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Mercury in the Environment: Field Studies from Tampa, Bolivia, And Guyana

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Mercury In The Environment: Field Studies From Tampa, Bolivia, And Guyana

by

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DEDICATION

To the past, present, and future:

Reverend Otis Howard

Beulah Allen Howard

Edward McArthur, Sr.

Raymond Howard, Sr.

Ora McArthur

Leanna McArthur

Loretta Howard

John Howard

Coach Arron Prather

All of those who will be impacted positively by my work

SANKOFA!

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"Write the vision and make it plan on tablets, that he may run who reads it. For the vision is yet for an appointed time; But at the end it will speak, and it will not lie."
-Habakkuk 2:2-3-

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The storm is over ...I feel as though I can make it now. *–Psalms 18-32-38-*

“Note to Reader”

The original of this document contains color that is necessary for understanding the data.
The original dissertation is on file with the USF library in Tampa, Florida.

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ABSTRACT

Tampa (US), Guyana (SA), and Bolivia (SA), are geographically, socially, economically, and politically unique which make them ideal sites to study issues of mercury and sustainability. Mercury's innate ability to bioaccumulate and biomagnify in aquatic and terrestrial ecosystems poses a severe threat to both human and environmental health. The most vulnerable populations affected by mercury consumption include coastal communities, children, women of child-bearing age, the indigenous poor and persons with high environmental/occupational exposure factors. Communities in the regions of Florida, Bolivia, and Guyana whose diets are high in fish and are environmentally/occupationally exposed to mercury may be at a higher risk of mercury intoxication, especially in the absence of education on the topic. Mercury loadings in rivers, streams, and mine tailing waters and sediments ranged from 0.9-114 ng/L and 29-2891 ng/g, respectively; whilst fish mercury loadings were 0.02-1.034 mg/kg wet wt. Although mining sites had the highest mercury sediment and water loadings there were no significant differences when compared to pristine sites in Guyana. Fish loadings above recommended EPA/WHO regulatory limits were observed at all sites and none had signage, informational warnings or educational material available. A pilot study that included four elementary schools in Tampa showed that Water Awareness Research Education (WARE), a community based participatory environmental educational program, is a sustainable solution to addressing issues of mercury exposure.

CHAPTER 1: INTRODUCTION

1.1 Motivation and Research Objectives

The burgeoning problem related to mercury (Hg) contamination in the environment has gained worldwide attention because of its detrimental effects on human health, especially childhood developmental disorders. In fact, according to the Global Mercury Assessment Program, mercury levels have increased considerably since the on-set of the industrial age[2]. Its atmospheric residence time is approximately 0.5-2 years [3, 4] which results in a complex global cycling mechanism. Its half-life in the human body is 30-80 [5, 6] days (whole body) which is dependent on mercury species, route of exposure, dose, and sex. The primary mechanism of Hg contamination at regional and global scales is atmospheric mercury transported chiefly from coal-fired power plants and artisanal mining; however, the principle route of human and animal exposure stems from fish consumption. Mercury's ability to bioaccumulate and biomagnify in aquatic and terrestrial ecosystems poses a severe threat to the health of humans and animals [7]. The most vulnerable populations affected by mercury consumption include coastal communities [8], children [9], women of child-bearing age [5], the indigenous poor [10] and persons with high environmental/occupational exposure factors (e.g. artisanal gold miners[11, 12], jewelers, fishermen[13], etc.).

Despite governmental, federal, and international agency concerns regarding the impacts of mercury on water, soil, biota, and human health, regulations and recommendations continue to provide contradictory information as well as insufficient means of disseminating vital information, thereby potentially lessening residents' ability to make well informed consumption decisions [14,15]. Developing countries face even more challenges with monitoring and enforcement of environmental regulations to protect human health and the environment from mercury contamination.

The main goal of this research was to improve our understanding of the factors contributing to mercury exposures in three geographically unique locations, Tampa, FL; Mahdia/Iwokrama, Guyana; and Lago Titicaca, Bolivia, and develop community oriented solutions that reduce exposure. The three objectives tested along with the tasks required were:

1. Objective 1: Characterize mercury loadings in three previously unmonitored freshwater bodies that represent different geologies, demographics, and regulatory frameworks.

    - *Task 1a:* Identify and characterize suitable study sites for this work.
    - *Task 1b*: Determine levels of mercury present in fish, water, and sediments located in/near some of the most vital water bodies in Florida, Bolivia, and Guyana. All sample matrices were analyzed for total mercury concentrations. Whilst sediment samples were further characterized by BET surface area analysis, electron dispersion spectroscopy, and X-ray diffractometry. Total mercury analyses were carried out using cold-vapor atomic absorption spectroscopy (CVAAS) and cold-vapor atomic florescence spectroscopy (CVAFS).
    - *Task 1c:* Understand the geochemical conditions that affect the fate of mercury.

2. Objective 2: Compare results and conditions at study sites to determine the role of socioeconomic factors in mercury loadings.

    - *Task 2a:* Document the socioeconomic, regulatory and geopolitical factors within the United States (Florida) and Internationally (Bolivia and Guyana) through a literature review

- *Task 2b:* Identify site similarities and differences in mercury loadings and human impacts

- Objective 3: Provide an Initial Evaluation of an existing CBPR project, WARE, for its ability to increase awareness of environmental, environmental health and sustainability concepts as they relate to mercury exposure.

    - *Task 3a:* Review educational literature and describe the WARE project.
    - *Task 3b:* Assess project activities through reflective journaling in terms of their ability to increase awareness of environmental, environmental health and sustainability concepts.
    - *Task 3c:* Recommend focal areas for improving and expanding the project to reach larger populations.

This dissertation has been arranged in the following format:

- Chapter 2, Background. The background is divided into three main sections which principally focus on the behavior of mercury in the environment, its usage, and toxicity.

- Chapters 3-5, Sample Areas: Florida, Guyana, and Bolivia, respectively. These Chapters give an overview of each study site within Florida, Guyana, and Bolivia and each site's relationship to mercury (inputs and any impeding issues) as well as the governmental policies governing mercury will be discussed. In addition, each chapter will provide a description of the targeted sampling area, the sampling protocol; materials used as well the analytical methods carried out followed by a general discussion of the results.

- Chapter 6, Sustainability: Community Engagement and Active Participation in Mercury Research. This chapter discusses the pilot initiative to broaden community awareness and participation in understanding issues of mercury at the elementary level.

- Chapter 7, Conclusion: Integrative Examination of Mercury. This chapter summarizes all of the data results with a given framework and followed by recommendations for future research.

CHAPTER 2: BACKGROUND

2.1 Introduction

This chapter provides an overview of mercury and its interactions within the environment and the associated health implications from its presence in our society. The principle focus will be on understanding its interactions with the air, water, sediment, and flora/fauna. Furthermore, an overview of its effects on human populations especially women of child-bearing age, children, and the indigenous will be discussed.

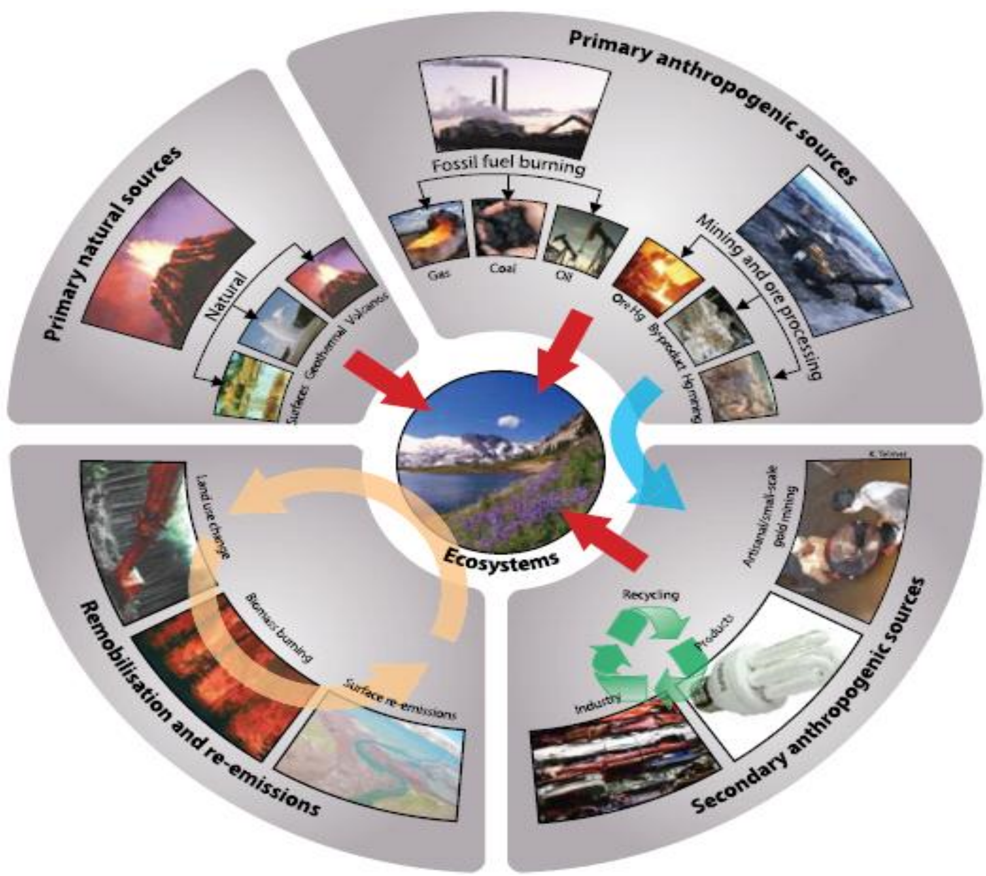

Figure 2.1. Primary, Secondary, and Remobilized/Re-emitted Natural and Anthropogenic Sources of Mercury Inputs to the Cycling of Mercury in the Ecosystem [16].

2.2 Overview of Mercury

Mercury is a global contaminant of increasing concern. Ranked 3rd out of 275 substances on the Agency for Toxic Substances and Disease Registry (ATSDR)[17], it is a Group XII transition metal that is released into the environment through natural and anthropogenic [18] sources. These sources can be divided into primary natural, primary anthropogenic, secondary anthropogenic, and remobilized/re-emitted sources (Figure 2.1). It is commonly found in three oxidation states (Hg^0, Hg^{1+}, and Hg^{2+}) in the environment and can form inorganic and organic species. The most abundant naturally occurring forms are metallic mercury (Hg^0), mercuric sulfide (HgS), mercuric chloride ($HgCl_2$), and methyl-mercury (CH_3Hg or MeHg). Exposure to each species negatively impacts the environment; however, methyl mercury is the most toxic form and can have detrimental effects on the human central nervous system and specific target organs [9, 19]. Since MeHg is lipophlic it readily bioaccumulates and biomagnifies in the environment. It also has a high affinity for sulfur containing compounds [20, 21].

Mercuric sulfide, commonly known as cinnabar, is a red mineral that once exposed to light turns black and is further refined by heating at temperatures above 540ºC to form the liquid metal mercury[2], Hg^0. This is the principle production method of mercury used in various industries and products. The world's most abundant mercuric sulfide deposits exist principally in Kyrgyzstan, Russia, Spain, Ukraine, Algeria, and Slovenia. It is estimated that nearly 600,000 tons of mercuric sulfide ore still exist [22]. The usage of metallic and other species of mercury ranges from fluorescent light bulbs, paints, facial bleaching creams, necklaces imported from Mexico, dental amalgams, some toys (e.g. infant teething rings, maze toys), light up shoes, switches, thermostats, industries (e.g. gold mining, pulp and paper milling, chlor-alkali) as well as in cultural and religious practices. This is due to its unique physical and chemical properties. Its' properties are often considered majestic or magical because it behaves as a "liquid" at room temperature yet it is still a solid. It is an excellent electrical conductor and resistant to corrosion. Unlike other metals (e.g. Zn, Co, Ni), mercury is not essential in the human body and is very toxic thus making it ideal for usage in vaccinations, pesticides, and antiseptics. It can form bonds with gold and silver which helps to produce a higher yield of recovery of the precious metals. As outlined in the physical and chemical properties of mercury in Table 2.1, the low aqueous solubility or low reactivity and high stability of mercury allows it to have a long atmospheric residence time. However, its low vapor pressure (0.2 KPa at -38.72ºC) allows it to be deposited readily as Hg^{2+} and re-emitted into the environment as Hg^0 via photoreduction. In addition, it can be transported to shallow sediment aquatic environments via particulate matter (wet or dry). Methylation of mercury occurs to a relatively high extent in aquatic systems [23-25], making fish consumption the leading route of human exposure today[26]. As a result, several exposure and consumption regulations have been established in the United States and internationally. These regulations have been detailed in subsequent section in Table 2.3 whilst the cycling of mercury in the environment has been described in Figure 2.2. The next section describes the cycling of mercury in the environment.

Table 2.1. Physical and Chemical Properties of Mercury (Taken from Benjamin [27]).

Property	Value	
Atomic number	80	
Electronic Configuration (n=)	$1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^2p^6d^{10}f^{14}\ 5s^2p^6d^{10}\ 6s^2$	
Electronic Structure	Rhombohedral	
Atomic mass (g/mol)	200.59	
Ionic/Atomic radius (Å)	1.02/1.76	
Boiling Point (K)	630 (357ºC, 675ºF)	
Melting Point (K)	234.43 (-38.72ºC, -37.7ºF)	
Density (g/cc @ 300K)	13.546	
Vapor Pressure (Pa @ -38.72ºC))	0.0002	
Enthalpy of Automization (kJ/mol @ 25ºC)	61.5	
Specific Heat (J/gK)	0.139	
Electronic Potential (-eV)	28.2	
Hardness Scale (Mohs)	1.5	
Molar volume (cm^3/mol)	14.81	
Flammability	Noncombustible liquid	
Description	Silver colored transition metal	
Alternate names	Mercurio, Quicksilver, Hydragyrum, Azogue	
Stability Constants for metal-ligand complexes (Log k)	$HgSO_4$	1.39
	HgCl	6.75
	$HgCl_2$	13.12
	$HgCl_3$	14.02
	$HgCl_4$	14.43
	$Hg(HS)_2$	37.72
Solubility Values of Solids(Log K_{s0})	$Hg(OH)_2(s)$	25.40
	$HgCO_3(s)$	22.52
	HgS (cinnabar)	52.01
Gibbs Free Energy, $G°_f$ (kJ/mol)	Hg (l)	0
	Hg_2^{2+} (aq)	153.6
	Hg^{2+} (aq)	164.4
	Hg_2Cl_2 (calomel)	-210.8
	HgO (red)	-58.5
	HgS (cinnabar)	-43.3
	HgI_2 (red)	-101.7
	$HgCl^+$ (aq)	-5.44
	$HgCl_2$ (aq)	-173.2
	$HgCl_3^-$(aq)	-309.2
	$HgCl_4^{2-}$ (aq)	-446.8
	$HgOH^+$ (aq)	-52.3
	$Hg(OH)_2$ (aq)	-274.9
	HgO_2-(aq)	-190.3

2.3 Mercury in the Environment

2.3.1 Mercury Cycle

The earth can be divided into four main spheres or layers: (1) atmosphere; (2) hydrosphere; and (3) lithosphere. These spheres are interconnected and each has its own unique property and ability to transport and retain heavy metal constituents (e.g. Pb, Hg, As) and other matter across its' boundaries thereby entering into the food chain. Prior to entering into the food chain several interactions occur within and between layers at the interfacial layer. The interfacial layer can be defined as the infinite thin boundary separating two phases or layers thus when a heavy metal constituent crosses this boundary it is considered to have been transferred to the other phase or enters into different spheres [28].

In the hyrdosphere, lithosphere, and pedosphere, the speciation of mercury is influenced by various abiotic (e.g. sorption, precipitation, photo induced volatilization, dissolved oxygen, pH, temperature, sediment surface characteristics, carbon dioxide levels) and biotic (methylation or demethylation) processes. Extensive research has been underway using both model and real conditions to understand this complexity. The biogeochemical processes thought to be involved in the cycling of mercury across these spheres is shown in Figure 2.2.

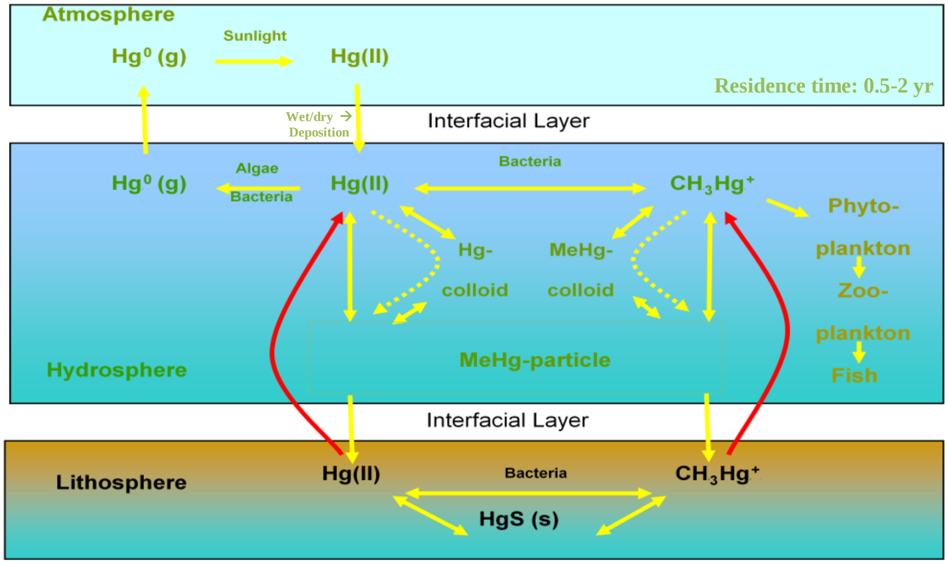

Figure 2.2. Biogeochemical Cycling of Mercury in the Atmosphere, Hydrosphere, and Lithosphere[1].

Once emitted into the environment through natural or anthropogenic activities as gaseous mercury, it resides in the air for up to 0.5-2 years [3, 4] . It is transported and distributed to the land and water bodies via wet, particulate, and dry deposition. In the hydrosphere, mercury undergoes biogeochemical and photo-oxidation transformation. It is then distributed between chemical species of inorganic divalent mercury (II) and organic mercury (methyl-mercury – CH_3Hg) with its dominant species being $HgCl_2$, $HgCl_4^{2-}$, Hg^{2+}, Hg, Hg species sorbed onto mineral oxides, and organo-mercurial species[29]. Organo-mecurial species are the most toxic. Mercuric mercury in particular, is then uptaken by phyto-plankton which are consumed by zoo-plankton thus entering into fish as it further bioaccumulates and biomagnifies to top predatory species (e.g. humans). Mercury also forms solid $HgS_{(s)}$ which is usually, but not always, found under reducing environments (either in sediment or in biofilms in the water column).

In the lithospheres microorganisms exist. These microorganisms such as sulfur-reducing bacteria (SRB) and methanogens are essential in the methylation and demethylation of mercury. In plants, uptake of mercury has been found to be plant specific. In general, mercury has the tendency to accumulate in roots, indicating that the roots serve as a barrier to mercury uptake; however, mercury concentrations in aboveground parts of plants appear to depend largely on foliar uptake of Hg^0 volatilized from the soil [30].

2.3.2 Atmospheric Mercury

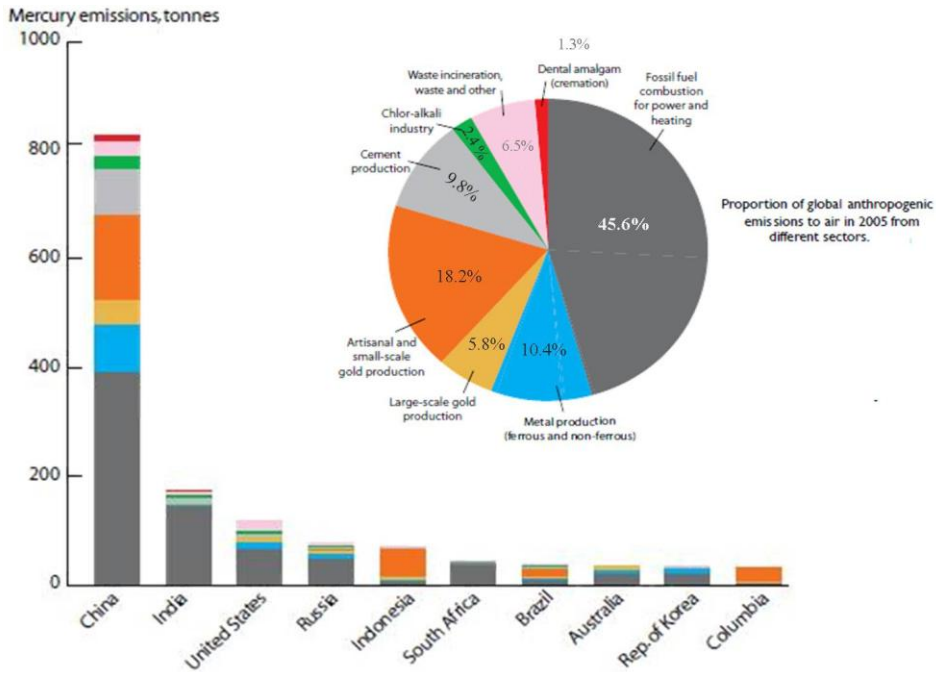

Figure 2.3. Global Mercury Emissions by Sector and Their Proportions in the Top Ten Countries with Highest Emission Rates. (Modified from United Nations Environmental Programme Global Atmospheric Mercury Assessment) [16].

Natural and anthropogenic emissions from volcanic eruptions, soil degassing/erosion, sea venting/evaporation, fossil fuel combustion, smelters, municipal/medical incinerators, are the main sources that introduce mercury into the atmosphere. Being a toxin as well as a commodity, Western Europe exports about 100 tons of mercury to Brazil each year, where it is latter emitted over the Amazon and undergoes trans-boundary dispersion [31]. According to the Global Mercury Assessment Program, atmospheric mercury levels have increased considerably since the on-set of the industrial age [2]. During the last 100 years, anthropogenic sources have contributed approximately 70% of the total mercury input to the environment [32]. Global mercury emissions by sector and their proportions are shown in Figure 2.3. Most of the mercury emission is derived from industrial or mercury processing sources which can be divided between 45.6% for fossil fuels (e.g. coal-fired power plants), 18.2% artisanal and small scale gold production, 16.3% for cement, waste incineration, and 10.4% metal production. However, Lacerda and Marins argue that out of the total estimated mercury emissions (116 $t \cdot yr^{-1}$), gold mining contributes 67.3% (77.9

t·yr^{-1}) to the atmosphere [33]. In 1997, it was reported that China, Venezuela, Philippians, and Indonesia are the countries with the greatest reported mercury inputs into the global atmospheric mercury load [33].

The dominant species of mercury released into the atmosphere from anthropogenic activities include Hg^0 (vapor), Hg^{2+}, Hg-particle, and HgO. Eighty percent of the total mercury that remains in the atmosphere is 20% Hg^0 whilst 60% is Hg^{2+}.[34] As it is distributed throughout the world by vertical wind dispersion it resides in the air for up to 0.5-2 years [4, 32] . The atmospheric transport of toxic chemicals, such as mercury, to other countries has been termed "the circle of poison" [35]. In large, it is still highly debated whether atmospheric Hg deposition is due to local, regional, or global sources [32]. However, it is certain that atmospheric mercury deposition is the primary route by which mercury enters into most freshwater systems. Water bodies in close proximity to mercury emitting sources such as coal-fired power plants and gold mining directly influence aqueous and fish mercury levels[36]. Such regional mercury emitters, have contributed to global mercury pollution due to the mobility of mercury in the air [31]. Comparative studies of mercury emission rates on gold mining in contrast to other industries and practices (e.g. chlora alkali plants, agriculture, slash and burn, , etc) in South America described by Lacerda and Marins shows that gold mining is the greatest contributor [33]. Recent estimates suggest that China is by far the largest contributor to atmospheric mercury load due to anthropogenic sources from coal combustion and gold mining, whilst the U.S. is the third although its emissions, are estimated to account for roughly three percent of the global total [16, 37].

Table 2.2. Environmental Mercury Fluxes from Global Mercury Models [16].

	Lamborg et al., 2002	Mason and Sheu, 2002	Selin et al., 2007	Mason, 2008	Friedl et al., 2008
Hg Fluxes (kt/yr)					
Natural emissions from land	1.0	0.81	0.5		
Re-emissions from land		0.79	1.5		
Emissions from biomass burning					0.675
(A) Total emissions from land	1.0	1.6	2.0	1.85[a]	
Natural emissions from ocean	0.4	1.3	0.4		
Re-emissions from ocean	0.4	1.3	2.4		
(B) Total oceanic emissions	0.8	2.6	2.8	2.6	
(C) Primary anthropogenic emissions	2.6	2.4	2.2		
Total emissions (A+B+C)	**4.4**	**6.6**	**7.0**		
(D) Deposition to land	2.2	3.52			
(E) Deposition to ocean	2.0	3.08			
Total deposition (D+E)	**4.2**	**6.6**	**7.0**	**6.4**	
Net load to land	1.2	1.72			
Net load to ocean (burial in sediments)	1.2 (0.4)	0.68 (0.2)			
Total net load (land+ocean)	**2.4**	**2.4**	**2.2**		
Other parameters					
Mercury burden in the troposphere (kt)	5.22	5.00	5.36		
GEM lifetime (yr)	1.3	0.76	0.79		

[a]Including Hg^0 emissions (0.2 kt/yr) in response to Atmospheric Mercury Depletion Events (AMDE's) in polar regions. Biomass burning is not included in the emissions from land in this Table.

Globally, environmental mercury fluxes from global models suggest that total mercury emissions from land, oceanic, and primary anthropogenic sources have decreased from 2002 to 2008 (Table 2.2).

2.3.3 Mercury in Water and Sediment

As mercury is deposited in the hydrosphere, it can be mobilized by physical perturbations, chemical or biogeochemical mechanisms (e.g. surface charging and dissolution), low ionic strengths or conductivity and the presence of strong sorbing ions in solution. According to model calculations by Duursma, tropical estuaries at steady state can act as sinks or sources for contaminants depending on the time period [38]. Their projections showed that at the onset of contamination the estuary would act as a sink whereas after a period of years it will begin to act as a source. The total inflow and distribution of dissolved and particulate contaminants from the river is not equal to the discharge along the estuary to the sea. Therefore, contaminants become immobile allowing bottom sediments to act as a buffer.

Natural sediments are a complex mixture of minerals/solid phases that exhibit a range of characteristics which influence heavy metal behavior. According to Lindsey [39] surface sediments in aquifers, lakes, and rivers principally contain minerals of iron, aluminum, and silica which also represent the most abundant mineral oxides in the environment. Mineral oxides (e.g. iron and aluminum oxides like goethite and gibbsite, respectively) play an important role in the speciation of mercury. Hence sediments and soils can act as potential sources or sinks for Hg.

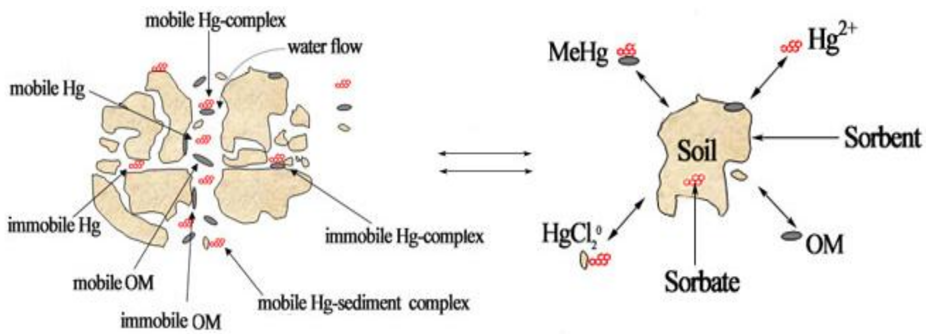

Figure 2.4. General Representation of Sorption of Mercury (Sorbate) to Natural Sediments and Soils (Sorbent) in the Presence of Organic Matter (OM) and Salts (Cl^-).

When in contact with water, mineral oxides form amphoteric surface groups (e.g. positive, negative or neutral surface charges); therefore, they can accept or lose protons depending on the pH of the water bodies. If acidic conditions exist, the overall number of positively charged surface sites would increase thus making mercury sorption to the mineral oxides decrease. This would allow mercury (Hg^+ or Hg^{2+}) species to remain in solution or the aquatic environment where they can be further transformed to the most toxic form, methyl mercury. However, while under more alkaline or "basic" conditions the positive sites would diminish and vice versa would occur for negatively charged surface sites. Therefore, mercury (II) sorption to clays [40-42], mineral oxides of iron [43-47], aluminum [46-48], and silicon [48-50] would typically increase as a function of pH until it reaches a maxima then decrease in higher pH regions. As a result, the excess mercury will sorb and/or interact with other sediment constituents (e.g. ions, heavy metals), attach to particulate matter/colloids (e.g. organic matter), transform to methyl mercury, or remain in the aqueous solution as $Hg^{2+}$and/or Hg (Figure 2.4). Soils high in clay, total iron, and carbon from the pristine forested area of French Guyana exhibited maximum mercury concentrations in upstream parts of the watershed that reached up to 500 $ng \cdot g^{-1}$ [51]. Methyl mercury sorption to mineral oxide surfaces of goethite and kaolin, on the other hand was found to be much lower than inorganic Hg^{2+} sorption [40]. In addition, the presence of chloride, sulfate, phosphate, other heavy metals (e.g. Ni(II), Pb(II)), and/or organic matter can influence mercury sorption to mineral oxide surfaces through various processes including competition for surface sites, changes in the surface charge, formation of ternary surfaces and formation of more stable aqueous complexes [45, 48-50, 52, 53]. Sediments containing high organic content or natural organic matter can form extremely strong complexes with mercury [54-56] thereby affecting the desorption or removal of mercury from the minerals as well as its bioavailability [57, 58]. Studies by Han et al. on the chemical speciation of dissolved mercury in surface waters of Galveston Bay determined that almost all of the dissolved mercury (> 99%) in Galveston Bay was complexed by natural ligands associated with dissolved organic matter [56]. Furthermore, the study determined that sulfides and thiolates are important binding sites for dissolved mercury in estuarine waters. Thereby suggesting that sulfide limits production and accumulation of MeHg in river systems. Similar findings were determined in the study of the behavior and fate of mercury in sediment and water samples collected from the estuarine Patuxent River [59]. These effects once again can vary depending on such factors as the temperature, pH, alkalinity, salinity, dissolved oxygen content, the form of mercury present, the geologic area, and the type of natural organic matter (NOM).

NOM or decaying waste from homes, industrial plants, animals, or run off that contain carbon compounds (e.g. plants, trees, leaves, grass clippings, peat,) is divided into two distinct groups, fulvic and humic acids. Fulvic acid, the hydrophilic or water-loving fraction of NOM, increases mercury sorption on iron oxide surfaces (e.g. goethite)[43] but decreases sorption of both Hg(II) and methyl mercury from aluminum silicate surfaces (e.g. kaolin)[40]. NOM has different functional groups (e.g. carboxylic, phenolic, thiol) that play important roles in complexing mercury thereby causing a distribution of binding affinities [60, 61]. Researchers found that dissolved organic matter (DOM) influenced the abiotic, photo-induced methylation rates of mercury [62]. Recent studies on mercury volatilization to Hg(0) found that the presence of NOM decreased volatilization in aqueous solutions, but that mercury volatilization in real lake samples was significant in sunlight [63]. Organic acids can dissolve silicon, Al, and Fe-bearing minerals which potentially can cause the mobilization and transport of metal contaminants.

Temperature and dissolved oxygen which are inversely proportional to each other are also important in controlling the mobilization of mercury. According to Ho and Wang[64], by increasing the temperature of your system there will be a net increase in chemisorption and diffusion processes, thereby playing a significant role in the overall sorption process[64]. It was further suggested that typically sharing and/or exchanging of electrons between the sorbent and sorbate is an endothermic process- thus increasing temperatures- may produce a "swelling" effect within the internal structure of your sorbent material which would enable metal ions to penetrate into new active sites of sorption on the sorbent surface.

2.3.4 Mercury in Fish

Overtime mercury does not degrade, it bioaccumulates and biomagnifies. In fish, methyl-mercury accounts for greater than 90% of the total mercury present [65]. Mercury bioaccumulation usually occurs in the fatty tissue of fish and is largely magnified in large predatory fish. The maximum contamination level determined by the US EPA and WHO for fish is 0.5 µg/g [66] and 2.5 µg/g [67] wet wt., respectively. Mercury concentrations vary by the fish species, fish size, type of water body (e.g. fresh, salt, pond, lake, river, ocean, bay), the specific geographic location, and atmospheric mercury deposition levels; however, it is well known that specific fish species such as salmon, shark, and King Mackerel, globally contain elevated levels of mercury. In certain locations like Florida high levels of mercury have been found in largemouth bass and other freshwater gamefish [68]. In studies of the Río Ramas, the largest tributary of the Lake Titicaca watershed on the Peruvian side in South America, pejerrey (Basilichthyes) and carachi (Orestias) exceed US EPA fish tissue-based water quality criterion levels of 0.50 $\mu g \cdot g^{-1}$ [66]. Also, Guyanese fish samples collected from two gold mining areas exceed these limits as fish total mercury levels ranged from 0.018-0.798 $\mu g \cdot g^{-1}$ [10].

Mercury accumulation in fish has been associated with many factors. Dittman and Driscoll found that in remote lakes the watershed area, elevation, and change in fish body condition influence fish total mercury loadings [69, 70]. Hutcheson et al. determined that mercury levels found in the dorsal muscle of largemouth bass (n=138) and yellow perch (n=97) from 15 lakes in Massachusetts were impacted from local mercury sources (e.g. medical and municipal waste incinerators)[69, 71]. Other researchers argue that there is a weak association between inorganic mercury loadings from the atmosphere and the accumulation of methyl mercury in aquatic biota and mosquitoes would be a more useful indicator for atmospheric mercury deposition to aquatic systems [70].

Mercury's presence in fish poses a severe threat to the health of animals and humans. The threat to humans has been directly linked to rate of consumption, species, age, and body weight. It has also been suggested that coastal communities which may consume larger amounts of seafood exhibit higher levels of methyl-mercury than inland populations [72].

2.4 Toxicity of Mercury

Since the early 1960's, environmental mercury pollution has gained increased attention. Mercury has been found to seriously impact human health. Human exposure to mercury can occur through inhalation, ingestion, and absorption through the skin but the principle route of exposure is through fish consumption [73-75]. The resulting effects of mercury depend on mercury species, duration, and source of exposure. The three forms of mercury (elemental, inorganic, and organic) each have its own unique profile of toxicity. For example, mercury exposures from fish and marine mammals/crustaceans contribute to elevated methyl-mercury levels whilst contact from dental amalgams, gold mining (other occupational exposures), Afro-Latin religious ceremonies, fossil fuels, and incinerators would be from elemental mercury [6]. In all, some effects may include dysarthria [76], loss of vision/hearing [9, 76], tremors, neurological/reproductive disorders [9], coma, kidney failure [77, 78], lung cancer [79, 80], congestive heart disease [81] as well as death in some cases [6]. With such tragedies like that in Minamata, Japan where over 3,000

Japanese residents died of methyl-mercury poisoning due to the consumption of mercury-laced fish, researchers have delved into understanding the complex nature of the pollutant.

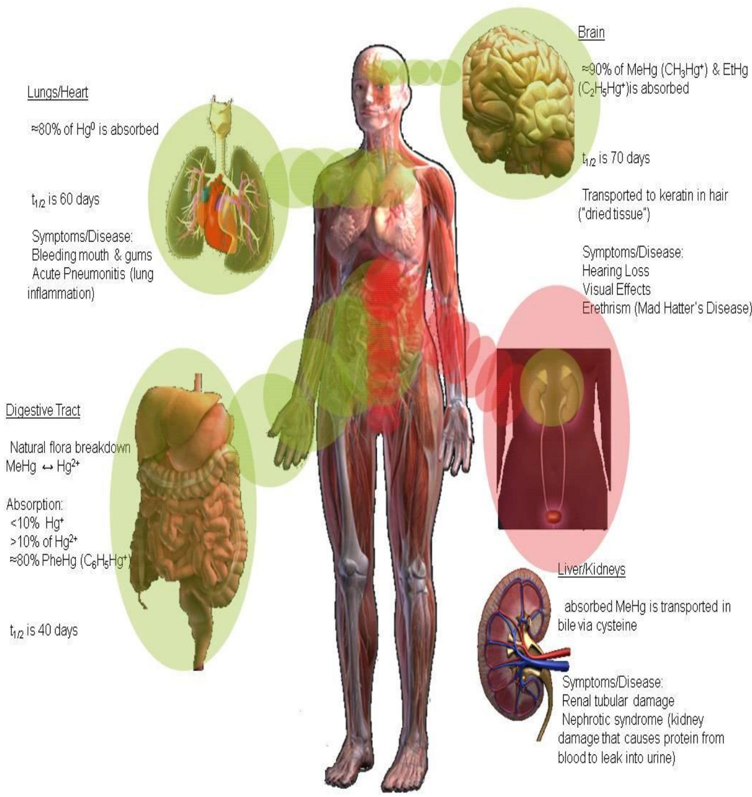

Figure 2.5 Mercury System Flow to Humans and the Associated Adverse Health Effects.

Once inhaled inorganic aerosols deposit in the respiratory tract and are absorbed depending on particle size. According to the Agency for Toxic Substances and Disease Registry (ATSDR) organisms retain approximately 80% of inhaled metallic mercury whilst 100% of the mercury is absorbed in the lung alveolus [82]. Thus the threshold limit for long term exposure to inorganic mercury is 50 $\mu g \cdot m^{-3}$ [83, 84]. While in the respiratory tract, mercury immediately begins to bind to specific target organs and target cells or sites where hormones bind. The target organs for mercury accumulation are primarily the brain, liver, and kidneys; however, distribution in the human body varies according to species and route of exposure. According to the World Health Organization (WHO) [85] daily consumption levels may be higher in contaminated areas as well as in locations where fish constitute a high proportion of the diet. Since methyl- and elemental mercury are lipophilic [86] they are readily distributed throughout the entire body. On the other hand, mercuric mercury (Hg^{2+}) is accumulated extensively in the kidneys [6, 75]. In all, mercury targets the kidneys, thyroid, central nervous system, heart, and brain[29]. Thus transport of inorganic mercury across the intestinal tract depends on solubility, dissociation in the gastrointestinal tract, intestinal pH, and the presence of essential nutrients ($Cu^{2+,}$ Zn^{2+}). During the transport process, target cells that bear receptors are capable of responding to the metabolic functions of hormones. These hormones (e.g. amines, thyoxine, peptides, proteins, etc.) help to regulate metabolic functions of other cells in the body and float in the blood or lymphatic fluid until they reach their target cell. It is believed that during this process mercury that is present within the blood stream or cells may bind to the hormones and/or inhibit proper flow of the regulatory chemicals thereby potentially leading to neurological damage and other health impairments such as myocardial infarction, lung disease, renal failure, among other disorders and diseases. In pregnant women, mercury can cross the blood-placenta barrier thereby entering into the brain of the developing fetus [5]. Mercury and inorganic constituents are then excreted via the kidneys (bile), liver, intestinal mucosa, sweat glands, salivary glands, feces, urine, hair, and breast milk. In particular, prior to elimination methyl-mercury is metabolized to inorganic mercury [87]. Its half-time in the whole body is 70-80 days. Therefore, at an excretion rate of less than 1% of the body burden per 24 hours, half of the body burden of mercury is eliminated [5]. Thus it will take approximately 365 days given a whole body half time of 70 days of regular intake of methyl-mercury to attain a steady state balance between uptake and excretion of methyl-mercury [5].

The effects of mercury vary depending on geographical location, sex, age, exposure routes, and pre-existing conditions. Health effects of mercury from various exposures and the effects on present health conditions in populations have been widely studied. Most of the literature examines the effects of MeHg due to fish consumption such as the Seychelles Islands, Faroe Islands, and Minamata, Japan. These studies have helped to establish the maximum contamination guidelines set by the US Environmental Protection Agency and the World Health Organization as seen in Table 2.3.

Table 2.3. Current Regulatory Limits and Guidelines for Mercury Set by Governing Agencies for the United States and Internationally.

	USEPA	WHO
Drinking Water MCL (μg/L – inorganic Hg) [4]	2	6[67]
Recommended Surface Water (ng/L)	12	
Permissible Hair (μg/g)	11.1	10-20[88]
Urine (μg/g)	below 10	
Fish (μg/g) dry weight (fish-type dependent)	0.5*	2.5[67]

*Same for US Food and Drug Administration
USEPA – United States Environmental Protection Agency
WHO – World Health Organization

Distributions of blood mercury levels within US census regions and coastal/noncoastal areas among women of childbearing age (18-40) differed according to region. Mahaffey detailed the regional differences in blood mercury levels in increasing order as [89]:

Northeast > South and West > Midwest

Even within a particular regional area levels can vary. For instance, as summarized in Figure 2.6, Florida's western coastal areas estimated 30-day mercury intake is higher than the state's eastern coast. This may be due to atmospheric mercury deposition rates being centrally focused in the southwestern portion of the state which has been shown to negatively impact the water and fish quality. This directly impacts women, children, and coastal communities. One in six women of child bearing age living in the coastal areas of the United States are more likely to have elevated blood mercury levels than non-coastal residents [89].

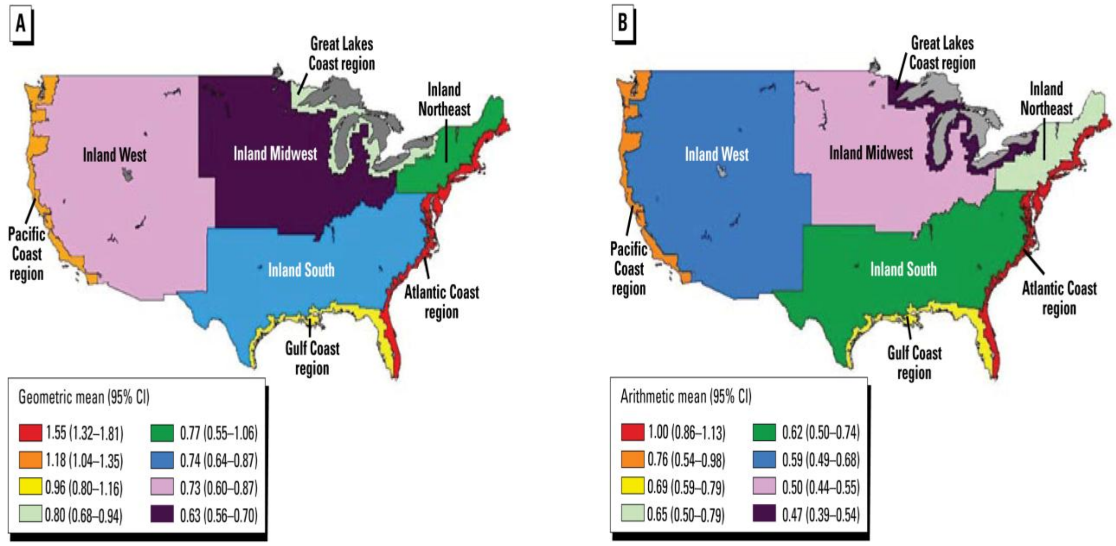

Figure 2.6. (a) Geometric and (b) Arithmetic Mean Blood Mercury (BHg) Concentrations (ugl-1) and Estimated 30-Day Mercury Intake (ug·kg^{-1}), Respectively with a 95% CI (Taken from Mahaffey et al.) [89].

Moreover, race/ethnicity, knowledge, occupation and income are also seen as factors associated with whole body mercury levels. The Centers for Disease Control suggest that across racial groups, minorities and Native Americans are at a higher risk of having elevated mercury levels [90]. Ethnic differences in fish consumption patterns and knowledge studied by Burger et al. suggest that African Americans in Florida [91, 92] are at a higher risk of having elevated mercury levels [91]. This may be due to fish consumption patterns [92, 93], preparation practices [93], and limited knowledge on fish advisory warnings [92]. Whilst studies by Karouna-Renier et al. [8], determined that coastal communities and indigenous populations were more susceptible to mercury intoxication due to increased consumptive behaviors of mercury laced foods. However, a cross-sectional study of fish consumption behavior within an inland American Indian reservation determined that 80% of the study's participants were unaware of tribal and state advisory messages thereby suggesting that risk communication and educational workshops are needed.[94] The examination of hair mercury levels from four coastal communities in Malaysia by Hajeb et al. [95] also showed similar positive correlations between hair mercury concentrations and fish consumption patterns for coastal communities as seen in the study by Karouna-Renier et al.[8] In addition, in many remote and urban areas around the world fishing is an important aspect of recreation, culture, and tradition which may also influence consumption behavior [96].

Outside of US borders, staple foods (e.g. cassava, potato, and rice) and fish consumption as well as ritualistic and occupational mercury pollution, mainly due to gold mining, has been seen to directly affect community MeHg levels. In Hindu, Asian, Afro-, Latin-, Caribbean, and Brazilian-based traditions such as Santeria, Palo, Voodoo, Babalao, and Espiritismo mercury is prescribed for various spiritual healings and health ailments. Mercury, often referred to as azogue or vidajan, can be bought easily in local markets in developing countries. Although banned in certain products, it can be readily bought in amulets or capsules over the counter in the United States from botanicas and bodegas, stores that sell spiritual and traditional items. Azogue, as it is commonly referred, requires religious participants to ingest, sprinkle, burn, or carry in sachets mercury for treatment of gastrointestinal/health problems, spiritual cleansing, protection from evil spirits, and good fortune as well as love [97].

On the other hand, Obiri [98] revealed that the consumption of cassava contaminated with mercury due to being grown in a gold mining area in Ghana may cause cancer in 10% of adults and children which is above acceptable cancer risk range (0.1% or one case of cancer out of one million people). Furthermore, Iraqi residents who consumed grains treated with a mercury fungicide during a famine in the 1970s died from mercury poisoning [85]. In Minamata, Japan, over 3,000 people suffered from physical deformities, emotional disorders, and death due to the consumption of fish that were contaminated from a chlor alkali plant that released mercury directly into Minamata Bay. Singh et al. observed that residents with elevated levels of mercury resided in gold mining communities located in the interior regions of Guyana (Isseneru and Kurpung) [99]. Due to elevated mercury levels in the body many researchers suggest that there is a need for increased risk communication and education measures.

Fish according to the American Heart Association (AHA) and other national and international health agencies, has numerous nutritional benefits, such as containing an excellent source of protein, vitamins, minerals, and especially omega-3 polyunsaturated fatty acids (PUFAs). These nutritional benefits are described to protect against several adverse health effects (i.e. coronary heart disease, stroke, and pre-term delivery) [100];

however, it can lead to the over consumption of mercury-laced fish. In fact, the AHA suggests that people with or without a known cardiovascular disease (CD) consume a variety of mainly oily fish at least twice a week which is more than the USEPA and WHO suggested consumption rates in terms of mercury in fish. According to the EPA and WHO, consumption of fish containing methyl-mercury should be limited to an intake of less than 0.5 µg/g and 2.5 µg/g drey weight, respectively which is based on three factors: (1) fish size and type, (2) regular dietary intake, and (3) location. The agencies recommend that pregnant woman and children reduce their intake of mercury-laced fish due to mercury's ability to be a neurotoxin. However, conflicting intake limits exist across the US and abroad despite the uniform guidelines set forth by the World Health Organization (which are not enforceable). These contradictions pose as a problem in conveying information to the general public so they can make informed decisions.

2.5 Mercury as a Commodity

Despite its properties as a toxin it is also a highly mined commodity. Its properties as previously mentioned in Section 2.1, make it ideal for usage in various products such as gold mining. In mining, mercury is used to recover gold. Its ease of availability, higher yield than simple gravitational techniques and inexpensive nature make it lucrative for small-medium scale miners to use[101].

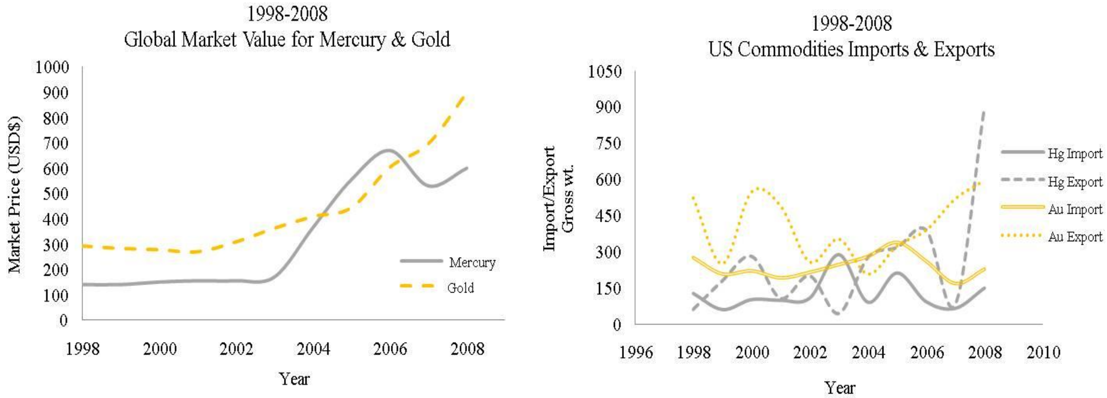

Figure 2.7. 1998-2008 (a) Global Market Value for Mercury and Gold; and 1998-2008 (b) US Commodities Imports and Exports Derived from USGS Minerals Statistics and Information Database [22, 102-106].

The average price for a single flask (35 kg or 76 lb) of mercury on the free market has nearly doubled since 2004 to its present historical high value of US$600 per metric ton [101, 105]. This rising price in mercury may be a direct result to the rising price of gold US$874.00 per ounce ton[101, 106] (ozt) as seen in Figure 2.7. The environmental and social implications of gold mining raise important questions on environmental sustainability. Almost 50% of gold is mined from indigenous lands and processed using mercury or cyanide [107], which is detrimental to the health of the environment and the people. It has been seen that the usage, handling, and management of tailings as well as the quantity of mercury used in small scale gold mining are principle issues of concern. It is commonly and conservatively estimated that for every 1 g of gold recovered there is 1-2 g of mercury lost to the environment [108]. The historical high prices of mercury and gold, it can be estimated that for every 2 g of mercury used the cost of mercury for a miner would only represent 0.1% of their revenue which is a negligible loss. At the same time, others suggest that it is the consumer's consumptive behavior and the capitalist economies hoarding of gold bullions as culprits to this environmental devastation. The United States formerly backing its money by gold has a surplus of gold in its banking reserves and could use this to supply the global demand for gold instead of the world continuously mining depleting underground sources. To help minimize the usage and environmental impact of mercury, governmental, non-governmental organizations (NGO), and large-scale mining companies are addressing these issues.

Governmental agencies have set bans, limits, and increased governmental regulations on the mining industry within its borders. On the other hand, non-governmental organizations are attempting to educate the public via campaigns like Oxfam America's "No Dirty Gold" campaign. It was initiated to (1) demand that mining corporations be more socially and environmentally responsible during the production of gold and (2) that consumers take responsibilities of their actions in the global distribution of mercury.

CHAPTER 3: FLORIDA

3.1 Introduction

In this chapter, a top down approach has been used to gain an understanding of the issues associated with mercury in the state of Florida as a whole to the isolated issues within the study site area, the Hillsborough River. Furthermore, the sampling approach, methodology, and data results from total mercury analyses, scanning electron microscopy/electron dispersion, x-ray dispersion, and surface area analysis will be presented and discussed.

3.1.1 Objective and Task

The objective of this chapter is to characterize mercury loadings in the Hillsborough River of Tampa, Florida as well as address the role that socioeconomic factors play in mercury loadings. The tasks to accomplish this objective include:

- *Task 1a:* Identify and characterize suitable study sites for this work.
- *Task 1b*: Determine levels of total mercury present in fish, water, and sediments by using cold-vapor atomic absorption spectroscopy (CVAAS) and cold-vapor atomic florescence spectroscopy (CVAFS).
- *Task 1c:* Identify the geochemical conditions that affect the fate of mercury by using BET surface area analysis, electron dispersion spectroscopy, and X-ray diffractometry.
- *Task 2a:* Document the socioeconomic, regulatory and geopolitical factors within the United States (Florida) and Internationally (Bolivia and Guyana) through a literature review

3.2 Mercury and Florida, USA (N.A.)

With a population of approximately 16 million, Florida is the fourth largest state in the US [109]. A tropical area [110], attracting more than 70 million tourists per year, it is the leader in commercial fishing in terms of fish catches per day (e.g. shrimp, lobster, scallops, etc.)[1]. In recent years, mercury has become a pollutant of increasing concern for the state.

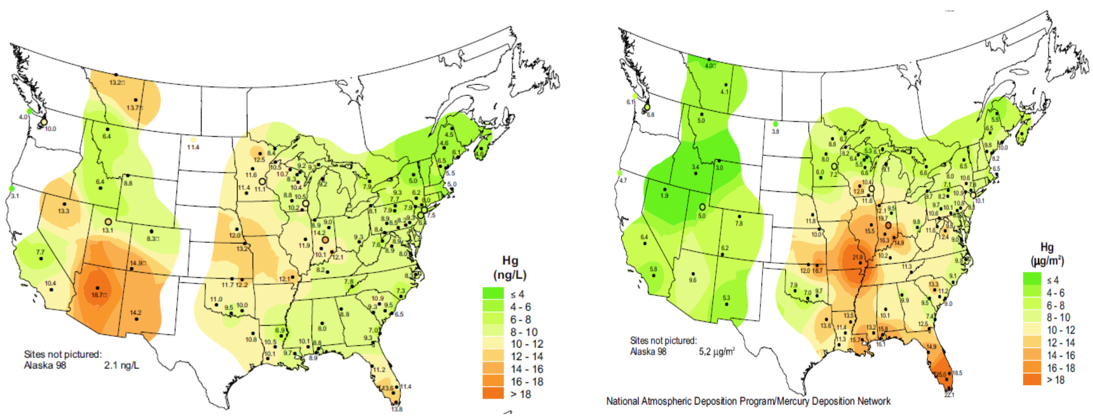

Figure 3.1. Taken from the National Atmospheric Deposition Program's Mercury Deposition Network (a) Total Mercury Concentrations ($ng \cdot L^{-1}$) and (b) Total Wet Mercury Deposition ($\mu g \cdot m^{-2}$) [111].

In the past six years, the Mercury Deposition Network (MDN) of the National Atmospheric Deposition Program (NADP) has reported the highest levels of total wet mercury deposition in the Florida Panhandle and Florida Peninsula [8]. In 2008, the total mercury concentrations in the United States determined that "hot spots" for mercury (areas containing >12 $\mu g/m^3$ Hg) are principally in Missouri, Indiana, Nevada, New Mexico, and Florida (Figure 3.1) **[111]**. However, wet mercury deposition was by far the greatest in Florida and Missouri. This may be due to weather conditions (e.g. heavy rains), local sources, as well as dispersion factors which are known to affect mercury deposition. Mercury deposition is still not well understood [112].

According to the Florida emissions inventory, municipal solid waste combustors (MSW), electric utility industries (coal fired power plants), and medical incinerators are the major local sources of atmospheric mercury for the entire state of Florida [113]. In 1994, the

Florida Atmospheric Monitoring Study (FAMS) initiated monitoring of wet and dry mercury deposition. revealed that background mercury levels were high and relatively constant throughout the state; however, the magnitude of deposition is considered to be seasonal with highest levels of deposition exhibited during the summer months of May through October [113, 114]. In 1996, the FDEP teamed with the Florida Center for Solid and Hazardous Waste Management (Center) to conduct mercury emission surveys within Florida hospitals to develop best management practices (BMPs) for handling mercury. The findings from this study determined that (1) not all of Florida's hospitals were in compliance with state mercury rules and recommended practices for properly handling and disposing of mercury/mercury containing devices; and (2) proper education and training for all hospital employees is drastically needed to accomplish a significant reduction in the amount of mercury in Florida's medical facilities. The most frequently used mercury-containing items in Florida's medical facilities included: fluorescent lamps (87%); sphygmomanometers (75%); high pressure sodium lamps (56%); thermometers (53%); mercury vapor lamps (46%); and metal halide lamps (44%) [115]. Research has indicated that not all of Florida hospitals were in compliance with applicable rules and recommended practices for properly handling and disposing of mercury and mercury-containing devices [115]. Therefore, it was recommended that proper educational training of all personnel was needed to accomplish a significant overall reduction in the amount of mercury in Florida.

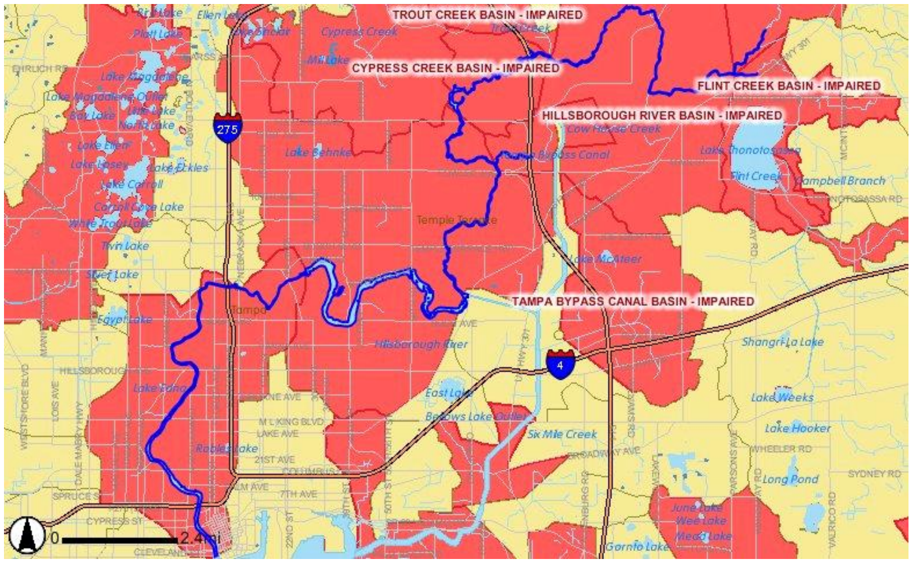

Figure 3.2. Hillsborough County Impaired Water Bodies Atlas (Areas in Red are Considered to be Impaired) [116].

In addition to atmospheric mercury deposition, Florida's entire coastline, as well as every lake and river in the state, is subjected to mercury consumption advisories. Historically, mercury has been a statewide issue for Florida fish especially for its marine (e.g. shark and king mackerel) and freshwater fish (e.g. largemouth bass) [117]. This has negatively impacted the fishing industry (sport and commercial fishing) in Florida. In 1999, the US EPA's Consent Decree listed 102 Florida water bodies as impaired by mercury and in need of total maximum daily loads (TMDLs). Currently more than two million acres of freshwater sources, mainly in the Everglades, have advisories recommending limited to no consumption of the large predatory fish [118]. Figure 3.2 outlines the impaired water bodies mainly due to mercury for Hillsborough County in red. The State's main contributor to increased local atmospheric pollutants of carbon dioxide and mercury is coal fired power plants [119]. In addition, municipal and medical incinerators, known contributors to the release of mercury to the environment, are a concern to Florida [115].

In recent years, mercury has also become a pollutant of increasing concern for Florida's Fish and Wildlife Commission (FFWCC) given its deleterious effect on human health, especially due to fish consumption. Approximately forty-eight mercury consumption advisories have been issued in the state of Florida for popular fish such as Snook, Gag

Grouper, Redfish, Cobia, Spotted Sea Trout, Flounder, Pompano, and King Mackerel[120]. The presence of extremely high levels have been reported in game fish found in the Florida Everglades (>1.5 μg g^{-1}) as well as in Largemouth bass within the Hillsborough River, Tampa Bay, FL (>1.8 μg g^{-1}). In 1995, the US Geological Survey (USGS) initiated and sponsored the Aquatic Cycling of Mercury in the Everglades (ACME) project, in order to understand the mercury problem in the Everglades alone. However, minimal studies have been conducted within the state for rivers in urban areas. For example, the Hillsborough River which originates at the Green Swamp and travels through urban areas before emptying into the Hillsborough Bay serves as a nursery and spawning location for over more than 100 species of fish. The FFWCC found it to have elevated mercury levels in largemouth bass species.

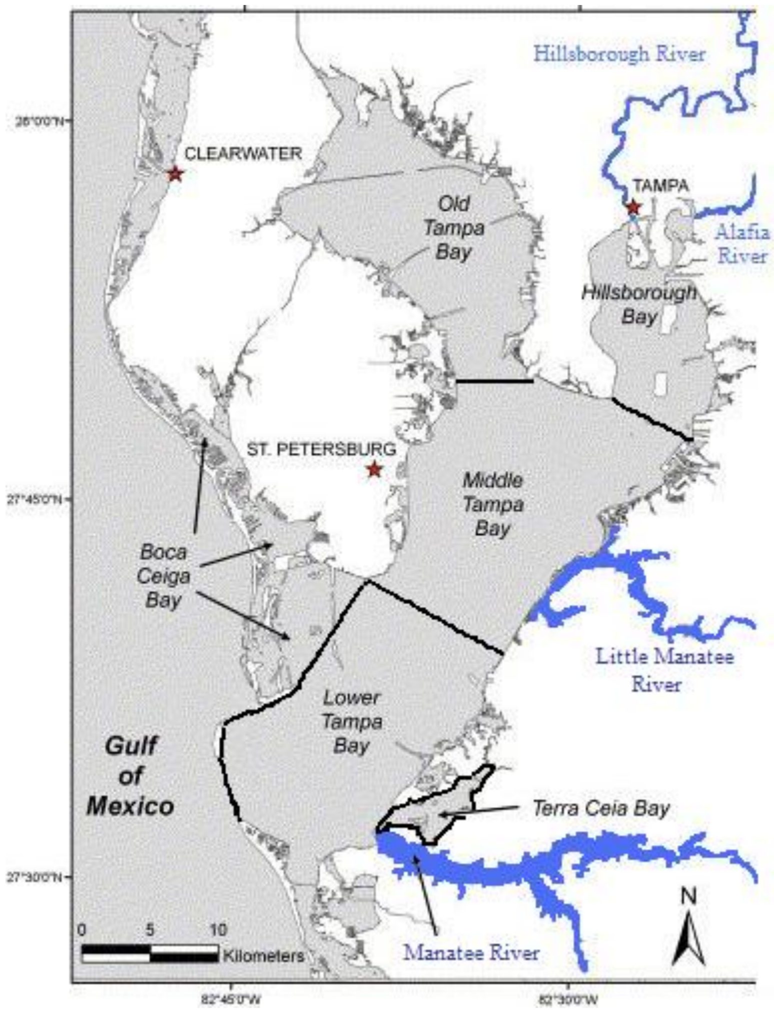

Figure 3.3. Map of the Tampa Bay Area (Modified from Malloy et al., [121]) and Its Geographic Segments (Old Tampa Bay, Hillsborough Bay, Middle Tampa, Lower Tampa Bay, Boca Ceiga Bay, and Terra Ceia Bay).

3.2.1 Tampa Bay, Florida, USA (N.A.)

Tampa Bay, a shallow "Y" shaped coastal embayment [122], located along the south western coast of Florida is the seventh largest commercial port in the United States and is one of the largest estuaries in Florida, encompassing more than 1000 square kilometers [123]. The Tampa Bay watershed supports the cities of Tampa, St. Petersburg, Clearwater, Bradenton and surrounding suburban communities [124]. Its seven segments depicted in Figure 3.3 (Old Tampa Bay (OTB), Boca Ciega Bay (BCB), Middle Tampa Bay (MTB), Hillsborough Bay (HB), Lower Tampa Bay (LTB), and the Manatee River(MR)) serves as a nursery and spawning location for over more than 100 species of fish[125].

Approximately 90% of all the species in the Gulf catch are estuarine-dependent, and spend all or a portion of their life in the estuarine zone [126]. If these waters become polluted or impaired then aquatic species will not mature and death is likely to occur. In an estuary, salt water and fresh water mix. This mixing as well as a sufficient amount of fresh water flow into the estuary is quintessential for the survival of aquatic fauna and the overall health of the river. Therefore, hydrologic and water quality changes caused by cumulative withdrawals and low flows from the Tampa Bay tributaries may generate negative impacts to freshwater and estuarine habitats and organisms especially in the Hillsborough, Alafia, and Palm/Tampa Bay Canal Rivers that drain into the Hillsborough Bay [127]. The shorelines of Hillsborough Bay are mostly impacted by high industrial and urban land use thus making it Tampa Bay's most impaired segment or tributary [127].

Historically, the Tampa Bay area has been affected by poor water quality conditions due to decades of pumping raw or barely treated sewage into the bay [124]. The highest levels of sediment-associated contaminants have been measured in coastal areas that are influenced by point sources of pollution, primarily from municipal and industrial sources [128]. Due to public concerns and a USEPA grant, Tampa established a water quality monitoring program that included the construction of a wastewater treatment plant and the Environmental Protection Commission of Hillsborough County (EPC) in the 1960s and 70's, respectively [124, 129]. In 1996, the Tampa Bay National Estuary Program determined that Tampa Bay sediments contained elevated levels of chromium, copper, mercury, nickel, and silver and were to be designated as priority contaminants of concern [130]. The primary sources of metallic contaminants to Tampa Bay have been identified as urban runoff, atmospheric deposition, and point sources (i.e. coal fired power plants and medicinal incinerators) [130]. Currently, efforts have been made to continue to minimize poor conditions as well as revitalize/restore Tampa Bay through the establishment of the Tampa Bay Estuary Program, Southwest Florida Water Management District's (SWFWMD) Surface Water Improvement and Management Project, as well as hospital BMPS for properly managing mercury and reducing its usage in the hospitals. It is also interesting to note that spatial and seasonal distributions of colored dissolved organic matter (CDOM) in Tampa Bay conducted by Chen et al. [129] showed that the Alafia and

Hillsborough Rivers were dominant CDOM sources. CDOM is important in controlling the attenuation of light. Natural organic and dissolved organic carbon (DOC) have been known to affect the transport and bio-availability of mercury [54, 55, 131] and organic pollutants. These factors highly influence the mobility/fate and transport of heavy metals in sediments, thereby affecting desorption kinetics from mineral oxides as well as its bioavailability [57, 132]. For example, Siciliano et al. found that dissolved organic matter (DOM) influenced the abiotic, photo-induced methylation rates of mercury [62]. This may be the cause for elevated fish mercury concentrations that exceed the USFDA health-based standards of 0.5 ng/g in 50-67% of all the lakes and streams in Florida [133].

Figure 3.4. Map of Hillsborough River System Tributaries (Modified from Pillsbury and Byrne[134]). Shaded Area Denotes the Hydrologic System for the Hillsborough River.

3.2.2 Hillsborough River, FL, USA (N.A.)

The Hillsborough River serves as the principle source of water for agriculture and drinking water for the residents of Tampa and its adjacent areas [135]. It is approximately 87 km and contains several freshwater (Crystal and Sulphur Springs) and non-freshwater (Black Water, Trout, and Flint Creek) sources or tributaries. The Hillsborough watershed or drainage basin spans a total of 379.9 m^2 [136]. The river's tributaries and hydrologic system have been depicted in Figure 3.4. Its headwaters originate at the Green Swamp which provides inputs to the Withlacoochee, Peace, and Ocklawaha Rivers. The Green Swamp, a centrally located 870 sq. mile wetland and upland, is very important in recharging the groundwater supply, providing flood protection during rainfall events, and acting as a natural treatment for runoff. Thus approximately 25% of its land area is protected by the Southwest Florida Water Management District (SWFWMD).

As the river travels southwest towards Hillsborough Bay, it begins to take form as several tributaries and springs add to the rivers flow. At Crystal Springs, despite recent reports of declining flow ($9.1x10^4$ m^3/day), it accounts for approximately 80% of the freshwater input to the upper Hillsborough River. Next, the river receives inputs from Blackwater Creek, an area known for phosphate mining and agriculture production. Once the river reaches Trout Creek it enters the Floridian aquifer as a direct result of a sink hole. Also at this location, the river is connected to the Tampa Bypass Canal. The Canal serves as a flood control measure for residents of the city of Temple Terrace before terminating at the Palm River (Figure 3.5). As the Hillsborough River travels south west towards Rowlett Park it begins to widen and the river flows under several bridges/overpasses allowing urban run-off to easily enter into the river. At Rowlett Park, there is the Tampa Hydroelectric Dam. Just before the dam, the river serves as the reservoir for Tampa Bay Water and Veolia Water North America, the drinking water treatment facility that supplies potable water to nearly 2 million residents of Tampa. Freshwater inputs from this point into the river are low as the dam is only periodically released. This poses a threat to aquatic life in the estuarine zone. From this point to just before draining into the Hillsborough Bay, the Hillsborough River's shoreline is extensively impacted by modifications to its shores by the filling of wetland habitats and increasing residential development. Reports from SWFWMD have indicated that the upland and riparian habitats along the river have been fragmented by agricultural and urban development. With an increasing urban population and tourism, the watershed's ability to serve as a water supply source for many recreational opportunities for area residents and tourists are in grave danger of pollution.

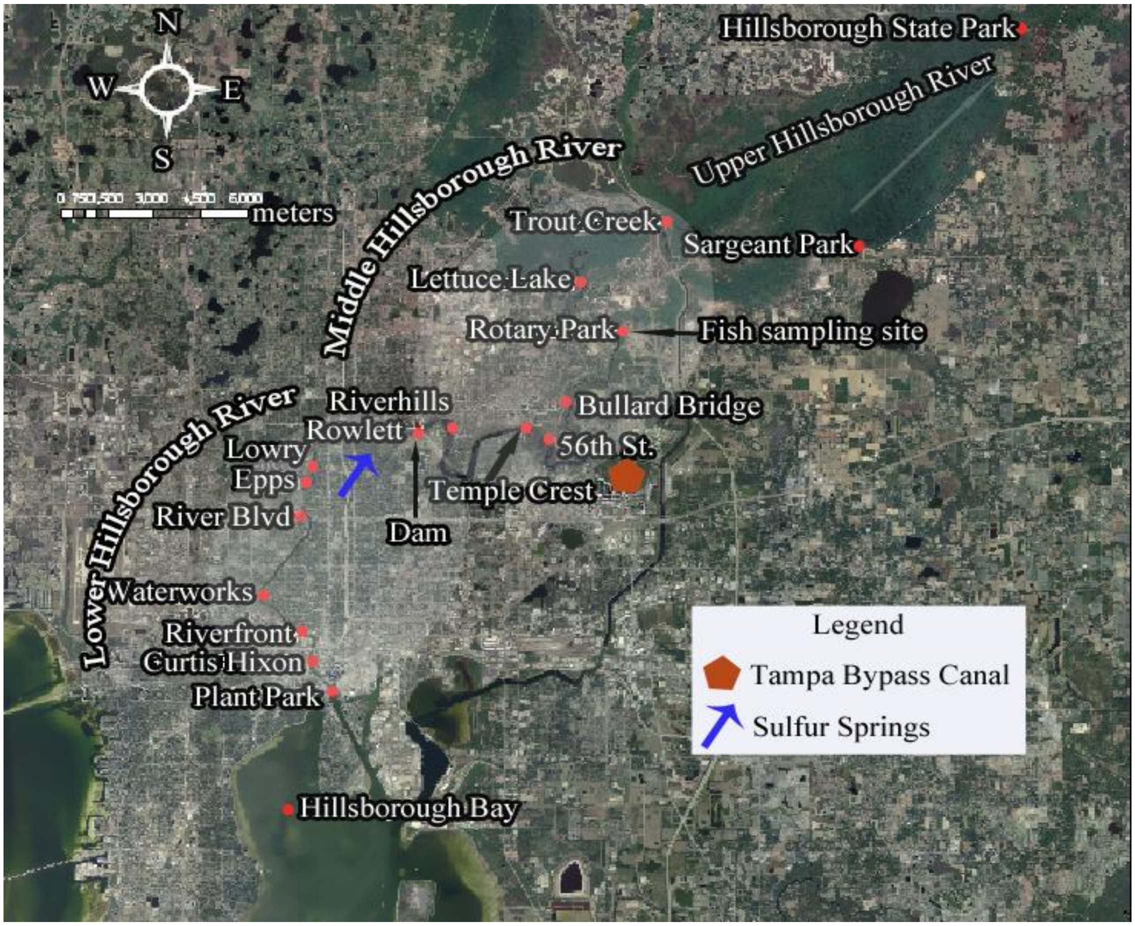

Figure 3.5. Sampling Locations (Noted by Red Points) Along the Hillsborough River, Tampa, FL. Divided Into River Distinctions (Lower, Middle, and Upper) with Important River Dynamics Emphasized.

3.3 Sampling Locations Hillsborough River

Nineteen sites along the Middle and Lower Hillsborough River (Figure 3.5) were selected for the collection of water, sediment, and fish between early 2008 and late 2009. Sampling events occurred after extreme weather events (e.g. extreme cold, heat, or rain events). In addition, sample collection was conducted over a two-day period during the morning hours.

In this study, the area was divided into three zones as depicted in Figure 3.5. The areas south of the dam were known as the Lower Hillsborough whilst regions north of the dam up to Lettuce Lake where known as Middle Hillsborough. Although, not truly part of the designated Upper Hillsborough, the state parks located at Trout Creek up to the Hillsborough River State Park were deemed as Upper Hillsborough River in this study. Water and sediment sampling of the Upper and Middle segments were carried out by traveling to each site by car whilst the Lower reaches were onboard a flat bottom Sea Ark 2472MVCC Jon boat. Fish samples were collected only from Middle Hillsborough River at Rotary Park. This site is a designated FDEP/FFWCC annual fish sampling location for the FDEP's Environmental and Monitoring Assessment Program (EMAP). Fish species selection was based on community consumption patterns and state regulatory target species (i.e. Largemouth Bass) identified in the Florida Fish and Wildlife Commission's (FFWC) and EMAP protocol.

3.4 Materials and Methods

Samples were collected following the Florida Department of Environmental Protection's (FDEP) sampling protocol. The sampling method described below has been divided into sections according to the sample matrix while the sampling sequence has been outlined in Figure 3.6.

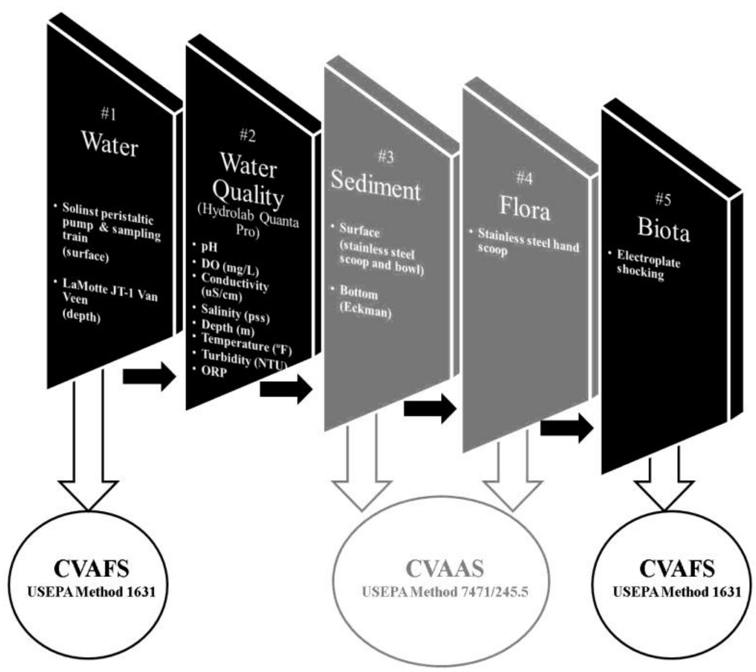

Figure 3.6 Sample Collection Flow Diagram with Method Analysis for Each Sediment Matrix.

The materials used in this work have been described in detail in the subsequent subsections. The matrix hold times and preservation requirements have been detailed in Table 3.1.

Table 3.1. Matrix Preservation Requirements and Hold Times.

Matrix Type	Preservation required	Hold Time
Air	- -	Vapor phase: 1 week Particle phase- indefinitely
Water	Total and Dissolved Hg: 5 mL/L 12N HCl or 5 mL/L BrCl Dissolved Hg: filtered through 0.45 µm capsule filter	Preserved with HCl: 90 days Preserved with BrCl: 300 days Unpreserved: 48 hours
Tissue, Sludge, Sediment, and Soil	Biota (e.g. tissue) – homogenize or freeze whole	Dry: indefinitely Wet: 1 year (if aliquoted) Biota: 1 year (if finely chopped or homogenized to a fine paste frozen)

3.4.1 Glassware/Sampling Kit

All Teflon bottles and glassware were cleaned using cleaning techniques described by the FDEP Method Hg-021-2.8, Procedure for High Level Mercury Glassware Cleaning [137] . This procedure has been outlined in Appendix C.

3.4.2 Reagents

Inorganic standards for trace level total mercury analysis were prepared in clean glassware from a 1000 ppm ($mg{\cdot}L^{-1}$) NIST certified standard in 10% HNO_3 purchased from SPEX Centriprep. Intermediate standards of 10 ppm and 200 ppb ($\mu g{\cdot}L^{-1}$) and a working standard of 1 ppb were prepared and preserved with BrCl . The working standard was used to make daily calibration standards. Standard reference materials of NIST1641d-1 (15.9 $\mu g{\cdot}L^{-1}$), DORM-2 (10 $\mu g{\cdot}L^{-1}$), and NIST3133-3 (3.4 mg/L) for water, fish, and sediment, respectively, were used for quality control and quality assurance purposes. Acid and reductant solutions for cold vapor atomic absorption analysis were 5% HCl and 10% w/v stannous chloride (LabChem Inc LC25180-1), respectively. Reductant for CVAFS was a 3% w/v stannous chloride solution prepared by slowing mixing trace metal grade hydrochloric acid with reagent grade di-hydride stannous chloride crystals ($SnCl_2 \cdot 2H_2O$) and purged with N_2 gas for at least 1 hour prior to sample analysis to dispel any traces of mercury in solution. A bulk volume of 5% hydrochloric acid solutions were made with 32% w/v HCL (Fisher brand) and diluted with MilliQ water. All reagents and calibration standards for CVAFS and CVAAS THg analysis were prepared fresh daily.

3.4.3 Water Sampling

Prior to in-field water collection, field equipment and sampling train kits underwent preparation procedures in the laboratory. Field equipment for water sampling consisted of coolers, Quanta-hydrolab, Solinst Model 410 peristaltic pump, 12V pump battery, a Trimble GPS system, and a La Motte JT-1 bottom water sampler (van Dorn). On the other hand, the sampling kit contained in a double sealed clean polyethylene storage bag was composed of (1) a 500 mL glass sampling bottle, (2) sample tubing (1-C-Flex, 1-silicon, and 1-Teflon), (3) 0.45 µm Whatman or Gilman filter, and (4) an extra clean storage bag. Before packaging, sampling kit tubing was rigorously cleaned following procedures outlined in Section 5.4-5.5 of the FDEP Method HG-015-2.10 (The Preparation of Sampling Kits for the Collection of Trace Level Mercury Water Samples, see Appendix). All sampling kits were placed in a clean dark lined cooler. The cooler used to transport the clean sampling gear was not used for the transport of environmental samples. Glass bottles did not require any pre-field or laboratory treatment as they were certified as clean from the manufacturer. For international sampling, 125 mL certified pre-cleaned I-Chem glass bottles were used to avoid total sample loss in case of accidental breakage during shipment to the USF Trotz Water Quality laboratory. In addition, since only total mercury analysis was conducted clear glass bottles were used for all water samples as amber bottles are expensive and are predominately used for methyl-mercury analysis. Although the use of amber bottles is important for methyl-mercury analysis, dark lined coolers were used to avoid any possible photo degradation of total mercury concentrations.

Using the ultra-clean sampling approach, surface grab by sampling train (filtered and unfiltered), surface grab without train, and depth water samples taken using a La Motte JT-1 were collected in 500 mL clear glass bottles (150 mL for international samples) and stored in a dark lined cooler. For samples that were grab collected without the use of a train, the mouth of the bottle was submerged into the water in the direction of the river flow. After water collection, simple water quality parameters (pH, DO, temperature, conductivity, salinity, TDS, and turbidity) were taken using a Quanta Hydrolab Pro. Samples were transported using ice packs. Upon arrival to the laboratory, water samples were preserved with BrCl produced in situ. In situ BrCl was produced within each sample by pipetting 5 mL of certified mercury-free HCl per one liter of sample and 20 mL of potassium bromide/potassium bromate ($KBr/KBrO_3$) per one liter of sample. Sample hold time for total mercury analysis is recommended to be 90 days; however, if samples are stored in glass or Teflon bottles and BrCl is used as a preservative the hold time can be up to 300 days[138]. The addition of bromine monochloride to water samples reduces Hg-loss that may occur due to organic matter in the sample as well condense mercury from sorbing to the walls of the bottle.

3.4.4 Sediment Sampling

Surface and bottom sediment samples were collected using a stainless steel bowl with a hand scoop and a Wildco 196-B15 Eckman bottom sediment grab sampler or van Veen, respectively. A clean hand- dirty hand or ultra clean sampling approach was employed for both surface and depth sampling. Depth and surface sediment samples were not collected at every sampling point. Prior to sample collection at each point, the equipment was rinsed three times with water from the sampling location. For easy transport, sediment samples were placed in doubly sealed plastic bags and stored in a dark lined cooler separate from water samples. As for surface samples, the top layer (≈ 2 cm) was discarded whilst the remaining 10 cm of sediment from the bottom of the water body were collected. All samples were stored on ice until arriving at the Trotz Water Quality Laboratory. Once in the laboratory, samples were weighed (before and after drying), decanted for excess water, dried in laboratory oven at 30ºC for 24-36 hours, ground in a mortar, and placed in doubly-bagged plastic storage bags until further analysis.

Sediment samples were digested following FDEP modified EPA Method 245.5 and 7471 for Total Mercury Analysis of Sludge, Sediment, and Tissue, sediments, then samples were analyzed for total mercury[139]. During the digestion phase, approximately 1.0 g of sediment was dissolved in 30% hydrogen peroxide and trace metal grade (TMG) nitric acid. This allowed the sediment matrix to breakdown any organic mercury present in the sample to its oxidized mercuric ion form (Hg^{+2}). Then, to ensure that complete oxidation to the Hg^{+2} state has occurred the liquid sediment was heated with 6% potassium permanganate and 6% potassium persulfate. Next, 4 mL of 20% hydroxylamine hydrochloride was added to each sample to reduce any excess potassium permanganate remaining in the digestate which can negatively interfere with mercury levels. Finally, the digestate was analyzed on a Varian 240FS coupled with a VGA77.

3.4.5 Biota Sampling

Biota samples containing Largemouth Bass (*Micropterus salmoides*, target species), Bluegill (*Lepomis macrochirus)*, and Redear Sunfish (*Lepomis microlophus*) were collected from a vessel off of the middle Hillsborough River using electroplate shocking techniques employed by the Florida Fish and Wildlife Conservation Commission (FFWCC). To avoid spawning issues only mature fish were retained for analysis. In the field, samples were processed for their species, sex, weight, and length. In addition, otoliths were carefully removed and placed in secure envelopes for age identification and migratory pattern studies for the FFWCC.

Furthermore, fish samples were carefully filleted, placed in doubly sealed plastic storage bags, and transported on ice to the laboratory for total mercury analysis. Tissue or fillet samples were carefully extracted to avoid contact with epidermal, dermal, and scales. Upon arrival to the laboratory whole samples were frozen until analysis. Thawed fish fillet aliquots of 0.2 g were collected using a stainless steel knife while rinsing with aqua regia ($HCl:HNO_3$; 3:1) and deionized water between samples. Aliquots of the preserved samples were then weighed into 60 mL Teflon (FEP) bottles for UV assisted digestion prior to analysis using a Tekran Model 2600 total mercury cold vapor atomic fluorescence spectroscopy (CVAFS). Standard digestion procedures, Method HG-007-1.9, adopted from the Florida Department of Environmental Protection Agency [140] in accordance with the US Environmental Protection Agency (US EPA) Method 1631 were followed to convert all mercury (Hg^0, $HgCl_2$ complexes, Hg^+, Hg bound to organics, Hg bound to minerals, etc.) in the sample to Hg^{2+}. Concentrations of mercury are expressed as mg/kg wet weight.

3.5 Analytical Procedures

3.5.1 Cold Vapor Atomic Adsorption Spectroscopy (CVAAS)

A Varian 240FS-AAS coupled with a Varian VGA77 attachment was used for the analysis of sediment and flora samples for total mercury, THg, analysis by the cold vapor technique also known as cold vapor atomic absorption spectroscopy (CVAAS). Methyl-mercury or mercury speciation was not conducted in this study. Before salinity samples were analyzed using the manual CVAAS technique, all samples were acidified with 0.5% HCl. Sediment and flora samples were also prepared before analyzing (see Section 4.3.2).

Due to the analytical sensitivity when testing for trace levels of mercury extreme precautions were exercised. Capillaries for the acid, reductant, and sample lines of the continuous vapor flow VGA77 were flushed with DI water before adjusting to an uptake rate of 1 mL/min, 1 mL/min, and 8 mL/min, respectively. A mercury flow-through cell attached to a Mark V burner head of the Varian 240FS was cleaned with 0.5% nitric acid, rinsed with DI water, and allowed to air dry for 24 hours before each analysis set. Optimal working conditions for the Varian 240FS-AAS equipped with a VGA77 have been outlined in Appendix A.

3.5.2 Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS)

Water and biota samples as described in Fig 3.6, were analyzed using the Tekran Model 2600 following the US EPA Method 1631. Some of the possible interferences with matrix analysis have been outlined below and special precautions were taken to reduce damage to the analytical instrument.

Gold and iodide are known to reduce mercury recovery from 100% to 0%, water samples collected from possible mining regions (mainly in Bolivia and Guyana) were pre-reduced with stannous chloride ($SnCl_2$) prior to analysis on the CVAFS. In addition, excess BrCl in each digested sample was reduced by the addition of 10% hydroxylamine hydrochloride before sample uptake by the Model 2600. The Tekran CVAFS, automatically adds a strong reductant, 3% stannous chloride ($SnCl_2$), to produce Hg^0. In solution, the Hg^0 is stripped to form a gaseous phase using ultra high purity (UHP) argon (Ar), a carrier gas. The gaseous mercury is then concentrated onto the dual gold coated sand traps to form an amalgam to be detected by the UV mercury analyzer within the Tekran Model 2600. To reduce potential negative interferences by oxygen and water vapor, UHP grade argon gas and soda lime traps are used, respectively.

In addition, fluid lines from the Tekran Model 2600 were routinely purged with aqua regia (3:1HNO_3 to HCl), then flushed with DI water followed by heating of the dual gold traps before and after any sample runs to remove any excess mercury that might be in the system.

3.5.3 Brunauer, Emmett, and Teller (BET) Surface Area Analysis

Sediment samples collected from the Hillsborough River were analyzed for surface area characteristics at the University of South Florida's Energy Systems Consortium's Clean Energy Research Center. Before performing gas sorption or BET analysis on samples, sediments were freed from contaminants (i.e. water and oils), by "surface cleaning" or degassing. Thus using a Quantachrome Autosorb-1 analyzer an aliquot (0.2-0.8 g) of each sediment sample was placed in its own glass cell and heated at 105ºC under vacuum for up to 3 hours. Then after each sample was brought to a constant temperature the mass was recorded. Next, the sediment sample was placed back into the Quantachrome Autosorb-1's evacuated sample chamber and exposed to small amounts of nitrogen (N_2) gas, the adsorbate. Since a multi-point BET analysis was performed, additional N_2 gas was introduced into the sample chamber to form a multilayer of absorbate onto the adsorbent. Once chemisorption was complete, the number of active surface sites which promote chemical reactions or strong chemical bonds between the adsorbate to specific surface locations or chemically active sites within the adsorbent were determined. Thus the proportionality between residual gas pressure and the saturation pressures at equilibrium (p/P_0) were used to generate cumulative areas.

3.5.4 X-Ray Diffractometry, Scanning Electron Microscopy/Electron Dispersive Spectroscopy

X-ray diffraction is a non-destructive analytical method used to determine the properties of solid matter and requires minimal sample preparation. The mineralogy of bulk and 38 µm sized-fractionated sediments and tailings were characterized using powder X-ray diffraction with a Bruker D4 Endeavor equipped with a LYNXEYE, a super speed detector. The D4 Endeavor was set to automatically load sixty-six samples and perform qualitative and quantitative crystalline phase and peak analysis with sample rotation enabled. Bulk and sized-fractionated sediments were prepared by drying at room temperature in a Thelco laboratory grade oven for approximately 24 hours. An aliquot of the bulk sample was removed whilst the remaining sample was sieved using a series of ASTM-E11 stainless steel sieves (mesh size 400) followed by grinding into a fine powder. Samples were then loaded into an 8.5 mm height, ø25 mm sample reception specimen holder ring using a top loading technique. Two types of specimen holder rings were used which were made of (1) low silicon and (2) steel (Bruker AXS holder # C79298A3244D82 and C79298A3244D84, respectively). Excess samples were stored in doubly sealed plastic bags and placed into a HDPE container. Once in the specimen holder ring, samples were smoothed and pressed to ensure uniform distribution, volume, and consistency for optimal analysis. Each sample completed a full scan at room temperature (25°C) with a step rate of 0.0125 steps/s from $2\theta = 2°$ to 120°. Once all samples were examined, their diffraction patterns were analyzed using the X'Pert HighScore version 2.2e software. The X'Pert software compares diffraction pattern results obtained from the Bruker D4 Endeavor to the International Centre for Diffraction Data's minerals and powder diffraction patterns database (ICDD PDF-4/PDF-2 reference files).

Surface characteristics and elemental composition analyses of sediment samples were determined using a Hitachi FE-SEM Model S-800/EDAX. The Hitachi field emission scanning electron microscope has a magnification power of 300,000 times the actual size of the specimen. The image is generated by scanning a very small electron beam over the sample. As the electrons are scattered from the specimen's surface, they are then collected by the detector thus generating an image and/or chemical characterization of microstructures less than 1 µm using an x-ray spectrometer. This spectrometer is commonly referred to as an energy dispersive spectrometer (EDS) or EDAX. The EDS collects x-rays that are generated from the scanned area by the electron beam. Since the atom of each element releases a unique amount of energy, the acquired x-rays are then used to determine the quantity of each element present in the sample. This is done by measuring the amounts of energy or peak intensities present in the x-ray beams being released by the scanned image of the sample.

To prepare samples for SEM/EDAX analysis, dried bulk samples were evenly distributed onto a thin strip of carbon tape that was adhered to the surface of a SEM designated 25 x 6 mm metal specimen mounting plate (Hitachi catalog # 16327). To minimize sample loading time and maximize sample analysis time, four thin strips of carbon tape were applied to the mounting plate. To avoid cross contamination between each sample application, a glass slide was used as a divider followed by light tapping of the specimen plate to remove any loose particles. After sample mounting, the specimen plate was then attached to the specimen holder. Following procedures outlined in the SEM/EDS protocol for the University of South Florida's Nanomaterials & Nanomanufacturing Research Center (NNRC), samples were carefully loaded into the Hitachi FE-SEM Model S-800/EDAX system. Since the Hitachi works under a high pressure vacuum of 90 torrs, the working conditions for the SEM were set between 17 to 20 keV to reduce the amount of particle charging at the surface and this eliminated the need for gold plating the sample using an Anatech Hummer X Sputter Coater.

3.6 General Results and Discussion

3.6.1 Total Mercury in Sediment and Water

Total mercury concentrations of filtered and unfiltered surface water samples, total mercury loadings in sediment, and other water quality parameters (pH, Temperature, Conductivity, Turbidity, Dissolved Oxygen) for the 18 different sampling points have been summarized in Table 3.2. On the other hand, depth water quality characteristics from the Lower reaches of the river below the dam have been summarized in Table 3.3.

Table 3.2. Total Mercury Concentrations in Unfiltered Water (uwTHg), Filtered Water (fwTHg), Sediment (sTHg) and Water Quality Parameters (pH, Temperature (Temp.), Specific Conductance (SpC.), Turbidity (Turb.) and Dissolved Oxygen (DO)) for Sample Sites. Water Quality Data is Reported for Surface Samples. Sampling Was Conducted June 2008.

Site	Lat.	Long.	Time	uwTHg	fwTHg	sTHg	pH	Temp.	Spc	Turb.	DO
				(ng/L)	(ng/L)	(ng/g)		(^{o}C)	(mS/cm)	(NTU)	(mg/L)
Lower Hillsborough River											
Hillsborough Bay	-82.4755	27.9113	13:24	1.5	ND	54	8.3	31.6	44.20	0	8.1
Plant Park	-82.4585	27.94276	10:45	0.9	0.0	59	8.1	29.1	38.60	0	6.3
Curtis Hixon	-82.4651	27.95235	11:00	2.2	0.9	119	8.1	29.3	33.50	0	6.1
Riverfront	-82.4671	27.96093	11:25	1.3	0.0	56	8.1	29.9	29.10	10	6.1
Waterworks	-82.4812	27.97241	11:40	4.1	ND	94	8.3	30.3	21.10	0	9.3
River Blvd	-82.4701	27.99696	12:00	2.8	0.7	86	8.3	30.6	15.60	17	9.4
Epps	-82.4667	28.00814	12:21	2.6	ND	68	8.4	29.8	9.79	1	11.3
Lowry Park	-82.4648	28.01269	12:43	2.9	2.5	ND	8.1	28.6	6.70	14	10.8
Rowlett	-82.4298	28.02431	7:46	5.1	ND	48	8.0	25.3	1.92	29	7.5
Lower Average				*2.6*	*0.8*	*73*	*8.2*	*29.4*	*22.28*	*8*	*8.3*
Lower Stdev				*1.4*	*1.0*	*25*	*0.1*	*1.8*	*14.91*	*10*	*2.0*
Middle Hillsborough River											
Riverhills	-82.3879	28.02088	9:31	3.7	ND	61	8.5	28.9	0.41	412	8.1
Temple Crest	-82.4192	28.02375	8:31	3.9	ND	62	8.6	29.4	0.46	34	6.8
56th Street	-82.3935	28.0242	9:02	4.1	ND	67	8.4	29.1	0.41	18	7.1
Bullard Pkwy	-82.3827	28.03279	9:58	4.5	ND	66	8.3	29.1	0.37	9	7.1
Rotary	-82.3632	28.05494	10:39	4.1	0.0	56	8.2	29.0	0.37	0	7.1
Lettuce Lake	-82.3775	28.06974	13:54	4.1	0.3	77	8.1	30.4	0.37	17	9.2
Trout Creek	-82.3489	28.08791	12:53	7.8	0.3	68	8.1	28.5	0.36	12	7.7
Sargent	-82.2858	28.08104	11:20	5.3	0.5	50	8.9	27.8	0.34	15	12.2
HR State	-82.2344	28.14886	12:00	3.1	0.0	63	8.0	24.4	0.37	23	7.8
Middle Average				*4.5*	*0.2*	*63*	*8.3*	*28.5*	*0.38*	*60*	*8.1*
Middle Stdev				*1.4*	*0.2*	*8*	*0.3*	*1.7*	*0.04*	*132*	*1.7*
All Average				*3.6*	*0.5*	*68*	*8.3*	*28.9*	*11.33*	*34*	*8.2*
All Stdev				*1.6*	*0.8*	*18*	*0.2*	*1.7*	*15.22*	*95*	*1.8*

*Samples that were below the detection limit were considered 0 ng/L. ND – not determined.

Table 3.3. Water Quality Parameters Just Above the Bottom of the Riverbed (pH, Temperature (Temp.), Specific Conductance (SpC.), Dissolved Oxygen (DO), and Turbidity (TURB)) for Sample Sites Accessed by Boat in the Lower Hillsborough River. Sampling Was Conducted on June 2008.

Site	pH	Temp.	Spc	DO	TURB	Depth
		(^{o}C)	(mS/cm)	(mg/L)	(NTU)	(m)
Plant Park	8.0	29.7	46.30	2.4	4	14.00
Curtis Hixon	8.0	29.9	44.50	2.8	ND	10.50
Riverfront	7.9	29.9	43.90	2.9	ND	8.30
Waterworks	7.7	29.9	39.00	1.3	4	5.00
River Blvd	7.5	29.8	38.30	0.8	0	6.60
Epps	7.3	29.3	34.00	1.2	0	8.00
Lowry Park	7.3	29.2	31.40	1.2	0	6.70
Average	*7.7*	*29.7*	*39.6*	*1.8*	0	*8.4*
Stdev	*0.3*	*0.3*	*5.60*	*0.9*	0	*3.0*

ND – Not determined.

Average total mercury concentrations of unfiltered surface water of all sites was 3.6±1.6 ng/L with the average of the upstream Middle Hillsborough (4.5±1.4 ng/L) being higher than that of the Lower Hillsborough river (2.6±1.3 ng/L). THg values ranged from 3.7 to 59.3 ng/L. The limited number of filtered samples yielded average concentrations in the Middle Hillsborough river (0.2±0.2 ng/L) were lower than those downstream (0.8±0.1 ng/L) and on average, the particulate associated mercury accounted for over 70% of the total mercury in water samples. The filtered THg concentrations seen in this study were relatively low compared to studies by others like Brigham et al. [141], who found filtered concentrations as high as 14.2 ng/L for the St. Marys River in the northeastern part of Florida. Higher dissolved mercury concentrations have been linked with higher percentages of wetlands in a given basin [141, 142]. Higher total mercury concentrations in unfiltered water in the middle Hillsborough was expected to be more impacted by nearby wetlands. However, lower levels tended to be exhibited in filtered water samples, though the sample size is small. Total mercury loadings in sediment averaged 68±18 ng/g and ranged from 48 to119 ng/g with Middle Hillsborough loadings being 63.3±7.6 ng/g and the Lower Hillsborough loadings being 73±24.6 ng/g. Table 3.4 compares the results obtained here with data from other places around the world.

Apart from the fact that the minimum sediment loading is higher than the minimum seen in most places, the data is within the range observed by others.

Table 3.4. Mercury Concentrations in Sediment and Water Samples from This and Other Studies.

Location	Sediment		Unfiltered Surface Water	
	Hg (ng/g)	Methyl Hg (ng/g)	Hg (ng/L)	Methyl Hg (ng/L)
Hillsborough River (this study)	48-119	-	0.9-7.8	-
Artisinal Au mines, Suriname [143]				
mine wastes	5.5-200	<0.02-0.83	11-930	0.05-3.8
streams below mines	110-150	1.2-1.4	-	-
uncontaminated baselines	14-48	0.03-0.08	6.4-10	0.08-0.28
Amazon basin [144-146]				
streams affected by mining				
upstream from mining	24-406	0.07-1.9	2.9-33	0.2-0.6
	67-93	-	2.2-2.6	-
Antarctica streams and lakes [147]			0.27-1.9*	
Mobile Alabama river basin [148]	3.1-104	0-3.8	0.2-3.8	0-1.5
US Streams [142]	0.84-4520	0.01-15.6	0.27-446	<0.01-4.11
Florida Bays [149]	1-219	-	3-7.4*	-

* filtered water samples

The average pH for all of the sites was 8.3±0.2 and ranged from to 8.1 to 8.9. The average temperature was 28.9±1.7 ^{o}C, and ranged from 24.4 to 31.6 ^{o}C. DO levels averaged 8.2±1.8 mg/L and ranged from 6.1 to 12.2 mg/L. For all sites the average specific conductivity was 11.33±15.22 and ranged from 0.34 to 44.2 mS/cm. The specific conductivity of the Middle Hillsborough ranged from 0.34 to 0.46 mS/cm and for the Lower Hillsborough River it ranged from 1.92 to 44.2 mS/cm. Turbidity averaged 34±95 NTU and ranged from 0 to 412 NTU with the average turbidity in the Middle Hillsborough being 60±132 NTU whereas in the Lower Hillsborough it was 8±10 NTU. The sites in the Lower Hillsborough River ranged in depth from 5 to 14 ft when sampled and water quality was also tested close to the bottom for these sites. The results showed that specific conductance ranged from 31 to 46.3 mS/cm and averaged 39.6 ±5.6 mS/cm, and DO levels ranged from 0.8 to 2.91 mg/L and averaged 1.8 ± 0.9 mg/L. Temperature and pH values averaged 29.7 ± 0.3 ^{o}C and 7.7± 0.3 pH units respectively. Differences in values between the two regions may be explained by several factors. Sampling in the Lower Hillsborough was done from a boat in the center of the river whereas in the

Middle Hillsborough it was done from the sides of the banks or from bridges over the center of the river. Additionally, sampling for each location was performed at different times of day, as reflected in the varying temperatures and DO levels at the surface. Photosynthesis, respiration and gas exchange influence DO levels and depend on variables like light, temperature, and nutrient availability and generally peak in the late afternoon [150, 151].

Table 3.5. Pearson Correlation Coefficients Between Total Mercury in Sediment and Unfiltered Surface Water and Water Quality Parameters for All Sites and p-Values Assuming a One Tailed Distribution for Two Samples of Unequal Variance.

Parameter	THg Sediment (ng/g dry weight)		THg unfiltered surface water (ng/L)	
	r_s	p value	r_s	p value
Conductivity (mS/cm)	0.27	<0.001	-0.75	<0.050
pH	-0.16	<0.001	0.20	<0.001
Turbidity (NTU)	-0.13	<0.100	0.05	<0.100
DO (mg/L)	-0.07	<0.001	0.25	<0.001
THg Sediment (ng/g dry weight)			-0.12	<0.001

To understand the relationships between mercury loadings and water quality, Pearson correlation coefficients between total mercury in sediment and unfiltered surface water and water quality parameters for all sites were calculated and reported in Table 3.5. The largest correlations were found with conductivity. The total unfiltered surface water mercury concentration decreased with conductivity whilst total sediment loadings increased with conductivity. Lange et al. [152] also found negative correlations between total unfiltered surface water concentrations and conductivity for lakes. Here, our sample sites ranged from low conductivity freshwaters to very brackish waters in the Hillsborough Channel, spanning an over 2 order of magnitude difference. Given that mercury forms complexes with chloride which influence sorption behavior to mineral oxide surfaces the correlation with specific conductivity is not surprising. Mercury (II) sorption to clays and mineral oxides of iron, aluminum and silicon, some of the most common sediment constituents, typically increases as a function of pH until it reaches a maxima then decreases in the higher pH regions [42, 47, 48, 50]. Kim et al. [46] found that at pH 6, mercury sorption decreased in the presence of sodium chloride due to the formation of aqueous mercury chloro- complexes, uncharged $HgCl_2$ in particular. Therefore, it would be expected that as the conductivity increases, the mercury loadings would decrease. The results show, however, that as the conductivity increases, the amount of mercury associated with the sediment increased and the amount in the water decreased. The presence of competing ions and natural organic matter, especially for the river sediments, likely play a role in loading behavior observed [40, 61 60]. Complexation of mercury with chloride and subsequent sorption to particulate fractions may explain the trend seen in this study. Although the entire river is fished, advisories are based on samples from the Rotary Park upstream of the dam and in the part of the river with more wetlands and forest coverage as well as lower conductivity. Since downstream THg and sTHg are not significantly greater than those upstream, it is likely that fish concentrations sampled in the Middle Hillsborough River probably give the most conservative estimate of mercury loadings.

Mineralogy and composition of complexing ligands in sediments and soils are also important factors that influence mercury mobility in the environment. Table 3.6 describes the mineralogical results of some of the samples and has been divided according to their sampling locale (e.g. Lower, Middle, and Upper Hillsborough River). All sample mineralogy can be found in the Appendix.

According to X-ray diffraction analysis data, quartz (SiO_2) and berlinite ($AlPO_4$) represent the dominant minerals for most of the samples from along the river. This is typical of natural sediments and similar to river bottom sediments obtained in other studies in Florida [153]. Samples collected from the lower reaches showed the presence of clays. Lowry Park, located just below the dam, showed a high semi-quantitative percent of kaolinite, ($Al_2Si_2O_5(OH)_4$,79%). On the other hand, gypsum, representing 25% of the composition of the USF Riverfront Park sample, contained 15% sodium chloride, and 5% mercury, chromium, and barium. The presence of mercury in this sample may be attributed to the site being in the vicinity of possible point sources of mercury (e.g. medical incinerator and coal-fired power plants) as well as the process by which gypsum is formed. Gypsum is formed by roasting calcium with sulfur dioxide that may have originated from sulfides such as mercuric sulfide. Similar findings were seen in the examination of the physicochemical characterizations of an abandoned mine area in Spain[154]. Gypsum is also a naturally occurring sediment in Florida. Zhong and Wang [155] observed that sediments with increased clay content reflected an increase in sediment mercury loadings whilst sediments containing quartz and calcium carbonate had minimal effects on mercury loadings. In comparison with sTHg levels based on river divisions, the Lower, more urbanized areas having higher average loadings (73 ng/g) contained the presence of strong ligands (e.g. Cl, SO_4, PO_4) and other metals influence which have been seen to affect sorption of mercury (II) to quartz and gibbsite [48]. Kim et al.[46] found that mercury sorption to Fe-,Al-oxides in the presence of sulfates is greatly enhanced as a result of the accumulation of sulfate ions at the substrate interface thereby reducing the positive surface charge that would inhibit mercury (II) sorption. The presence of phosphates in the upper reaches of the river may be due to inputs from the phosphate mines or agricultural run-off from local farms close to the rivers headwaters. Phosphates tend to increase mercury loadings in sediments and fish. The study of mercury present in rock phosphate by Jackson et al. [156] determined that discharges of mercury liberated during the manufacturing of fertilizer caused mercury levels in sediments to increase to (<1. 7 mg/kg) white mollusks (<50 mg/kg) and fish (pelagic and demersal, 7.6 mg/kg) levels were greater than US EPA permissible limits. This may be the reason for increased levels of mercury in largemouth bass collected at Rotary Park.

Table 3.6. Mineralogical and Semi-Quantitative Results Obtained by X-ray Diffraction for Samples from Upper, Middle, and Lower Segments of the River.

	Sample Name	SemiQuant [%]	Compound Name	Chemical Formula
Upper	Sargent Park	42	Berlinite	$AlPO_4$
		58	Quartz	SiO_2
	HR State Park	40	Silica	SiO_2
		58	Berlinite	$AlPO_4$
		1	Tin Selenide	$SnSe$
	Rotary Park	50	Quartz low	SiO_2
		50	Berlinite, syn	$AlPO_4$
Middle	Riverhills	98	Quartz	SiO_2
		2	Silver Telluride	Ag_2Te
		1	Aluminum Uranium	Al_3,U
	Rowlett Park*	100	Quartz, syn	SiO_2
Lower	Lowry Park	79	Kaolinite	$Al_2Si_2O_5(OH)_4$
		21	Quartz, syn	$Si\ O_2$
	Riverfront	15	Sodium Chloride	$Na\ Cl$
		48	Quartz	$Si\ O_2$
		5	PHC	$K_5H(CN_2)_3$
		25	Gypsum	$Ca(SO_4)_2H_2\ O$
		6	MCB, Platinum Zinc (1%)	$Hg, Cr, Ba_2, Pt_3\ Zn$
	Curtis Hixon	61	Quartz	SiO_2
		36	Berlinite, syn	$AlPO_4$
		4	Magnetite	Fe_3O_4

SEM/EDAX analysis confirmed that silica and oxygen, the elements that form quartz, as being the most abundant or major constituents in most of the samples. Constituents within a sample containing greater than or equal to 10% of the weight percent are considered major whilst those between 1 and 10% are minor and all others are trace. Based on weight percentages for silicon and oxygen a 1:2 (Si:O) ratio exist thus assuming that indeed SiO_2 is the dominant mineral in most of the samples which was confirmed by XRD analysis. The semi-quantitative results for each major, minor, and trace constituents were examined for a single sampling location within each of the river divisions (e.g. Upper- Sargent Park; Middle – Rotary Park; and Lower – Riverfront Park) and are shown along with SEM high resolution images in Figure 3.7. All SEM images captured at low and high resolutions showed that the sediments along the rivers course before emptying into Tampa Bay were different but all were anamorphous and porous. All in all, bulk fractions of sediments exhibited large grains of quartz with aggregates of Fe-(hydro)-oxides and aluminum-(hydro)-oxides which was in agreement with X-ray diffraction results.

Scanning electron spectroscopy and energy dispersion spectroscopy is not popularly used for elemental determination in sediment or soil sample characterization. Although, Roach et al.[157] was unable to show the physical distribution of heavy metals in kaolin soils using EDX, Bautier et al. [158] successively used it to directly characterize elemental constituents within amporphous phase soils mainly composed of Fe- and Al-oxyhydrides using TEM-EDX. In Figure 3.7a, Sargent Park characteristic x-ray peaks were associated with Si, C, O, Al, and Ca, where calcium and aluminum were minor constituents. In addition, the sediments contained large pores measuring about 48.9 µm in diameter which means that there are more surface sites available for possible sorption of mercury. Rotary and Riverfront (Figure 3.7b-c) normalized element quantification results show the presence of trace amounts of mercury and tellurium (Tl). Elements 80 and 81, mercury and tellurium, respectively, have relatively similar electron energies and are distinguishable at energy is above 15 keV; however, to prevent particle charging and the need to gold coat sediments peaks were not collected at higher energy levels. In addition, carbon weight percentages were seen to be uniform (≈ 40% C) for most of the samples and considered major constituents. This uniform carbon weight percentage can be attributed to the presence and use of carbon tape for mounting samples to the specimen holder. The SEM image of bulk characteristics from Riverfront Park were obtained at a magnification of x70 but when magnified to x800 the skeletal remains of a microorganism was present which increased carbon weight percent to 48.55%.

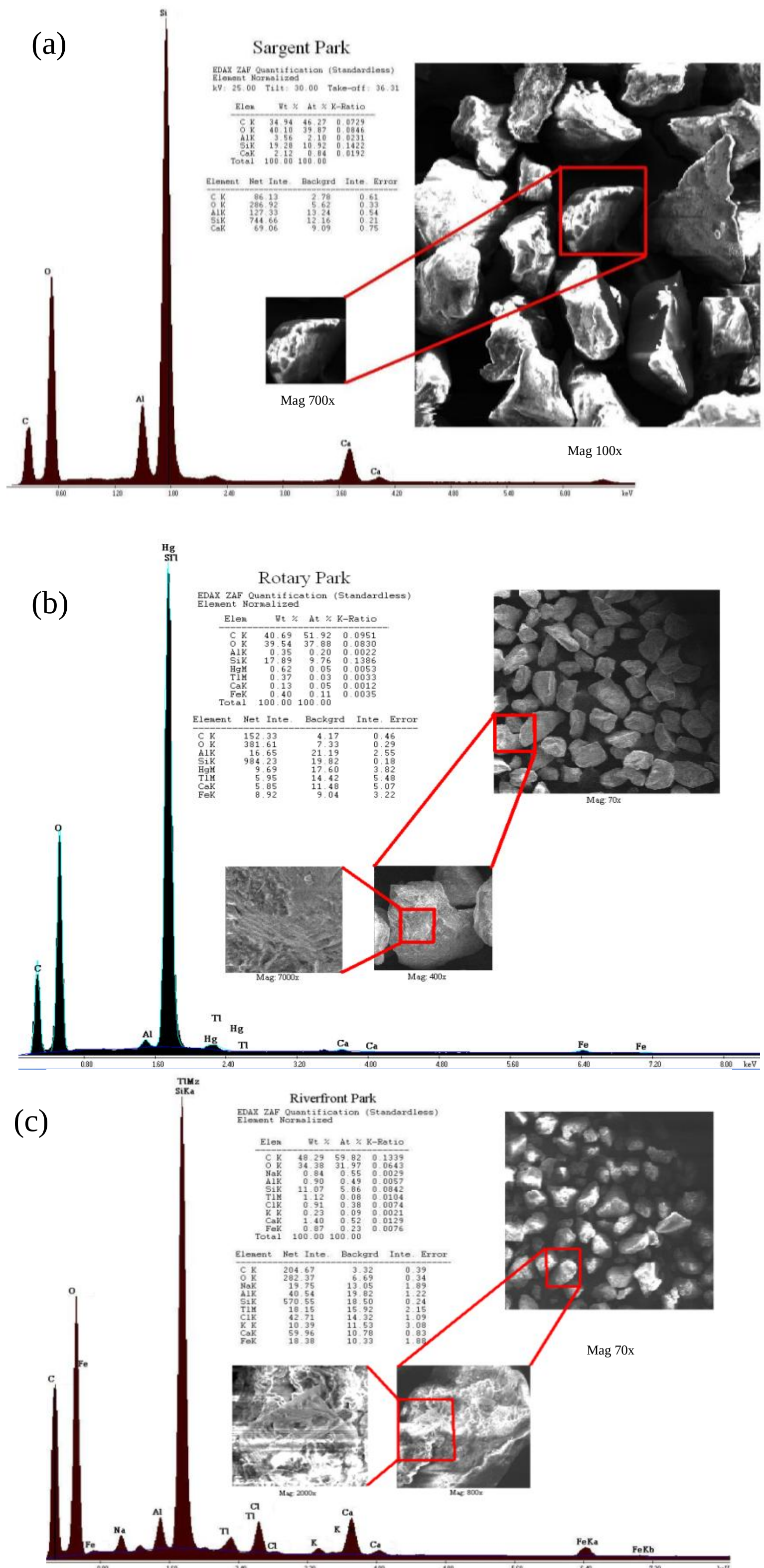

Figure 3.7. SEM/EDAX Standardless Quantification of Normalized Elements from Sediments Collected from (a) Sargent Park; (b) Rotary Park; and (c) Lowry Park.

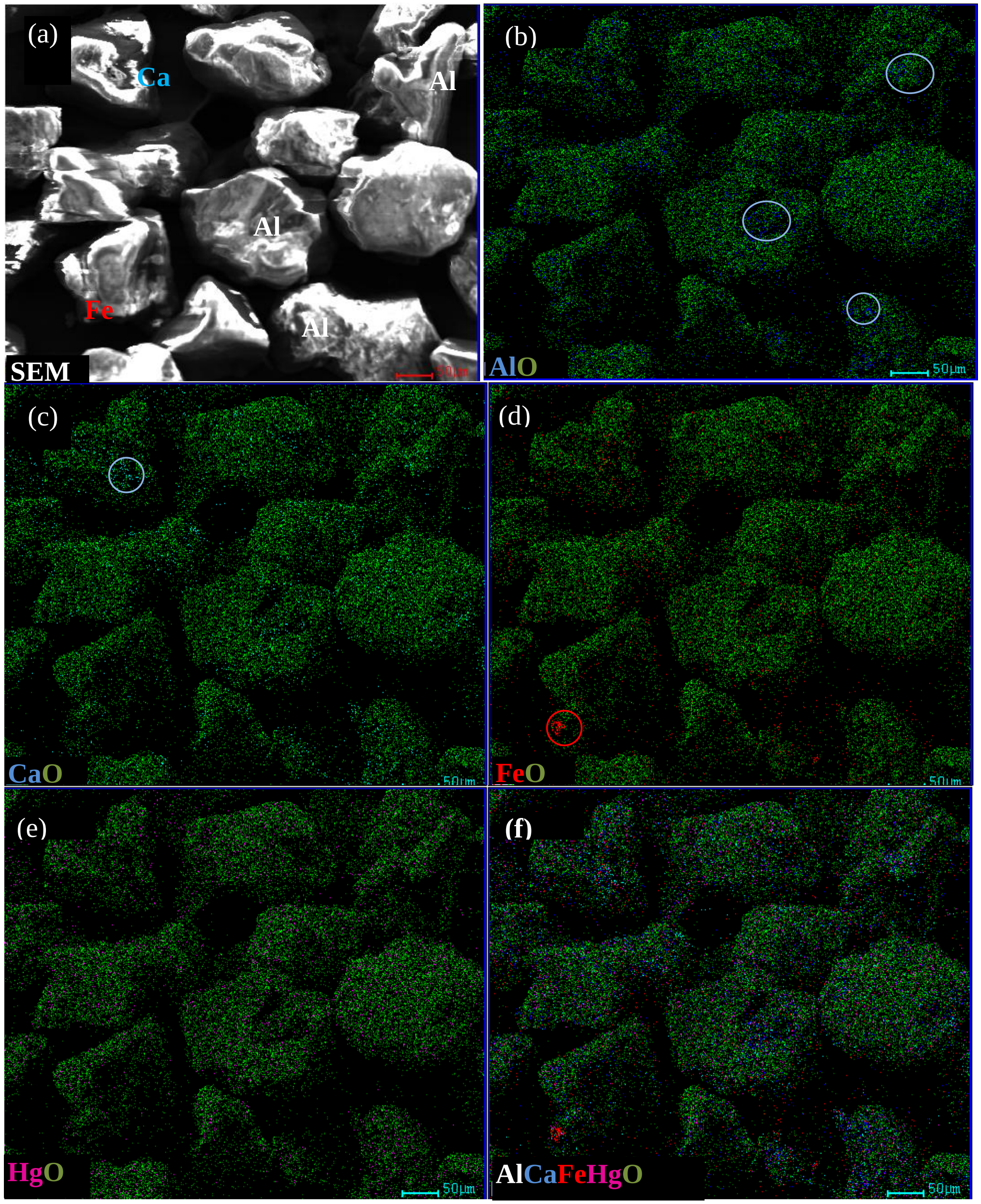

Figure 3.8. SEM Image and Element Maps for Rotary Park Sediments. (a); Magnification x150 of SEM Image; and Spot Images of Major and Minor Constituents of (b) Al; (c) Ca; (d) Fe Clusters; (e) Hg; and (f) AlCaFeHgO.

Furthermore, SEM imaging and quantification software can be used in combination with elemental mapping with EDX to determine heavy metals and elemental aggregates or dispersal within a sample. Elemental maps for select samples were collected and Figure 3.8 corresponds to sediments collected from Rotary Park, the annual site for the FFWCC

Environmental Mercury Assessment Program. The distribution of each major and minor element was independently overlaid with oxygen in order to clearly see the single element in each of the maps (Figure 3.8b-e); however, the last spot map is an overlay of all of the major and minor elements (Figure 3.8f). From the SEM semi-quantification results it was determined that silicon was most abundant in the samples so no elemental map was created for it. Elemental maps for aluminum, iron, and calcium showed that the elements were in clusters. Aluminum and calcium tended to be clustered within the voids whilst iron was seen to group together at the surface. Mercury was scattered throughout the samples.

3.6.2 Total Mercury Loadings in Fish

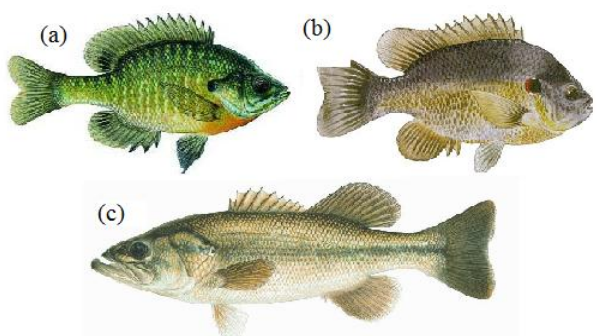

Figure 3.9. Fish Species Collected from the Hillsborough River, Tampa, FL Include (a) Bluegill, (b) Redear Sunfish, and (c) Largemouth Bass.

Looking mainly at lakes, researchers have correlated fish loadings with water quality parameters and found alkalinity, calcium, chlorophyll *a*, conductance, magnesium, pH, total hardness, total nitrogen, mercury concentration in water and total phosphorus to be some main factors of influence [159, 160]. Scudder et al. [142]found that total mercury loadings in LMB found in streams across the US were positively correlated with amount of wetlands present, amount of methyl mercury in water and sediment, specific UV absorbance and negatively correlated with dissolved sulfate concentrations and pH of unfiltered water. Fish were only sampled from one location in this study which was upstream of a dam; however, water quality parameters and sediment loadings were collected along a wider selection of the river, including areas below the dam which were also heavily fished by local residents. Fish species of largemouth bass, redear sunfish, and bluegill are depicted in Figure 3.9.

Table 3.7 summarizes the characteristics and total mercury loadings associated with fish species and body condition. Average mercury loadings in LMB (n=20), bluefish (n=10) and redear sunfish (n=8) were 0.56± 0.22 mg/kg, 0.17± 0.4 mg/kg and 0.1± 0.07 mg/kg wet weight, respectively. After categorization by species, these loadings were compared with fish length, weight, and age data. Scatterplots and correlation data are shown in Figures 3.10 and 3.11. Positive associations were found with both weight and length for all species. The largest correlations were found for the LMB. Mercury loadings were also positively associated with age for the largemouth bass (age data was only available for this species). Historical data from the FFWC at the same sample location (for 2003-2007 and a total of 154 fish) also show strong correlations of fTHg with largemouth length, weight and age (r_s = 0.72, 0.56 and 0.45 respectively with $p < 0.001$). Fish data compared (mercury loading versus fish weight) with historic FFWC data is plotted in Figure 3.12.

Table 3.7. Summary of Fish Characteristics (Length, Weight, Fish Body Condition (fbC), Age) and Total Hg (fTHg) Concentrations Sampled on 2/26/08 at Rotary Park#, Tampa, Florida.

Species	N	L_{range} (mm)	L_{avg} (mm)	W_{range} (g)	W_{avg} (g)	Age* (years)	fbC_{range}	$fTHg_{range}$ (mg/kg wet wt.)	$fTHg_{avg}$ (mg/kg wet wt.)
LMB	20	249-495	347±61	307-1841	618±61	2-6	1.09-1.52	0.22-0.97	0.56±0.22
BLUE	10	163-209	184±14	59-183	105±35	ND	1.24-2.00	0.12-0.24	0.17±0.04
RESU	8	126-243	168±41	30-262	88±82	ND	1.07-1.83	0.02-0.21	0.10±0.07

LMB – Largemouth bass, BLUE – Bluefish, RESU – Redear sunfish
#28.05406 LAT and -82.36419 LONG
* Age was determined by the Florida Fish and Wildlife Commission
ND – Not determined.

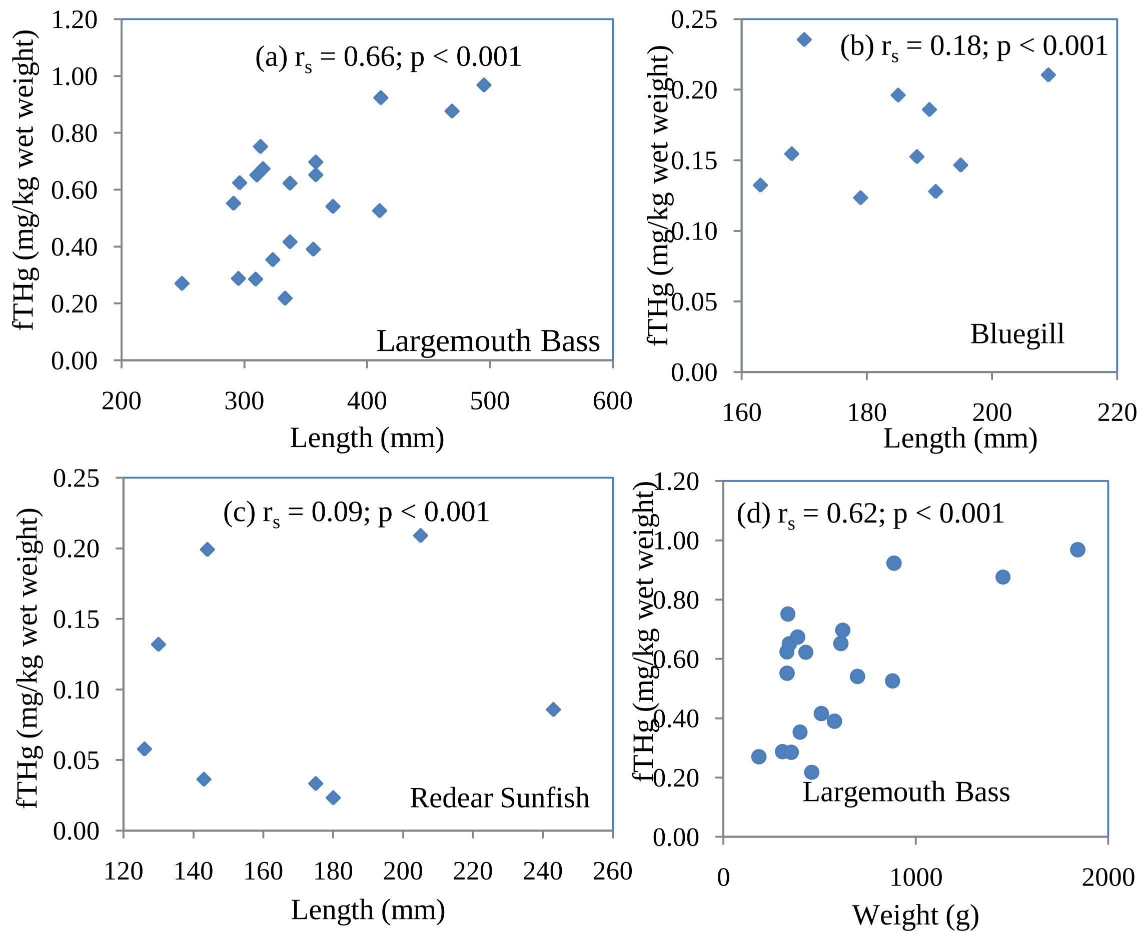

Figure 3.10 (a-d): Scatterplots of Total Mercury Loadings (fThg) in mg/kg Wet Weight as a Function of Length, Weight, and Age, for Each Fish Species. Pearson Correlation Coefficients, r_s, and p-Values Are Shown. p-Values Were Calculated Assuming a Two Tailed Distribution for Two Samples of Unequal Variance.

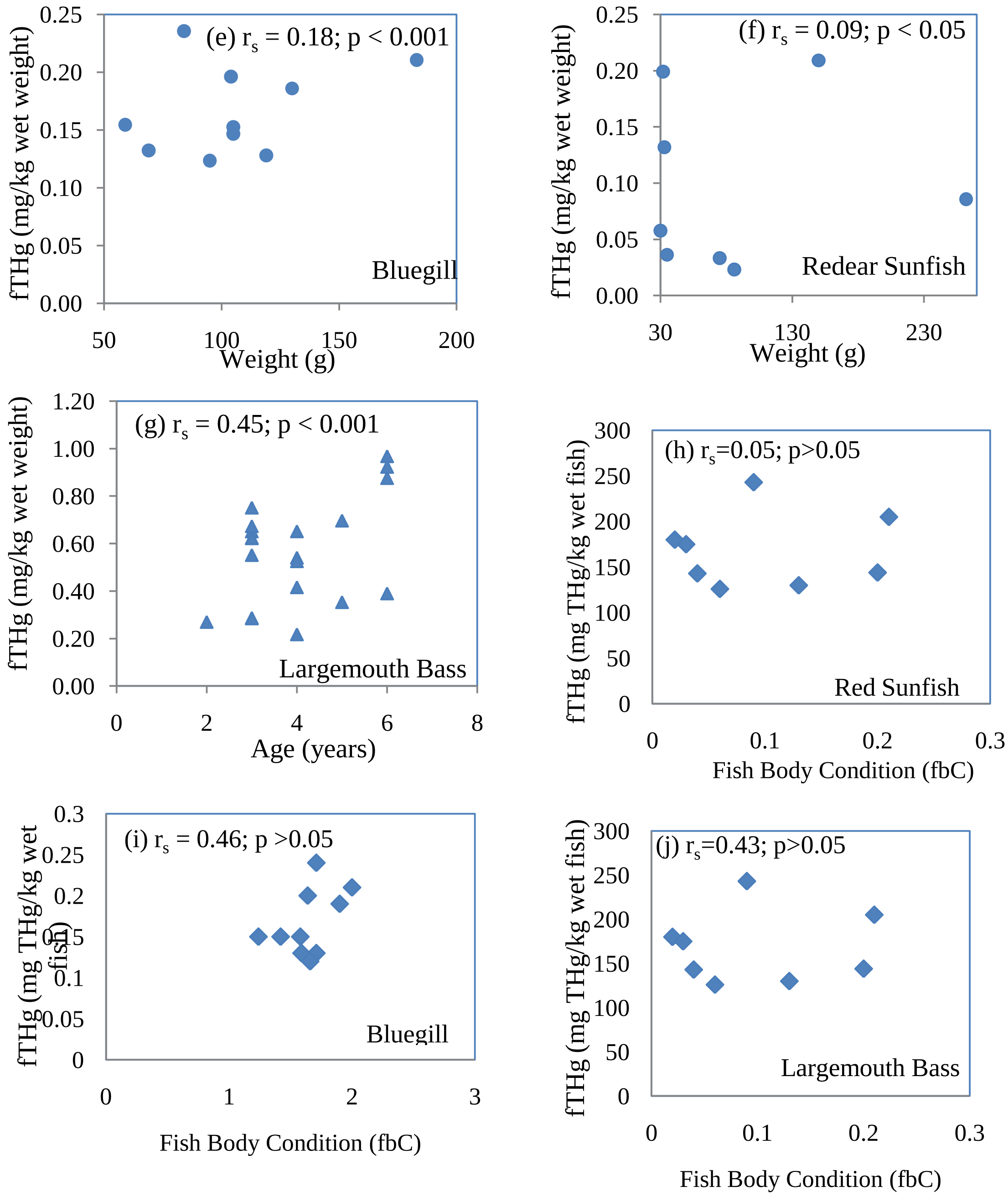

Figure 3.11 (e-j): Scatterplots of Total Mercury Loadings (fThg) in mg/kg Wet Weight as a Function of Length, Weight, and Age, for Each Fish Species. Pearson Correlation Coefficients, r_s, and P Values Are Shown. P Values Were Calculated Assuming a Two Tailed Distribution for Two Samples of Unequal Variance.

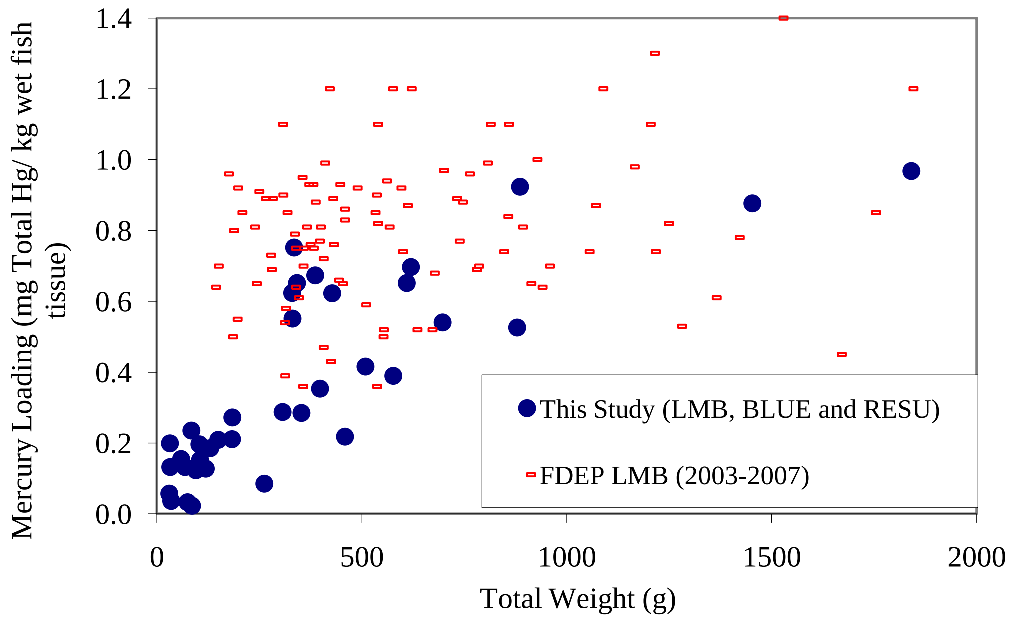

Figure 3.12. Scatterplot of Mercury Loading Versus Fish Weight for Samples Taken at Rotary Park for This Study (20 LMB out of 38 Fish Total) and By the Florida Fish and Wildlife Commission (FFWC) Between 2003 and 2007 for LMB Only. LMB – Largemouth Bass; BLUE – Bluegill; RESU – Redear Sunfish (Weight of BLUE and RESU Are All Less Than 262 g).

A recent mercury survey of concentrations in fish in the Western United States found that average concentration of piscivorous fish was 0.26 mg/kg wet weight for [161]. This is lower than the average LMB concentrations seen at the site studied in the Hillsborough River. Others have found average LMB loadings similar to those observed in this study in other rivers, streams and lakes as well as their correlation with fish length, weight and age [142, 152, 159, 160]. A long term study of fTHg in the middle Savannah River, from 1971 to 2004 found average LMB concentrations of 0.55 mg/kg wet weight which is similar to that found here [162]. Paller et al. [162]observed decreased concentrations when a Chlor Alkali point source input ceased, but subsequent increases in fish loadings were attributed to atmospheric deposition and releases from tributaries draining wetland areas. There are no known industrial sources that drain into the Hillsborough River and the most upstream portion, referred to in this work as the Upper Hillsborough River, starts in the Green Swamp (it was not studied because of its public inaccessibility). The higher methylation rates attributed to wetland areas combined with the damming of the river could contribute to the concentrations of LMB observed in this study [142, 160, 163].

Additionally, in fishery studies, researchers use weight, length, and body condition as an index to assess fish nutritional well-being, fitness as well as the relative suitability of its habitat [164] which has the ability to potentially reflect seasonal and longer term nutritional trends. Equation 2 best explains the calculation for body condition (K) [165]

$$K = 10^5 \times W \times L^{-3}; \qquad \text{Equation 1}$$

where W is the body weight (g) and L is the standard length (cm). Therefore, if K is greater than or close to 1 it is assumed that the fish is in good condition or receiving sufficient food and nutrition. Researchers have shown that fish body conditions can be comparable to the levels of stored fat as well as the incidence of disease [166, 167]. In addition, various factors (e.g. sex, body shape, sample collection method, environmental pollution, seasonal changes, disease, and parasites) can affect fish body conditions. Suns and Hitchin have shown that higher mercury levels tend to decrease enzyme protein synthesis where as Lizama [168] argues that fish condition affects mercury levels. Average fish body conditions were 1.27, 1.46, and 1.65 for largemouth bass, red sunfish, and bluegill, respectively. Largemouth bass average fish body conditions were similar to those found by Lizama et al.[168]. Negative correlations existed between fish body conditions and total mercury concentrations. Striped bass fish conditions studied by Hinner[169] were negatively correlated with total mercury concentrations as was seen by Cizdziel[170].

3.6.3 Health Implications

The US Environmental Protection Agency [171] suggests consumption of fish with methyl mercury concentrations in the range 0.12–0.47 mg/kg wet weight should be limited to one meal (227 g or 8 oz. of cooked fish) per week for the average adult. Fish containing 0.47-0.94 mg/kg wet weight should be limited to consumption once per month and levels greater than 0.94 mg/kg should not be consumed [171]. Since the majority of mercury seen in fish is methyl mercury [172, 173] total mercury concentrations can be assumed to be equal to methyl mercury. Therefore, 86% of all of the fish (n=38) seen in this study had total Hg loadings that would warrant a fish advisory and 32% having loadings that should limit consumption to once per month if using the EPA fish consumption guidelines stated above.

The Florida Department of Agriculture and Consumer Services (2009) issued a joint statement with other state agencies (Department of Health, Department of Environmental Protection) emphasizing the benefits of eating fish soon after the release of a 2009 USGS survey of mercury levels of fish in streams across the US [174]. That USGS survey was picked up by mainstream media because of the high percentage of fish found with mercury levels above EPA recommended limits. Whilst the EPA recommends acceptable mercury exposure through fish consumption based on toxicological tests, state and local agencies are responsible for protection of their own populations. The Florida Department of Health issues annual fish consumption advisories (where one meal refers to 170 g of cooked fish as opposed to the EPA’s value of 227 g of uncooked fish) for specific fish in a given water body tested, and the county agencies use that information to best protect human health. The 2008 Florida fish consumption advisories for LMB and Bluegill in the Hillsborough River recommend a maximum one meal per month for everyone and for the Redear Sunfish, the consumption could be one meal per week for all, except women of child bearing age and young children who should only consume one meal per month [175]. For the purposes of this study, 227 g is used to refer to fish weight where this can be treated as either uncooked or cooked given that some forms of preparation like boiling do not alter fish weight [176]. The following discussion uses the data collected in this chapter to evaluate the efficacy of the above fish consumption advisory.

Toxicological and epidemiological studies are used to develop a reference does (RfD) which is an estimate of the daily exposure to a certain chemical that would likely not pose any appreciable risk of deleterious effects in the human population and sub groups of at risk individuals over a lifetime [171]. Hence, a comparison of actual dose to the RfD can be used to determine the deviation from the safe value. This is captured by a Hazard Index (H) which is the ratio of Dose (D) to Reference Dose (RfD) and is generally used to determine the toxic effects of fish consumption where values less than 1 are considered non toxic. H can be calculated using Equation 2:

$$H = \frac{D}{RfD} = \frac{C \times I/W}{1000 \times RfD} \qquad \text{Equation 2}$$

Where C is the concentration of mercury in fish (mg/kg wet weight of fish); D is the dose of mercury from fish (mg/kg.day); I is the ingestion rate of fish (g/day); W is the average body weight which is 70 kg for an adult and 16 kg for a child, RfD is the estimated single daily chemical intake rate that appears to be without risk if ingested over a lifetime. EPA [171] recommends a RfD value for methyl mercury loadings of 1×10^{-4} mg/kg-day. Using this equation, we calculated the hazard index for a range of fish Hg loadings and ingestion rates relevant to this study. The three ingestion rates used represent a 227 g portion of fish consumed on a monthly (~8 g/day), weekly (32 g/day) and daily basis which were based on findings by Halfhide [177] on the Hillsborough River.

Table 3.8 Child Hazard Index (H) and Critical Fish Concentration (C) Assuming H = 1. Calculations Assumed a Rfd = 1 X 10^{-4} mg/kg Day for Different Ingestion Rates (I, g/day), Fish Mercury Concentrations (C, mg/kg Wet Weight) and Body Weights (16 kg for a Child). Ingestion rates of 8, 32 and 227 g/day correspond to a meal of fish once per month, week and day respectively.

Child Hazard Index (H)				
Ingestion Rate (g/day)	H C = 0.1 mg/kg	H C = 0.27 mg/kg	H C = 0.97 mg/kg	C (mg/kg) H =1
8	0.47	1.28	4.59	0.21
32	2.03	5.47	19.66	0.05
227	14.19	38.31	137.62	0.01

Table 3.9 Adult Hazard Index (H) and Critical Fish Concentration (C) Assuming H = 1. Calculations Assumed a Rfd = 1 X 10^{-4} mg/kg Day for Different Ingestion Rates (I, g/day), Fish Mercury Concentrations (C, mg/kg Wet Weight) and Body Weights (70 kg for an Adult). Ingestion rates of 8, 32 and 227 g/day correspond to a meal of fish once per month, week and day respectively.

Adult Hazard Index (H)				
Ingestion Rate (g/day)	H C = 0.1 mg/kg	H C = 0.27 mg/kg	H C = 0.97 mg/kg	C (mg/kg) H =1
8	0.11	0.29	1.05	0.93
32	0.05	1.25	4.49	0.22
227	0.32	8.76	31.46	0.03

Table 3.8 and 3.9 provides the results of these calculations. The last column in each table lists the mercury loadings in fish, C (mg/kg wet weight), that would be considered hazardous for the given ingestion rate. Using the measured fish loadings observed in this study, none of the Bluegill or Redear Sunfish would be considered hazardous at an ingestion rate of 227 g/month for adults; however, at this ingestion rate children should not eat anything greater than 0.21 mg/kg which would represent fish 16% of those fish sampled. For the LMB, all would be considered hazardous for children at an ingestion rate of 227 g/month. This suggests that the published advisory is under protecting children. At an ingestion rate of 227 g/week, fish above 0.01 mg/kg and 0.22 mg/kg should not be consumed by children and adults respectively and the local advisory adequately protects both populations and possibly overprotects adults in the case of Bluegill consumption. All of the fish sampled in this study would be considered hazardous if ingested at 227 /day for children and all of the LMB would be considered

hazardous to adults if ingested at 35 g/day (not shown in the table). The outcomes do not change much if we used concentrations that were 95% of the values measured to represent the methyl mercury fraction or if a meal was treated as 170 g. For example, at 170 g, 90% of the LMB would be considered hazardous to children as opposed to all for an ingestion rate of 1 meal per month. These results are particularly problematic in light of evidence from our concurrent study of fishing habits and knowledge along the river [177]. Results of that study indicate that a large proportion of the population surveyed fishes multiple times per week and have not seen any fish consumption guidance. Hence, it is likely that exposures to mercury exceed recommended levels.

Whilst statewide fish consumption advisories based on mercury loadings provide guidance to reduce human exposure, these are not necessarily easily translated to local scales and may miss vulnerable populations. As shown above the advisories may also limit consumption unnecessarily. Regardless, the lack of signage at the areas sampled and the high percentage of fisherfolk unaware of advisories for the given water body[177] imply that more effective forms of outreach are needed to impact human health. The challenge is to design this process so that the public can make informed decisions based on personal habits and the local characteristics of the water body. Further studies are needed to measure fish mercury loadings in other parts of the river which are heavily fished and which have different characteristics than the Rotary Park site of this study. Below the dam in the lower Hillsborough river where parameters like conductivity may be influential.

3.7. Summary

Nineteen sites along the Hillsborough River were selected for analysis because of ease of access and in larger scope water and sediment mercury loadings are not regularly monitored.

The average unfiltered surface water total mercury concentrations were 3.6±1.6 ng/L with the average of the upstream Middle Hillsborough (4.5±1.4 ng/L) being higher than that of the Lower Hillsborough River (2.6±1.3 ng/L). Total mercury loadings in sediment averaged 68±18 ng/g and ranged from 48 to119 ng/g with Middle Hillsborough loadings being 63.3±7.6 ng/g and the Lower Hillsborough loadings being 73±24.6 ng/g). Average LMB loadings were similar to those observed in other water bodies in the US; however, 86% of all of the fish (n=38) seen in this study had total Hg loadings that would warrant a fish advisory and 32% having loadings that should limit consumption to once per month if using the EPA fish consumption guidelines. XRD analysis confirmed that sediments exhibited large grains of quartz with aggregates of Fe-(hydro)-oxides and aluminum-(hydro)-oxides which may affect the mobility of mercury in soils.

CHAPTER 4: GUYANA

Figure 4.1. Administrative Regions of Guyana. Mahdia and Iwokrama are located in the Potaro-Siparuni (8) While the Konashen District is in the East Berbice-Corentyne (6).

4.1 Introduction

This chapter examines the use of mercury in the gold mining region of Guyana and its associated environmental and health implications. A presentation of the sampling approach and total concentrations in water, sediment, and fish samples collected from pristine and mined areas will be discussed.

4.1.1 Objectives and Tasks

Overall, the objective of this chapter is to characterize mercury loadings in select areas within Guyana, South America to assess the impact of gold mining activities. The tasks to accomplish this objective include:

- *Task 1a:* Identify and characterize suitable study sites for this work.
- *Task 1b*: Determine levels of total mercury present in fish, water, and sediments by using cold-vapor atomic absorption spectroscopy (CVAAS) and cold-vapor atomic florescence spectroscopy (CVAFS).
- *Task 1c:* Identify the geochemical conditions that affect the fate of mercury by using BET surface area analysis, electron dispersion spectroscopy, and X-ray diffractometry.
- *Task 2a:* Document the socioeconomic, regulatory and geopolitical factors within the United States (Florida) and internationally (Bolivia and Guyana) through a literature review.

4.2 Guyana (S.A.)

Guyana located between Suriname and Venezuela is a tropical climatic area known for its biodiversity, extensive rainforests, and many rivers. Its name in Amerindian means the "land of many rivers". It is geologically rich especially in gold which is Guyana's leading export and accounts for 11% of the country's gross domestic product (GDP) [178]. In addition, timber, bauxite, and diamond represent other major exports [179]. Being the only English speaking country in South America, it has a population of about 772,298 of which 90% of the population reside on the Atlantic coastal region which has most of the arable land (2% of total land area). The dominant religion is Hindu and is composed of four ethnic groups (East Indian, 43.5%; African descent, 30.2%; mixed 16.7%; and Amerindian, 9.1%). On the other hand, the interior regions are mainly inhabited by the indigenous. Guyana is divided into ten distinct regions and further separated into six mining districts. Figure 4.1 depicts the regions placing special emphasis on the Potaro-

Siparuni (Region 8) and East Berbice-Coretyne (Region 6) locations studied within this work. Whilst in Figure 4.3, the location of the sample sites and the delineations for the mining districts are depicted. The six mining districts in Guyana are as follows: Berbice Mining District 1, Potaro Mining District 2, Mazaruni Mining District 3, Cuyuni Mining District 4, Northwest Mining District 5, and Rupununi Mining District 6 with the bulk of gold mining currently occurring in Districts 2 to 4. The approximately 960 km long Essequibo River starts in the Acarai Range located in the southernmost part of the country (on the border with Brazil) in District 6's Konashen area and passes through Districts 2, 3, and 4 prior to emptying into the Atlantic ocean. The Essequibo drainage basin is approximately 50,000 km^2 and has a maximum depth of about 40 m with an average annual rainfall of 3,000 mm/yr [180, 181]. The Essequibo River and its tributaries drain two current protected areas in central Guyana, the Kaieteur National Park and Iwokrama International Centre for Rain Forest Conservation and are the main surface waters of an even larger biodiversity conservation corridor proposed by Conservation International - Guyana.

The Guiana Shield refers to a belt of greenstone underlying 21% of the total land area of Brazil, Colombia, French Guiana, Guyana, Suriname and Venezuela combined (Table 4.1). The area is bounded by the Amazon River and Japura-Caqueta River in the south, the Sierra de Chiribiquere to the west, the Orinoco and Guaviare Rivers to the north, and the Atlantic Ocean to the east. Sixty three percent of the total land in these six South American countries remains as intact forests (76% of which are tropical forests), with the smaller Guianas – French Guiana, Guyana and Suriname showing the least amount of deforestation [182].

Table 4.1. Land and Forestry Coverage and Gold Production of Countries of the Guiana Shield (Adapted from Hammond DS, 2005 and USGS, 2008)

Country	Total Land (km^2)	Land in GS* %	Land as IF* %	2006 Gold Production (kg)
Brazil	8,456,510	14	64	45,000
Colombia	1,038,710	16	47	15,700
French Guiana	88,150	100	90	2,000
Guyana	214,980	100	79	6,406
Suriname	156,000	100	90	9,362
Venezuela	882,060	51	56	12,400
Total	10,836,410	21	63	90,868

*GS refers to Guiana Shield and IF refers to Intact Forest.

Biological diversity, especially of endemic species, has driven the establishment of conservation areas in the region, including World Heritage Sites like the Central Suriname Nature Reserve that covers 10% of Suriname's land. Larger efforts are underway to protect the standing forests through international payment mechanisms established to combat global climate change within Guyana's Low Carbon Development Strategy. The Guiana Shield is also rich in gold, having one of the largest lower-grade deposits, and it ranks one of the fastest growing regions of gold production where the scale of mining ranges from large (> 500, 000 t ore/yr) to medium (50-500,000 t ore/yr) to small (<50 t ore/yr) [182]. In the case of Guyana, classifications are made according to property size: 2-52 km^2 - large, 0.6-4.9 km^2 - medium, and 0.1 km^2 – small [183]. Rising gold prices has led to the spread of mining activities throughout areas of the Guiana Shield which have had, and continue to have detrimental social and environmental impacts, many times in, or close to areas considered protected or inhabited by indigenous groups [182, 183 184 185]. In countries like Guyana which experienced significant increases in gold exports from the large OMAI mine which used the cyanide heap leaching procedure and operated there for ten years, gold production from small and medium scale mines which use mercury amalgamation procedures, are rising sharply as are the number of mining permits disbursed versus the use of more efficient procedures and safe practices or the discovery of richer deposits (Figure 4.2). Gold mining, logging, and the opening of new roads threaten biodiversity and mined areas have shown extremely slow rates of recovery under current practices [184, 186].

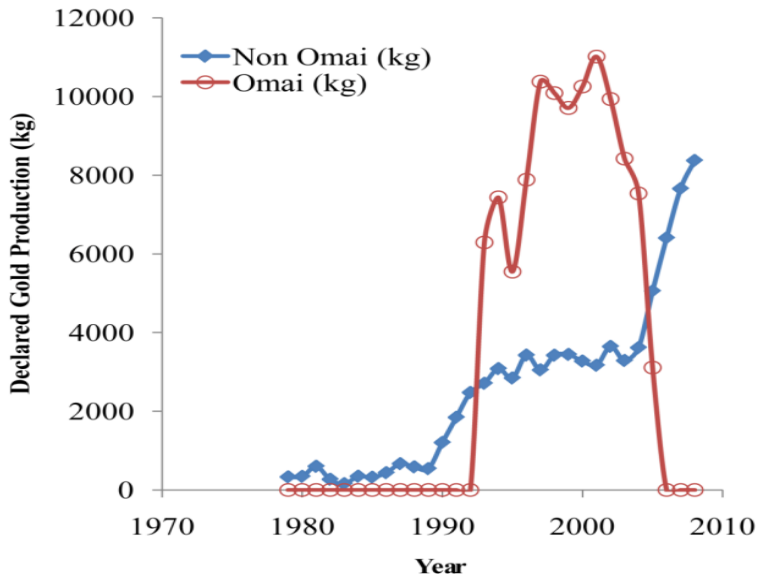

Figure 4.2. Guyana Declared Gold Production 1979 – 2008 from Large Sscale OMAI Mine and Small to Medium Scale Mines (Non Omai)[187].

Brazil is the only country in the Guiana shield to ban mercury use in gold mining, and the miners and their excessive mining habits have migrated to the Guianas where environmental regulation on mercury use is lacking or lacks proper enforcement mechanisms [183, 185]. Small-scale gold mining was estimated to contribute more than 10% of annual global anthropogenic Hg loading to the atmosphere in 2005 [188]. Mercury is recognized as a global contaminant known to cause deleterious neurological, developmental and other health effects [9]. Based on toxicological studies, the following guidelines have been established for mercury: 1 μg/L for drinking water [67], 1μg/m^3 for air [189], 0.77 μg/L for the protection of aquatic life through chronic exposure [190], and 0.3 mg methyl mercury/kg wet weight of fish for human consumption [190]. Epidemiological studies indicate neurological damage when total mercury concentrations are greater than 50 μg/g in adult hair or 10-20 μg/g in maternal hair [191]. Higher mercury concentrations in hair and urine samples have been found in or close to small to medium scale mining communities in the Guiana Shield [10, 192] and in some instances correlated with neurocognitive outcomes [193]. Higher hair mercury loadings seen in indigenous populations, many times in areas upstream from mining, have been linked to fish consumption habits [194, 195] although very little work has looked at contributions from thimerosal preserved vaccinations or nutritional deficiencies [196] or other local environmental conditions (e.g. slash and burn agriculture or wood fires in homes).

Early work in Brazil found higher concentrations of mercury in fish, sediment and water around small and medium scale gold mining communities when compared to non mining areas [144, 197 11, 198, 199]. Hilson [200]summarizes other studies that support these observations around the world. Others have also found some upstream non-mined environments to have higher loadings in Brazil [201]and Wasserman [202]argues that mercury releases from actual amalgamation are too insignificant to be the cause of loadings seen in soils in the Amazonian environment and that it is human induced activity, some from gold mining like land clearing, that releases mercury from soils into aquatic systems ([203, 204]. Though limited by its exclusion of the impact of mercury deposition, Beliveau et al. (2009) found that slash and burn agriculture altered the fractions of soil mercury was associated with, but did not result in and major loss of mercury to waterways. Deforestation and other land use changes are indeed being used as indicators for increased mercury levels in carnivorous fish [205]. Miller et al. [206] describes the ensuing debate within the scientific journals on whether the high mercury levels seen in Brazil resulted from gold mining or deforestation (and soil erosion) since both activities were prevalent and the soils from the area naturally had high background mercury levels compared to other parts of the world [207]. Some studies in the less deforested Guianas also found higher mercury loadings closer to, or downstream from mining although localized deforestation would have been an issue at mining sites [143, 206, 208, 209]. Mercury loadings in forest soils, river sediment and lateritic soils along the Sinnamary River in French Guiana did not show any significant variations around mining sites [210] whilst the type of soil (oxisol versus utisol) found in the ECEREX reserve in French Guiana influenced mercury loadings with oxisols having higher values [211].

Tessier et al.[51] found that during a rainfall event, atmospheric mercury distribution in the pristine Amazonian forested area of French Guyana exhibited concentrations from 2-100 ng/m^3. This was significantly higher than previous background levels determined by the Centre National de la Recherche Scientifique (CNRS) thereby suggesting that the exchange of gaseous mercury between the forest canopy and free atmosphere play a key role in the cycling of mercury in tropical environments [51]. Furthermore, rainforest ecosystems naturally emit large amounts of reactive gases and aerosols that can enhance the oxidation of mercury and precipitation washout.

4.3 Mining in Guyana and Environmental Regulations

In Guyana, artisinal gold miners make up approximately 95% of all the miners whilst the remaining is from large scale operations. Although, representing only 5% of the mining operations, large scale and multinational companies from major production industries (e.g. bauxite, diamond, timber, and sugar) account for 80% of the domestic economy [212]. In the large-scale mining sector, miners use sophisticated equipment and cyanide (HCN) to extract gold from ore such as the former OMAI Gold LTD. located in Region 8. This method of extraction is quite costly. Therefore, due to economical factors, limited technology, and ease of availability, small and medium scale miners principally use the more primitive technologies which employ the use of elemental mercury for gold extraction and gravitational agitation or whole ore amalgamation.

Gold mining appears to be a lucrative profession in Guyana and has impacted Guyana's social economics and environment. Since the rise in gold prices in the late 1980s, small scale operations in Guyana have increased significantly[206]. As of 2005, Guyana had 3,715 medium-scale prospecting permits and 41 prospecting licenses for large scale operations [213]. However, according to the Household Income and Expenditure Survey described by Ifil [212], regions 1, 2, 5, 8, and 10 where increased mining activities are present and most Indigenous groups reside, the highest unemployment rates of 16.7, 15.5, 14.6, 19.4, and 15.2 percent, respectively, exist. Of the total population, women within these regions represent the highest in unemployment [212].

Efforts to reduce mercury released in small and medium scale gold mines have been underway in Guyana since 2004. In accordance with the United Nations Environment Programme's (UNEP) Governing Council Decision 23/9 IV of the International Chemical

Programme, Guyana has established mercury partnerships within the Amazonia, Guiana Shield, Caribbean Region, and nationally to reduce environmental contamination and health effects associated with mercury exposure. These partnerships have been outlined in Table 4.2. Historically, the use of mercury has been seen to impair waterbodies within Guyana. Some of the programs advocate the use of alternative mercury technologies that propose the use of cyanide which may develop even more environmental issues than mercury. In 2001, the tailings dam breach by OMAI Gold Ltd., a large cyanide leaching facility, caused an immense amount of damage to the riverine communities along the Essequibo River, the principle drinking water supply for these communities [214]. The partnership programs have focused solely on addressing mercury handling practices, "clean" technologies, and sustainable gold production measures in an effort to raise heightened awareness. However, most of the programs with the exclusion of some of the World Wildlife Federation (WWF)-Guianas programs, have focused on key stake holders, miners, and governmental/university officials thus minimizing the importance of women, children, and the indigenous, the most vulnerable populations to mercury poisoning.

Table 4.2. Mercury Partnerships and Programs Within Guyana Aimed to Reduce Mercury Exposure.

Partnership/Program	Partnership Countries	Focus
Regional Awareness Raising Workshop on Mercury	Caribbean Region PPC*: Basel Regional Centre, CARICOM, CEHI*, UWI*	workshops developed to raise magnitude of problem and address strategies to address mercury issues
Regional Action Plan for the Prevention and Control of Mercury Contamination in the Amazon Ecosystems	Amazon Cooperation Treaty Organization	Proper handling of mercury, clean technologies, and sustainable economic develop of gold production
Use of Mercury Free Technologies in Mining	Guyana Shield (Guyana, Suriname, and French Guiana) and WWF**	Workshops, demonstration projects, panel discussions, and public awareness video aimed at reducing impacts of small and medium scale mining on the environment
General Environmental Capacity Development Mining Project (GENCAPD)	CIDA, GGMC, Guyana EPA, Guyana Gold and Diamond Miners Association, IAST, Ministry of Health, UG ***	Human and fish mercury studies in some mining districts; regulations and codes of practices (e.g. use of retorts and illegal mining concessions prohibited), public video, miner workshops

*PPC- Proposed Partnership Communities requested that they play more integral part of awareness campaign; CEHI - Caribbean Environmental Health Institute; UWI - University of the West Indies. ** WWF- World Wildlife Federation. ***CIDA – Canadian International Development Agency; GGMC- Guyana Geology Mines Commission; EPA- Environmental Protection Agency; IAST- Institute of Applied Science and Technology; and UG- University of Guyana.

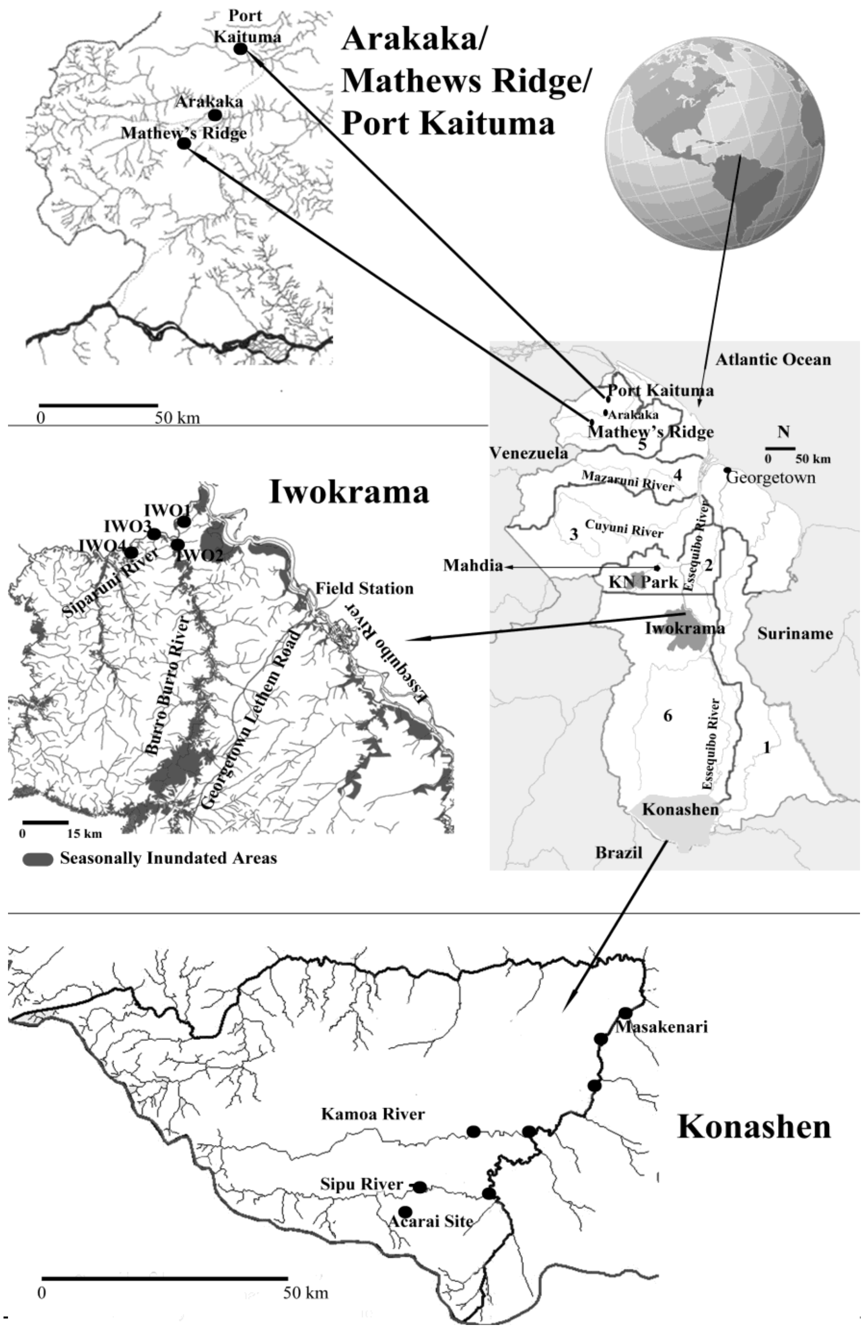

Figure 4.3. Study Sites in Guyana's Pristine Locations of Konashen District and Iwokrama and Mine Impacted Areas of Mahdia and Arakaka/Mathew's Ridge/Port Kaituma (KN- Kaiteur National Park).

4.4 Sampling Area

The study sites for Guyana depicted in Figure 4.3 include four distinct areas: Mahdia, Iwokrama, Arakaka/Mathew's Ridge/Port Kaituma, and the Konashen Community Owned Conservation Area. The sites within Guyana were chosen based on several factors which include areas centrally located in gold mining regions and those that are considered pristine and protected from anthropogenic activities.

4.4.1 Mahdia

Mahdia is the central town for mining and is currently the largest mining area in the country. Located in District 2, Mahdia's rich abundance of gold serves as a major source of income for residents and migratory workers. The area is undergoing severe deforestation and soil erosion possibly as a result of extensive mining activities. The small scale mines within Mahdia as well as other small and medium scale mines in Guyana use the following conventional gold mining process: (1) clearing of the concession by logging; (2) land dredging or the use of hydraulic pressure to extract low grade gold bearing ore thus forming large pits; (3) collection of ore placed on a sluice box for manual or mechanical gravitational agitation to settle gold deposits; (4) metallic mercury is combined with the final concentrate (settled gold/ore deposits) oftentimes directly on the sluice mats or with the concentrate that is shaken off of the sluice mats; (5) followed by a roasting technique or the recovery of gold by burning off of mercury from the gold. Safety precautions during the recovery phase (e.g. use of retorts to limit atmospheric releases of mercury) and practices of mercury application during the mining process (directly on the mat or after the mat is shaken) vary by each concession or mine camp. It has been estimated that for every 1 kg of concentrate there is 14 grams of mercury required to form an amalgamate [215]; however, oftentimes approximately 30 grams of mercury is rubbed directly onto the mat or the final concentrate retained on the sluice mats [108] which is considered an illegal mining practice.

Within the town center of Mahdia, mercury can be easily bought over the counter in the local market. In addition, there is limited amount of paved access roads as well as no access roads to the mine sites. Along the outskirts of town are local garbage dump sites where several plastic and Styrofoam containers are seen lining the streets.

4.4.2. Arakaka/Matthew's Ridge/Port Kaituma

The 21,755 km^2 area of the Northwest district towns of Arakaka and Matthew's Ridge with populations less than 1000 persons, have been mined extensively for manganese, diamond, and gold; however, the dominant commerce today is gold mining [108]. This area is a part of Mining District 5 and small-medium scale gold mining occurs in Arakaka while Matthew's Ridge serves as the central location of residency for many of the miners and their families. Port Kaituma served as the port for manganese cargo when the mine was operating and is now another residence for many in the mining industry. Residents and workers surveyed within this area depend extensively on rain catchments and springs for potable water, consume fish from the rivers and the majority of those involved in the mining business used mercury [216]. Hair and fish samples have also been found to have high levels of mercury [216, 217]. Sediment and soil samples were collected from Port Kaituma, Pakera Creek located in Matthew's Ridge and various water bodies in Arakaka as well as from an active gold mine in Arakaka in April 2005 in conjunction with the Institute of Applied Science and Technology (IAST) under a WWF-Guianas sponsored project.

4.4.3 Konashen Community Owned Conservation Area

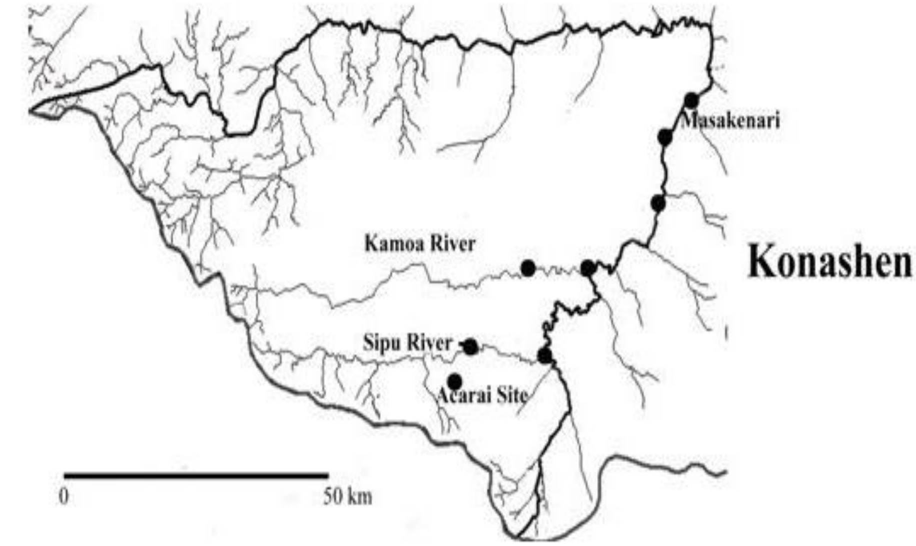

Figure 4.4. Map of Sampling Areas Along the Essequibo River (Kamoa River, Sipu River, Acari Mountain Creek, Masakenari River) Within the Konashen Community Owned Conservation Area (COCA).

The Konashen Community Owned Conservation Area (COCA) sampling sites have been outlined in Figure 4.4. COCA is comprised of 6,250 km^2 of some of the most pristine expanses of evergreen forests in the northern part of South America with over 319 species of birds, and 119 species of fish, including four that may be new to science (Alonso et al., 2008). The area is primarily underlain by sedimentary rocks and sand and houses the headwaters of the Essequibo River, and drains the Kassikaityu, Kamoa, Sipu and Chodikar rivers. The area's main mountains include the Acarai, Wassarai, Yashore, Kamoa and Kaiawakua with elevations reaching 1,200 meters above mean sea level. The Konashen District supports 200 Amerindians known as the Wai Wai who rely heavily on the Essequibo and its tributaries for daily water activities (e.g. drinking, bathing, eating, and cultivating the land) and who have teamed up with the GOG via the Ministry of Amerindian Affairs and Conservation International Guyana (CI-Guyana) to develop and implement a sustainable management plan for the area. It is the second largest out of five "consensus areas" in Guyana. Apart from slash and burn agriculture there is no current mining or industrial development in the area COCA, however, the local population speculated on certain areas being old mining sites and also on the existence of illegal mining activities. Hammond et al. [182] indicates that registered mines exist less than 200 km east of the COCA along the Brazilian border in Mining District 1. In October 2006, during the dry season, sediment samples were collected from the banks of the Sipu River (SR), Acarai Mountain Creek (AM), Kamoa River (KR), and Essequibo River (ER), the sites have been identified in Figure 7 and have been described in more detail elsewhere (Trotz, 2008). Samples were also collected in creeks and swamps in these areas. This sampling was done during a Conservation International Rapid Assessment Program (Alonso et al., 2008) and sample sites coincided with the various camp locations. In 2007 a COCA-managed water quality monitoring program was established using a subset of the sampling sites identified in this study.

4.4.4 Iwokrama International Centre for Rain Forest Conservation and Development

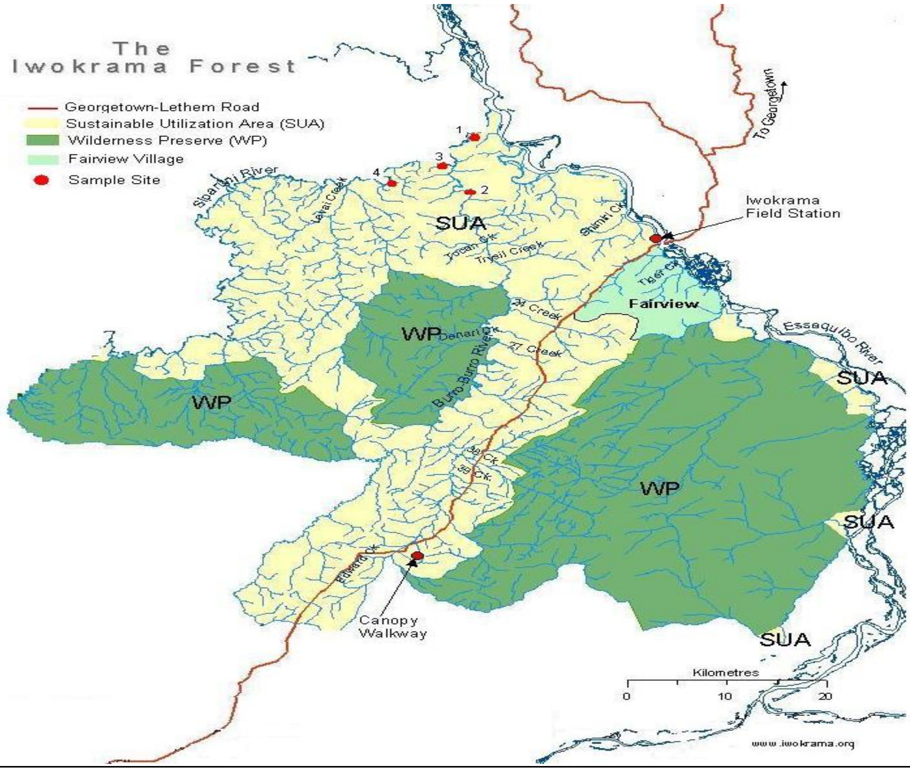

Figure 4.5. Location of Sample Sites Along the Essequibo and Siparuni Rivers Within the Protected National Park of Iwokrama, Guyana (S.A.) and Regional Borders (Modified from Iwokrama).

Iwokrama is located in the heart of the Guiana Shield and is the home to the Makushi Amerindian tribe as well as a diverse species of flora and fauna. It is one of four protected areas in Guyana, and by far the largest. Encompassing approximately 3,710 square kilometers (1,430 mile^2), it borders the Pakaraima Mountains to the west, the Essequibo River to the east, the Siparuni River to the north while the Burro-Burro River runs through its center. The Iwokrama International Centre for Rain Forest Conservation and Development (IIC) was established following the IIC Act (1996) to provide for the sustainable management and utilization of the rainforest. The highest point on the Iwokrama Mountain is close to 1,000 m. In addition to being the home of the Makushi indigenous group totaling roughly 250 people in Fairview Village (15 communities south of the Iwokrama forest combine to give a total indigenous population greater than 5000 people), IIC is known for its extensive biodiversity which includes 475 species of birds, over 400 species of fish, and over 90 species of bats [218]. As one of the few protected lowland tropical rainforests in the Amazon, IIC serves as an ecotourism site and research area for sustainable livelihoods, biodiversity and ecosystems services research. The site supports a sustainable utilization area which includes certified logging operations under the Forest Stewardship Council (FSC). The Iwokrama Reserve is partly bordered by rivers and more in the north is surrounded by areas designated for small to medium scale gold mining (land mining on opposite side of rivers) although regulations are in place preventing this activity given its proximity to Iwokrama. Sampling of five locations occurred in March 2009 on the Siparuni and Burro Burro rivers, although not as far as the mining creeks (Figure 4.5). Based on observations and recollections of Iwokrama staff, sampling was done at areas that may have been illegally mined and at areas that will be consistently monitored for water quality under an environmental monitoring program established in 2009.

4.5 Materials and Methods

In compliance with the United States Department of Agriculture (USDA) and the University of South Florida's Division of Environmental Health and Safety's agreement for foreign importing soils and sediments, all sediment and water samples were handled with proper care.

4.5.1 Glassware/Sampling Kit

All glassware and sampling kits were prepared as discussed in Chapter 3.4.1.

4.5.2 Reagents

All reagents and lab instrument calibration standards were prepared with trace metal grade (TMG) solutions supplied from Fisher Scientific. Mercury soil standard reference material (NIST SRM 1944, 3.40 mg/kg dry wt.) and freshwater standard reference material (NIST-1641 d, 200 x dilution; 8010 ng/L THg) were used for quality control and quality assurance. Stock solutions for mercury calibration were made from a 10 mg/L mercury nitrate standard preserved in 5% nitric acid (Fisher Scientific). A more detailed understanding of reagent preparation has been described in Chapter 3.4.2.

4.5.3 Water and Sediment Sampling

Water and sediment sampling was conducted along the Essequibo River and in tributaries at its main northern and southern watersheds. The areas covered included (1) unmined land (Konashen and Iwokrama) and (2) actively mined areas (Mahdia and Arakaka/Mathew's Ridge/Port Kaituma). Mahdia and Arakaka/Mathew's Ridge/Port Kaituma samples were collected directly from mining pits and tailings ponds.

A Quanta HYDROLAB multi-sensing system was used to measure depth (± 0.003 m), pH (± 0.2 pH units), dissolved oxygen (± 0.2 mg/L), specific conductance (±1% of reading ±1 count), temperature (± 0.2^{o}C), and turbidity (±5% of reading ±1 NTU) in the field and was calibrated using Fisher Scientific standards for pH, conductivity and turbidity and temperature-stable air saturated water for 100% DO_{sat}.

Sediment samples collected from Iwokrama were carried out using a Wildco 196-B15 standard Ekman bottom grab sampler and transferred in Ziploc bags for easy transport. In Konashen and Mahdia, sediments from the edge of rivers or from select areas within individual mining sites, respectively, were collected in Ziploc bags using a stainless steel scoop. All of the samples were stored on ice or refrigerated in the field and shipped on ice to the USF laboratory. The sediment was dried at 35ºC in a THELCO Laboratory oven prior to homogenization using a pestle and mortar and stored in Ziploc bags in the laboratory. All sediment samples were analyzed on a 240FS VARIAN DUO Atomic Absorption Spectrometer (CVAAS) coupled to a VGA77 Cold Vapor Accessory. Using the FDEP SOP # HG-020-5.12 digestion procedure [219] samples were predigested followed by CVAAS analysis procedures outlined in the FDEP HG-008-3.16 Method [219] for total mercury concentrations in sediment and waste by Cold Vapor Atomic Absorption Spectrometry (CVAAS). This method is based on US EPA Method 245.5/7471 [220].

4.6 General Results and Discussion

Total mercury loadings in sediment and soil samples and surface water quality data are provided in Table 4.3 with averages for the different areas given in Table 4.4 (value ± standard deviation (SD)). Fifty three sediment and soil concentrations ranged from 29 to 1200 ng/g and averaged 215±187 ng/g for all sites. Twenty seven samples taken from active gold mining areas (Arakaka and Mahdia) had sediment and soil concentrations that ranged from 29 to 601 ng/g and averaged 226±171 ng/g. Thirty five samples taken from active gold mining areas plus Mathew's Ridge and Port Kaituma had sediment and soil concentrations that ranged from 29 to 1200 ng/g and averaged 229±223 ng/g. Eighteen sediment and soil samples taken from conservation areas (Iwokrama and Konashen) had mercury loadings that ranged from 53 to 301 ng/g and averaged 187±77 ng/g. The highest loadings seen in the Iwokrama samples (IWO2, IWO3 and IWO4) were actually taken at locations which local staff suggested might be old mining camps which might explain why sample IWO1 was only 53 ng/g.

Some soil and sediment samples were taken from places which prevented the collection of water quality data because of high solids density. For the water quality data collected, pH values ranged from 3.9 to 7.3 pH units with lowest values observed around tailings ponds in Mahdia. The pH of water samples in Iwokrama and Konashen ranged from 4.8 to 6.3 pH units with the lower values observed in small creeks and swamp environments. The average pH for these conservation areas was 5.7±0.5 pH units. In the Mahdia mining samples, pH ranged from 3.9 to 7.3 pH units and averaged 6.6±1.1 pH units. Dissolved oxygen levels for Iwokrama and Konashen varied between 1.2 and 10 mg/L and averaged 6.5±1.7 mg/L. The lower value of 1.2 mg/L dissolved oxygen was associated with a seasonal pool in Konashen. Dissolved oxygen levels measured in Mahdia varied from 3.5 to 5.7 mg/L and averaged 4.7±0.8 mg/L. Turbidity values for Iwokrama and Konashen varied from 0 to 51 NTU and averaged 14±15 NTU and for Mahdia it ranged from 12 to 178 NTU and averaged 70±55 NTU. Mercury sediment and soil loadings were slightly positively correlated with pH (correlation co-efficient = 0.2; p value < 0.001) whereas no significant correlations were found with dissolved oxygen or turbidity.

Mercury (II) sorption to clays and mineral oxides of iron, aluminum and silicon, some of the most common sediment constituents, typically increases as a function of pH until it reaches a maxima then decreases in the higher pH regions [42, 48, 50, 221] and may explain the observed correlation. The presence of competing ions and natural organic matter, especially for the river sediments, likely play a role in loading behavior observed [40, 222, 223].

X-ray diffraction analysis revealed that sediments and soils collected from pristine locations were mainly quartz and Al-oxides whilst mining areas in Mahdia were rich in clays (kaolinite and Halloysite), phosphates, and Al- and Fe-oxides (goethite). In natural aquatic systems, lakes and rivers particularly abundant in Fe-Al- (hydr)oxides are effective at uptaking mercury[224]. Mercury peroxide (HgO) peaks were obtained in samples collected by hydrologic pumps and in tailings. No mercury was observed in samples collected from within the pits which suggest that mercury was being added, most likely from the miners. It has been generally observed that the formation of $Hg(OH)_2$ is pH-dependent[224]. The presence of mercury around these areas may further indicate that miners are not recovering mercury using appropriate technologies or applying mercury directly onto gravitational sluice box mats which is an illegal practice. Appendix F highlights all of the minerals determined from most of the sites.

Table 4.3. Sediment Total Mercury Loadings (sTHg in ng/g dry weight) and Water Quality Parameters for Samples Taken at Iwokrama, Konashen, Arakaka/Matthew's Ridge/Port Kaituma.

Area			sTHg (ng/g)	Surface Water			Longitude	Latitude
				pH	DO (mg/L)	TURB (NTU)		
Iwokrama	Iwokrama	IWO1	53	5.42	6.91	19.1	N04.78912	W058.87139
		IWO2	225	5.60	6.85	13.0	N04.73200	W058.85048
		IWO3	298	5.70	7.62	32.2	N04.76645	W058.88126
		IWO4	120	5.95	10.00	28.8	N04.74021	W058.92834
Konashen	Essequibo River	GR-ER-11	209	6.28	5.29	11.6	N01.62.976	W058.62.447
		GR-ER-12	176	6.34	5.97	12.1	N01.64.733	W058.61.826
		GR-ER-16	198	6.04	5.7	0	N01.68.102	W058.62.934
	Acarai Creek	GR-AM-01	290	4.74	1.2	0	N01.42.180	W058.95.221
		GR-AM-02	131	5.74	7.59	10.7		
		GR-AM-03	121	5.50	7.5	0		
		GR-AM-04	301	5.20	8.25	2.5	N01.38.989	W058.94.489
	Kamoa River	GR-KR-02	220	6.01	6.53	28	N01.53.189	W058.82.967
		GR-KR-04	121	6.09	6.91	51		
		GR-KR-05	163	6.05	6.62	34		
		GR-KR-06	92	5.19	6.36	5.7	N01.53.427	W058.82.692
		GR-KR-07	262	4.78	6.22	8.6		
		GR-KR-12	115				N01.53.193	W058.81.922
	Sipu River	GR-SR-06	271	5.65	7.43	5	N01.43.072	W058.92.941
Arakaka/Mathew's Ridge/Port Kaituma	Arakaka	S270405-0103	130	-	-	-	N0735.431	W059.58.714
		S270405-0401	180	-	-	-	N07.35.761	W060.00.260
		S270405-0805	61	-	-	-	N07.34.784	W060.00.186
		S270405-0704	98	-	-	-	N07.35.193	W060.01.188
		S270405	110	-	-	-	N07.35.574	W059.59.378
		S270405-0302	41	-	-	-	N07.34.799	W060.00.130
		Mine tailings	300	-	-	-	-	-
	Mathew's Ridge	S030505-2107	1200	-	-	-	-	-
		S020505-1804	200	-	-	-	N07.29.448	W060.08.452
		S020505-1602	190	-	-	-	N07.29.359	W060.11.120
		S040505-2309	200	-	-	-	N07.28.956	W060.09.238
		S030505-2006	290	-	-	-	N07.30.129	W060.08.044
		S020505-1703	583	-	-	-	N07.29.448	W060.09.214
	Port Kaituma	S050507-2502	168	-	-	-	N07.41.881	W059.55.450
		S050507-2704	364	-	-	-	N07.41.917	W059.53.559
		S070505	142	-	-	-	N07.42.517	W059.53.223

Table 4.3 (Continued). Sediment Total Mercury Loadings (sTHg in ng/g Dry Weight) and Water Quality Parameters for Samples Taken at Mahdia.

Mahdia	Mine 1	11, by pump	331	6.59	4.28	47.7	N05.380.23	W059.13596
		12, sluice box	127	-	-	-	-	-
		12B, LHS, sluice box	143	-	-	-	-	-
		12C, RHS, sluice box	81	-	-	-	-	-
		12D, camp	134	-	-	-	-	-
		Diosmp	114	-	-	-	-	-
		Topsoil	253	-	-	-	-	-
		Topsoil B	111	-	-	-	-	-
	Mine 2	14, pit	29	7.33	3.85	14.5	N05.29134	W059.13186
		14B, tailings 2	150	7.25	4.07	12.3	N05.29117	W059.13206
		15, tailings 1	222	3.87	3.51	178	N05.28982	W059.13229
		16, sluice box	49	5.95	4.25	14.6	N05.29007	W059.13061
		17, tailings 3	66	7.05	4.99	34	N05.26475	W059.13805
	Mine 3	18, tailings	409	7.31	5.66	116	N05.26437	W059.13745
		19, by pump	443	-	-	-	-	-
	Mine 4	20	508	6.73	5.45	80.2	N05.26443	W059.13791
		21, by pump	471	7.11	5.5	95	N05.25819	W059.13311
		Tailings	601	7.21	5.59	104	N05.25814	W059.13308
	Mine 5	22, by pump	72	-	-	-	N05.27391	W059.13372
		22b, sluice box	127	-	-	-	-	-

Table 4.4. Average Values of Total Mercury Loading, sTHg (ng/g dry weight), pH, Dissolved Oxygen, DO (mg/L), and Turbidity, TURB (NTU) Found in Each Study Area.

Location (# samples)	sTHg ± SD (ng/g)	Surface Water		
		pH± SD	DO± SD (mg/L)	TURB± SD (NTU)
Iwokrama (4)	174±109	5.7±0.2	7.8±1.5	23±9
Essequibo River (3)	194±17	6.2±0.1	5.6±0.3	6±7
Acaria Creek (4)	211±98	5.3±0.4	6.1±3.3	3±5
Kamoa River (6)	162±67	5.6±0.6	6.5±0.3	25±19
Sipu River (1)	271	5.65	7.43	5
Arakaka (7)	116±87	-	-	-
Mathew's Ridge (5)	416±440	-	-	-
Port Kaituma (3)	225±128	-	-	-
Mine 1 (8)	162±85	6.59	4.28	47.7
Mine 2 (5)	103±81	6.3±1.5	4.1±0.6	72±116
Mine 3 (2)	426±24	7.31	5.7	116
Mine 4 (3)	527±92	7.0±0.1	5.5±1.7	93±6
Mine 5 (2)	100±39	-	-	-
All sites (53)	215±187			
Conservation Areas (18)[a]	187±77	5.7±0.5	6.5±1.7	15±14
Gold Mining Areas (27)[b]	226±171	6.6±1.1	4.7±0.8	70±55
Mining Areas (35)[c]	229±223			

[a] Conservation areas include Iwokrama and Konashen only.
[b] Mining areas include Arakaka and Mahdia (Mines 1-5).
[c] Mining areas include Arakaka, Mathew’s Ridge, Port Kaituma and Mahdia (Mines 1-5).

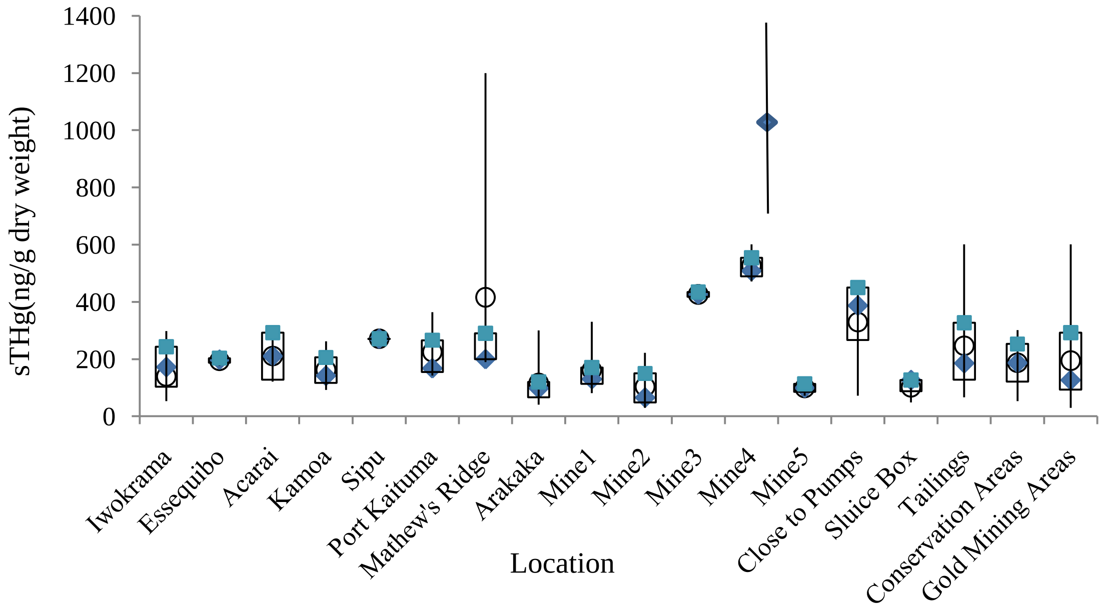

Figure 4.6. Box Plot of Total Mercury Loading on Sediments and Soils, sTHg (Ng/G Dry Weight), By Area Sampled Showing Values That Fall Within the 25th and 75th Percentile (Box), the Minimum and Maximum Loading (Line) and the Median (Diamond). Close To Pumps, Sluice Box, and Tailings Are Averages for Samples from Active Gold Mining Areas (Arakaka and Mines 1-5 in Mahdia). Conservation Areas Include Iwokrama, Konashen (Essequibo, Acarai, Kamoa and Sipu), and Gold Mining Areas Include Arakaka and Mahdia (Mines 1-5).

Figure 4.6 shows a box plot of the sediment and soil total mercury loadings by site. The highest sediment loading of 1200 ng/g was actually observed in Mathew's Ridge at a water source for the area. No active gold mines existed in Mathew's Ridge at the time of sampling, however, Mathew's Ridge was once a manganese mine and it is possible that the manganese oxides in the soil and sediment serve as sorption sites or sinks for mercury [225]. Aside from Mines 3, 4, and the high Mathew's Ridge sample, the loadings seen at mining and non mining areas in this study all lie between 29 and 364 ng/g with no significant difference seen between loadings found in conservation areas versus mining areas or areas close to mining. If only active gold mining areas are compared with the conservation areas higher loadings are seen in the gold mining areas.

Arakaka and Mines 1-5 were the sites with active gold mining and samples were taken from the sluice boxes and/or other areas around each of those sites. Mines 3 and 4 had the highest sediment loadings for the active gold mining sites studied in Mahdia. Figure 4.7 shows an image of the sediments representative of these mines as well as the average mercury loadings observed. The iron oxides were clearly prevalent in Mines 3 and 4 and to a lesser degree in Mine 5. Further spectroscopic analyses of collected samples are currently under investigation. In Thailand, Pataranawat et al. [226] surveyed areas around an active gold mining site that uses mercury amalgamation methods and found extremely high localized levels in soils, especially close to recovery areas (~ 10,000 ng/g) which they attributed to volatilization of Hg and dry deposition nearby. The mine sampled in Arakaka, and Mines 1, 2, and 5 in Mahdia, were also larger than Mines 3 and 4 and hence the recovery process was done fairly far from the pits and sluice boxes sampled. In addition to ore type and mine size, other factors like mercury handling and practices could influence the loadings observed. At each mining site it was observed that varying degrees of management practices and worker awareness and attention to handling of mercury were carried out; however, through informal discussions at all sites it was stated that retorts were used during recovery. Unfortunately, no soil samples were taken from the retort stations or mercury recovery areas.

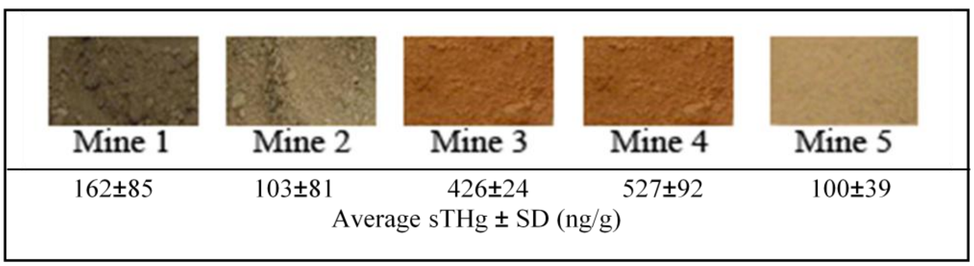

Figure 4.7. Photographs of Sediment Samples Collected in Mahdia from 5 Different Mines. The Average Sediment Loadings of the Various Sites at Mines 1-5 Were 162±85, 103±81, 426±24, 527±92, and 100±39 ng/g Respectively.

Figure 4.6 also plots data for specific areas around the mining sites, directly under the sluice box, in various tailings ponds, and close to hydraulic pumps. The sediment close to the sluice box had the lowest average mercury loadings of these three categories and the sediment close to the diesel powered hydraulic pumps had the highest average loadings. The pump samples were taken at the points where water was first pumped into the mining pit and included water recycled from tailings areas and water collected in flooded forest floors or creeks. Hence, the higher loadings seen close to the pump samples could be due to the fact that, 1) they burned diesel which could be a local source of mercury; 2) they received water and likely fines from tailings which may have been exposed to mercury during the mining process; and 3) they inundate a forest floor which could provide an environment conducive to mercury release from topsoil.

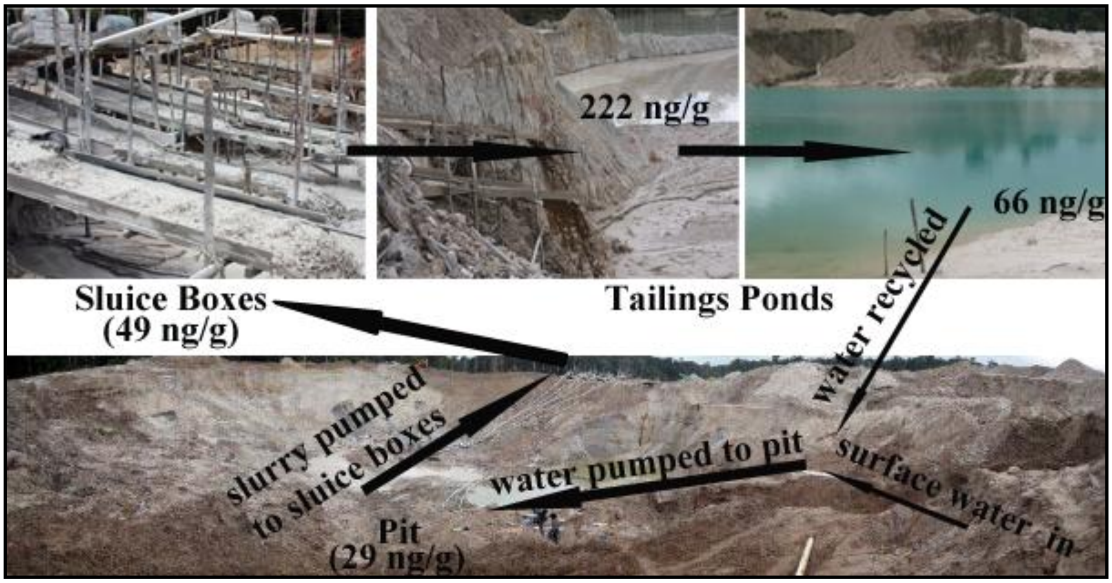

Figure 4.8. Diagram of Mine 2 in Mahdia, Showing Main Mining Processes and Areas Sampled Including: 1) The Pit Where High Pressure Water is Used to Make A Slurry With the Ore; 2) Sluice Boxes Fitted With Mats That Trap Gold Bearing Ore As Slurry Passes Over; and 3) Tailings Ponds Where Sediment is Allowed to Settle, Sometimes With the Help of Flocculants.

For one mine in Mahdia, samples were taken from the pit, sluice box and tailings ponds and the sediment total mercury loading increased at each stage as shown in Figure 4.8. The designations used here to identify different tailings areas may not match those designations used by miners, however, it reflects various locations within the mine site that are separated by some type of makeshift boundary/earthen dam. Researchers have found that forest soils in the Guianas have total mercury loadings in the range of 30 to 800 ng/g [210, 211]. Forest and overburden removal constitutes one of the first steps in the mining process and the low loading seen in the pit (29 ng/g) likely reflects the low background concentration of mercury in the ore. Between the sluice box and the first tailings pond area the loading increased from 49 ng/g to 222 ng/g and this could be due to inputs of mercury from the sluice box, atmospheric deposition, or an increase in the concentration of finer particles. The sample from the sluice box was taken prior to passing over the black mat which collects denser gold bearing ore. Although the application of mercury to this mat is illegal in Guyana, miners sometimes apply mercury to increase gold recovery. However, surveys of miners done simultaneously with this sampling exercise did not reveal this practice in Mahdia.

The turbidity of the water sampled in the first ponded area was high (178 NTU) indicating a high percentage of fines which have been positively correlated with mercury loadings downstream from artisinal gold mines in Suriname and Guyana [143, 153]. Miners are encouraged to apply flocculating agents to their tailings and this likely occurred at Mine 2, prior to the last two tailings pond locations (Guyana Geology and Mines Field Officer, Colin Mathis, Personal Communication). This could explain the observation that as the tailings moved further away from the sluice box, from one pond area to the next, the mercury loading decreased as did the turbidity.

Table 4.5. Range of Mercury Concentrations Seen in Sediment from This and Other Studies.

Location	sTHg (ng/g)
Arakaka (this study) Mathews Ridge (this study) Port Kaituma (this study)	41-300 190-1200 142-364
Mahdia mine wastes (this study)	29-601
Konashen river and creek sediments (this study)	92-301
Iwokrama river sediments (this study)	53-298
US Streams (2009) [174]	
unmined basins	0.90-2480
mined basins	0.84-4520
Brazil Summary (2003)[206]	
channel sediments[a]	<20 – 19800
soils[b]	30-406
French Guiana Sinnamary River (2000) [210]	
forest soils	50-480
river sediment	10-1550
lateritic soils	40-180
French Guiana (2008) [211]	
oxisol at ECEREX reserve	300-800
utisol at ECEREX reserve	30-300
French Guiana (2003) [209]	
coastal and ECEREX non mining area	<150
upstream from mines	<400
streams below mines	50-6200
French Guyana (2003) [208]	
Litany River (uncontaminated)	74-150
mining tributaries	254-350
Artisinal Au mines Suriname [143]	
mine wastes	5.5-200
streams below mines	110-150
uncontaminated baselines	14-48
Essequibo and Mazaruni rivers, Guyana (2003) [206]	
Essequibo River (mining)	4-225
Mazaruni River (mining)	5-707

[a] – Summary of studies done up to 1995, [b] – summary of studies done up to 2000.

Table 4.5 summarizes the more recent studies on mercury loadings in the less deforested Guianas where the highest sediment loadings observed have been in tributaries of small or medium scale mining activity [143, 206, 208], but where high levels have also been recorded at remote areas [209]. For the most part, the higher end of the range of sediment loadings in US streams[174] and in Brazil (as summarized by Miller et al. [206]) are greater than values observed in the sediments from the Guianas, even in active gold mining sites that use mercury. The upstream sediments and uncontaminated baselines found in other studies of the Guianas in Table 4.5 includes coastal areas and the range of loadings varies from 14 to 150 ng/g whereas the sediments from mining sites or tributaries downstream from mining sites ranged from 5.5 to 6200 ng/g [143, 206, 208, 209]. Soil loadings in the ECEREX reserve area and Sinmarry river in French Guiana ranged from 30 to 800 ng/g with higher loadings seen in forest soils and more specifically in oxisols [210, 211].

The mercury loadings of sediment and mine tailings observed in this study fall within the range of loadings observed in similar sites throughout the Guianas [143, 206, 208-210], however, the loadings observed at the conservation areas were not as low as those seen in some uncontaminated baselines for river sediments in this region [143, 208, 209]. The Iwokrama samples were taken from the rivers on its periphery where mining likely occurs on lands outside its jurisdiction. The three highest samples were identified by staff as areas where they thought may be impacted by some sort of historical mining activity. Hence, it is very likely that the levels reflect mining and it may be unfair to classify those samples as representative of an uncontaminated baseline. It does serve as a baseline from which future and more extensive monitoring programs can reference. Sampling for mercury within the site itself will provide important information on the impact of various income generating activities like the sustainable logging and can be used to better understand the dynamics of coupled human natural systems. Samples in Konashen were taken from areas where the Wai Wai had relatively little recollection of mining activity and in the Essequibo headwater region with low population density (0.032 persons/km^2) and not much through traffic. These samples can therefore be considered an uncontaminated baseline for sediment loadings in the southern drainage area of the Essequibo River. Though the Wai Wai practice slash and burn agriculture which also could release mercury rich topsoil to the rivers, most of the sample sites were taken upstream of village plots in areas considered amongst the most pristine in the world. It should be noted that Konashen borders the Brazilian gold producing state of Para (mining activity concentrated some distance away) and also lies approximately 200 km west of registered mines in Guyana, and the influence of atmospheric releases from those areas on

Konashen is unknown. Using published geospatial data on registered gold mines and logging activity in Guyana, Konashen is the farthest from registered gold mines and logging activity of all sites sampled [227].

4.7 Summary

The Essequibo River as well its northern and southern tributaries were identified as collection sites due to limited data for the areas. Moreover the sites represented lands that were considered protected and pristine (Konashen and Iwokrama) and actively mined (Mahdia and Arakaka/Mathew's Ridge/Port Kaituma).

Preliminary findings show that mercury concentrations from fifty three sediment and soil samples ranged from 29 to 1200 ng/g and averaged 215±187 ng/g for all sites. Eighteen sediment and soil samples taken from conservation areas (Iwokrama and Konashen) had mercury loadings that ranged from 53 to 301 ng/g and averaged 187±77 ng/g which confirmed suspected presence of old mining camps and sites. Active gold mining areas had sediment and soil concentrations that ranged from 29 to 1200 ng/g and averaged 229±223 ng/g.

X-ray diffraction analysis revealed that sediments and soils collected from pristine locations (Iwokrama) were mainly quartz and Al-oxides whilst mining areas (Madhia) were rich in clays (kaolinite and Halloysite), phosphates, and Al- and Fe-oxides (goethite). Mercury peroxide (HgO) was observed in XRD analysis of samples collected from mine area hydrologic pumps and in tailings.

CHAPTER 5: BOLIVIA

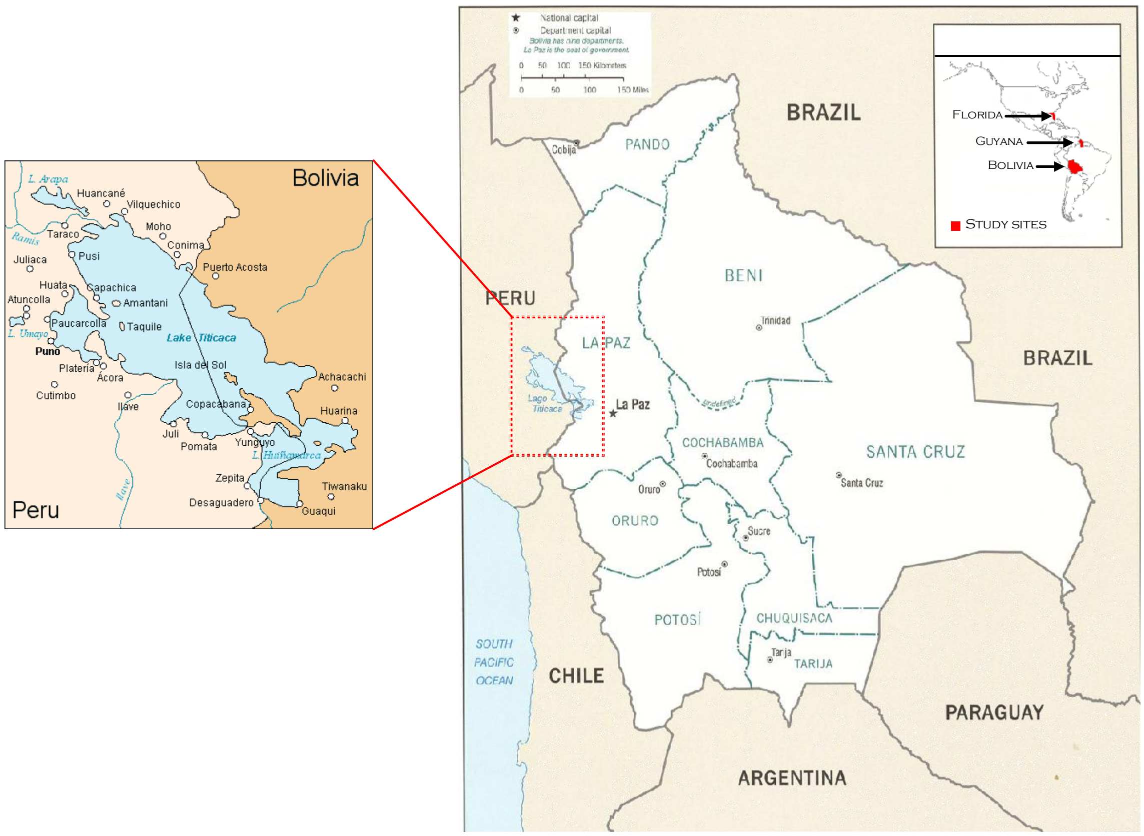

Figure 5.1. Nine Departments of Bolivia With Respect to Other Sampling Locations and An Enlargement of the Sampling Area Within Bolivia, Lago Titicaca.

5.1. Introduction

This chapter highlights the social and economic benefits of mercury to Bolivia. In addition, a presentation of the sampling approach and analysis of water, sediment, and fish samples for total mercury concentrations and mineralogy are presented.

5.1.1 Objectives and Tasks

The objective of this chapter is to investigate mercury loadings in Lake Titicaca, a water body in Bolivia with little characterization with respect to mercury as well as address the role that socioeconomic factors play in mercury loadings. The tasks to accomplish this objective include:

- *Task 1a:* Identify and characterize suitable study sites for this work.
- *Task 1b*: Determine levels of total mercury present in fish, water, and sediments by using cold-vapor atomic absorption spectroscopy (CVAAS) and cold-vapor atomic florescence spectroscopy (CVAFS).
- *Task 1c:* Identify the geochemical conditions that affect the fate of mercury by using BET surface area analysis, electron dispersion spectroscopy, and X-ray diffractometry
- *Task 2a:* Document the socioeconomic, regulatory and geopolitical factors within Bolivia through a literature review

5.2 Bolivia

Bolivia, one of the poorest countries in South America is landlocked with an area of 679, 619 km^2 and is bordered by Argentina, Brazil, Chile, Paraguay, and Peru [228]. With a population of 9.7 million[229] and approximately 70% of its population classified as poor and indigenous[230], it is the world's third-largest cultivator of coca and producer of cocaine[229]. Divided into nine departments (Beni, Chuquisaca, Cochabamba, La Paz, Oruro, Pando, Potosi, Santa Cruz, and Tarija), it is ethnically, linguistically, and geographically diverse (Figure 5.1) [230, 231]. Ethnically, Bolivia is composed of many indigenous tribes and mestizos (mixed racial ancestry, Spanish and indigenous background). In terms of linguistics, the primary language is Spanish; however there are over 40 indigenous languages which Quechua and Aymara represent the two dominate indigenous dialects and tribes[229, 231]. Geographically, its highland plateau or Altiplano (elevation of over 6,000 m) rests within the rugged Andes Mountains where weather conditions are frigid and semiarid [229]. Located in this area is the world's highest and South America's largest commercially navigable freshwater lake, Lake Titicaca. On the other hand, its lowlands experience humid tropical conditions as it resides in the Amazon Basin. It is also volcanically and tectonically active [230, 232]. The indigenous groups (Aymara and Quechua) traditionally live in the Altiplano and the valley of the high Andes. It is ranked 113th out of 177 countries on the UN Human Development Index and a large proportion of its population has limited access to education, health, and affordable housing [233]. Fish protein consumption accounts for 62% of the diets of rural inhabitants residing in the Peruvian Amazon which is similar to other Andean Amazon basin communities [234]. Additionally, the Andean Amazon Rivers Analysis Monitoring (AARM) Institut de Recherche pour le Development (IRD)-Bolivia have initiated Hg measurements in water of the Bolivian catchment [235]; however, minimal results are published but it is believed Hg contamination of fish resource in the Andean Amazon could impact the health of Bolivians.

During the early 1980s, the country experienced an economic crisis. Therefore to help stimulate economic growth, cut poverty rates, as well address issues of inequality, Bolivia enacted several reforms to spur private investment. In the 1992 US Commerce Department's Overseas Business Report, it was estimated that the United States imported over $209 million in tin, gold, and wood from Bolivia, making the US Bolivia's major trading partner [236]. This accounts for more than one-fifth of Bolivia's imports and exports. The report further concluded that the US made over $100 million in the sale of mining equipment to Bolivia which has since doubled[236]. Since this was in large a success to the US economy, US investors with the assistance of Bolivian partners have built several businesses directly involved in mining of tin, gold, and silver.

Mining contributes 4.5% to the GDP [237] of Bolivia and has impacted its environment due to unregulated and unsustainable practices. High mercury concentrations and fluxes have been estimated to be highest during the dry seasons in the Bolivian Amazon basin at the Andean piedmont as well as along the upper Madeira Rivers where gold mining activities occur [238]. In addition, studies on the Peruvian side of Lake Titicaca suggest that the lake is impaired by mercury. Studies have found up to 0.4 mg/kg of Hg are in mackerel fish [66] in Peru's Puno Bay. The Bolivian side of Lake Titicaca, fed by the Río Suches, has yet to be analyzed for total mercury content.

5.3 Mining in Bolivia

In Bolivia, less than 4% of the forty-eight percent of rural land is usable for cultivation due to the arid lands thus the people depend on mining as a means of economic survival[236]. From 1900-1980, tin (Sn) was the principle commodity of high regard because of its usage in weaponry during war. This industry was operated by the country's only mining company, COMIBOL. However, due to the fall in Sn prices in 1985, the exploitation of other precious metals, principally gold, increased significantly.

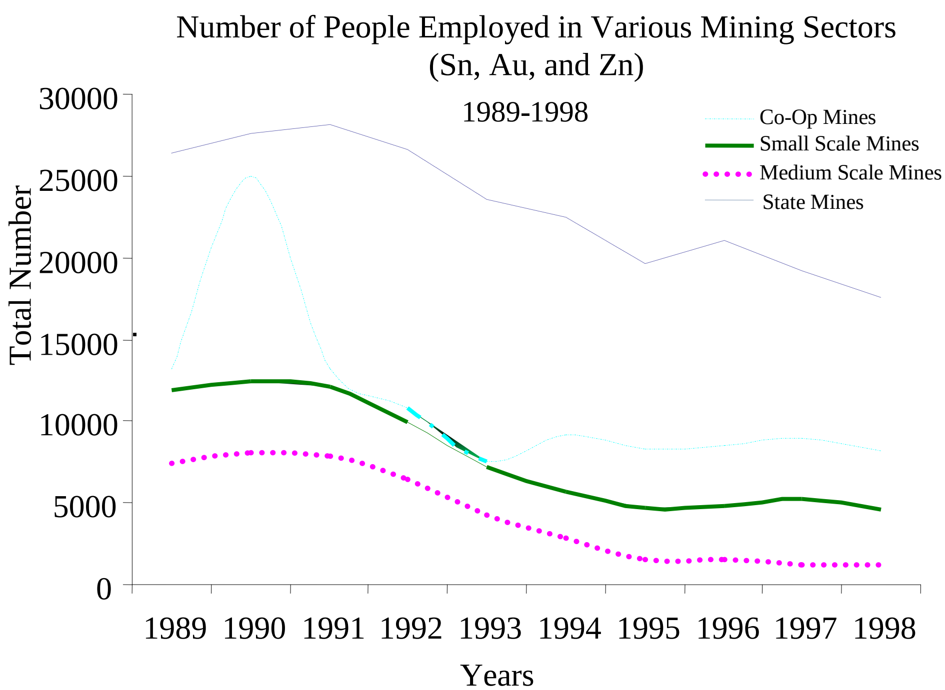

Figure 5.2. Total Number of Persons Employed in Various Mining Sectors in Bolivia from 1989-1998 Bbased on Reports by Bocangel [239].

With the United States as the single largest investor in Bolivia, the import and export of mining equipment and supplies regained momentum.

From 1971 to 1980, the mining sector employed over 20,000 workers and began to increase until 1986 when the economic crisis took a toll on the Bolivian economy and tin demand dropped (Figure 5.2). However, over the past fifteen years mining cooperatives have grown steadily. With a mining workforce of over 45,000 registered miners, Bolivian mining cooperatives contains about 506 mines of which 376 mines are associated with extraction of alluvial gold, tin, and tungsten (La Paz Department), 109 in base metal (zinc, lead, and cooper) (Oruro and Potosí), and 21 mines recovering ulexite (hydrated sodium calcium borate hydroxide) and non-metallic minerals (Uyuni Salt Flats) [237]. These cooperatives belong to the Federación Nacional de Cooperativas Mineras (FENCOMIN). On the other hand, medium scale miners mainly associated with mining and smelting employs approximately 3,500 miners and belongs to the Medium Scale Miners Association whilst private small-scale miners are affiliated with the National Mining Chamber (Cámara Nacional de Minería) and employs 3,500 miners as well [237].

COMIBOL's closure in 1989 was marked by a sharp emergence in employment within mining cooperatives. Cooperative mines or co-ops are composed of many teams or cuadrillas, groups of one to ten miners that are in operation independent of the cooperative. They produce, process, and trade their own findings. The cooperative, organized into groups by the mineral being extracted, is the lead organization that supplies essential mining supplies and equipment such as compressed air, technical assistance, and trading to the cuadrillas in exchange for a percentage of the net value of their sales. However, in the gold cooperatives more primitive technologies that require the use of mercury are utilized. In addition, skilled labor, security/safety, or technical assistance are not provided. In all of the cooperatives, operation/ownership is controlled by former COMIBOL workers, their families, and even in some rare cases seasonal migrants who in a large part are the indigenous poor. These cooperatives have a total disregard for the safety and well-being of its workers as well as the environment. The methods of exploitation do not have proper environmental impact assessments, protocols for waste management (e.g. tailings dams or ponds, water treatment prior to discharge), or closure plans in place. In the gold cooperatives, the structure of organization is more complex and contains many laws of regulation established by the chief gold cooperative.

These cooperative types contain both formal and informal miners (barranquilleros). For example, the barranquilleros are the “scavengers or gravel scratchers” of the gold mines. They reprocess the tailings of the cooperatives in search of gold that was mistakenly lost during extraction by the formal miners. All of their practices can immense amount of damage to the people and their environment.

5.4 The Mining Culture and the Exploitation of the Poor and Indigenous Populations

The culture of mining is complex and oftentimes with no real alternatives. Miners working to produce generous earnings for their families join the profession with a clear understanding of the daily risks associated with their profession. In fact, before entering into the mines the miners believe that one must exclude the outside world from the mines including God known as Pachamama to the indigenous Andean communities. Then as the miner enters into the mine one must close the door and submit to the mining devil, El Tío, by providing an offering before beginning work. Miners usually provide offerings of tobacco, liquor, and coca leaves to simultaneously ask for protection and high mineral recovery. Traditionally, El Tío (The Uncle), lord of the underworld resembles the shape of a goat and is similar to Legba in the Voodoo religion [240]. However, it is unconfirmed whether the use of mercury for ritualistic practices is performed among inner mine offerings or community sacrificial ceremonies which involve slaughtering a llama and smearing its blood on the outside of the mine doors in hopes that El Tio will grant refuge to the miners [241].

In Bolivia, mining has caused extensive soil erosion and pollution of freshwater systems [242]. It has stimulated the economy, but continuously exploits the indigenous population, women, and children who play an integral part in the mining process. Some 90% of all mining children begin working in the mines at age six or seven to earn a salary of Bs. 4 (approximately, US$0.50 per day), and work seven days a week between seven to eight hours or until a palo, 0.10 g, of gold is obtained with only one thirty minute break [243, 244]. According to the Bolivian Code for Boys, Girls and Adolescents General Labor Law, fourteen years of age is the legal minimum age for employment. In addition, minors are prohibited from conducting dangerous, unhealthy and physically exhausting work especially in underground mines. Women and children under 18 years of age are only allowed to work during the day [244]. Furthermore, the Ministry of Planning and Sustainable Development in Bolivia estimates that 60% of children employed in mining and other practices do not attend school [244]. Often grouped as informal miners or barranquilleros, they are exposed daily to deplorable and deadly conditions. These conditions warrant the use of special apparatuses and personal protective equipment which are not supplied by the co-op officials. Due to financial hardships, miners often do not use them or improvise (e.g. using several layers of clothes to cover their nose and mouth to act as a breathing apparatus). The cooperatives do provide cost based medic services or sanitation posts at the mine sites. Due to financial reasons the informal miners prefer to use home remedies and/or chew on coca leaves to relieve any pain and exhaustion experienced from the deplorable working conditions.

5.5 Sampling Area

5.5.1 Lago Titicaca, Bolivia (S.A.)

Figure 5.3. Lago Titicaca (Lake Titicaca) and Its Two Southeasterly Quarters Known to the Indigenous, Quechua, as Lago Huinaymarca (2) and Lago Chucito (3).

Lake Titicaca, also known in Spanish as Lago Tititaca, is an ancient nearly closed, basin lake that resides in the tropical belt of South America's high-altitude Altiplano basin (>3,800 meters above sea level) of the Andes Mountains. Jointly controlled and bordered by Peru, it occupies a total surface area of 8,400 sq. km [245, 246] which is shrinking due to increasing evaporation rates suspected to be caused by increasing humidity and lack of rain [236] amplifiers to regional climate change [235247, 248]. It is divided into three main areas (Figure 5.3) known as (1) Lago Mayor (6,500 km^2), (2) Lago Menor (1,400 km^2), and (3) Bahia de Puno (500 km^2). The maximum depth of the lake is 288 m which is in the Lago Mayor division [246] whilst the shallower areas are Lago Menor (20- 30 m) and Bahia de Puno [246]. Bahia de Puno and Lago Mayor reside mainly on the Peruvian side of the lake where as Lago Menor is on the Bolivian side. Bahia de Puno is the most contaminated and Lago Menor is the most understudied. Precipitation accounts for 55% of the inflowing water to Lago Titicaca whilst 45% of its inflowing water comes from rivers and streams [246]. The major rivers flowing into the lake include the Río Ramis (74 m^3/s), Río Coata (47 m^3/s), Río llave (38 m^3/s), Río Huancané (19 m^3/s), Río Suches (11 m^3/s), Río Keka, and Río Tiwanaku[246]. On the other hand, evaporation as well as the Río Desaguadero or translated into English as the "river that removes water" acts as the lake's only means for naturally releasing water flow or overflow.

During the summer months of December to March, the lake is subjected to the influence of the intertropical convergence zone (ITCZ) and experiences monsoon weather events as North-East and South-East trade winds converge to form large bands of clouds or thunderstorms. Average temperatures for the areas surrounding the lake are between 3-12ºC (37-54ºF) but can go lower. In addition, it is characterized by its unique flora and fauna. The lake spans a distance of 190 km in length and 80 km in width. It has been characterized to contain over 30 native fish species that represent 28 genus *Orestia* and 2 benthic catfish species of *Trichomyceterus dispar* and *Trichomyseterus rivulatus* [249]. Exogenous species of pejerrey (*Basilichthyes bonariensis*) and trucha (*Salmo gaidneri*) were intentionally introduced into the lake in 1939 to help with issues of declining fish stocks. Such phenomenons have been frequently seen to occur globally in many freshwater systems.

The lake is essential to many Bolivians and Peruvians. Serving as the primary water supply for over 1,000,000 people living in the lake region in both Bolivia and Peru, it is known by the indigenous as "father of life" or the sacred "gift" from God. Residents in the capital city of LaPaz and the communities in the LaPaz department principally receive their fish from this area. Residents have also described ice melts and rain waters as additional sources of water. It is managed by the Proyecto Especial del Lago Titicaca (PELT) and the Autoridad Autonoma Binacional del Lago Titicaca (ALT) which formed as a result of the severe drought experienced in 1982-1983 [246]. PELT is a Peruvian management program for water resources, fisheries, and farming in Peru where as ALT is a binational master plan for water resource management and protection-prevention of floods in Bolivia and Peru[246].

5.5.2 Site Description

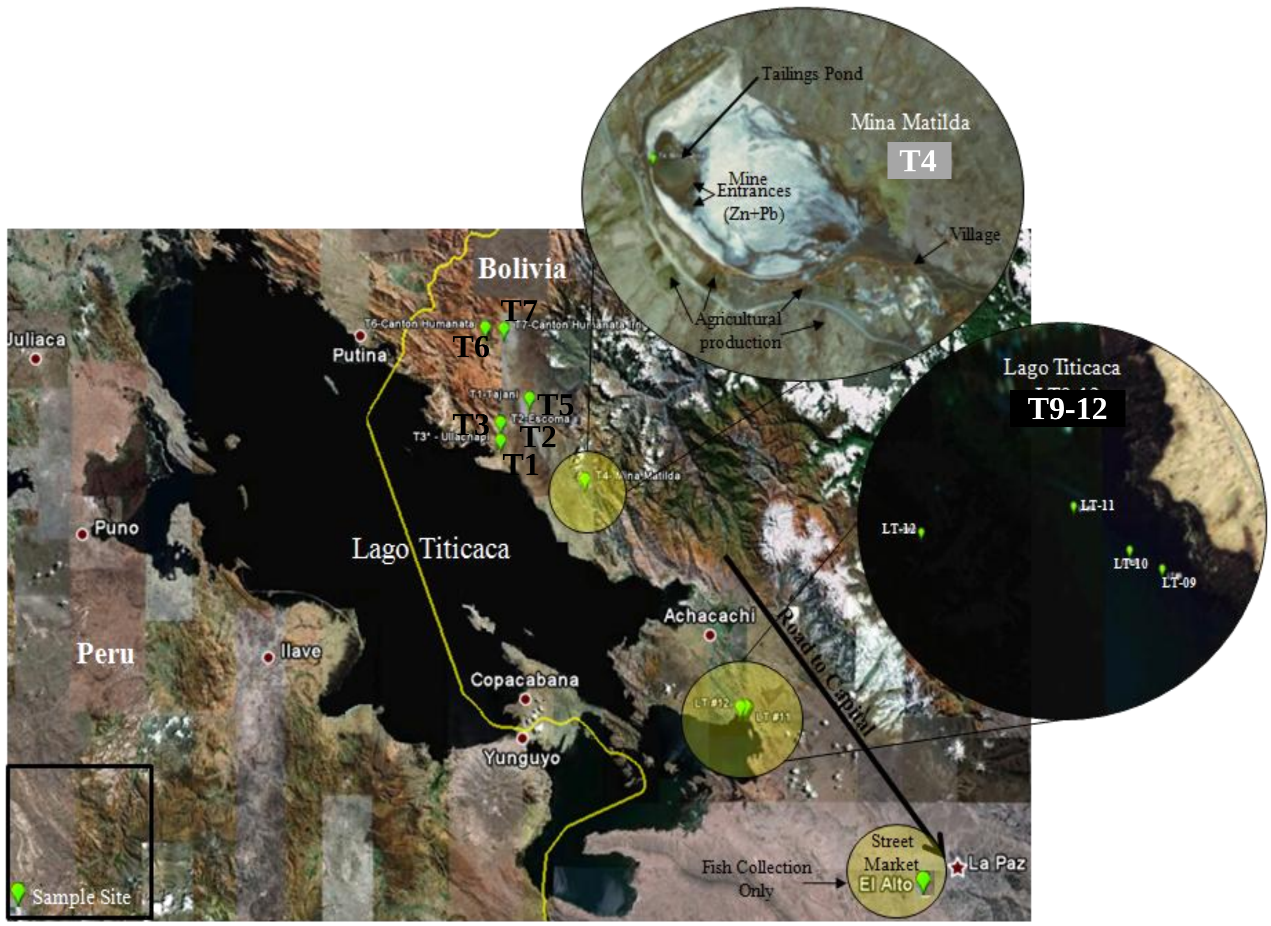

Figure 5.4. Digital Mapping of Sample Points of the Tributaries of Lago Titicaca with Enlargements of the Tin (Sn) and Lead (Pb) Mining Concessions and Lago Titicaca (from Google Earth).

In July 2009, over a period of three days, water and sediment samples were collected from twelve locations in Lago Titicaca and its rivers and streams (Río Suches, Río Alcamarini, and mountain streams). Sample collection was done in collaboration with ACDI/VOCA, Universidad Tecnologica Boliviana, and the University of South Florida. This area was highly populated by Quechua and Ayamará who do not speak fluent Spanish. Therefore, the ACDI/VOCA representative acted as the translator for Quechua and the Unversidad Tecnologica Boliviana researcher was the Spanish translator. The sites have been denoted in Figure 5.4 as LT1-LT7 for streams and rivers whilst LT9-12 represent samples collected directly from the lake. Fish samples of known origin, genera and habitat were bought at a popular outdoor market in the Lago Titicaca area.

The area around the lake can be classified as arid containing several hills with mature slopes rising to over 800 meters above the lake. The lands directly surrounding the lake (T1-T4) are poor for rearing livestock (e.g. sheep, llamas, and alpacas). Potatoes are grown close to the lake at Escoma (T2) and sampling areas T6-T7 contain several agricultural plots for the production of potatoes and quinoa, a staple product, as well as livestock (mainly llamas). Canton Humanata (T6-7) is fed by river water from the Río Alcamarani and Río Suches. It is also interesting to note that sampling areas T6 and T7 had an intricate system of piping and raised fields, an ancient farming practice. River levels along the lower reaches of the Río Suches were low and residents were subjected to extreme water restrictions.

During sampling, the average daily temperatures were between 20-23ºF where as night temperatures fell below freezing. In addition, since ambient temperatures ranged between -5-23ºF and refrigeration systems were limited in the area, samples were transported in a cooler to the Laboratorio de Calidad Ambiental of the Instituto de Ecología of the facultad de Ciencias Puras of the Universidad Mayor de San Andrés for drying prior to shipping to the US for analysis by CVAAS.

5.6 Materials and Methods

5.6.1 Glassware and Field Supplies

I-Chem certified pre-cleaned glassware (250 mL) was used for surface and depth water samples. Sediment samples were collected using a stainless steel scoop and bowl. Geographic data points were collected using a handheld Garmin eTrek using the Universal Transverse Mercator (UTM) World Geodetic System (WGS) 1984.

5.6.2 Reagents

A bulk solution of potassium bromide/potassium bromate was prepared from reagent grade solids dissolved in water. $KBr/KBrO_3$ was combined with concentrated Fisherbrand hydrochloric acid in situ to preserve all water samples.

5.6.3 Water and Sediment Sampling

Water and sediment sampling points have been shown in Figure 5.4. Samples were collected from a zinc and lead mine, Minera Potosí (T4), a mountain stream in the town of Matilda-Aqua Calientes (T4-b) , in the town of Canton Humanata (T7) along the Río Alcamarini which drains into the RioSuches, along the Río Suches (T1-Tajani, T2-Escoma, and T3-Ullachapi), just before it drains into the Lago Tititca, and Lago Titicaca (LT9-LT12). Only unfiltered surface and depth water samples were collected directly into certified 150 mL pre-cleaned I-CHEM glass bottles. Due to limited access and timing conflicts, depth and surface sediment and water samples were not collected at every sampling point. Water samples from rivers and streams entering into Lago Titicaca were collected along shore where as lake samples were collected from onboard a wooden makeshift row boat. All handling operations were performed using ultra clean techniques employed by the US EPA. Prior to sample collection at each site, the equipment was rinsed three times with water from the sampling point. Samples were then acidified with bromine monochloride prepared in situ. All acidified samples were stored in a dark lined cooler for laboratory shipment. Water quality measurements of pH, specific conductivity (SpC), temperature, dissolved oxygen (DO), saturated dissolved oxygen percent (DO_{sat} %), salinity, total dissolved solids (TDS), turbidity, and depth were collected in the field using a Hydrolab Quanta multiprobe. GPS measurements were taken at each sampling point along with a corresponding sediment sample.

As for surface sediment samples, the top 2 cm were discarded while the remaining sample was placed in doubly sealed plastic bag and stored in a dark lined cooler separate from water samples. No water samples were collected at Mina Matilda (T4-b) due to concerns with health and safety.

All sediments and tailings were dried and water samples were analyzed by the Laboratorio de Calidad Ambiental del Instituto de Ecología de la facultad de Ciencias Puras del Universidad Mayor de San Andrés in LaPaz following the US EPA Method 1631 and for Trace Metal Analysis of Mercury in Water. Sediments and tailings were transported to the University of South Florida and analyzed using a Varian 240FS coupled with a VGA77 following Method 7471.

5.6.4 Fish Sampling

Bolivian fish samples of trucha (*Salmo gaidneri*) and pejerrey (*Basilichthyes bonariensi*) were obtained at the largest local market in the Alto Plano region. Based on fishermen accounts these samples came directly from Lago Titicaca where fishermen mainly use nets and traps. In Lago Titicaca, trucha and pejerrey are the dominate species and non-native to Bolivia. These species were introduced into the lake in the 1940s and 1950s as a means to help with fish management issues [66]; however, over-fishing is still an issue as the principle source of protein in the region is fish. Samples were weighed, measured, identified for gender, and filleted in the field then transported to the Laboratorio de Calidad Ambiental del Instituto de Ecología de la facultad de Ciencias Puras del Universidad Mayor de San Andrés in LaPaz. To ensure similar digestion procedures as

Hillsborough River samples, the laboratory was provided a copy of the FDEP digestion and analytical procedures. Otoliths for age identification were not collected.

5.7 General Results and Discussion

5.7.1 Total Mercury Loadings in Water and Sediment

Twelve locations in the Lago Titicaca, Bolivia area were sampled. Water chemistry (pH, Temp, SpC, DO, and TURB) and unfiltered water THg (uwTHg) concentrations were investigated to gain a general understanding of the possible influences water chemistry have on water mercury loadings. Table 5.1 (uwTHg Lago Tititcaca) and Table 5.2 (uwTHg rivers and streams) summarizes the water chemistry measurements. Data results were grouped into two categories (1) Lago Titicaca and (2) Rivers and Streams of Lago Titicaca. Due to previous mine closures and hostile relations among miners and government officials only sediment was collected for site T4b, Minera Potosí.

Table 5.1. Depth (DUF) Unfiltered Water Quality Parameters (pH, Temperature (Temp.), Speceific Conductivity (SpC.), Dissolved Oxygen (DO), and Turbidity (TURB) for Sample Sites Access by Rowboat in Lago Titicaca. Sampling Was Conducted June 2009.

Site	uwTHg (ng/l)	sTHg (ng/g)	pH	Temp. (°C)	SpC. (mS/cm)	DO (mg/L)	TURB (NTU)	Depth (m)
T9 DUF	0.3	919	7.0	9.9	3.5	3.7	17	7.0
T10 DUF	37.0	854	8.0	9.9	2.0	2.0	15	14.7
T11 DUF	0.3	878	8.0	10.3	2.0	2.4	6	10.8
T12 DUF	20	ND	8.1	12.7	1.3	5.5	7	8.0
Titicaca Average	*14*	*883*	*7.8*	*10.7*	*1.9*	*3.4*	*11*	*10.1*
Titicaca Stdev	*17*	*33*	*0.5*	*1.3*	*1.4*	*1.6*	*6*	*3.4*

Lake pH ranged from 7.0 – 8.1 with an average of 7.8±0.5 where as rivers and streams of Lago Titicaca averaged 6.1± 1.0 (5.1-7.6). Lake averages were similar to natural and manmade lakes studied in Brazil[250]. The lowest pH value was seen in sample T6 which was collected from Canton Humanata, a potato and quinoa farming and llama rearing community just downstream from a suspected gold mining area along the Río Alcamarani (just before the river entererd into the Río Suches). Samples T1 (Tajani) and T2

(Escoma) located on the Río Suches about 5-10 miles from entering into the Lago Titicaca, also displayed low pH values (5.40 and 5.70, respectively) which may have be the reason for the small size potatoes grown in the area. The low pH also may be attributed to the river serving as a disposal site for municipal and industrial/electrical waste products. At Tajani (T1), the river is used for irrigation of potatoes and onions. Optimal growth for potatoes is in slightly acidic soils; however, if too acidic smaller potatoes are produced. In addition, low water levels were exhibited along this segment of the river; therefore, residents only received water every 3-4 days. Matilda-Aqua Calientes (T4-a), located just downstream from Minera Potosí or Mina Matilda (T4-b), a zinc and tin mine had a pH value of 6.27 but exhibited the highest temperature out of all of the samples, hence the town's name translated in English means "Hot Waters". Average temperatures in the lake were slightly lower than those observed by Gilson at similar depths (11.61-12.31°C)[247] . The overall sample pH ranges (5.1 to 8.1) in this study when in comparison to the Río Ramis watershed that enters into Lago Titicaca on the Peruvian side are within the exhibited ranges of 3.17-8.60 (lowest levels were in mining areas) [66]. Additionally, average river and stream waters represented the lowest temperatures compared to lake temperatures. Turbidity (TURB) averaged 11±6 NTU in Lago Titicaca and ranged from 6 to 17 NTU. The results also revealed that Matilda-Agua Calientes had the highest levels of specific conductivity and salinity, 1.64 mS/cm and 0.82 ppt, respectively, Conductivity in lake samples ranged from 1.3-3.5mS/cm which is expected since salt concentrations in the lake have been seen to be considerably higher than fresh waters[247].

Table 5.2. Surface Unfiltered Water Quality Parameters (pH, Temperature (Temp.), Speceific Conductivity (SpC.), Dissolved Oxygen (DO), Turbidity (TURB), and Salintiy for Sample Sites Access the Banks of Rivers and Streams (RS). Sampling Was Conducted June 2009.

Rivers and streams (RS) of Lago Titicaca(T)										
Area		uwTHg (ng/L)	sTHg (ng/g)	pH	TEMP (°C)	SpC (mS/cm)	DO (mg/L)	TURB (NTU)	Salinity (ppt)
Tajani	T1	63.0	170	5.70	5.70	0.22	10.55	14.9	0.10
Escoma	T2	67.0	132	5.40	10.75	0.22	9.82	15.6	0.10
Ullachapi	T3	44.0	358	7.60	9.43	0.22	11.36	19.1	0.10
Matilda-Agua Calientes	T4-a	114.0	1568	6.27	15.47	1.64	7.31	16.2	0.82
Minera Potosi	T4-b	--	2891	--	--	--	--	--	--
Canton Humanata	T6	63.0	757	5.05	5.56	0.27	10.67	15.2	0.20
CH Irrigation	T7	45.0	24	6.86	5.57	0.23	11.61	18.1	0.11
RS Average		66.0	843	6.1	8.70	0.50	10.21	16.5	0.20
RS Minimum		44.0	24	5.1	5.56	0.20	7.32	14.9	0.10
RS Stdev		25.5	1048	1.0	4.00	0.60	1.61	1.7	0.30

Given the small sampling size, mercury loadings in the unfiltered waters within the rivers and streams of Lago Titicaca ranged from 0.3-114 ng/L and sediment loadings ranged from 24-2891 ng/g. Mercury loadings from this site have been compared with water quality parameters in Table 5.2 whilst comparison to other areas is shown in Table 5.3 and Pearson correlations in Table 5.4.

Table 5.3. Mercury Concentrations in Sediment and Water Samples from Lago Titicaca and Other Studies.

Location	Sediment		Unfiltered Surface Water	
	Hg (ng/g)	Methyl Hg (ng/g)	Hg (ng/L)	Methyl Hg (ng/L)
Lago Titicaca and rivers and streams that flow into it (this study)	9.3-2891	-	0.3-114	-
Río Ramis, Lake Tititcaca (Peru)		-	30-259	-
Antarctica streams and lakes [147]			0.27-1.9*	
Amazon basin [144-146]				
streams affected by mining	24-406	0.07-1.9	2.9-33	0.2-0.6
upstream from mining	67-93	-	2.2-2.6	-
Río Pilcomayo Basin, Bolivia (agricultural area located near mines)[251]	339-4270	-	75-260	-
Upper Madeira Rivers of Bolivian Amazon Basin[238]				
rivers affected by mining-Andean piedmont			7.22-8.22	
upstream from mining-outlet of Andean basin			2.25-6.99	
Beni Basin (Bolivan Amazon Basin) [238]	-	-	2.24-10.86*	-
Mato Grosso, Brazil (Poconé mines area)[252]	23-198		18-160	
US Streams [142]	0.84-4520	0.01-15.6	0.27-446	<0.01-4.11
Florida Bays [149]	1-219	-	3-7.4*	-

* Filtered samples (0.45um filters used).

Water parameters were compared against total mercury loadings using the Pearson correlation coefficient assuming a one tailed distribution for two samples of unequal variance to determine if a linear relationship exists. Strong positive correlations were exhibited between sTHg loadings and dissolved oxygen as well as salinity, total dissolved solids and conductivity concentrations for rivers and streams of Lago Titicaca. This may be indicative of the presence of anaerobic bacteria such as sulfate reducing bacteria which are principal mercury methylators. Compeau and Bartha[253] determined that in the presence of high salt concentrations typically mercury levels in sediments increased. Weak associations between unfiltered water total mercury levels and most water parameters existed. Weak associations existed for unfiltered water total mercury and conductivity were consistent with studies by Lange et al.[159]. Temperature showed a positive linear relationship with sTHg concentrations.

Table 5.4. Pearson Correlation Coefficients Between Total Mercury in Sediment and Unfiltered Surface Water and Water Quality Parameters for All Sites in Bolivia and p Values Assuming a One Tailed Distribution for Two Samples of Unequal Variance.

Parameter	THg Unfiltered Surface Water (ng/L)		THg Sediment (ng/g dry weight)	
	r_s	p-value	r_s	p-value
Conductivity (mS/cm)	-0.306	0.4233	0.8372	0.0049**
pH	-0.7441	0.0215*	0.2227	0.5647
Turbidity (NTU)	-0.5464	0.1279	0.1979	0.6098
DO (mg/L)	-0.9618	0	-0.1724	0.6574
TDS (g/L)	-0.3046	0.4255	0.848	0.0039**
Salinity (ppt)	-0.2925	0.4449	0.8623	0.0028**
Temperature (°C)	0.2378	0.5377	0.705	0.0339*
sTHg (ng/g dry weight)	0.1154	0.7674		

Significance tests for correlations: *$p < 0.05$; **$p < 0.01$.

Total mercury loadings in waters were similar to those found in areas considered to be impaired by mercury. High levels may be likely from suspension of particulate matter from stream beds and the natural weathering of soils and sediments. According to study findings by Zehetner and Miller [254], climatic gradient changes in Andean soil ecosystems can contribute to various soil leaching regimes. High elevations exhibiting cool and humid conditions similar to the Alti Plano can lead to the accumulation of organic matter that has been shown to increase mercury loadings in soils and sediments [255]. High levels at Minera Potosi (2891 ng/g) may be due to the mineral processing of tin which is usually associated with sulfides and these can form strong bonds with mercury as well. During the tin extraction process the crushed ore is roasted by heating to remove any impurities such as arsenic and sulfides. If mercury is present it can be released into the atmosphere. Despite the relative small sample size (n=4), average Lake Titicaca sediment mercury loadings were 888 ±33 ng/L which were within similar values found by Miller in the Río Pilcomayo Basin in Bolivia (located in Southeast section of country flowing through

Paraguay northward toward Sucre) [251]. However, loadings were higher than those found in the Pocone mine areas in the Brazilian Amazon [252].

5.7.2 Total Mercury Loadings in Fish

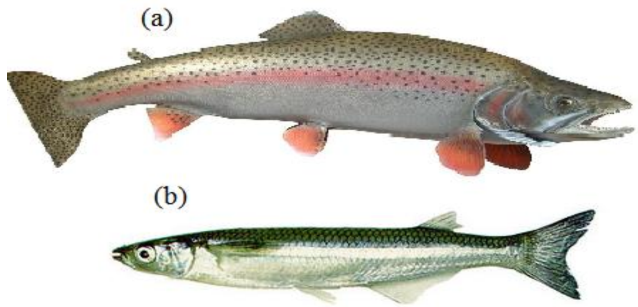

Figure 5.5. Fish Species (a) Trucha (*Salmo Gaidneri*) and (b) Pejerrey (*Basilichthyes boariensis*) Collected from Lago Titicaca Area.

Total mercury in fish (fTHg) in units of mg of mercury per kg of wet fish weight along with average fish characteristics (sex, length, fish condition, and weight) have been summarized in Table 5.5. The average mercury concentrations in trucha (*Salmo gaidneri*) and pejerrey (*Basilichthyes boariensis*) collected from Lago Titicaca were 0.06 and 0.38 $mg{\cdot}kg^{-1}$, respectively (depicted in Figure 5.5). Average mercury loadings for pejerry were three times higher than trucha. Gammons et al. [66] examined mercury fish loadings on the Peruvian side of the lake which showed that pejerrey, the most popular fish of Lago Titcaca, represented more than 27% of the fish species that exceeded fish mercury tissue-based water quality criterion levels of 0.3 mg/kg.

In the Tapajós river basin in the Brazilian Amazon, large predatory fish species showed average total mercury concentrations of 0.69 mg/kg, wet wt. (n=43) [256]. This average is about two times greater than the average values exhibited in this study which may be a result of the intense mining activities; however, it does suggest that there may be possible inputs of mercury from the local mines.

Table 5.5. Summary of Fish Characteristics (Length, Weight, Sex, and Fish Body Condition (fbC)) and Total Hg (fTHg) Concentrations Sampled on 06/2009 from the Lago Titicaca Aarea in Bolivia.

Species	N	L_{range} (mm)	L_{avg} (mm)	W_{range} (g)	W_{avg} (g)	Sex (M: F)	fbC_{range} --	fbC_{avg}	$fTHg_{range}$ (mg/kg wet wt)	$fTHg_{avg}$ (mg/kg wet wt)
Pejerry	10	292-415	336	185-522	298.1	7:3	1.4-1.8	1.9	0.20-0.76	0.38
Trucha	10	225-375	299	203-946	496.1	5:5	0.7-0.9	0.8	0.03-0.1	0.06

There are multiple drivers or conditions that can lead to increased mercury levels in larger predatory and omnivorous fish. Both trucha and pejerrey have similar feeding behaviors but their body shapes are different. These driving forces can be grouped into consumption behavior and water biogeochemical processes which can ultimately affect fish growth and spawning. In fishery studies, researchers use weight, length, and body condition as an index to assess fish nutritional well-being, fitness as well as the relative suitability of its habitat [164] which has the ability to potentially reflect seasonal and longer term nutritional trends. Equation 1 from Chapter 3 best explains the calculation for body condition (K) [165]. If K is greater than or close to 1 it is assumed that the fish is in good condition or receiving sufficient food and nutrition. Fish body conditions can be comparable to stored fat as well as the incidence of disease [166, 167]. In addition, various factors (e.g. sex, body shape, sample collection method, environmental pollution, seasonal changes, disease, and parasites) can affect fish body conditions. The fish's body condition influences the levels of mercury[168]. Higher mercury levels tend to decrease enzyme protein synthesis which reduces stored fat in fish [257].

Fish body conditions and total mercury concentrations for pejerrey and trucha have been determined in Table 5.5; however, ontogenetics, changes in body shape, seasonal, and sex differences were not taken into consideration. Despite the small sampling size, the K_{avg} for perrrey and trucha were 0.8 and 1.9, respectively. Fish species were considered to be in good condition and free of whirling disease, a fish disease that causes skeletal deformations and neurological damage, as well as white spot disease (mostly seen in trout species that once affected the area in the 1980s). The body condition for trucha is about two times that of pejerrey which suggests that the two exogenous species may be in competition; thus trucha maybe outcompeting pejerrey for food. During the 2002 United

Nations International Year of the Mountains, the Food and Agriculture Organization (FAO) found that trucha introduced into five Andean water bodies represented 48% of the species of fish present and had rapidly adapted to the food organisms; therefore, out consuming its competitors such as pejerrey [258]. Figure 5.6a-b illustrates the relationship of mercury loadings to fish body conditions for pejerrey and trucha. There appeared to be a strong correlation between fTHg and fish body condition (fbC) in trucha and not pejerrey.

The Pearson equation was applied to fish data results determine whether a linear relationship between fish characteristics and total fish mercury loadings exist. When examining weight and length independently, Berzas Nevado et al.[259] and Cizdiel et al. [170] determined that fish Hg levels increase when fish species undergo starvation. Therefore, thinner fish (in relation to weight and height) have higher mercury levels than robust fish which have been shown by Nicholls et al. to have fewer protein synthesis enzymes [260]. Figure 5.6c-f, show that there is a positive relationship that exist between fish length and weight; therefore, as the length of the fish increases so does the concentration of mercury in the fish. Similar observations were seen by dos Santos et al. [261] in the examination of six carnivorous fish species Pimelodidae family (*Brachyplatystoma filamentosum*, filhote), (*Brachyplatystoma flavicans*, dourada) and (*Pseudoplatystoma* sp., surubim); the Sciaenidae family (*Plagisocion squamosissimus*, pescada branca); the Cichlidae family (*Cichla* sp., tucunaré); and the Clupeidae family (*Pellona* sp., sarda).

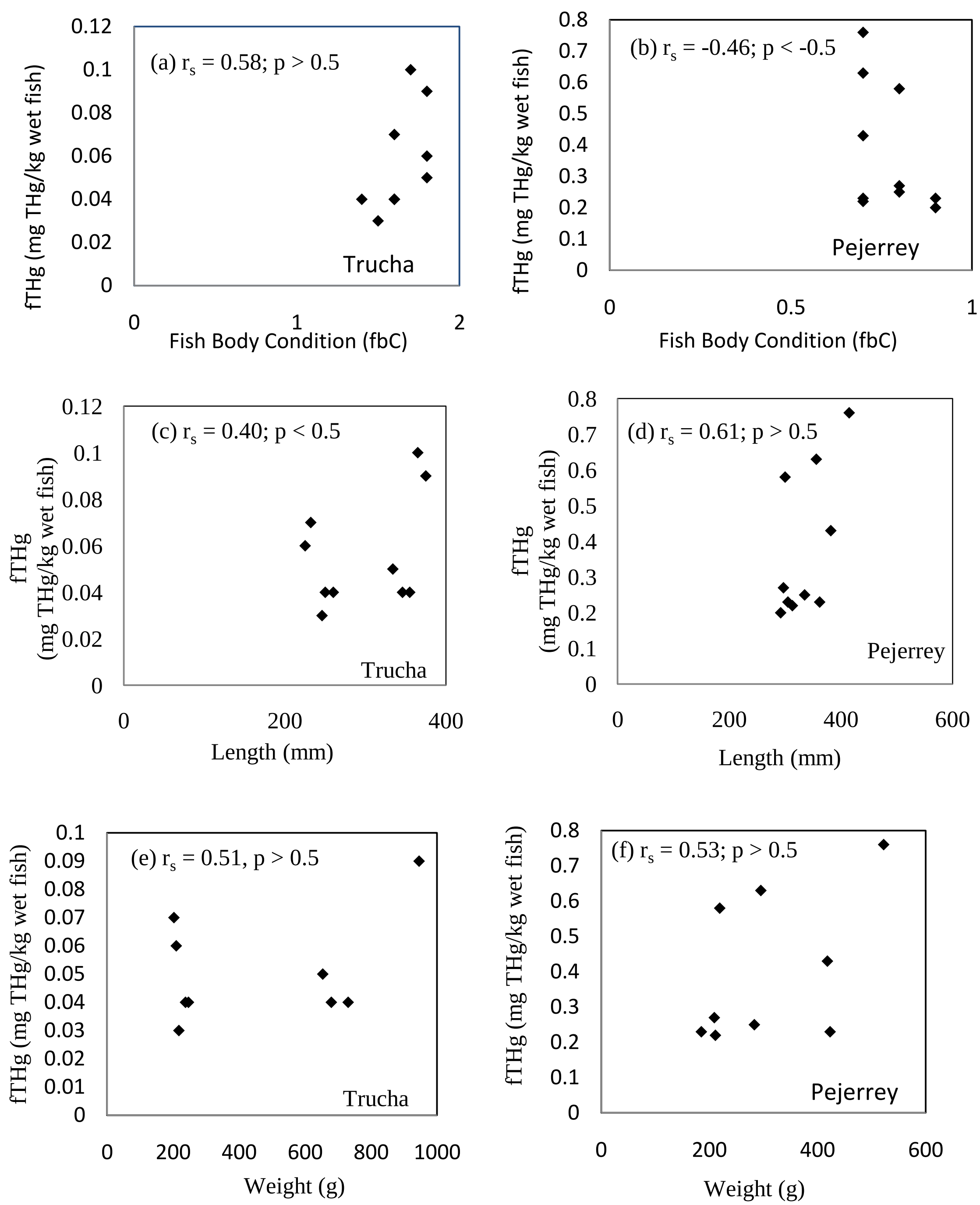

Figure 5.6 (a-f). Scatterplots of Total Mercury Loadings (fthg) in mg/kg Wet Weight As a Function of Length, Weight, and Age, for Each Fish Species. Pearson Correlation Coefficients, R_s, and p-Values Are Shown. p- Values Were Calculated Assuming A Two Tailed Distribution for Two Samples of Unequal Variance.

5.7.3 Health Implications Associated with Fish Consumption

The hazard index (H), which is commonly used to assess the potential implications of noncancerous adverse health effects that are expected to occur, have been applied here. A hazard index value of greater than 1.0 indicates that an adverse human health effect will occur whilst values less than 1.0 assume no adverse effects. H can be calculated using Equation 2 from Chapter 3.5.1. Although the consumptive behavior was not obtained in this study, a general assumption that aboriginals or natives from similar ethnic groups of Peru and Bolivia had similar body mass and consumption rates was applied. Studies have revealed that there is genetic relationship between the Quechua and Aymara[262, 263]. They undergo similar environmental stress factors which include low partial pressure of oxygen, poor nutrition, cold weather, socioeconomic problems, and geographic isolation [264]. Average body mass values of 22 kg for children [265, 266] and 66 kg [264] for adults was used in this study. These values were based on research findings on the average body mass of Peruvian Quechua who have migrated to the cities as well as live in rural areas. Consumption rates of 3.4 to 4.8 kg of fish per week (486 and 686 g/day of fish, respectively) were assumed and based on rates of consumption determined by McClain and Llerena [234] for highland and lowland indigenous populations in Peru. Moreover, lower level ingestion rates were based on a daily serving of two fish fillets weighing 112 g (4 oz.) and 227 g of fish being consumed on a monthly single daily serving basis and. Fish concentrations (C) in Table 6 were derived from the total mercury analysis values of fish samples collected in this study. Low and high fish total mercury concentrations for all samples (C= 0.03 mg/kg, trucha, and C=0.76 mg/kg, pejerrey) were used as well as the average total mercury concentration for pejerrey (C=0.38 mg/kg).

The hazard index values have been reported in Table 5.6 and 5.7 for indigenous children and adults, respectively. Given the current high concentrations of total mercury in trucha at the assumed consumption rate between 486 and 466 g fish/day have a hazard index above one. This indicates that a large proportion of the Amerindian population's consumption behavior places them at a higher risk of experiencing adverse health affects associated with the consumption of fish. However, this may be a high estimate for

Bolivian Amerindians living in the Lago Titicaca area as the Quechua and Ayamara residents also consume other protein sources such as alpaca and llama [266]. Although Wantanabe et al.[267] determined that Bolivians living in the lowlands and highlands didn't exhibit high mean levels of urinary mercury, women were seen to have the highest levels and dietary consumption behaviors were responsible for variations in concentrations. A fish mercury concentration less than 0.003 mg/kg would be needed in order for no adverse health effect to be exhibited. Adverse health effects associated with mercury intoxication may be difficult to identify as studies have showed that the Amerindians are faced with several health issues such as obesity[268], cardiovascular disease[269], and dyslipidemia (high blood cholesterol and triglcerides) [270] which all have been seen to exacerbate mercury levels in the human body[87].

There were no observed postings of informational signage and/or warnings. However, residents have indicated in informal communications that they believed that upstream mining activities along the Rio Suches and the streams from the mountain areas were possibly affecting the fish.

Table 5.6. ChildHazard Index (H) and Critical fish concentration (C) for Lago Titicaca, Bolivia Assuming H = 1. Calculations Assumed a RfD = 1 x 10^{-4} mg/kg per day for Different Ingestion Rates (I, g/day), Fish Mercury Concentrations (C, mg/kg wet weight) and Body Weight (22 kg for a Child).

Ingestion Rate (g fish/day)	H	H	H	C (mg/kg)
	C=0.02 mg/kg	C=0.38 mg/kg	C=0.76 mg/kg	H=1
	child	Child	child	child
8	0.11	1.38	2.76	0.28
227	3.10	39.21	78.42	0.01
486	6.63	83.95	167.89	0.005
686	9.35	118.49	236.98	0.003

Table 5.7. Adult Hazard Index (H) and Critical Fish Concentration (C) for Lago Titicaca, Bolivia Assuming H = 1. Calculations Assumed a RfD = 1 x 10^{-4} mg/kg per day for Different Ingestion Rates (I, g/day), Fish Mercury Concentrations (C, mg/kg wet weight) and Body Weight of 66 kg for a Typical Indigenous Adult.

Ingestion Rate (g fish/day)	H		H		H		C (mg/kg)	
	C=0.02 mg/kg		C=0.38 mg/kg		C=0.76 mg/kg		H=1	
	child	adult	Child	adult	child	adult	child	Adult
8	0.11	0.04	1.38	0.46	2.76	0.91	0.28	0.83
227	3.10	1.02	39.21	12.95	78.42	25.90	0.01	0.03
486	6.63	2.19	83.95	27.73	167.89	55.46	0.005	0.014
686	9.35	3.09	118.49	39.14	236.98	78.28	0.003	0.010

5.8 Summary

Water and sediment samples were collected from twelve locations in Lago Titicaca and its rivers and streams (Río Suches, Río Alcamarini, and mountain streams). Average mercury loadings in the unfiltered waters within the rivers and streams of Lago Titicaca were 66±22.5 ng/L and sediment loadings ranged from 24-2891 ng/g. Positive correlations were exhibited between sTHg loadings and dissolved oxygen as well as salinity, total dissolved solids and conductivity concentrations for rivers and streams of Lago Titicaca. This may be indicative of the presence of anaerobic bacteria such as sulfate reducing bacteria which are principal mercury methylators. However, weak associations between unfiltered water total mercury levels and most water parameters existed. Sediments were mainly composed of quartz, aluminum, and iron; however, in agricultural and mining areas mercury complexes were seen in the XRD analysis. This was further confirmed by total mercury analysis showing that these areas were the most impacted.

Mercury concentrations for trucha (*Salmo gaidneri*) and pejerrey (*Basilichthyes boariensis*) collected from Lago Titicaca fish market were 0.03-0.76 mg/kg, wet weight with highest levels exhibited in pejerrey. Fish body weight and legnth showed a linear correlation with total mercury concentrations. Although, total mean values do not exceed permissible limits set forth by the WHO and US EPA, special attention, monitoring, and communication may be needed to address any possible health effects or concerns.

CHAPTER 6: BUILDING COMMUNITY PARTNERSHIPS FOR SUSTAINABILITY AND SCIENCE EDUCATION

6.1. Introduction

Studies have revealed that communities and vulnerable populations with increased exposures to environmental pollutants are not appropriately receiving the necessary information [15, 72, 91, 177, 271]. Despite governmental, federal, and international agency concerns regarding the impacts of mercury on water, soil, biota, and human health, regulations and recommendations provide contradictory information. Moreover, there is an insufficient means of disseminating vital information which can potentially lessen the ability of residents' to make well informed consumption decisions [14,15]. However, evidence has shown that community based participatory research programs are effective in bridging gaps in knowledge, improving well-being, and increasing efforts of sustainability [272].

Water Awareness Research and Education (WARE) is a Community Based Participatory Research (CBPR) program aimed to increase environmental/environmental health/sustainability awareness through the use of local stormwater ponds in Tampa, Florida. Over the course of time spent doing the graduate research presented in chapters 3-5, I have actively participated in all of WARE's activities, from its conception to its implementation and constant expansion and improvement efforts. It became evident that education has a significant role to play in fostering sustainable healthy communities and I merged my mercury research with many WARE activities. This chapter discusses the important role of education in furthering sustainability concepts, including mechanisms for broadening participation like CBPR and Informal Science Education (ISE). It details the WARE project and uses personal reflective journaling to assess its effectiveness and applicability to promoting sustainability concepts as they relate to mercury exposures.

6.1.1. Objectives and Tasks

The objective of this chapter was to provide an initial evaluation of an existing CBPR project, WARE, for its ability to increase awareness of environmental, environmental health and sustainability concepts as they relate to mercury exposure.

The tasks include:

- *Task 3a:* Review educational literature and describe the WARE project.
- *Task 3b:* Assess project activities through reflective journaling in terms of their ability to increase awareness of environmental, environmental health and sustainability concepts.
- *Task 3c:* Recommend focal areas for improving and expanding the project to reach larger populations.

Chapter 6 is limited to a project already being implemented mainly in East Tampa, a community that is a part of the Hillsborough River watershed presented in Chapter 3. The extension of educational components to sites in Bolivia and Guyana is discussed in Chapter 7.

6.2. Background

6.2.1. Sustainability and Education

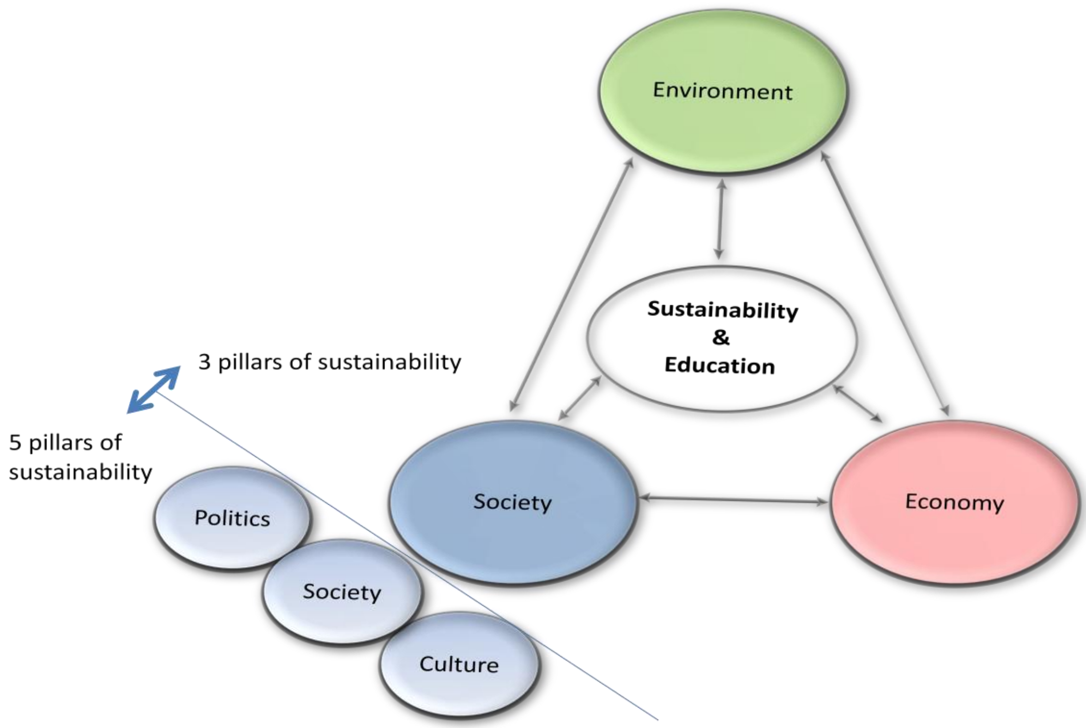

Figure 6.1. Pillars of Sustainability With Education Being the Principle Force Joining All Sectors. Traditionally, 3 Pillars Have Been used (Environment, Economy, and Society), But Researchers Have Extended it to 5 Pillars (Environment, Economy, Society, Culture and Politicsl) [273].

The United Nations has termed the years 2005-2014 as the Decade of Education for Sustainable Development. Their overall goal is to integrate the principles, values, and practices of sustainable development into all aspects of education and learning. Several definitions of sustainability exist and probably the most popular definition, and the one adopted by this work, comes from the 1987 Brundtland Report commonly known as Our Common Future. The Brundtland Report states that “sustainability is the development by which the needs of the present are met without compromising the ability of future generations to meet their own needs.” It is achieved through the incorporation of three to five areas, referred to as pillars - environment, economy, society, culture and politics with traditional emphasis on the first three [273] as shown in Figure 6.1. Education plays a critical role in ensuring sustainability concepts are understood, and applied and sustainability is achieved. Emphasis on environmental education, therefore, would address one of the five pillars identified above. Approaches that integrate all five pillars into educational material would eventually be necessary to adequately address sustainability issues.

From the report of the United Nations Conference on Human Environment, Stockholm Recommendation 96, it is critical that the development of environmental education be implemented globally and is strongly related to the basic principles outlined in the United Nations Declaration on the New International Economic Order, a set of proposals that promote increasing assistance in development [274]. Given that high quality environmental education is seen as an important first step for sustainability, researchers have found it effective to target youth to initiate change, especially when a participatory research approach is used [275]. In assessing the results of the research on mercury conducted for this work and its relevance to local community health, the role of education became important if one wanted to initiate change in local behavior. The next few sections describe the state of education, especially in the sciences, and the approaches that various groups are using to deliver high quality education.

6.2.2 State of Science Education

Science education is important in developing critical thinking so that students and communities can make well informed decisions in everyday life (e.g. nutrition, consumption, and health practices). Environmental education provides a good mechanism for developing critical thinking that also teaches across the school curriculum [276]. Figure 6.2 shows the total number of students enrolled by educational level for Bolivia, Guyana and the United States in 2008. These countries have adult literacy rates greater than the world average (Table 6.1) and from the data presented in Figure 6.2, there is a decrease in the number of students enrolled as a function of level in the system. This justifies the targeting of primary and secondary students, although not to the exclusion of tertiary students.

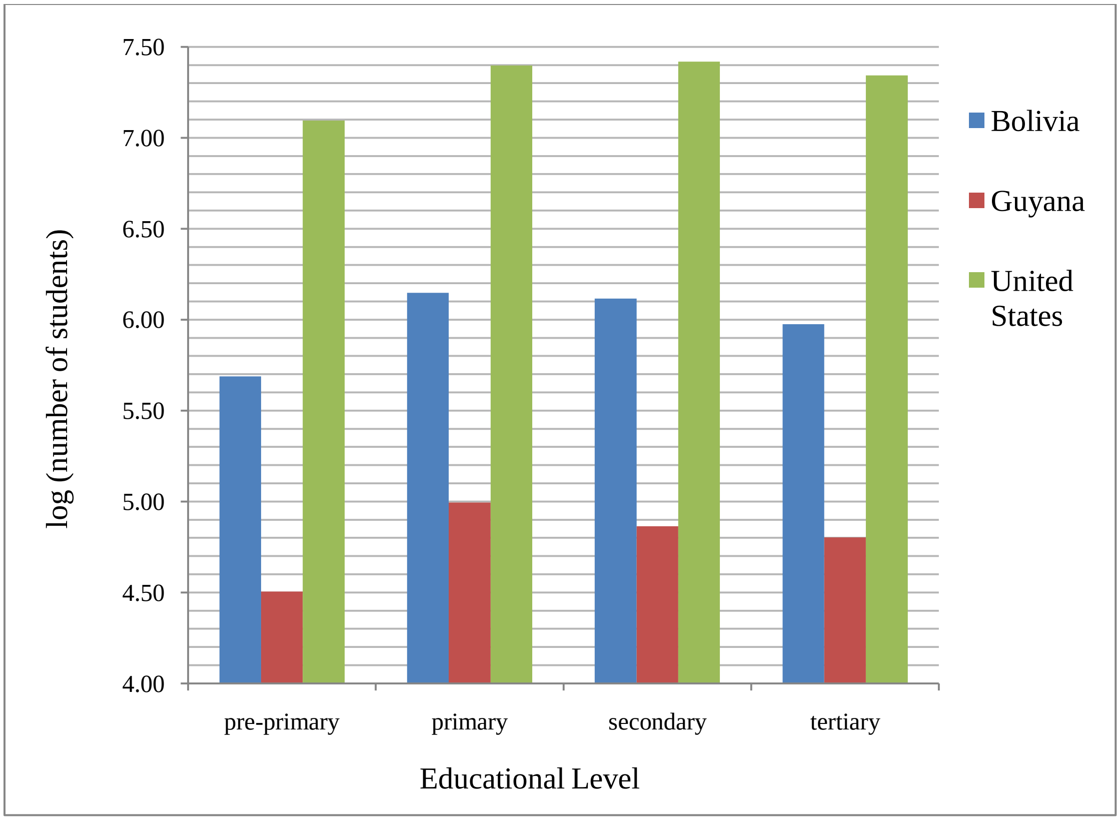

Figure 6.2. 2008 Data for the Number of Students Enrolled Per Education Level in Bolivia, Guyana and the United States. The Data Presented was Obtained from UNESCO (www.uis.unesco.org) Which Obtains Raw Data from UNESCO Member States.

While general education is essential for all, demographics, ethnicity/race, and gender differences and inequalities have been major issues throughout the world's education systems. In rural areas in developing countries and inner cities or urban poor neighborhoods of the US, students receive education of lower quality [277, 278]. The World Bank's basic and primary education project [279] determined that students from rural developing areas are often left out of education reforms and usually only receive primary level education if at all and have to relocate for higher level training. The schools or districts within these areas are usually faced with many issues such as poor quality infrastructure, transport, and availability of quality teachers. Therefore, the funding for science education [280] as well as a focus on sustainability is limited to non-existent.

Table 6.1. Demographics for the United States, Bolivia and Guyana and the World.

Demographics and Economic Development Comparison					
Country	Total Pop. (2007)	Urban Pop. (2010)	GDP (2007)	Poverty Index	National Poverty Line (2000-2006)
	(millions)	(% of total)	(US$ billions)	Rank (N=177)	% below
United States	308.7	82.30	13,751.40	--	--
Bolivia	6.7	66.5	13.1	52	65.2
Guyana	0.7	28.5	1.1	48	35
World	5,290.50	2.60	54,583.90	--	--

Country	Health		Education				
	Public Expenditure on Health (2006)	Life Expect ancy at birth	Public Expenditure on Education (2000-2007)	Educational Attainment Levels (2000-2007) *			Adult Literacy (1999-2007)
	(% of total government expenditure)	(years)	(% of total government expenditure)	(% of the population aged ≥ 25)			% aged >15
				L	M	H	
United States	19.1	79.1	13.7	14.8	49	36.2	99 #
Bolivia	11.6	65.4	18.1	61.6	23.8	14	90.7
Guyana	8.3	66.5	15.5	--	--	--	98.8#
World	--	67.5	--	--	--	--	83.9

** Educational levels are defined according to the UNDP HDI Report. L - less than upper secondary; M- upper secondary or post secondary non-tertiary; and H – tertiary. # data obtained from the CIA*

6.2.3 Broadening Participation in Science Education in the US

The American Competitiveness Initiative (ACI) and the America Competes Act reflect the concerns that the US is in danger of losing its position of world leadership in science and technology. If one were to look at worldwide patent filings over the past two decades, the United States still ranks number one in terms of patents granted and patents still in force (Figure 6.3). Since 1995, however, China has significantly increased both the number of patents filed worldwide and the number of patents filed in the U.S. (Table 6.2). If growth rates of patents filed in the U.S. is a reflection of advancement in STEMs research, it is not difficult to imagine that in another 20 years, the patents filed by China will surpass those of the U.S.

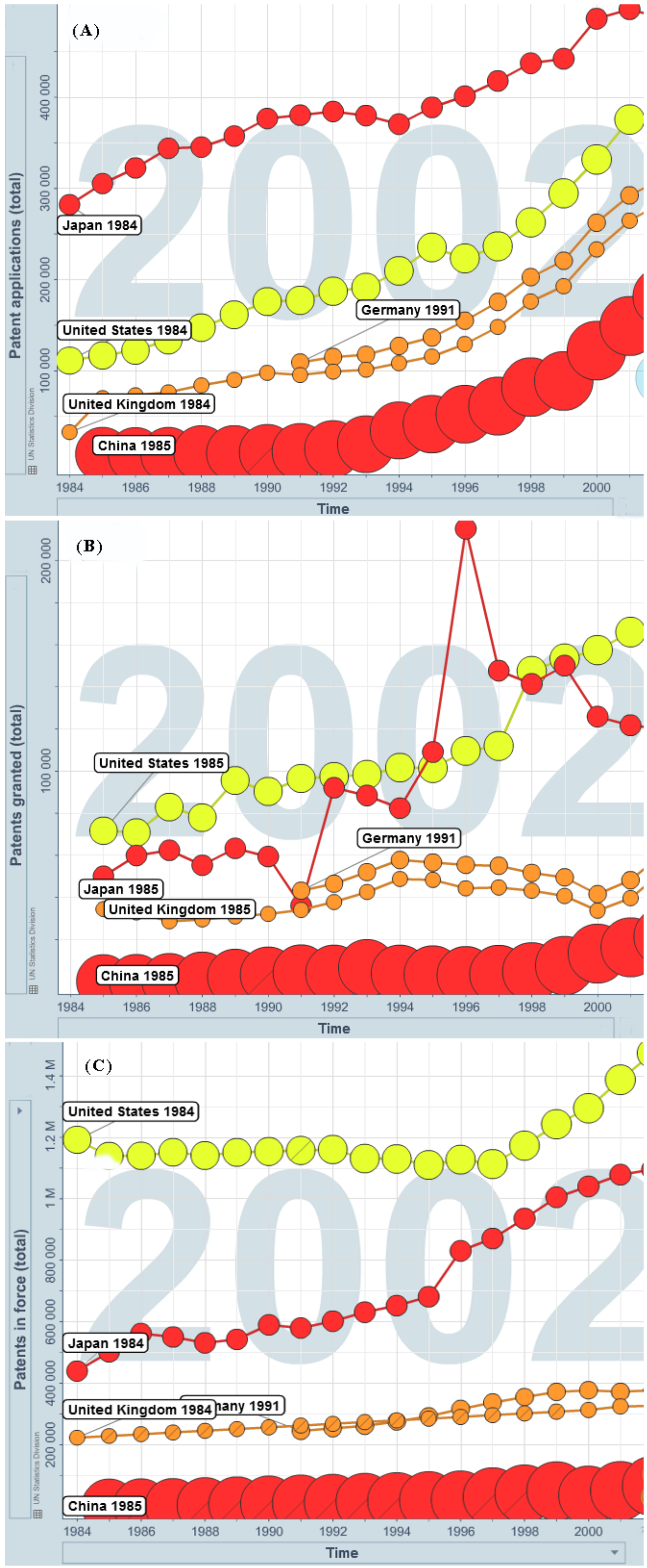

Figure 6.3. Comparisons of Patents (A) Applied for, (B) Granted and (C) in Force for the United States, Japan, Germany, the United Kingdom and China from 1984 to 2001. Figures Were Ceated Using Gap Minder World on 3/4/10 and the Size of the Circle is Representative of Population Size. (www.gapminder.org).

Table 6.2. Patents Filed In the U.S. In 1995 and 2008. Data Taken From The USPTO Technology Monitoring Team Report, "Patents By Country, State, And Year - All Patent Types. Granted: 01/01/1977 - 12/31/2008. Http://www.uspto.gov/web/offices/ac/ido/oeip/taf/cst_all.htm, Accessed 3/4/10.

Country	Year		% increase
	1995	2008	
Japan	22871	36679	60
U.S.	64510	92000	43
China	63	1874	2875
Germany	6874	10086	47
UK	2685	3843	43

In addition to low spending on education and focus on standardize testing reforms, science education in the US lags in the participation of young girls, one of the most vulnerable populations [281, 282]. This translates into serious underrepresentation at faculty levels, positions that are important for being role models. Table 6.3 and Figure 6.4 show demographics for faculty in the Civil Engineering discipline, which includes environmental engineering, at the top 50 programs in the U.S.. The percentage of female faculty is only 12.7% whereas that for minority female faculty is almost non-existent (e.g. 0.4 % for Black women).

Table 6.3. Demographics Of Civil Engineering Faculty At The Top 50 Departments in The US for The Year 2007. Taken from http://chem.ou.edu/~djn/diversity/Faculty_Tables_FY07/CivilEngTable2007.pdf.

	White	Black	Hispanic	Asian	Native American	Total
Number of Faculty	1067	25	65	212	0	1369
Percent of Grand total	77.9%	1.8%	4.7%	15.5%	0.0%	100.0%
Number of Female Faculty	138	5	8	23	0	174
% of Female Faculty in Race	12.9%	20.0%	12.3%	10.8%	0.0%	12.7%
% of Grand Total of Female Faculty	10.1%	0.4%	0.6%	1.7%	0.0%	12.7%

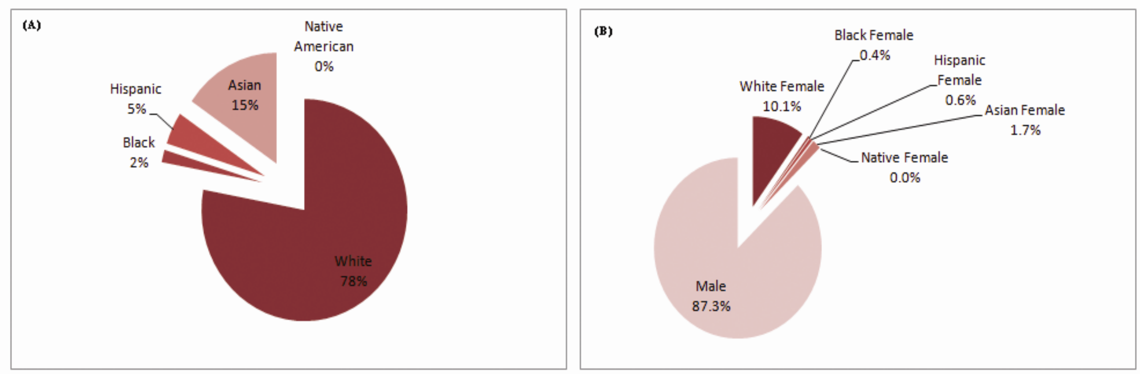

Figure 6.4. Demographics of Civil Engineering Faculty at the Top 50 Departments in the US for the Year 2007 by (A) Ehnicity and (B) Ethnicity of Female Faculty. Total Number of Faculty was 1369. Taken from http://chem.ou.edu/~djn/diversity/Faculty_Tables_FY07/CivilEngTable2007.pdf.

Federal agencies, including the National Science Foundation (NSF) recognize thatretaining world leadership requires Broader Participation (BP) in STEMs fields to take advantage of rapidly changing demographics. NSF defines broadening participation in terms of individuals from underrepresented groups as well as institutions and geographic areas that do not participate in NSF research programs at rates comparable to others [283]. Proposals are generally assessed according to the following criteria[283]:

- How well does the activity advance discovery and understanding while promoting teaching, training, and learning?
- How well does the proposed activity broaden the participation of underrepresented groups (e.g., gender, ethnicity, disability, geographic, etc.)?
- To what extent will it enhance the infrastructure for research and education, such as facilities, instrumentation, networks, and partnerships?
- Will the results be disseminated broadly to enhance scientific and technological understanding? What may be the benefits of the proposed activity to society?

"Social class, race, ethnicity, national origin, and gender have significant influences on opportunities to learn and develop in the U.S. society. Being born into a racial majority group with high levels of economic and social resources—or into a group that has historically been marginalized with low levels of economic and social resources—results in very different lived experiences that include unequal learning opportunities, challenges, and potential risks to learning and development [2849]*."*

Some of the challenges identified by the National Research Council [285] in engaging nondominant groups in the sciences include:

- Inadequate science instruction in most elementary schools, especially those serving children from low-income and rural areas.
- Girls often do not identify strongly with science or science careers.
- Students from nondominant groups perform lower on standardized measures of science achievement than their peers.
- Although the number of individuals with disabilities pursuing post-secondary education has increased, few pursue academic careers in science or engineering.
- Learning science can be especially challenging for all learners because of the specialized language involved.

According to the National Science Foundation (NSF) [282], not all students are actively engaged and new approaches to learning in the classroom or in informal education settings (e.g. clubs, summer camps, and after school programs) is needed in order to spark interest and increase science and engineering participation. Despite low district and governmental funding, Kodrzycki's report[286] on education in the 21st century in the United States , determined that federal and state educational boards have focused on standards-based reforms and choice as a result of low scores on standardized tests and unacceptable performance levels of low income and minority groups [286].

The National science education standards established by the National Research Council (NRC) [287] state that it is essential that adequate district and state funding be provided to create environments in which students of all grade levels and teachers can be active learners. Informal science is a burgeoning field that operates across a broad range of venues and envisages learning outcomes for individuals, schools, families, and society. Environmental education is central to effective community involvement in participatory research [288].

The NSF portfolio includes 23 BP focus programs (e.g. Scholarships in Science, Technology, Engineering and Mathematics), 18 BP emphasis programs (e.g. Research Expereinces for Undergraduates; Informal Science Education), and 18 BP potential programs (e.g. Graduate Teaching Fellows in K-12 Education). Based on research and experiences with BP, NSF [283] recommends that:

- Partnerships between science-rich institutions and local communities show great promise for structuring inclusive science learning across settings, especially when partnerships are rooted in ongoing input from community partners that inform the entire process, beginning with setting goals.

- Learners thrive in environments that acknowledge their needs and experiences, which vary across the life span.

- Adult caregivers, peers, teachers, facilitators, and mentors play a critical role in supporting science learning. The means they use to do this range from simple, discrete acts of assistance to long-term, sustained relationships, collaborations, and apprenticeships.

- Informal settings provide space for all learners to engage with ideas, bringing their prior knowledge and experience to bear.

- Learning experiences should reflect a view of science as influenced by individual experience as well as social and historical contexts. They should highlight forms of participation in science that are also familiar to nonscientist learners—question asking, various modes of communication, drawing analogies, etc.

- Programs, especially during out-of-school time, afford a special opportunity to expand science learning experiences for millions of children. These programs, many of which are based in schools, are increasingly folding in disciplinary and subject matter content, but by means of informal education.

Banks et al. [284] proposes 4 principles of formal and informal education delivery to broaden participation. These are:

- Learning is situated in broad socio-economic and historical contexts and is mediated by local cultural practices and perspectives.

- Learning takes place not only in school but also in the multiple contexts and valued practices of everyday lives across the life span.

- All learners need multiple sources of support from a variety of institutions to promote their personal and intellectual development.

- Learning is facilitated when learners are encouraged to use their home and community language resources as a basis for expanding their linguistic repertoires.

The discussion thus far emphasizes the importance of broadening participation in STEMs fields, identifies barriers to broadening participation, and summarizes approaches needed to increase broader participation. The next section discusses an overarching approach, Community Based Participatory Research that can intersect all of Bank's principles.

6.2.4 Community Based Participatory Research

According to Finn [289] participatory research has three key elements: *people, power* and *praxis* and Table 6.4 summarizes their meaning.

Table 6.4. Elements of Community Based Participatory Research.

Element	Dictionary Definition	Research Interpretations
People	(noun): persons indefinitely or collectively; persons in general (verb): to furnish with people; populate.	The process of critical inquiry is informed by and responds to the experiences and needs of people involved [290]
Power	(noun): ability to do or act; capability of doing or accomplishing something. (verb): to give power to; make powerful.	Power is knowledge and knowledge creates truth and therefore power [291].
Praxis	(noun): practice, as distinguished from theory; application or use, as of knowledge or skills.	The inseparability of theory and practice and critical awareness of the personal-political dialectic.

Community-based participatory research (CBPR) is becoming more popular with support and funding from various foundations and national agencies [292]. Some CBPR definitions used by the national agencies include:

National Institute for Environmental Health Sciences (niehs.gov) - *"CBPR is a methodology that promotes active community involvement in the processes that shape research and intervention strategies, as well as in the conduct of research studies"* [293].

Office of Behavioral and Social Sciences Research (OBSSR) - *"Community-based participatory research (CBPR) is an applied collaborative approach that enables community residents to more actively participate in the full spectrum of research (from conception – design – conduct – analysis – interpretation – conclusions – communication of results) with a goal of influencing change in community health, systems, programs or policies. Community members and researchers partner to combine knowledge and action for social change to improve community health and often reduce health disparities. Academic/research and community partners join to develop models and approaches to building communication, trust and capacity, with the final goal of increasing community participation in the research process. It is an orientation to research which equitably involves all partners in the research process and recognizes the unique strengths that each brings"* [294].

The Agency for Healthcare Research and Quality (ahrq.gov) - *"CBPR is a collaborative process of research involving researchers and community representatives; it engages community members, employs local knowledge in the understanding of health problems and the design of interventions, and invests community members in the processes and products of research. In addition, community members are invested in the dissemination and use of research findings and ultimately in the reduction of health disparities"* [295].

Centers for Disease Control and Prevention (cdc.gov) - *"CBPR is a joint effort that involves researchers and community representatives in all phases of the research process. The joint effort engages community members, employs local knowledge in the understanding of health problems and the design of interventions, and invests community members in the processes and products of research. In addition, the collaborative is invested in the dissemination and use of research findings to improve community health and reduce health disparities"* [296].

Table 6.5 summarizes some of the publications on CBPR that relate to environmental studies, many of which have linkages to community health. The studies highlighted involve multiple participants, some who belong to the community under study and use various tools to implement the research (surveys, monitoring, disseminating, assessing). Eight guiding principles have been identified for environmental health CBPR and these are summarized in Table 6.6. These guiding principles are and can be used to guide the development and execution of CBPR projects in areas not directly related to public health.

Table 6.5. Examples of CBPR Studies with Environmental Linkages.

Study summary	Reference
Water/natural resource management	
Local Responses to Participatory Conservation in Annapurna Conservation Area, Nepal. *Participants:* Non-governmental organization, community groups in Non-Tourist and Tourist villages. *Tools:* Surveys. *Conclusion:* The Conservation agency must devise strategies and initiatives appropriate to specific social groups so as to optimize their input in participatory conservation.	Khadka, D.; Nepal S. K. (2010)[297]
Assessing water use and quality through youth participatory research in a rural Andean watershed. *Participants:* Youth from schools in the Andean region in Colombia, NGO, university research center, technician at municipal telecenter. *Tools:* Surveys, Monitoring, Assessment, Youth led community workshops. *Conclusions:* The approach involving youth in research stimulated improved management of both land and water resources for small rural watersheds.	Garcia , C. E. R.; Brown S. (2009) [275]
Scientific perceptions and community responses in a participatory water management endeavor. *Participants:* a team of multidisciplinary scientist representing ICAR Participatory water management endeavor Research Complex for Eastern Region (ICAR-RCER), Patna, Bihar, India, (b) group of scientists/consultants mainly based in different Universities of U.K led by Rothemsted, U.K., and (c) an Indian NGO and its apex bodies. *Tools:* Surveys, Feedback *Conclusions:* A more differentiated communication and a conceptual framework, can help researchers and practitioners to make better choices and more informed decisions when designing their research, communication and dissemination approaches. Flexibility in participatory approaches are very important which comprises of a blend of top-to-down and bottom-to-up approaches with scope for innovation.	Singh, A. K. et al. (2008) [298]
Air	
Combining community-based research and local knowledge to confront asthma and subsistence-fishing hazards in Greenpoint/Williamsburg, Brooklyn, New York. *Participants:* Community-based organizations: El Puente and The Watchperson Project in the Greenpoint/Williamsburg neighborhood in Brooklyn, New York, Scientists *Tools:* Series of asthma health surveys and tapped into local knowledge of the Latino population to understand potential asthma triggers and to devise culturally relevant health interventions. *Conclusion:* Problem definition, information collection, and data analysis-all geared toward locally relevant action for social change. U.S. EPA Cumulative Exposure Project in the neighborhood.	Corburn, J. (2002)[299]
Airborne concentrations of PM(2.5) and diesel exhaust particles on Harlem sidewalks: a community-based pilot study. *Participants:* Residents of the dense urban core neighborhoods of New York City (NYC), Columbia University in New York (the Center for Environmental Health in Northern Manhattan; Harlem Center for Health Promotion and Disease Prevention; a community-based organization, West Harlem Environmental Action (WE-ACT). *Tools:* Surveys, traffic surveys, portable monitors worn by study staff. *Conclusions:* A new paradigm for community-based research involving full and active partnership between academic scientists and community-based organizations is feasible.	Kinney P. L. et al. (2000)[300]
Diesel exhaust exposure among adolescents in Harlem: a community-driven study. *Participants:* High school students from WE ACT's Earth Crew Youth Leadership Program, seventh-grade students from Thurgood Marshall Academy, researchers at Columbia University, and health care providers at Harlem Hospital Center and Columbia Presbyterian Medical Center. *Tools:* In-person surveys, Urine sample analysis, Statistical Analyses. *Conclusions:* Community driven research initiatives are important for empowering communities to make needed changes to improve their environments and health.	Northridge, M. E. et al. (1999)[301]

Table 6.6. Guiding Principles for Community Based Participatory Research. Based on the Work of Israel et al., [302].

CBPR Guiding Principles	Explanation
1. Recognizes community as a unit of identity	A community may be a geographic area, a shared ethnic/racial or other identity.
2. Builds on strengths and resource within the community	CBPR supports and expands existing social processes (community skills, assets, existing structures like community boards) to address community needs.
3. Facilitates collaborative partnerships in all phases of the research	Investigators and communities work together to define the problem, collect data, and interpret results. It is truly an empowering process for all involved.
4. Integrates knowledge and action for mutual benefit of all partners	All involved need to determine the mutual benefit of the process and develop an intervention or guide policy.
5. Promotes a co-learning and empowering process that attends to social inequalities	Researchers need to enhance their capacity and learn from the process.
6. Involves a cyclical and iterative process	Research goals develop over time through many iterative processes used to reflect and evaluate and redefine.
7. Addresses health from both positive and ecological perspectives	Builds on problems identified by the community, which are often linked by additional sources of data (e.g., epidemiological surveys, environmental stressors).
8. Disseminates findings and knowledge gained to all partners	Community members co-author reports, publications, and other forms of media that reach and are useful to the community

6.2.5 Water Awareness, Research and Education project (WARE)

The Water Awareness, Research and Education project (WARE), is a pilot project funded through the Environmental Protection Agency's People, Prosperity, Planet (P3) program from 2008-2011. WARE's goal is to develop a model of partnership that broadens participation in STEMs fields, improves community awareness of environmental health issues, and delivers K-20 education that integrates sustainability concepts. The model of the collaborative partnerships required to sustainably manage an environmental system with an example of a stomwater pond in East Tampa has been described in Figure 6.5. It is based in Hillsborough County, Florida and involves stakeholders from the K-12 educational system, community groups, the University of South Florida, and government agencies. Hillsborough County Public Schools (HCPS) is the eighth largest public school district in the country. The demographics of the city and its counties are given in Table 6.7.

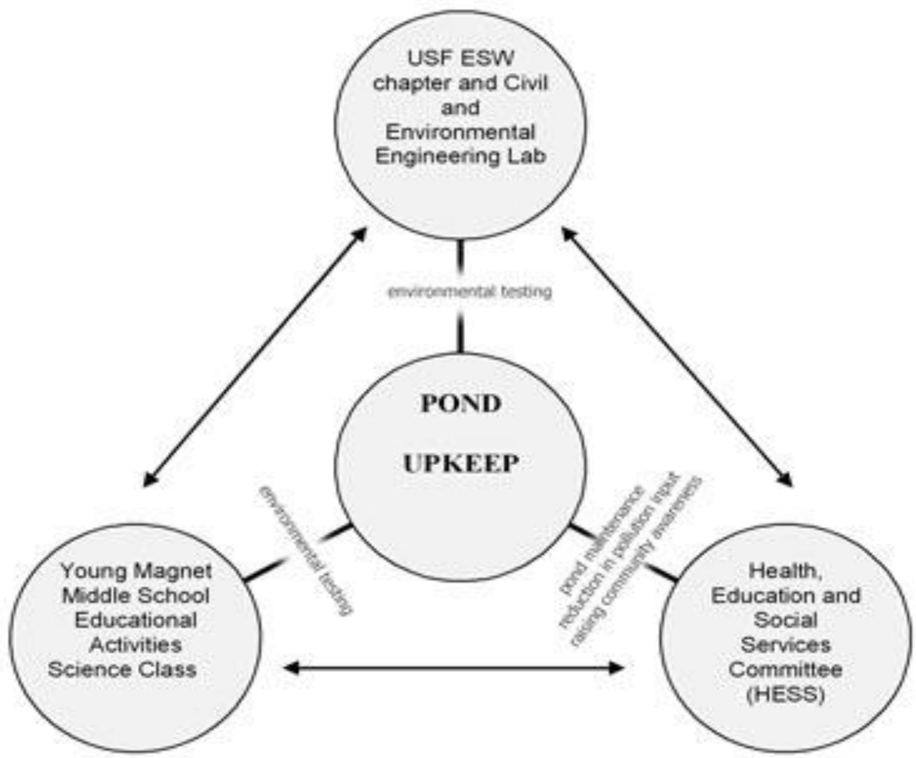

Figure 6.5 Collaborative Partnerships Required to Sustainably Manage Environmental Systems With an Example of Stormwater Ponds in East Tampa Used as An Example.

Table 6.7. Summary of Demographic Data for Florida, The City Of Tampa, and Counties That Make Up The Tampa Metropolitan Statistical Area. Data Taken from The U.S. Census Bureau [303].

People QuickFacts	City of Tampa	Florida
Population, 2006 estimate	332,888	18,089,888
Persons under 5 years old, percent, 2000	6.80	5.9
Persons under 18 years old, percent, 2000	24.60	22.8
Persons 65 years old and over, percent, 2000	12.50	17.6
Female persons, percent, 2000	51.20	51.2
White persons, percent, 2000 (a)	64.20	78
Black persons, percent, 2000 (a)	**26.10**	**14.6**
American Indian and Alaska Native persons, percent, 2000 (a)	0.40	0.3
Asian persons, percent, 2000 (a)	2.20	1.7
Native Hawaiian and Other Pacific Islander, percent, 2000 (a)	0.10	0.1
Persons reporting two or more races, percent, 2000	2.90	2.4
Persons of Hispanic or Latino origin, percent, 2000 (b)	**19.30**	**16.8**

People QuickFacts	Hillsborough County	Pasco County	Pinellas County	Hernando County	Tampa MSA
Population 2008 estimate	1180784	471028	910260	171689	2733761
Persons under 5 years old percent 2008	7.1	5.9	5	5	6.1
Persons under 18 years old percent 2008	24.5	21	18.8	19	21.7
Persons 65 years old and over percent 2008	12.1	21	21.1	26	17.5
Female persons percent 2008	50.7	51.5	51.9	52.1	51.3
White persons percent 2008 (a)	77.9	91.6	84.9	91.8	83.5
Black persons percent 2008 (a)	16.6	4.6	10.4	5.6	11.8
American Indian and Alaska Native persons percent 2008 (a)	0.6	0.4	0.4	0.3	0.5
Asian persons percent 2008 (a)	3.1	1.9	2.8	1.1	2.7
Native Hawaiian and Other Pacific Islander percent 2008 (a)	0.1	0	0.1	0	0.1
Persons reporting two or more races percent 2008	1.7	1.3	1.4	1.2	1.5
Persons of Hispanic or Latino origin percent 2008 (b)	22.8	10.5	7.2	9.2	14.6
White persons not Hispanic percent 2008	57	81.8	78.4	83.2	70.0

WARE initially focused on stormwater ponds in East Tampa, a seven square mile economically disadvantaged urban area in Florida with a majority African American population. Florida established a system to reinvigorate communities in which 50% of the property is in disrepair, which requires that any additional increase in tax revenue collected by the city or county go into a kitty that is used to reinvest in the community. The East Tampa Community Revitalization Partnernship (ETCRP) serves as an organizational medium for the area's 13 different neighborhood groups. Although the city has fiduciary responsibility for how money is used, the partnership has a lot to say about how funds are invested. The stormwater beautification project was one of the first funded and involved the redesign of 3 stormwater pond areas so that they became community friendly open green spaces as opposed to "eyesores where rubbish was dumped". Though not explicitly conceived as a CBPR project, it fits in well with the principles outlined in Table 6.7. Moreover, it also addresses all four principles for delivering education that broadens education as listed by Banks et al[284].

Prof. Trent Green from USF's department of architecture was contracted to redesign the areas and to date (March 2010), two ponds have been completed (Fair Oaks Lake and Robert L. Cole Sr., Community Lake). The close proximity of the ponds to local schools provided a natural fit for building curriculum around the ponds that provided a field site location for students to not only learn about science and engineering, but to also provide a "service" to the community through monitoring and interventions to maintain pond health. Additionally, through community education and awareness, local pollutant inputs to storm water will be reduced; an activity that not only impacts local pond water quality, but also water quality in the Tampa Bay. Figure 6.6 shows East Tampa with details on the flow of stormwater through the various pond systems and the pilot schools. Young Middle Magnet for Math and Science (highlighted) is located opposite to the Robert L. Cole Sr., Community Lake on Martin Luther King Boulevard between 17th and 19th streets. Through local community input, the project grew to include Lockhart Elementary, a magnet school for the performing arts, and King’s Kids Christian Academy, a private elementary school. These three schools fall within East Tampa and hence the City of Tampa. By August 2009, the project expanded to a new suburban area of Tampa, New Tampa, owing to the fact that the science resource teacher changed schools from Lockhart Elementary to Chiles Elementary. Though not considered a part of the City of Tampa, New Tampa is a part of Hillsborough County. Chiles has a stormwater pond on its property.

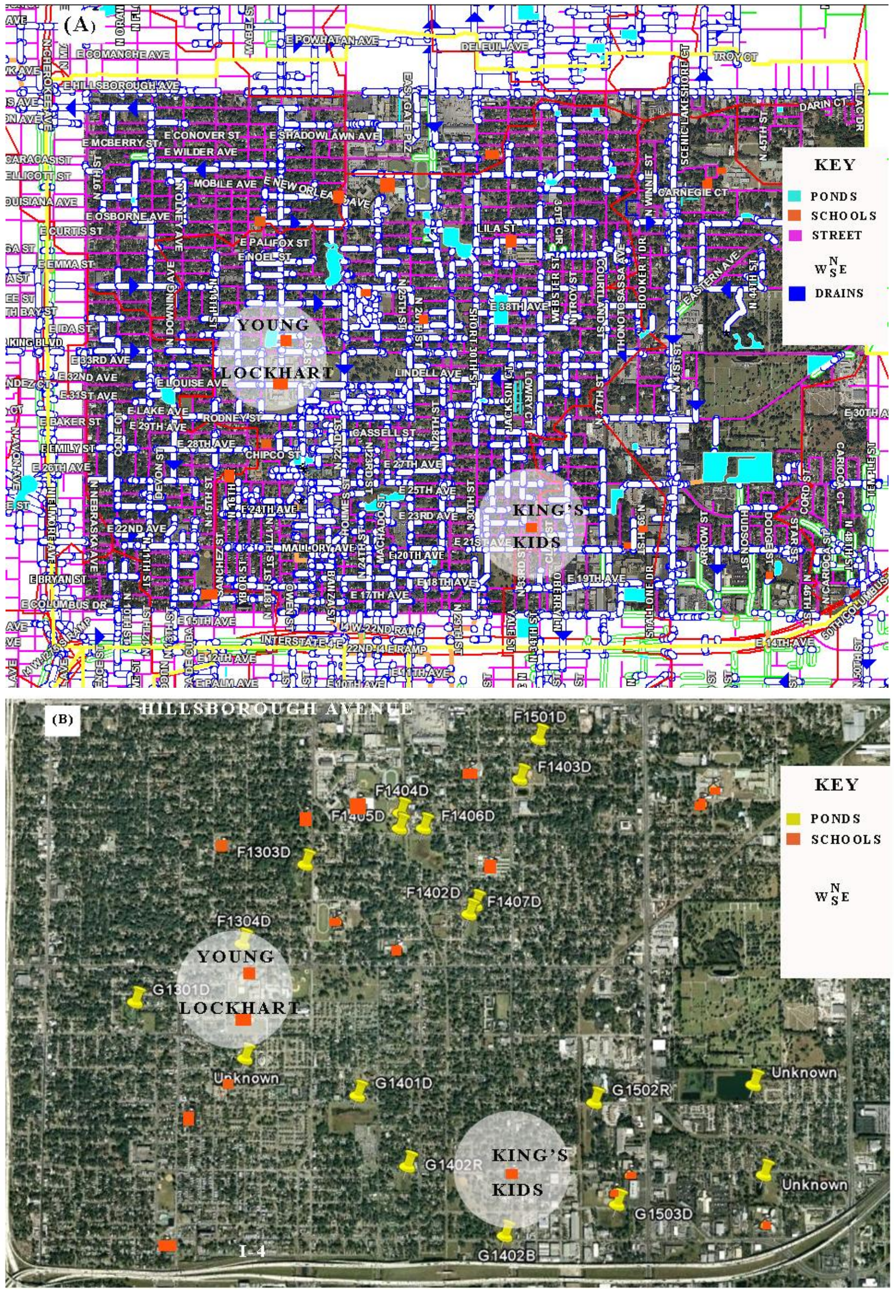

Figure 6.6. Maps of East Tampa Showing The Proximity of Schools in East Tampa to (A) Stormwater Ponds With Stormwater Drainage System (Obtained From The City Of Tampa Stormwater Department) and (B) Stormwater Ponds Without Drainage Pipe Overlays (Mapped Using Google Earth. Pond Codes Correspond to City of Tampa Codes and Represent Sites That Exist in Google Earth With Pictures of The Ponds).

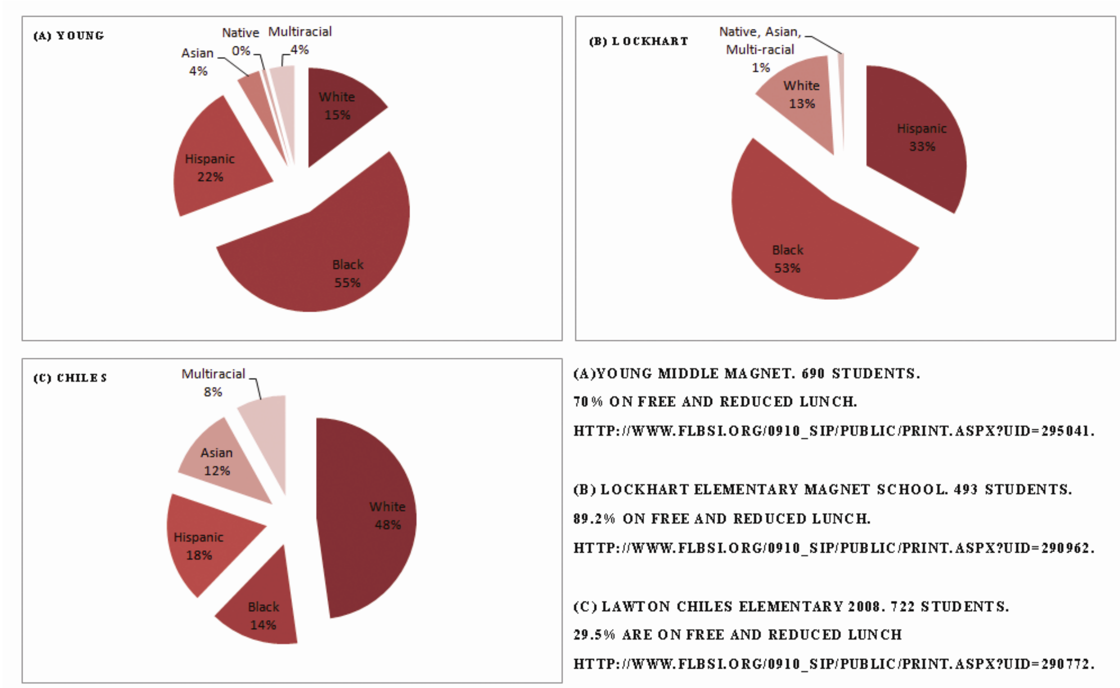

Figure 6.7. 2008-2009 Demographics of (A) Young Middle Magnet, (B) Lockhart Elementary and (C) Lawton Chiles Elementary.

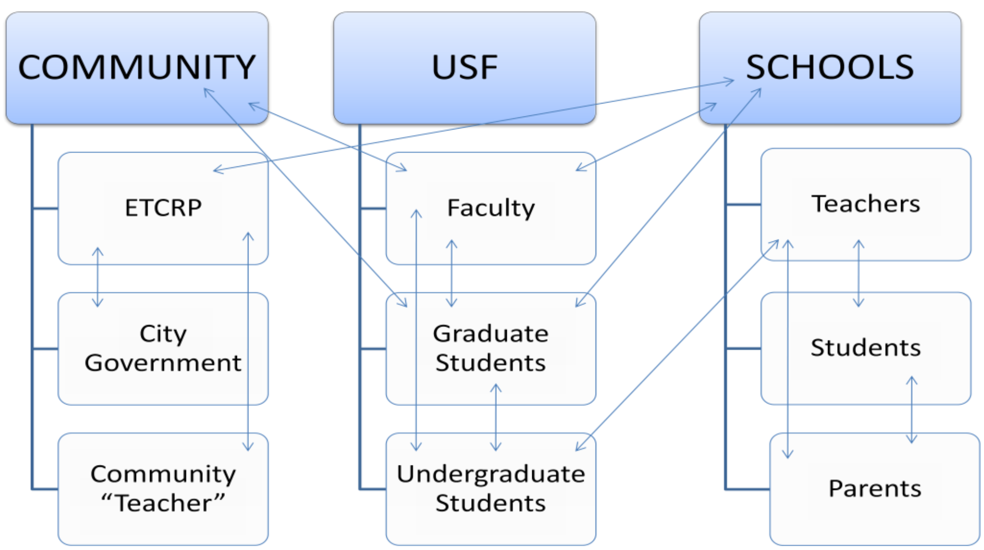

Figure 6.8. Organizational Chart for WARE, Indicating Areas of Interaction of The Members of Each of The Three Participatory Groups (Community, USF, Schools). Arrows Indicate Mutually Beneficial Interactions Between Various Members.

Tables 6.8 and 6.9 summarize the roles of each of the partners and their method of dissemination as of March 2010 whilst Figures 6.7 and 6.8 describe the demographics of the various participating schools and the organizational flow, resppectively. WARE's organizational flow uses two way arrows to indicate the mutually beneficial interactions between each partnering member. Furthermore, the funds provided by the EPA allows for a stipend for four K5-7 science teachers and a "community teacher" to spend 160 hours of out of school time on WARE activities. It also funds some community participation (e.g. to lead bus tours of the neighborhood) and equipment purchases. WARE is a long term project with multiple feedback loops for improvement. With time there will likely be changes to the participatory groups, member roles and the dissemination activities. To date, this is already occurring. For example, when conceived in 2007 WARE involved one school and as of 2009 it involves three, one of which is not in East Tamp so it has also expanded to another community. In 2007 WARE involved one class at USF and during the 2010/11 academic year a new undergraduate class will be added that was developed by faculty and a community member with specific requirements for service learning in East Tampa.

Table 6.8. WARE Participants As of March 2010, Their Roles and Ways in Which They Disseminate WARE Generated Materials.

Participatory Group Type	Participatory Group	Member	Role	Dissemination
Community	ETCRP	ETCRP Chair	Link between community, U.S., and schools; Provide guided tours of community; Assess and improve WARE. Share WARE with others; Support funding for WARE.	ETCRP community meetings & meeting minutes (monthly); speeches; newsletter; workshop; publication with team.
		ETCRP HESS Committee	Provide opportunities to interface with the community.	Community Survival Day (August of each year).
	City of Tampa	City of Tampa	Share data and resources of area and stormwater infrastructure; Implement projects supported by the ETCRP (educational kiosk).	Email to members of East Tampa Community and communicate to members of city government.
	Community Teachers	Community teacher	Develop curriculum & educational material; Communicate with community members	Radio, community interactions.
USF	Faculty	Engineering Architecture	Design pond structures including kiosks and public outreach learning modules.	Radio; newspaper articles; Ware-easttampa.com & ESW website; booths at EPA EXPO, USF Engineering EXPO, Going Green Tampa Bay, Community Survival Day, School events; Workshops, Class material development; Teaching & training; Educational community Kiosk, K5-7 class activity; Journal publications, conference presentations.
	Graduate Students	Graduate student (ESW) and graduate directed research	Develop and participate in all WARE activities; Assist teachers during school times; Mentor K5-12 students;	
		Graduate (directed research)	Develop and participate in WARE activities; Assist teachers during school times.	
	Undergraduate Students	Undergraduate laboratory student	Conduct stormwater pond water quality analyses, present data to class and as a report; Share project information with K5-12	Great America Teach-In (K5-12) class activity; Class presentations.
		Undergraduate researcher	Conduct stormwater pond analyses and understand water flows in area; prepare materials for K-12 students and for outreach activities; contribute to design of educational kiosks.	Newspaper articles; WARE & ESW website; booths at EPA EXPO, USF Engineering EXPO, Going Green Tampa Bay, Community Survival Day, School events; Educational community Kiosk; K5-7 class activity; Journal publications, conference presentations.

Table 6.9. Cont'd WARE Participants As of March 2010, Their Roles and Ways in Which They Disseminate WARE Generated Materials.

Schools	Teachers	Middle school science teachers	Develop curriculum; Teach; Develop publication/educational materials; Participate in various activities like science fairs, community EXPOs etc..	Newsletters; Ware-easttampa.com; booths at School events & science fairs; Educational community Kiosk; class activities; Publications.
		Elementary school science teachers	Develop curriculum; Teach; Develop publication/educational materials; Participate in various activities like science fairs, community EXPOs etc..	Newsletters; Ware-easttampa.com; booths at School events & science fairs; Educational community Kiosk; class activities; Publications.
	Students	Middle school students	Participate in class time activities, field trips, and special programs.	Newsletters; Radio; booths at USF Engineering EXPO & School events; Science Fairs; Educational community Kiosk.
		Elementary school students	Participate in class time activities, field trips, and special programs.	Newsletters; Radio; booths at USF Engineering EXPO & School events; Science Fairs; Educational community Kiosk.
	Parents	Parents	Participate in various activities like science fairs, community EXPOs etc..	

6.2.6 WARE Activities

The National Science Foundation supports constructivism as a promising new learning technique for science and engineering education[281]. Constructivism purports that learners actively construct new concepts based on past and present experiences. It relies on a cognitive structure or mental model in which the learner can transform information to facilitate the construction of hypotheses to make well informed decisions [304].

Active participation that involves all sensory functions and understanding of the eight different types of intelligences (naturalist, musical, logical, interpersonal, linguistic, intrapersonal, spatial and kinesthetic) has been used to create better ways of teaching complex subjects like science. Multiple intelligences address the varied learner's cognitive learning ability by using the student's strength rather than their weakness to teach new ideas and concepts.

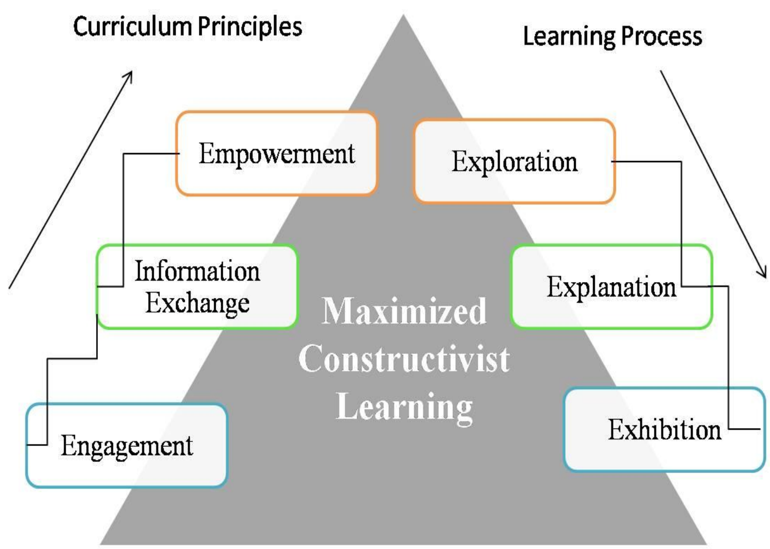

Figure 6.9. Maximized Constructivist Learning Approach for the Water Curriculum Principles. (Adopted from Christie [305]).

The curriculum was correlated with Florida's Sunshine State Standards and Grade Level Expectations stated in the students' science book and based on a maximized constructivist learning approach adopted by Christie [305].

This approach can best be described in Figure 6.9 which uses a step up and step down approach to learning and teaching sustainability concepts. The curriculum's main principle of design works to increase engagement, information exchange between the student and his/her instructor, peers, and parents, followed by a step up to empowerment. Zimmerman [306] explains that empowerment is considered the highest point of learning and occurs when individuals, communities, or organizations gain mastery over their lives. Thus at this peak, students have gained an understanding and now modify their actions or seek other opportunities. Unlike the curriculum, the learning process uses a step down approach. In other words, a big question is explored then explained in a simplified manner using various media types that finally allows the student to draw a conclusion to make well informed decisions as well as feel a sense of influence on others which helps to create a sense of community [307].

The objectives of the water curriculum can be best described according to the UN Tibilisi declaration and Belgrade Charter's Global Framework for Environmental Education [308] which include helping to increase Knowledge, Awareness, Attitude, Participation, and Skills (KAAPS). KAAPS represents:

- *Knowledge*: obtaining basic understanding of the total environment, its associated problems and humanity's critically responsible presence and role in it.
- *Awareness*: about the environment and environmental issues.
- *Attitude*: students and groups become socially, politically, and environmentally conscious and are motivated to protect and improve our environment.
- *Participation*: develop a sense of responsibility and urgency regarding environmental problems to ensure appropriate action to solve those problems.
- *Skills*: acquire skills for monitoring, identifying, and possibly solving environmental problems.

An overview of the WARE curriculum for the schools is given in Table 6.10. This material is continually being improved and adapted as the project progresses. Teachers and USF faculty and graduate students are the main persons in charge of this activity. The curriculum is divided into six sections. Section I of the curriculum explores the global and local perspectives of water followed by Sections II and III which highlight a low level understanding of water chemistry as well as the issues of quality, quantity, and sanitation/health. Sections IV and V, map the flow of water through natural and engineered treatment processes so that learners can draw a parallel understanding between the two approaches.

Each lesson within an individual section was designed to:

- Relate real-world issues to activities in the classroom,
- Focus on sustainable approaches to solving the real-world problems,
- Stress conceptual interrelatedness,
- Provide appropriate tools and environments to assist learners interpretation of the perspectives of the world, and
- Guide student investigative learning if necessary.

Table 6.10. Water Awareness Research and Education Classroom Curriculum Overview.

1. Section I: Water Matters (A brief introduction of global and local perspectives)
a. Define water, its uses
b. Conservation and Sustainability
2. Section II: The Chemistry of Water
a. Phases of water
b. Water as a universal solvent
3. Section III: Water Quality, Quantity, and Public Health
a. Point source vs. non point source contamination
b. pH, DO, turbidity, biological indicators, temperature, nitrates, phosphates
c. Typical usage values and crisis in the world
d. Water related illnesses
4. Section IV: Water Cycle (natural system)
a. Emphasis placed on aquifer and surface water storage
5. Section V: Water Treatment (engineered systems - student makes connection to water cycle)
a. Drinking water
b. Wastewater (i.e. stormwater and reclaim water concepts introduced)
6. Section VI: Water Monitoring
a. Retention pond emphasis
b. Rotation schedule development for the following subgroups:
Lead engineer, field assessor, field sampler, lab analyst, and data analyst

Student programs and lessons were designed as a series of activities which included an introductory presentation followed by actively engaging hands on exercises. Each lesson was modified appropriately for each grade level and designed to meet at least one of the Florida Sunshine State Standards and Grade Level Expectations (SGLEs) listed in Table 6.11.

Table 6.11. Sunshine State Standards Grade Level Expectations and Benchmarks for Grades 3-8 That Were Used in Curriculum Design.

Sunshine State Standard Grade Level Expectation and Benchmarks	Description
SC.D.1.2.2-3	Knows that 75% of the surface of the Earth is covered by water and knows that the water cycle is influenced by temperature, pressure, and topography.
SC.G.2.2	The student understands the consequences of using limited resources.
SC.3.N.1.3: SC.H.1.2	Keeps records as appropriate, such as pictorial, written, or simple charts and graphs, of investigations conducted.
SC.7.E.6.6	Identifies the impact that humans have had on Earth, such as deforestation, urbanization, desertification, erosion, air and water quality, changing the flow of water.
SC.7.E.6.In.e	Recognizes that humans have had an impact on Earth, such as polluting the air and water and expanding urban areas and road systems.
SC.7.E.6.Su.e:	Recognizes that polluting the air and water can harm Earth.
SC.7.E.6.Pa.c:	Recognizes that ground on the Earth's surface changes over time.

6.3 Methodology

There are several challenges involved in evaluating environmental education programs[309, 310]. Heimlich [310] argues that environmental education programs aimed at behavioral change are complex and that there is not enough to measure changes in an individual's knowledge or behavior, yet it should be a measure of the program's ability to serve the environment. More importantly, the broader good should be to change the public's perception. Pre and post surveys of students and teachers were carried out for most of the WARE activities by the student organization, Engineers for a Sustainable World. The surveys were used to assess whether the targeted concepts were successfully conveyed by the specific activity. Given that WARE is a CBPR project, evaluation of the impacts on all involved requires long term evaluation tools.

Reflective journaling according to education theorist John Dewey [311], fosters a meaningful learning environment that actively engages students with content in an interpersonal manner. It is a learning strategy that provides opportunities for internal and structural analysis, thus creating an environment for significant learning. Rogers [312] found that the use of reflective journaling is a good tool for learning, fostering personal growth, and professional development. Gil-Garcia and Cintron [275] contend that reflective educators are aware that taking time and energy to reflect on, and improve one's work is absolutely essential to the comprehension of the process of teaching itself.

Reflective journaling was used to assess WARE activities in which I was involved for their effectiveness and applicability to promoting sustainability concepts as they relate to mercury exposures. Each of the main activities contained a set of reflections that were best grouped into student, teacher learning and the effectiveness of the technology used. A series of questions and free responses were developed to identify partnership weaknesses and teaching effectiveness, and modifications required for enhanced understanding. Table 6.12 provides an example of the questions of the reflective journal. This reflective tool was used for the in class activities and the other WARE activities described next. Note that while Table 6.10 refers to many different activities, the only ones assessed during the reflective exercise are those in which I was involved as a graduate researcher and member of ESW.

Table 6.12 Example of The Reflective Journal Assessment Tool.

Personal Perceptions

- What were your expectations before activity?
- Where you prepared, if not why not and how can you plan better in the future?
- Did you convey concepts using appropriate language?

Perceived Student perspectives (free response)

- Did students appear confused?
- How did they respond to lecture?
- Where they able to recall this exercise and what they learned in the subsequent week?

Perceived Teacher perspectives

- Were teachers actively involved?
- Did teachers want to learn more?
- Were teachers able to aid in learning based on your presentation before the activity?

In class time activities included both classroom lectures and field sampling exercises. Students received various styles of lectures (i.e. group discussions, think tank subgroups, power points, music, movies) that were to build concepts before applying to infield analyses or classroom experiments. As part of the classroom discussions student interests and strengths were assessed via a questionnaire in order to break them into appropriate teams for the design competition. The teams included: field assessment team; analytical wet chemists; audio/visual engineers and graphic design artists; data reporters or scientific journalists. Each team had a specific set of tasks; however, all teams had to work with one another to produce a 3-5 minute video and final report that would be showcased at the EPA P3 Design Competition in Washington, D.C (Spring 2011).

Students applied knowledge obtained from discussions and training sessions to field analysis skills to address the environmental and social issues associated with the stormwater retention pond located directly across from the school. The students learned how to utilize the Quanta Hydrolab probe to assess water samples for various parameters (temperature, pH, conductivity, dissolved oxygen, turbidity, etc.). Using these skills, the students were able to regularly monitor the status and progress/decline of the stormwater pond water quality. Spatial and temporal changes for their own collected data were used to discuss pond mechanisms. In addition to the field activities, the students had an opportunity to create and design a website to post their research findings and conclusions, along with the chance to build a small-scale model of the stormwater pond following completion of the beautification.

Community Outreach and Active Engagement activities refers to activities that engaged the community (East Tampa and beyond) through face to face interaction with WARE members. A five hour booth exhibit at the East Tampa Community Survival Day delivered environmental awareness information through handouts from local environmental agencies and various activities related to water. For example, a hands-on activity using various materials (sand, wood chips etc.) was used to demonstrate what happens to water when it falls to the earth. The booth was visited by approximately 700 community members in August 2008 and 2009. This was a partnership between the ESW and HESS committee to help to raise awareness on environmental issues in the community. In addition to developing the booth content and activities, USF faculty, graduate and undergraduates manned the booth each year, directly connecting with community members who were not a part of WARE's classroom activities. Similar activities were performed during the University of South Florida Engineering EXPO in February 2009 and 2010, and the Lockhart Elementary Night of Ecology in February 2009. Engineering EXPO is open to all schools in the area, so the community reached is much wider than East Tampa. Middle school students from WARE helped to manage the booth at USF. The Lockhart Elementary Night of Ecology was visited by approximately two hundred people, mainly parents of students from the school.

Field trips were set-up to enhance student lectures by showing them real world applications of concepts covered in the classroom. Field trips included:

- Bus Tours – historical narrative of the East Tampa community done by the chair of the ETCRP and a visual presentation of the stormwater ponds in the area with time allotted for sampling exercises.
- Howard Curren Advanced Wastewater Treatment plant – students toured the Howard Curren Advanced water treatment plant to see how other engineered systems clean water before being discharged into the Bay
- Florida Aquarium Tours – tours were divided into age appropriate activities which included mangrove in-house planting (G3-G4), behind the scenes water quality monitoring (G5-8), and an aquarium exhibition scavenger hunt.

Special programs refer to video productions, community kiosks/informational signage, competitions, and summer exploration projects. Videos were produced by the Young Middle Magnet students and the graduate researcher. This was used for the EPA P3 Design Competition in April 2009 and is now shown during community outreach activities. Graduate researchers also produced a laboratory video intended for primary level audiences that showcases the preparation and analytical tools required to determine the levels of environmental contaminants in various media samples (e.g. water, sediment, and fish). For example, one video was related to an in class sampling exercise in which Chiles Elementary students prepared fish samples (fish were collected from their stormwater pond by a caretaker who normally fishes there and a local market) following the beginning steps of an actual laboratory standard operating procedures manual for preparing fish samples for digestion to determine the amount of mercury present. After viewing the video segment, students are given the analytical data results to determine the total mercury loading in their fish sample. Using previous information as well as guidelines from the state of Florida, students draw their own conclusions on whether they should eat the fish as well as the frequency.

Currently, community kiosks are under development as informal science education centers at the stormwater ponds. Figure 6.10 highlights the mercury informational signage developed from a partnership with the Southwest Florida Water Management District (SWFWMD) as well as the schematic of the first kiosk, designed by the USF architecture department. The City of Tampa has agreed to finance this project and it will be installed in March 2010. In addition to conceptualizing the kiosk, the WARE members (community members, teachers, students, university faculty/students, and a graphic designer) worked on the content to be displayed on the four separate panels, the door and the rain barrel. This first kiosk will be located at the Robert S. Cole Jr. Community Lake opposite Young Middle Magnet.

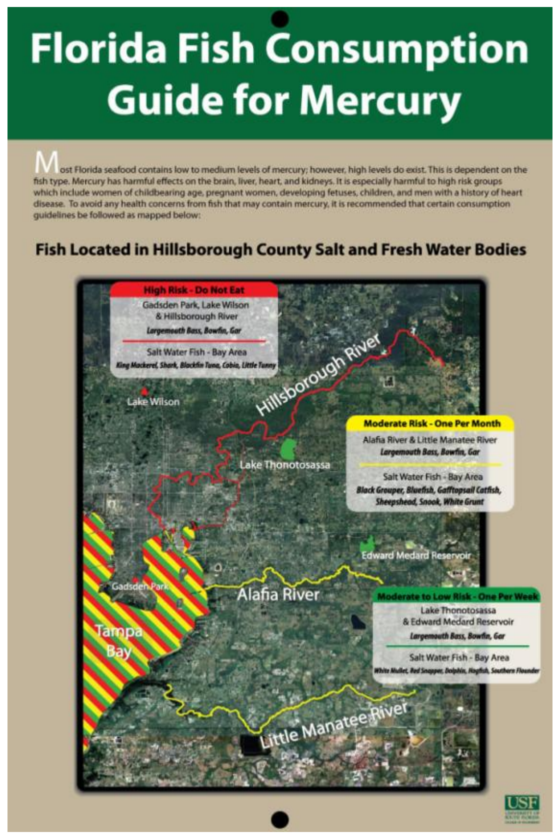

Figure 6.10. Sketch of Educational Kiosk to be Located at the Robert S. Cole Community Lake in East Tampa. Prepared by Prof. Trent Green of the USF Architecture Department and Mercury Informational Signage as Joint Collaboration with the Southwest Florida Water Management District (SWFWMD).

After students were introduced to several WARE curriculum topics and sustainability concepts a competition was held at each school in Spring 2010 to assess their ability to describe what they had learned. The competition requested that the students turn themselves into reporters and convey the importance of the WARE program or discuss an environmental topic they learnt and felt comfortable with conveying (the empowerment phase). Two to three students from each of the schools were selected to discuss the WARE project live on the WMNF radio station on Sunday February 14th, an activity arranged and coordinated by the graduate researcher and a community member. Nine students from Young, King's Kids, and Chiles attended along with their parent/s and one of the teachers from Chiles Elementary. Some of the students from Young were selected based on their previous and extended engagement with the class and WARE program. Each student was asked a question on the air and presented along with USF faculty and the graduate researcher. WMNF (88.5 FM) is a community radio broadcasting and internet streaming station located four blocks away from Young Middle Magnet. Its Sunday morning program has a listenership of about 15,000 persons.

In addition to projects that incorporate the media, a two week summer apprenticeship program was implemented by the graduate researcher in 2009. It involved four middle school African American girls, two of whom were from Young and participated in WARE the previous spring, and two from Lockhart Elementary who participated as well. Students were first reintroduced to concepts of mercury more in depth than what was given in lessons during the academic year. Presentations were open to parents, teachers, and community members followed by lab tours. Students received USF laboratory safety training certification and additional briefings such as field safety. Students then performed field preparation protocols and spent 3-days in the field collecting water and sediment samples. While in the field each student assumed ownership of a specific role after being clearly informed of each task involved for the particular role. This was done to ensure team effectiveness. Though not directly involved in the analysis, students prepared sediment samples (e.g. appropriately labeling containers and data sheets, collecting wet and dry mass, drying, and cooling samples) for analytical analyses using a CVAAS. Students were also allowed to label all glassware and insert sample identification information into the analytical computer systems, but were not allowed to come in contact with chemical reagents or carry out analyses.

6.4 Results and Discussion

In 2009, regular classroom visits were made once a week to each of the schools for the first six months then biweekly for the remaining academic year. Partnership based progress and update meetings and educational sessions were held once a month for one hour. Classroom activities were designed to be completed within 45 minutes. The sections below summarize the findings from each reflective journal used to assess the in-class activities as well as the evaluation of the progression of the WARE program.

6.4.1 In Class Activities

Section I: Water Matters (A brief introduction of global and local perspectives)
Lesson Overview (Building on Awareness and Attitude)
During Lesson 1, "Water Matters", students were shown a video documentary presentation on my travels throughout the world. The intent of the documentary was to bring about environmental awareness issues dealing with water as well as encourage positive attitudes and perceptions.

Reflection:
Middle School
Instructors and ESW members co-taught about the global and local perceptions of water. Students were able to understand the hardships associated with water access, rights, quality, and quantity. However, there was still a negative perception about people who were not able to obtain water and had to get the resources from contaminated lakes. The children thought that it was easy for people to move to obtain better resources and that it was available to everyone at all times except if you did not pay your bill on time. Teachers had to step in to use age appropriate language to conclude the lesson.

Elementary School
Students were extremely captivated and more compassionate than the middle school students. The think tank discussion involved in this lesson was a little too much for the students to handle and their behavior became a little disruptive. Teachers then had to redirect the students' focus to

behavior. Despite minor behavioral issues, the video production was well perceived. Students and teachers also inquired about other issues relating to health, sanitation, and food.

Section II: The Chemistry of Water

Lesson Overview (Building on Knowledge)

The phases of water were discussed on the chalk board and using an interactive computer model. Students were then asked to develop a model of a water molecule using marshmallows, toothpicks, and balloons as well as perform various tests to characterize its properties. Middle school students were taught from a college textbook and assigned a homework assignment to review the periodic table of elements, learn abbreviations for important elements (carbon, oxygen, hydrogen, sulfur, nitrogen, phosphorous, mercury, lead, zinc, and cadmium), molecular weight, atomic mass, and atomic number.

Reflection:

Middle School

ESW affiliates were well prepared and had handouts for students. It was assumed that the students understood that there was a periodic table of elements; therefore, the first lesson dealt with how to appropriately read the table of elements followed by how to write the electron configuration for the important elements we were to focus on. Students were asked to review the table of elements and based on their handouts answer three questions ready for the next meeting date. Unfortunately, not all students returned the assignment and there was little teacher assistance. In the next lesson, students explored the components of water and the bonding structure using toothpicks and marshmallows. ESW members identified quickly that there was an extreme need to make modifications to this lesson for the following year. The lesson took over the allotted 45 minutes, clean-up was not smooth, and students were eating the marshmallows while in the classroom laboratory which is strongly prohibited.

Elementary School

ESW members were extremely shocked that students identified immediately that water was "H_2O" but did not know what "H", "2", and "O" represented; therefore, an explanation was given by using balloons to construct a water molecule . Students were separated into teams of three to create their molecule. After spending too much time on blowing up the balloons, students were spatially arranged with their water molecule to represent the different phases of water (solid, liquid, and gas) and bonding orientations.

Section III: Water Quality, Quantity, and Public Health

Overview (Building on Knowledge, Awareness, Attitude, and Participation)

Students were to understand the differences in point source vs. non point source contamination; the importance of various water parameters (pH, DO, turbidity, biological indicators, temperature, nitrates, phosphates, heavy metals), typical values seen in the world, and water related illnesses.

Reflection: Elementary and Middle Schools

This lesson was quite interactive and the lesson surpassed the allotted design time. All students were actively engaged and participated in the lesson. Teacher assistance was needed to help students setup various tests. Students worked well with each other and with educators. Students performed different water quality tests and then collectively drew a large illustration of the effects. Although students understood the big picture, the experimental setup had students puzzled.

Section IV: Water Cycle (natural system) & Water Treatment (engineered systems - student makes connection to water cycle)

Overview (Building on Knowledge, Awareness, Attitude, and Participation)

Student emphasis was placed on aquifer and surface water storage and drinking/wastewater (i.e. stormwater and reclaim water concepts were introduced).

Reflection: Elementary and Middle School

Each year students are taught about the water cycle; therefore, middle school students were not enthusiastic about the lesson. On the other hand, elementary students enjoyed the water cycle song.

The lessons and activities in this section were all well received. Students were given an age appropriate PowerPoint presentation that they were to read aloud, examine the figures, and discuss natural and engineered systems. Then based on the reading students were to put together a filtration system using a media of their choice that they believed would work best. Some teachers and students were intrigued by the filtration process and even identified this exercise with home water purification systems.

Section VI: Water Monitoring

Overview

This section served as a lesson that would be taught the entire second semester. Students were to focus on the retention pond and rotate work schedules based on the following subgroups:

Lead engineer, field assessor, field sampler, lab analyst, and data analyst.

Each group had a specific task and a team leader. The team leader was responsible for getting information from all the other teams. Leaders would remain the same for a week and students would rotate based on their likes analysis conducted in the beginning of the semester. Lead field samplers had to package samples using a chain of custody form that would be sent to USF for further metals analysis.

Reflection: Elementary and Middle School

Memory recall from the previous lessons was good; however, students were not focused on their specific tasks within their groups and equipment malfunctions were an issue.
Teacher and students took the initiative to construct a water sampler and tested samples using water analysis test kits on a more frequent basis.

Table 6.13 describes the reflections on WAREs incorporation of the Guiding Principles for CBPR Research as listed in Table 6.6.

Table 6.13. Reflections on WAREs incorporation of the Guiding Principles for CBPR Research Listed in Table 6.6.

CBPR Guiding Principles[302] (Taken from Israel et al)	Reflections on WARE
1. Recognizes community as a unit of identity	Initially and core focus: Partnership with East Tampa, a seven square mile community with 13 different neighborhood associations and a strong governing community group, the ETCRP. Expansion: Other locations in Tampa due to movement of WARE members out of East Tampa or East Tampa schools. Future: Redefine the communities involved with WARE, and link communities via website which would eliminate geographic boundaries and extend WARE to other cities, states and countries (e.g. the sites in Guyana and Bolivia that were discussed in Chapters 4 and 5).
2. Builds on strengths and resource within the community	Development of teacher and student training and community awareness of environmental issues; background material for larger grants that build on the partnerships developed with WARE and that involve other faculty from USF from education and health; working with engineering faculty and the chair of the ETCRP to develop a future USF class based on community engagement and know that workshop attendance enhanced both faculty and community member understanding of community engagement opportunities.
3. Facilitates collaborative partnerships in all phases of the research	Investigators and communities work together to define the problem, collect data, and interpret results. It is truly an empowering process for all involved.
4. Integrates knowledge and action for mutual benefit of all partners	All involved need to determine the mutual benefit of the process and develop an intervention or guide policy.
5. Promotes a co-learning and empowering process that attends to social inequalities	Researchers need to enhance their capacity and learn from the process.
6. Involves a cyclical and iterative process	As descrbied earlier, WARE has grown and continues to evolve since its inception. Improving outcomes (e.g. learning of students and engagement of community) is a constant process and there are multiple places where review and repackaging is implemented.
7. Addresses health from both positive and ecological perspectives	WARE was conceived by members of the ETCRP, the City of Tampa, USF faculty, faculty from Young Middle Magnet, and members of USF's ESW student chapter. It initially builds on problems identified by the community, which are often linked by additional sources of data (e.g., epidemiological surveys and environmental stressors).
8. Disseminates findings and knowledge gained to all partners	Table 6.8 lists the various dissemination activities in which each WARE member played a role. The monthly meetings were the most accessible place for sharing all of the information on the project to date even though the material is posted to the website, including pictures of all activities.

Although, the metrics used to collect empirical data are a short-term outcome for individual program achievements with partners, it does not address the long term impacts of effectively promoting change in behaviors. Therefore, the total success of the project is highly unknown at this time. Students are able to discuss and address environmental concepts, especially in smaller participant sizes and with the community (e.g. summer apprenticeships and community outreach programs), and the best overall responses were seen within the special programs. This may be due to personal mentoring relationships that developed and additional team building exercises that were not a part of the main curriculum (e.g. canoeing, ropes course, student guided horseback riding, concerts in the performing arts, museum exhibitions, and botanical garden and state park field trips). Sullivan et al. [313] found similar results for high school girls who explored careers in engineering and technology during a summer internship program. Additionaly, in a week long computer science camp entitled "CS Girls Rock", Graham and Latulipe [314] found that after one week girls in grades 9 and 10, having developed a strong bond with university student mentors, were more interested in science and wanted to take computer science course electives. Chickering and Gamson[315] argue in the "Seven Principles for Good Practice in Undergraduate Education" which can span across all levels of education that learning is enhanced in a team setting. Additionally, community outreach and engagement were also tools that all members enjoyed which gave each student as well as teachers a sense of ownership in tackling a real world problem and helping to build self confidence. Seifer ascertained that service-learning or active community outreach programs benefit students, faculty, communities, higher education institutions, as well as other relationships among all stakeholders[316]. This is suggestive that the curriculum's principle design of active engagement leading to information exchange and empowerment can be achieved.

Students who participated in the summer field exploration program were self motivated to participate in science fair competitions as well as student presentation on their roles in environmental sampling. One student who entered into the state science fair won first place in her school and has since moved on to compete in the district fair. Studies by Feldman argue that people learn through taking part in apprenticeship experiences and that assigning different roles to different participants effectively develops proficient researcher skills[317]. Moreover, studies have shown that strong links exist between high-quality programs that go beyond core literacy and numeracy skills often found in in-school programs.

In addition, there was seen to be a greater impact factor on girl participation. This may be attributed to program coordinators being females who did not resemble the perceived normal scientist or engineer thereby inspiring and empowering participation.

6.4.2 Partnership Progression and Evaluation

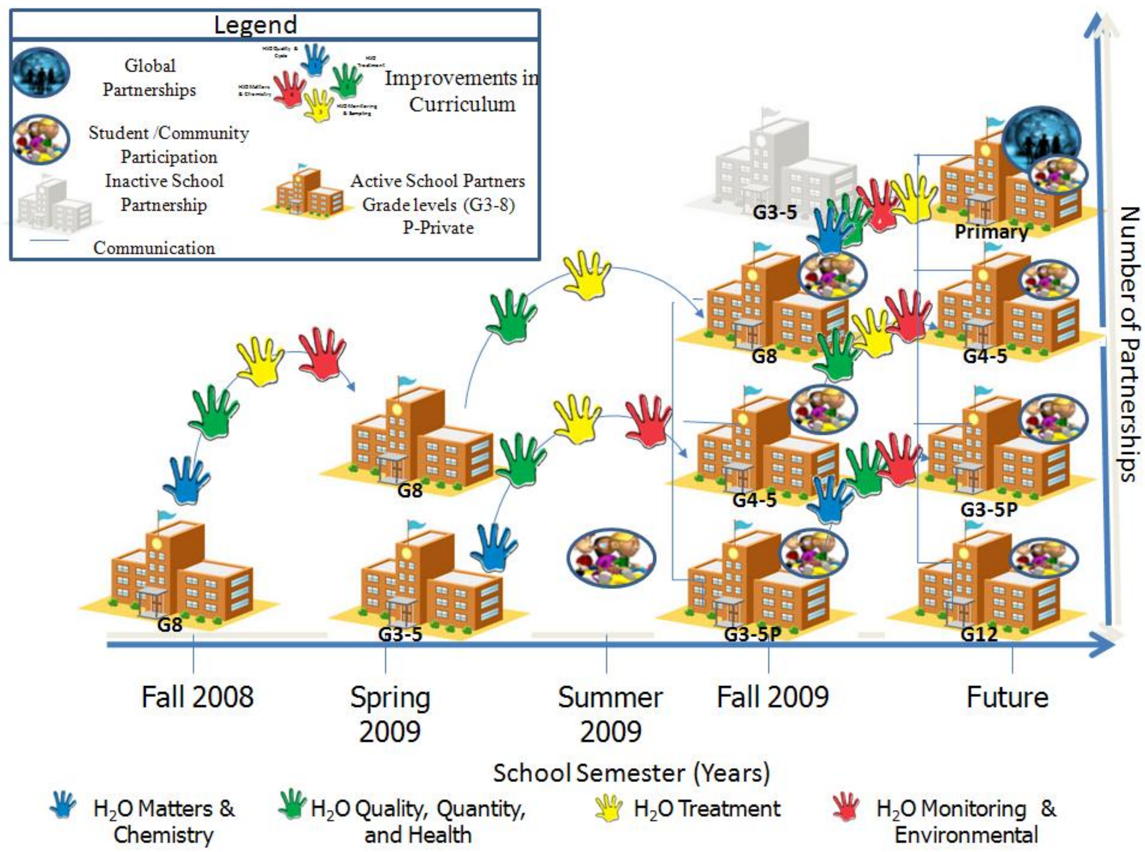

Figure 6.11. Schematic of Growth in Partnerships and The Need for Curriculum Development Gathered from Reflective Journal Entries.

Since it is difficult to determine the measure of success based on student knowledge, the progression and evaluation in partnerships has been examined. Figure 6.11 highlights the progression of the program and the changes needed to be made to each of the lessons based on reflective journals and teacher input.

The program has expanded from its inception in 2008 from one school to three schools (with ~60 student participants and four teachers), a university based student organization, radio and TV personalities, university professors, local government officials, and active east Tampa social and civil engagement community members. Although, the program has grown and students have become actively involved there is a need for internal restructuring and strengthened communication amongst all vital partners. Some of the program downfalls include conflicts in participation or project sustainability, scheduling, administration, and effective communication amongst all partners. However, the expertise of each partner has been effective at developing new activities and engaging the students. Stakeholder feedback although discussed informally in meetings is needs to be in a formal and uniform manner.

6.5 Conclusion

A six step curriculum developed with the assistance of teachers and community members was designed and incorporated into the classroom to serve as a tool for teaching sustainability concepts with an initial focus on water quality of stormwater ponds. The study revealed some key findings from researcher reflective journals. Partnerships from all areas of society (GK-12 schools/students, university professors/students, community members, and governmental agencies) are critically important in educating and addressing issues of sustainability.

The collaborations established in the WARE Program have led to a heightened awareness of the importance of partnerships in teaching on sustainability with a focus on stormwater ponds with respect to their function, water quality issues and an overall understanding of heavy metal pollutants such as mercury. Students, teachers, and community members' increased awareness has resulted from the direct involvement in a formal capacity (presentations inside and outside of school) as well as an informal capacity (East Tampa Community Survival Day, USF Engineering Expo, field trips, field training, team building exercises, and mentoring). Moreover, this may be used as an effective teaching tool for the required graduate course hours in instructed methods to help build the graduate students' confidence in explaining complex concepts to different audiences and therefore engaging them in decision making processes related that can improve environmental quality and community health.

CHAPTER 7: INTEGRATED EXAMINATION OF MERCURY

7.1 Introduction

Mercury cycles through the environment in a complex global network depicted in Figure 7.1. As mercury is introduced to the atmospheric environment from natural and anthropogenic sources, it is transported around the world via patterns of wind dispersion, atmospheric deposition, volatilization, and suspension which ultimately leads to bioaccumulation and biomagnifcation up the food chain. Figure 7.2 presents pathways for mercury in commerce. Human activities like coal combustion, ore refining, manufacturing processes, small scale gold mining, religious practices as well as the chemical characteristics of mercury facilitate the transport of mercury throughout the world. Laws, regulations, technologies and informed human decisions and actions can all minimize the negative impacts of mercury and vary both spatially and temporally. The traditional (economic, social, environmental) and non-traditional (economic, political, socicultural, community participation, environmental) pillars of sustainability capture the critical areas to address in producing a sustainable outcome [273]. In this chapter the five pillars of sustainability are used to compare the field sites which vary geographically, politically, economically, socioculturally, demographically and geologically. Chapter six presented education as essential for ensuring sustainable outcomes and included a program being developed for an area within the Tampa, Fl field site. This discussion on education is expanded to the Guyana and Bolivia field sites.

7.1.1. Objectives, Tasks and Approach

The objective of this chapter is to compare mercury occurrence, use and exposure associated with field sites in Bolivia, Guyana and the USA using the pillars of sustainability as critical areas for consideration. These three countries differ in terms of demographics, geography, geology, politics, economics, commerce, history and culture. The tasks and approaches are:

- Summarize major characteristics of each study site/country through literature review.

- Compare mercury occurrence, use and exposure associated with the different field sites using the pillars of sustainability as critical areas for consideration. Literature reviews, data analysis (from Chapters 3-6), and personal observations were used to assess mercury as it relates to:
  - Economic Sustainability – Are the drivers for mercury use sustainable for the different levels of participants?
  - Political Cohesion – Is there political support, commitment and processes to attain sustainable outcomes?
  - Community Participation – How do the principles of Community Based Participatory Research (CMBR) guide activities at local sites?
  - Environmental Sustainability – Are there negative impacts on environmental compartments thereby impacting ecosystem and human health?
  - Socio-Cultural Impacts – How is socio-cultural behavior influenced by current practices and how can the sustainable outcome respect those customs?

- Propose potential partnerships for Guyana and Bolivia that can contribute to reaching sustainable outcomes for reducing mercury impacts on the local and global environment.

7.2 Results and Discussion

Environmental, social and economic conditions have geospatial and temporal variability. The concept of sustainability addressed in the context of this work has been derived from the Brundtland Report and McConville and Mihelcic [273] and pays particular attention to human needs. A need is a socially constructed term that depends on the specific society/community. The definition of need in this study is one including food, clothing, shelter, a healthy environment and economic stability. These needs are limited by the carrying capacity of society, the economy, and the environment.

Table 7.1 compares the characteristics of the different study sites presented in Chapters three to five, located in Florida, Bolivia and Guyana. The following sections discuss their similarities/differences as they impact mercury presence and potential exposure for the given areas.

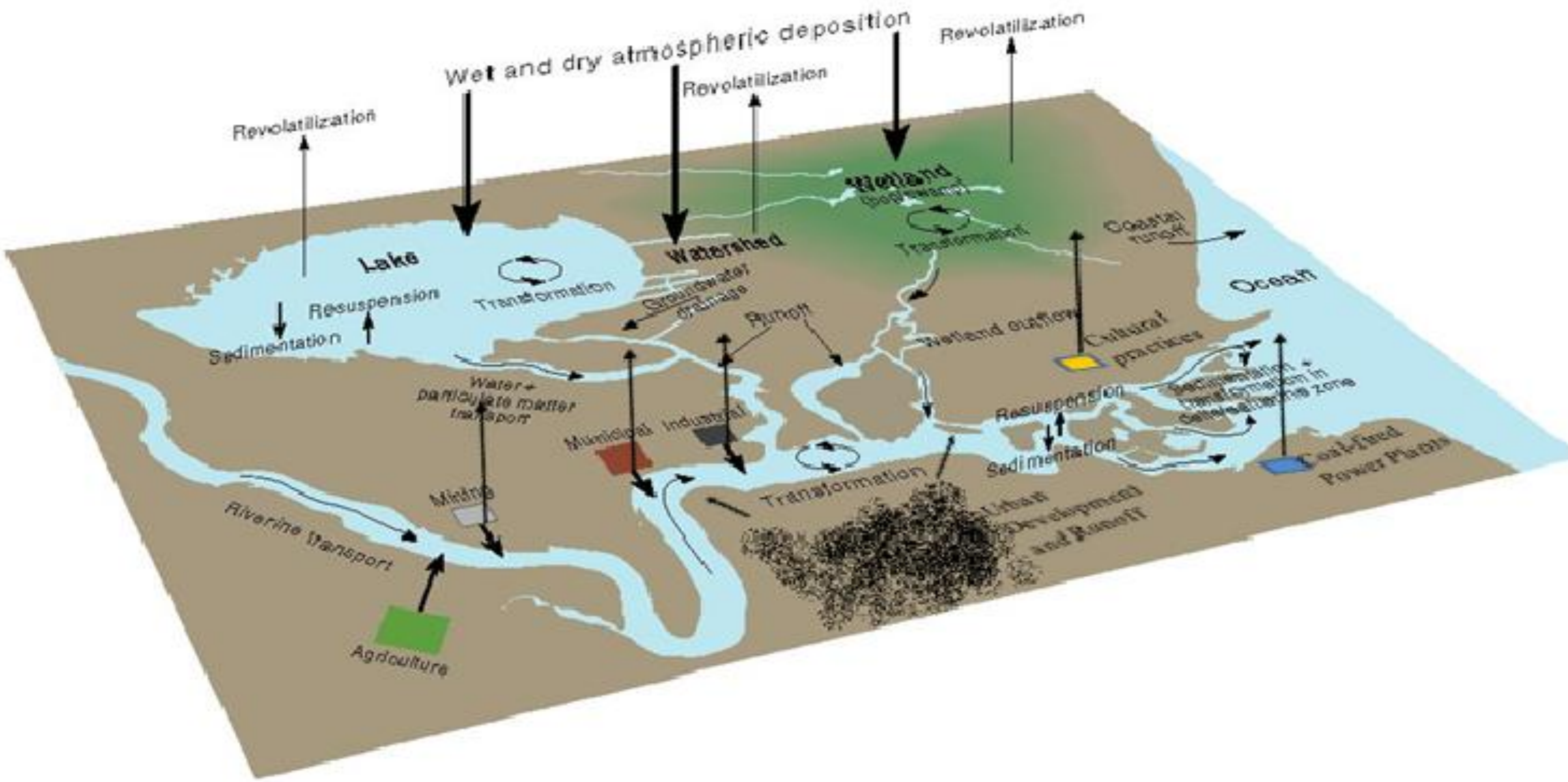

Figure 7.1. The Presence of Mercury in the Global Environment

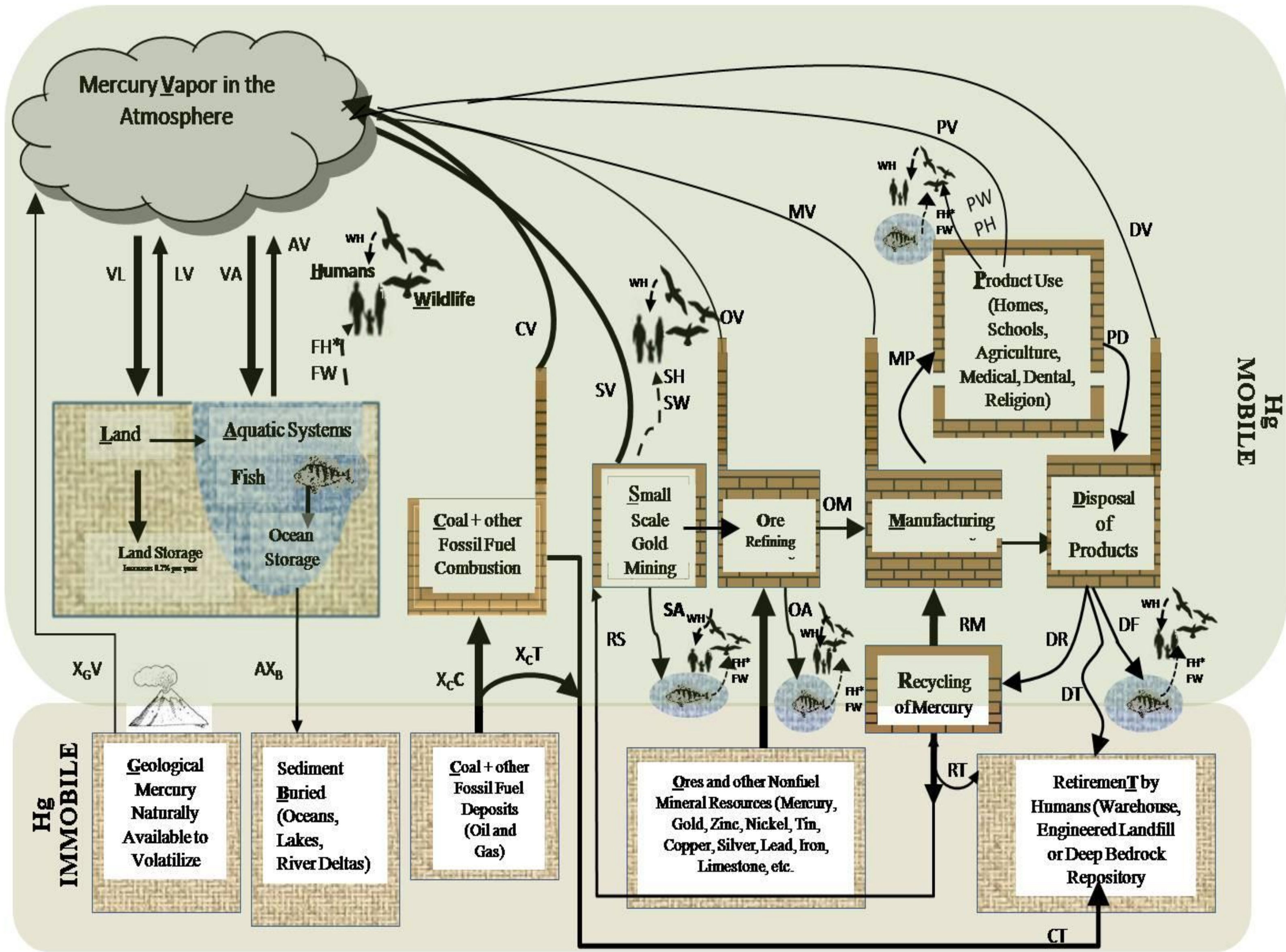

Figure 7.2. Pathways of Mercury Transport in the Environment (Modified from Swain et. al [318]).

Table 7.1 Site Comparison of Social, Environmental, and Economic Factors in Florida, Bolivia and Guyana.

Factor	Tampa, FL *	Bolivia ¥	Guyana¥
Population	State - 17, 019,068 Tampa – 303,000	▪ 9,775,246 (July 2009 est.)	▪ 752, 940
Geography	▪ Located in US ▪ Coastal (1926 km) ▪ Land Area – 140,512 sq km ▪ Water Area - 11,157 sq km ▪ 22nd largest state in US	▪ Located in Central South America ▪ Landlocked ▪ Land Area – 1,083,301 sq km ▪ Water Area – 15, 280 sq. km ▪ 28th largest country in world	▪ Located in Northeast region of South America ▪ Coastal (459 km) ▪ Land Area: 196,849 sq km ▪ Water Area: 18,120 sq km
Language	English	Spanish, Quechua, Ayamara	English, Amerindian dialects, Creole, Hindi
Climate	Semi tropic Three seasons	Varies with elevation Arid – Altiplano Two Seasons (rainy and dry)	▪ Tropic, hot humid ▪ Two Seasons (rainy and dry; rainy: May to August and November to January)
Natural Resources/Major Commodity	▪ Oranges ▪ Phosphate	▪ Sn, Zn, Pb, Fe, Au, natural gas, petroleum, Li	▪ Sugar, gold and diamonds, bauxite, shrimp, timber and rice (60% of GDP)
Major Weather Events	▪ Hurricanes ▪ Flooding	▪ Droughts (Altiplano) ▪ Volcanic eruptions ▪ Flooding (North-East)	▪ Flooding
Environmental Issues	▪ Water availability ▪ Water quality and Total Maximum Daily Loads ▪ Everglades restoration	▪ Mercury ▪ Soil Erosion ▪ Water pollution/privatization	▪ Mercury ▪ Water pollution ▪ Deforestation
Food Source of Concern wrt Hg Loadings	Fish	Fish, potato, llama, alpaca, quinoa, coca	▪ Fish, rice, cassava
Economy	▪ HDI – 13ᵠ (very high development) ▪ 40% of all US Exports to Latin and South America ▪ 75% of US orange production ▪ Tourism ▪ CPI – 7.5#	▪ HDI – 113ᵠ (medium development) ▪ Export commodities: natural gas, soybeans, crude oil, Zn, Sn, Au (low) ▪ CPI – 2.6#	▪ HDI – 114ᵠ (medium development) ▪ 60% of GDP from sugar, gold, bauxite, shrimp, timber, and rice ▪ CPI – 2.7#
Political Society Major Laws Affecting Mercury	Democracy 1st Arican American President The Clean Air Act, The Florida Management of Mercury-Containing Lamps and Devices Destined for Recycling , The Clean Water Act, Impaired Waters Rule Mercury Export Ban Act; EPA Clean Air Mercury Rule	Republic (new constitution state 1st Indigenous President (Ayamara) Social Unitarian State) Environment Regulation on Mining Activities 1995; Mining Code 1997; General Environmental Law, 1992; International Labor Organization, 1991 [239]	Republic Forest Bill 2009, Mining Law, Amerindian Act 2006, and the Environmental Protection Act 2006. Additionally the Land Law, the Iwokrama Act, National Infrastructure Policy
Principle Sources of Mercury Exposure	Coal fired power plants Municipal/Medical Waste Incinerators	Gold and tin mining Volcanic Eruptions	Gold mining activities Deforestation or Land Degradation.

*Information collected from State of Florida (www.stateofflorida.com). ¥Obtained from CIA World Factbook. ᵠObtained from UN 2009 Human Development Report (http://hdr.undp.org/en/statistics/) where the closer the Human Development Index (HDI) is to 1 the more "developed" it is. #Obtained from Transparency International for 2009 where the closer the Corruption Perceptions Index (CPI) is to 10 (on a scale of 0 to 10), the least corrupt it is (http://www.transparency.org/policy_research/surveys_indices/cpi/2009).

7.2.1 Economic Sustainability, Political Cohesion and Community Participation

Mercury is used to extract several precious metals and is found in various household products. It is also used in ritualistic practices in Afro Caribbean and Amerindian religions and for obtaining gold (e.g. jewelry). Human consumption and consumerism can inadvertently cause destruction to the environment. Currently, consumption of resources and capital in developed countries are being utilized at a faster rate than they are being replenished by natural geological and biological processes. On the other hand, developing countries allow developed nations to establish industries and exploit their lands to meet the demands for the developed world's hunger and in an effort to increase the developing country's gross domestic product (GDP). The Human Development Index (HDI), an indicator that measures development and human progress based on health, education, and purchasing power, ranks Bolivia and Guyana as 113th and 114th out of 182 countries, respectively. These two countries are classified as being medium development whereas the United States is classified as having a high HDI. The GDP for Guyana, Bolivia, and the US is $13, $11, and $13,751 billion US dollars respectively. Compared with the US, Guyana and Bolivia are at a severe market disadvantage.

According to the Environmental Kuznet's Curve (EKC) which is based on a consumption theory, the growth of the economy results in a degradation of the environment until the desired economic development is obtained[319, 320]. This was further supported by Beckerman[321] who stated that there is "clear evidence that, although economic growth usually leads to environmental degradation in the early stages of development, in the end the best- and probably the only-way to attain a decent environment in most countries is to become rich." The World Bank, one of the main lenders to developing countries for infrastructure improvements, argues that the EKC is based on a static assumption that economic development hurts the environment[322]. Mechanisms like the Clean Development Mechanism (CDM) created under the Kyoto Protocol negotiations provide opportunities for developing countries to "leapfrog" technological development. Through binding agreements with developed country industries they can acquire the newest, most efficient and clean technologies since their lack of infrastructure makes it more cost effective to implement them and get the carbon credits versus making improvements in existing developed world infrastructure. With the absence of any binding agreement at the 15th Conference of Parties, mechanisms like the CDM remain under utilized. The Human Development Report presented by the United Nations Development Programme [233] has stated that:

"Today's consumption is undermining the environmental resource base. It is exacerbating inequalities. And the dynamics of the consumption-poverty-inequality-environment nexus are accelerating. If the trends continue without change — not redistributing from high-income to low-income consumers, not shifting from polluting to cleaner goods and production technologies, not promoting goods that empower poor producers, not shifting priority from consumption for conspicuous display to meeting basic needs — today's problems of consumption and human development will worsen.\ The real issue is not consumption itself but its patterns and effects on sustainable development."

According to the World Bank [323], 20% of the world's richest or highest income countries (e.g. United States) account for 76.6% of the total consumptive expenditures whilst the middle (e.g. Guyana and Bolivia) and lowest countries (e.g. Haiti) contribute to 21.9% and 1.5% of consumer expenditures respectively (Figure 7.3). Globally, the historic production of mercury dates back to fourth century BC during Egyptian times and increased as the Spanish silver mining expeditions evolved in the 1600s and further climaxed during World War II in the 1900s[324]. Also during World War II, tin production in Bolvia and export to the US increased[325]. Cinnabar (HgS), the product mined to obtain mercury, has been produced in Idirija (present day Slovenia) and other locations (e.g. as well as Kyrgyzstan, Russia, and Ukraine) for 500 years , Almaden for 2000 years, and used in Guyana for over 500 years and China for over 2000 years . Gold and silver were mined in Bolivia by the Tiwanacu and Incan peoples long before Spanish arrival in 1545 [326]. Recent reports indicate that Bolivia has at least 3 million troy ounces of gold worth in claims that have been untouched[327]. The historic use of mercury has been shown to be devastating to humans, animals, and the environment.

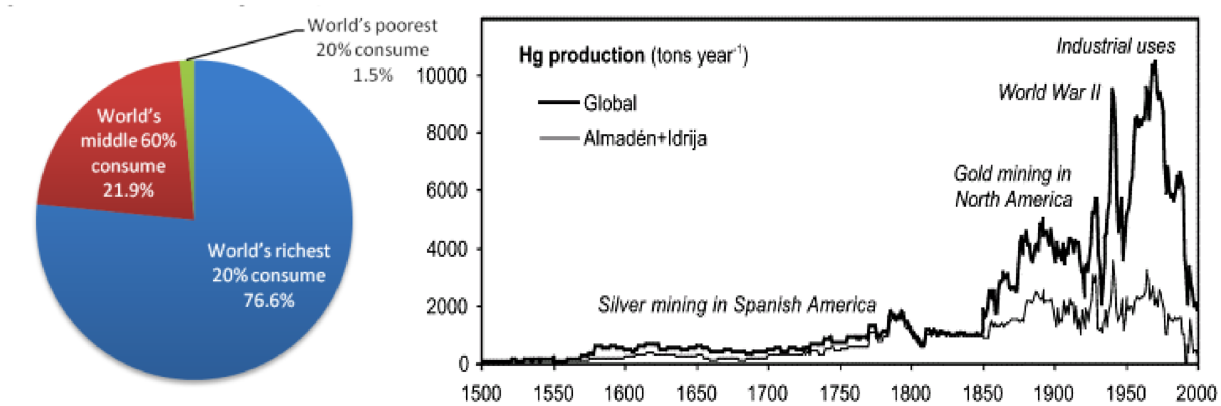

Figure 7.3 World Consumption Behavior (a) Total Consumption[323] and (b) Mercury Consumption from (1500-2000, Taken from Hylander[324]).

Figure 7.4 highlights the reported current consumption, production, price, and legislation of mercury from 1970–1997 in the United States. In 1970, when mercury consumption and prices were at a peak, mercury was identified as a hazardous pollutant under the Clean Air Act. Following this legislation, the production rate decreased but consumption continued to soar until 1992 when the EPA banned land disposal of high mercury content wastes and the National Defense Stockpile (NDS) suspended mercury sales [328].

The World Mercury Ban established by the European Union passed a regulation banning the export of elemental mercury in 2007. Senator Barack Obama (D-IL) and Senator Lisa Murkowski (R-AK) introduced the Mercury Export Ban Act (MEBA) of 2008 (S.906) that prohibits the sale of federal stockpiles of elemental mercury and prohibits the export of elemental mercury from the US, effective January 1, 2013 [329]. The provisions of the MEBA call for:

- All Federal agencies to immediately cease conveying, selling or distributing elemental mercury under Federal control or jurisdiction to any other federal agency, any state or local government agency, or any private individual or entity except for transfers to facilitate storage or transfers of coal.
- The prohibition of elemental mercury from the United States starting on January 1, 2013.
- The Federal government's provision of long-term management and storage of any elemental mercury generated within the United States.

Balistreri and Worley [329] argue that payment for sequestration of mercury in the US offers less drawbacks than the export ban which will encourage local mercury use, discourage mercury recovery from byproduct and waste sources and result in a surplus of mercury in the domestic market, even at a zero price. The impact of a mercury ban on artisanal gold mining can be dramatic given the number of people employed and dependent on this way of life, and their already poor economic situation. In the absence of capacity building efforts that provide either alternative mining methods or alternative livelihoods, one can imagine the destruction of these communities if mercury becomes scarce as well as the destruction due to current mining activities.

Ironically, the US provision never called for an export ban of mercury compounds commonly found in the waste stream. Table 7.2 summarizes the reports from Congress that describe the possibilities of mercury compounds being extracted for mercury from waste products such as electronic components. Figure 7.5, shows an increase in mercury exports which may be due to the large cost associated with storing toxic waste which is a part of the provisions for the MEBA. Additionally, the European Union on October 22, 2008, expanded the mercury export ban to include certain mercury compounds and mixtures (e.g. metallic mercury (Hg_0), mercury (I) chloride (HgCl); mercury(II) oxide (HgO); cinnabar ore (HgS); and mixtures of metallic mercury with other substances, including alloys of mercury having a mercury concentration of at least 95% by weight. This new ban will be effective on all exports from the European Union after March 15, 2011.

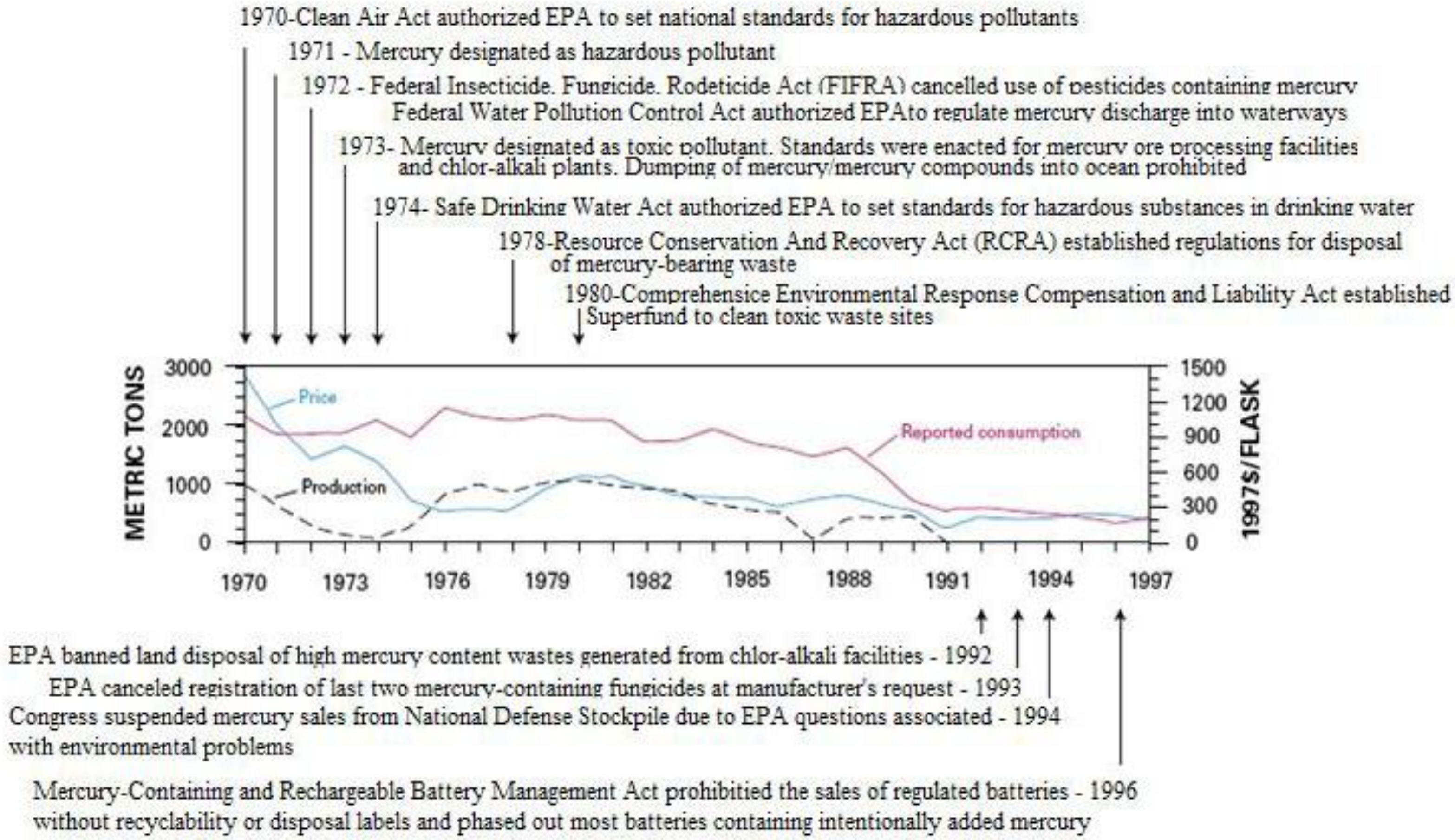

Figure 7.4. Legislation, Consumption, and Production of Mercury in the US from 1970-1997. A FLASK is Equivalent to 1,216 ozs (34.5 kg) of Mercury.

Table 7.2. Summary of Information on Mercury Compounds Required in the Mercury Export Ban Act of 2008.

	Produced in US		Imported						
Compound Name	Source Sector	kg in 2004	Source	Quantity (annual)	Purposes and Uses	Quantity used annually in US	Quantity used 2010 and after	Sources and quantities exported in last three years (2006, 2007, 2008)	Potential for export for regeneration of elemental mercury
Mercury (I) Chloride	Air pollution by product at mines,	25,000 Hg	Data for individual compounds not currently available	Data for individual compounds not currently available	1. Processed for elemental regeneration	Data for individual compounds not currently available	Data for individual compounds not currently available	Data for individual compounds not currently available	Likely, unlikely
	chemical manufacturing	1.3			2. Calomel (mercury (I) chloride) electrodes				
Mercury(II) nitrate	Chemical Manufacturing	88.7			1. Preparation of other mercuric products 2. Analytic reagent (test kits)				Somewhat likely
Mercury (II) oxide	Chemical manufacturing; Battery recycling	32.5			1. Batteries 2. Synthesis of other compounds 3. Analytical reagent				Somewhat likely
Mercury (II) sulfate	Chemical manufacturing; Waste Treatment	260.8 (amount from waste treatment unknown)			1. Gold and silver extraction 2. Reagent				Somewhat likely
Mercury (II) Sulfide	Naturally occurring; chemical manufacturing; waste treatment	0.6 (amount from waste treatment unknown)			1. Extraction of elemental mercury 2. Pigment				Somewhat-Unlikely
Mercury (II) acetate	chemical manufacturing	41.3			1. Manufacturing of organomercuric compounds 2. Catalyst or reagent				Unlikely

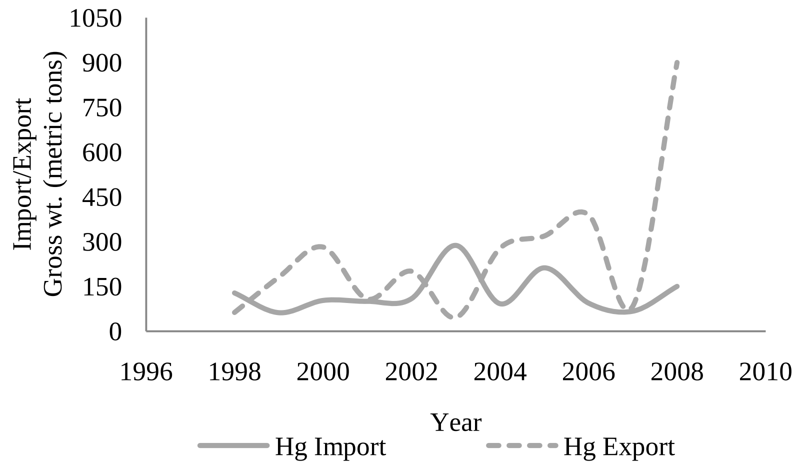

Figure 7.5. 1998-2008 US Commodities Imports and Exports Report for Mercury (Data Collected from USGS Minerals Database [330-332]) .

Aside from the direct extraction of mercury, the use of mercury in the mining industry helps to drive the economies of Guyana and Bolivia where mining and timber and oil account for 60% of the GDP. The US economy was once backed by gold and contains one of the largest reserve holdings of gold alongside Germany, the International Monetary Fund, France, Switzerland, and Italy. In a global economy that has been on edge due to the wake of financial collapses, gold prices have soared to alarmingly historical high rates above $1200/oz (Figure 7.6) and mining activities in developing countries (e.g. Guyana) have increased (Figure 7.7). The amount of wealth remaining in the developing country and the sectors of the societies which benefit remains questionable.

Many environmentalists argue that this is due to consumer *wants* rather than *needs* [107] as this industry's chemical usage and waste management have impacted the environment and affected the health of many inhabitants which include miners, non-miners (both local and global) as well as animals. According to the World Summit on Sustainable Development in Johannesburg, many stakeholders in the mining sector as well as consumers should be held responsible for their consumptive behaviors and not blame the corporations.

Figure 7.6. 10 Year Gold Price in USD per Ounce. Last Closing Price was $1,134.80 on 03/05/2010.

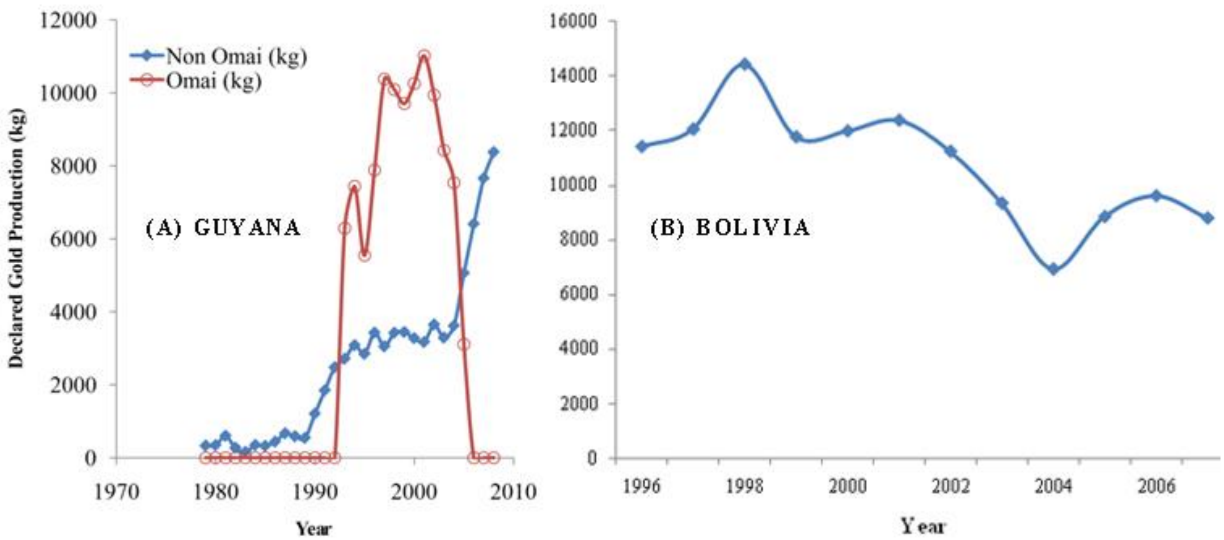

Figure 7.7. Declared Gold Production for (A) Guyana: 1979 – 2008 from Large Scale OMAI Mine and Small to Medium Scale Mines (non Omai) (GGMC, 2009) and (B) Bolivia: 1996-2007 Data Obtained from USGS "The Mineral Industry of Bolivia in 2007 (2002, 1997, and 1996) Taken from http://minerals.usgs.gov/minerals/pubs/country/sa.html Accessed 3/4/10."

Some governments are taking measures to reduce mercury usage by developing legislation that requires the use of "clean technologies". Many of the clean technologies can be classified as gravity based [333] and can also lead to additional destruction to the environment. In addition, human health can also be compromised, since "clean technologies," still require the removal of forest cover. In Guyana, WWF-Guianas with the assistance of the Guyana Geology Mines Commission Guyana Environmental Capacity Development (GENCAPD) program established training on gravity based mercury free technologies that promise similar yields[108]. Without incentives in Guyana for using these technologies, no miners currently use them even though the GENCAPD (funded by the Canadian International Development Agency (CIDA)) project is over ten years old. Interesting to note is that the largest claims in mining concessions held in Guyana are registered to Canadian mining companies. These larger concessions normally utilize cyanide leaching techniques, a process whereby mercury forms a complex with cyanide that is recovered in a chemical plant. A 1995 tailings dam spill from the OMAI gold mine released 3 million m^3 of cyanide slurries into freshwater systems [326]. It remains the largest such catastrophe in Guyana that affected water supply and fish consumption of downstream communities. The country's Environmental Protection Agency was formed more or less as a result of this spill. Hence, international aid from CIDA is assisting with improving sustainability practices amongst small to medium scale miners whilst large scale Canadian registered mining operations failed to institute sustainable practices in Guyana.

According to 2009 reports in one of the country's local newspapers, Stabroek News [334], the government of Guyana is trying to enforce more stringent regulations that would better manage mining site activities, make mercury use in mining illegal and institute better management of tailings for rehabilitation/reforestation. This top down approach results from Guyana's current government's Low Carbon Development Strategy (LCDS) released in June 2009 that was developed in conjunction with the consulting firm McKinsey & Company with financial backing from the Clinton Foundation's Climate Initiative. The LCDS was developed to take advantage of the United Nations Framework Convention on Climate Change's (UNFCCC's) "Reducing Emissions from Deforestation and Forest Degradation in Developing Countries; and conservation, sustainable management of forests and enhancement of forest carbon stocks in developing countries" (REDD+) mechanism to pay countries with standing forests for their ecosystem services, mainly their ability to reduce CO_2 emissions from avoided deforestation activities [335, 336]. An estimated 20% of global annual CO_2 emissions comes from deforestation with power plant emissions being the largest at 24% [336]. One of the few substantial outcomes of

COP 15 held in Coppenhagen in December 2009 was the commitment of funding from the most developed nations for REDD+ which would be managed by the Forest Carbon Partnership Facility (FCPF) of the World Bank. An estimated $175 million is currently pledged for the various funds to support REDD+ [337]. According to the World Bank's FCPF website, the first set of proposals for initial REDD+ funding (Readiness Plans, R-PLANS) of approximately $300,000 US are now in their second phase of review (as of March 2010) and will be used as pilot studies for various aspects of REDD+, including financing and monitoring exercises.

Guyana will be one of the first, if not the first country to receive funding from the FCPF. The government of Guyana also entered into a bilateral agreement with Norway for REDD+ like initiatives under the LCDS in November 2009. Norway has pledged $250 million US over five years with an initial installment of $30 million [334, 338]. The LCDS estimates annual payments greater than $580 million US under the REDD+ program in a tiered approach that would reach this value after 2020 [338]. To put this amount of money in perspective, a recent application by a Canadian company for a gold mining permit in the Marudi Mountain area estimates mining of 1 million ounces of gold over five years. The proposed recovery technique is "gravity separation using mobile screen and concentrator units." At current prices over $1000/ounce, the revenue generated in one year would equal the entire 5 year Norwegian pledge. Many other new mining applications are in the pipeline for Guyana. Mahdia, one of the sites presented in Chapter 4, was once to be mined by large scale mining operations. The grade of the ore and gold prices at the time (around 2000) converted the concessions into small to medium scale mines all of which use mercury recovery techniques. Now that gold prices have more than tripled since the larger mining interests left, it remains to be seen if the medium to small scale local miners will be "squeezed" out of areas. Given Guyana's experience with OMAI, left without any remedial action since closure in 2005, it is unknown whether the larger scale, international mining operations would be any more sustainable than the small to medium scale miners.

In January 2010, the government of Guyana proposed regulations that would require gold miners to obtain approval from the Guyana Forestry Commission for new mining activity. Gold miners would have to identify their intentions six months prior to mining activity, something that has raised major concerns amongst the mining community and resulted in well organized protests in

Bartica and Mahdia in January and February 2010. Miners believed that the LCDS would force at least 80% of the local miners out of a job. Some of the regulations being enforced all of a sudden have actually been part of Guyanese law for over a decade. Lack of interest or provision of proper resources by the government to the agencies in charge of regulation like the Guyana Geology and Mines Commission (GGMC) has resulted in little to no action being taken to ensure proper mining practices. There has been very little government investment in technical capacity building that could improve the small to medium scale gold mining sector through partnerships with the local university and technical training institutes.

The NGO WWF-Guianas has supplied equipment to both the GGMC and the University of Guyana over the past five years that is being used to monitor mercury levels of miners whenever they declare their gold. The last equipment purchase capable of mercury detection by a governmental institution (Institue of Applied Science and Technology) was over twenty years ago in the form of a Cold Vapor Atomic Absorption Spectromter. The very recent move to enforce standards, institute new mining regulations, and commit to capacity building is very interesting in assessing sustainability as it really shows the impact of political will and political engagement. Given this sudden and almost immediate change in governmental strategy towards mining, a more in depth discussion of the LCDS process follows with linkages to sustainability issues raised in Chapter 6 through the Community Based Participatory Research (CBPR) process.

Chapter six described the principle guidelines required for successful CBPR projects and Table 7.3 summarizes the relationship between those principles and LCDS activities based on published material, reviews of publicly accessible material posted on the official LCDS website, newspapers, blogs, website postings and personal communications.

Table 7.3. Linking Principles of Community Based Participatory Research (CBPR) with Guyana's Low Carbon Development Strategy.

CBPR Guiding Principles (Israel et al.[302])	Application to Guyana's LCDS Process
Recognizes community as a unit of identity	Based on the impact of the LCDS on livelihoods of all Guyanese, the community represents the entire country. The main participants are the President and Office of the President, the LCDS appointed steering committee, Guyana Office of Climate Change, Indigenous groups, Forestry Commission, Non Governmental Organizations (especially Conservation International and WWF-Guianas). Partnering members also include the international financing community (e.g. FCPF and Norway), members of the Guyanese diaspora, and foreign research institutions.
Builds on strengths and resources within the community	CBPR supports and expands existing social processes (community skills, assets, existing structures like community boards) to address community needs.
Facilitates collaborative partnerships in all phases of the research	The LCDS has potential for engagement and empowerment for all involved (Conservation International [335]). Organized civil protests by mining gold communities in 2010 suggest that collaborative partnerships are not yet in place for all members of the communities that will be affected by the LCDS.
Integrates knowledge and action for mutual benefit of all partners	The initial development of the LCDS took a very top down approach that is politicized in a country sensitive to these associations. The draft LCDS was shared with the Guyanese public after it had been drafted by members of the government and McKinsey & Company.
Promotes a co-learning and empowering process that attends to social inequalities	The LCDS has the potential to do this if communities are truly allowed to participate in the decision making and implementation processes.
Involves a cyclical and iterative process	The LCDS was released to the Guyanese population in June 2009. Listening sessions throughout the country were held between June 2009 and September 2009. The draft LCDS proposal stated that the website would be used to collect comments from the public that would be considered by the LCDS steering committee. This was never made available. An updated draft document was published in December 2009 and it did not address many issues raised in the consultations and this has resulted in non support from the indigenous groups.
Addresses sustainability from all five pillars*	The LCDS is a binding mechanism that affects all Guyanese. It should build on problems identified by the citizens of Guyana, but for the most part in its current state it has not adequately engaged all Guyanese so that they can meaningfully contribute to its design.
Disseminates findings and knowledge gained to all partners	A large publicity campaign followed the release of the draft LCDS in June 2009. All media types were used, consultation sessions were held throughout Guyana, and the LCDS website hosts many of the documents and meeting minutes. The accessibility of these materials is questionable as the consultation sessions revealed that indigenous communities wanted the information translated into their own language and others stated that the material was difficult to understand.

*modified Principle 7 that is better suited to Guyana and the LCDS.

"The citizens of forest countries – especially those who depend on the forest for livelihoods – must be active participants in framing a solution. In the same way as there is no solution to climate change without forestry, there is no solution to deforestation without the support of forest populations."

His Excellency President Bharrat Jagdeo's in the Foreward of The Little Red Book (Parker et al.[336])

There is no doubt that Guyana's President Jagdeo has championed REDD+ development and implementation and argued for developing countries to be equally involved in the framing of REDD+. His insistence on developing country participation at the international level fails to transfer to local affairs on the ground with respect to the LCDS or Guyana's R-PLAN under review by the FCPF. The official Government of Guyana LCDS website (http://www.lcds.gov.gy/) has provided meeting minutes from the "consultation sessions" held with various communities throughout Guyana between June and September 2009, reaching an estimated 7,000 persons [339]. These consultation sessions were organized by the Guyana Office of Climate Change in the Office of the President and included a steering committee of various representatives of Guyanese society, though key representatives were missing like members of the opposition parties and members from the educational sector. Dow et al. [339] provide a thorough summary of the consultation process in their report, including commentaries raised through local newspapers. They discuss areas for improvement that would better engage and benefit Guyanese and make note of the fact that the government developed the LCDS prior to widespread local consultations, an action that could cause future drawbacks. Dow et al.'s [339] document was published in September 2009 and therefore missed newspaper headlines in which citizens responded to new mining guidelines needed to meet LCDS commitments. Recent newspaper headlines include, "Bartica goes gold! …Thousands protest mining proposals [340]" and "GUYANA: Pro-Forest Measures Anger Miners [341]".

The second draft of the LCDS was released in December 2009 and does not address many of the limitations identified by Dow et al., 1990. In fact, it states that the independent observers applauded Guyana's transparent consultation process and refers the reader to the original report by Dow et.al[342] to learn about the stressed limitations. In addition to the January and February protests organized by gold miners, some indigenous groups have called for a halt to implementation of the LCDS and REDD+ projects as reported by the Stabroek News on March 10th, 2010 under the caption, "Indigenous leaders call for hold on LCDS, REDD+ projects." According to the article, the June to September consultations were inadequately administered to the indigenous groups and land rights issues need to be resolved prior to their support for LCDS and REDD+ related projects.

The second draft of the LCDS published in December 2009 [338] states that "The government has been working with the *mining sectors* to identify ways to embark on wide-ranging reform of the mining regulations and their enforcement to ensure that mining operations promote higher standards of environmental sustainability alongside economic development. Further information will be outlined in the REDD+ Governance Development Plan, by October 2010." It is alarming that this would be printed in the second draft and not more than one month later, mining protests are occurring around the country. In June 2009 the Technical Advisory Panel (TAP) reviewed Guyana's first draft R-PLAN submitted to the FCPF and concluded that since mining is the major cause of deforestation and forest degradation a functional working relationship that addresses integrated land use assessment is urgently needed between the GGMC and Forestry Commission and other related parties. The second R-PLAN is currently under review by the FCPF and the protests of miners and attitude of the President of Guyana to proceed with or without the consent of miners implies that more work needs to be done to forge a meaningful partnership.

The World Bank has applauded Guyana's implementation of the LCDS consultation process in news releases displayed on the LCDS website. However, on reading the meeting minutes from the LCDS "consultation sessions" and viewing the corresponding posted recorded videos it becomes quite evident that communities were not involved in the creation of the LCDS and were merely being consulted/informed after it was developed by a multinational company in collaboration with the local Guyanese government. These criticisms have been raised in Guyana and abroad through various media outlets like newspapers, websites/blogs (globalwitness.org; lcdsguyana.com; http://guyanaforests.blogspot.com), especially since there is widespread concern that lack of transparency in developing countries will prevent the funding from reaching the communities that inhabit and depend on the forested lands or for even reaching the local population exclusive of the government. Guyana scores 2.7 on the Corruption Perceptions Index which has been developed by Transparency International with a value of 0 being the most corrupt and a value of 10 being the most corrupt [343]. The LCDS is the governing document that includes REDD+ projects which are managed through the FCPF. Four institutions will manage the LCDS, all of them government associated. FCPF funding would go directly to an office within the Guyana Ministry of Finance, which raises questions on accountability on what specific investments (how contracts would be awarded etc..) will be made to improve livelihoods of the wider population, especially those directly dependent on forested lands.

The potential is there for meeting the CBPR principles, however to date the LCDS has failed to satisfy these in their entirety. The LCDS is in its early stages of development and the entire REDD+ funding mechanism is also new. Using the CBPR principles as a guide would actually enhance the LCDS and its proper development. The TAP review [344] of Guyana's R-PLAN does suggest that there needs to be "a clearer understanding by GoG [Government of Guyana] that this kind of information sharing is only the beginning of a process that has much larger aims. The purpose of full consultations is to involve the various sectors of society in discussing, identifying, and understanding in an interactive way, their level of knowledge about climate change and sustainable development linked to REDD." They recommend that the government develop a strategy for moving stakeholder involvement from a "consultation" mode to a more inclusive, interactive "consultation/participation" approach."

Like Guyana, Bolivia is also a potential site for REDD+ funding. In 2008 the Bolivian government filed a Readiness Plan Idea Note (R-PIN) and are further behind Guyana in being a REDD+ pilot site. The review of their R-PIN highlighted issues of engagement like those discussed above and suggested that "In the two main areas, Amazon forest and the dry Chiquitano, forest indigenous peoples are the main players, and their participation needs to be secured through better stakeholder consultation during the whole readiness process, not only in the implementation of a REDD mechanism." The potential influence of REDD+ on gold mining practices in Bolivia remains to be seen, but the widespread adoption of new ways of doing things is possible.

Mining has always been a major driver in the Bolivian economy and in 1952, when the sector represented 97% of foreign exchange earned, the government nationalized mining and placed it under the management of CAMIBOL. Low world market prices and management decisions resulted in CAMIBOL's decline with an approximate loss of 20,000 workers from the industry and by 1990, foreign investment was once again encouraged in Bolivia through international monetary mechanisms[345]. The mines are owned by the state with some mining concessions to private Bolivian cooperatives and foreign mining companies. In 2006 President Evo Morales of Bolivia nationalized the hydrocarbon industry with mining next on the agenda. Figure 7.6 compared gold exports from Guyana and Bolivia. Whilst the Guyanese exports correlated with the rise in gold prices, this was not necessarily seen in the Bolivian case which is likely influenced by political changes. As exports from a large foreign investor, OMAI, decreased, the small to medium scale mining declarations increased significantly as did the number of permits and people involved in the industry. Whilst OMAI used cyanide, the small to medium scale miners use mercury for gold recovery.

Table 7.4 lists the companies registered as large scale gold mines in Guyana and Bolivia, where the former is much more open to private and foreign investment. Ineffective efforts at water privatization in Bolivia are cited throughout the world (famous examples include documentaries Flow & Blue Gold) as an example of engaged and active citizenry that fights and wins over multinational enterprises. The same actively engaged and organized citizenry in the form of mining cooperatives have delayed nationalization efforts of the Bolivian mining sector. Many of the cooperatives began during CAMIBOL's decline. The National Association of Medium-Scale Miners, The National Association of Small-Scale Miners and the National Federation of Mining Cooperatives are the three main groups representing the Bolivian mining sector [239]. The most common types of small-scale mining operations in Bolivia are cooperatives working in alluvial gold deposits (dwindling resources), cooperatives working in primary gold deposits and informal mining (gravel scratchers, individual miners, tailings re-treatment, 'pirquiñeros') [239]. This informal sector uses the least technically advanced methods of mining, unwarranted amounts of unrecovered mercury, and with no safety precautions for human health [239]. Civic engagement/activism in Guyana pales in comparison to Bolivia. The recent protests by members of the Guyana Gold Miners Association against the LCDS suggest that the association is becoming more engaged; however, their initial intent is to continue their regular modes of operation.

Non-governmental organizations like the MEDMIN Foundation in Bolivia have focused on the development and application of technologies for the reduction of environmental impacts caused by mining operations, especially in artisan and small scale mining [239]. An example project was the construction of a collective dam to receive tailings from 40 separate flotation plants which serviced approximately 8,000 miners who were producing approximately1,500 t/day (almost 100 times the amount of gold produced annually) [333]. In Guyana, WWF-Guianas is the organization that has been leading the charge in terms of improving the practices of small to medium scale gold mining.

Table 7.4. Gold Companies in Guyana and Bolivia.

Gold Companies in Guyana	Gold Companies in Bolivia
* Argus Metals Corp. * Caerus Resource Corporation * Gold Port Resources Ltd. * Goldstone Resources Ltd * Guyana Goldfields Inc. * Iamgold Corporation * Infinito Gold Ltd. * Newmont Mining Corp * Sacre-Coeur Minerals, Ltd. * Shoreham Resources Ltd. * Takara Resources Inc. * Uramet Minerals Limited * Valgold Resources Ltd. * Victoria Gold Corp. * Vista Continental Corp	* Eaglecrest Exploration Bolivia S.A. * Empresa Minera Inti Raymi S.A. * Empresa Minera Paititi S.A.

Gold production employs over 10 million individuals and could contribute to a country's economic development, but there is great debate over the need to mine for gold. According to Lehman Brothers and Ali[107], the total amount of gold above ground is far larger than the known unmined reserves. Figure 7.8 shows that unmined reserves only account for 50,000 tons of the total gold reserves. Non-governmental agencies such as Oxfam-America and Earthworks have launched campaigns such as "No Dirty Gold." This campaign encourages consumers to be cognizant of their behaviors and proactive in demanding corporate responsibility in ventures that destroy the lands. As the world's market rate for gold increases the rate of mercury use will increase; however, resources are indeed finite so additional measures will need to be taken to address the needs of small scale miners and their families. Fair trade, historically applied to agricultural products, has been proposed for gold to eliminate "middle men" and directly connect miners with jewelers [346]. The illegality of practices at many small to medium scale operations complicates support for fair trade. Gold and Hilson [346] argue that rather than directly link miners with jewelers, emphasis should be placed on strengthening the small scale mining sector to meet regulations and practices that better benefit them and the environment.

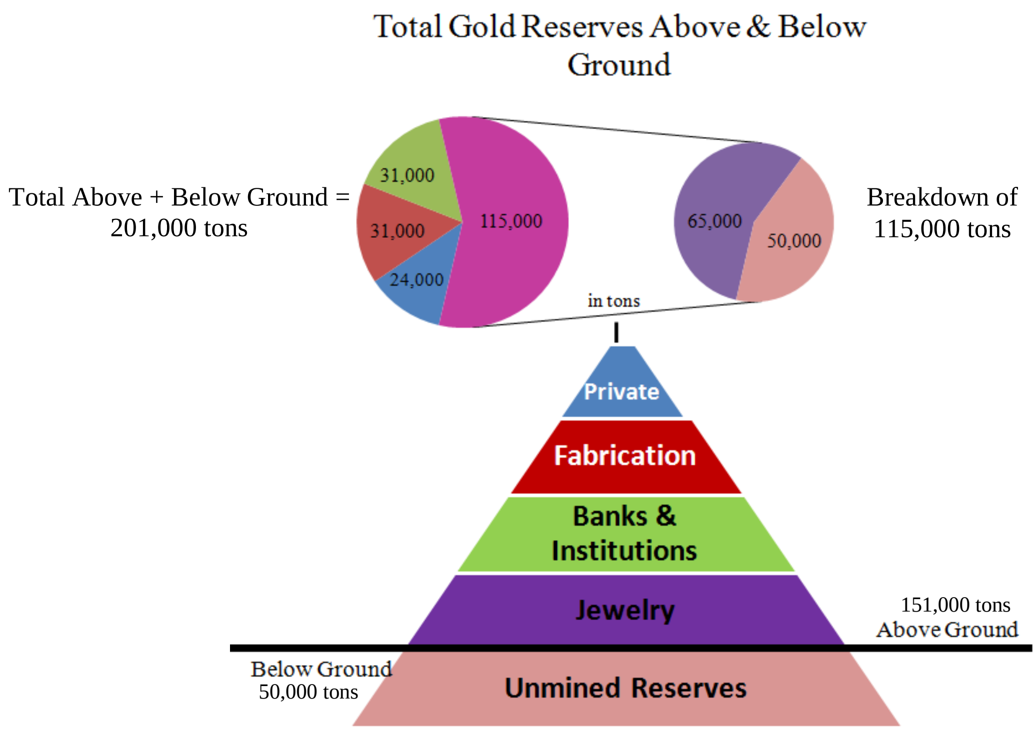

Figure 7.8. Gold Reserves Above and Below Ground (Modified from Lehman Brothers and Ali[107]).

The field sites in Guyana and Bolivia were mainly in the remote parts of the country, many times close to or in mining areas. In the case of Guyana, the gold mining sites used mercury amalgamation methods. Phosphate, titanium and zirconium are the two main mined commodities in Florida, none of them using mercury in the process [330]. The Hillsborough River, the field site in Tampa, Florida was an urban river with mercury inputs coming mainly from atmospheric deposition (incineration of medical waste and burning of fossil fuels), either directly or through stormwater runoff. The closest mining related activity to the Hillsborough River would be phosphate and vermiculite mining, a cement plant and a gypsum plant. Like mines in Guyana and Bolivia, the Floridian mines result in removal of forest cover, changes in hydrological processes, degradation of river water quality, and release of hazardous materials (e.g. radon and uranium) as a result of tailings exposure. The pollutants released are not considered global pollutants of concern because they are neither transported like mercury nor are they as toxic. Proximity of urban communities to these locations, existence of enforceable environmental regulation, and activism of environmental watchdog groups continuously work to ensure more sustainable practices by these mines. The mining of phosphate used for agriculture and food production is also probably perceived differently by the public than the mining of gold used to fill the vaults of banks or for individual glorification.

Mercury emissions regulations have been established for power plants using a cap and trade design under the 2005 EPA Clean Air Mercury Rule (CAMR). The CAMR takes effect in 2010 and establishes that a 69% overall reduction in emissions be achieved by 2017[347]. Legislative processes in the US are strongly influenced by special interests like the utilities. In addition, the laws passed in Florida depend heavily on the political party in power. For Florida, emissions from utilities and incinerators are the main contributors to mercury pollution. This poses a concern for local citizens like those living in East Tampa, some of whom fish in the Hillsborough River. In framing the concept of political cohesion, economic sustainability, and community participation as it relates to mercury use and exposure in the Tampa, Florida, one must ask who makes decisions on acceptable pollutant levels, who has access to and can access information to make informed decisions for health protection (e.g. each year the Florida Department of Health posts fish advisory levels for water bodies in Florida on its website, but many minority communities lack access to computers and internet connections) and who is engaged in the development of research agendas to study these phenomena.

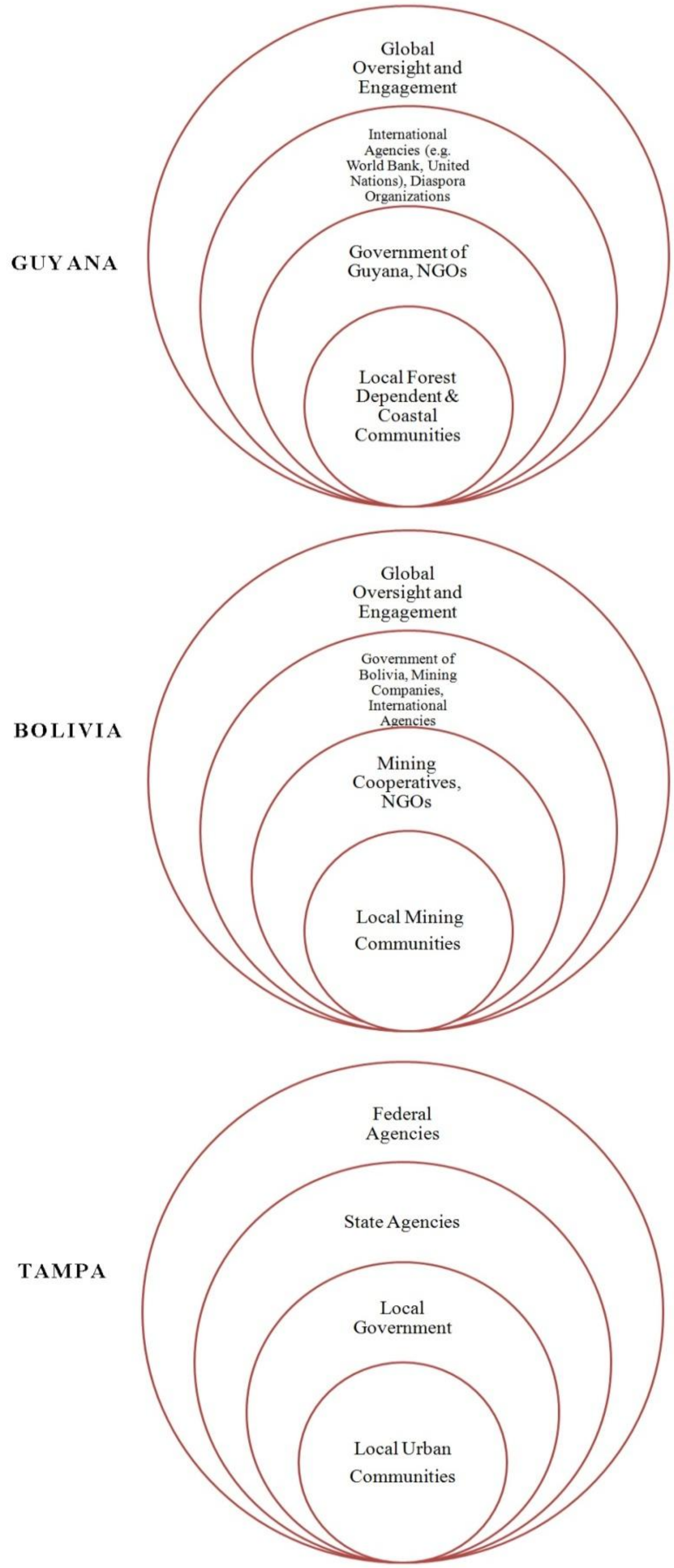

Figure 7.9. Various Players Who Influence Sustainability as it is Related to Mercury Use and Exposure.

Figure 7.9 depicts the various players at the different field sites who influence sustainability as it relates to mercury use and exposure. The previous section discussed actions across the gamut of players as they related to political cohesion, economic sustainability and community participation. In Section 7.3 the last two sustainability pillars, environmental sustainability and socio-cultural impacts, are discussed mainly within the smallest sphere, the local community, in Figure 7.9.

7.3 Environmental Sustainability and Socio-Cultural Impacts

In this study, environmental sampling and analyses were done to determine mercury loadings and potential exposures to humans. Table 7.5 describes the analytical tests performed in the various sites described in greater detail in Chapters 3-5.

Table 7.5. Environmental Analysis Performed at Field Sites in the USA, Bolivia and Guyana.

	Tampa, FL					Bolivia					Guyana				
Waterbody Analyzed	Hillsborough River					Lake Titicaca					Essequibo River and tributaries				
Media Collected	Sediment, water, fish					Sediment, water, fish					Sediment, water				
Analytical Test	CV-AFS	XRD	CV-AAS	SEM /EDAX	BET	CV-AFS	XRD	CV AAS	SEM/ EDAX	BET	CV-AFS	XRD	CV-AAS	SEM/ EDAX	BET
	√	√	√	√	√	√	√	√			√	√	√		

CVAFS – Cold Vapor Atomic Fluorescence Spectromtery; XRD – Xray Diffraction; CVAAS – Cold Vapor Atomic Absorption Spectrometry; SEM/EDAX – Scanning Electron Microscopy/Elemental Analysis; BET – Surface Area.

Table 7.6 summarizes the results for total mercury in unfiltered water samples and total mercury in sediment samples. Guidelines for mercury to consider are: 1000 ng/L for drinking water [348] and 770 ng/L for the protection of aquatic life through chronic exposure [190]. The unfiltered water samples for the Hillsborough River (0.9-7.8 ng/L) and for Lake Titicaca (44-114 ng/L) measured total mercury concentrations below both of these regulatory guidelines. Most uncontaminated surface waters usually have total mercury concentrations below 4 ng/L, so the Lake Titicaca samples are high relative to Hillsborough River and high relative to uncontaminated baselines. River water is not drunk directly from the Hillsborough River, but in the communities around Lake Titicaca, untreated river water is a source of drinking water. Water samples were not analyzed for Guyana, but communities there also directly drink river water in addition to rain catchment and well water.

Mercury loadings in sediment samples for the sites in Tampa, Guyana and Bolivia ranged from 50-119 ng/g, 29-1200 ng/g, and 132-2891 ng/g respectively. Unmined US basins had total mercury loadings between 0.9-2480 ng/g [174]. The total mercury loadings in the Hillsborough River were lower than the loadings observed in the Titicaca area and for most of the Guyana samples, even the remote, unmined, conservation areas like Kanashen. Cadwell et al. studied mercury in sediments from arid lands in New Mexico and found that mercury levels were temporal with higher loadings seen during the drier seasons [349]. This may be a contributing factor to the higher levels of mercury seen in the Titicaca area when compared to Guyana. The higher loadings around Titicaca could also be due to greater use of mercury by miners and worse modes of disposal/recovery. According to Bocangel [239], some artisanal miners in Bolivia grind ore with mercury in such a way that a "flowering effect" occurs requiring a greater amount of mercury and extensive dispersal of mercury in the environment with the spent ore. The mines visited in Guyana (1 in Arakaka, 5 in Mahdia) all used sluice boxes with mats for collecting heavy gold containing ore. Mercury application occurred either on the mat (illegal), or in a "jig box" after the mat was shook. Where and how the gold was recovered from the amalgam was never observed by our team and questions remain on whether retorts were generally used. Compared to some of the mining practices highlighted by Bocangel [239] in Bolivia less mercury would be used and released from the Guyanese processes.

Iwokrama and Konashen would be considered extremely remote, sparsely populated environments with no industrial activity; however, there is a logging industry in Iwokrama. Their sediment loadings for mercury range up to ~ 300 ng/g whereas the highest loading seen in the Hillsborough River was 119 ng/g. Samples from some mining sites in Guyana were surprisingly low and could be due to the nature of the sediment materials or to the fact that mercury was used in such a way that it minimized contamination. Cohen et al. [350] found soil total mercury concentrations across the greater Everglades to range from 2-917 ng/g with the average being 162 ng/g ± 141 ng/g. Other studies of soils in Florida have found mercury loadings that range from 0.62-430 ng/g with the average being 12.6 ± 34.4 ng/g [351]. Sediment Quality Assessment Guidelines (SQAG) for coastal waters in Florida recommend a Threshold Effects Level (TEL) of 130 ng/g and a Probable Effects Level (PEL) of 696 ng/g [352]. The TEL represents the upper limit of the range of sediment contaminant concentrations not considered to represent significant hazards to aquatic organisms and the PEL defines the lower limit of the range of contaminant concentrations associated with adverse biological effects.

The Hillsborough River and Guyana samples, with the exception of a sample from the Phillips Tailings which was 1200 ng/g, would fall below the PEL guideline. There is actually no regulatory limit on sediment mercury loadings, but given the complex biogeochemical mercury cycle, higher loadings could result in increased availability for consumption by organisms.

Drinking water is definitely a route of mercury exposure to animals and humans. Sediments on the other hand would be a route of exposure through absorption through the skin or ingestion (e.g. on improperly washed food). Samples from surface tailings would also be a source of mercury that could potentially contribute to air emissions. More importantly, mercury in sediments can be transformed into mercury loadings in fish. Cohen et al. [350] has correlated total mercury sediment loadings with mercury concentrations in fish and has further justified measuring total mercury loadings by citing the cost effectiveness of both (n = 600).

The consumption of fish is the primary route of exposure to mercury in the world. Patterns of exposure vary by consumption pattern, market values, geographic location, method of preparation, and ethnicity/race whilst concentrations vary by fish species, fish size, and locale (polluted and unpolluted waters, fresh vs. marine, etc.). Fish harvesting in the developed world is composed of 92% marine fish, 5% freshwater, and 3% aquaculture[318]. Swain et al. [318] estimated that over one third (85×10^6 t) of the global marine harvest enters international trade with fifty percent coming from developing nations. High value tuna and piscivorous fish usually have higher mercury concentrations in the global markets.

Table 7.6 Mercury Results from Sites in The USA, Guyana, and Bolivia Reported for Unfiltered Water Total Mercury (uwthg) and Sediment Total Mercury (sTHg).

Location	uwTHg (ng/L)	sTHg (ng/g)
Tampa, Florida (US)		
Hillsborough River, Tampa, Florida	0.9-7.8	50-119
Guyana (SA)		
Arakaka		41-300
Mathews Ridge		190-1200
Port Kaituma		142-364
Mahdia mine wastes		29-601
Konashen river and creek sediments		92-301
Iwokrama river sediments		53-298
Bolivia (SA)		
Lago Titicaca		
Rivers and Streams of Lago Titicaca	44-114	132-2891
Mine waste and stream (downstream of mine)	114*	1568-2891
US Stream [174]		
unmined basns		0.90-2480
mined basins		0.84-4520

*No water sample was collected for mine site

Table 7.7 Fish Length (L), Weight (W), and Total Mercury Loading (fTHg) from Tampa, Fl, Guyana, and Bolivia.

Area	Species	N	L_{range} (mm)	L_{avg} (mm)	W_{range} (g)	W_{avg} (g)	$fTHg_{range}$ (mg/kg wet wt)	$fTHg_{avg}$ (mg/kg wet wt)
Bolivia	Pejerrey	10	292-415	336	185-522	298.1	0.20-0.76	0.38
	Trucha	10	225-375	299	203-946	496.1	0.03-0.1	0.06
Tampa	LMB	20	249-495	347	307-1841	618.1	0.22-0.97	0.56± 0.22
	BLUE	10	163-209	184	59-183	105.3	0.12-0.24	0.17 ± 0.4
	RESU	8	126-243	168	30-262	88.7	0.02-0.21	0.10 ± 0.07
Guyana*	Zipfish**	20	--	--	--	--	--	0.429
	Sunfish***	13	--	--	--	--	--	0.276
	Various	168	--	--	--	--	0.02-1.034	0.439

*Taken from World Wildlife Fund Guianas and Guyana Institute of Applied Science of Technology Guyana Project Report done in the Mathew's Ridge area[353].
** Zipfish is local name for *Dora micropeus* and *Hemiodus unimaculatus*.
*** Sunfish is local name for *Crenicichia lugubris* and *Cynodon gibbus.*

Total mercury loadings in fish samples are summarized in Table 7.7 for sites in Bolivia, Tampa and Guyana. Fish mercury levels in Florida ranged from 0.02 – 0.97 mg/kg wet weight with highest levels exhibited in largemouth bass whilst in Bolivian mercury concentrations were from 0.03 to 0.76 mg/kg wet weight with Pejerrey having the highest levels. Mercury loadings in fish usually correlate positively with fish weight, but this was not the case for the Trucha which had lower loadings than Pejerrey despite heavier weights. Using data results from the mining areas of Isseneru and Kurupung in Guyana mercury levels for various species were 0.02 – 1.034 mg/kg wet weight [353] (average = 0.439 mg/kg wet wt). According to Singh et al[353], 90% of the population surveyed in Isseneru can be considered at risk and may display adverse health effects.

Section 3.6 discussed the Hazard Index which relates the mercury loading in fish to the human consumption rate required to ensure there are non cancerous health effects to children and adults.

The study of hair mercury loadings amongst an indigenous riverine population close to an amalgamated gold mining operations in the Bolivian Amazon revealed loadings lower than other Amazonian communities [354]. Barbieri et al. [354] (2009) sampled hair from and interviewed 150 members of the area (population of 829) and found that on average they ate 10.5 meals of fish per week with that of children aged 1-5 being 12.52 meals per week. Average hair concentrations were 3.02 μg/g with the highest found amongst the Garimperos (miners), but still for the most part below the 10 μg/g unofficial level used by researchers (The WHO level is 50 μg/g) [355]. Unfortunately, Barbieri et al. [355] did not report mercury loadings in fish, water or sediment for the community surveyed. The number of fish meals consumed per week is significantly greater than that observed by the Guyana study discussed above which suggested 3-4 meals of fish per week. One meal per day, per week and per month were all found to represent consumption habits of fisherfolk along the Hillsborough River [177]. Tables 7.8 and 7.9 compare the Hazard Index for a given fish mercury loading and also the fish mercury loading that would be required to obtain a Hazard Index of 1 (above 1 would be of concern) assuming a Reference Dose (RfD) value of 1 x 10^{-4} mg/kg-day and that one serving of fish is 227 g.

Table 7.8. Hazard Index (H) and Critical Fish Concentration (C) for Children Assuming H = 1. Calculations Assumed a Rfd = 1 x 10^{-4} mg/kg day for Different Ingestion Rates (I, g/day), Fish Mercury Concentrations (C, mg/kg Wet Weight) and Body Weight (16 kg for a Child). Ingestion rates of 8, 32, and 227 g/day correspond to 1 meal per month, week, and day.

Ingestion Rate (g/day)	H C = 0.1 mg/kg	H C = 0.38 mg/kg	H C = 0.56 mg/kg	C (mg/kg) H =1
	child	child	child	child
8	0.47	1.80	2.65	0.21
32	2.03	7.70	11.35	0.05
227	14.19	53.91	79.45	0.01
341	21.28	80.87	119.18	0.00

Table 7.9. Hazard Index (H) and Critical Fish Concentration for Adults (C) Assuming H = 1. Calculations Assumed a Rfd = 1 x 10^{-4} mg/kg day for Different Ingestion Rates (I, g/day), Fish Mercury Concentrations (C, mg/kg Wet Weight) and Body Weight (70 kg for an Adult). Ingestion rates of 8, 32, and 227 g/day correspond to 1 meal per month, week, and day.

Ingestion Rate (g/day)	H C = 0.1 mg/kg	H C = 0.38 mg/kg	H C = 0.56 mg/kg	C (mg/kg) H=1
	adult	adult	adult	adult
8	0.11	0.41	0.61	0.93
32	0.46	1.76	2.59	0.22
227	3.24	12.32	18.16	0.03
341	4.86	18.48	27.24	0.02

Assuming a consumption rate of 10.5 meals per week (341 g/day), the mercury loading in fish should be 0 for children and 0.02 mg/kg for adults. This ingestion rate has been observed in Bolivia, though not necessarily at the sites tested for this study. Using the average Trucha and Perrejey loadings, the Trucha should be consumed by children at a rate of ~ 1 meal per week and Perrejey less than once per month. The average weight of a Bolivian adult and child may be different than the values used above. Regardless, the high ingestion rates would raise concerns if common in the areas studied in this research. Using the average LMB loading seen for the Florida site, children should consume LMB less than once a month and adults once a month. For the mercury loadings in fish ranging from 0.1 to 0.56 mg/kg, H>1 for ingestion rates of once per week for both children and adults. Many of the fish mercury loadings reported in Tables 7.8 and 7.9 fall within this range, suggesting that ingestion rates should be adjusted accordingly to protect human health or fish selection should adjust to favor fish with lower loadings (e.g. trucha vs perrejey or bluefish vs LMB). It should also be noted that the serving size for children is probably different from that of adults and this was not considered here, however this can be easily adjusted in Table 7.8.

Awareness of mercury in fish and the recommended ingestion rates was beyond the scope of this study. There was no information posted at any of the study sites that discussed fish mercury loadings and human consumption. For non mining indigenous populations like the Wai Wai at Kanashen or the villagers in Fairview, Iwokrama, fishing is part of the culture and changing that to other forms of protein would be complicated when compared to mining areas in Guyana where access to the city is easier. This challenge is not unique to these populations as fishing communities around the world are grappling with changes in behavior needed to sustain one's health in the light of increased pollutant levels in fish.

Other routes of human exposure to mercury do exist and differ according to geographic location and setting (urban or rural in a developed or developing country). Table 7.10 identifies the main routes of exposure for the different field sites. The environmental sampling conducted for this work is limited to the first row and were discussed above in terms of water and fish. The inhalation and absorption routes are based on direct observation and literature review. Figure 7.10 shows images of mercury storage and use in retorts in a mining site in Guyana. The poster was from the GENCAPD project cosponsored by the Guyana EPA. The retort is placed in a fire at various locations around the mining site, sometimes closer to where miners live and cook. The mercury is recovered by collecting the vapor under water. With the given retort set up, there are many opportunities for inhalation exposure as the system is not 100% closed. Figure 7.11 shows the open torching of amalgam at a local shop in a Guyanese gold mining area. This would contribute to inhalation exposure for those in close proximity to the burning, including children. It also shows a gold miner handling pure mercury by hand at an eating establishment. The mercury is worn on his person for spiritual reasons and contributes to both inhalation and absorption exposure.

Table 7.10. List of Activities that Contribute to Various Exposure Pathways in Study Sites in Bolivia, Guyana and Tampa.

Exposure Route	Lake Titicaca Bolivia	Kanashen, Iwokrama Mahdia, Mathew's Ridge Guyana	Tampa, Fl USA
Ingestion	River water, Fish, Other food	River water, Fish, Other food	Fish, Other food
Inhalation	Soil & dumped waste emissions, Amalgam burning, Stored mercury	Forest fires, Soil & dumped waste emissions, Amalgam burning, Stored mercury, Wood burning stoves in house (Kanashen)	Incinerators, Coal Fired Power Plant, Cement manufacture, Landfill emissions, Soil emissions, Phosphate mines, Crematoriums, Religious practices
Absorption	Soil, Mercury for amalgamation, Handling of mercury containing materials/waste	Soil, Mercury for amalgamation, Handling of mercury containing materials/waste	Soil, Handling of mercury containing materials/waste

Figure 7.10. Mercury Use at a Mine in Mahdia, Guyana with Posters Done by the GENCAPD Project in Conjunction with the Guyana EPA. (A) Mercury is Stored in a Safe Place, (B) A Retort with the Amalgam Heated Over a Fire in a Closed Container and the Vapors Collected Under Water, (C) Retort is Burned in a Fireplace in the Mining Camp.

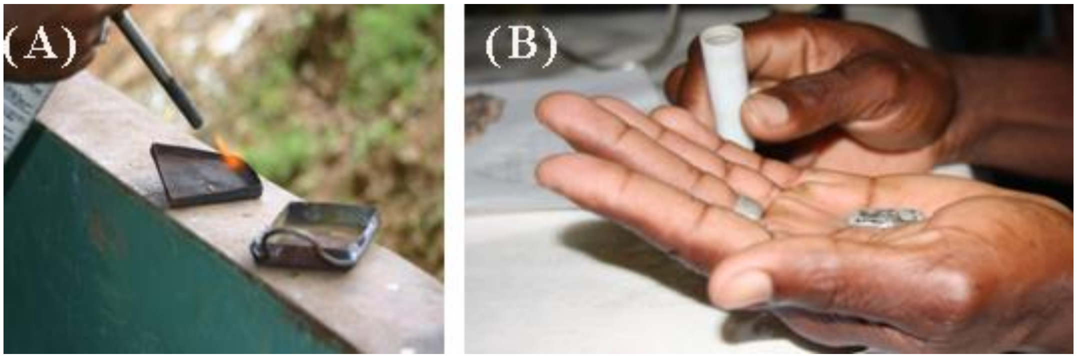

Figure 7.11. Pictures from Guyana Showing Direct Exposure to Mercury Through (A) Using a Blow Torch in an Open Space to Clean Gold, and (B) Carrying Mercury on Person for Spiritual Reasons.

Gold mining occurs on almost 50% of indigenous lands[107] and a greater percent occurs on lands that impact the environment of indigenous populations. The technologies employed by artisanal miners in Guyana and Bolivia use mercury to extract precious metals and result in environmental degradation with little effort at reclamation or remediation. Amerindians represent 9% of the population in Guyana and to date own ~14% of the land in the country which are titled under the State Lands Act, however, criticisms remain on the failure of the government of Guyana to recognize Amerindian land rights in accordance to international provisions[178]. In Bolivia, there have been similar sentiments with the Ayamara and Quechua populations though the dynamics is probably different given indigenous leadership in the form of President Evo Morales.

According to the 1999 National Emissions Inventory Database for Hazardous Air Pollutants, mercury emissions for Hillsborough County were estimated to be 1,224.50 kg/yr. Advancement in technology has probably lowered this value as the most recent estimates for mercury emissions for the entire state of Florida are 7,500 kg [356]. As CAMR takes effect, emissions from the main sources (coal powered fuel plants, incinerators, cement manufacturers) will drop significantly and sources like solid waste landfills which now only contribute 1% of emissions, will account for a larger percentage of emissions. In time, as less mercury is used in our products, source emissions from landfills will also decrease. Compared to the Guyana and Bolivia sites, direct handling of mercury by individuals in Tampa is not common nor is inhalation exposure, although breakage of mercury continaing bulbs or compact fluorescent lights (CFLs) is increasingly popular within the closed home environment as well as old storage in school science laboratories.

The levels of mercury found in fish are a health concern for all of the communities studied. Enforcing policy measures may affect the livelihoods of miners, subsistence fisherfolk, and their families. Health according to the World Health Organization is a state of complete physical, mental , and social well-being and not merely the absence of disease or infirmity[357]. Mercury bans may not be practical measures of control if miners are given no other alternatives to generate an income if not equal or greater to then what they receive while working in the mines. This is especially true if gold demand continues to increase as do gold prices. Bans on exports in the US can also create leakage. Around the world, the illegality of mercury use may lead to an increase in the use of time, energy, effort, and resources oncriminalizing current practices rather than spurring innovation and capacity building. Instead of updating old technologies (e.g. "mercury free gold') as has been the case in Guyana and Bolivia, truly green engineering should be used. Green engineering is defined by Mihelcic and Zimmerman[358] as the "design, discovery and implantation of engineering solutions with an awareness of potential benefits and problems in terms of the environment." Given the emphasis on mercury use in the gold mining industry, the sociocultural change needed to reduce the main driver, gold demand, cannot be ignored.

7.4 Education

For all of the sites studied monitoring data on environmental mercury loadings is sparse as is the awareness of local communities on their exposure to mercury through various pathways. For example, in locations where the smartphone is available a new downloadable application, "Mercury in Fish for the iphone" that sells for 0.99 cents (Figure 7.12) indicates that there probably is an already aware and concerned global population interested in monitoring and making informed decisions on things that affect their health and that are within their immediate control. The application collects the latest data on mercury loadings in 125 fish and provides consumption guidance based on the consumer characteristics. This application uses a GUI or graphical user interface and allows its users to switch between different guidelines (FDA, EPA, and WHO) and it receives "real time" mercury warnings along with images of the fish in question which would be useful for fisherfolk. In Figure 6.1 sustainability and education share the same sphere, the implication being that they are directly intertwined. The pillars of sustainability represent five different areas that must all be considered in order to assess the most sustainable outcome. Education that addresses and integrates those five pillars plays an important role in reaching the most sustainable outcome. Chapter 6 presented an evolving model for raising environmental awareness in Tampa, increasing community and personal engagement on local issues and forging partnerships through a CBPR process. The model mainly focuses on East Tampa, a distressed urban community that has formally organized its resources to reinvest in, and improve the community.

The Water Awareness Research and Education (WARE) project is a long term commitment to a partnership that evolves as all participants grow and learn through the work. Based on the partnerships already established in the other study sites that enabled the research presented here, Figures 7.13 and 7.14 extend WARE to Guyanese and Bolivian sites. The figures list the various participants representing the local community, the university and the NGO community. The NGO community has been identified as key players for strengthening civic engagement in developing countries, especially places where actions are highly politicized (Trotz, 2008).

Figure 7.12. A Smartphone Application, "Mercury in Fish", for Quantifying Mercury Exposure from Fish. http://www.pcworld.com/appguide/app.html?id=289697&expand=false. Accessed 2/10/10.

For immediate implementation, it would be best to work with agencies that have built trusting relationships with the indigenous populations and/or mining communities within each of the areas as well as integrates indigenous culture into the program design. In Guyana, agencies already actively involved in the community like the WWF-Guianas, Conservation International and Iwokrama Center for Biodiversity Research along with university and community officials in the indigenous and mining communities can form a joint collaboration. In Bolivia, ACDI/VOCA, the Universidad Tecnologica Boliviana, AARM, the University of South Florida, health care workers, and the indigenous community (Ayamara and Quecha) would be ideal partners in an effort to increase active participation in modernizing the ancient practices of mining and yet be beneficial to the economy.

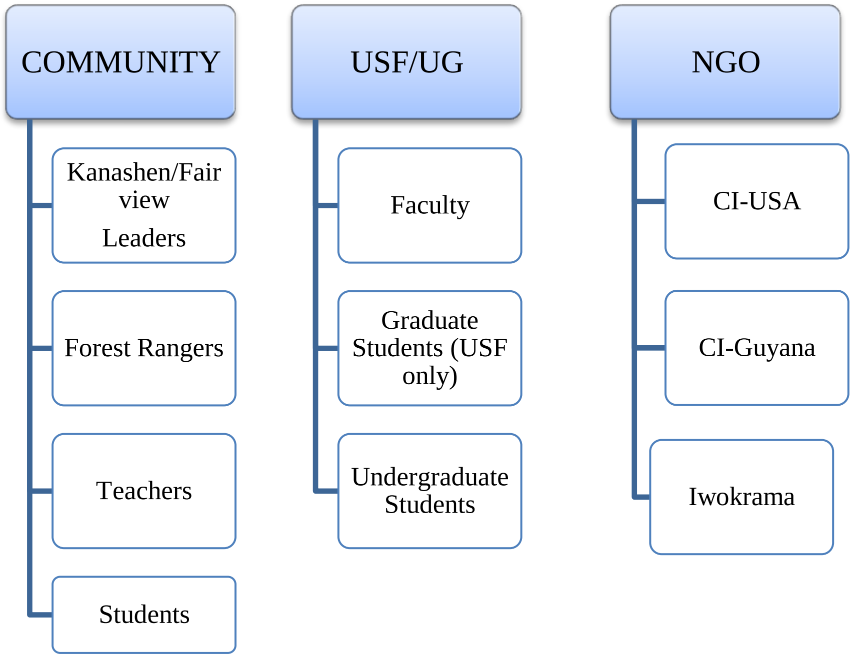

Figure 7.13. Potential Partnership Structures with Conservation International (CI) in Guyana.

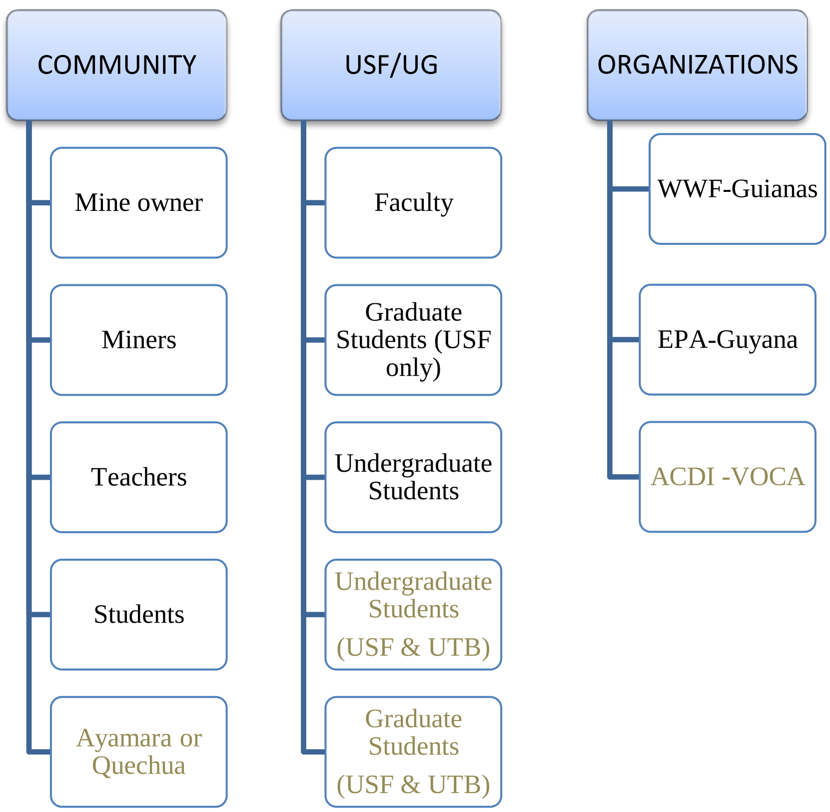

Figure 7.14. Potential Partnership Structures for Guyana and Bolivia Where Bolivian Partnerships are Faded.

7.5 Conclusion

This chapter discussed mercury in study sites in Bolivia, Guyana and Tampa, Florida, three countries that differ in terms of demographics, geography, geology, politics, economics, commerce, and culture. Despite the many differences, mercury occurrence, use and exposure for the sites were discussed in terms of the five different pillars of sustainability and Tables 7.11 and 7.12 summarizes the main findings for the different study sites in terms of: (1) economic sustainability, (2) political cohesion, (3) community participation, (4) environmental sustainability, and (5 and 6) socio-cultural aspects.

Education is a key to integrating the pillars of sustainability to create sustainable solutions and promote sustainable development. Community Based Participatory Research principles capture the sustainability pillars and if implemented correctly have the capacity to generate awareness and action around the issue of sustainability. Based on the experience from the WARE model in Tampa, partnerships for Guyana and Bolivia were proposed that can implement similar capacity building programs to raise awareness on sustainability, including mercury use, occurrence and exposure.

Table 7.11 (A) Summary of Mercury Use, Occurrence and Exposure in Bolivia, Guyana and Tampa, Florida as They Relate to the Five Pillars of Sustainability.

Pillars of Sustainability	Bolivia	Guyana	Tampa, Fl
Economic Sustainability	High gold prices increase mining activity and mercury use and many artisanal miners inefficiently use mercury and use it in such a way that environmental contamination results. The impact of mercury use on human health (women and children also mine in Bolivia) can decrease the profits made from mining which are few or non existent to begin with. Cooperatives and NGO collaborations help to devise sustainable solutions for improved mining.	High gold prices increase mining activity and mercury use since it is still the most readily available and cheapest way to produce gold for artisanal miners. New rules making mercury use in mining illegal may not stop artisanal miners from using mercury and may criminalize a larger portion of the Guyanese workforce in order to meet new international monitoring mechanisms for forest preservation.	CAMR requires utilities and industry to reduce emissions through implementation of new technology and a mercury export ban is underway. The cost versus effectiveness of these measures at reducing community exposure to mercury is unknown.
Political Cohesion	Mining cooperatives are engaged and active groups who are against mining nationalization and who form cohesive bargaining units. Bolivia has a history of community engagement and activism on unfairness as it relates to basic human needs (e.g. water).	Highly politicized environment with minimal, but growing, community activism around environmental issues.	Various governmental agencies make decisions on mercury, many times special interest lobbying plays a role in outcomes. Minimal engagement of local communities in these decision making processes. Awareness of some communities on mercury impacts is non existent. East Tampa has a strong community group and serves as a good model for developing CBPR projects that raise awareness on mercury.

Table 7.12. (B)Summary of Mercury Use, Occurrence and Exposure in Bolivia, Guyana and Tampa, Florida as They Relate to the Five Pillars of Sustainability.

Pillars of Sustainability	Bolivia	Guyana	Tampa, Fl
Community Participation	Mining cooperatives represent a large group of miners though artisanal miners who are the most reckless with mercury are not a part of any of the legally recognized groups. NGO presence has tried to develop sustainable solutions for mining that require buy in and participation of large groups of individual miners.	Top down decisions clash with local communities and new international funding mechanisms have opened the door for the creation of truly engaged and participatory decision making processes. To date this has not been 100% implemented, especially as it related to forest communities and miners. NGOs have been instrumental at forging better community participation in all aspects of projects.	The WARE project is a model underway for increasing awareness of mercury related issues and in general creating a more engaged public that critically incorporates sustainability concepts into decision making processes.
Environmental Sustainability	Mercury from mining activities impact ecological, animal and human health	Mercury from mining activities and deforestation impact ecological, animal and human health	Mercury emissions from utilities account for most local loadings.
Socio-Cultural Impacts	Local customs increase risk of exposure (fish consumption habits, spiritual use) and education through CBPR can potentially allow local communities to make better informed decisions.	Local customs increase risk of exposure (fish consumption habits, spiritual use) and education through CBPR can potentially allow local communities to make better informed decisions.	Local customs increase risk of exposure (fish consumption habits) and education through CBPR can potentially allow local communities to make better informed decisions.

CHAPTER 8: CONCLUSION

8.1 Introduction

Mercury and concepts of sustainability are mainstream issues that require the active participation and engagement of all members of society to help improve current conditions for future generations. These relationships are quintessential in acquiring, assessing, and disseminating information required to reduce exposure factors as well as make well informed decisions. This section provides a summary of the experimental results, conclusion, and recommendations for future work.

8.2. Summary of Results and Conclusions

The main goal of this research was to improve our understanding of the factors contributing to mercury exposures in three geographically unique locations, Tampa, FL; Mahdia/Iwokrama, Guyana; and Lago Titicaca, Bolivia, and develop community oriented solutions that reduce exposure. The three objectives and summary of the findings for this work have been provided below:

Characterize mercury loadings in three previously unmonitored freshwater bodies that represent different geologies, demographics, and regulatory frameworks.

- 86% of the total mercury loadings in fish collected from the Hillsborough River (Tampa, Florida), warrant an advisory warning if following the US EPA fish consumption guideline, especially for largemouth bass. Sediments (50-119 ng/g) contained levels highest in areas just after the dam in the urban reaches but all values were similar to levels found in Florida Bays.

- In Guyana, the conservation and actively mined areas along the Essequibo River exhibited sediment and soil concentrations ranging from 29 to 1200 ng/g with lower average levels seen in conservation areas.
- From twelve locations in Lago Titicaca and its rivers and streams (Río Suches, Río Alcamarini, and mountain streams) water and sediment samples were collected. Average mercury loadings in the unfiltered waters within the rivers and streams of Lago Titicaca ranged from 0.3-114 ng/L and sediment loadings ranged from 24-2891 ng/g. In comparison to other sites, it is suggestive that mercury is of concern for the area.
- For all sampling sites a positive linear correlation existed between total mercury in sediment with pH, DO, and turbidity.

Compare results and conditions at study sites to determine the role of socioeconomic factors in mercury loadings.

- There are varying socioeconomic, regulatory and geopolitical factors within Florida, Bolivia and Guyana; however, limited to no informational signage exist and mercury hazard index data suggest that children are being under protected.
- Critical adjustments are needed within internataional and domestic regulatory frameworks to include universal mercury and health guidelines that reduce loop holes in clauses.
- Mercury loadings in fish from both Bolivia and Florida may cause adverse health effects to residents if consumption rates remain the same and larger predatory fish are consumed.
- Community partnerships and active participation is needed to address issues of sustainability.

Implement partnerships between education and local community sectors that focus on increasing an awareness of sustainability concepts in a mutually beneficial manner that informs on mercury contamination and reduces exposure.

- Education is a key to integrating the pillars of sustainability to create sustainable solutions and promote sustainable development. Community Based Participatory Research (CBPR) principles capture the pillars of sustainability.
- Florida represented the model location for CBPR Suitable local partnerships were identified and have since grown. Current partnerships exist with 3 schools and 4 teachers from East and New Tampa (Hillsborough County Public Schools), the City of Tampa Economic and Urban Development, East Tampa Civic and Community leaders, University of South Florida professors and student organization (Engineers for a Sustainable World), 88.5 WMNF radio personalities, and the Southwest Florida Water Management District.
- An environmental curriculum with a principle focus on stormwater ponds and various special programs were designed with the assistance of various partners.
- The curriculum utilized constructivism theory of learning and a teaching philosophy of inquiry based learning to provide a broader impact and actively encourage active community participation.
- All stakeholders or partners are quientessential in addressing various avenues of the project; however, there is room for growth and improvement and this is allowable in the design of WARE.
- The WARE program can probably be modified appropriately and be used in Bolivia and Guyana with potential partners being local non-governmental organizations that have built a relationship with the indigenous (ACDI-VOCA, Iwokrama, WWF-Guianas,)

8.3 Reccomendations for Future Work

Table 8.1 summarizes recoomendations for future work using the five pillars of sustainability presented in Chapter 7.

Table 8.1. Reccomendations for Future Work Using the Pillars of Sustainability

Pillar	Recommendations
Societal (political cohension, sociocultural respect, and community participation)	• CBPRs be used to create sustainable solutions and promote sustainable development • Improve and expand existing partnerships • Universal Health Guideline • Develop cyber infrastructure for international and interdisciplinary linkages for CBPR type projects • Use principles of cogeneration of knowledge
Environmental	• Analyze coca, potatoes, cassava (Yucca) and quinoa products for mercury and additional heavy metals to understand • Additional sample collection and monitoring to capture temporal variation and more spatial coverage • Fish consumption habits and fish loadings relevant to immigrant communities in the US
Economical	• Use CBPR to reduce mercury consumption • Create alternative means of income to reduce Hg exposure • Through sustainability education enhance self reflection on individual role (e.g. jewelry preference) in outcomes and impacts around the world. • Extend Life Cycle Analysis approaches to incorporate socio-cultural, political and community empowerment indicators.

This dissertation has presented several opportunities to conduct additional research and build partnerships within each of the given areas. Table 8.1 summarizes some of the opportunities according to the pillars of sustainability. A list of recommendations for future work within the context of the areas studied within this work are as follows:

Tampa, Florida:

- A regular monitoring program can be established for the Hillsborough River as well as the upper Hillsborough Bay as a joint collaboration between the Florida Department of Environmental Protection and the United States Geological Survey to help expand the data in the South Florida Information Access Program.
- Use regular monitoring programs as a means to educate and actively engage the community to promote sustainability.
- Temporal sampling of environmental media.

- Improve existing partnerships within the Hillsborough County School District.
- Develop a road map of mercury in the Tampa area by collecting air and flora samples along the Hillsborough River and Hillsborough Bay.
- Partner with state agencies (e.g. Hillsborough County Environmental Protection Commission, Department of Health, FDEP), film/media specialist, schools, non-profit organizations that represent the interest of the communities to promote knowledge and awareness of mercury and other environmental issues.

Guyana:

- Work with local agencies to gain access to interior regions and to analyze results in country instead of transporting to US for analysis.
- Survey mining and pristine areas for mercury concentrations in air, water, sediment, and staple products produced in vicinity of area.
- Collect and analyze fish for total mercury concentrations.
- Obtain results on worker and community consumption behaviors and exposure to mercury to develop appropriate measures of exposure.

Bolivia:

- Collect additional samples from the Altiplano Region of Lago Titicaca ensuring that a larger sampling size is obtained.
- Obtain fish samples and water samples from locations where river and streams entering into the lake as well as in the Desagudero.
- Analyze coca, potatoes, and quinoa products for mercury and additional heavy metals to understand human health risks.
- Perform community surveys on consumption practices and knowledge of mercury and sustainability to begin to appropriately assess health hazards.
- Develop stronger relationships with ACDI/VOCA and other agencies that work in indigenous communities to build a similar community based participatory program as in Tampa.

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Appendices

Appendix A: Equipment and Supplies List.

Table A-1. Catalog and Price List for Sampling Supplies and Field Equipment.

Item Detail	Company	Qty	Price	Cat #
Silicone Tubing	Fisher	2	$39.70	`
Teflon Tubing (1/8 in x 3/16 in) (case of 2 - $52.92)	Fisher	2	39.70	8050-0187
Cole Parmer C-Flex Tubing (3/8 in x 5/8 in)	Fisher	2	76.96	NC 9781223
Whatman Polycap Filters (0.45µm) (assuming 1 filter/sample) Gelman AquaPrep Filter	Fisher Fisher	24 Or 24	19.35/ea 30.08/ea ($258.50/case of 10)	05-714-036 12176 (Gelman #); GWSC04510 (Fisher #)
Plastic Storage Bags	Fisher	1 1	110.18 45.96	01-816-1E (9x12) 01-816-1D (5x8)
500 mL disposable glass bottles (case of 12)	Fisher	2	25.86 (Alternate) 24.15	02-912-013 (Alternate) 05-719-171
Solinst Portable Peristaltic Pump	Fisher Solinst	1	999.00	NC9611459 Model #410
Extra Battery -Werker 12V 5AH AGM Battery W/ .187 Terminal - WKA12-5F	Batteries Plus	1	29.99	WKA12-5F
LaMotte Water Sampler Model JT-1 (Vandorn water sampler)	Fisher LaMotte	1	205.58	S45085J CODE1077
Ekman Bottom Grab Sampler	Wildco	1	485.00	196-B12 Standard w/case
Quanta Hydro lab	Hach	1	4500.00	
Stainless Steel Bowl	Wal Mart	1	9.96	Durapet: Stainless Steel Pet Bowl, 1ct
Stainless Steel Scooper	Wal Mart	1	4.96	
Trimble Ranger Handheld GPS Garmin GPSMAP 76S	Trimble Walmart	1 1	$5500 w/case $299.00	Includes warranty and base maps for SA,NA,CA
Powder Free Nitrile gloves (1 pk = 100 gloves)	Fisher	2 2	9.27 9.26	19-130-1597C (M) 19-130-1597B (S)
Marking Pens	Fisher	1	13.73	13-379-4 (black)
Clipboard w/storage	Wal Mart	1	18.99	
Waterproof Field Notebook (alternative: Nalgene* PolyPaper* Pocket Data Books; 1 pk. = 4)	Fisher	2 (1)	52.40 (70.04/pk)	6303-1000 (alt: 6306-0500)
Potassium Bromate (ACS Reagent Grade) (5g)	Fisher	1	13.47	AC424070050
Potassium Bromide (ACS RGrade) (500g)	Fisher	1	70.15	AA4001336
Hydrochloric Acid (ACS Plus) (500 mL)	Fisher	1	14.75	A144-212
Eppendorf Pipette 100-1000 uL	Fisher	1	221.90	05-402-90
Eppendorf Pipette 500-5000 uL	Fisher	1	222.19	05-402-91
Eppendorf pipette tips 100-1000 uL	Fisher	1	49.85	05-403-68
Eppendorf pipette tips 500-5000 uL	Fisher	1	21.77	05-403-29
Turbidity Standard 40 NTU	Hach	1	122.01	NC9943238
Conductivity/TDS Standard, 500µS/cm	Hach	1	13.18	224132
Conductivity Standard, 150 mS/cm	Hach	1	26.29	22491532
Turbidity Standard, 10 NTU	Hach	1	62.48	R88010004C

Appendix B: SOP for CVAAS and Analytical Parameters

CVAAS MERCURY ANALYSIS

STANDARD OPERATING PROCEDURE (SOP)

Safety Guidelines

In compliance with the USF Division of Environmental Health and Safety Agreement soil/sediment and biological samples should be handled accordingly.

All samples must be handled with care due to strict USDA and USF guidelines. In addition, mercury compounds are highly toxic if inhaled, swallowed, or absorbed through the skin; therefore laboratory safety and field safety measures must be adhered to at all times. Appropriate attire should be worn when handling mercury or potentially mercury contaminated samples from all matrices. Proper attire includes the following:

- Lab coat
- Gloves/Protective eye gear
- Closed toed shoes
- Long pants
- Nasal/Mouth Mask

While in the laboratory all samples should be handled under the ventilation/fume hood at all times. Work surfaces/areas must be cleaned. *Note: Untreated samples should not be retained longer than 12 months from receipt unless proper authorization has been granted from PPQ.**

According to the USDA Compliance Agreement (details are outlined in the *Foreign and Domestic Soils SOP Manual*) all foreign and domestic soil samples must be stored and locked at all times in the securely locked freezer in ENB 227A.

Appendix B Continued

Storage Regulations

According to the United States Department of Agriculture Animal and Plant Health Inspection Services the following guidelines must be adhered to when shipping domestic and foreign samples to the Civil and Environmental Engineering Department at the University of South Florida.

In preparation for the shipment of foreign soil samples to the University of South Florida the following must be followed:

1. Individual soil samples must be stored in doubly bagged and sealed Ziploc or other tightly closed, doubly contained containers. The samples must then be contained in a sturdy, leak proof container (i.e. a cooler) to prohibit the possible spillage or escape of pest while in transit to the university.
2. Samples should be labeled and accompanied with a copy of the Soil Permit and have a PPQ Form 550 clearly displayed on it as follows:

   "Contents Soil Samples"
3. All foreign and domestic soil shipments must be sent via a bonded carrier
   Samples from Guyana will be shipped by via Fedex in Guyana. The port of entry in the US will be Memphis or Miami.
4. Record Soil Shipments in binder kept in KOPP 227A. Once samples are received and properly stored decontaminate shipment containers.

Mercury Standards and Reagents

All standards and reagents have been outlined below:

- Reagent Water: Reagent Referenced as water in method.
  - 5%HCl or 5% HNO_3

- Aqua Regia: (soil digestion)
  - *Prepare immediately before use.*
  - Add volume of 3:1 concentrated HCl to concentrated HNO_3.

- Sulfuric acid, 0.5 N:
  - Dilute 14.0 mL of concentrated H_2SO_4 to 1L.

- Stannous sulfate: (CVAA)
  - Add 25 g stannous sulfate to 250 mL of 0.5 N H_2SO_4.
    - This mixture is a suspension and should be stirred continuously during use.
  - A 10% solution of stannous chloride can be substituted for stannous sulfate.

- Sodium chloride-hydroxylamine sulfate solution: (soil digestion)
- Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL.
- *Hydroxylamine hydrochloride (NaCl/NH_2OH) may be used in place of hydroxylamine sulfate.*

- Potassium permanganate, mercury-free, 5% solution (w/v): (soil digestion)
- o Dissolve 5 g of potassium permanganate in 100 mL of ultra pure deionized water (DI water with resitivity of 18.1MΩ).
- Ultra-pure deionized water (18 MΩ minimum)

- Stock mercury standard—NIST-certified 10,000-ppb aqueous Hg solution (NIST-3133).

Appendix B Continued

Standards Preparation

All standards should be taken through the digestion process even if using the EPA Method 6971 Modified by Environmental Express for use with there digestion bottles.

- Take the 10,000 ppb stock aqueous Hg solution (NIST-3133) and dilute it down to 500 ppb Hg using the reagent water (5% HCl or 5% HNO_3; however be consistent) in a 100 mL flask
- Using the 500 ppb Hg working solution make dilutions to obtain 350 ppb, 250 ppb, 150 ppb, 100 ppb, 50 ppb, and 25 ppb. Follow the aforementioned method. However, a smaller flask size can be used (i.e. 10 mL; however, please be advised there is a higher error associated with smaller sizes and is not recommended).

Interferences with CV-AAS Analysis

Interferences and contamination of water samples may occur. The following list describes the potential hindrance to total mercury results:

- Waters containing sulfide, chloride, copper and tellurium (concentration levels unknown)
  - Copper – Only concentrations as high as 10 mg/Kg have no effect on recovery of mercury from spiked samples.
  - Chlorides - high concentrations require additional permanganate (as much as 25 mL) due to the oxidation steps conversion of chloride to free chlorine, which also absorbs radiation of 253 nm.

    - Reduced by using excess hydroxylamine sulfate reagent (25 mL) or purging dead air space in the digestion vessel before adding stannous sulfate (or stannous chloride)

- Organic compounds (broad band UV absorbance ~253.7 nm)

- Volatile materials (e.g., chlorine) that absorb at 253.7 nm will cause a positive interference.
    - To remove any interfering volatile materials, dead air space in the digestion vessel should be purged before addition of stannous chloride solution.
- Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

- Low level mercury sample preparation, digestion, and analysis may be subject to environmental contamination if preformed in areas with high ambient backgrounds (i.e. locations where mercury was previously employed as an analytical reagent in analyses such as total Kjeldahl nitrogen (TKN) or chemical oxygen demand (COD))

Mercury Standard Methods

The following is a condensed version of the digestion procedure for mercury using the plastic digestion tubes from Environmental Express. The procedure is based on EPA Methods 245.1 and 7470. EPA Method 245.1 is applicable for aqueous samples and TCLP extracts. The procedure for hair, soils, oils, and sediments are based on EPA Method 7471. Only sample preparation steps are outlined below:

Oils, Hair, Soils, and Sediments:

- Add 30 mL of each standard solution or appropriate amount of standard spiking solution to give desired concentration when diluted to 30 mL to environmental express 100 mL digestion vessel. The standards should be made in 3% HNO_3.
- Weigh 0.60 ± 0.05 g of homogenized sample into a tube.
- Add 30 mL of 3% HNO_3 solution
- To each tube add 0.5 mL of concentrated HNO_3 and 2.0 mL of concentrated HCl
- Lay cap on tube and digest at 95°C for 10 minutes.
- Add 3 mL of 5% $KmnO_4$ and let stand for 15 minutes. If sample does not maintain purple or brown color, add an additional 3 mL of $KMnO_4$ solutions to all samples, blanks and standards. If the sample still does not maintain color, discard set and dilute the sample prior to digestion.
- Heat samples at 95°C for 30 minutes.
- Let samples cool to room temperature and add 3.0 mL of 12% $NaCl/NH_2OH$ solution.
- Cap tubes and shake. If color does not dissipate, incrementally add 0.5 mL of 12% $NaCl/NH_2OH$ solution until color is gone.
- Analyze using the Varian 240FS/VGA77

Appendix B Continued

Table B-1. Analytical Parameters for Varian 240FS/VGAA77 CVAAS.

Parameters (Varian 240FS)	
Wavelength (nm)	253.7
Slit Width (nm)	0.5
Lamp Current	4
Integration time (s)	3
Vapor Generator (VGA 77)	
Acid uptake tube (mL/min)	1
Reductant uptake tube (mL/min)	1
Sample uptake tube (mL/min)	8
Argon* or Nitrogen Gas	99.99% pure
Permissible pressure range***	43-57 psi
Reagents	**Usage**
5% Hydrochloric Acid, (from concentrated)	Acid Line, Reagent Water*, Preservation*
20% (w/v) Stannous Chloride	Reductant Line
5% Nitric Acid, concentrated**	Reagent water, preservation

Notes:
* - used in this study
** - suggested (Varian, 1985)
*** - recommended pressure is 50 psi

Appendix C: SOP for CVAFS and Analytical Parameters

CVAFS MERCURY ANALYSIS

STANDARD OPERATING PROCEDURE (SOP)

Water:

- Pour 100 mL aliquot of preserved sample into a 125 mL fluropolymer container.
- Add BrCl was not added as preservative add accordingly
- Clear water & filtered samples - add 0.5mL of BrCl
- Brown water and turbid samples- add 1.0 mL BrCl
- If yellow color disappears because of consumption of organic matter or sulfides add more BrCl until permanent (12 h) yellow color is obtained
- Digest at room temperature for 2 hours in UV cabinet
- Please see Method 1631 or equipment guidelines for reduction and purging preparation procedures
- Analyze following FDEP Method 1631

Tissue, Sludge, Sediment, and Soil:

- Sediment and soil samples should be sieved through ASTM certified sieves
- Digestion by hot re-fluxing HNO_3/H2SO_4 followed by BrCl oxidation will be conducted for biota, wood, paper, tissue, municipal sludge, other primarily organic matrices (excluding coal)
- Weigh the required amount into a digestion vessel

Table C-1. Mass of Sample Required for Analytical Testing for CVAFS Analysis.

Matrix	Required Mass
Biota	0.2-0.4 g
tissue (e.g. fish), plant material, or sludge	0.5-1.5 g
Wood, paper, and CRMs	0.2-0.4 g

- Under fume hood, add 8.0 mL concentrated HCl and swirl

Appendix C Continued

- Add 2.0 mL HNO_3 and cap the vessel.
- Allow to digest at room temperature for 4 hours or overnight

Table C-2. Method Parameters for Tekran Model 2600 CVAFS.

Tekran Model 2600 Method Parameters							
#	Start	Cmd	Command	Value	Duration	End Time	Note
0	4	12	MFC	100 ml/min	600	604	MFC: 100 ml
1	4	11	Pump	20%	600	604	Pump: 20%
2	4	8	V4: WashPmp	ON	600	604	Wash Pump ON
3	5	5	V1:Vent	ON	190	195	V1: Vent A
4	7	21	A/S Up	5Spd	0	7	A/S Up
5	8	22	A/S Move	Sample Tube	2	10	A/S Move to
6	9	24	A/S Down	5Spd	0	9	A/S Down
7	125	6	V2:Load-A	ON	60	185	V2: Load ON
8	145	21	A/S Up	5Spd	0	145	A/S Up
9	146	22	A/S Move	ON	3	149	A/S Move
10	147	24	A/S Down	5Spd	4	151	A/S Down
11	200	1	Heater-A	85%	30	230	Heater-A: 85%
12	205	21	A/S Up	5Spd	2	207	A/S Up
13	206	22	A/S Move	Wash Stn	3	209	A/S Move
14	20	24	A/S Down	5Spd	4	211	A/S Down
15	7230	3	Fan-A	ON	35	265	Fan-A ON
16	265	1	Heater-A	0%	80	345	Heater-A: 0%
17	265	2	Heater-B	100%	30	295	Heater-B: 100%
18	275	14	AD24 Start	100%	50	325	AD24 Start
19	340	4	Fan-B	ON	40	380	Fan-B ON
20	355	20	Done	Done	0	355	Done

Appendix D: Analytical Parameters for Bruker D4 Endeavor XRD

Table D-1. Analytical Parameters for Bruker D4 Endeavor XRD Scans.

Operator	Operator Setting Value
Raw Data Origin	BRUKER-binary V3 (.RAW)
Scan Axis	Gonio
Start Position [°2Th.]	2.0000
End Position [°2Th.]	120.0000
Step Size [°2Th.]	0.0250
Scan Step Time [s]	2.0003
Scan Type	CONTINUOUS
Offset [°2Th.]	0.0000
Divergence Slit Type	Fixed
Divergence Slit Size [°]	0.2000
Specimen Length [mm]	10.00
Receiving Slit Size [mm]	0.1000
Measurement Temperature [°C]	25.00
Anode Material	Cu
Generator Settings	40 kV, 40 mA
Diffractometer Type	Unknown
Goniometer Radius [mm]	200.50
Dist. Focus-Diverg. Slit [mm]	91.00
Incident Beam Monochromator	No
Spinning	No

Appendix E: Standards Preparation Procedure

All standards were made on a weight basis in 100 mL PTFE (teflon) bottles and diluted with DI water. The minimum concentration that can be analyzed was 0.5 ppt and the maximum 250 ppt.

Table E-1 Standards Preparation Procedures for CVAAS Analysis.

Concentration (ppt)	1 ppb Hg Stock Required (uL)	DI required (mL)
0.5	50	100
2	200	99.8
3	300	99.7
5	500	99.5
10	1000	99
15	1500	98.5
20	2000	98
30	3000	97
50	5000	95
100	10 000	90
200	20 000	80
250	25 000	75

**Note: Samples should be diluted with DI only.*

Formula:

$$C_{stock} * V_{stock} = C_{desired} * V_{flask}$$

Ex. 1: 0.5 ppt Hg desired

$1\,000 \text{ ppt} * V_{stock} \text{ mL} = 0.5 \text{ ppt} * 100 \text{ mL}$

$V_{stock} \text{ mL} = 50/1\,000 = 0.05\text{mL}$

$V_{stock} \text{ uL} = 0.05 \text{ mL} * 1000 \text{ uL/mL}$

$V_{stock} = 50 \text{ uL}$

therefore, 50 uL of 1 ppb Hg working stock is required.

** 1 ppb = 1 000 ppt**

Appendix F: Cleaning Procedures

Containers used to store the reagents are cleaned thoroughly with solutions of 5% Aqua Regia and distilled water before use. All containers are rinsed twice with this acid solution, followed by rinsing with de-ionized water at least six times. All beakers, measuring cylinders, volumetric flasks, glass pipettes and plastic pipette tips (Eppendorf) are also subject to the same cleaning procedure before use.

Narrow mouth 60 and 125 mL Teflon (FEP) bottles with leak proof Tefzel caps are used to digest the preserved samples for digestion. The bottles are cleaned with 5% Aqua Regia solution to the brim, capped, and stored under the UV cabinet for at least 24 hours prior to use. The bottles are emptied and rinsed thoroughly with distilled water, (at least six times) before use. The Tefzel caps are also treated with the same degree of cleaning.

Appendix G: Fish Data Results

Table G-1. 2008 Hillsborough River, Florida Total Fish Mercury Levels Extended

Large Mouth Bass *(Micropterus salmoides)*						Red Sunfish (Red Drum)					
#	Age	THg (mg/kg)	Length (mm)	*Fish Body Condition	Weight (g)	#	Age	THg	Length (mm)	*Fish Body Condition	Weight (g)
1	2	0.27	249	1.19	184	31	--	0.20	144	1.07	32
2	3	0.29	295	1.20	307	32	--	0.04	143	1.20	35
3	3	0.28	309	1.20	353	33	--	0.06	126	1.50	30
4	5	0.35	323	1.18	398	34	--	0.13	130	1.50	33
5	6	0.39	356	1.28	577	35	--	0.02	180	1.47	86
6	4	0.22	333	1.24	459	36	--	0.03	175	1.40	75
7	4	0.42	337	1.33	509	37	--	0.21	205	1.74	150
8	3	0.62	296	1.27	330	38	--	0.09	243	1.83	262
9	3	0.55	291	1.34	331	Bluefish *(Pomatomus saltatrix)*					
10	3	0.65	310	1.15	342	#	Age	THg	Length (mm)	*Fish Body Condition	Weight (g)
11	3	0.62	337	1.12	428	21	--	0.15	168	1.24	59
12	3	0.67	315	1.23	386	22	--	0.19	190	1.90	130
13	5	0.70	358	1.35	620	23	--	0.13	191	1.71	119
14	3	0.75	313	1.09	335	24	--	0.21	209	2.00	183
15	4	0.65	358	1.33	610	25	--	0.13	163	1.59	69
16	4	0.54	372	1.35	697	26	--	0.15	195	1.42	105
17	4	0.53	410	1.28	879	27	--	0.24	170	1.71	84
18	6	0.92	411	1.28	886	28	--	0.15	188	1.58	105
19	6	0.88	469	1.41	1452.5	29	--	0.20	185	1.64	104
20	6	0.97	495	1.52	1841	30	--	0.12	179	1.66	95

Appendix G Continued

Table G-2. 2003 Historical Fish Mercury Data for Hillsborough River, Florida. (Collected and analyzed by FFWCC and FDEP. Data Results provided by Mr. Doug Adams and Ted Lange)

2003 Historical Fish Data Results							
LABID	Date Sampled	Species	TL	TW	AGE	SEX	THg (DEP)
303047	3/26/2003	LMB	257	234	1	M	0.650
303048	3/26/2003	LMB	272	305	2	M	0.580
303049	3/26/2003	LMB	289	347	2	M	0.360
303050	3/26/2003	LMB	287	303	2	M	0.540
303051	3/26/2003	LMB	277	304	2	M	0.390
303052	3/26/2003	LMB	316	415	2	M	0.430
303053	3/26/2003	LMB	332	528	2	M	0.360
303054	3/26/2003	LMB	292	397	2	M	0.470
303055	3/26/2003	LMB	338	626	3	F	0.520
303056	3/26/2003	LMB	327	501	3	M	0.590
303057	3/26/2003	LMB	334	543	4	M	0.500
303058	3/26/2003	LMB	353	663	3	M	0.520
303059	3/26/2003	LMB	376	771	6	M	0.690
303060	3/26/2003	LMB	364	668	6	M	0.680
303061	3/26/2003	LMB	402	949	5	F	0.700
303062	3/26/2003	LMB	388	904	6	M	0.650
303063	3/26/2003	LMB	396	838	8	M	0.740
303064	3/26/2003	LMB	458	1356	4	F	0.610
303065	3/26/2003	LMB	428	1272	5	F	0.530
303066	3/26/2003	LMB	487	1661	4	F	0.450

Appendix G Continued

Table G-3. 2004 Historical Fish Mercury Data for Hillsborough River, Florida. (Collected and analyzed by FFWCC and FDEP. Data Results provided by Mr. Doug Adams and Ted Lange)

2004 Historical Fish Data Results							
LABID	Date Sampled	Species	TL	TW	AGE	SEX	THg (DEP)
304084	3/24/2004	LMB	320	444	2	M	0.650
304085	3/24/2004	LMB	305	388	3	M	0.770
304086	3/24/2004	LMB	309	421	2	M	0.890
304087	3/24/2004	LMB	263	240	2	M	0.910
304088	3/24/2004	LMB	299	357	2	M	0.810
304089	3/24/2004	LMB	262	273	2	M	0.890
304090	3/24/2004	LMB	316	373	2	F	0.750
304091	3/24/2004	LMB	285	298	2	M	1.100
304092	3/24/2004	LMB	243	179	2	F	0.800
304093	3/24/2004	LMB	280	299	2	F	0.900
304094	3/24/2004	LMB	257	199	2	M	0.850
304095	3/24/2004	LMB	319	422	3	M	0.760
304096	3/24/2004	LMB	324	435	2	M	0.660
304097	3/24/2004	LMB	247	189	2	F	0.920
304098	3/24/2004	LMB	237	166	2	M	0.960
304099	3/24/2004	LMB	351	587	2	M	0.920
304100	3/24/2004	LMB	391	849	7	M	1.100
304101	3/24/2004	LMB	374	805	7	M	1.100
304102	3/24/2004	LMB	432	1205	7	M	1.300
304103	3/24/2004	LMB	489	1836	7	F	1.200

Appendix G Continued

Table G-4. 2005 Historical Fish Mercury Data for Hillsborough River, Florida. (Collected and analyzed by FFWCC and FDEP. Data Results provided by Mr. Doug Adams and Ted Lange).

2005 Historical Fish Data Results							
LABID	Date Sampled	Species	TL	TW	AGE	SEX	THg (DEP)
105127	1/27/2005	LMB	473	1745	4	F	0.850
105128	1/27/2005	LMB	295	348	3	M	0.700
105129	1/27/2005	LMB	351	591	3	F	0.740
105130	1/27/2005	LMB	381	798	4	M	0.990
105131	1/27/2005	LMB	350	603	3	M	0.870
105132	1/27/2005	LMB	432	1412	4	M	0.780
105133	1/27/2005	LMB	406	1240	4	M	0.820
105134	1/27/2005	LMB	408	1208	3	F	0.740
105135	1/27/2005	LMB	367	884	4	M	0.810
105136	1/27/2005	LMB	366	754	4	M	0.960
105137	1/27/2005	LMB	405	1046	3	F	0.740
105138	1/27/2005	LMB	335	530	3	M	0.820
105139	1/27/2005	LMB	331	558	3	M	0.810
105140	1/27/2005	LMB	323	544	3	M	0.520
105141	1/27/2005	LMB	357	723	3	M	0.890
105142	1/27/2005	LMB	375	737	3	M	0.880
105143	1/27/2005	LMB	293	337	3	F	0.610
105144	1/27/2005	LMB	287	309	3	M	0.850
105145	1/27/2005	LMB	314	397	3	F	0.720
105146	1/27/2005	LMB	259	187	2	F	0.550

Table G-5. 2006 Historical Fish Mercury Data for Hillsborough River, Florida. (Collected and analyzed by FFWCC and FDEP. Results Provided by D. Adams)

2006 Historical Fish Data Results

LABID	Date Sampled	Species	TL	TW	AGE	SEX	THg (DEP)	LABID	Species	TL	TW	AGE	SEX	THg (DEP)
306008	3/15/2006	LMB	315	401	4	M	0.990	306055	RBSU	168	73	--	--	0.180
306009	3/15/2006	LMB	322	438	4	M	0.930	306056	RBSU	162	72	--	--	0.160
306010	3/15/2006	LMB	329	527	4	M	0.900	306057	RBSU	165	79	--	--	0.200
306011	3/15/2006	LMB	321	530	4	M	1.100	306058	RBSU	171	93	--	--	0.320
306012	3/15/2006	LMB	375	729	4	F	0.770	306059	RBSU	176	94	--	--	0.270
306013	3/15/2006	LMB	357	691	5	M	0.970	306060	RBSU	182	105	--	--	0.180
306014	3/15/2006	LMB	272	271	3	F	0.690	306061	RBSU	198	147	--	--	0.190
306015	3/15/2006	LMB	343	612	4	M	1.200	306062	SPSU	145	71	--	--	0.700
306016	3/15/2006	LMB	346	552	4	M	0.940	306063	SPSU	148	73	--	--	0.360
306017	3/15/2006	LMB	327	450	4	F	0.830	306064	SPSU	152	86	--	--	0.410
306018	3/15/2006	LMB	337	524	4	F	0.850	306065	SPSU	153	79	--	--	0.670
306019	3/15/2006	LMB	251	230	3	F	0.810	306066	SPSU	152	91	--	--	0.170
306020	3/15/2006	LMB	328	480	4	M	0.920	306067	SPSU	155	94	--	--	0.230
306021	3/15/2006	LMB	221	135	2	M	0.640	306068	SPSU	161	102	--	--	0.350
306022	3/15/2006	LMB	291	327	3	M	0.790	306069	SPSU	170	108	--	--	0.550
306023	3/15/2006	LMB	281	257	3	M	0.890	306070	SPSU	163	97	--	--	0.410
306024	3/15/2006	LMB	406	1062	4	F	0.870	306071	SPSU	164	100	--	--	0.380
306025	3/15/2006	LMB	395	848	4	F	0.840	306072	SPSU	167	125	--	--	0.480
306026	3/15/2006	LMB	388	777	4	F	0.700	306073	SPSU	168	122	--	--	0.290
306027	3/15/2006	LMB	411	1156	4	F	0.980	306074	WAR	172	128	--	--	0.410
306038	3/15/2006	RESU	196	154	--	--	0.230	306075	WAR	166	111	--	--	0.410
306039	3/15/2006	RESU	189	127	--	--	0.370	306076	WAR	165	104	--	--	0.370
306040	3/15/2006	RESU	193	159	--	--	0.270	306077	WAR	166	116	--	--	0.520
306041	3/15/2006	RESU	225	246	--	--	0.250	306078	WAR	178	142	--	--	0.410
306042	3/15/2006	RESU	222	239	--	--	0.500	306079	WAR	176	147	--	--	0.630
306043	3/15/2006	RESU	212	223	--	--	0.390	306080	WAR	178	149	--	--	0.510
306044	3/15/2006	RESU	215	214	--	--	0.320	306081	WAR	180	147	--	--	0.600
306045	3/15/2006	RESU	231	295	--	--	0.430	306082	WAR	200	205	--	--	0.540
306046	3/15/2006	RESU	273	525	--	--	0.430	306083	WAR	175	146	--	--	0.500
306047	3/15/2006	RESU	173	99	--	--	0.240	306084	WAR	205	243	--	--	0.700
306048	3/15/2006	RESU	182	120	--	--	0.270	306085	WAR	211	240	--	--	0.570
306049	3/15/2006	RESU	161	83	--	--	0.130	306086	BLUE	156	60	--	--	0.370
306050	3/15/2006	RBSU	152	55	--	--	0.120	306087	BLUE	181	114	--	--	0.240
306051	3/15/2006	RBSU	152	65	--	--	0.110	306088	BLUE	192	140	--	--	0.440
306052	3/15/2006	RBSU	150	57	--	--	0.110	306089	BLUE	187	125	--	--	0.200
306053	3/15/2006	RBSU	146	58	--	--	0.180	306090	BLUE	200	163	--	--	0.290
306054	3/15/2006	RBSU	144	49	--	--	0.140	306091	BLUE	206	209	--	--	0.500

Appendix G Continued

Table G-6. Historical Fish Mercury Data for Hillsborough River, Florida. (Collected and analyzed by FFWCC and FDEP. Data Results provided by Mr. Doug Adams and Ted Lange)

2007 Historical Data Results							
LABID	Date Sampled	Species	TL	TW	AGE	SEX	THg (DEP)
507001	5/2/2007	LMB	242	176	3	M	0.5
507002	5/2/2007	LMB	283	269	3	F	0.73
507003	5/2/2007	LMB	308	378	4	M	0.88
507004	5/2/2007	LMB	297	329	3	F	0.75
507005	5/2/2007	LMB	316	372	5	M	0.93
507006	5/2/2007	LMB	304	346	4	M	0.95
507007	5/2/2007	LMB	305	365	3	F	0.76
507008	5/2/2007	LMB	301	349	3	F	0.75
507009	5/2/2007	LMB	317	390	3	F	0.81
507010	5/2/2007	LMB	314	412	5	M	1.2
507011	5/2/2007	LMB	312	362	3	F	0.93
507012	5/2/2007	LMB	358	567	5	M	1.2
507013	5/2/2007	LMB	328	450	5	M	0.86
507014	5/2/2007	LMB	389	919	5	F	1
507015	5/2/2007	LMB	432	1080	5	F	1.2
507016	5/2/2007	LMB	297	330	3	M	0.64
507017	5/2/2007	LMB	224	141	2	F	0.7
507018	5/2/2007	LMB	389	931	5	F	0.64
507019	5/2/2007	LMB	438	1195	5	F	1.1
507020	5/2/2007	LMB	474	1519	6	F	1.4

Appendix G Continued

Table G-7. 2009 Historical Fish Mercury Data for Bolivia (Analyzed in Bolivia)

2009 Bolivia Fish Results						
LABID	Sample ID	Length (mm)	Weight (g)	*Fish Body Condition (K)	Sex (M/F)	fTHg wet weight (mg/kg)
Trucha *(Salmo gaidneri, n = 10)*						
26-1	1 TG	365	834	1.7	M	0.10
26-2	2 TG	355	731	1.6	F	0.04
26-3	3TG	375	946	1.8	M	0.09
26-4	4TG	334	654	1.8	F	0.05
26-5	5TG	346	680	1.6	F	0.04
26-6	6 TP	225	210	1.8	M	0.06
26-7	7 TP	232	203	1.6	M	0.07
26-8	8 TP	246	218	1.5	F	0.03
26-9	9 TP	250	247	1.6	M	0.04
26-10	10 TP	260	238	1.4	F	0.04
	Average	*299*	*496*	1.9	*M(5); F(5)*	
Pejerrey *(Basilichthyes bonariensi, n = 10)*						
26-11	1 PG	382	418	0.7	M	0.43
26-12	2 PG	356	295	0.7	F	0.63
26-13	3 PG	297	209	0.8	M	0.27
26-14	4 PG	362	423	0.9	F	0.23
26-15	5 PG	415	522	0.7	M	0.76
26-16	6 PP	300	219	0.8	F	0.58
26-17	7 PP	313	211	0.7	M	0.22
26-18	8 PP	335	283	0.8	M	0.25
26-19	9 PP	305	185	0.7	M	0.23
26-20	10 PP	292	216	0.9	M	0.20
	Average	*336*	*298*	*0.8*	*M(7); F(3)*	*0.38*

Appendix H: Field Notes and Water Quality Data

Table H-1. Guyana (Mahdia) Water Quality, Total Mercury Concentrations and Field Notes

	Sample Name	[THg] (µg/kg)	Temperature (°C)	Conductivity (mS/cm)	DO (mg/L)	DO Sat (%)	pH	TDS (g/L)	Turbidity (NTU)	Salinity (ppt)	ORP	UTM Coordinates		Elevation (m)	Notes
Mine 1	11	331	27.78	0.058	6.59	86	4.28	0	47.7	0.03	99				Tailings - from hydraulic pump motor
	12	127	27.78	0.058	6.59	86	4.28	0	47.7	0.03	99	N05.38023	W059.13596	90	Near sluice box
	12B	143	27.78	0.058	6.59	86	4.28	0	47.7	0.03	99				
	12C	81	27.78	0.058	6.59	86	4.28	0	47.7	0.03	99				
	12D	134	27.78	0.058	6.59	86	4.28	0	47.7	0.03	99				
	Dio's Smp	114	27.78	0.058	6.59	86	4.28	0	47.7	0.03	99				At mine entrance
Mine 2	Top Soil	253													Top soil of pit; close to land dredging
	Top Soil B	111													Topsoil of pit opposite Top soil A; close to land dredging
	14	29	29.8	0.106	7.33	90.2	3.85	0	14.5	0.005	139	N05.29134	W059.13186	83	recirculation water
	14B	150	29.06	0.104	7.25	93.4	4.07	0	12.3	0.5	142	N05.29117	W059.13206	79	
	15	222	28.49	0.288	3.87	3.51	3.51	0.2	178	0.14	290	N05.28982	W059.13229		By tailings
	16	49	29.62	0.06	5.95	73.7	4.25	0	14.6	0.03	113	N05.29007	W059.13061	80	Bottom of pit water going into pit from higher ground
	17	66	31.44	0.025	7.05	94.2	4.99	0	34	0.04	109	N05.26475	W059.13805	81	Mine 2.
Mine 3	18	409	34.05	0.03	7.31	84.9	5.66	0	116	0.03	75	N05.26437	W059.13745	83	Tailings
	19	443													By hydraulic pump motor
Mine 4	Tailings	601	31.07	0.024	7.21	85.2	5.45	0	104	0.03	69	N05.26443	W059.13791	82	Tailings
	20	508	32.18	0.018	6.73	91.3	5.5	0	80.2	0.02	63	N05.25819	W059.13311	88	Area where two mines meet
	21	471	30.62	0.02	7.11	96.3	5.59	0	95	0.02	52	N05.25814	W059.13308	73	By hydraulic pump motor and adjacent to cooking area
Mine 5	22	72	--	--	--	--	--	--	--	--	--	N05.27391	W059.13372	85	By hydraulic pump motor
	22b	127	--	--	--	--	--	--	--	--	--				Directly from sluice box

Appendix H Continued

Table H-2. Guyana (Iwokrama) Water Quality, Total Mercury Concentrations and Field Notes

Iwokrama														
#	[THg] (μg/kg)	Temp (°C)	Cond. (mS/cm)	DO (mg/L)	DO Sat (%)	pH	TDS (g/L)	Turbidity (NTU)	Salinity (ppt)	ORP	UTM Coordinates		Elev. (m)	Notes
1	53	26.63	0.022	6.91	81	5.42	18.5	19.1	0.02	104	N04.78912	W058.87139	56	Taken near brush
2	225	26.1	0.024	6.85	83	5.6	0	13	0.02	93	N04.73200	W058.85048	55	Water is visibly darker in this area; reported to have been an old mining camp area
3	298	27.4	0.022	7.62	87	5.7	0	32.2	0.02	89	N04.76645	W058.88126	42	Close to mining community. Water is bubbly & frothy.
4	120	27.1	0.022	10	98.4	5.95	0	28.8	0.02	73	N04.74021	W058.92834	56	Abandoned mining area across from sampling location;
5		27.99	0.014	7.86	99.7	6.4		13.2	0.02		N04.67193	W058.68386		Iwokrama Field Station and housing

Appendix I: XRD Minerological Profiles

Table I-1. Hillsborough River XRD Mineralogical Profile.

Sample ID	Sample Name	SemiQuant [%]	Ref. Code	Compound Name	Chemical Formula
HR1	Sargent Park	42	01-075-1072	Berlinite	$AlPO_4$
		58	01-081-0066	Quartz	SiO_2
HR2	River Blvd	100	01-086-1562	Quartz, low	SiO_2
HR3	56th Street	42	01-085-0930	Quartz	SiO_2
		6	01-075-0589	Silicon	Si
		52	01-089-4201	Berlinite	$AlPO_4$
HR4	HR State Park	40	00-033-1161	Silica	SiO_2
		58	01-076-0232	Berlinite	$AlPO_4$
		1	01-089-4781	Tin Selenide	SnSe
HR5	Rowlett Park*	100	01-083-3468	Quartz, syn	SiO_2
HR6	Rivercrest*	65	01-085-0930	Quartz, syn	SiO_2
		35	01-076-0226	Berlinite	$AlPO_4$
HR7	Lettuce Lake	41	00-005-0490	Quartz, low	$Si\ O_2$
		45	01-087-0086	Berlinite, syn	$Al\ PO_4$
		15	01-087-0580	PAFH	$K\ (AsF_5(OH))$
HR8	Rotary Park	50	03-065-0466	Quartz low	SiO_2
		50	01-076-0228	Berlinite, syn	$AlPO_4$
HR9	Water Works	30	00-033-1161	Silica	SiO_2
		32	00-046-1045	Quartz, syn	SiO_2
		3	01-074-0154	SPF	$Na\ P\ F_6$
		3	01-084-0855	Aluminium Arsenate	$AlAsO_4$
		32	01-075-1072	Berlinite, syn	$AlPO_4$
HR10	Curtis Hixon	35	03-065-0466	Quartz low, syn	SiO_2
		26	00-033-1161	Silica	SiO_2
		36	01-076-0227	Berlinite, syn	$AlPO_4$
		4	01-075-0449	Magnetite	Fe_3O_4
HR11	Trout Creek	59	03-065-0466	Quartz low, syn	SiO_2
		41	01-071-1041	Berlinite	$AlPO_4$

Appendix I Continued

Table I-2. Hillsborough River XRD Mineralogical Profile (2).

Sample ID	Sample Name	SemiQuant [%]	Ref. Code	Compound Name	Chemical Formula
HR12	Riverhills	40	01-085-0796	Quartz	SiO_2
		27	00-046-1045	Quartz, syn	SiO_2
		2	01-081-1824	Silver Telluride	Ag_2Te
		1	03-065-0928	Aluminium Uranium	Al_3,U SiO_2
		31	01-085-0695	Silicon Oxide	
HR13	Riverfront	15	01-077-2064	Sodium Chloride	Na Cl
		37	01-085-0865	Quartz	Si O_2
		5	01-088-1431	PHC	$K_5H(CN_2)_3$
		25	00-036-0432	Gypsum	$Ca(SO_4)_2H_2$ O
		2	01-087-0095	MCB	Hg, Cr, Ba_2
			01-087-0095	Copper Oxide	Cu $O_{4.267}$
		4	03-065-3257	Platinum Zinc	Pt_3 Zn
		11	00-046-1045	Quartz, syn	Si O_2
HR14	Lowry Park	79	01-074-1784	Kaolinite	$Al_2Si_2O_5(OH)_4$
		11	00-046-1045	Quartz, syn	Si O_2
		10	00-033-1161	Silica	Si O_2
HR15	Bullard Parkway	29	00-005-0490	Quartz, low	Si O_2
		36	01-079-1095	Aluminum Phosphate	$Al(PO_4)$
		29	01-076-0225	Berlinite, syn	$AlPO_4$
		5	01-086-0365	Lead Arsenate	$Pb(As_2O_6)$
HR16	Epps Park	64	01-085-0798	Quartz	Si O2
		13	01-075-0278	Aluminum Oxide	Al O
		19	01-076-0314	Aluminum Arsenate	Al As O4
		4	01-089-4088	Manganese Sulfide	Mn S

*Unresolved peaks exist in lower sections of scan

PAFH - Potassium Arsenic Fluoride Hydroxide

PHC - Potassium Hydrogen Cyanamide

SPF - Sodium Phosphorus Fluoride

MCB - Mercury Chromium Barium

Appendix I Continued

Table I-3. Hillsborough Guyana (Iwokrama) River XRD Mineralogical Profile.

Sample ID	Sample Name	SemiQuant [%]	Ref. Code	Compound Name	Chemical Formula
IWO1	Iwokrama 1	---			
IWO2	Iwokrama 2	--	01-083-2187	Quartz	$Si\ O_2$
			01-087-0082	Berlinite, syn	$Al\ (PO_4)$
			01-072-1064	Aluminium Phosphate	$AlPO_4$
			01-089-1362	Gallium Arsenic Oxide	$Ga(AsO_4)$
			01-070-1797	Mercury Hydrogen	$Hg_2\ (H_2PO_4)_2$
			01-075-1700	Phosphate Threadgoldite	$Al\ (UO_2)_2(PO_4)_2(OH)\ (H_2O)_8$
IWO3	Iwokrama 3	--	01-083-2187	Quartz	SiO_2
		--	01-072-1064	Aluminum Phosphate	$AlPO_4$
		--	01-071-1041	Berlinite	$AlPO_4$
		--	01-083-2476	Germanium Oxide	GeO_2
		--	01-080-1255	Iron Arsenic Carbonyl	$(Fe_2(CO)_8As)_2(\ Fe_2(CO)_6)$
			01-082-2122	Copper Bromide	Cu Br
IWO4	Iwokrama 4	--	01-085-0796	Quartz	SiO_2
		--	01-074-0154	SPF*	$Na\ P\ F_6$
		--	03-065-3271	Aluminum Neptunium	$Al_3\ Np$
		--	01-071-1041	Berlinite	$Al\ PO_4$
		--	01-082-2455	Brucite, syn	$Mg\ (OH)_2$
		--	01-078-0283	MGT	$Hg\ Ga_2\ Te_4$

*SPF - Sodium Phosphorus Fluoride MGT - Mercury Gallium Telluride

Appendix I Continued

Table I-4. Guyana (Konashen) River XRD Mineralogical Profile.

Sample Area	Sample Name	SemiQuant [%]	Ref. Code	Compound Name	Chemical Formula
Essequibo	ER-11	25	01-085-0794	Quartz	SiO_2
		75	01-080-0886	Kaolinite	$Al_2(Si_2O_5)(OH)_4$
	ER-12	--	--	------------------------------	----------------------
	ER-16	69	01-077-1060	Silicon Oxide	SiO_2
		1	01-086-0666	Potassium Manganese	$K_{O.27}MnO_2(H_2O)$
		1	01-082-2122	Copper Bromide	Cu Br
		28	01-072-1064	Aluminum Phosphate	$AlPO_4$
		1	03-065-3492	Aluminum Chromium	$AlCr_2C$
		1	03-065-0682	Zinc Oxide	ZnO
Acari Creek	AM-01	32	00-005-0490	Quartz, low	SiO_2
		6	00-052-0922	ACS	$AlCrCu_2$
		1	03-065-0022	Gold Indium Lutetium	Au_2 In Lu
		6	01-087-0628	Osbornite	TiN
		50	01-087-0084	Berlinite, syn	$Al(PO_4)$
		5	01-089-0437	MMS	$(Hg_{0.67}Mn_{0.33})S$
	AM-02	23	00-005-0490	Quartz, low	SiO_2
		29	01-087-0082	Berlinite, syn	$Al(PO_4)$
		25	01-085-1123	Mercury Peroxide	HgO_2
		23	00-033-1161	Silica	SiO_2

Appendix I Continued

Table I-5. Guyana (Konashen) XRD Mineralogical Profile (2).

Sample ID	Sample Name	SemiQuant [%]	Ref. Code	Compound Name	Chemical Formula
Acari Creek	AM-03	15	00-033-1161	Silica	SiO_2
		16	00-046-1045	Quartz, syn	SiO_2
		16	01-076-0225	Berlinite, syn	$AlPO_4$
		53	01-077-1060	Silicon Oxide	SiO_2
	AM-04	--	--	--	--
Kamoa River	KR-02	25	00-046-1045	Quartz, syn	SiO_2
		16	01-086-1664	Lanthanum Cobalt Oxide	$LaCoO_3$
		27	01-076-0228	Berlinite, syn	$AlPO_4$
		2	01-077-2367	Magnesium Iron Oxide	$(MgO)_{0.593}(FeO)_{0.407}$
		27	01-086-1560	Quartz low	SiO_2
		4	01-073-1593	Metacinnabar	HgS
	KR-04				
	KR-05	6	01-089-0437	MMS	$(Hg_{0.67}Mn_{0.33})S$
		39	01-071-0910	Beryllium Fluoride	BeF_2
		24	01-071-1041	Berlinite	$AlPO_4$
		2	01-077-2368	Magnesium Iron Oxide	$(MgO)_{0.432}(FeO)_{0.568}$
		29	00-046-1045	Quartz, syn	SiO_2
	KR-06	61	01-077-1060	Silicon Oxide	$Si\ O_2$
		19	03-065-0466	Quartz low, syn	$Si\ O_2$
		15	01-084-0854	Aluminum Phosphate	$Al\ P\ O_4$
		1	01-077-0191	Zinc Oxide	Zn O
		1	03-065-3844	Copper Tin Phosphide	$Cu_4\ Sn\ P_{10}$
		4	01-089-0437	MMS	$(Hg_{0.67}\ Mn_{0.33})\ S$
	KR-07				
	KR-12				
Sipu River	SR-06	47	01-077-1060	Silicon Oxide	SiO_2
		13	00-046-1045	Quartz, syn	SiO_2
		10	01-076-0314	Aluminum Arsenate	$AlAsO_4$
		16	01-071-1041	Berlinite	Al P O4
		14	01-085-1123	Mercury Peroxide	Hg O2

*MMS - Mercury Manganese Sulfide ACS- Aluminum Chromium Copper

Appendix I Continued

Table I-6. Guyana (Mahdia) XRD Mineralogical Profile.

Sample ID	Sample Name	SemiQuant [%]	Ref. Code	Compound Name	Chemical Formula
Mine 1	11, pump	3	01-086-0666	Potassium Manganese	$K_{0.27}MnO_2(H_2O)$
		29	01-087-0082	Berlinite, syn	$Al(PO_4)$
		33	00-046-1045	Quartz, syn	SiO_2
		34	01-085-1123	Mercury Peroxide	HgO_2
	12, sluice		00-003-0249	Goethite, syn	$Fe^{+3}O(OH)$
	12B, LHS				
	12C, RHS				
	12D, camp				
	Diosmp				
	Topsoil		01-076-0227	Berlinite, syn	$AlPO_4$
			01-084-0853	Aluminum Phosphate	$AlPO_4$
			03-065-3020	Indium Sodium	In Na
			01-075-1522	Quartz	$Si\ O_2$
			01-089-6538	Kaolinite	$Al_2(Si_2O_5)(OH)_4$
			01-089-5895	Copper Oxide	Cu O
			01-070-1797	MHP*	$Hg_2\ (H_2PO_4)_2$
Mine 2	14, pit		00-011-0252	high quartz	SiO_2
			01-083-2475	Germanium Oxide	GeO_2
	14B, tailing		01-076-0226	Berlinite, syn	$AlPO_4$
			01-083-2476	Germanium Oxide	GeO_2
			01-085-1123	Mercury Peroxide	$Hg\ O_2$
	15, tailings				
	16, sluice				
	17, tailings				
Mine 3	18, tailings				
	19, pump				
Mine 4	20				
	21, pump				
	Tailings				
Mine 5	22, pump		00-013-0375	Halloysite	$Al_2Si_2O_5(OH)_4$
			00-001-0527	Kaolinite	$Al_2Si_2O_5(OH)_4$
			00-032-0661	Mercury Selenate Hydrate	$HgSeO_4 \cdot H_2O$
Mine 6	22b, sluice		01-084-0854	Aluminum Phosphate	Al P O4
			01-071-1610	Nickel Chromium	Ni Cr F6
			03-065-2573	Fluoride	As2 Fe
				Arsenic Iron	

*MHP- Mercury Hydrogen Phosphate

Appendix I Continued

Table I-7. Bolivia (Lago Titicaca, Rivers, and Streams) XRD Mineralogical Profile.

Sample ID	Sample Name	Ref. Code	Compound Name	Chemical Formula
B1	Tajani	00-033-1161	Silica	SiO_2
		00-031-1780	Mercury methyl mercaptide	$C_2H_6HgS_2$
B2	Escoma			
B3	Sojo Sojo	01-083-2465	Quartz, syn	SiO_2
		00-005-0143	Kaolinite	$Al_2Si_2O_5(OH)_4$
		00-002-0050	Illite	$2K_2O_3MgOFeO(Al_2O_3)_{24}\cdot(SiO_2)_{12}\cdot H_2O$
				$Na(AlSi_3O_8)$
		01-084-0982	Albite low	
B4	Aqua Caliente			
B4B	MinervaPotosí			
B6	Villa Tacata	01-083-2466	Quartz, syn	SiO_2
		00-029-0713	Goethite	$Fe^{+3}O(OH)$
		00-029-1497	Nontronite-15A	$Na_{0.3}Fe_2Si_4O_{10}$
		00-001-0665	PHI	$(OH)_2\cdot 4H_2O$
		00-033-0118	Stistaite	$KIO_3\cdot HIO_3$
		00-001-1240	Copper Tin	SbSn
		00-004-0770	Magnesium	Cu_3Sn
		00-036-1471	Potassium Bromide	Mg
				K Br
B7	Canton Humanata	00-033-1161	Silica	SiO_2
		00-011-0237	Boron Phosphate	BPO_4
		01-087-0088	Berlinite, syn	$Al(PO_4)$
		01-088-2470	MBCCO	$HgBa_2Ca_2Cu_3O_{8.16}$
B8	Lago Titicaca			
B13	Río Beni			

*PHI - Potassium Hydrogen Iodate MBCCO- Mercury Barium Calcium Copper Oxide

Appendix J: BET Surface Area Analysis

Table H-1. BET Surface Area Analysis for Hillsborough River, Tampa, FL

Sample Name/units	*Unit*	*Kemiron Standard*	*5650 56th St. Overpass*	*HS1 HR State Surface*	*RCT1 River-crest*	*TRT1 Trout Creek Park*	*RTY1 Rotary Park*	*ROW1 Rowlett Park*	*SRG1 Sargent Park*	*CRH1 Curtis Hixon Park*	*LWY1 Lowry Park Zoo Area*
Vial	G	10.529	10.523	10.53	10.523	10.523	10.298	10.298	10.523	10.298	10.526
Vial+sample	G	10.609	10.829	11.119	11.31	10.708	10.416	10.463	10.705	10.375	10.676
Vial+sample+wool	G	10.627	10.846	11.131	11.326	10.722	10.432	10.474	10.707	10.387	10.699
Sample	G	0.08	0.306	0.589	0.787	0.185	0.118	0.165	0.182	0.077	0.15
Wool	G	0.018	0.017	0.012	0.016	0.014	0.016	0.011	0.002	0.012	0.023
Outgas at 105°C	Hr	3	2	2	3	2	2	2	2	2	2
Vial+sample+wool after outgassing	G	10.608	10.844	11.13	11.321	10.722	10.429	10.473	10.709	10.386	10.694
Sample after outgassing	G	0.061	0.304	0.588	0.782	0.185	0.115	0.164	0.184	0.076	0.145
Surface area	m^2/g	33.34	0.4341	0.2622	0.1897	0.7674	0.9796	0.822	0.7917	2.822	0.1897
Correlation Factor	a.u.	0.9996	0.997419	0.997822	0.995877	0.865925	0.988688	0.758537	0.481354	0.966952	0.9958

About Author

Joniqua A'ja Howard received her Bachelor's of Science degree from Hampton University in Computer and Electrical Engineering. She then went on to obtain her Master's of Science degree in Environmental Engineering from the University of South Florida where she continued to pursue her Doctoral degree. Throughout her academic tenure she has conducted global research examining various aspects of water, sanitation, and sustainability in many remote areas of the world such as Mexico, Tanzania, Guyana, Trinidad and Tobago, and Bolivia. She has received travel grants and fellowship awards from the National Science Foundation and the University of South Florida. She was the co-founder and former president of the Engineers for a Sustainable World USF Chapter and has since been an active member. She has served as a mentor to several youth in the community, co-coordinator for a professional development organization (MSPHDS) and co-coordinator for a community based participatory research program.