# Trihalomethane Formation in Rural Household Water Filtration Systems in Haiti

by

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## Abstract

The Florida-based non-governmental organization Gift of Water, Incorporated (GWI) produces, distributes, and provides technical assistance on household water filtration systems in rural Haiti. The GWI purifier utilizes chlorine in the form of bleach as a disinfectant, a cotton filter for sediment removal, and a granulated activated carbon (GAC) filter for chemical removal. Because of the chlorination step, GWI is concerned with the possible production of trihalomethanes (THMs). THMs are disinfection by-products (DBPs) associated with potential human health effects.

During the month of January, 2001, water sources in Haiti were visited. Raw source waters were analyzed for physical parameters, and purified finished waters were collected for analysis at MIT. Results of that analysis determined that no finished water sample was above World Health Organization (WHO) guideline values for concentrations of the four individual THMs. In addition, only one finished water sample was above the WHO guideline value and USEPA standard for total THM concentration. Total THM concentration correlated with the total usage of the carbon filter, and conductivity of the water, as shown in the following equation:

$$\text{TTHM } (\mu\text{g/L}) = 0.14 \text{ (Total Usage)} + 21 \text{ (Conductivity)} - 9.6$$
$$R^2 = 0.780$$

The most important variable in TTHM concentration was determined to be total usage of the GAC filter. Reliable GAC filter replacement is thus critical to maintaining low concentrations of THMs in finished waters in Haiti. Other mitigation strategies to reduce THM production are presented herein for completeness. In addition, three critical factors that lead to GWI program success were determined: dedicated and responsible staff, planned distribution of purifiers, and purifiers as part of a larger community development initiative.

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# Chapter 1: Introduction

## 1.1 Haiti Disinfection Project

Over one billion people in the world lack access to safe water, and over three billion lack access to adequate sanitation [WHO, 2001]. In Haiti, only 45 percent of the rural population has access to safe water, only 16 percent of the rural population has access to safe sanitation, and the morality rate for children under five is 129 per 1,000 live births [UNICEF, 2001].

To address this need for safe water in Haiti, MIT Master's of Engineering (M. Eng.) students teamed with the Florida-based non-governmental organization (NGO) Gift of Water, Inc. (GWI). GWI has been working in Haiti on point-of-use rural household filtration since 1995. Four related projects were developed and researched by M. Eng. students during the 2000 – 2001 academic year. The projects researched included: (1) chlorine generation in Haiti, conducted by Nadine van Zyl; (2) disinfection by-product formation and critical factors for program success, conducted by the author; (3) alternate forms of disinfection, conducted by Peter Oates; and (4) program sustainability, conducted by Farzana Mohamed.

## 1.2 Trihalomethane and Critical Factors Project

This thesis investigates trihalomethane production in the GWI purifier system. Trihalomethanes (THMs) are disinfection by-products (DBPs) formed when chlorine reacts with natural organic matter in the source water. Studies have detailed potential human health effects from lifetime exposure to low levels of THMs. GWI is concerned about THMs because their purifier system chlorinates twice: once in the raw water for biological inactivation, and then again in finished water to form the residual necessary to prevent recontamination in unclean containers.

In order to investigate THM formation, source and finished water samples were collected during a field month in Haiti in January, 2001. Source water samples were analyzed for a variety of physical parameters easily tested in Haiti. These parameters included pH, turbidity, nitrate, and temperature. Source water was then purified using a GWI purifier. The owner of the purifier was asked how often they used the purifier, the age of the carbon and cotton filter in the purifier, and whether they have had any problems with the purifier. Finished water samples were collected and analyzed at MIT using a gas chromatograph (GC). The purpose of the THM study was twofold: (1) to determine if THM concentrations were above the World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) standards; and (2) to develop an equation based on easily measured source water parameters that GWI could use to estimate THM concentration in finished waters.

An additional focus of the thesis was to observe the program “in action” and determine critical factors of program success. Thus, Chapter 2 provides a socio-political framework of Haiti and Chapter 3 an introduction to the purifier and to GWI. Chapter 4 moves to the THM focus with an introduction to chlorination and THM formation, which continues in Chapter 5 with THM toxicology. Chapter 6 combines the two foci with the field observations and data. Chapter 7 moves back to THMs with the analysis results and Chapter 8 discusses THM mitigation strategies. Chapter 9 then summarizes recommendations for both parts of the thesis.

# Chapter 2: Historical and Cultural Context

Haiti encompasses 27,750 square kilometers of the western third of the island of Hispaniola in the Carribean Sea. It shares the island with the Dominican Republic, and is near Cuba, Jamaica, and Florida. Haiti's current population is about 8 million people, with the largest population center the capital, Port-au-Prince.

Isolated by culture and language from its neighbors, Haiti remains "the most African of Afro-American countries [USAID, 1985]." Haiti is also full of apparent contradictions. From being the second free state and the poorest country in the hemisphere, to the mixture of Vodoun and Catholicism, to a history that is both proud and contentious, to a people who are living in severe poverty but are welcoming and friendly, Haiti is both a vibrant and a difficult place.

Figure 2.1: Map of Haiti

## 2.1 Haitian History and Culture

Prince [1995] detailed the complexity of Haiti's complicated and tortuous history. Columbus first landed in the new world at Cap-Haiten, on the northern coast of Haiti, in 1492. He promptly exploited the native Taino population to mine for gold to send back to Spain. In 1548, 56 years after Columbus had landed, the population of Taino had dropped from 500,000 to less than 500 due to slavery, hunger, disease, and suicide. In 1519, with the gold mines worked out, sugar and cattle farming began to thrive. 864,000 slaves were brought to Haiti from Africa between 1519 and 1549. By 1559 only 400,000 slaves remained, due to the death rate of slaves in transport to, and hardship of life in, Haiti.

During this time period, French pirates landed at La Tortue, an island off the north coast of Haiti. The French began to fight with the Spanish over control of Hispaniola, eventually taking control of the western portion of the island in 1697. In 1801, slave leaders Francois-Dominique Toussaint L'Ouverture, Jean Biassou, and Jean Francois led a revolt that resulted in Haiti declaring independence on January 1, 1804. Thus, Haiti became the first black republic in the world and only the second free state in the western hemisphere.

France officially recognized Haiti in 1825, on the condition that France would be compensated for lost income due to "confiscation" of property. Thus, Haiti began its existence with 150 million dollars of debt to France that was only repaid in full in 1922.

A number of different political leaders were in control of the country from 1804 to 1915. The political situation reflected the social tension between blacks and mulattos and between Haiti and the Dominican Republic. Leaders came into and out of power quickly, and established the precedent for dictatorships and "kleptocracies" in Haiti. In 1915, the United States occupied Haiti after seven different presidents were in power from 1910 to 1915. Ostensibly the U.S. occupied to stabilize the political system, but economic recognition of Haiti's strategic importance also played a role. The U.S. left Haiti in 1934, leaving behind a U.S. supported dictator, improved infrastructure, a U.S. trained police force, and increased tension between the mulatto and black communities.

A number of dictators held office in Haiti from 1934 to 1956. In 1956, Francois Duvalier, with support from the black middle class and isolated rural poor, won the presidency in the first election in Haiti that women were allowed to vote in. The Duvalier regime lasted from 1956 to 1986, with Duvalier's son, Jean Claude, succeeding him after his death in 1971. The Duvalier regime was characterized by excessive wealth at the expense of the Haitian people, rule by private militia, amendment of the constitution, and on-and-off support from the United States.

Maguire [1996] discussed Haiti's recent history. In 1986, a combination of popular uprising, supported by the liberation theology of the Catholic Church, and withdrawal of U.S. support led Jean Claude Duvalier to flee to France in exile. In February 1991, after a period of civil unrest, a young priest named Father Jean-Bertrand Aristide was inaugurated into the presidency in what is widely regarded as the first democratic election in Haiti. His Lavalas (cleansing flood) party only survived until a coup in September of 1991. Aristide escaped to the U.S., and the army was again in power.

In October 1991, the U.S. established economic sanctions against the military regime governing Haiti that significantly hurt the civilian population. Responding to pressure from an increased number of "boat people" attempting to escape the military regime to Florida, and following the established diplomacy of "nobody really cares about Haiti except as it impacts on southern Florida," the U.S. occupied Haiti once again in 1994. On October 15, 1994 Aristide was reestablished as the Haitian president, with only one and a half years left in his constitutionally mandated five year term. Aristide was replaced by his successor, Rene Preval, in 1996, with civil unrest and poverty still playing a large role in Haiti.

Aristide was reelected President on November 26, 2000, with civil unrest, low voter turn-out, and the questioning of the legitimacy of the election all indicating that Aristide has lost popular support and the ability to effectively govern the country. His inauguration was February 7, 2001. The questioning and unrest surrounding his reelection does not lead to much hope for Haitian politics changing for the better in the near future.

### 2.1.1 Economics

Maguire [1996], detailed some economic indicators in Haiti as well. Seventy-five percent of the population of Haiti is involved in sustenance agriculture, although urban migration to Port-au-Prince has increased over the last few years. Poverty is widespread, with over 75 percent of the country in "absolute poverty." Economic disparity is extreme, with one percent of the country owning 45 to 55 percent of the wealth. The foreign debt weight of Haiti is also extreme.

Population growth is currently among the highest in Central America at 5 children per woman. The growing tourism industry of the 1980's was abruptly shut down when Haiti was, incorrectly, blamed for bringing HIV to the U.S. via Miami.

### 2.1.2 Religion

Courlander [1960] observed the following while investigation religion in Haiti. Haiti is predominantly Catholic, with a small 10 percent Protestant minority. Although the majority of the population is Catholic, Vodoun is extremely widespread throughout the country. Despite first appearances, this is not the anachronism that it seems. Vodoun and Catholicism are blended in a religion that sees the Catholic God as "destiny," and the Vodoun *loa* (spirits) as responsible for the here-and-now.

Africans in Haiti came predominantly from Dahomey, with other groups from Togoland, Nigeria, and the Congo River basin. These cultures provided the framework for the Afro-Haitian religious belief system. As Catholicism became rooted in Haiti, the Dahomean supreme being, Nananbuluku, was replaced with the Catholic God. "Though God is the supreme creator, giver, and taker, it is the *loa* who must be supplicated and mollified." The *loa* are the myriad local and African pantheons of gods and goddesses that exemplify day-to-day concerns. The Vodoun priest, the *houngan*, maintains his own independent temple, the *hounfor*. Some common elements bind the individual temples, including the possession, or "mounting" of the human body by one of the *loa*.

Water is intrinsically tied to the Vodoun relationship with the *loa*. "The land where the loa live" is "the place below the water." The route to *loa* worship is through water: "tales are heard everywhere of persons who, drawing water from the spring at night, heard the voices of loa or the sound of singing and drumming coming up from somewhere below," and "virtually all the tales about human beings who visited the land of the *loa* describe them as descending into a river or disappearing into a waterfall." Water is also used to entice *loa* to ceremonies, to call the cardinal points, and to bathe the *loa* in the ceremonies. The baptism of Catholicism integrates well with this water worship.

Courlander wrote in 1960 that "the Catholic attitude of tolerance-by-necessity in Haiti won for it most of the country's four million souls. Today, many a Haitian who participates in the rites of Vodoun on Saturday worships in a Catholic chapel on Sunday. The Protestant churches in Haiti, on the contrary, have demanded that their converts become new people." This statement is true to this day. However, the Catholic and Protestant churches work extremely well together. Due to the absence of government support for infrastructure, the churches have stepped into this role. In rural areas, churches are often the only organizations that support community development projects. Both Catholic and Protestant churches work with GWI to provide safe water.

## 2.2 The Environment, Water Supply, and Public Health

In Haiti, the links between environmental damage, water supply, and public health are dramatic and problematic. Centuries of deforestation have reduced baseflow in surface water supplies, which results in lower river flows. Thus, pollution from inadequate sanitation is more concentrated, which in turn affects public health.

### 2.2.1 The Environment

The United States Agency for International Development's (USAID) Haiti: Country Environmental Profile begins with the statement that "few countries in the world face a more serious threat to their own survival from environmental catastrophe than Haiti [1985]." The report continued by noting that overpopulation, overexploited natural resources, and trends toward further environmental degradation were so significant that “the chance for reversing this trend ... is diminishing daily.”

The USAID report continued by discussing the role of geology. Due to its position in the tropics and the mountainous terrain, extreme weather and temperature conditions predominant in Haiti. Elevation ranges from sea level to the highest peak of 2,684 meters, and rainfall varies from 300 mm to 3000 mm across the country. In addition, tropical storms, hurricanes, droughts, and floods are common. The prevalence of mountainous terrain means that 63 percent of the 27,000 $km^2$ land area has a slope greater than 20 percent. Due to the numerous mountains and two narrow peninsulas, Haiti’s rivers are mostly short and swift flowing, with the exception of the 290 km Artibonite River. The broken and steep landscape gives rise to numerous streams and rivers with torrential flow in rain, but no permanent flow. Haiti has two rainy seasons, in the spring, and in the fall.

Covered with lush forest in the nineteenth century, deforestation due to peasant farming of marginal lands, production of charcoal, and export forestry crops has resulted in only 185,000 hectares (6.7 percent) of forested land remaining. Twelve of the thirty major watersheds in Haiti were deforested by 1978. Thirty-eight percent of the forested land remaining is in the south-east, where the rivers in those protected watersheds drain to the Dominican Republic. Evidence is accumulating that baseflows in rivers are decreasing across Haiti due to the loss of groundwater recharge caused by deforestation. The actual amount of land currently used for agriculture is six times that of land judged to be “good” for agriculture. One-third of the total land in Haiti is unusable because of erosion or salinization due to farming, grazing, or tree cutting.

### 2.2.2 Water Supply

USAID [1985] states that “water resources, though not precisely known, are believed adequate to meet basic domestic needs.” Currently, irrigation and drinking water systems predominantly use surface water sources for supply. These sources are in danger, due to deforestation and overuse. The abundant limestone formations in Haiti are believed to hold significant amounts of groundwater, however. USAID recommended two policies to address safe water supply in Haiti:

(1) improve water retention by reducing hillside farming and grazing; and (2) investigate safe groundwater development that does not result in salinization of aquifers.

The Haitian Ministry of Public Works has two branches that oversee water supply development: CAMEP and SNEP [USAID, 1985]. CAMEP supplies the Port-au-Prince metropolitan area and SNEP the remainder of the country. The majority of the government funding is allocated to CAMEP, which supplies the Port-au-Prince area from 17 springs and three wells. The quality of the raw and distributed water is generally good, as all sources but one have a disinfection unit (in various states of repair). SNEP receives little funding from the government, although much support from the international community. UNICEF, USAID, CARE, Plan International, and many other NGOs work with SNEP, or on their own, to secure rural water access.

During the January field month, we noted that CAMEP was drilling new deep wells in the Dumay area. These wells are intended to supply the fountain system in Port-au-Prince. Residents in the Dumay area were worried about the possibility that these new deep wells will interfere with their own fountain system and shallow wells.

A survey by USAID [1996] of Cite Soleil found that the infamous Port-au-Prince slum is currently supplied by trucked water that residents pay for, or by the priests' reservoirs, which are free. Residents also walk across the national route, a busy and dangerous road, to collect water. A male resident responded to the survey by saying, "these details, it's a woman's concern because we don't cook, clean the house or wash clothes." This quote illustrates the fact that in Haiti, women and children of both sexes are responsible for the collection of water. Once collected, Cite Soleil residents added Clorox or Jif (a Dominican Republic bleach), sometimes in combination with lemon juice, to disinfect the water. Some residents boiled their water. Residents attributed the following diseases to dirty water: diarrhea, malaria, typhoid, polio, cholera, dysentery, skin problems, vertigo, colic, stomach problems, cancer, female genital infections, TB, parasites, and malnutrition.

### 2.2.3 Public Health

A number of different international aid agencies have accumulated data detailing access to safe drinking water and sanitation in Haiti, and the health effects of contaminated water. Although the absolute values of the numbers differ, approximately half the Haitian population lacks access to safe water and 75 percent lacks access to safe sanitation (Table 2.1). The high infant mortality, child mortality, and stunting rates detail the effects of this lack. The Pan-American Health Organization (PAHO) [1999] noted that one-half of all deaths in Haiti are in children under five. Diarrheal diseases, acute respiratory illnesses, and malnutrition are the leading causes of childhood death. Nearly half of 6 – 11 month olds have diarrhea.

**Table 2.1: Water and Public Health Metrics in Haiti**

| Metric | UNICEF (2001) | UNCSD (1997) | PAHO (1999) |
|---|---|---|---|
| Access to safe water: | 46 % | 39 % | 43 % |
| Rural | 45 % | | |
| Urban | 49 % | | |
| Access to sanitation | 28 % | 50 % | 27 % |
| Rural | 16 % | | 16 % |
| Urban | 50 % | | 43 % |
| Stunting seen in children | 32 % | 41 % | |
| Infant Mortality | | 76 / 1000 | 74 / 1000<br>101 / 1000 |
| Under 5 Mortality | | | 131 / 1000 |
| Birth Rate | 4.2 / woman | | 4.8 / woman |
| Maternal Mortality | | 600 / 100,000 | 457 / 100,000 |
| Life expectancy | | | 54.5 years |
| GNP per capita | US$460 | US$304 | US$310 |
| Population | | 7,500,000 | 8,000,000 |
| Urban Population | | 32.6 % | |
| Population in poverty | | 75.5 % | 65 % |

Data from a 1980 USAID study described in USAID (1985) details the incidence breakdown of water borne diseases by area in Haiti (Table 2.2). Rates of diarrhea range from 3.8 to 350 cases per 1,000 people. Thus, in the worst areas, one third of people have diarrhea, and one tenth of people have intestinal illnesses.

**Table 2.2: Incidence of Water Borne Disease by Area in Haiti**

| Area | Diarrhea / 1000 | Intestinal / 1000 | Typhoid / 1000 |
|---|---|---|---|
| Part-au-Prince | 10.2 | 7.2 | 0.7 |
| Gonaives | 7.7 | 5.1 | 0.3 |
| Port-de-Paix | 30.3 | 145 | 7.6 |
| Hinche | 69.4 | 74 | 10 |
| St-Marc | 37 | 13.7 | 11.6 |
| Petit-Goave | 42 | 194 | 0.3 |
| Belladere | 350 | 109 | 27.2 |
| Jacmel | 24.6 | 11.7 | 6.7 |
| South Department | 5.6 | 12.2 | 0.3 |
| North Department | 3.8 | 4.8 | 0.9 |

One last note on public health in Haiti is the role of infectious diseases. Paul Farmer established a clinic in Haiti as a medical student at Harvard Medical School. His work in infectious disease clinics in the developing world has continued, investigating TB and HIV in clinics in Haiti, Peru, and Russia. Infectious diseases are still the world's most common cause of death, with three million people worldwide dying of tuberculosis alone [Farmer, 1999]. PAHO [1999] estimated that 7 to 10 percent of the urban population, and 3 to 5 percent of the rural population of Haiti was seropositive for HIV. Farmer's research confirmed these numbers, noting that the highest seropositive rate is in low socioeconomic status urban residents. His work on combating TB and HIV in rural, poverty stricken areas led him to write a book that examined "inequalities in the distribution and outcome of infectious diseases" and concluded that "inequalities have powerfully sculpted not only the distribution of infection diseases but also the course of health outcomes among the afflicted [Farmer, 1999]." His books are powerful statements on the links between poverty and disease.

## 2.3 A Case Study

In the January 17, 2001 issue of the Philadelphia Weekly, Victor Fiorillo and Liz Spikol detailed the following events in a feature article.

In 1996, the city of Philadelphia signed a contract with Joseph Paolin & Sons to dispose of incinerator ash. Amalgamated Shipping Corp. was subcontracted and 14,000 tons of ash were loaded onto the barge, Khian Sea. The Khian Sea circled the Caribbean for 18 months, unable to find a place to dump the ash, and landed at Gonaives, Haiti on New Year's Eve, 1987. The contents were described as fertilizer, and corrupt government officials signed the contract. The next day the government rescinded the contract, but 4,000 tons had already been dumped on the beaches at Gonaives. In November 1988, the Khian Sea arrived in Singapore without the ash. The captain later admitted they had dumped the balance, 10,000 tons, into the sea.

The ash was unloaded by Haitian workers onto the beach, and then transferred inland by Haitian workers to an enclosed, but not covered, area. The ash was removed on April 5, 2000, not by Philadelphia, but by the Haitian Government and the New York City Trade Waste Commission. Before the ash could be removed, Haitian workers treated it with VAPAM HL, a treatment to purge the ash of its toxicity. The ash now sits on a barge outside of Florida.

Workers and families complain of skin and genital rashes and malaise. The Lonely Planet guidebook warns tourists against visiting the beaches in Gonaives. The investors in a Haitian-American business plan to produce salt in Gonaives backed out when they heard of the waste site.

The United States has a long history of involvement within the political affairs of Haiti. Our interventions, intended for humanitarian reasons or for other more complicated political and economic reasons, have affected Haiti both negatively and positively. The above example exemplifies the most negative aspects of the relationship between the wealthiest country in the hemisphere and the most impoverished. This thesis details a significantly more positive relationship between the United States and Haiti.

# Chapter 3: Gift of Water and the Purifier Design

## 3.1 Gift of Water, Inc. (formerly Industry for the Poor)

The general objective of Gift of Water (GWI) is: "Industry for the Poor empowers impoverished families in rural Haiti to purify their own water through the sustainable development of a maintenance network and small scale enterprises [GWI, 2000]."

### 3.1.1 Beginnings

In 1985, Thomas P. Warwick (Phil) became involved with a solar distillation project in Haiti that was large, impractical, and cost prohibitive. Later, in medical mission trips to the Dominican Republic, Phil worked on a water project for three years, and the beginnings of the current GWI purifier were developed [GWI, 2000].

In May 1995, Phil and his family decided to incorporate Industry for the Poor and work to provide safe drinking water in Haiti. In November 1995, GWI began by assessing medical conditions and health problems in Dumay, Haiti with Adopt-a-Village Medical Missions [GWI, 2000]. Three concurrent studies were undertaken and presented in Wilson [1996]: (1) an epidemiological survey of families in the area; (2) an analysis of primary care medical records; and (3) water quality analysis of well and captage sources in the area. Captage is a Kreyol word for a structure containing or transporting a groundwater spring. The epidemiological study showed high levels of gastro-intestinal problems in childhood that declined in the 20 to 35 year old age bracket and then rose again with increasing age. Analysis of the primary care records showed that gastro-esophageal reflux disease (heartburn), a presumed indicator of contaminated drinking water, was extremely prevalent in the 20 to 35 year old range. Parasites, another indicator of contaminated drinking water, were prevalent in the 1 to 5 year old range, but not the 0 to 1 year range, presumably because breastfeeding protects against diseases caused by contaminated drinking water. Water quality analysis of eight wells near Dumay showed that all were contaminated with coliform bacteria. Based on an economic analysis, the study recommended home-based water purification as the most economical of the alternatives, which included boiling, high quality purification, low quality purification, new wells, and the home-based system.

GWI [2000] details the history of purifiers in Haiti. In August 1996, 52 families in Dumay purchased the first purifiers for H$2 (approximately US$0.40), and the first six Haitian technicians were trained to monitor the program. By March 1997, 96 percent of the families using the purifier chlorinated properly and 84 percent of the purifiers showed negative total coliform tests. The decision was made to expand and 229 purifiers were installed in Haiti in August 1997.

In August 1997, 13 Haitians were trained to assemble the purifiers in a factory facility in Dumay. Seven hundred twelve additional unassembled purifiers were sent in February 1998, 1,600 more in December 1998, and another 1,600 in November 1999. Thus, by the end of 1999, approximately 4,000 purifiers had been shipped to Haiti. Some pre-assembly work also occurs in a Florida workshop organized by a GWI staff member. Workers at the workshop include juvenile offenders and differently-abled staff. The latest shipment of purifiers to Haiti was held up in customs for approximately one year and was eventually released in April, 2001.

In November 1997, the purifier was independently verified by Brevard Teaching & Research Laboratories (BTR). BTR independently assembled the purifier, collected water from three surface water sources in Florida, and purified the water. Raw water was sampled for total dissolved solids (TDS), pH, residual and total chlorine, nitrate, nitrite, and total coliform. TDS increased approximately 10 to 20 percent through the purifier, pH increased approximately a log unit to become more basic through the purifier, and nitrate/nitrite increased by approximately 50 percent. Fecal and total coliform were always below the detection limit after purifying, but were as high as 2700 colonies per 100 mL in the raw source water.

BTR also analyzed the finished water samples for total THMs (TTHMs). The results are all below the USEPA standards, except for Sample 4 (Table 3.1). Please see Chapter 5 for discussion of the standards for, and health effects of, total trihalomethanes.

**Table 3.1: TTHM and Residual Chlorine Results, Florida Water**

| Sample Number | TTHM (μg/L) | Residual Chlorine |
|---|---|---|
| 1 | 12.7 | 3.25 |
| 2 | 21.4 | 3.5 |
| 3 | 27.7 | 3.25 |
| 4 | 200.0 | 0.9 [1] |

In July 1998, the newly independently verified purifier became the first Haitian-made purifier to be approved by the Haitian Ministry of Health [GWI, Undated]. Gift of Water states in their literature that monitoring studies have shown greater than 90 percent correct use, greater than 98 percent consistent use of the purifier, and a 90 percent drop in water-related illnesses among children under five who use the purifier [GWI, 2000].

GWI sampling data, collected in Dumay, Haiti over a period off almost three years is not completely consistent with the 90 percent correct usage figure quoted in GWIs literature (Table 3.2) [GWI, 2000]. Correct usage, as defined by GWI, is based on whether the correct amount of chlorine is in the top and bottom buckets of the purifier. Values for this metric in Dumay varied from 45 to 90 percent over three years. Values for this metric in our sampling in January, 2001 are detailed in Table 6.5, and show a 20 to 100 percent correct usage rate.

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[1] pH in the raw water of this sample was measured at 2.6, which may account for the low residual chlorine.

**Table 3.2: GWI Testing Results, Dumay, Haiti 1996 -1999**

| GWI Sampling Date | % Chlorine Residual Correct | % Negative Total Coliform Test |
|---|---|---|
| December 1996 | 45 | 9 |
| March 1997 | 88 | 67 |
| May 1997 | 90 | 73 |
| August 1997 | Not sampled | 60 |
| January 1998 | Not sampled | 93 |
| June 1998 | Not sampled | 79 |
| October 1998 | Not sampled | 62 |
| March 1999 | 79 | 71 |
| October 1999 | Not sampled | 67 |

In January, 1999 GWI began working with a number of different sponsors to expand to additional rural communities. Seven communities, together with sponsors, now have established purifier programs (Table 3.3).

**Table 3.3: Communities in Haiti with Purifier Programs**

| Village | Number of Purifiers | Data Began | Sponsor |
|---|---|---|---|
| Dumay | 1,800[2] | August 1996 | Adopt-A-Village Bethel Foundation |
| Les Palmes | 600 | January 1999 | Haiti Twinning Program Church |
| Barasa | 50 | January 2000 | Catholic Center at Illinois University |
| Fon Veret | 50 | October 2000 | Matt Cyr |
| Ferriere | 50 | July 2000 | Catholic Church |
| Bas Limbe | 50 | August 2000 | Medical Mission |
| Demiere | 50 | September 2000 | Dennison University |
| Total: | 2,650 | | |

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[2] Different technicians in Dumay quoted different total numbers of purifiers. 1,800 is an average number.

Of note is that 4,000 purifiers have been shipped to Haiti, but only approximately 2,650 are accounted for in the seven communities. Phil Warwick is working to investigate this discrepancy [Warwick, personal communication].

GWI [2000] also details that the initial cost of the purifier is US$15.29 per family in Haiti. This includes the purifier, monitoring, educational programs, and shipment of materials. Families pay approximately H$2 for the purifier, and sponsors cover the difference. The usage and maintenance cost per purifier is US$0.42 per month. The sponsors work in conjunction with the local partner in the community and GWI as the technical advisor to establish the program. Due to extra transportation and monitoring costs in the first year, the total cost for the first year of operation is approximately US$50 per filter.

Currently GWI employs Trudi Onek as General Administrator, Sisi Towers as Workshop Manager, and two differently abled workshop employees. Salaries are very fair and competitive, family time and bringing young children to work is encouraged, and employee needs are honored. The President of the Board, Thomas P. Warwick (Phil), and the rest of the Board do not take a salary. Bill Gallo volunteers to lead the sampling trips to Haiti and also does not take a salary. In Haiti, GWI employs technicians in each community who visit homes with purifiers, solve problems, and implement the program on the ground. The technicians are supervised by a volunteer water committee of approximately ten people in each community. In addition, each community has one contact person, such as the priest or nun, who acts as the liason between GWI and the community. Thus, a network of people support the program on the ground.

A recent donation appeal, sent by Phil Warwick, detailed GWIs [2000] continued vision, successes, concerns, and financial accountability. Phil details how water "remains the #1 killer of children today" and how "education and monitoring programs are *more important* than the actual number of purifiers shipped." He states "our vision provides education, monitoring, and growth." In program successes of the past year, Phil details how six out of seven areas in Haiti meet an 80 percent correct and consistent usage standard.

In summary, although there are a number of inconsistencies, including: (1) the actual number of purifiers in Haiti; (2) data supporting the 90 percent correct usage statement; and (3) epidemiological data supporting the 90 percent drop in childhood disease statement [GWI, 2000], GWI clearly has developed a responsible organization that is promoting public health in Haiti.

## 3.2 Purifier Design

The purifier itself is two 15-liter buckets connected by a check valve. Above the check valve in the top bucket is a cotton filter. Below the check valve in the bottom bucket is a carbon filter.

The top bucket has a capacity of 15 liters, with a spare 2.6 inches to the top of the bucket. The "cotton" filter is a five micron spun polypropylene sediment filter purchased from Eagle Spring Filtration in Holly Hill, Florida (Figure 3.1). The filter is 25 cm long, with the string 0.1 inch in diameter and 500 feet in length when unwound. The core of the cotton filter is 1.4 inches of diameter, with 0.25" x 0.25" hollow inner squares. There are eight squares around the diameter and 23.5 in the length. A plug at the top prevents water from flowing down through the core of the filter. A plug at the bottom connects the cotton filter to the check valve.

**Figure 3.1: Cotton Filter**

**Figure 3.2: Carbon Filter**

The carbon filter is 4.8 cm in diameter and 21 cm long. There were 220 grams of granulated activated carbon (GAC) in the filter analyzed in lab. The GAC is 12/40 bituminous GAC purchased from Eagle Spring Filtration.  The ratio of diameter to the length of the carbon filter is 4.4.

To use the purifier, water is collected in the top bucket, and bleach is added.  The amount of bleach added is measured through one of two systems:  (1) a bleach container that is opened, and the cap is filled and poured into the bucket; or (2) a mouthwash-type container that is squeezed into a top receptacle and then poured into the bucket.  The amount of bleach added using the second mechanism was 6. 8 - 8.6 mL in lab, depending on how it was squeezed and if there was leakage.

The top bucket with the bleach in it is allowed to sit for 30 minutes.  It is then placed on the bottom bucket and water flows through the cotton and then the carbon filter.  Five drops of chlorine (0.04 milliliters) are added to the bottom bucket before filtration to form the residual.

Phil Warwick determined the chlorine demand of Haitian water when designing the purifier.  He found the highest chlorine demand to be 5 ppm.  Adding 3 ppm as a safety factor because bleach is stored for one month and can degrade, and a margin of error of 2 ppm leads a necessary chlorine addition concentration of 10 ppm.  To calculate the actual amount of chlorine added to the top bucket of the purifier the amount of chlorine in bleach is multiplied by the amount of bleach added to the top bucket, and divided by the amount of water.  The amount of chlorine in bleach is determined by taking the amount of sodium hypochlorite (NaOCl) in bleach (0.0525 kg / L), multiplying it by the molecular weight of chlorine (35.5) and dividing by the molecular weight of NaOCl (74.5).  The result is 12.5 mg/L (ppm) of chlorine added.  This is close to the 10 ppm recommended by GWI.  The Center for Disease Control (CDC) recommends a residual chlorine level of 0.5 – 2.0 mg/L, but notes some raw water may have very high demand [2001].

$$\begin{array}{l}\text{Chlorine} \\ \text{Concentration}\end{array} = \frac{0.0525\text{ kg NaOCl}}{\text{Liter Bleach}} * \frac{35.5\text{ g Chlorine}}{74.5\text{ g NaOCl}} * \frac{0.0075\text{ L Bleach}}{15\text{ L water}} = 12.5\text{ ppm}$$

Phil Warwick also noted that water at the bottom of the filter begins to taste like chlorine at the end of six months as the residual chlorine breaks through the GAC [personal communication]. This mechanism is thought to ensure the GAC is regularly changed. Based on the literature and research in Haiti, we did not find this mechanism to be occurring.

## 3.3 Bench Scale Model & Testing

### 3.3.1 Bench Scale Model

A 1/30th scale, 500 mL bench scale model of the purifier was constructed in order to test Haitian water at MIT using samples of less that 15 liters of volume. The top bucket was constructed by drilling a hole in the bottom of a plastic 1-liter bottle and inserting a rubber stopper with tubing through it. Above the stopper a model cotton filter made of 1/30th the total amount of cotton wrapped around a 5 x 21 square piece of 10-square-per-inch plastic canvas was attached. A rubber cap secured the top end of the cotton from leakage. The water flowed into a flask from which water could be collected and then flowed through a model GAC filter. The GAC filter was constructed using 1/30th of the weight of the carbon and placing it in a plastic vial that maintained the diameter to length ratio of the original filter. The original screen was secured around the bottom of the vial and a collection bottle placed beneath the carbon filter. Bleach was diluted by a factor of 30.

**Figure 3.3: Bench Scale Model**

### 3.3.2 Chemical Analysis

Raw source water was mailed to MIT from one of the fountains in Dumay, Haiti at the end of November and was stored at room temperature in plastic bottles with head space. It was received at MIT and placed in the refrigerator in early December. On December 29, 2000 that water was used to test the bench scale model. Triplicate samples were collected into 45 mL volatile organic analysis (VOA) vials before chlorination, after first chlorination but before filtration, after the cotton filtration, after GAC filtration, and after the final chlorination. These samples were analyzed for pH, turbidity, TOC, and trihalomethanes.

pH was measured with a Orion Model 720A meter calibrated at pH 7, 4, and 10. Turbidity was measured with a HF Scientific DRT-15CE turbidity meter. TOC was measured with a Schmidzu TOC-5000.

The results show that pH decreased with initial chlorination and then increased through the purifier (Table 3.4). The unexpected decrease in pH from sample 1 to sample 2 can be explained by the fact that pH was analyzed five days after the sample was taken. Turbidity decreased through the cotton filter and then increased through the GAC filter and with final chlorination. This is due to the reduction of particulate matter through the cotton filter, and then flowthrough of GAC into the finished water. TOC decreased with initial chlorination, increased through the cotton filter due to shedding of the filter, and decreased through the GAC filter.

**Table 3.4: Turbidity, pH, and TOC of Haitian Water through Bench-Scale Purifier**

| Sample | pH | Turbidity (NTU) | TOC (ppm) |
|---|---|---|---|
| 1: Raw Water | 7.8 | 0.25 | 1.47 |
| 2: Post Chlorination | 7.67 | 0.27 | 0.80 |
| 3: Post Cotton Filter | 7.91 | 0.18 | 1.26 |
| 4: Post GAC | 8.22 | 0.20 | 0.83 |
| 5: Finished Water | 8.39 | 0.24 | 0.82 |

The THM chromatographs are shown in Figures 3.4 – 3.8. All graphs are at the same scale both vertically (peak height) and horizontally (time), and because no standards were run with these samples, the graphs detail relative trihalomethane concentration only. As can be seen, raw water contained no volatile organics compounds (no peaks), but after initial chlorination occurred, a whole range of compounds (peaks) was created. The cotton filter removed many of the compounds (peaks), and then the GAC filter removed almost all of the compounds (peaks).

Final chlorination resulted in the creation of chloroform at elution time 2.96 minutes, bromodichloromethane at 3.54 minutes, and chlorodibromomethane at 4.37 minutes.

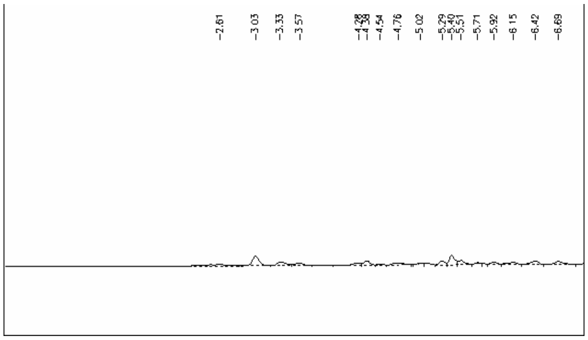

**Figure 3.4: GC Run, Raw Water**

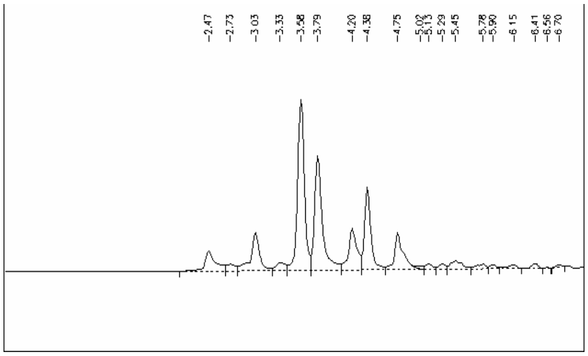

**Figure 3.5: GC Run, Post Cotton Filter**

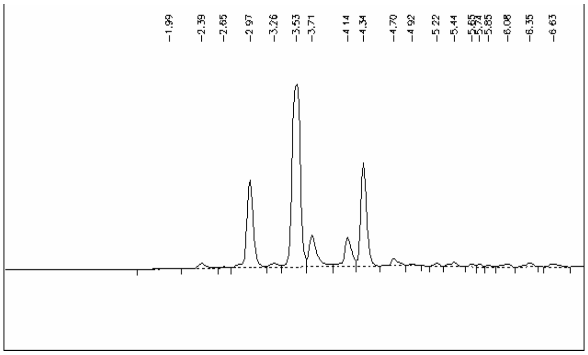

**Figure 3.6: GC Run, Post Chlorination 1**

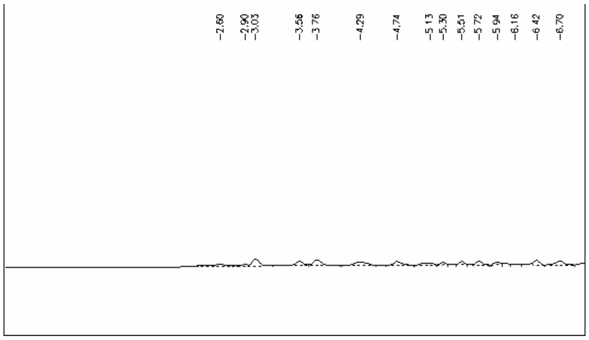

**Figure 3.7: GC Run, Post Carbon Filter**

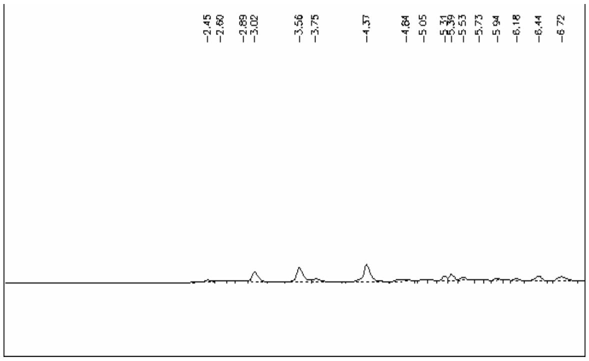

**Figure 3.8: GC Run, Post Chlorination 2**

### 3.3.3 Bacteriological Analysis

In addition to the bench scale modeling, Charles River water was run through the real purifier, and bacteriological analysis was conducted.

Total coliform bacteria are part of the *Enterobacterceae* family, but their actual defininition is based on an analysis protocol, not a biological definition They are defined as aerobic and facultatively anaerobic, gram-negative, non-spore-forming, rod-shaped bacteria that ferment lactose with gas formation within 40 hours at 35 C. In the U.K., they are defined as gram-negative, oxidase-negative, non-spore-forming rods capable of growing aerobically on agar containing bile salts and able to ferment lactose within 48 hours at 37 C with the production of both acid and gas [Lynch, 1998].

The Family *Enterobacteriaceae* consists of the tribes Eschericheae, Klebsielleae, and Proteae with genera and species branching from those tribes [Kauffman, 1966]. Fecal coliform are organisms in the genera *Escherichia* and *Klebsiella* that are able to ferment lactose with the production of acid and gas at 44.5 C within 24 hours. These organisms are the subset of total coliform that are of fecal origin. This test does not differentiate between human and animal fecal origin, however [Maier, 1999].

The Haiti M. Eng. student group tested pre- and post-filter samples using a PathoScreen medium and Lauryl Tryptose Broth with Bromcresol Purple (LT/BCP) medium in November 2000. The PathoScreen medium detects hydrogen sulfide-producing bacteria that are associated with fecal contamination and the presence of coliform. A powder pillow is opened, mixed with the sample and incubated for 48 hours. The Lauryl Tryptose Broth detects total coliform, with the Bromcresol Purple fluorescing in the presence of *E. coli*. Duplicate samples of pre-filtration Charles River water were both positive for both the PathoScreen and LT/BCP tests. Duplicate samples of post-filtration water were both negative for the PathoScreen and LT/BCP tests.

The combination of chemical and bacteriological testing clearly shows that when used correctly, the purifier effectively disinfects and purifies water.

# Chapter 4: Chlorination and the Formation of Trihalomethanes (THMs)

"The first documented drinking water treatment can be found in Egyptian hieroglyphics, describing procedures to purify water. The basic principles were the same then as they are today: boiling, chemical treatment, and filtration were recommended treatments [Calderon, 2000]."

Until 1908, when chlorine was first introduced in the United States, the same mechanisms as mentioned in Egypt were utilized for drinking water treatment. Chlorine revolutionized water purification, is credited with the reduction of infectious disease, and is currently the most widely used chemical for disinfection in the U.S. [Gordon, 1987].

Gaseous chlorine ($Cl_2$) or sodium hypoclorite (bleach, NaOCl (aq)), reacts with water to form hypochlorous acid and hypochlorite ion.

$$Cl_2(g) + H_2O \longleftrightarrow HOCl + H^+ + Cl^-$$

$$NaOCL\ (aq) + H_2O \longrightarrow Na^+ + OCl^- + H_2O$$

Hypochlorous acid and hypochlorite ion hen react with water according to pH.

$$HOCl + H_2O \longleftrightarrow H_3O^+ + OCl^-$$

Chlorine is a strong oxidizing agent and reacts with a wide variety of reducing compounds to consume chlorine, making it unavailable for disinfection. The set of reactions is called the "chlorine demand." Sulfur, manganese, iron, sulfate, nitrate, and iodine can all react with chlorine and prevent it from inactivating biological compounds.

In addition to reacting with the compounds above, hypochlorous acid also reacts with bromide in the water according to the following reaction:

$$HOCl + Br^{-} \longrightarrow HOBr + Cl^{-}$$

Chlorine is the most common disinfection agent in the U.S. because of its effectiveness in inactivating bacteria. Gibbons [1999] details that hypochlorous acid inactivates bacteria by attacking the respiratory and transport systems, and nucleic acid activity. It inactivates viruses by attacking the protein coat. Sufficient chlorine is added in the purification process to ensure residual is left throughout the distribution system, so that regrowth in the pipes is prevented.

To inactivate pathogens or microorganisms, chlorine must be present in sufficient concentration and have enough time to react. This is mathematically shown by [Gibbons, 1999]:

$$C\ (mg/L) \times t(\mathrm{min}) = k\ \ factor$$

To inactivate *E. coli*, a k factor of 0.04 at neutral pH is needed. For *Giardia lamblia*, k is generally greater than 50, indicating *G. lamblia* may be the limiting factor in the disinfection process.

In 1974, Rook discovered that hypochlorous acid and hypobromous acid react with naturally occurring natural organic matter to create four compounds (chloroform ($CHCl_3$), bromoform ($CHBr_3$), bromodichloromethane ($CHCl_2Br$), and chlorodibromomethane ($CHClBr_2$)). These four compounds are collectively termed trihalomethanes (THMs). Early days of research into THMs and chloroform received much attention because chloroform was shown to be an animal carcinogen [Simpson, 1998]. As time has passed, chlorination of drinking waters has become equated with increased mutagenic activity due to an array of halogenated compounds and has spurred much concern and research [Simpson, 1998]. Hubbs [1986] found that approximately 10 to 20 percent of disinfection by-products (DBPs) were THMs. The others were collectively termed TOX (total organic halogen). A different study of 35 water treatment plants showed that THMs accounted for 50 percent of the DBPs on a weight basis, while haloacetic acids (HAAs) accounted for 25 percent, and aldehydes 7 percent [Gibbons,1989]. Thus, THMs are often used as an indicator organism for other disinfection by-products.

## 4.1 Trihalomethanes (THMs)

### 4.1.1 Background

Rook noted in 1974 that hypochlorous and hypobromous acid reacted with natural organic matter in the water supply to form the four THM compounds. This discovery led to a field of research to determine how THMs are formed and how to mitigate THM formation.

Hubbs [1986] details in a summary article that increased THM production occurs with:

- higher temperatures (not as many precursors and lower k values in the winter);
- higher pH (the last step of THM formation is base-catalyzed);
- higher humic acid concentration (not fulvic acid concentration); and
- higher chlorine dose.

### 4.1.2 Brominated Compounds

The role of the bromide ion in the formation of THMs is critical. Without bromide in the raw water, the three brominated THMs are not formed. A number of studies and articles begin with the assumption that only chloroform concentrations are important because the raw water has no bromide. Bromide itself is a naturally occurring ion found most commonly in ocean water and waters near the ocean. While chlorine acts preferentially as an oxidant, bromine is a more effective halogen substituting agent, so bromide not only causes a shift towards the more brominated species, but also increases the total THM yield [Sketchell, 1995]. Bromine incorporation values decline, however, at higher dissolved organic carbon (DOC) concentrations where more precursor reactive sites are available and utilized by the chlorine in excess [Sketchell, 1995].

Once formed, hypobromous acid is capable of participating in reactions analogous to those of chlorine. Nokes [1999] shows that as the bromine:chlorine ratio increases, the molar percent $CHCl_3$ decreases exponentially, the $CHCl_2Br$ and $CHClBr_2$ molar percents increase and then fall off, and the $CHBr_3$ molar percent increases (Figure 4.1). The relative cancer risk (using EPA potency factors) associated with these trends, indicates that the highest cancer risk is at a $[Br^-]$/[chlorine] ratio of 0.15.

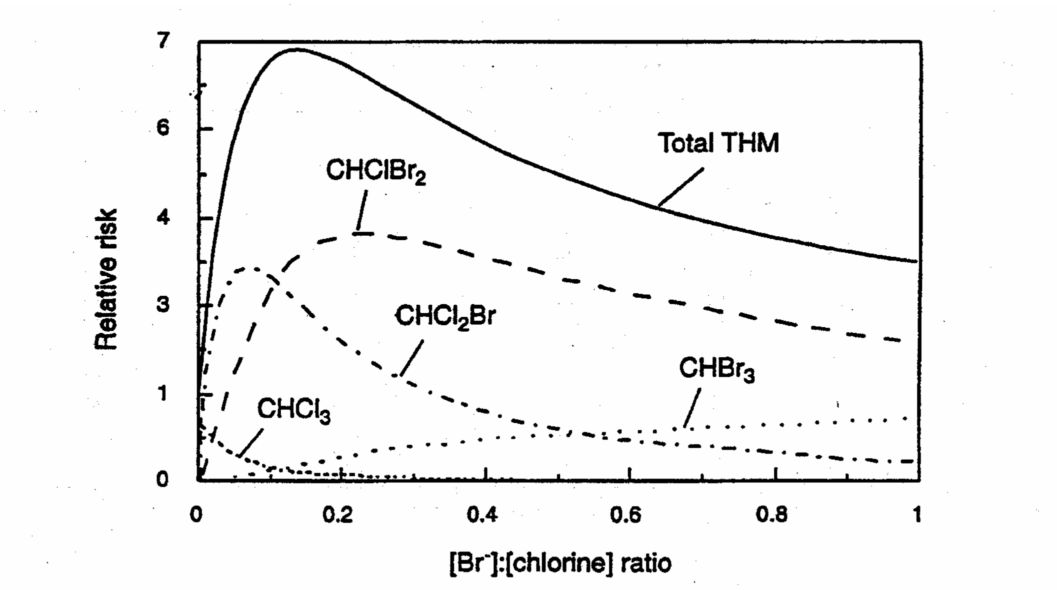

**Figure 4.1: Relative Cancer Risk Due to $[Br^-]$ / [chlorine] Ratios**

Ichihashi's [1999] results agree with Nokes. Ichihashi finds that below a NaOBr / NaOCl ratio of 0.04, $CHCl_3$ is the dominant species followed in descending order by $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$. Above a ratio of 0.1, $CHBr_3$ is the dominant species, followed in descending order by $CHClBr_2$, $CHCl_2Br$, and $CHCl_3$. Ichihashi produces the same graph as Nokes. These findings suggest that the rate of substitution of bromide is greater than that of chloride. The same graph is produced using KBr / NaOCl, strongly supporting the argument that $Br^-$ is first oxidized to $OBr^-$ by $OCl^-$ and then $OBr^-$ reacts with naturally occurring matter. Additionally, Ichihashi finds that the concentration of $CHBr_3$ is seven times higher in the presence of NaOCl than with only NaOBr, showing that NaOCl promotes the formation of $CHBr_3$, possibly by the hypochlorite reacting with the humic acids to produce precursors and the hypobromite reacting then with those precursors.  Also, although the amount of TTHM produced changes with pH, the relative percent of the species distribution remains constant.

### 4.1.3 Granulated Activated Carbon

“Activated carbon adsorption using either granular activated carbon (GAC) or powdered activated carbon (PAC) is commonly used to remove dissolved organic contamination, especially halogenated hydrocarbons [Morawski, 1997].”  The mechanical resistivity and the lifetime of the carbon are important properties when considering GAC filtration of THMs.  Synthetic carbons obtained from polymers have better mechanical resistivity than carbon from natural precursors. Three different prepared GAC samples were analyzed to compare their adsorpability.  All three were prepared by heating phenol resin to 1000 C in the presence of nitrogen or carbon dioxide. Chemical modification of these three by nitric acid to from a hydrophilic surface allowed significantly more adsorption of THM.  The following adsorption rates for TTHM were determined with these modifications [Morawski, 1997]:

| | |
|---|---|
| Carbon 1: | 40 mg/g |
| Carbon 2: | 120 mg/g |
| Carbon 3: | 77 mg/g |

Using commercially available carbon, Nakano [1997] designed a point-of-use activated carbon and microfilter unit to remove THMs.  They determined that THM breakthrough occurred early in the throughput volume, followed by musty odor and finally residual chlorine (Figure 4.2).

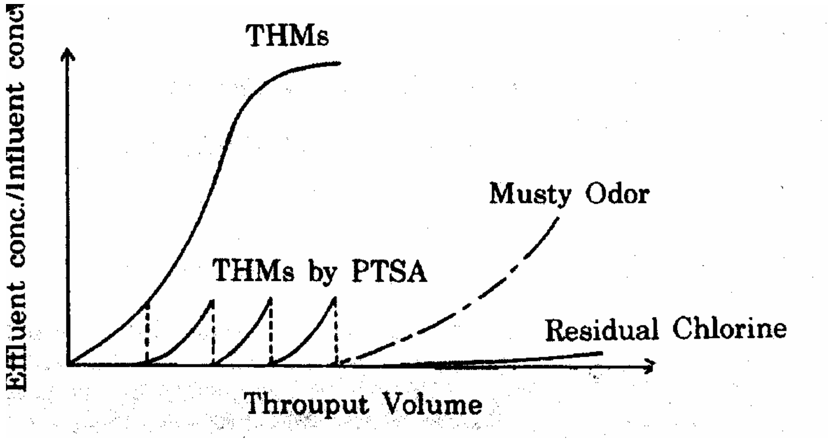

**Figure 4.2: Breakthrough of THMs and Residual Chlorine through GAC**

Adsorption quantities for the four different commercial natural carbons used ranged from 0.4 to 1.8 mg chloroform / gram carbon [Nakano, 1997]. Adsorption quantities of $CHBrCl_2$ and $CHBr_2Cl$ were higher than chloroform. Heating the activated carbon to 70 degrees C at regular intervals reduced adsorbed chloroform by 97 percent.

Morawski [2000] also found that $CHBr_3$ preferentially adsorbed into carbon spheres, followed by $CHBr_2Cl$, $CHBrCl_2$, and then $CHCl_3$. The adsorption of $CHCl_3$ from a mixed THM solution was depressed compared to a pure solution of $CHCl_3$ by 60 percent. The total adsorbed amount of all four THMs was about twice that of the capacity of pure $CHCl_3$.

### 4.1.4 Humic Acids as THM Precursors

Although humic acids are known to be THM precursors, little is known about the actual mechanism and what types of humic acids react with hypochlorous and hypobromous acid to form THMs. This is an active and debated point in the current literature, as described below.

C. Lin [2000] found that unfractionated commercial humic acids had 165 µg THMFP / mg DOC. THM formation potential (THMFP), detailed in Standard Methods [APHA, 1995], is a laboratory analysis that chlorinates raw water and then analyzes THMs one week later. When fractionated, the hydrophobic fraction was 190 µg THMFP / mg DOC and the hydrophilic 130 µg THMFP / mg DOC.  The high reactivity of the hydrophilic fraction to form THMs is important to note.  Exposure to powdered activated carbon led to a reduction in THMFP of approximately 20 percent in each fraction.

Galapate [1999] found that in treated industrial wastewater samples, the hydrophilic (nonhumic) portion of the DOC had an average of 8.5 µg THMFP / mg DOC and the hydrophobic portion an average of 36 µg THMFP / mg DOC.  This is consistent with the general view and with Lin, although Galapate found lower values.  However, because the DOC content of the hydrophilic fraction was significantly higher then the hydrophobic fraction, the hydrophilic fraction actually had a higher contribution to the total THMFP, as they did in Lin's work.

Marhaba [2000] fractionated dissolved organic material (DOM) from a conventional surface water treatment plant in northern New Jersey and found that the hydrophilic acid fraction was the most reactive THM precursor and the hydrophobic neutral fraction were the most reactive haloacetic acid (HAA) precursor.  Removing the hydrophilic acid fraction removed 70 percent of the THMFP and removing the hydrophobic base fraction removed 60 percent of the haloacetic acid formation potential (HAAFP).  Coagulation and sedimentation in the plant were found to reduce the THMFP 30 percent and the HAAFP 55 percent.  Hydrophilic acid fraction was 53 percent of the DOM and hydrophobic base was 7 percent of the DOM.

Bergamaschi [1999] used carbon isotopes as a tool to identify the source of THM precursors. They found that maize releases almost twice the amount of DOC as *Scirpus* (another grain), forming more than twice the amount of THM from their leachates.  This indicates that plant type may be an important variable in managing DOC released into watersheds.

Galapate [1997] found that in the Kurose River in Hiroshima Japan, the sources of THM precursors were mainly point sources such as domestic wastewater, industrial effluent, and agricultural drains, but not treated domestic sewage.  After rainfall, however, the dominant source of THM precursors was runoff containing water-soluble organic compounds extracted from forest litter and top soil, but not road dust or agricultural soil.

Fujii [1998] found that, despite the “generally accepted conceptual model for THM formation [that] assumes that aromatic forms of carbon (such as resorcinol) are primary precursors to THMs,” COC aromaticity alone cannot explain fully or predict THM precursor contact. This study was conducted in reduced peat soils beneath shallow ground water that would have a tendency to release greater aromatic carbon relative to near surface oxidized peat soils.

Although humic acids are known as one precursor of THM formation, the actual reaction is complicated and removal technologies aimed at targeting specific fractions of the humic acids are just beginning to be developed. Thus, determining the fractionation of humic acids in Haitian raw water will not yet provide usable data to determine trihalomethane production or mitigation strategies.

### 4.1.5 THM Formation in the Distribution System

The production of THMs continues after processing is complete. El-Shafy [2000] studied THM formation in a water distribution system in the Czech Republic, and found that formation of THMs in the treatment plant only accounted for 45 percent of the THMs in the tap. In the distribution system, residual chlorine dropped as THM levels increased, with linear $R^2 = 0.913$. Rodriguez [2001] also found that THM concentrations varied significantly (from 1.5 - 4 times) between finished waters and system extremities.

Thus one important consideration in Haiti is the formation of THMs in the purifier after chlorination is complete and before the water is used. At the high temperatures typical in Haiti, this could be significant.

### 4.1.6 Other Disinfection By-Products

A number of other DBPs are formed by the reaction of chlorine with raw water. Iodinated THM’s are “formed when iodide (from natural sources, sea-water intrusion or brines) is present [Cancho, 1999].” “The low odor and taste threshold concentrations of iodoform (0.02 and 5 µg/l, respectively) could explain how ITHMs at concentrations between 0.02 - 1 µg/l are able to cause medicinal taste and odor problems in drinking water [Cancho, 1999].”

HAAs are another DBP formed during the chlorination process. Dojlido [1999] found that their formation was depended on organic matter concentration, chlorine concentration and, more importantly, increasing water temperature. Unlike THM’s, boiling does not reduce them, except for trichloroacetic acid, $CCl_3COOH$, which decomposes into $CHCl_3$ and $Cl_2$ when boiled.

THMs have widely been used as an indicator of total DPB formation. Recently, however, organizations have begun to regulate the DPBs separately. For this study, THM levels were used as an indicator of total DPB formation.

# Chapter 5: Toxicology

## 5.1 Toxicity

The identification of DBPs as ubiquitous in chlorinated drinking water led to a flurry of research into potential human health effects. The effects of the four THMs have been studied individually and synergistically.

### 5.1.1 Individual THM studies

Chloroform is the most studied THM because of historical identification, occupational exposure, and industrial importance. It was "recognized as a liver toxin many years ago," and although Fawell [2000] details some studies where in vitro genotoxic effects were seen, in vivo studies showed inactivity. Thus, "the weight of evidence supports the view that chloroform is not genotoxic [Fawell, 2000]." The body of evidence supports the mechanism that chloroform promotes the formation of tumors by causing cell death and reparative cell proliferation. Chloroform is oxidized to trichloromethanol, which on the elimination of hydrogen chloride, produces phosgene. Phosgene can react with water to produce carbon dioxide and hydrogen chloride. It can also react with cellular macromolecules, causing damage to the cell.

Fawell [2000] also described mechanisms for the other three THMs. Bromodichloromethane increased kidney tumors in male and female rats and male mice, increased liver tumors in female mice, and increased intestinal tumors in male and female rats, all when administered in corn oil. A recent EPA study showed no significant increase in incidence of tumors in rats administered bromodichloromethane in drinking water instead of corn oil. In vivo studies of genotoxicity have been negative. No clear pathway for the mechanism of carcinogenicity has been developed, although kidney and liver tumors probably result from non-genotoxic tissue damage and reparative cell proliferation.

Chlorodibromomethane increases liver tumors in female and male mice when administered in corn oil. It is not regarded as likely to be carcinogenic in humans. It is reasonable to suggest the mechanism of action is the same as chloroform given the increase seen in fatty metamorphosis in the liver at doses causing increased liver tumors.

Bromoform increases adenomatous polyps and carcinomas of the large intestines in male and female rats following administration in corn oil. These are significant because they are rare in control animals. The weight of evidence is inconclusive about whether bromoform is genotoxic in vitro and in vivo, but suggests it is not genotoxic in vivo.

One large caveat on these studies is that Fawell [2000] notes that "the toxicity and carcinogenicity of these substances is profoundly affected by dosing in corn oil. New studies suggest that dosing in drinking water would not result in increases in tumors." Thus, there is "significant doubt about how appropriate the use of mathematical models, which assume linearity to low doses, is in determining the risks of carcinogenicity following exposure through drinking water." Linearity of the dose-response curve can not be assumed because carcinogenicity appears to be dependent on the method of dosing.

### 5.1.2 Interactions Between THMs

Because THMs are present as a mixture, much discussion has occurred concerning the combined effects of THMs.

Fawell [2000] states that the "proportional approach proposed by WHO, to allow for the fact that the THMs are almost invariably present as a complex mixture, would seem to be both scientifically defensible and prudent." Calderon [2000] agrees with the need to investigate the complex mixture of THMs. He states "addressing the mixtures area is where there is a great need for greater communication and collaboration between epidemiologists and toxicologists." da Silva [1999] states that for the additive toxicity method assumed in the WHO guideline values to be valid, the combined effects of THMs should be dose-additive and mechanisms of action should be the same.  He also states that this approach assumes no toxicokinetic or toxicodynamic interactions between the THMs.  This is not a valid assumption, given the data discussed below.

A number of studies have compared the individual THMs to mixtures of THMs.   Pegram [1997] found that $CHBrCl_2$ could activate transformation to mutagenic intermediates at low concentrations, while $CHCl_3$ could not.  This demonstrated that THMs can induce effects via different mechanisms, and as such should not be regulated as if they share a common mechanism.

da Silva [1999] investigated the venous blood concentrations of THMs following exposure to single THMs and a quaternary mixture.  The metabolism time increased from 2.62 to 8.15 times, consistent with the order of metabolism of bromoform, then chlorodibromomethane, then bromodichloromethane and chloroform.  da Silva [1999] concludes with: “the results of the present study suggest that co-exposure to THMs can interfere with their respective metabolic fates.”

### 5.1.3 Human Epidemiological Studies

A few human studies on the effects of THMs have been conducted.   King [2000] noted that males exposed to chlorinated surface water for 35 to 40 years had increased colon cancer risk compared to those exposed less than 10 years (1.53 times).  THM levels higher than 75 μg/L were associated with double the risk of colon cancer in males.  No relationships between THMs and colon or rectal cancer were seen in females, and no relationship was seen between THMs and rectal cancers in males.  The author notes that the results of this study are only partially congruent to other studies.  King [2000] also associated total and specific THMs with increased stillbirth risk.  The strongest association was with bromodichloromethane exposure – the  risk of stillbirth doubled as exposure level increased from less than 5 μg/L to greater than 20 μg/L.

Overall, however, there is much contention over the effects of THMs on humans.

### 5.1.4 Exposure in Humans

T. Lin [2000], in a study in south Taiwan, identified that exposure to THMs through ingestion was 47.9 μg/day, with exposure from inhalation (summation of shower, pre and post cooking and cooking activities) accounting for 30.7 μg/day. The shower alone averaged 26.4 μg/day, with pre and post cooking 1.56 μg/day, and cooking 3.29 μg/day. Thus, inhalation in the developed world is a significant factor in THM exposure.

Aggazzotti [1998], conducted studies in swimming pools, because of high levels of chlorination in public pools. Subjects rested for one hour in the pool area at average environmental exposure of 0.1 μg/L. Uptake after rest was 30 μg/h. After one hour of swimming, uptake was 221 μg/h.

Because rural Haitian households do not have showers, a major exposure route in the developed world is not a factor in Haiti. Thus, the cooking and drinking factors form the major exposure route in Haiti.

## 5.2 Standards and Guideline Values

In response to concerns about potential human health effects of THMs, both international and governmental organizations have established exposure standards. Following are details about the World Health Organization and the United States Environmental Protection Agency standards.

### 5.2.1 World Health Organization

One of the primary goals of the WHO [1998] is that “all people, whatever their stage of development and their social and economic conditions, have the right to have access to an adequate supply of safe drinking water.” The first International Standards for Drinking-Water was published in 1958, followed by revisions in 1963 and 1971. In 1984, the publication was revised again to incorporate risk-benefit approaches in the formulation and enforcement of national standards and was retitled Guidelines for Drinking-Water Quality. A second edition of the Guidelines was released in 1993 and a third is currently being developed [WHO, 1998]. The WHO regulates the individual THMs separately and in total.

The WHO International Agency for Research on Cancer (IARC) has determined the cancer risks of the three brominated THMs (Table 5.1). Only bromodichloromethane is considered to be carcinogenic is humans when calculating guideline values.

**Table 5.1: IARC-WHO Carcinogenicity of THMs**

| | Animals | Humans | Classification |
|---|---|---|---|
| Bromodichloromethane | Sufficient evidence for carcinogenicity. | Inadequate evidence for carcinogenicity. | Possibly carcinogenic in humans: Group 2B. |
| Chlorodibromomethane | Limited evidence for carcinogenicity. | Inadequate evidence for carcinogenicity. | Not classifiable in humans: Group 3. |
| Bromoform | Limited evidence for carcinogenicity. | Inadequate evidence for carcinogenicity. | Not classifiable in humans: Group 3. |

#### 5.2.1.1 Chloroform

The WHO has reviewed the literature on chloroform and reached the following conclusions [1998]:

1. The human population is exposed to chloroform through food, drinking-water, and indoor air in roughly equal proportions.
2. Most available evidence indicates there is no gene mutation or direct damage to DNA from chloroform.
3. Liver tumors in mice are associated with, and kidney tumors in rats might be associated with, a threshold mechanism of induction by chloroform.
4. Evidence for colon and bladder cancer in humans caused by chloroform is considered to be limited.

The lowest dose of chloroform causing liver damage was 15 mg/kg over a period of 7.5 years, due to chloroform-laced toothpaste used in beagles. Other adverse impacts, in the in kidney cortex and histopathological effects, have been observed at levels around 30 mg/kg [WHO, 1998].

To determine the safe total daily intake (TDI) level for chloroform, the WHO carried out the following calculation:

$$15\frac{mg}{kg}\times\frac{1}{100}\times\frac{1}{10}\times\frac{6}{7}\times\frac{1}{2}\times 60\ kg\times\frac{1\ Day}{2\ Liters}=195\ (rounded\ to\ 200\ \mu g\ /\ L)$$

This calculation was based on the following numbers:

| | |
|---|---|
| 15 mg/kg: | Least observed adverse exposure level (LOAEL) in beagles. |
| 1/100: | To account for intra- and interspecies variations. |
| 1/10: | To account for use of LOAEL instead of no observed adverse exposure level (NOAEL). |
| 6/7: | Because the dogs were only dosed six days per week. |
| 1/2: | Only half daily chloroform intake comes from water. |
| 60 kg: | Average weight of human. |
| 1 day/2 liters: | Average amount a human drinks per day. |

This value is similar to the standard calculated by extrapolation of increased cancer risk of 1 in 100,000 from rat and mouse experimental data [WHO, 1998].

In addition, the WHO specifically and repeatedly states in the standards that: “It is cautioned that, where local circumstances require a choice to be made between meeting microbiological guidelines or guidelines for disinfection by-products such as chloroform, the microbiological quality must always take precedence. Efficient disinfection must *never* be compromised [WHO, 1998].”

#### 5.2.1.2 Other THMs

Dibromochloromethane and bromoform standards were also calculated using the TDI formula. Both guideline values were determined to be 100 μg/L: the chlorodibromomethane from extrapolation of the histopathological effects in rat livers and the bromoform from histopathological lesions in rat livers [Fawell, 2000; WHO, 1998].

Bromodichloromethane is considered by WHO to be a potential human carcinogen, and therefore the guideline value is calculated based on an increased lifetime cancer risk of 1/100,000. The guideline value for bromodichloromethane was determined to be 60 μg/L by applying a linearized multistage model to the kidney tumors of male mice [Fawell, 2000]. Of note is the fact that the compound was administered in a corn oil gavage which may have amplified the carcinogenicity. Thus, this guideline value is likely to be conservative.

#### 5.2.1.3 WHO - TTHM

The sum of the four WHO THM standards is 460 μg/L. Yet, WHO also incorporates potential interactions in the human body caused by the four compounds working in conjunction. In addition to the individual guidelines, the sum of the four THMs' actual value divided by their guideline value cannot be greater than one.

### 5.2.2 USEPA

The disinfection / disinfection by-products (D/DBP) rule was designed to be implemented in three stages (Table 5.2). However, the implementation schedule has been delayed and the standard is still 100 μg/L. The current proposal is to implement Stage 1 on January 1, 2002 [USEPA, 2001].

**Table 5.2: D/DBP Implementation Schedule, USEPA**

| Date | TTHM Standard | HAA Standard |
|---|---|---|
| Initial | 100 μg/L | |
| Stage 1: November 1998 | 80 μg/L | 60 μg/L |
| Stage 2: May 2000 | 40 μg/L | 30 μg/L |

The USEPA has calculated cancer potency factors for the four THMs, which can be used to calculate probability of cancer for varying exposure levels (Table 5.3).

**Table 5.3: USEPA Cancer Potency Factors**

| Compound | Cancer Potency Factor |
|---|---|
| Chloroform | 0.0061 mg/kg/day |
| Bromodichloromethane | 0.062 mg/kg/day |
| Chlorodibromomethane | 0 mg/kg/day (not cancerous) |
| Bromoform | 0.0079 mg/kg/day |

Masters [1998] completed a risk assessment for chloroform utilizing these potency factors as follows. First, he calculated the Chronic Daily Intake (CDI):

CDI (mg/kg-day) = average daily dose (mg/kg) / body weight (kg)

= 0.1 mg/L * 2 L / 70 kg

= 0.00286 mg/kg-day

and then the risk from the CDI and the potency factor:

Risk = CDI * Potency

$$= 0.00286 \times 6.1 \times 10^{-3} mg/kg-day$$

$$= 17.4 \times 10^{-6}$$

Or, over 70 years, an upper bound estimate of the probability of cancer due to chloroform is about 17 per 1,000,000. Dividing by the 70 years of exposure is 2.48 x $10^{-7}$, or 0.24 cancers /

1,000,000 population per year. The rate of cancer in the US is now 1,930 / 1,000,000 per year. Thus, the extra cancer from chloroform is calculated to be negligible.

Of interesting note are the TTHM standards in other countries (Table 5.4). Values range from 1 to 100 μg /L, depending on the country.

**Table 5.4: Worldwide TTHM Standards**

| Country | TTHM Standard | Source |
|---|---|---|
| Sweden | 20 μg/L guide, 50 μg/L limit | Kuivinien [1999] |
| Germany | 10 μg/L | Rodriquez [2001] |
| Canada | 100 μg/L | Rodriquez [2001] |
| EU | 100 μg/L | Simpson [1998] |
| Netherlands | 1 μg /L | Graveland [1998] |

The Center for Disease Control [2001] states the following about THMs:

> Another concern about chlorination of water is the health effects of trihalomethanes. Trihalomethanes are disinfection byproducts that are formed when hypochlorite is used to treat water with organic material in it. Research suggests that, over a lifetime, the risk of bladder cancer increases with chronic consumption of trihalomethanes. In populations in developing countries, however, the risk of death or delayed development in early childhood from diarrhea transmitted by contaminated water is far greater than the relatively small risk of bladder cancer in old age.

Thus, although some countries stringently regulate TTHM concentrations, both the CDC and WHO strongly state that the danger due to bacterial contamination of drinking water in childhood in developing countries is far greater than the risk of cancer later in life.

## 5.3 THM Sampling Studies and Models

A plethora of studies have been conducted analyzing the THMFP of a certain water plant or subarea or region. These models were investigated to provide a guideline to developing an equation to model the production of THMs in Haiti.

## 5.3.1 THM Sampling Study Results

TTHM results found in a wide variety of studies show most TTHM concentrations are below the USEPA standards and far below the WHO guideline values (Table 5.5). The percentage of brominated compounds varied widely across studies, with higher concentrations in areas near ocean water due to the concentration of bromine in sea spray.

**Table 5.5: TTHM Results in Targeted Studies**

| Site | TTHM Results | Notes | Author |
|---|---|---|---|
| Hong Kong | All samples below 100 µg/L. | Highest percentage of brominated (64%) compounds was on an island. | Yu [1999] |
| Florida: bottled, municipal, and well water | All samples below 25 µg/L. | Few brominated compounds. | Gibbons [1999] |
| Athens, Greece | All samples below 80 µg/L.<br>One sample above 100 µg/L. | Brominated compounds were 90 %.<br>Higher TTHM concentration in summer. | Golfinopoulous [1998]<br>Golfinopoulous [2000] |
| Taiwan | Samples below 100 µg/L if TOC less than 4 mg/L. | | Chang [1998] |
| Taiwan | Samples ranged from 3.53 – 191 µg/L. | 90 % of residents do not drink tap water, but drink mountain or spring water, can smell chlorine. | Kuo [1997] |

An interesting case is Australia, which would like to regulate a wide range of DPBs, more in fact than either the USEPA or WHO does (Table 5.6) [Simpson, 1998]. However, as can be seen, there is not enough data to regulate a number of the compounds. Simpson [1998] investigated DBPs in predominantly surface water sources throughout Australia. THMs ranged from 25 – 191 µg/L (all below the Australian standard of 250 µg/L). The speciation differences between chlorinated and chloraminated waters are of note. In chlorinated water, 46 percent of DBPs were THMs, and 42 percent were chloroacetic acids (CAAs). In chloraminated supplies, 24 percent were THMs and 54 percent were CAAs.   Simpsons' results indicate the limiting DBPs in Australia will be chloroacetic acid and chloral hydrate.

**Table 5.6: Australian DBP Standards**

| Compound | Standard (µg/L) | Compound | Standard (µg/L) |
|---|---|---|---|
| Chloral hydrate | 20 | Cyanogen Chloride | 80 |
| Chloroacetic acid | 150 | Dichloroacetic acid | 100 |
| Chlorophenols |  | Formaldyhyde | 500 |
| 2-chlorophenol | 300 | Halocetonitriles | ID |
| 2-4 dichlorophenol | 200 | MX | ID |
| 2-4-6-trichlorophenol | 20 | Trichloroacetic acid | 100 |
| Chloroketones | ID[3] | Trihalomethanes | 250 |
| Chloropicrin | ID |  |  |

## 5.3.2 THM and THMFP Models

A number of models have been developed to determine TTHM or THMFP mathematically from source water characteristics. This allows for calculation of TTHM or THMFP without the need for intensive sampling.

Golfinopoulous [1998] developed a model depending on chlorophyll a, pH, bromide concentration, season, temperature, and chlorine concentration according to the following equation:

$$\begin{gathered} TTHM = 13.54\ln(\text{chlorophyll a}) - 14.47\,pH + 230.25[Br^-] + 139.62[Br^-]^2 \\ - 25.28\,(\text{Summer}) + 110.55\,(\text{Spring}) \\ - 6.59\,(\text{Temperature} * \text{Spring}) + 1.48\,(\text{Temperature} \times [\text{Cl}]) \end{gathered}$$

---

[3] In Development:  There is currently insufficient data to develop a standard.

This model was accurate within 20 percent, and indicated that TTHM concentration increased with chlorophyll a concentration, bromide ion concentration, whether samples were taken in the spring, temperature, and chlorine concentration. TTHM concentration decreased with pH, sampling in the summer, and temperature and spring.

Rodriquez [2001] developed a model for THM production in finished water in three plants and THM production in points in the distribution system. For two of the plants, temperature (C) was the only significant variable noted, with the equations of the form:

$$\text{TTHM} = 0.057\ \text{Temp}^2 + 21.3$$

Thus here TTHM concentration increased with temperature. For the third plant temperature (C), pH, and flow rate were determined to be significant to form the equation:

$$\begin{aligned} TTHM &= 0.680 \times THM\ (\text{raw water}) + 0.031 \times \text{Temp}^2 \\ &\quad - 34.8\,pH - 0.0015\,Q + 298.2 \end{aligned}$$

Where again TTHM concentration increased with temperature, decreased with pH, and decreased with flow. The equations added terms for TTHM concentrations when leaving the treatment plant when adapted for TTHM concentrations at the tap. Despite the increase of TTHM distribution system, few samples at the tap were above 100 µg/L. All samples were below 60 µg/L before distribution.

Korshin [1997] investigated the link between UV absorbance and DBP formation, because aromacity of natural organic matter (NOM) is destroyed as chlorine attacks chromophores in the NOM. Total organic halogen (including HAA) formation was linear with change in UV absorbance at 272 / cm by the equation TOX = 10834 delta UV 272. THM formation was linear with the change in UV, but was extremely pH-dependent with increasing slope at increasing pH and the best-fit line did not pass through the origin. Korshin concluded that when free chlorine species first attach UV-absorbing groups, these reactions generate little chloroform. The chloroform is produced later as subsequent reactions proceed. All samples were completed in water with no bromine, thus chloroform was the only THM species formed.

Garcia-Villanova [1997] determined a model for water in two treatment plants using River Torres water in the city of Salamanca, Spain. Temperature (C), year of study, and pH were the only variables significant to chloroform production based on the following equation at the end of the distribution system. The coefficients were calculated, but included in the final equations as variables.

$$\ln CHCl_3(\mu g/L) = \alpha_1(\text{Year}\,1\,\text{or}\,2) + \alpha_2 D + \beta_3 T^3 - \beta_4 T^4 + \chi pH^2 + \varepsilon$$

Observed versus fitted values had a r squared value of 0.99.

As can be seen, some simple and some extremely complicated models to determine TTHM have been developed. One of the goals of the Haiti THM project was to develop a model that used only parameters that could easily be tested in the field and could also be understood mechanistically.

# Chapter 6: Field Sampling and Observations

From January 7th through January 28th, 2001, the four students in the Haiti M.Eng. group and a GWI guide, Bill Gallo, spent time in Haiti completing field work. There were three goals associated with my portion of the field work: (1) completing water quality sampling; (2) observing the program in operation; and (3) meeting and speaking with the people involved in managing the program.

All three goals were accomplished by visiting six of the seven communities in which GWI has programs for periods of 1 to 4 days each.

## 6.1 Sampling Plan

In each community visited, two concurrent studies were completed.

1) GWI Testing

GWIs standard testing procedure samples chlorine concentration in the top and bottom bucket, and collects a finished sample for bacteriological analysis. This sampling protocol is random, and purifiers to be tested are chosen by pulling purifier numbers out of a hat.

Chlorine concentrations were measured with a colorometric pool test kit that tests for residual chlorine. The kit has two receptacles: technicians fill the left side with water from the top bucket and the right side with water from the bottom bucket. After the addition of one drop of testing solution, the color in the left receptacle (top bucket) should be orange, and in the right receptacle (bottom bucket) light yellow. These colors correspond to correctly adding a capful of bleach in the top bucket and five drops of bleach in the bottom bucket. The receptacles are rinsed with the purifier water prior to use. Correct or incorrect color was recorded with + or – signs.

For bacteriological contamination testing, finished water (from the spout of the purifier) was added to Lauryl Tryptose broth in autoclaved glass bottles and kept in a cooler filled with 2 to 4 inches of 35 C water for 48 hours. After 24 and 48 hours the bottles were investigated for a color change from clear brown fluid to cloudy fluid. The color change indicates presence of total coliform. Color change was recorded as a positive coliform test.

The results of this testing were used to calculate the percent correct usage of the community. GWIs goal is 70 percent correct usage in each community. This test was conducted in all communities except Dumay.

2) THM Testing

To determine the amount of THMs generated in the purifier, a two-pronged approach was taken: (1) raw source water was collected, analyzed before purification, and filtered through a purifier; and (2) finished water from the purifier was collected and analyzed at MIT. This data was also used to model the formation of the THMs mathematically.

Raw source water was analyzed for color, turbidity, pH, temperature and nitrate in Haiti (Table 6.1).

**Table 6.1: Raw Water Analysis Parameters in Haiti**

| **Parameter** | **Method of Analysis** | **Calibration Procedure** |
|---|---|---|
| Color | Visually | Not necessary |
| Turbidity | LaMotte Model 2020 Portable / Benchtop Turbidimeter | At 1 and 10 NTU's weekly. |
| PH | ColorpHast pH Strips: 5 – 10 and 0 – 6 | Not necessary |
| Temperature | Envirosafe Celsius Thermometer | Not necessary |
| Nitrate | LaMotte Nitrate-N Test Kit | Not necessary |
| Raw Water THM | Collected one 45 mL VOA vial, analyzed at MIT | Not necessary |

Other parameters noted at the source were:

- Description of the source.
- Distance of walk to the source.
- Difficulty of walk to the source.
- Estimated flow per source.
- Estimated number of people using the source.
- Soil description, including whether or not the soil reacted with vinegar, an indication of limestone (or $CaCO_3$) soils.

Source water was then collected using clean, locally available containers and transported to a nearby purifier. The purifier was emptied, cleaned, and chlorinated, and the source water run through the purifier. Finished water was collected into two 45 mL VOA vials from the spout and checked for the correct amount of chlorine using the pool test kit. Through a translator, the family was asked the following questions:

1. How many people use the purifier?
2. Who collects the water for the purifier?
3. How many times per day is the purifier used?
4. Where do you normally get water for the purifier?
5. Do you have any problems with the purifier?
6. How old is the cotton filter?
7. How old is the carbon filter?

In addition, characteristics of the villages such as number of children in schools and community development projects were noted.

## 6.2 Results: By Village

### 6.2.1 Ferriere

Ferriere is a small community near the Dominican Republic border in the north of Haiti. It is about a three-hour drive east of Cap Haitien. About one hour south of the ocean, Ferriere is a flat, small community. Houses are placed near each other on grided side streets and one main road. We were not able to meet the American nun who works and lives there, Sister Pat, because she was in the U.S. at the time.

The local Catholic Church, through Sister Pat, does quite a bit of community organizing here. There is a water committee, maternal health programs, and other community education activities. The Church put in nine identical hand-pump groundwater wells throughout the community fifteen years ago. The Church also purchased and installed a large ceramic filter for the town that did not work. They then went to GWI for another method to provide clean drinking water. Groundwater depth was 17.2 feet in one open well (not used for drinking water supply). Villagers can also always purchase clean water in the Dominican Republic.

**Figure 6.1: Well in Ferriere**

Soils in Ferriere are conglomerate alluvium, with some clay present. The soil did not react with vinegar, indicating that no limestone was present. Due to the number of the wells installed by the church, the longest distance to water is a 15-minute walk along flat paths. The wells have never run dry and are easy to pump. We did not see anyone waiting in line for water longer than a few minutes. Samples were collected from two different public wells and run through the purifier of a water committee member (F-1) and one of the technicians (F-2). Temperature of the groundwater in the wells was 29 degrees Celsius. Nitrate was 44 ppm at F-1, which was near a large agricultural field. Nitrate was 0.0 ppm at F-2. Turbidity was low in both wells: 0.00 in F-1 and 1.08 in F-2. pH was 7.5 in both wells. The water committee member's purifier is used for 13 people in the family, filled twice per day, and two family members walk to carry the water from the well. The technician's purifier is used for five people in the family, used once every two days, and the girl who works for the family collects the water.

The two technicians for Ferriere, Mary-Marthe and Suzanne, are dedicated and well respected. They visit homes with purifiers four times per week, have designed uniforms they wear while they work, and have a good understanding of the purifiers. They purchase Jif (a bleach from the Dominican Republic) at H$17 a gallon and resell it at cost to the community. Both are widows, and were selected by Sister Pat and the water committee to be the technicians based on their skills and their need.

**Figure 6.2: Mary-Marthe & Purifier**

On rounds with Suzanne, we noticed that all but one of the purifiers was covered with homemade cloth (some quite fancy), or plastic. In addition, everyone knew how to help Suzanne complete her chlorine testing. They gave her a cup to help her test and understood the results. Houses were spaced close together and rounds were easy to complete.

Of interesting note is that the top bucket in Sister Pat's house had the wrong amount of chlorine – only five drops instead of five mL. In addition, the program began in May of 2000 and carbon filters had not been changed except when they had broken.

### 6.2.2 Bas Limbe

Bas Limbe is approximately one hour west of Cap Haitien on the northern coast. The community is larger and more spread out than Ferriere, and is significantly more mountainous. The Rectory where Father Dubois lives is at the top of the largest hill, overlooking the town, and with a view of the ocean. Father Dubois runs a radio station for the valley and likes electronics. He was polite to us, but it was clear the water project really is not his focus. A medical team from Indiana who visits twice per year noticed a high incidence of diarrheal diseases, and sponsors the water project here because they feel the diarrhea is caused by poor water supply.

Although water is not scarce in Bas Limbe, many people walk long distances to collect what they consider a clean source of water for their drinking water. There is one pump in the center of town that people use. There are also spring-fed sources up in the hills and in the town that people walk to, as well as a private well at the rectory.

The first sampling site in Bas Limbe (BL-1) is a spring flowing into a shallow pool in the valley. Turbidity was the highest found in Haiti at 4.21, probably due to the medium brown alluvium silty clay of the cutout falling into the water. pH was 6.5, temperature was 18 C, nitrate was 2.2 ppm, and the source is approximately five minutes flat walking from the main road. The purifier closest to the source serves 12 persons, is used twice per day, and the adults carry the water from the source. They have had problems with the spigot leaking; and on the day we were there the purifier was in pieces, and there was no chlorine in the house. The age of the cotton and carbon filters were seven months. After 30 minutes, some suspended solids had settled to the bottom of the bucket. When we returned to collect the finished sample, the family had not run the purifier. We started it and returned the next morning to collect the finished water.

**Figure 6.3: Spring in Bas Limbe (BL-1)**

The second sampling site (BL-2) was from the public town pump in the center of town. The well is located approximately 10 feet from a small (five foot wide) river and close to the main path in town. Although this pump was harder to pump than in Ferriere, there was good flow. Temperature was 27 C, pH was 7.0, nitrate was 1.1 ppm, and turbidity was 2.62. The purifier closest to the well serves 20 neighbors. It was set up in one house, and all the kids in the vicinity were familiar with it. The purifier is run twice per day, with the youngest and oldest children sharing the task of collecting water. They have had problems with a broken check valve, and the cotton and carbon filters were each six months old. There was prepared water, correctly chlorinated, in the purifier when we arrived.

**Figure 6.4: Well in Bas Limbe (BL-2)**

The third sampling site (BL-3) is a 15-minute hike up a small river to a spring flowing into the river. It was difficult walking up through the river itself and there were a significant number of women and children walking up and down to collect water. Women were washing clothes in the river. The turbidity of the spring water was 0.09, pH was 6.25, temperature 25 C, and nitrate 2.2 ppm. Soils were the same medium brown silty clay as in the other two sites. The purifier used for this sample was the original Bas Limbe purifier in the Rectory. The carbon and cotton filters were seven months old. This purifier is used twice per day and the employees fill it with the private well water from the backyard. The cotton filter was discolored to yellow because of the sediment from water in the well.

**Figure 6.5: Spring in Bas Limbe (BL-3)**

After I collected the finished sample in BL-3, the employees poured out the spring water and reran the purifier with well water. This is a something I noticed across Ba Limbe. As we were rounding to do the GWI testing, we asked people where they collected their water from to use in the purifier. People very specifically had one spring or source or well they used. They felt this one was clean for a specific (unknown) reason. This did not correlate at all with distance to source. People from the other side of town walked one hour to the spring in BL-3, whereas people near the spring in BL-3 walked 30 minutes to the opposite side of town to a different spring. Some education about safe water sources could be useful here. In addition to the springs and wells, there are a number of surface and runoff streams in Bas Limbe. No one said they used this for drinking water, but it could be possible some people use this easily obtained water in the purifiers.

The two technicians in Bas Limbe are younger men who clearly were not comfortable interacting with the community. On rounds here, we found a number of the houses without chlorine, unused purifiers lying in pieces, and the technicians did not know how to use the chlorine tests kits. An unusually large number of children followed us around Bas Limbe, our record was 43.

To address these issues, Bill Gallo led a meeting with Father Dubois, Mary-Marthe (who accompanied us from Ferriere), the technicians, and us. Father Dubois mentioned that he feels the water committee, the technicians, and himself all have different directions and ideas. He feels out of the loop and unsupported, especially because he was overruled on how much to charge families for the purifiers and for the chlorine. Thus families were not paying enough for the chlorine to recoup the cost of purchasing the gallon. The technicians asked for bicycles in the meeting (the technicians in Dumay have them because of the distances they cover). Bill mentioned bicycles might be forthcoming if they reached the 70 percent correct usage rate. It was decided at the meeting that the Bas Limbe technicians would stay with Mary-Marthe and Suzanne in Ferriere for a week, and then Mary-Marthe would visit Bas Limbe once per month to work on improving the program.

### 6.2.3 Fon Veret

Fon Veret is a small community about two hours west of Port-au-Prince on the Dominican Republic border. The first thing you notice in Fon Veret is the swath cut through the center of town from flooding due to Hurricane George. There is a 50-meter wide section in the valley between the mountains to either side where nothing is living. It is filled with an outwash of 2-to-6-inch diameter limestone rocks that are very difficult to walk on. The town is built on an old river bed. The river has been dry since the time Haiti was a French colony, but the path of the water in George killed 500 people.

**Figure 6.6: Hurricane Damage in Fon Veret**

A young American teacher of English and juggling named Matt Cyr is the person who organizes the water program here. He lives in the Rectory with Father Belneau, who is supportive of the program, but is already overcommitted as he has one parish, ten sub-parishes, two sermons each Sunday, and is the head of the Development Committee in Fon Veret. The two technicians in Fon Veret are Dieumaitre and Helene. Both gave up day jobs to become technicians and are dedicated and serious.

Water is scarce in this part of Haiti and there is only one source available, about a 30 minute walk up one of the mountains. In addition to that, some people have cisterns that they use for personal use and to sell at around H$1 per 5 gallon bucket to people in the community. The rectory obtains water from a source seven kilometers away that they can drive to and fill up multiple containers at once. Two samples were taken in Fon Veret, one from a cistern and one from the Karetye source up the mountain.

**Figure 6.7: Karetye Source in Fon Veret (FV-1)**

Matt suggested a sunrise hike to Karetye for FV-1. At 4 AM the path to Karetye was literally a highway of small children walking up and down collecting water before school. Young children carried one-gallon jugs in each hand, older girls and women carried 5-gallon buckets on their heads. The path up the mountain is steep and difficult to walk on because of the two to three-inch-diameter limestone rocks. This source was the only place we saw a Haitian (a boy) slip on the path and spill his water. The path follows a river that runs dry before the valley. At a particular bend in the river, about 30 minutes up, people stop and collect water. There were approximately 100 people there at 5:30 AM. Turbidity was 0.00, pH 6.0, nitrate 13.2 ppm, and temperature 16 C. The soil was limestone rock and boulders with very little alluvial topsoil. Farmers on the hill created dams in the river to collect the sediment. They then laid the sediment on the rock about one inch thick and 12 inches wide in rows to grow crops on the mountain. Karetye water was filtered through the Rectory purifier which was three months old, used by three to many guests, and run twice per day.

The second sample in Fon Veret (FV-2) was taken from the church cistern. One side of the roof of the school drains into a large cistern. The turbidity of the cistern water was 0.26, the temperature 21.5 C, pH 6.0, and nitrate 2.2 ppm. Cistern water was filtered through a neighboring purifier used by a family of four, three times per week. The mother collects the water and the filter is three months old. This family has a cistern, although it is 50 years old and leaks.

**Figure 6.8: Cistern in Fon Veret (FV-2)**

**Figure 6.9: Roof Draining to Cistern**

Fifty-two purifiers were sent to Fon Veret in October, 2000. The purifiers were delivered in the middle of the night and left in the rocks. Matt mentioned that he scrambled around trying to find all the pieces and that he noticed a number of the carbon filters had leaked significantly. He estimates that 1,200 families in the immediate vicinity would want a purifier, and that there are 6,000 total families in the surrounding area. Matt purchases chlorine by the gallon in Port-au-Prince, and there is a bleach distributor in Fon Veret who sells it at cost.

Walking around on rounds we noticed that this was a wealthier village in general than the others; the houses were more solid, people had shoes, and there were more animals, radios, and elderly people. Also, more students were in school and so many fewer children followed us around here. In addition, many people said "Hello, how are you?" to us, a product of Matt's English classes. Many of the purifiers in the area were covered.

Matt very much wanted to have a Water Committee meeting with Bill before we left. Bill agreed, and six members of the water committee, Matt, Bill, Wilburn (a Master Technician from Dumay), and we met in the Rectory. After a prayer and excessive thank you's, the technicians spoke about problems they were having. Helene mentioned that some families did not listen to suggestions and that it is hard to find water to fill the purifier. In addition, people were questioning her about how to use already randomly chlorinated cistern water in the purifier.

Dieumaitre mentioned that all the families receive the technicians well, that families sent thank yous, and that stomach acid is no longer a problem.

The topics the water committee spoke of were:

1. The first proposal the water committee brought up was a plan to build additional cisterns using donated local labor and money from a sponsor. Bill approved of the idea, but mentioned this was not GWIs expertise, and the water committee could decide to do this on its own.
2. They also suggested uniforms for the technicians, and Bill spoke of Marie-Marthe and Suzanne.
3. They brought up the fact that Helene and Dieumaitre had not yet been paid for their months of work. People spoke at length of how technicians are paid: Matt raises money as the sponsor which is given to GWI, which is sent to Nathan Dieudonne as part of the Bethel Foundation, which is then distributed to the technicians from Dumay. In addition, the technicians had been told they would receive their salary frozen at the exchange rate of 17 Gourde (3.4) / U.S. Dollar. As of January 2001, the exchange rate was roughly 21 Gourde / U.S. Dollar. Nathan did not seem to be aware of this conversion when we spoke with him.
4. They asked when purifiers would be let through customs and Bill spoke of needing signatures and the fact that buckets would be purchased in Haiti from now on to prevent this from happening again.
5. At the end, Matt showed Bill a letter from Phil that outlined some agreements between GWI and Fon Veret. The letter was cc'd to Bill, but Bill never had seen it before. In addition, the technicians had a few questions for Wilburn.

I found this water committee very impressive - they were thoughtful, had great ideas, and were well organized. I realized that this was the only water committee we had contact with in Haiti and I wondered how often GWI meets with the committee, because I found they could be very helpful.

### 6.2.4 Barasa

**Figure 6.10: Barasa Agriculture**

Barasa is a small mountaintop community about 45 minutes from Fon Veret with an amazing view down the mountain into the Dominican Republic. The program has been unsteady here, for water availability is the worst we saw in Haiti, and in many seasons it is difficult to collect five gallons at once. There are two water sources here, one stream about a 30 minute walk named Sen Lwi and cistern water in town. Sen Lwi is so slow moving that someone dug out a ponded area so that you can put a one-gallon bucket flat to fill it. It is also surrounded by animal feces from the donkeys that are led there to collect water. Turbidity was 0.09, pH 6.0, nitrate 13.2 ppm, and temperature 16.5 C. The soil is alluvium clay and limestone, with large rock and boulders. This is the only source we visited where we saw no girls or women collecting water. At this site, we saw only boys, who ran cutting the switchbacks and drummed on the plastic bottles. The littlest ones had strings tied around their hands and the neck of the bottle because their hands were not big enough to grasp it. In the dry months people wait to fill their bottles here.

**Figure 6.11: Source Sen Lwi (B-2)**

Sample B-2 was collected from Sen Lwi and run through Mr. Dondon’s purifier. Between 4 to 9 people use the purifier, which is run once per day. Members of the family collect water from the cistern out back, which was installed in 1991 and is 12.7 by 10.5 feet by an unknown depth. The purifier was 13 months old and the carbon filter had been changed at 9 months, so the new carbon filter was 4 months old.

Sample B-1 was collected from Mr. Dondon's cistern and also run through Mr. Dondon's purifier. The turbidity in the cistern was 0.10, pH was 6.0, temperature 16 C, and nitrate 4.4 ppm. The cistern runs dry in February, and then the family walks to the source.

In Barasa, there is one person who sells the bleach out of his home, two technicians, and one advisor. The program seems to be running better here than before, but the program here is still difficult because of the lack of water. The area is large and spread out, with three circuits for the technicians. Matt had taught here for one year before moving to Fon Veret and lived with the advisor to the program, Mr. Dondon. Mr. Dondon is on the water committee and used to be a technician, but conflict of interest and led GWI to suggest he become an advisor.

### 6.2.5 Les Palmes

Les Palmes is not only a mountainous community, it is on top of the mountain, in the mountaintop valleys, and then on the next peaks, too. Les Palmes covers a large area about two hours west of Port-au-Prince and then two hours up a "road" to the top of the mountain. When we first arrived Father Bruni, an amazingly energetic priest, fed us and then immediately set us to work feeding 900 school children in the elementary school adjacent to his Rectory. He showed us the additions to the Rectory, the running water, and second floor, asked if we noticed the new second elementary school coming up the hill, showed us the site for the high school that is under construction, and the new cistern pump system. All of this had happened in about a year. Before he was in the Church, Father Bruni was a tap-tap (imagine a pick-up truck with many Haitians in back driven by a rabid New York taxi driver on roads that are really just a collection of potholes and you have the picture) driver and after becoming a priest he was an avid supporter of Aristide in his first presidency. His assignment to Les Palmes six years ago could be seen as punishment by the Church, for although his talents are incredibly useful in Les Palmes, it is a remote parish. He no longer advocates for any political party. He is currently negotiating to leave Les Palmes in three years instead of the standard six year second rotation.

Bail, Father Bruni's English-speaking assistant, who is planning to move to the U.S. where his wife lives, organizes the water program here. There are eight technicians, Bail, 600 purifiers, and nine circuits.  Currently, Bail is training one of the technicians to take on the lead role when he leaves.  On rounds, I was impressed with the ability of the technicians, the knowledge of the families, and the distance and elevation these technicians hike to do their rounds.  The houses are far apart because the first 400 purifiers were distributed by Father Bruni in Church without thinking of placement or training.  After (most of) the 400 purifiers were accounted for, circuits were set up, and technicians trained.  The second batch of 200 purifiers was distributed to fill in gaps within the first set of purifiers.

Bail spoke about the program as he organizes it in Les Palmes and mentioned:

1. Each month all the families meet together with Bail and the other technicians and talk about the purifier.  How it is important to always drink clean water, for if you stop drinking clean water after you are used to it, then you will get sick easier.  They answer questions about what to do if you are leaving for a bit.  They suggest bringing water with you or boiling water before you drink.  If people do not come to meetings, they must turn in their purifier.
2. Families are encouraged to share purifiers.
3. Each house is visited once per week by a technician.  There are three technicians for every 200 purifiers.  They are paid H$240 - 250 / month.  When they visit a home, they ensure the families know how to use the purifier, check the water in the purifier, and fix any problems.  When they leave, they ensure that the purifier is working.
4. Common problems with the purifier are uncapped carbon filters that leak and cracked buckets.  A new bucket is H$10.   In addition, people want purifiers for their families in other areas.  It is hard to keep the purifiers in Les Palmes.
5. Bail said “we never change carbon” when asked about carbon replacement.
6. Technicians meet once per week.  They are reminded to speak kindly to the families.
7. Bail hires technicians based on three factors:  1) Can they read and write?  2)  Are they a leader?  3)  Are they a good person?  There are no women technicians in Les Palmes.
8. The Water Committee assembles names of families to get new purifiers.  There are 11 members, three women and eight men, who meet once per month (before the large family meeting).  There are now Protestants on the Water Committee, although there were not any at the beginning.

9. The members of the Water Committee sell chlorine for their area. Bail purchases 10 - 20 gallons of bleach at a time in Port-au-Prince.
10. The doctor in the community has noticed less diarrhea and has community groups talking about women and health. The doctor is waiting for 200 purifiers to distribute.
11. Bail envisions 6,000 purifiers for the community of Les Palmes, installed in batches of 200 with three new technicians each.

One interesting note is that Bail and the Les Palmes technicians were the only people I noted who used the GWI data collection sheets. Also, Father Bruni did not know the correct directions for purifying and his purifiers had low chlorine.

Bail mentioned there are approximately 100 captages in Les Palmes and a number of springs and sources. The French organization InterEd installed the captages. Four samples were collected in Les Palmes: one from a cistern, one from a captage, one from a spring, and one from a stone captage structure.

The first sample, LP-1, was collected from the cistern in the back of the Rectory. Runoff from the school roof is stored in the captage and pumped via pipes indoors to the Rectory. The turbidity of the water was 0.35, pH was 5.5, temperature 17.5 C, and nitrate 1.1 ppm. The purifier in the Rectory is run twice per day and serves 15 people. The carbon and cotton filters were 9 months old.

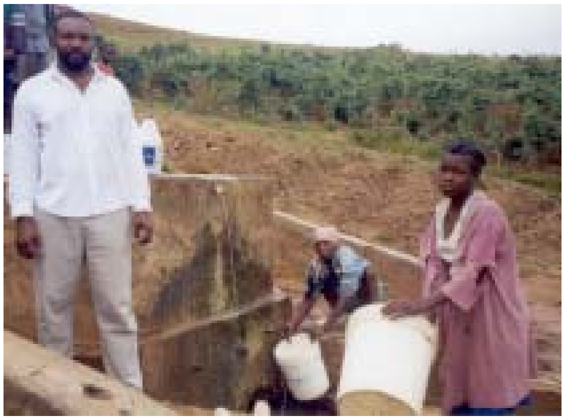

**Figure 6.12: Les Palmes Captage (LP-2)**

The second sample, LP-2, was collected from a captage that runs freely 24 hours a day throughout the year. The soils in the area were red, iron rich, and good for farming. They do not react with vinegar. The turbidity of the captage water was 0.95, pH was 5.5, nitrate 6.6 ppm, and temperature 16 C. The captage water was run through a nearby purifier which serves six people and is used once every three days.  The girl in the family collects the water, always from the captage.  The carbon and cotton filters were both one-year old.

The third sample, LP-3, was collected from a spring formed at a limestone hillside outcrop overlain by unconsolidated soils. Only 2.5 gallons of water could be collected here, so we ran the purifier with half the chlorine.  The turbidity of the water was 2.3, pH was 4.75, nitrate 4.4 ppm, and temperature 15 C.   The nearest purifier was 10 minutes away, served four people, and was run once every three days.  The family normally used captage water from LP-2, and the cotton filter was stained red. The cotton and carbon filter were both one-year old.

**Figure 6.13:  Les Palmes Spring  (LP-3)**

The fourth sample, LP-4, was collected from a stone structure, at the bottom of a hill, into which one reaches to collect the water.  It is a steep walk down a gravely flat hill about 20 minutes from the road.  When we arrived, approximately 10 people were collecting water and washing here. The turbidity of the water was 0.65, the pH 6.25, the nitrate 17.6 ppm, and the temperature 20 C. The soil was limestone.  This water was collected and run through Father Bruni’s purifier in his bedroom.  This purifier is used once per week, normally using cistern water, and the cotton and carbon filters were one-year old.

**Figure 6.14:  Les Palmes Captage (LP-4)**

### 6.2.6 Dumay & Surrounding Area

Dumay is a lush, fertile valley surrounded by mountains on one side and bordering the outskirts of Port-au-Prince on the other. Bananas, mangos, sugarcane, chives, vegetables, and other crops are grown in the valley with small irrigation ditches flowing with water surrounding the crops. Water is piped from three captages (installed by Plan International) halfway up the hillside down to Dumay proper. Captage water runs freely by gravity feed 24 hours a day, seven days a week, and is a source of envy in other communities. The captages are essentially stone huts with one vertical pipe rising up that captures groundwater springs as they rise to the surface. Horizontal underground pipes run down the mountain to free flowing fountains, thus preventing surface contamination of clean groundwater.

Captages are from 6 to 30 feet deep, and need to be cleaned every one to two months. A technician is lowered into the pipe and removes the blockage (possibly iron bacteria) from the pipes. The fountains stop when the pipes are blocked up. The technicians mentioned that each captage flows to different fountains, although this seems. It seems more possible that the pipes would join together and then distribute at the base of the hill. One of the three captages was blocked when we were there, and the fountain directly downstream had stopped flowing, but none of the others. The technicians mentioned that this particular captage only served the one fountain.

**Figure 6.15:**
**Dumay Captage & Technician**

The captages serve Dumay itself, in the valley at the foot of the mountains. The surrounding communities: Roche Blanche to the north, Pond Dumay, Gallet-Doulla, and Peniaer (bordering on Port-au-Prince) to the west are all served by hand-pump wells that were installed by a variety of NGO groups. Peniaer also has a captage system that Wilbern mentioned was installed by the

Duvalier government 15 years ago. Of interest is a large cement water tower installed by CARE in Roche Blanche, 50 feet up with a 14 x 4 x 6 foot water storage tank. It is next to a pump well that was locked and had a diesel pump next to it. Water was pumped up to the tower and then flowed down to shower stalls and taps. Parts of the pump were stolen, however, and the tower and the well were no longer usable. There were still four inches of water in the tower, because the outlet pipe is four inches above the bottom of the tank.

There are a number of technicians in Dumay, including all of the Master technicians, who have more responsibility for the operation of the program than the regular technicians. They form a close knit, friendly group who are often seen talking and working near Nathan’s church. There are nine circuits that technicians rotate through, in Dumay and the nearby surrounding villages. The technicians in Dumay have bicycles to assist them in their rounds. The technicians in Dumay are not only responsible for the Dumay area, but also train all of the technicians and assist in organization of all of the community projects. Of note is that in Dumay and the surrounding area children were seen drinking from roof runoff and from captage fountains as they collected water. In addition, animals were seen drinking from well areas. Education by the technicians about safe water practices is needed.

A total of six samples were taken in Dumay, spread out over the many subcommunities in the Dumay area. The first sample, D-1, was taken in Gallet from one of five identical pump wells installed five years ago. The pH was 6.25, turbidity 2.1 NTU, nitrate 8.8 ppm, and temperature 24.5 C. The walk to the well was short and flat, and the well was easy to pump. The valley is limestone rock. Thirteen people in the family use the purifier, which is run twice per day. The purifier was 18 months old and the carbon had never been changed.

D-2 was taken in Peniaer from the same type of pump well, installed two years ago by Plan International. The well is on flat easy walking ground. The pH was 8.0, turbidity was 3.0 NTU, nitrate was 17.6 ppm, and temperature was 25 C. Ten people use the purifier, which is run twice per day. The age of the purifier and the filters was 15 months.

D-3 was taken in Pond Dumay from the same type of pump well. The walk to the source is flat and easy, with good flow in the well. pH was 7.5, turbidity was 1.4 NTU, nitrate 22.0 ppm, and temperature 24 C. Six people use the purifier, which is run twice per week. The age of the purifier and the filters was 15 months.

Figure 6.16: Dumay Pump Well

D-4 was taken in Dumay from the captage fountain water. pH was 8.0, turbidity was 1.3, nitrate 8.8 ppm, and temperature 23.5 C. Three people use the purifier that this water was run through. The purifier is used two times per week and both the purifier and the carbon filter were four years old. This was the oldest carbon filter seen. Additional water from the same captage was collected, (D-5) and run through a less aged purifier. A family of 6 use the D-5 purifier twice per week, and the carbon was six months old.

Figure 6.17: Dumay Captage Fountain (D-4, D-5)

The last sample in Dumay, D-6, was collected at the Duvall pump well, with good flow and easy access. pH was 8.0, turbidity was 0.40 NTU, nitrate 17.6 ppm, and temperature 25.5 C. The purifier used was also four years old, but the carbon had been changed twice, most recently three months ago. This purifier is used twice per day by 7 people.

#### 6.2.6.1 Family Meeting

We happened to be in Dumay on a day that the technicians had called a meeting for families from one area that was doing poorly. Approximately 80 people, about 75 percent women, came to the church in their best clothes for a meeting. The technicians stood up front and, in lecture style, talked to the group for approximately 45 minutes. A number of people walked in late, many people were distracted, the room was hot, it was difficult to hear, and our presence was a distraction for those around us. A rough outline of the lecture, as translated by Wilbern, is as follows:

> The water in the pump is not good for children and persons because of bacteria. This is a big project, Americans come to help us. We must keep the purifiers clean. Children should not drink from the pump. Chlorine must be new when you use it. Leave chlorine in the top for 30 minutes. Do not take water from side of road - put clean water in the purifier. Ice made with bad water will make you sick. Life is life. The Master technicians organize schools to talk about not having bad water, diarrhea. The system is of much importance for every family. It is very expensive to help and much, much trouble to continue. You must know importance. Babies die. Every person in Dumay now spends not too much money on doctor - this is a responsibility. American people are busy and pay ticket to come here so we don’t have to boil water anymore. Without Clorox, the purifier will not work.

The lecture revolved around these themes and was repeated, emphasizing responsibility. Talking with Matt in Fon Veret about the style of this meeting, he mentioned that this is how school is normally conducted in Haiti. A teacher drills students in subjects using a repetitive, lecture format (often in French, while most students only speak Kreyol). Although people were obviously bored during the meeting, Matt mentioned this style is normal and would be expected. From my U.S. perspective, I would love to recommend demonstrations, a question and answer period, or a participatory activity to involve the group, but that might not be appropriate. The meeting was initiated by the technicians because they saw a problem and wanted to correct it. Neither Nathan nor GWI were involved in the planning. The Haitian technicians obviously understand and are managing the water program here. This is exactly what GWI envisions.

#### 6.2.6.2 Carbon Filter Records

Nuphie is the technician / secretary who collects the reports from the other technicians and maintains the record book on filter maintenance. I spoke with Remus and Nuphie about carbon replacement practices in Dumay. The Dumay program began in 1996 with 50 purifiers. Currently there are 1,800 systems in Dumay. Remus and Nuphie mentioned that carbon is changed every six to eight months, when the color of the water changes to yellow on the bottom or the family can feel the taste of chlorine in the water. In different places carbon is changed at different times. The longest time is one year, the shortest six to eight months. If the filter is broken and the carbon flows through, it is changed immediately. Carbon filters are brought to the shop and refilled by Nuphie or the technician. Remus and Nuphie estimated that 15 carbon filters are changed per month. Nuphie keeps a record book of all maintenance, including cracked buckets, carbon changes, and other minor repairs. Nuphie, Remus, and I looked in her record book to determine the number of filter changes that occurred per month (Table 6.2).

Although it can be seen that Nuphie and Remus's estimate of approximately 15 per month is correct for the recent time period, if there are actually 1,800 purifiers that need carbon changes once every six months, that equals 300 carbon changes per month, or 10 per day. There is a certain percentage of carbon changes that probably remain unrecorded, yet the discrepancy is very high and the age of the filters we found in Dumay (up to 4 years old) indicates that this data is accurate. In addition, Phil Warwick recently checked and noticed that the factory still has most of the GAC that was shipped, indicating little was used to refill filters [personal communication].

**Table 6.2: Carbon Changes per Month in Dumay, Haiti**

| | 1998 | 1999 | 2000 | 2001 |
|---|---|---|---|---|
| January | | 4 | 9 | 2 |
| February | | 0 | 3 | |
| March | | 0 | 2 | |
| April | | 5 | 3 | |
| May | | 7 | 3 | |
| June | | 4 | 21 | |
| July | | 5 | 4 | |
| August | | 1 | 6 | |
| September | | 0 | 10 | |
| October | | 4 | 10 | |
| November | 2 | 0 | 16 | |
| December | 1 | 0 | 13 | |

#### 6.2.6.3 Administrative Center

Dumay is also the administrative center of the GWI project in Haiti. GWI works with Pastor Nathan Dieudonne, who organizes the Haitian end of the money transfers, import of equipment, and organizational duties. Both the assembly factory and some records are located in Dumay

The assembly factory is a large room with a cement floor, stacks of purifiers, some machinery, and a large bucket of granulated activated carbon. The factory employs ten employees.

**Figures 6.18, 6.19: Dumay Assembly Factory**

### 6.2.6.4 Medical Missions

While we were in Haiti, a medical mission team was visiting Dumay. The Ohio based group comes once per year for one week. They noted ringworm and the need for antibiotics, not water-borne diseases, as the most common medical complaints. The staff sees approximately 250 patients per day, some from as far away as Port-au-Prince. This particular group obtained medicines by donation from drug representatives in return for attending dinners and other promotional activities. Nathan mentioned that there are four separate medical mission groups that come to Dumay, one for each season. The medical mission building, as well as the school and the water project factory, were built by U.S. soldiers during the occupation. Nathan's church also has a bus that was flown down in the bay of an empty airplane during the same occupation.

The technicians also serve as informal medical advisors. While sampling in Dumay one day, Remus was approached by a woman and small child who were very weak and had sores on their legs and faces. The woman asked Remus what to do, mentioning that she had seen doctors in both Port-au-Prince and the medical mission who had nothing to offer. He spoke with her for a bit and we left. He mentioned to me that there was nothing he could do either - the woman and child were suffering from complications of HIV.

The fact that technicians are approached for medical information shows that they are seen as knowledgeable and respected within their communities.

## 6.3 Summary of Source Water Data

Analysis of the source water data shows that the purifiers are used, on average, daily, and the average carbon filter age is slightly under one year. Nitrate levels were very high, for the WHO standard is 10 ppm, and the average was above this. Turbidity was low for standards of using the water in the purifier, and all water was clear in color.

**Table 6.3: Source Water Quality Summary**

| Parameter | Average | Range | Standard Deviation |
|---|---|---|---|
| PH | 6.6 | 4.7 – 8.0 | 1.0 |
| Turbidity (NTU) | 1.17 | 0 .00 – 4.21 | 1.19 |
| Temperature (C) | 21.7 | 15 - 29 | 4.67 |
| Nitrate (ppm) | 10.3 | 0 - 44 | 10.6 |
| Size of family using purifier | 8.2 | 1 - 20 | 5.0 |
| # times / week purifier used | 7.3 | 1 - 14 | 6.0 |
| Age of carbon filter (weeks) | 47.4 | 13 - 208 | 43.1 |

Also of interesting note is the distribution of type of source ( Table 6.4). Most of the sources were protected from surface water contamination.

**Table 6.4: Summary of Source Type**

| Source Type | Number of Samples |
|---|---|
| Cistern | 3 |
| Captage | 3 |
| Well | 7 |
| Spring | 4 |
| Surface Water | 2 |

Lastly, four out of the five communities sampled using the GWI methodology reached the 70 percent correct usage rate, and two of five reach the advertised 90 percent correct usage rate (Table 6.5).

**Table 6.5: Percentage Correct Usage by Community**

| Village | Percent Correct Usage |
|---|---|
| Ferriere | 100 |
| Bas Limbe | 20 |
| Fon Veret | 75 |
| Barasa | 90 |
| Les Palmes | 77 |

## 6.4 Critical Factors for Project Success

The following common factors for successful program implementation were determined from the January visit to the six communities detailed above. They are meant as observations and potential recommendations.

### 6.4.1 Staff

Dedicated, respected, and well-selected technicians are vital to the success of the program. In Ferriere, Mary-Marthe and Suzanne are greeted warmly on a home visit, and they perform the testing with ease. They visit homes four times per week. In Dumay, Wilburn and Remus are warmly greeted and command respect from community members.  The opposite is true in Bas Limbe, where the technicians were incompetent with the testing and were not greeted warmly.  The importance of good hiring of technicians should be stressed to the project leader in the community.  Mary-Marthe and Suzanne were selected by Sister Pat.  Dieumaitre and Helene in Fon Veret gave up other jobs after they interviewed and were hired.

When the project leader in the community has a vested interest in water issues and is familiar with U.S. style paperwork, and with the English language, the program runs more smoothly.  Bail in Les Palmes, Matt in Fon Veret, Sister Pat in Ferriere, and Nathan in Dumay all supervise their projects well, and function as good cultural translators between GWI and the French / Kreyol speaking technicians.  When the project leader is uninterested, as in Bas Limbe, the project lacks enough support.

### 6.4.2 Purifier Distribution

Staged, planned, and local distribution of purifiers is also critical.  In Ferriere, where 50 purifiers were distributed in a small area, rounds were comfortable, and easily completed multiple times per week.  In Les Palmes and Bas Limbe, rounds were difficult and time consuming because the purifiers were very far apart in mountainous areas.  Bail's plan of further implementation in Les Palmes is very sound.  The addition of 200 purifiers at a time to localized areas will simplify the project in many ways.  Eventually, each project may reach the size of Dumay, which has a large area to cover due to the number of purifiers. The distance problem has been solved in Dumay be simply giving the technicians bicycles.

### 6.4.3 Purifiers as Part of the Community

A number of people we saw were sharing their purifier with neighbors.  This is a simple and effective way for GWI to reach a greater number of people for less capital costs.  Because most of the families only use the purifier for drinking water, 15 liters is adequate storage for many people to use the water without excessive filtration per day.  The cost of the chlorine can be shared.  The only issue is the necessity of replacing the carbon filter earlier because of higher use.  If the standard to change the carbon filter is changed to a per use rather than a time unit this would be accounted for, although that change schedule might be difficult to implement.

In addition, the water program seemed to have more support when it was part of a larger community development plan.  Sister Pat has sponsored many health related programs in Ferriere, and the GWI program ties well into her larger work with the community and education. In Bas Limbe, it does not fit with the radio program focus of community development, for there are no other programs to work with and support the water project.  In Dumay, the technicians are seen as respected community members, greeted by everyone, and are able to form community with their presence.   In Fon Veret, Matt with his community support gives the purifier project support.  This is a tenuous metric, but measuring the “readiness” of the community for the project seems vital to the success of the project.

### 6.4.4 Challenges

Although there are many successes in the GWI program, there are a few challenges that are of note.

- A number of community leaders were not using their purifier correctly (Sister Pat, Nathan, Father Bruni).  This is a result of both the leaders not knowing the correct procedure, or their staff not knowing the correct procedure.  This is a problem because the support of the community leaders is essential, and if they become ill by waterborne disease that undermines credibility.

- Carbon filters were not actually being replaced.  Generally, the technicians knew how to and when to, but it was still not happening.

- In Barasa, the lack of available water indicates that the first priority there should be water access, rather than water treatment.  Perhaps working with Plan

International, or other international water supply agencies, to assess safe water systems would be more appropriate.

- No one in GWI speaks fluent Kreyol. This makes effective communication difficult because many subtleties of feeling and opinion are likely missed. In addition, more contact with GWI could be a positive factor for communities. The hiring of a full-time, in-country, Haiti-wide organizer who is fluent in Kreyol could improve many situations.

- Good technicians will not continue if they are never paid. A system of effective distribution of salaries outside of Dumay should be determined.

The GWI program is an effective and vital project in Haiti. Although there are some challenges, there are also many successes. Some simple modifications to the project implementation could help the program reach its potential.

# Chapter 7: THM Results and Modeling

A total of 19 finished water samples were brought back to MIT from Haiti. Seventeen of these samples were analyzed for TTHM and provided the basis for the development of equations to model TTHM concentration in the GWI purifiers.

## 7.1 Sampling Methodology

Trihalomethanes were sampled using a Tekmar LSC 2000 purge-and-trap system connected to a Perkin Elmer AutoSystem XL gas chromatograph (GC). The column was a J & W DB-5 nonpolar, phenylmethypolysiloxane column with a 0.32 mm inner diameter and a length of 60 meters. The electron capture dectector (ECD) was manufactured by Perkin Elmer. A trihalomethane mix standard was purchased and sampled at 1, 2.5, 5, 10, and 25 ppb to obtain standard curves. In addition, either a 10 ppb chloroform standard (before February 15, 2001) or a 5 ppb trihalomethane standard (February 15, 2001 onwards) was made fresh each analysis date and run at the beginning and end of each day, as well as approximately every 6 runs of the GC. Q-water was obtained by passing reverse osmosis water through an Aries Vaponics 110 volt system with one OR-1 and two MR-1 ion-exchange cartridges in series, then through a TOC remover. Q-water was run first each day to clear the GC column, and then after every standard and after each finished sample. The GC was kept at 150 degrees when not in use to clean the column.

The purge-and-trap protocol began with samples being purged for 4 minutes at room temperature, and then desorbed up to 175 degrees Celsius to the GC. The trap was baked at 200 for 7 minutes to clear the sample. The GC protocol began at 80 degrees Celsius, climbing to 120 degrees Celsius in 4 minutes at the rate of 10 degrees per minute, then climbing to 150 degrees Celsius in 1.5 minutes at the rate of 20 degrees per minute. The 150 degrees was held for 1.5 minutes for a complete sampling time of 7 minutes per GC run. The carrier gas was methane / argon mix. TurboChrome software on a Windows 3.1 platform was used for peak analysis and integration. If necessary, integration of the peaks was corrected manually. The THMs were easily separated using this protocol (Table 7.1).

**Table 7.1: Elution times of THMs in GC**

| | |
|---|---|
| Chloroform | 2.98 minutes |
| Bromodichloromethane | 3.52 minutes |
| Chlorodibromomethane | 4.31 minutes |
| Bromoform | 5.32 minutes |

Conductivity was measured with a VWR Scientific Conductivity Meter, Model 2052, calibrated at 718 micromhos/cm. Nitrate was measured with a colorometric LaMotte Nitrate-N Test Kit. The result obtained by matching the color of the sample to the standard color chart was multiplied by 4.4 to obtain nitrate. Because nitrate was a visual inspection, the quality assurance of the data is not as high as the meter readings.

Sodium concentration was measured using a Perkin Elmer AAnalyst 100. Using the emission procedures recommended in the AAnalyst 100 handbook, the wavelength was 589.0 nanometers, the slit 0.2, and the gas mix was air / acetylene. Standards were calibrated from 0.5 to 1000 mg/L, and raw data was converted to mg/L (ppm) based on the equation from the standard curve. The $R^2$ value of the standard curve was 0.98. Sodium concentration was converted to bromide concentration using the relative concentrations in seawater of sodium and bromide as defined by Riley [1971]: sodium is present in sea water at 11.05 g/L and bromide at 0.068 g/L.

## 7.2 Quality Assurance / Quality Control

A number of QA / QC procedures were used to ensure accurate data in the THM analysis. This include the assembly of standard curves, the analysis of duplicate samples and lab splits of the same sample, and daily analyses of standard samples to ensure accuracy.

### 7.2.1 Standards Curves

Standards curves were created for each compound, and an equation to convert peak area from the gas chromatograph to µg/L was determined.

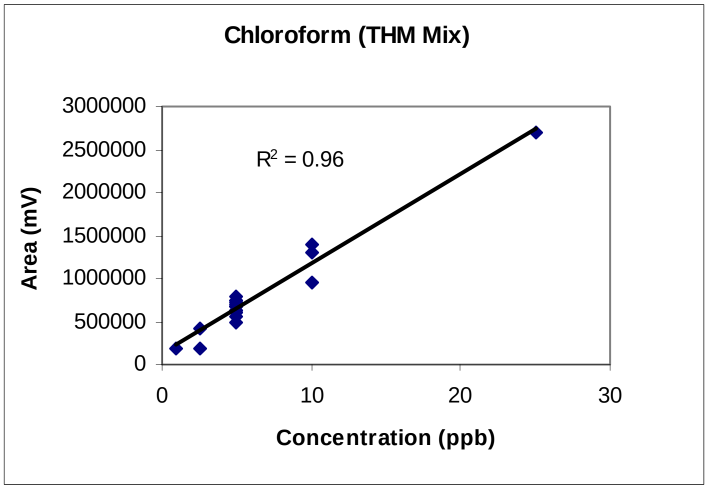

**Figure 7.1: Chloroform Standard**

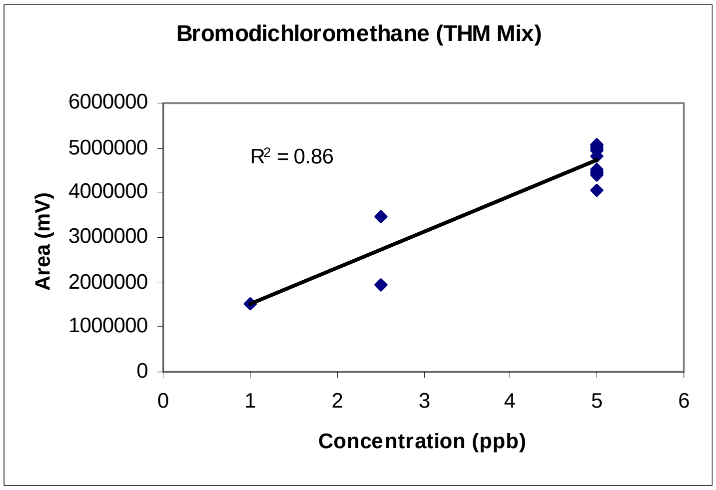

**Figure 7.2: Bromodichloromethane Standard**

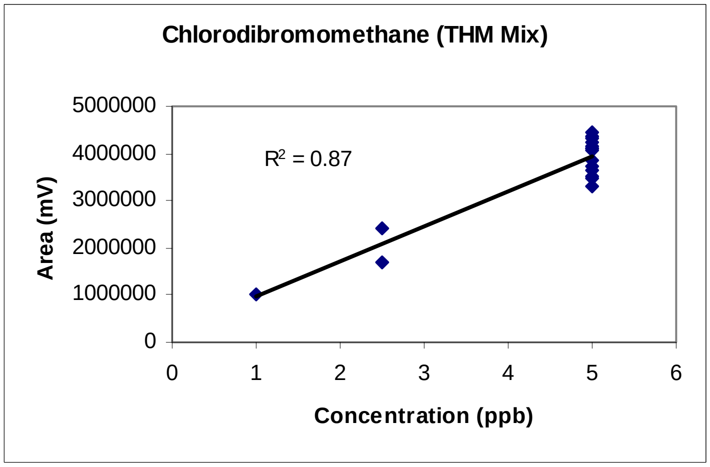

**Figure 7.3: Chlorodibromomethane Standard**

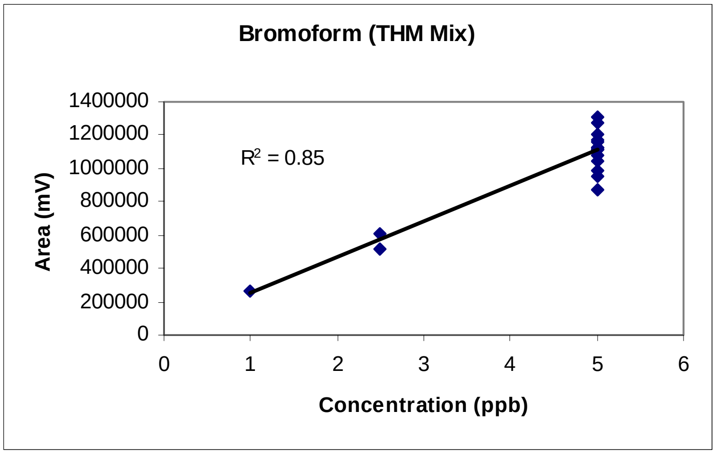

**Figure 7.4: Bromoform Standard**

As can be seen, the $R^2$ values for the standards curves were 0.95 for chloroform and near 0.85 for the brominated compounds. The linear fit equations from these graphs were used to convert area in mV to concentration in µg/L or ppb. Below is the average, standard deviation, and the percent of the average that is the standard deviation. As can be seen, all standards run were within 12 percent precision.

**Table 7.2: Standard Error**

| Compound | Chloroform | Bromodichloro methane | Chlorodibromo methane | Bromoform |
|---|---|---|---|---|
| Average | 663,000 | 4,750,000 | 3,960,000 | 1,110,000 |
| Standard Deviation | 80,000 | 303,000 | 351,000 | 119,000 |
| Percent SD | 12 percent | 6 percent | 9 percent | 11 percent |

### 7.2.2 Duplicate and Split Samples

Ten percent of the samples were split and analyzed twice in the lab, and ten percent of duplicate field samples were analyzed. All but one of the samples was within 20 percent error (Table 7.3).

**Table 7.3: Duplicate and Split Sampling Results**

| | | Percentage Errors = (Original - Duplicate) / Original | | | |
|---|---|---|---|---|---|
| D-3 Finish | Field Dup | 0.06 | 0.16 | 0.08 | -0.09 |
| D-3 Finish | Lab Split | -0.04 | 0.16 | 0.12 | 0.12 |
| LP-4 Finish | Field Dup | -0.11 | -0.17 | -0.20 | -0.27 |
| LP-4 Finish | Lab Split | -0.04 | 0.00 | -0.01 | -0.02 |

### 7.2.3 Standard Gas Chromatograph

The THM mix standard was well resolved (Figure 7.5). The four THMs elude between 2.97 and 5.32 minutes. This standard was run at the beginning and end of each sampling day, as well as approximately every six samples.

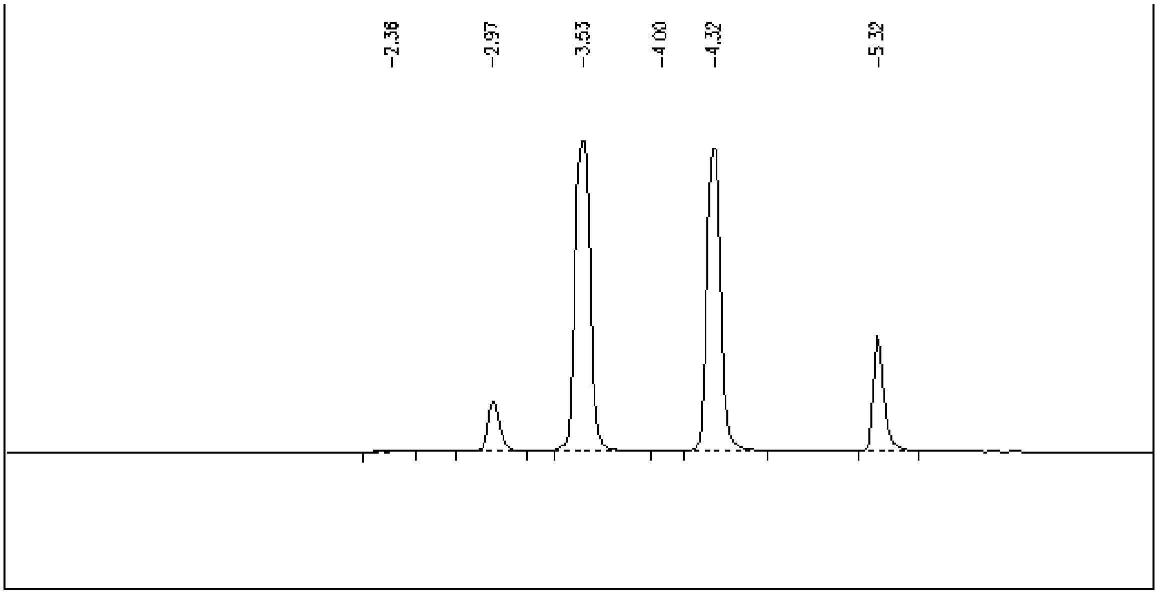

**Figure 7.5: Standard 5 ppb THM Mix Chromatograph**

In addition, because of the storage time in Haiti, the THM samples were held beyond the EPA recommended holding time of 14 days. Holding times were 16 – 39 days, depending on sample. Samples were, however, kept cold throughout the Haiti trip and after return to MIT. Prepared standards were left in the refrigerator for 34 and 42 days. The chromatograph from the 34 day holding time sample looked exactly as above. The 42 day holding time sample exhibited extra peaks along the baseline, indicating processes are occurring to make those compounds in the sample. The peak areas of the four THM peaks, however, are the same as found initially. Thus, although the holding times are over the EPA suggested time, the chromatographs from the standard samples are accurate.

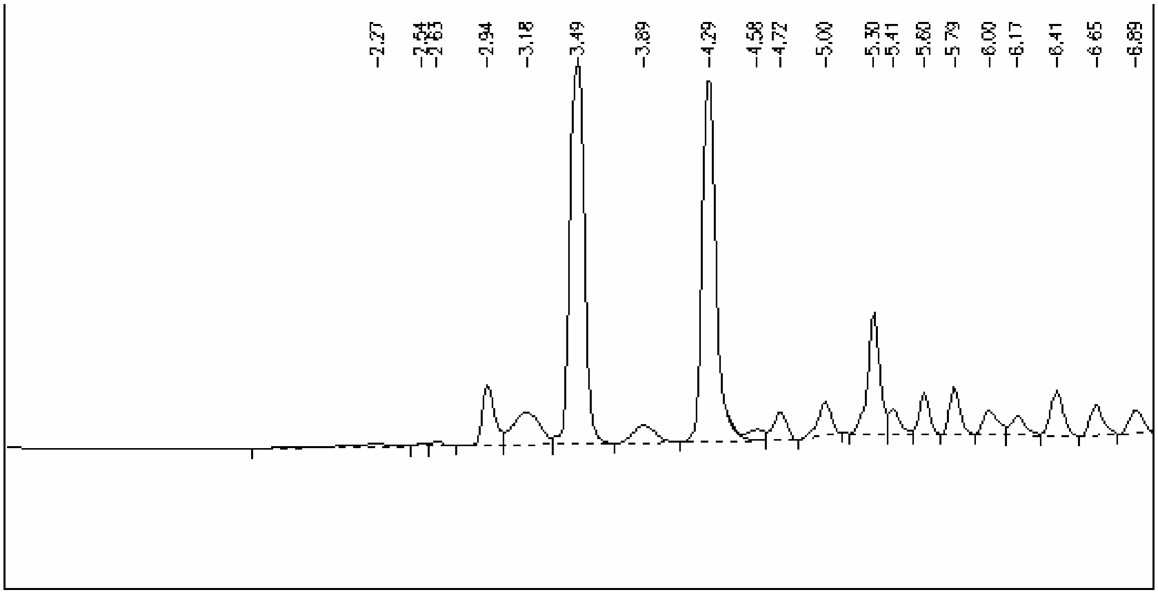

**Figure 7.6: Standard Chromatograph, 42 Days Old**

### 7.2.4 Summary of QA/QC

In summary, percentage error can be considered to be less than 20 percent, for the standard curves, duplicate and split samples, and holding time analysis all (except one sample) show error less than 20 percent.

## 7.3 Results

THMs were observed in all seventeen of the finished water samples analyzes (Figure 7.7 and Table 7.4). Two samples, one from Dumay (D-2) and one from Bas Limbe (BL-1) were dropped from the sampling procedures because of, respectively, leakage in the VOA vial and no chlorine residual in the bottom bucket.

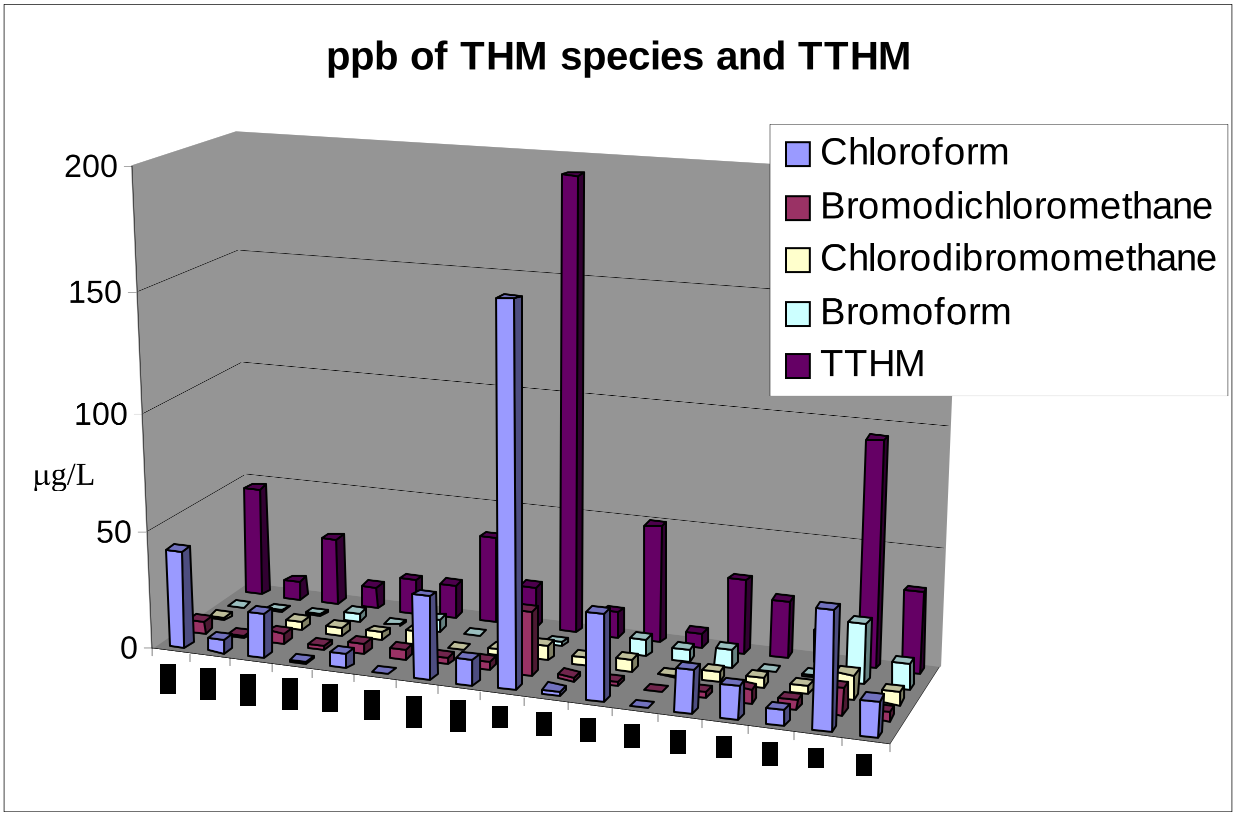

**Figure 7.7: THM species and TTHM in 17 Haitian Samples**

All samples met the WHO guideline values of 200 µg/L for chloroform, 60 µg/L for bromodichloromethane, 100 µg/L for chlorodibromomethane, and 100 µg/L for bromoform. However, sample D-1 exceeded the WHO guideline value that states the sum of the four THMs' actual value divided by their guideline value cannot be greater than one. The sum of the four THMs' actual value divided by guideline value in sample D-1 was 1.37. In addition, all but one, D-1, met the USEPA standard of 100 µg/L for TTHM.

### Table 7.4: THM Speciation in mol/L and µg/L in Haitian Samples

| Sample | $CHCl_3$ | | $CHBrCl_2$ | | $CHClBr_2$ | | $CHBr_3$ | |
|---|---|---|---|---|---|---|---|---|
| | µg/L | mol/L | µg/L | mol/L | µg/L | mol/L | µg/L | mol/L |
| LP-1 | 42 | 0.35 | 5 | 0.03 | 1 | 0.01 | 0 | 0.00 |
| LP-2 | 6 | 0.05 | 2 | 0.01 | 0 | 0.00 | 1 | 0.00 |
| LP-3 | 19 | 0.16 | 5 | 0.03 | 4 | 0.02 | 1 | 0.00 |
| LP-4 | 1 | 0.01 | 2 | 0.01 | 3 | 0.02 | 4 | 0.01 |
| FV-1 | 6 | 0.05 | 5 | 0.03 | 3 | 0.02 | 1 | 0.00 |
| FV-2 | 0 | 0.00 | 4 | 0.02 | 6 | 0.03 | 5 | 0.02 |
| BL-2 | 35 | 0.29 | 3 | 0.02 | 0 | 0.00 | 0 | 0.00 |
| BL-3 | 11 | 0.09 | 4 | 0.02 | 2 | 0.01 | 1 | 0.00 |
| D-1 | 158 | 1.32 | 27 | 0.17 | 7 | 0.03 | 2 | 0.00 |
| D-3 | 2 | 0.02 | 2 | 0.01 | 3 | 0.07 | 4 | 0.02 |
| D-4 | 36 | 0.30 | 2 | 0.01 | 5 | 0.02 | 7 | 0.03 |
| D-5 | 0 | 0.00 | 0 | 0.00 | 1 | 0.00 | 6 | 0.02 |
| D-6 | 18 | 0.15 | 2 | 0.01 | 4 | 0.02 | 7 | 0.03 |
| B-1 | 14 | 0.12 | 6 | 0.04 | 4 | 0.02 | 0 | 0.00 |
| B-2 | 6 | 0.05 | 4 | 0.02 | 3 | 0.01 | 1 | 0.00 |
| F-1 | 49 | 0.41 | 11 | 0.07 | 10 | 0.05 | 25 | 0.10 |
| F-2 | 15 | 0.12 | 4 | 0.02 | 5 | 0.03 | 11 | 0.04 |

Brominated compounds were commonly seen. Some samples, such as LP-1 and D-1, contained predominantly chloroform, with little brominated compounds. This was commonly seen when investigating THM production from fresh water sources. Other samples, such as LP-4 and D-5, were bromoform-dominated samples. This was more commonly seen with source water that is near the ocean or had been desalinated. Samples such as D-4 and F-1 are mixed. In the literature review, no study determined and developed a model from samples with the amount of variation in percent brominated compounds (5 – 100 percent) as found in the Haiti samples (Table 7.5).

**Table 7.5: TTHM and Percent Brominated in 17 Haitian Samples**

| Sample | **TTHM µg/L** | **TTHM mol/L** | **Percent Brominated** | **Source Type** |
|---|---|---|---|---|
| LP-1 | 48 | 0.39 | 9 | Cistern |
| LP-2 | 8 | 0.06 | 19 | Captage |
| LP-3 | 29 | 0.21 | 24 | Spring |
| LP-4 | 9 | 0.05 | 85 | Spring |
| FV-1 | 15 | 0.10 | 48 | Surface |
| FV-2 | 14 | 0.07 | 100 | Cistern |
| BL-2 | 37 | 0.31 | 5 | Well |
| BL-3 | 18 | 0.13 | 30 | Spring |
| D-1 | 193 | 1.53 | 13 | Well |
| D-3 | 11 | 0.06 | 70 | Well |
| D-4 | 50 | 0.37 | 17 | Captage |
| D-5 | 6 | 0.02 | 100 | Captage |
| D-6 | 31 | 0.21 | 30 | Well |
| B-1 | 24 | 0.17 | 33 | Cistern |
| B-2 | 14 | 0.09 | 42 | Surface |
| F-1 | 95 | 0.63 | 35 | Well |
| F-2 | 34 | 0.21 | 43 | Well |

### 7.3.1 Brominated Compounds Investigation

To begin understanding why there was a large range of percent brominated compounds and their affect on finished water TTHM concentrations, characteristics of source water were analyzed at MIT.

The first step was to quantify the bromide ion concentration in the source water. To this end, conductivity and sodium concentration were measured in raw source water samples. These were measured because both of these parameters can correlate with bromide ion concentration.

The bromide concentration and the conductivity varied significantly across Haiti (Table 7.6). In Les Palmes, Fon Veret and Barasa (all mountainous inland communities) bromide concentrations were very low. In Dumay, slightly inland and in a valley, bromide concentrations were slightly higher. In Bas Limbe, very close to the ocean, bromide concentrations were higher yet. In Ferriere, near the ocean and in the east of the country, bromide concentrations were quite high. In addition, when bromide concentrations are compared to bromoform concentration in the finished water (Table 7.6), the three samples with highest bromide concentrations and conductivity values also have the highest bromoform concentration in ppb: samples D-6, F-1, and F-2.

**Table 7.6: Bromide Concentration and Conductivity in Haitian Samples**

| Sample | Bromide Concentration μg/L | Bromoform Concentration (ppb) | Conductivity μmho/cm |
|---|---|---|---|
| B-1 | 0.01 | 0 | 96 |
| B-2 | 0.07 | 1 | 417 |
| BL-2 | 0.38 | 0 | 608 |
| BL-3 | 0.16 | 1 | 551 |
| D-1 | 0.12 | 2 | 402 |
| D-3 | 0.15 | 4 | 437 |
| D-4 | 0.17 | 7 | 572 |
| D-5 | 0.17 | 6 | 572 |
| D-6 | 0.55 | 7 | 646 |
| F-1 | 1.34 | 25 | 1537 |
| F-2 | 0.94 | 11 | 864 |
| FV-1 | 0.03 | 1 | 272 |
| FV-2 | 0.02 | 5 | 96 |
| LP-1 | 0.02 | 0 | 65 |
| LP-2 | 0.04 | 1 | 110 |
| LP-3 | 0.05 | 1 | 40 |
| LP-4 | 0.20 | 4 | 763 |
| D-2[4] | 0.21 |  | 759 |
| BL-1 | 0.18 |  | 521 |

---

[4] D-2 and BL-1 are raw samples whose corresponding finished samples were not analyzed for THMs due to VOA vial leakage and no residual chlorine, respectively.

In addition, the bromide concentration and conductivity results were correlated ($R^2 = 0.75$, Figure 7.8). This indicates that conductivity, a parameter easily measured in the field, can be used as a rough indicator of bromide concentration by setting bromide concentration equal to 0.0008 times the conductivity and then subtracting 0.16.

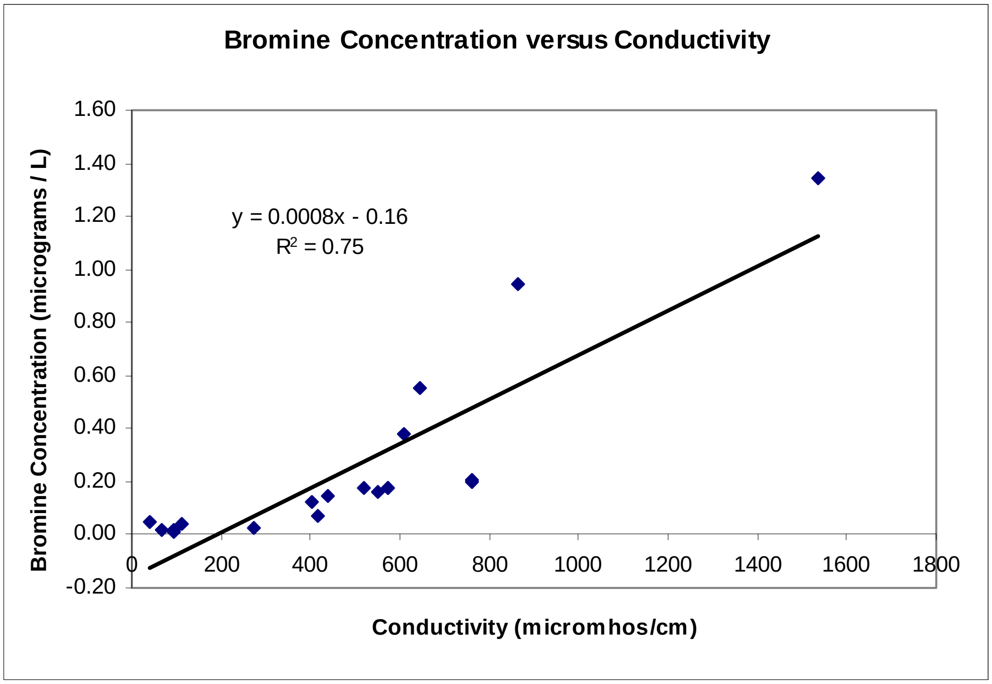

**Figure 7.8: Conductivity / Bromide Correlation**

# 7.4 Mathematical Model

The data obtained from source water in Haiti, from the GC for TTHM and individual THM concentrations, and from analysis of conductivity and bromide concentration of source water at MIT was then used to create a mathematical model to predict the concentration of TTHM in finished, purified water.

## 7.4.1 Derivation of TTHM Model

In order to anticipate TTHM production in Haiti, TTHM concentration, in micrograms per liter, was regressed against the source water variables collected in Haiti and at MIT. The units of micrograms per liter (ppb) were used for TTHM concentration because both the USEPA and

WHO standards are expressed in ppb. Slightly better $R^2$ values were obtained regressing against TTHM in molar concentration, because the molar concentration unit does not include the conversion from moles to ppm that is different for each species of THM. For example, two compounds with the same molar concentration will lead to different ppb concentrations because the lighter compound will have less ppb by weight than the heavier compound. Thus, although molar concentration would a more precise unit to use, the ppb unit was used due to the standards.

The first regression calculated was microgram per liter TTHM against total usage of the carbon filter. Total usage was calculated by multiplying the number of times the purifier was used per week by the age of the carbon filter in weeks. Thus, a unitless integral number was developed to account for the age and usage of the GAC. The concentration of TTHM in the finished water versus the number of times that the carbon filter has been used was well fit with a linear equation ($R^2$ value of 0.75, Figure 7.9). This shows that 75 percent of the variance in the TTHM concentration in the finished water can be attributed to total usage of the carbon filter. This indicates that each time the carbon filter is used, more TTHMs breakthrough, which is a reasonable result. A certain volume of GAC can only adsorb a finite amount of a compound.

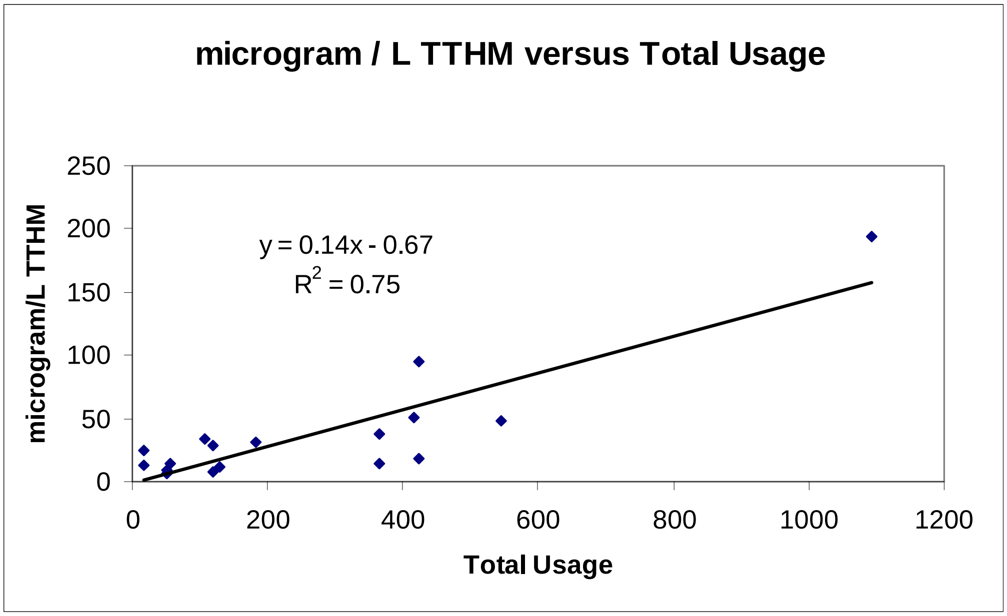

**Figure 7.9: TTHM Concentration and Total Usage of the Carbon Filter**

The $R^2$ value of 0.752 does indicate a relationship between TTHM concentration and total usage.

Because the last step of the formation of THMs is base-catalyzed, it is expected that as pH increases, so does the final concentration of THMs. When pH was added to the regression, the $R^2$ value increased to 0.756 from 0.752. This small increase indicates that pH (which ranged from 4.75 – 8.0 in the source water), was not a significant factor in the final concentration of TTHMs.

Turbidity of the source water was the next variable included within the regression. Increasing turbidity could be an indicator that there is an increased amount of NOM, the precursor material of THMs, in the source water. When turbidity and total usage were regressed against TTHM concentration, the $R^2$ value was 0.758. This indicates that turbidity accounts for less than one percent of the variance in the production of TTHMs. Increasing turbidity could be an indicator that there is an increased amount of NOM, the precursor material of THMs, in the source water. However, turbidity of all source water was fairly low in Haiti. All water was clear to the eye, and the turbidity values of the 17 samples in the regression ranged from 0 – 2.62 NTU. Thus in the ranges tested, turbidity had little effect on the production of THMs. All source water tested in Haiti was from a clear source that people walked long distances to reach. If water with the higher turbidity of the water in the easily accessible drainage ditches throughout the communities was used in the purifier, there could be increased THM production due to high turbidity levels.

Source water temperature in Celsius was the next variable investigated. The literature shows that as temperature increases, so does the concentration of TTHMs due to the increased rate of reactions. When total usage and source water temperature were regressed, the $R^2$ value was 0.764. This indicates that source water temperature accounts for 1.2 percent of the variance in the final TTHM concentration. The equation for this correlation is:

$$\text{TTHM } (\mu g/L) = 0.14 \text{ (Total Usage)} + 1.1 \text{ (Temperature)} - 23$$

$$R^2 = 0.764$$

Thus, as temperature increases, the final concentration of TTHM increases slightly, but not significantly.

The next variable investigated was the bromide concentration. The literature clearly shows that as the bromide concentration increases, not only does the speciation of the four THMs shift toward the brominated compounds, but the TTHM concentration increases as well. When total usage and bromide concentration were regressed, the $R^2$ value increased to 0.797 from the $R^2$ value of total usage alone of 0.752. Thus, bromide concentration accounts for 4.5 percent of the variation in the TTHM concentrations. The equation for this correlation is:

$$\text{TTHM } (\mu\text{g/L}) = 0.14 \text{ (Total Usage)} + 27 \text{ (Bromide Concentration)} - 7.1$$
$$R^2 = 0.797$$

The increased value of TTHM concentration with increasing bromide concentration is an expected value.

However, bromide concentration is not a parameter that can easily be measured in the field. Bromide concentration is related to conductivity, however (Figure 7.8). Conductivity can easily be measured in the field in Haiti. When total usage and conductivity were regressed, the following correlation was found:

$$\text{TTHM } (\mu\text{g/L}) = 0.14 \text{ (Total Usage)} + 21 \text{ (Conductivity)} - 9.6$$
$$R^2 = 0.780$$

Thus, conductivity does not provide as good a correlation as bromide concentration, but it still indicates that conductivity accounts for 3.8 percent of the TTHM concentration.

The last variable compared with the total usage regression was nitrate concentration in ppm. When nitrate concentration and total usage were regressed the following correlation was found:

$$\text{TTHM } (\mu\text{g/L}) = 0.14 \text{ (Total Usage)} + 0.72 \text{ (nitrate)} - 7.9$$
$$R^2 = 0.781$$

Thus, increasing nitrate concentration increases the TTHM concentration. Possibly, this occurs because nitrate concentration is related to the NOM in the source water. With more NOM precursors in the source water there will be more TTHM concentration. This value indicates that nitrate concentration accounts for 3.9 percent of variability of the TTHM concentration.

Hence, in addition to the dependency on total usage, the most important variables are bromide concentration, followed by nitrate concentration, conductivity (an indicator of bromide concentration), and then temperature (Table 7.7). pH and turbidity account for less than one percent of the variability.

**Table 7.7: Source Water Variables Accounting for Variability of TTHM Concentration**

| Variable | Increase in $R^2$ as compared to $R^2$ of total usage | Percent of variability in TTHM concentration (as compared to total usage) |
|---|---|---|
| pH | 0.004 | 0.4 |
| Turbidity (NTU) | 0.006 | 0.6 |
| Temperature (C) | 0.012 | 1.2 |
| Bromide Concentration (ppb) | 0.045 | 4.5 |
| Conductivity (μmho/cm) | 0.038 | 3.8 |
| Nitrate Concentration (ppm) | 0.039 | 3.9 |

The next step was to regress all of the variables in combination to determine the combination of variables with the highest $R^2$ value (Table 7.8). The highest combination $R^2$ value was with all five variables for 0.811.

**Table 7.8: Multiple Regression $R^2$ Values**

| **Variables** | **$R^2$** |
|---|---|

| | |
|---|---|
| Total Usage | 0.752 |
| Total Usage, Conductivity | 0.780 |
| Total Usage, Nitrate | 0.781 |
| Total Usage, Temperature | 0.764 |
| Total Usage, pH | 0.756 |
| Total Usage, Turbidity | 0.758 |
| Total Usage, Conductivity, Nitrate | 0.785 |
| Total Usage, Conductivity, Temperature | 0.781 |
| Total Usage, Conductivity, pH | 0.783 |
| Total Usage, Conductivity, Turbidity | 0.795 |
| Total Usage, Nitrate, Temperature | 0.785 |
| Total Usage, Nitrate, pH | 0.781 |
| Total Usage, Nitrate, Turbidity | 0.801 |
| Total Usage, pH, Turbidity | 0.763 |
| Total Usage, pH, Temperature | 0.765 |
| Total Usage, Turbidity, Temperature | 0.769 |
| Total Usage, Conductivity, Nitrate, Temperature | 0.786 |
| Total Usage, Conductivity, Nitrate, pH | 0.787 |
| Total Usage, Conductivity, Nitrate, Turbidity | 0.805 |
| Total Usage, Conductivity, pH, Temperature | 0.784 |
| Total Usage, Conductivity, pH, Turbidity | 0.802 |
| Total Usage, Conductivity, Turbidity, Temperature | 0.800 |
| Total Usage, Nitrate, pH, Temperature | 0.791 |
| Total Usage, Nitrate, pH, Turbidity | 0.801 |
| Total Usage, Nitrate, Turbidity, Temperature | 0.802 |
| Total Usage, pH, Turbidity, Temperature | 0.769 |
| Total Usage, Conductivity, Nitrate, Temperature, Turbidity | 0.806 |
| Total Usage, Conductivity, Nitrate, Temperature, pH | 0.791 |
| Total Usage, Conductivity, Nitrate, Turbidity, pH | 0.810 |
| Total Usage, Conductivity, Temperature, Turbidity, pH | 0.803 |
| Total Usage, Nitrate, Temperature, Turbidity, pH | 0.808 |
| Total Usage, Conductivity, Nitrate, Temperature, Turbidity, pH | 0.811 |

Yet, the highest $R^2$ value (with all the variables) is only 0.3 higher than the values for total usage / conductivity (0.780) and total usage / nitrate (0.781). And the value for total usage by itself is 0.752. Thus, the use of six variables in the equation increases the complexity of the equation so much that a mechanistic understanding of why more THMs are generated can no longer be determined. Thus, the more accurate measure of TTHM concentration will be one of the two variable equations.

For completeness, the equation derived using the six variables is as follows:

$$\text{TTHM } (\mu\text{g/L}) = 0.13(\text{total usage}) + 0.64(\text{nitrate concentration}) + 0.45(\text{temperature}) \\ + 17\ (\text{conductivity}) + 8.8\ (\text{turbidity}) - 5.6\ (\text{pH}) + 7.0$$

$$R^2 = 0.811$$

Thus, TTHM concentration will increase with total usage as breakthrough in the GAC occurs, with nitrate concentration and turbidity with increased NOM, with conductivity with increased brominated compound production, and with temperature with increased rates of reactions. pH is an anomaly, because it would be expected that with increased pH the last base-catalyzed reaction to form THMs would increased. Instead, this equation shows that TTHM concentration decreases with pH.

Because the above equation has a higher $R^2$, it is tempting to say it is a more accurate predictor of THMs than the other regression equations generated. However, with the addition of four extra variables, there is only a gain of 0.03, or three percent, in the $R^2$. And one of the variables, pH, does not have a mechanistic explanation for the sign. A much simpler, more accurate measure of TTHM concentration would be to use either the total usage / conductivity equation ($R^2 = 0.780$) or the total usage / nitrate equation ($R^2 = 0.781$).

Nitrate is measured with a colormetric test kit that has a large error because the user must match color against standards that are 2 ppm apart. Conductivity, on the other hand, can be measured with a meter. Thus, the conductivity reading is likely to be more accurate, and therefore the conductivity equation is a preferred equation to model. Bromide concentration provides a more accurate measure of the bromide in the water than conductivity does, but because it is not possible to measure in the field, the conductivity equation is more applicable.

The total usage / conductivity regression equation is (again):

$$\text{TTHM } (\mu\text{g/L}) = 0.14 \text{ (Total Usage)} + 21 \text{ (Conductivity)} - 9.6$$
$$R^2 = 0.780$$

with conductivity in μmho/cm and total usage an integral number calculated by multiplying the age of the carbon filter in weeks by the number of times the purifier is used per week.

When the calculated value from this total usage / conductivity model is compared to the observed value from GC measurements of actual Haitian water there is a small amount of spread in the lower concentrations, but the fitted linear total usage / conductivity regression equation explains 78 percent of the total spread (Figure 7.10).

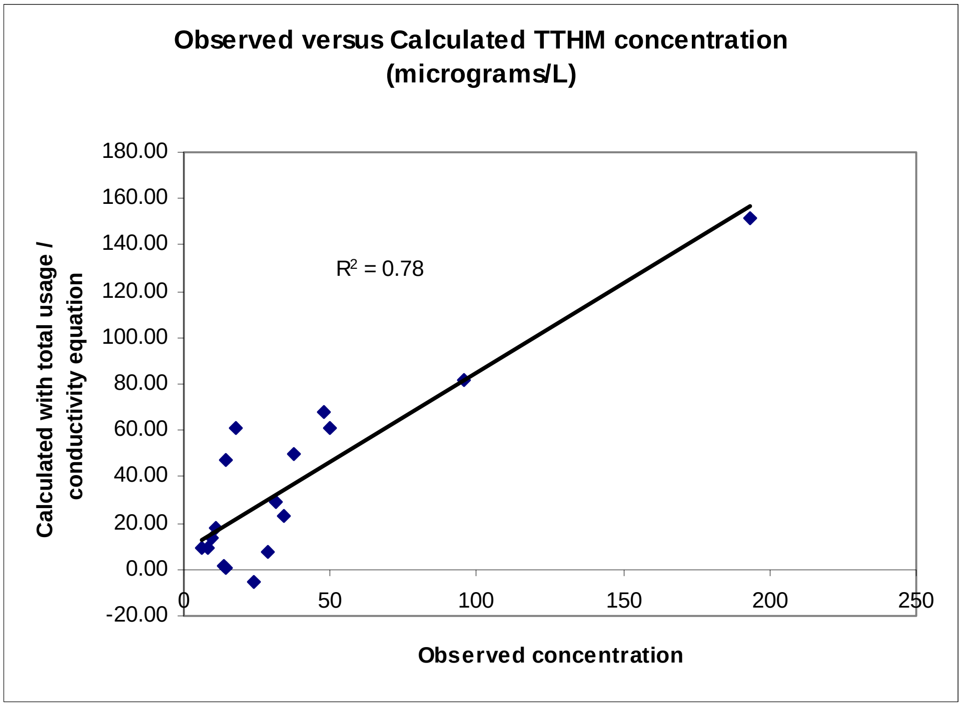

**Figure 7.10: Comparison of Calculated and Observed TTHM Concentration**

Thus, increased conductivity and increased carbon use can be used to model increased TTHM concentration (μg/L) in the finished water after filtration with a GWI purifier. This simple equation can be used to estimate TTHM production in water throughout Haiti, but only if GWI continues using the GAC currently purchased and distributed. Solving this equation for TTHM equal to the USEPA standard of 100 μg/L allows calculation of the total usage number when the purifier water first exceeds USEPA standards (Table 7.9). The average case uses the average conductivity to calculate the total usage at the USEPA standard. The total usage is then converted to carbon age in weeks by dividing by the average number of times the purifier is used per week. The worst case uses the highest conductivity seen in Haiti and the highest usage of the purifier per week for the same calculation. The best case uses the lowest conductivity seen in Haiti and the lowest usage of the purifier per week for the calculation. The worst case scenario shows that the carbon filter should be changed every 0.75 years, or 9 months, in order to ensure that the USEPA standard is not exceeded. Thus, GWIs policy of changing the carbon every six months includes a safety margin against even the highest potential use of the purifier in areas with the highest conductivity.

**Table 7.9: Average, Best, and Worst Case Carbon Change Scenarios**

| Scenario | Total Usage at USEPA Standard | Times per week filter is used | Convert Total Usage to carbon age at USEPA standard |
|---|---|---|---|
| Average:<br>Conductivity: 470 μmho/cm | 712 | 7.3 | 97 weeks<br>1.9 years |
| Worst Case:<br>Conductivity: 1.5 μmho/cm | 552 | 14 | 39 weeks<br>0.75 years |
| Best Case:<br>Conductivity: 40 μmho/cm | 776 | 1 | 776 weeks<br>14.9 years |

However, as was found in Haiti, carbon is not changed every six months. In addition, it would be more accurate for the carbon change to occur based on usage of the filter because of the large range (used 1 – 14 times per week) of usage, not a time scale, which assumes the same use of the filter across Haiti. This would complicate the carbon change process, however, and currently the first goal is to ensure the carbon is changed at all. Thus, it is recommended that GWI take one of two courses: (1) work with the technicians to implement the current policy of carbon changes every six months; or (2) implement a new two-step policy that includes the technicians accessing the number of times per day the purifier is used. If that number is greater than one, carbon should be changed every six months. If that number is equal to or less than one, carbon should be every year. This would ensure a safety margin, and necessitate less carbon changes. The two-step policy adds a complexity that, given the current carbon change rate, may not be feasible. Thus the simpler every-six-months policy may be the best option.

### 7.4.2 Model for Bromodichloromethane

Both the WHO and the USEPA define bromodichloromethane (BCDM) as the most cancerous of the four THMs. The WHO guideline value of 60 μg/L for BCDM is the lowest of the four guideline values. Therefore, calculation of an equation to model BCDM concentration is important.

To begin the development of this equation, total usage was regressed against BCDM concentrations in the finished waters. The $R^2$ value of this regression was 0.65. Then, multiple regressions were completed (Table 7.10). The $R^2$ values of total usage / conductivity / pH and total usage / nitrate / pH are both 0.70. This value is quite close to the $R^2$ value of 0.71 for all of the variables regressed against BCDM concentration. As before, the simpler the equation, the easier it is to use and the more likely it can be explained mechanistically. Thus, the six variable equation will not be used.

As before, the method of measurement for conductivity is more accurate than that for nitrate. Thus the total usage / conductivity / pH equation will be used. That equation is as follows:

$$\text{BDCM } (\mu\text{g/L}) = 0.018 \text{ (Total Usage)} + 3.6 \text{ (Conductivity)} - 1.7 \text{ (pH)} + 10$$

$$R^2 = 0.70$$

With total usage an integral number, conductivity in μmho/cm, and pH in log units.

### Table 7.10: Multiple Regression $R^2$ Values for Bromodichloromethane

| **Variables** | **$R^2$** |
|---|---|
| Total Usage | 0.65 |
| Total Usage, Conductivity | 0.65 |
| Total Usage, Nitrate | 0.66 |
| Total Usage, Temperature | 0.65 |
| Total Usage, pH | 0.67 |
| Total Usage, Turbidity | 0.65 |
| Total Usage, Conductivity, Nitrate | 0.67 |
| Total Usage, Conductivity, Temperature | 0.66 |
| Total Usage, Conductivity, pH | 0.70 |
| Total Usage, Conductivity, Turbidity | 0.65 |
| Total Usage, Nitrate, Temperature | 0.67 |
| Total Usage, Nitrate, pH | 0.70 |
| Total Usage, Nitrate, Turbidity | 0.66 |
| Total Usage, pH, Turbidity | 0.67 |
| Total Usage, pH, Temperature | 0.68 |
| Total Usage, Turbidity, Temperature | 0.65 |
| Total Usage, Conductivity, Nitrate, Temperature, Turbidity, pH | 0.71 |

The two equations with 0.70 $R^2$ both contained total usage, pH, and a variable that is related to the concentration of bromide ion or possibly NOM in the raw water. This equation is similar to the equations modeling TTHM concentration, except that, with lower pH, more BDCM is formed. pH is an important factor in the formation of brominated THMs because the reaction that creates hypobromous acid occurs at acidic pH, as shown in the formula below. At high, basic pH sodium hypochlorite will exist as hypochlorite ion, and will not react with bromide ion to form hypobromous acid.

$$HOCl + Br^{-} \longrightarrow HOBr + Cl^{-}$$

The BDCM model equation can be solved for the total usage associated with the WHO standard of 60 μg/L for the average, worst case, and best case scenarios (Table 7.11). The worst case scenario requires a carbon change every 0.4 years. This is more often than the current protocol of every six months, yet due to the low BDCM values seen in Haiti (no one value was even half the guideline value), the combination of variables leading to high BDCM concentrations did not occur in the actual samples collected for this study. Thus, the six month recommended change of carbon need not be modified.

**Table 7.11: BDCM Average, Best, and Worst Case Carbon Change Scenarios**

| **Scenario** | **Total Usage at WHO Standard** | **Times per week Filter is Used** | **Convert Total Usage to Carbon Age at WHO Guideline** |
|---|---|---|---|
| Average:<br>Conductivity: 470 μmho/cm<br>pH: 6.6 | 330 | 7.3 | 45.3 weeks<br>0.9 years |
| Worst Case:<br>Conductivity: 1.5 μmho/cm<br>pH: 4.75 | 292 | 14 | 21 weeks<br>0.4 years |
| Best Case:<br>Conductivity: 40 μmho/cm<br>pH: 8 | 353 | 1 | 353 weeks<br>6.8 years |

When the calculated value from this total usage / conductivity / pH model is compared to the observed value from GC measurements of actual Haitian water, there is a small amount of spread in the lower concentrations, but the fitted linear total usage / conductivity regression equation explains 70 percent of the total spread (Figure 7.11).

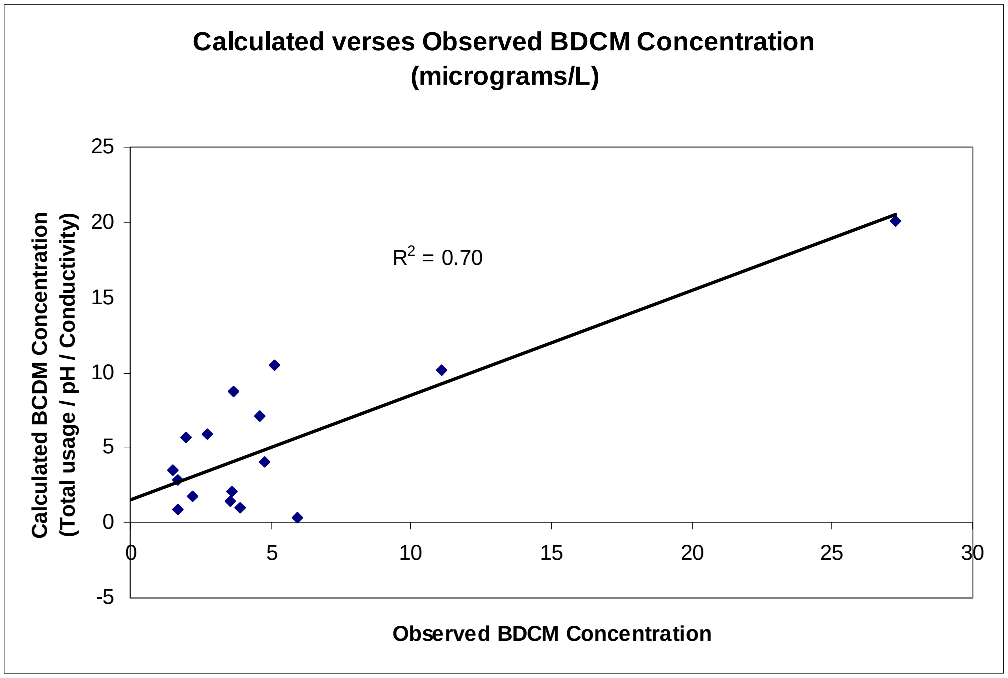

**Figure 7.11: Comparison of Calculated and Observed BDCM Concentration**

## 7.5 Extra Compound in Les Palmes

An interesting note is that an extra compound was found in three of the Les Palmes samples. It was found in one raw and two finished water samples. This indicates there is a compound in Les Palmes water that is entering the carbon and breaking through the carbon. The extra peak eludes at 3.26 minutes (the second peak from the left in Figure 7.12). This peak has not been identified although, based on elution time, it is not TCE.

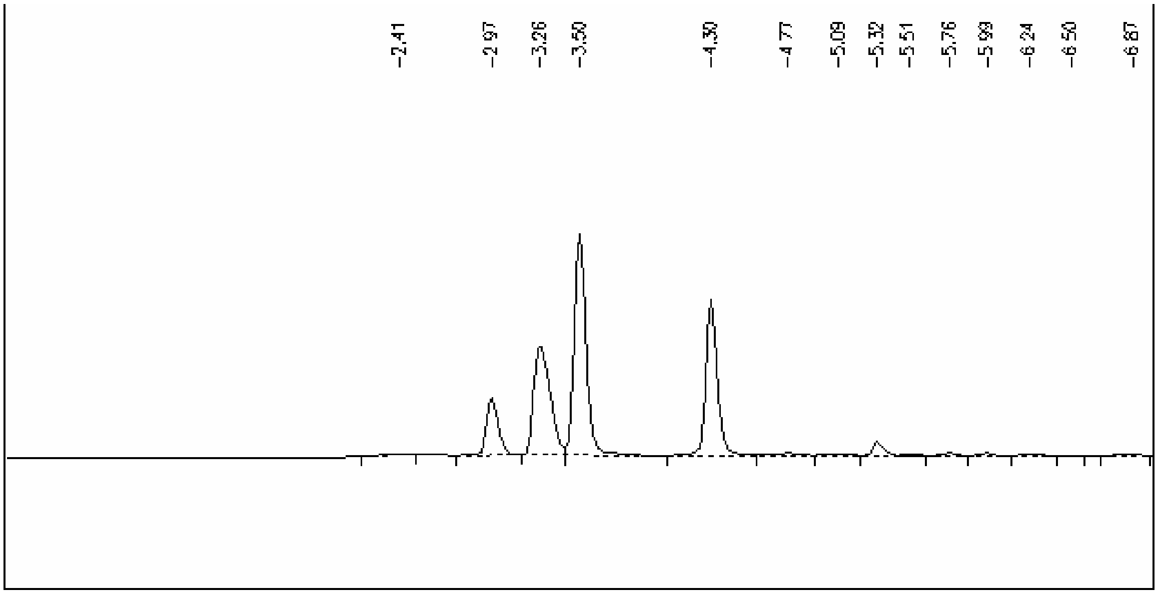

**Figure 7.12: Extra Peak in Les Palmes Samples**

# Chapter 8: THM Mitigation Strategies

The main approaches currently investigated and used to prevent THMs reaching the tap are grouped into the following categories:

1. Disinfection by-product (DBP) precursor removal
2. Disinfection process control / alternative disinfection processes
3. Physical processes: Ultraviolet light, membrane filtration
4. Advanced oxidation processes
5. Removal of DBPs from finished water
6. Quenching agents

These approaches are described below, with consideration of their potential applicability in Haiti.

## 8.1 DBP Precursor Removal

The goal of DBP precursor removal treatment is to remove the natural organic matter in the raw water that provides the reaction sites for the hypochlorite and hypobromite to react with and form THMs.

Gerlach [1999] investigated soil passage and found that "the alteration of dissolved organic matter (DOM) over a wide distance in subsurface flow improves the treatment in a low expenditure plant consisting only of powdered activated carbon addition, a filtration strip, and residual chlorination if necessary. This is due to an improved adsorbability and an efficient removal of THM precursors via subsurface flow."

Westerhoff [2000] also ran (waste)water through packed columns as a means to reduce TOC and THMFP. He found that the DOC was reduced by a factor of 3 to 5, depending on the soil. The TTHMFP fell from 508 µg/L to 220 and 344 µg/l respectively. Yet the reactivity of the DOC, the (µg TTHMFP / mg DOC) increased from by a factor of two. This indicates that the structure of the DOC shifted towards aromatic, high molecular weight, more humic matter due to removal of low molecular weight non-THMFP material during filtration.

Thus, two studies have found that THMFP is reduced by filtering raw water through a column of soil or sand, because fractions of the raw DOC adsorb to the column material. Because of the necessity of having an additional sand filter in each household, DBP precursor removal would be difficult to install in each Haitian household as a THM mitigation strategy, however.

## 8.2 Disinfection Process Control / Alternative Disinfection Processes

Although chlorine is the most common disinfectant, in recent years alternative disinfectants have been investigated in order to reduce DBP formation. These alternative disinfectants include: chlorine dioxide, ozone, and chloramines. These disinfectants were investigated to determine their potential applicability in the GWI system.

### 8.2.1 Chlorine Dioxide

Gordon [1987] detailed that chlorine dioxide is a gas at room temperature, with a boiling point at 11 C and a freezing point of -59 C. Liquid chlorine dioxide is explosive at -40 C, as is concentrated vapor. Because no storage medium has been successful, chlorine dioxide must be manufactured at the point-of-use. Chlorine dioxide is, however, soluble in water, remaining in solution as a dissolved gas. Aqueous solutions are stable if kept cool, sealed, and protected from light.

Gordon [1987] continued by describing that chlorine dioxide reacts as an oxidant or by electrophilic substitution. Chlorine dioxide does not react with natural organic matter to form THMs, and production of TOX is only 1 to 25 percent of the production with chlorine. Of concern, however, is the reaction with phenol and phenolic compounds in industrial wastewaters to form chlorophenolic tastes and odors. Chlorate ion and chlorite ion are also potential by-products.

Hubbs [1986] found that chlorine dioxide was more effective against viruses than chlorine. In addition, chlorine dioxide could be 2 to 70 times less concentrated than chlorine to inactivate coliforms in the distribution system. C. Chang [2000] found that disinfection was effective with 1 to 5 mg/L of chlorine dioxide in only 1 to 2 minutes, but below 1 mg/l substantial colonies remained after 3 minutes. pH did not influence disinfection efficiency, but increased concentrations of organic precursors did reduce the percentage of bacteria inactivated.

C. Chang also found that $ClO_2$ is a stronger oxidant that $Cl_2$. Thus, in bromide containing waters, the chlorine dioxide oxidizes bromide to form hydrobromous acid, which then reacts with the humic acids to form bromoform. A disinfection combination of $ClO_2$ and $Cl_2$ in the absence of bromide led to formation of only chloroform, but in the presence of bromide all four THMs were formed. As the $ClO_2/Cl_2$ ratio increased less THMs were formed. Irradiation led to a decrease in all THMs, with increasing irradiation time causing increased reduction in THMs. [Li, 1996] Heller-Grossman [1999] found that in bromide-rich lake water chlorine dioxide disinfection produced insignificant quantities of THMs.

Aggazzotti [1998] noted that in Modena, Italy water treated with chlorine dioxide produced no THMs. Sansebastiano found THMs in the distribution systems of two Italian plants after chlorination in 27 out of 50 samples. Mean concentration was 0.34 µg/L with a range of 0 - 6 µg/L. After chlorine dioxide treatment of the same raw waters, THMs were only found in 2 of 50 samples. Mean concentration was 0.073 µg/L with a range of 0 - 3.5 µg/L. TOX was also reduced from 3.7 - 71 µg/L range with a mean of 22.7 µg/L with chlorine to 5 – 22 µg/L range with a mean of 14.5 µg/L average when chlorine dioxide was used.

Although the literature is clear that using chlorine dioxide significantly reduces the production of THMs, especially when no bromide is present, due to the difficulties of production and storage, chlorine dioxide can not be recommended for use in point-of-use systems in Haiti.

### 8.2.2 Ozonation

Hubbs [1996] details the benefits of ozonation as follows:

1. High germicidal effectiveness.
2. Time required for disinfection is short.
3. Ameliorates odor, taste, and color problems.
4. Only residual is dissolved oxygen (no THMs are formed).
5. Transformation of resistant substances into biodegradable products.
6. Unaffected by ammonia content.

The drawbacks, however, include that ozone cannot be stored, leaves no residual, and reacts with inorganics, including chlorine, chlorine dioxide, and chloramines. Thus, ozone cannot be used in conjunction with other disinfection procedures. Only 0.5 - 4 mg/L of ozone are usually needed to disinfect water. Hubbs [1986] concludes by saying that in small community water systems, ozone and UV light were inferior to chlorination from the operation and maintenance standpoint. Yu [1999] also notes the drawback of the lack of an ozone residual.

Graham [1999] notes that ozone reacts with humic matters through direct reactions or indirect reactions with ozone decomposition products. Ozonation causes structural changes to the humics that lead to a rapid decrease in color and UV-absorbance due to loss of aromaticity and depolymerization. These loses also lead to a small reduction in TOC, and slight decrease in the high molecular weight fractions with a corresponding increase in the smaller fractions.

Although the lack of formation of any THMs is a strong benefit, ozone could not be used as a disinfectant in Haiti due to inability to store and transport it and the lack of residual. Residual is necessary in Haiti because purified water can become recontaminated by contact with unclean containers.

### 8.2.3 Chloramine

Chlorine in the presence of ammonia or other nitrogenous material produces a mixture of chloramines (mono-, di-, and trichloramine) depending on the pH. First introduced as a disinfectant in the early 1900's, chloramine disinfection was popular in the 1930s in the U.S. Interest has recently been renewed because chloramination produces fewer THMs and TOX, has a stable residual, and does not have the odor of chlorinated water. Disadvantages are the reduction in disinfection caused by preferential reactions with chlorine and nitrogenous organics.

Chloramination is less effective than chlorination at inactivating bacteria, viruses, and protozoans, because it is highly dependent on pH, temperature, and contact time. However, chloramination has been found to reduce THMs and with a long contact time has the same inactivation as chlorine. Hubbs [1986] concludes that TOX and THM, following treatment with chloramines, are believed to be universal lower than with chlorine. He states that manipulation to reduce disinfection by-products can be accomplished without sacrificing the primary goals of the disinfection process using chloramines.

The chemical reactions forming the chloramines are [Jacangelo, 1987]:

Monochloramine: $NH_3 + HOCl \longleftrightarrow NH_2Cl + H_2O$

Dichloramine: $NH_2Cl + HOCl \longleftrightarrow NHCl_2 + H_2O$

Trichloramine: $NHCl_2 + HOCl \longleftrightarrow NHCl_3 + H_2O$

Jacangelo [1987] noted that dichloramine is more effective at inactivating bacteria than monochloramine, and that monochloramine is more effective at inactivating viruses than dichloramine. However, hypochlorous acid and hypochlorite ion are more effective than both chloramines in inactivating both viruses and bacteria.

Heller-Grossman [1999] noted that in bromide-rich lake water, chloramination created only one-third of the THMs that chlorine did. Simpson [1998] mentioned that in Australia only chlorine and monochloramine are used for disinfection, and THM levels were lowest in monochloramine samples. In three samples from the same area, THM levels were 189 µg/L from chlorination and

6 μg/L due to chloramination. Tanaka [1994] added ammonium chloride and sodium hypochlorite to form monochloramine at the seawater intake of a desalination system. No THMs were seen in the chloramine disinfected seawater or in the reverse osmosis permeate water after secondary chlorine disinfection.

Straub [1995] investigated inactivation of MS-2 coliphage and E. coli due to monochloramine and cupric chloride alone and in combination. Addition of 0.1 - 0.4 mg/l cupric chloride reduced the time from 120 to 10 minutes to inactivate 3 log10 MS-2 with 5 mg/L monochloramine. A 6 log 10 reduction in E. coli was seen after 10 minutes with the addition of 0.8 mg/L cupric chloride, compared to 60 minutes with only 5 mg/L monochloramine.

The reduction of THMs and the maintenance of bacteriological inactivation are strong benefits of using chloramines in the GWI system. Because chloramines are produced by the reaction of chlorine and ammonia, it could be possible for GWI to manufacture chloramines to distribute throughout Haiti.

## 8.3 Physical Processes

Three types of physical processes were investigated to determine their applicability in Haitian households: coagulation, filtration, and aeration.

Chang [1999] investigated the use of polyelectrolyte coagulants to remove natural organic materials (NOMs). One particular chlorine-resistant polymer, polydiallyldimethylammonium chlorine (p-DADMAC), was investigated as a primary coagulant in the presence of higher turbidity water. Chang found that the addition of p-DADMAC reduced turbidity, TOC, and THMs. Childress [1999] also investigated enhanced coagulation with ferric chloride to obtain removal of THM precursors. Childress found that optimal removal of precursors occurred at high coagulant doses (>16 mg/L) and low pH conditions.

Siddiqui [2000] found that microfiltration reduced THMFP by approximately 10 percent, ultrafiltration reduction THMFP by 50 percent, and nanofiltration by 90 percent. However, nanofiltration on its own led to filter fouling. The use of nanofiltration with pretreatment by microfiltration and/or coagulation was recommended. Chellam [2000] found that low rejection of bromide ion by some nanofiltration membranes resulted in a shift to the brominated species, which is of concern because of the increased carcinogenicity of the brominated compounds.

Roberts investigated diffuse aeration for trihalomethane control and found it not appropriate because of the rapid saturation of air bubbles as they rise through the columns. He concluded that surface aeration, because of the much larger volume and large equilibrium capacity, offers a good alternative for THM control.

Although air stripping is clearly not appropriate for individual households in Haiti, the addition of a coagulation step is something that could be considered. It would necessitate a third bucket so that the water could settle and then be poured into the top bucket. Filtration is not appropriate given the rapid fouling reported in the literature.

## 8.4 Advanced Oxidation Processes

Advanced oxidation processes use a mixture of processes to achieve biological inactivation and minimize the use of chlorine. Some of the processes are: biological activated carbon, ozonation, and other oxidation processes.

Nishijima [1998] describes BAC (biological activated carbon) treatment as "one of the most promising processes for the removal of synthetic organic chemicals and precursor of DBP by simultaneous adsorption by activated carbon and biodegradation by bacteria attached on activated carbon." Preozonation converts organic substance into biodegradable organics which are then absorbed onto the BAC. Levels of removal are maintained even after saturation because of biodegradation on the BAC [Sketchell, 1995]. Although treatment reduced both chloroform and bromodichloromethane, the proportion of brominated species increased. The raw amount of brominated compounds increased. Table 8.1 details the THMFP removal from from many different processes.

**Table 8.1: Removal of THMFP from AOP Methods**

| Method | Percentage THMFP Removal | Author |
|---|---|---|
| Sand Filtration | 23 | Graham [1999] |
| Ozonation / Sand Filtration | 20 – 64 | Graham [1999] |
| Ozonation only | 8 – 24 | Nishijima [1998] |
|  | 47 | Ito [1998] |
|  | 68 | Kleiser [2000] |
| Spent GAC | <15 percent | Vahala [1999] |
| BGAC | 66 | Sketchell [1995] |
| Ozonation / BGAC | 32 | Nishijima [1998] |
|  | 40 | Graham [1999] |
| BAC, hyperfiltration | <1 μg/L | Graveland [1998] |
| UV | 14.4 | Ito [1998] |
| H2O2/UV (short irradiation) | +20 | Kleiser [2000] |
| H2O2/UV (long irradiation) | 75 | Kleiser [2000] |
| $O_3$/UV, $O_3$/ $H_2O_2$, $H_2O_2$/UV | 55.2- 67.1 | Ito [1998] |
| $H_2O_2$-UV-$O_3$ | 81.3 | Ito [1998] |
| UF-$O_3$-BACF | 86.5 | Park [1997] |

Although AOPs are the most advanced and newest technologies, they are extremely complicated and have side effects such as increased brominated compound concentrations that make them unsuitable for use in Haiti.

## 8.5 Removal of DBPs from Finished Water

Granulated activated carbon is one method to remove DBPs from finished water. This is the method used by GWI and recommended by Parrott, of the Virginia Cooperative Extension [1998]. GAC will remove pesticides, radon, THMs, and volatile organic chemicals, but not nitrate, bacteria or metals. It is further noted that “setting up a regular maintenance schedule for filter replacement is necessary, because there is no easy method for detecting that a filter is no longer working effectively." Calculations in Section 4.1.3 detail that the GWI carbon filter can effectively remove approximately 100 mg of chloroform if no brominated compounds are present.

In addition, Batterman [2000] found that storage, pouring, and serving of tap water at temperatures below 30 C cause minor (less than 20 percent) reduction in THMs. When boiled, however, volatilization losses approached 75 percent and reached 90 percent when water was boiled and served. Kuo [1997] also found that 61 - 82 percent of THMs could be removed by boiling. Thus, boiling will reduce THM concentration, but that is not an effective strategy in Haiti because of the lack of fuel and the already extensive deforestation.

## 8.6 Quenching Agents

Quenching agents are strong oxidizers that prevent the formation of THMs after the chlorine has inactivated the microbial contamination.

Batterman [2000] investigated the use of combined $Ag^+/H_2O_2$ as a quenching agent. After seven days incubation, TTHM and THAA concentrations with the secondary disinfectant were 85 and 90 percent lower than without the addition of $Ag^+/H_2O_2$. He then confirmed that $H_2O_2$ was "the sole agent responsible for quenching THM and HAA formation." The mechanism of quenching was proposed to be the reduction of chlorine to chloride with the addition of sufficient $H_2O_2$. It is possible that naturally occurring iron in the sample water acted in concert with the $H_2O_2$ as described by Tang [1997]. Tang combined $H_2O_2$ with $Fe^{2+}$ (Fenton's Reagent) to achieve a reduction in bromoform of 65 – 85 percent. As the easiest THM to oxidize, bromoform was the only THM tested. The proposed mechanism involves oxidation of $Fe^{2+}$ by the $H_2O_2$ to form $Fe^{3+}$, $OH^-$, and OH. The OH then reacts to oxidize the bromoform. Tang did not study the effects of the $H_2O_2$ without the $Fe^{2+}$.

The quenching agent of hydrogen peroxide has possibility for use in Haiti if it is locally available. A simple addition of hydrogen peroxide after the chlorine could be added to the purifier methodology. Strong oxidizers can have other side effects, however, and should be used cautiously.

## 8.7 Summary

Off all of the mitigation strategies described here, those with the greatest potential for application in Haiti are:

- Quenching by hydrogen peroxide.
- Coagulation
- Chloramination

If THM levels become a problem in Haiti, or GWI determines they would like to investigate mitigation of THMs, then the use of hydrogen peroxide, coagulates, or chloramination are all viable options to investigate.

# Chapter 9: Recommendations

The following chapter summarizes the results of the two foci of this thesis and provides recommendations for further studies.

## 9.1 Trihalomethane Concentration Mitigation

Only one of 17 finished water samples from Haiti was above the USEPA standard of 100 μg/L, and no sample was above the WHO guideline values. Both the CDC and the WHO stress that, in developing countries, bacteriological inactivation is critical, and THM standards therefore secondary. Based on the TTHM concentration results of this study, no action to change the purification process or mitigate TTHM production is recommended.

TTHM can be calculated from simple parameters from the equation:

$$\text{TTHM } (\mu\text{g/L}): = 0.14 \text{ (total usage)} + 21 \text{ (conductivity)} - 9.6$$
$$R^2 = 0.780$$

With conductivity in μmho/cm and total usage an integral number.

If mitigation becomes a necessity in the future, the use of hydrogen peroxide, coagulates, or chloramination are all viable options to investigate for TTHM mitigation.

## 9.2 Critical Factors of Program Success

Three factors were identified as critical to ensure program success in community. These factors were:

1. Dedicated and well selected staff;
2. Localized purifier distribution; and
3. The purifier as part of the community.

GWI organizes a well-structured and vital project that with a few modifications could be even more successful.

## 9.3 Further Studies

Three studies are recommended herein for further study:

1. Epidemiology Study: A full scale study to determine the actual health benefits of the purifier is needed. Although these studies are difficult to implement in the developing world, the full benefit of the purifier will not be known without one.

2. Chlorine Demand Study: Currently significantly more than the CDC recommended amount of chlorine is added to the purifier. Although this may be necessary, a new study to investigate chlorine demand across Haiti will help to optimize chlorine addition.

3. GAC Study: This thesis clearly shows that the GAC is critical in THM removal. Studies to determine the characteristics of the actual GAC used by GWI would be a valuable addition to this thesis. If the type of GAC is changed, the equations mentioned herein are no longer valid.

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