pb, Zn and Cd, accounts for 3.9%; and steel and iron production may emit up to 10.4%. Burning of natural vegetation to clear agriculture lands may represent an important diffuse source of Hg to the atmosphere in Brazil and is on the order of 7.5% of the total. That leaves gold mining. It is presently the major source of anthropogenic Hg to the atmosphere in Brazil averaging 67.3% of the total annually. Mercury emissions from gold mining are more or less restricted to the Amazon region which results in emission per area rates of approximately 16 g/km, larger than in industrial areas.

Air, soil, water, bottom sediments, fish, plants, bird feathers, and human hair and urine have been analysed by researchers attempting to map Hg pathways, concentrations, and critical exposure situations. (Akagi et al., 1995; Akagi et al., 1995; Boas, 1997; Boischio et al., 1995; Barbosa et al., 1995; Cleary, 1990; Hacon et al., 1997; Hacon et al., 1995; Lacerda and Marins, 1997; Lacerda et al., 1993; Malm et al., 1995; Malm et al., 1990; Martinelli et al., 1988; Melamed et al., 1997; Palheta and Taylor, 1995; Pfeiffer et al., 1991; Pfeiffer et al., 1989; Rodrigues and Maddock, 1997; Reuther, 1994; Von Tumpling Jr et al., 1995). Not suprisingly, elevated Hg concentrations have been detected. Malm (1995) summarized that people working in gold dealer shops are the critical group concerning Hg<sup>0</sup> risk due to inhalation of vapours, whereas riverine communities which consume Hg contaminated fish are the risk group with respect to methylmercury. However, due to detection limit constraints and rapid dilution in the environment, Hg contamination has been difficult to detect in carrier media - riverine sediments, river water, and in the atmosphere - beyond the localized heavy Hg contamination zones.

Other sources of pollutive Hg in the Amazon basin are mine tailings, biomass burning, deforestation, and agricultural landuse (Hacon et al., 1995). Veiga et al (1994) estimated that 90 tons Hg/a are released to the atmosphere in the Amazon by biomass burning although this was disputed by Lacerda (1995) who estimated it to be less than 17 tons Hg/a. Recently, Roulet et al (1998) have turned attention to natural sources of Hg in the Amazon and have suggested that perturbations of this source by landuse is the dominant control on Hg in Amazonian Waters and that Hg loading to the Tapajós river was unrelated to upstream gold mining operations. Telmer (1999) has confirmed that the source of Hg in the Tapajós river is natural but also states that, contrary to Roulet et al., gold mining is by far the dominant cause of increased suspended sediment loading to the river and that deforestation and agriculture are

at best secondary sources. This has major implications for remediation and prevention. Simply halting the use of mercury is surely a step in the right direction but regional mercury pollution will only be reduced when the dredging is stopped or contained.

## **1.2. Targeted Study Area Background**

Many regions in the Amazon face enormous social and environmental problems derived from recent gold rushes that left highly contaminated areas and no economic alternatives for local communities living on these sites. Cachoeira do Piriá, in the Eastern part of Pará State is an example of this unfortunate situation. The easy access to the area and the abundance of alluvial gold attracted more than 3,000 artisanal miners over the last two decades. The wealth produced during the golden years of mining, however, was unfortunately squandered, and has left a legacy of environmental damage and an impoverished village. In spite of this the municipality of Cachoeira do Piriá was created in 1996 and its inhabitants continue to struggle to eke out a subsistence from agriculture and gold mining. News of a new gold rush in the region (Fogão) and a new government policy distributing agricultural plots to the landless, has recently attracted more people to the region and exacerbated the situation.

## **2. ONGOING RELATED WORK**

### **2.1. Tailings in Cachoeira do Piriá, Eastern Pará, Brazil; Marcello Veiga (UBC) and Terezinha Cid da Souza (DNPM)**

Preliminary monitoring programs conducted jointly by the Brazilian National Department of Mineral Production (DNPM) and University of British Columbia (UBC) in Cachoeira do Piriá have detected high mercury levels in sediments of the drainages reaching Igarapé do Macaco, a darkwater tributary of the Piriá River and source of fish for the region. Mercury contaminated tailings are widespread as a result of misuse of mercury in the amalgamation process, use of copper plates to amalgamate whole ore, and inappropriate disposal of tailings into the creeks. Residential occupation of former open pit mines, building houses on top of contaminated tailings and using water and fish from the polluted drainages have worsened health hazards considerably.

### **2.2. Emissions of Sediment and Mercury in Amazonia, 1970-2000 as Determined from Space; Kevin Telmer (Uvictoria) and Maycira Costa (Instituto Nacional de Pesquisas Espaciais (INPE), Brazil)**

Hydraulic mining in the remote regions of the Amazon dump huge amounts of river bottom and river bank sediment into the otherwise naturally clear flowing rivers, rendering them the colour of coffee and milk (Telmer, 1999). Samples collected from the impacted region in 1997/98 show a strong relationship between the concentration of suspended sediment and riverine mercury – a potential toxicity problem for the fish eating riparian communities in the region. The suspended sediment load is visible with LANDSAT imagery (Telmer et al., 1998). Contrary to former belief, the sediment erosion and not the miner's use of mercury seems to be the cause of the mercury problem. Satellite imagery has great potential to reconstruct historical mining activity, useful for locating impacted areas and

estimating historical mercury fluxes and, perhaps more importantly, to monitor present and future mining activity. To accomplish this LANDSAT data for the Tapajós River Basin, Pará, Brazil for the period 1975-2000 has been acquired. "Cloudless" scenes dating from 1975 through to 1995 will augment the 1997 scenes already in possession to form a time series of imagery. A supervised classification using a maximum likelihood algorithm effectively links the "ground truth" collected in 1997 to the concurrent satellite images. This relationship will now be extrapolated to other images and other times in order to reconstruct the sediment and Hg emission history and well as monitor future mining activities.

### **2.3. Sources and fate of lead and mercury in lake sediments: combining isotopic and sequential extraction evidence. Part of the Multi-disciplinary study of metal cycling, primarily Hg, in aquatic and terrestrial environments, Toxic Substances Research Initiative (TSRI) sponsored by Health Canada.**

Lead and mercury, along with other metals, often has an upcore enrichment trend in many freshwater lake sediments which has been interpreted as the result of modern atmospheric pollution at both a global and regional scale. Lake sediments in Kejimikujik Park NS, exhibit this same trend generally, however, the degree of upcore enrichment is highly variable, some showing little enrichment and others enrichments of 2 to 100 times. This is contrary to simple atmospheric deposition models that predict less variable enrichment. Why is Beaverskin Lake so much more enriched than Big Dam East? Preliminary results from Kejimikujik Park collected in 1998 clearly illustrate the problems with the atmospheric models and provide evidence for the increasingly accepted theory that the distribution of metals with depth in lake sediments must reflect not only depositional history but post-depositional diagenetic processes caused by physiochemical and biochemical processes as well (microbial decomposition, bioturbation, molecular diffusion, porewater advection...). The isotopic composition of lead and an understanding of where that lead is held in the lake sediment matrix, determined by sequential extraction, is a powerful technique to assess the original source of lead, and its depositional and postdepositional history. Anthropogenic versus natural lead inputs to the environment can be quantitatively described with such data. Sequential extraction techniques can also be successfully applied to Hg in lake sediments, isotopic methods are more difficult with Hg but can be investigated.

## **3. PREVIOUS RELATED WORK**

### **3.1. Mercury in the Tapajós River Basin - The Significance of Suspended Sediments from Alluvial Gold Mining, Pará, Brazilian Amazon;**

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The Tapajós River Basin (Figure 1) resides entirely within the southern Amazon Basin in Brazil. With a mean discharge of 7,200 m<sup>3</sup>/s (Gleick, 1993) and a drainage area of 520,000 km<sup>2</sup> (determined by GIS) it is one of the larger tributaries of the Amazon River. The Crepori River is a medium sized tributary of the Tapajós River with a drainage area of roughly 50,000 km<sup>2</sup> (determined by GIS) and a mean discharge of 700 m<sup>3</sup>/s (minimal estimate using the area/discharge relationship for the Tapajós Basin). The Crepori River begins in pristine uplands in the central Tapajós basin, flows north bisecting the area of Garimpo activity known as Creporizão and then continues on to confluence with the Tapajós River some 250 km south of Itaituba, the largest town on the Tapajós River and the centre for the Amazon's gold economy.

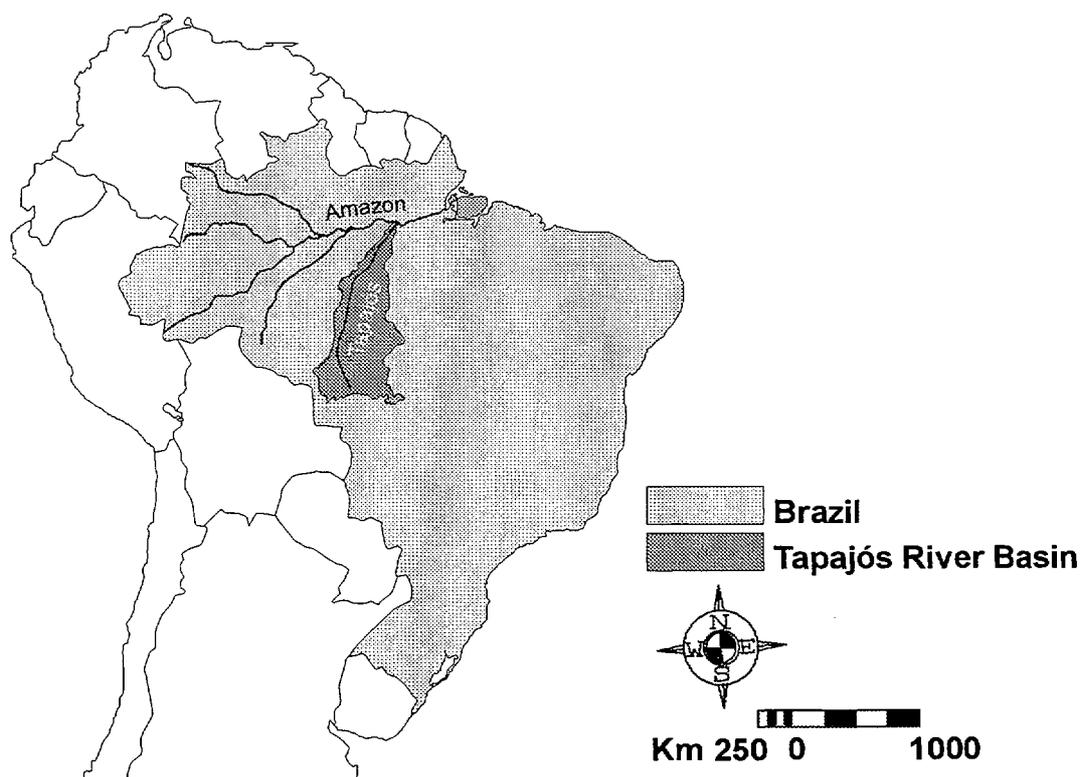


Figure 1: The Tapajós River Basin.

Water samples from the Reserva Garimpeira do Tapajós, the Tapajós River and Pristine Streams were taken along the length of rivers and from the mouths of their major tributaries at as close to one instant in time as possible - in this case 2 weeks - twice, once during low water stand in October 1997 and during high water stand in May of 1998. 51 samples were collected per campaign, not including duplicates, 29 from a 1:50,000 area surrounding the garimpeiro community of Creporizão and 21 from a larger 1:250,000 scale area also centred around Creporizão. This strategy was adopted to capture both detailed (impacted) and regional scale (background) geochemistry.

All samples are filtered through 0.45µ membranes to separate the dissolved from suspended load and are then treated and stored at 4°C (in iced coolers in the field) for chemical analyses. Water for the determination of Hg is processed immediately to avoid any

Hg loss by volatilization. Water is filtered by syringe pressure through a millipore sterivex syringe-tip cartridge filter (durapore membrane cat. no. SVHV010RS) and collected as a separate aliquot in centrifuge falcon tubes that have been pre-injected with a precise amount of BrCl by pipette to stabilize and oxidize all Hg species to Hg<sup>2+</sup>. In this case 0.75ml of a 1:5 solution of BrCl was used to create a final BrCl sample concentration of 1%. Samples collected for anion analysis are filtered through the same sterivex cartridge as that used for Hg and collected in 60ml high density polyethylene (HDPE) bottles with polypropylene closures and need no chemical preservative. The samples for determination of cations, and trace elements are filtered through 47mm-0.45u ashless mixed cellulose-ester (nitrate and acetate) millipore membranes (cat no. HAWP 047 00) by syringe pressure and collected in 125ml HDPE bottles. They are precisely acidified with strong ultrapure HNO<sub>3</sub> to a pH below 2 within 8 hours of collection. Exactly the same amount of acid is added to each aliquot by pipette to eliminate analytical noise and reduce potential contamination. The cellulose membranes from the cation aliquots (a total of 250ml of filtrate) and the residues are retained and collected in small polyethylene vials for the determination of total suspended solids. Further details on sampling methodology can be found in Telmer and Veizer (1999) and Telmer (1997).

Dissolved Hg is subsequently analysed by hydride generation and ICP-MS or by Cold Vapor Atomic Fluorescence Spectrophotometry for very low concentration samples. For the suspended load, a fixed volume of sample is pushed through 47mm pre-ignited glass fibre membrane. The membrane and its load are then analysed for Hg directly by ignition on a Milestone AMA 254 Mercury Analyser. An evaluation of Hg analyses capability using the Milestone AMA 254 can be found in Hall and Pelchat (1997). A byproduct of this operation is the determination of particulate organic carbon (POC) by LOI on the same sample.

Dissolved mercury concentrations are elevated in waters affected by mining operations when compared to concentrations in pristine rivers (Figure 2). However, essentially all dissolved mercury concentrations fall below 0.1 ppb. Mercury bound to suspended sediment tells another story. Particulate Hg fluxes average 600 and 200 times those of dissolved mercury in impacted and pristine waters, respectively, and thus, particulate bound Hg represents the major pathway of river-borne mercury (Figure 2). Total Hg fluxes in impacted waters average 15 times greater than those of pristine waters (Figure 2) but can be up to 100 times greater indicating that mining has a profound impact on transport rates of riverine Hg. However, suspended load Hg concentrations are proportional to the concentration of total suspended solids and the histogram of Hg concentration in total suspended solids (Figure 3) shows that the majority of samples, regardless of source, either impacted or pristine, have a consistent concentration of Hg suggesting that the source of mercury is the sediment itself and not mercury discharge from Garimpos. This observation is further supported by observed Hg concentrations of 50 to 300 ppb in regional laterite profiles - this is not unusual and falls within the normal range of surficial materials world-wide.

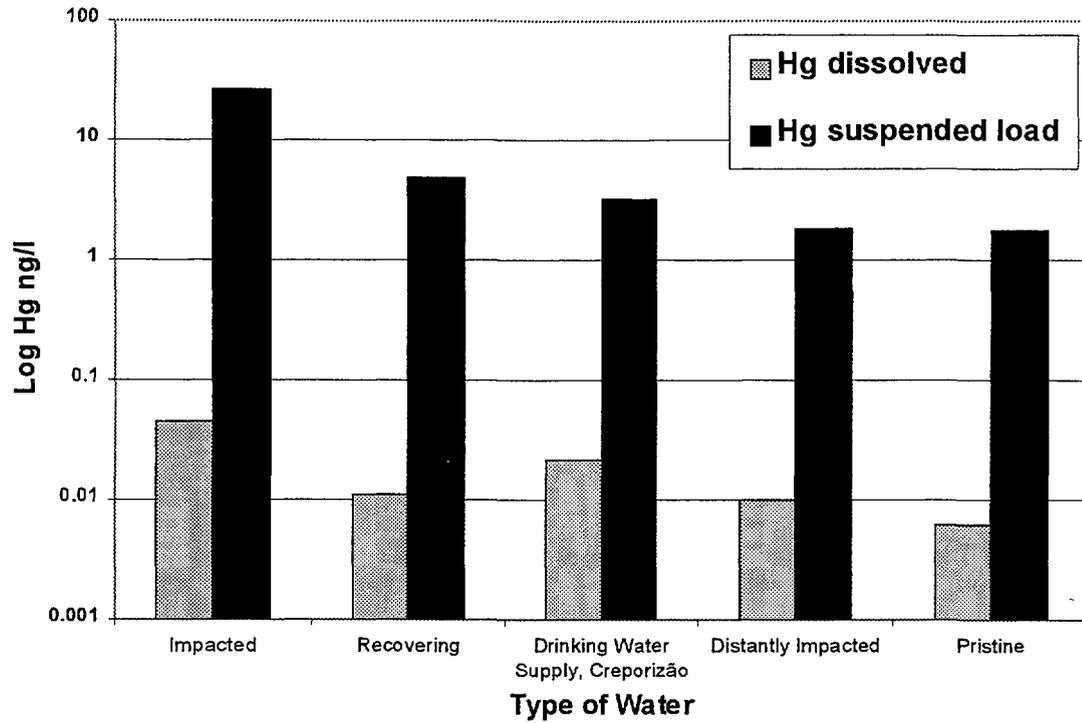


Figure 2: Burdens of Hg per litre of water in the dissolved and suspended load of (a) waters directly impacted by gold mining operations; (b) waters that were directly impacted by gold mining in the past but are now recovering; (c) the main municipal water supply in the gold mining community of Creporizão on the banks of the Rio Creporí; (d) waters that receive gold mining effluent from distant upstream tributaries (e) pristine waters.

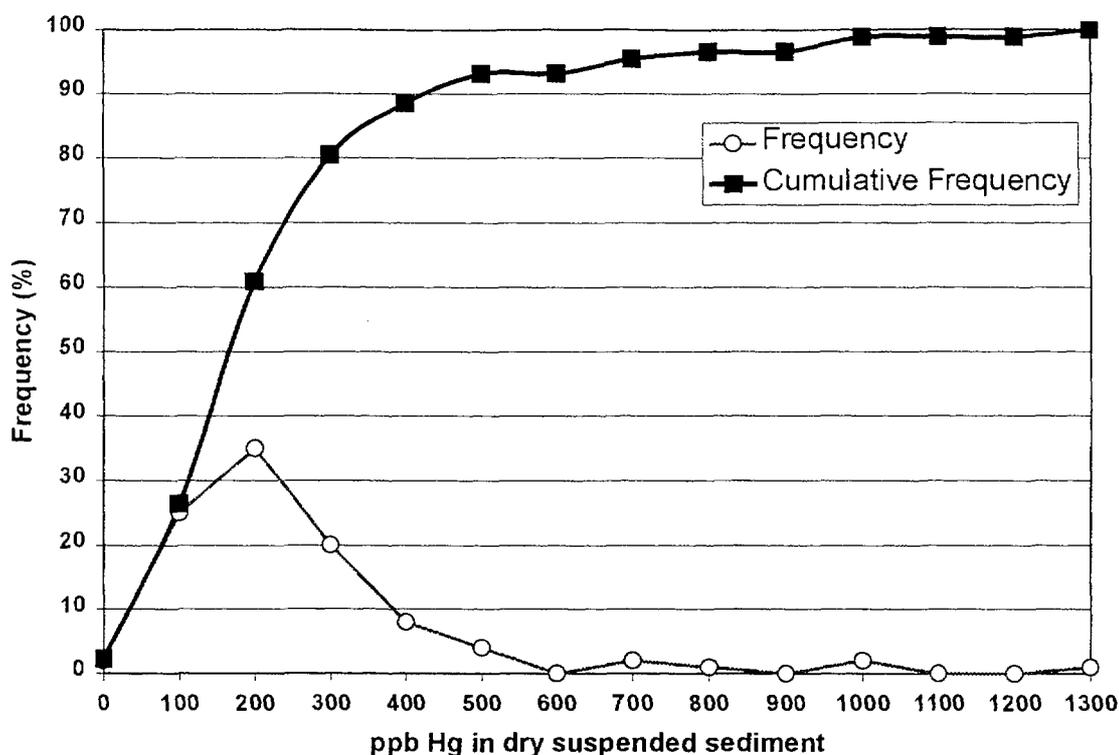


Figure 3: Frequency diagram (histogram) of the concentration of Hg in dry suspended sediment of all waters sampled in this study - 87 samples.

Roulet et al (1998) have correctly identified burdens of riverine Hg to be controlled dominantly by particulate matter but they are incorrect in their assertion that the Hg content of Tapajós waters is independent from upstream goldmining activities. On the contrary, gold mining activities are the greatest source of particulate matter to the Tapajós system. Figure 4 is an enhanced satellite image showing a suspended sediment plume with TSS concentrations of 400-600 mg/l emitting from the Rio Creporí into the Tapajós River. Background TSS concentrations in the Tapajós waters upstream of the plume are ~7 mg/l. This scenario exists for other smaller tributaries and also on a large scale in the Alta Floresta area in the upper Tapajós basin. Further these mining induced sediment plumes have been contaminating the Tapajós system for 20 years and so in basin storage of historical mining emissions of fine sediment must also be considered in any Hg source apportioning theories.

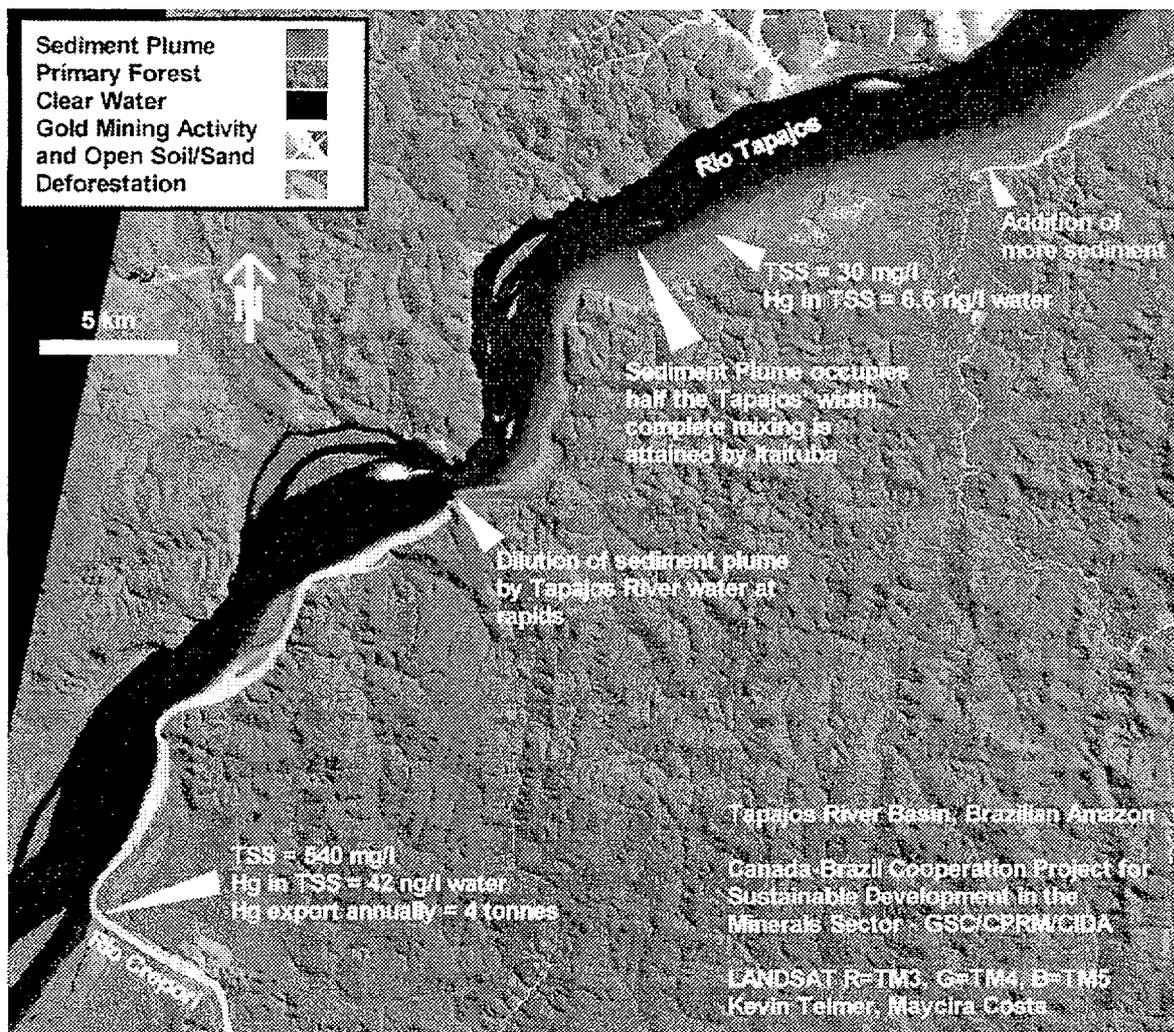


Figure 4: Landsat TM image enhanced to show the Creporí river discharging its enormous mining-induced sediment load into the Tapajós River.

Presently, Hg released by garimpeiros is almost exclusively atmospheric as mercury is no longer used directly in sluice boxes. Although a portion of the Hg released to the atmosphere may find its way back into the river, the calculated annual export of mercury from the Creporí River, 4 tonnes, is difficult to account for by Garimpo discharge alone. This is not to say that direct discharge of mercury is insignificant. Analyses of river sediments shows localized hot spots of contamination. But the regional problem - riverine mercury at 100 times background levels is dominantly caused by the enhanced physical erosion of garimpo sluicing and dredging operations than by direct mercury discharge. This has major implications for remediation and prevention. Simply halting the use of mercury is surely a step in the right direction but regional mercury pollution will only be reduced when the dredging is stopped or contained.

#### 4. SCOPE

**4.1. Is the regional source of Hg in the Amazon allocthonous, or autocthonous, and how significant are human disturbances? Tertiary ferralitic soils and modern podzolization or diffuse deposition from global anthropogenic sources?**

**4.2. Which dissolved organic substances dominate riverine Hg transportation?**

**4.3. Are the presence/absence of these substances predictors of Hg bioaccumulation?**

**4.4. How is pH related? It co-varies with DOC, are both important predictors of Hg bioaccumulation?**

**4.5. Pathway of Hg into organisms – where is it methylated? Where is it uptaken? At what trophic level?**

**4.6. Can invertebrates (worms) be used for bioassays?**

#### 5. OBJECTIVES

**5.1. Short-term objectives: Identify the dissolved organic carbon compounds such as tannic and fulvic and humic acids that most actively form soluble Hg-organo-complexes.**

**5.2. Long-term objectives: Determine the biotic and abiotic mechanisms responsible for the methylation of Hg-organo complexes in the Amazon.**

#### 6. METHODS

A very generalized schematic diagram of the method is below in Figure 5. Notably this is preliminary and does not reflect the final experimental design. In particular the separation of DOC into its constituents will have to be investigated in detail perhaps with the aid of Nuclear Magnetic resonance (NMR) analysis to first characterize the DOC. Other analysis such as C/N ratios and S content of DOC may also be useful preliminary information upon which to design the chromatographic platform.

# Analytical Method

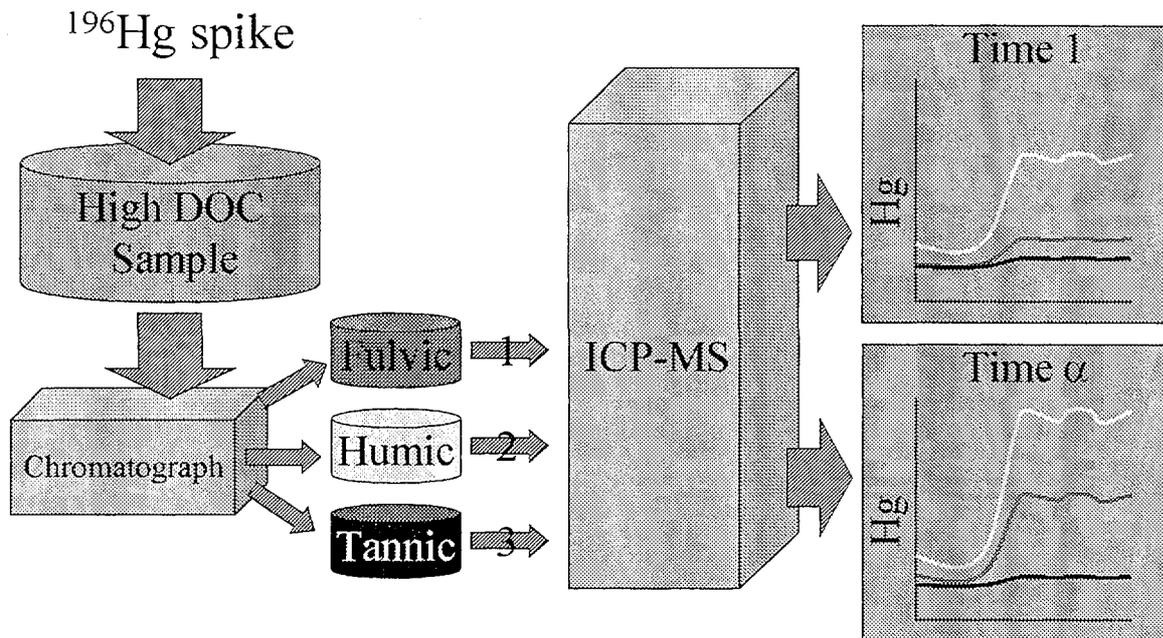


Figure 5: Analytical Method

Total mercury and mercury isotopes will be analyzed by ICP-MS in the aqueous geochemistry lab at the University of Victoria. The concentration of total Hg in solid materials will also be confirmed by "gold-trap" atomic absorption. The isotopic tracer will reveal which organic acids are the most prominent pathways of Hg-organo complex formation and their rate of uptake under the various conditions examined. Hg concentrations will also be correlated with the behavior of other elements. Functional groups of the organic complexes will be characterized by molecular size fractions and related to their Hg carrying capacity.

## 7. RESULTS AND DISCUSSION

See previous and ongoing work Section 1.2.

## 8. PLANS FOR 2000/2001

**8.1. Write research proposals to acquire financial support for a full undertaking of the CRP proposed.**

**8.2. Elaboration, and coordination of research activities and work distribution between the Universidade Federal do Pará (UFPA), Center for Research and Mercury Analysis at the Departamento Nacional de Producao Mineraiis (DNPM), University of Victoria (UV), the University of British Columbia (UBC), and the Universidad Nacional Experimental de Guayana.**

**8.3. The ICP-MS facility at the University of Victoria will purchase isotopically enriched Hg standards and run tests to determine detection sensitivity levels.**

**8.4. Dark, high DOC water from the Amazon and/or Orinoco basin, will be collected and analyzed for total Hg, DOC, and the structure of DOC.**

**8.5. Appropriate chromatographic methods will be developed and tested for the separation of DOC into its components.**

## **9. OPTIONAL PLANS**

**9.1. Incorporate rate of methylation into experimental design using  $^{196}\text{Hg}$  and simple exchange column separation of  $\text{Hg}_{\text{total}}$  from MeHg.**

**9.2. Survey of Hg and trophic level of fish in Venezuelan hydroelectric reservoirs by direct ignition atomic adsorbtion.**

**9.3. Laser ablation fish otolith experiments to determine first, if otolith structure is sufficiently homogenous at ablation scales to produce meaningful results, second, the distribution of Hg in fish otoliths from tropical and temperate fish.**

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