Chlorine Demand in Haitian Water Supplies

by

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Abstract

Gift of Water, Inc., an NGO committed to providing safe drinking water in Haiti, has developed a two bucket filtration system that uses a combination of bleach and physical filters to disinfect and purify water. Currently 5 ml of 5.25 percent bleach are used for disinfection in the top bucket, and five drops of bleach are added to the bottom bucket. For health, economic and social reasons, it would be beneficial to reduce the amount of bleach used for disinfection.

In order to establish a safe reduction of bleach it is necessary to determine the chlorine demand of Haitian drinking water supplies. Chlorine demand is the amount of bleach that must be added to achieve a desired residual concentration. This residual is based on the concentration necessary to destroy pathogens of concern over the half hour contact time that Gift of Water recommends.

During the month of January 2002, water from 13 sources in Haiti was chlorinated with 1 ml, 3 ml, 5 ml, and 10 ml of bleach and tested for free and total chlorine residuals. The water was also tested for six water quality parameters: ammonia concentration, iron concentration, temperature, pH, conductivity, and turbidity.

Chlorine residual measurements were higher than expected, most likely due to stratification in the buckets, causing some or all of the bleach in each bucket to be "held up" at the surface rather than fall to the bottom and mix along the way. Due to the high readings, the chlorine demand of the system cannot be determined from this study; However the implementation of mixing is recommended, either through the use of a third bucket to pour water onto bleach in the top bucket or by creating a paddle made of the same material as the buckets that will be used to stir the water.

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1 Introduction

1.1 Haiti

Haiti occupies 27,750 square kilometers of land on the west side of the island Hispaniola in the Caribbean (Figure 1). The Dominican Republic occupies the eastern side of the island. Haiti has a population of 8 million people, approximately 2 million of whom live in the capital city of Port-au-Prince (World Bank Group, 2002; Lonely Planet, 2002).

(US Central Intelligence Agency, 2001)

Figure 1 Map of Haiti.

Haiti is the poorest nation in the Western Hemisphere. Seventy-five percent of the population lives in absolute poverty, mostly living off of subsistence agriculture (Maguire et al., 1996). The distribution of wealth is exceptionally unbalanced, with one percent of the population owning approximately half the wealth. The nation also has a large foreign debt.

There is very little infrastructure of any sort in Haiti, including roads, electricity, and water supply. There is also a lack of adequate medical care. The average life expectancy is only 53 years and the infant mortality rate is 73 in 1000 live births (World Bank Group, 2002). Waterborne disease is a major cause of illness in the population, and particularly of death in children under the age of five.

1.1.2 Water Needs in Haiti

Haiti simply does not have the resources to create an infrastructure for water sanitation and delivery. Not only has Haiti been economically devastated by political instability and long-term debt, but it has also been environmentally ravaged. Extensive deforestation has reduced surface water levels and left many areas where rivers once ran, dry. People often have to journey over 45 minutes just to reach a source for drinking water, and once the water is collected, they must travel back home carrying gallons of water. Where surface water is the primary source of drinking water, it is generally used for washing as well. In order to retrieve water that is free from soaps, people must travel further upstream for their drinking water.

International aid agencies have stepped in to ameliorate the situation somewhat. Agencies from Japan, the United States, and elsewhere have installed groundwater wells in villages, as well as piped water from mountain springs down to some villages located in valleys. This helps bring the water closer to the people; however it does not solve a related problem, which is the quality of the water.

Because the water that people collect is untreated, there is no assurance that it does not contain pathogens that can cause severe illness or death. In developed nations, government agencies often regulate the disinfection and delivery of water. However in Haiti the government agencies responsible for water and sanitation do not have the resources to ensure safe drinking water for the Haitian population.

Because no national or even regional solutions to the lack of clean water infrastructure are foreseeable, it was necessary to develop a means of producing safe drinking water on a local level. Point-of-use water filtration systems (water purifiers which are utilized in the home or other site of water usage) have been successful in bringing health to people in many developing nations.

1.2 Gift of Water, Inc.

The non-profit organization, Gift of Water, Inc. (GWI), known prior to 2000 as Industry for the Poor, Inc (IPI), has been working on point-of-use water treatment in Haiti since 1995 (Gift of Water, Inc., 2000). GWI was created by Phil Warwick, a Florida engineer, to provide water filtration in countries lacking water treatment and sanitation infrastructure. Initially, the organization worked with Adopt-a-Village Medical Mission to analyze epidemiological studies, and found that gastro-intestinal problems were common and believed to be caused by bacteriological pathogens in drinking water sources.

In response to this finding, Industry for the Poor, Inc. performed a cost analysis in order to begin development of an in-home gravity-driven water filtration system intended to remove pathogens and volatile chemicals (Gift of Water, Inc., 2000). In 1996, GWI began a pilot program in Dumay, a town near Port-au-Prince, with 56 families purchasing filters (Gift of Water, Inc., 2000). In addition, 12 filtration systems were donated to the University Hospital in downtown Port-au-Prince. There was a significant decline in gastro-intestinal diseases with the use of the filter, particularly in young children, who are considered the most vulnerable.

Gift of Water, Inc. then began to expand its program. It hired six local technicians, who were trained to provide technical assistance to the families using the filter (Gift of Water, Inc., 2000). In 1997, a factory was built in Dumay to assemble the filters locally, with parts shipped from the US.

The cost of the filter is heavily subsidized by GWI in order to make it affordable to Haitian families. The apparatus costs US$15.29, but families are only required to pay approximately US$1.85 (Gift of Water, Inc., 2000). Operating expenses for the filter include replacement chlorine and granular activated carbon, and run families approximately US$0.42 per year.

Overall, the Gift of Water, Inc. filter and its use have been deemed a success. Since the Haitian Ministry of Health has approved the filter, GWI's program has reached seven villages, providing filtration systems that serve over 22,000 people (Gift of Water, Inc., 2000). The filters and the education provided by the program are thought to be responsible for a 90 percent decrease in water related diseases in children under five. The trained local technicians monitor each family that owns a filter to ensure that filters are used correctly and consistently.

1.2.1 The Gift of Water, Inc. Filter Setup

The Gift of Water, Inc. filtration system is comprised of two five gallon plastic buckets, stacked on top of each other, and two types of filters through which water must pass (Figure 2). Both buckets are 36 cm high with a diameter of 28 cm. The top bucket contains a polypropylene filter through which water must pass before traveling through a check valve into the lower bucket. This filter is designed to reduce turbidity and remove suspended solids from the water. On the other side of the check valve, attached to the lid of the bottom bucket is a granular activated carbon (GAC) filter, intended to remove chlorination by-products and other chemicals from the water. There is a spout on the bottom bucket to obtain water, as dipping unsterile cups into the bucket could cause contamination of the filtered water.

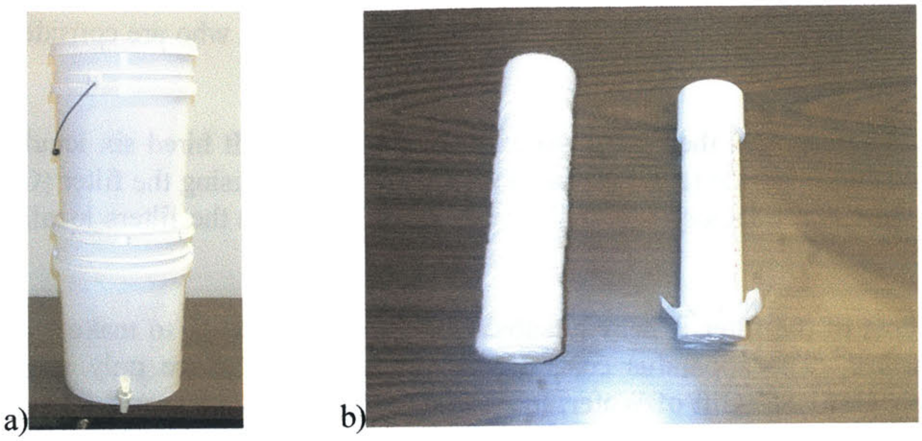


Figure 2 a) A full filtration system setup. b) The two filters used in the system, from left to right, the polypropylene filter and the granular activated carbon filter.

The water is chlorinated in both the top and bottom buckets. In the top bucket, 5 ml of 5.25 percent sodium hypochlorite solution (Clorox bleach) is currently added to approximately five gallons of water. A lid is placed on the bucket to prevent contamination and the bleach is allowed to act for half an hour. In Haiti, people are told to let the bucket sit for the amount of time it takes to cook a pot of beans (Lantagne, 2001a). After half an hour, the top bucket is placed on the bottom bucket and the check valve is opened to allow water to pass through the two filters into the bottom bucket. Five drops of bleach (0.2-0.25 ml) are placed in the bottom bucket in order to provide a chlorine residual to prevent the regrowth of bacteria and other pathogens. The water is considered finished and safe to drink after it has all passed into the bottom bucket.

1.3 Purpose of Study

The purpose of this study was to determine the chlorine demand in Haitian drinking water sources in order to establish the most efficient amount of chlorine to use in the Gift of Water, Inc. filtration system. Minimization of the amount of chlorine in the top bucket is beneficial in a number of ways, but enough chlorine must be added to ensure that pathogens of concern are destroyed. Since it is important to have a chlorine residual in water that sits for a time before being used, a reduction of chlorine in the bottom bucket was not considered in this study.

A reduction in the amount of sodium hypochlorite added to the top bucket can be beneficial in several ways. First, chlorine and disinfection-by-products can have negative effects on human health. The World Health Organization (WHO) and the Centers for Disease Control and Prevention (CDC) have determined that the benefits of chlorine, primarily killing pathogens and reducing water-borne diseases, are worth the cost of ingesting chlorinated compounds (Centers for Disease Control and Prevention, 2002b; World Health Organization, 1997). To fully reduce risk, however, the amount of chlorine used in disinfection should be minimized. The addition of chlorine to water creates harmful by-products, such as trihalomethanes, some of which are known carcinogens. A field study conducted on the use of the Gift of Water, Inc. filter found that trihalomethanes are present in all finished water samples, but generally meet the World Health Organization (WHO) standards for each compound (Lantagne, 2001b). However it was found that one sample did not meet the WHO standard for total trihalomethanes, the sum of the concentrations of all four trihalomethane species: chloroform, dibromochloromethane, bromodichloromethane, and bromoform.

The GAC filter in the Gift of Water, Inc. filtration system is intended to remove disinfection by-products, including trihalomethanes. The filter has a limit to the amount of chemical it can remove, and when that limit is reached there is breakthrough of chemical compounds in the finished water. For this reason, Gift of Water, Inc. has designed its program so that the filter is changed periodically. Unfortunately, field research determined that, in practice, the GAC filters were not replaced as often as needed (Lantagne, 2001b). Although this problem is beginning to be addressed, minimizing the amount of chlorine used in the Gift of Water, Inc. filtration system will make it possible to reach the WHO trihalomethane standards for a longer period of time with the same GAC filter.

Minimizing the chlorine addition to the Gift of Water, Inc. filtration system could also have economic benefits and might allow for a wider distribution of GWI's program (Warwick, 2002). 5.25 percent bleach is not extremely stable, particularly in the heat and sunlight of Haiti. There is concern within GWI over whether the strength of the bleach has diminished and may not provide enough germicidal strength. Phil Warwick took this possibility into account when he determined the amount of chlorine that should be added to the top bucket, and therefore included a safety factor in his recommendation (Lantagne, 2001b). A lower concentration bleach solution would deteriorate more slowly, thereby providing GWI with more confidence in the strength of their bleach solution (White, 1986). The safety factor for bleach instability could thus be reduced when using a lower concentration solution.

Gift of Water, Inc. is currently investigating the generation of chlorine in Haiti. Currently bleach is imported from the Dominican Republic or the United States. If Gift of Water, Inc. does implement chlorine generation, the organization will most likely turn to the recommendations of a study completed by Nadine van Zyl one year ago in conjunction with GWI. The study recommends the use of the SANILEC-6 unit, made by Exceltec International Corporation. This generator, however, would create a lower concentration sodium hypochlorite solution (0.8%), with the benefits of stability described above and a shorter storage time because it can be delivered and used by costumers soon after generation (van Zyl, 2001). van Zyl has recommended a reduction in the final expected concentration in the Gift of Water top bucket from 16 ppm to 5 ppm, and calculated that 10 ml of the generated solution be added to the top bucket of the filtration system. In order to determine if this lower concentration of chlorine provides adequate disinfection, the chlorine demand of the drinking water sources in Haiti must be determined.

Finally, a reduction in the amount of chlorine used in the Gift of Water, Inc. filtration system can have a social impact as well. The introduction of chlorine into a community that has always drunk water without the addition of chemicals can be difficult. The education that Gift of Water provides through training sessions and technician visits has helped people understand the importance of chlorination; however there may be reluctance on the part of some Haitians to use the filter. Reducing the amount of chlorine added while still achieving the same health benefits might increase the social acceptance of the filtration system. With less chlorine, there is less breakthrough of chlorinated compounds into the finished water, and therefore less of a chemical taste. If the water doesn't taste strongly like chemicals, more people are likely to subscribe to the use of chlorine for disinfection.

Overall, lowering the amount of chlorine used in the Gift of Water, Inc. filtration system will have a positive impact. A reduction in the chlorine input can provide health, economic, and social benefits. However, in order to lower the amount of bleach used for disinfection and still guarantee safe drinking water, it is necessary to understand the chlorine demand of the water in order to assure that there will always be enough chlorine residual to inactivate pathogens. This study investigates the chlorine demand of Haitian water supplies.

2 Chlorination

2.1 Sodium Hypochlorite

Hypochlorite was one of the first forms of chlorine used for disinfection. It is found in one of two forms, calcium hypochlorite (CaOCl) and sodium hypochlorite (NaOCl). The bleach used in the Gift of Water, Inc. filtration system is a 5.25 percent solution of sodium hypochlorite. When bleach is mixed with water, the following reaction occurs,

$$NaOCl + H_2O \rightarrow HOCl + Na^+(OH)^- \qquad \textbf{Eq. 1}$$

creating the germicidal species hypochlorous acid (White, 1986).

Sodium hypochlorite is a powerful oxidant and is of great value for disinfection. However, a solution of sodium hypochlorite is not completely stable. A high concentration solution will deteriorate much faster than a weak solution (White, 1986). Spontaneous decay can take place within a bleach solution through the interaction of hypochlorous acid and hypochlorite ion (Hoffman et al., 1981). Hypochlorous acid can oxidize hypochlorite ion through the following reaction:

$$OCl^- + 2\,HOCl \rightarrow ClO_3^- + 2\,HCl \qquad \textbf{Eq. 2}$$

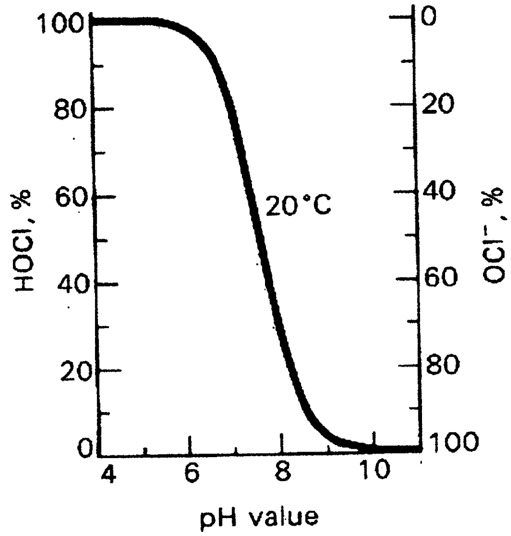
The pH is driven down by the formation of hydrochloric acid, which causes more HOCl to form and react with OCl^-. For this reason, higher concentration solutions will degrade faster because there is more HOCl available for this oxidation reaction to occur. For example, the half-life of sodium hypochlorite is approximately 60 days for an 18 percent available chlorine solution, whereas a 3 percent available chlorine solution has a half-life of 1700 days (Lawrence and Block, 1968). These times are highly dependent on other parameters as well. Sodium hypochlorite solutions will degrade faster at higher temperatures, under UV radiation, and in the presence of metals such as copper, nickel, cobalt, and iron.

The stability of sodium hypochlorite is of considerable concern in the Gift of Water, Inc. filtration system. Currently, the majority of bleach in Haiti is imported from the United States or the Dominican Republic. By the time the bleach has traveled into Haiti and to the villages in which it will be used, a significant amount of time has elapsed and the bleach has had an opportunity to degrade. This is particularly problematic in a tropical country like Haiti, where heat and sunlight can accelerate the degradation of the sodium hypochlorite solution.

2.2 Disinfectant Species

The most germicidal chlorine species is hypochlorous acid, HOCl, which dissociates to form hypochlorite ion, OCl^-. HOCl destroys pathogens approximately 40-100 times more effectively than OCl^- (White, 1986; Metcalf & Eddy, 1991).

The ratio of HOCl to OCl^- is dependant upon the pH of a water sample (Figure 3). At a low pH there will be more hypochlorous acid. As the pH rises, the acid will dissociate into H^+ and hypochlorite ion (White, 1986). As the pH falls again, hypochlorous acid reforms.



(Metcalf & Eddy, 1991)

Figure 3 Dependency on pH of the ratio of HOCl to OCl^-.

At higher temperatures the curve in Figure 3 moves to the left, because the tendency of hypochlorous acid to dissociate is greater at higher temperatures (Table 1). Water temperatures in Haiti range from approximately 17-27°C. Thus, at higher temperatures there is less HOCl present at a given pH than there would be at lower temperatures (Liptak, 1974).

Temperature	K_i X 10^8
°C	mol/L
0	1.49
5	1.75
10	2.03
15	2.32
20	2.62
25	2.9

(Metcalf & Eddy, 1991)

Table 1 Values of the ionization constant, K_i, of hypochlorous acid at different temperatures.

Chloramines are produced when ammonia is present in a water sample. There are three species of chloramines, which are collectively called combined chlorine: monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine or nitrogen trichloride (NCl_3). They are formed through the following reactions that occur stepwise:

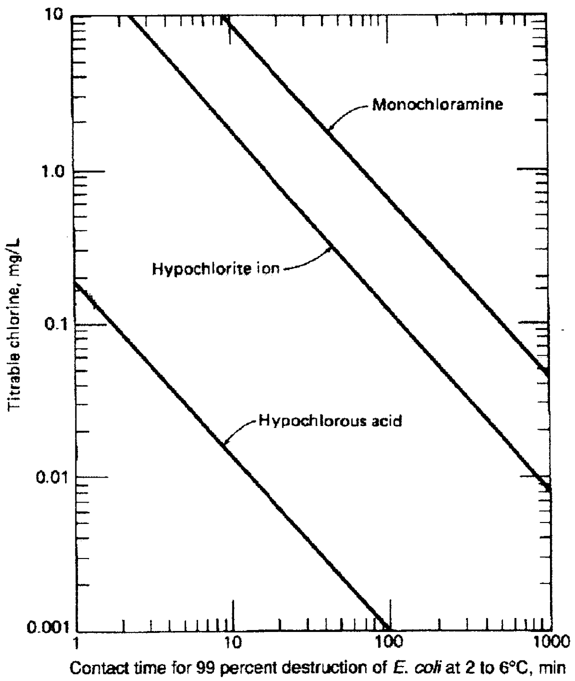
Formation of monochloramine: $NH_3 + HOCl \rightarrow NH_2Cl + H_2O$ **Eq. 3**

Formation of dichloramine: $NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$ **Eq. 4**

Formation of trichloramine: $NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$ **Eq. 5**

The three chloramine species are present in different proportions depending on the pH of the water. When the pH is greater than 8.5 monochloramine is the dominant species. When the pH is less than 4.5 trichloramine is generally predominant. Between pH 4.5 and 8.5 both monochloramine and dichloramine exist, however above pH 6 monochloramine is the more abundant of the two (Bitton, 1999).

These species are significantly less germicidal than hypochlorous acid, (Figure 4). However, if given sufficient contact time, monochloramine can be as effective at destroying pathogens as hypochlorous acid (Metcalf & Eddy, 1991). Trichloramine is virtually non-germicidal. In the Gift of Water, Inc. filtration system, the contact time is fixed at half an hour, so it is important to account for the reduced germicidal ability of any chloramines produced during the use of the filter.



(Metcalf & Eddy, 1991)

Figure 4 Germicidal efficiencies of hypochlorous acid, hypochlorite ion, and monochloramine.

The presence of dichloramine and trichloramine in finished drinking water is not desirable. These species both produce an offensive odor. Trichloramine creates such an odor at the low concentration of only 0.02 ppm. Because of the smell and taste, the presence of these compounds in drinking water might dissuade a person from chlorinating their water.

When referring to the amount of chlorine in a water sample, HOCl and OCl^- are collectively referred to as free residual. A measurement of chloramines is called combined residual. The addition of the two is total residual.

2.3 Available Chlorine

Available chlorine (Av Cl_2) is a phrase that was created in order to compare the potential oxidizing power of various chlorine compounds (White, 1999). As White said , "the term 'available chlorine' has no place in the field of water and waste treatment." However, available chlorine is used to describe the concentration of chlorine that is necessary to kill certain pathogens, so it is important to have an understanding of the term.

The initial definition of available chlorine was based on the iodometric method, in which the amount of iodine liberated from potassium iodide in a solution containing chlorine is proportional to the oxidizing power of the chlorine (White, 1999). All chlorine with a valence of +1 should react to liberate iodine from potassium iodide to produce elemental iodine. It takes one Cl^+ atom to create one molecule of elemental iodine, I_2.

The concept of available chlorine can be quite confusing as the oxidizing species is Cl^+, but available chlorine is a calculation of the weight of Cl_2 needed to liberate the same amount of I_2 from potassium iodide (White, 1999). For this reason, available chlorine is thought of in terms of Cl_2 not Cl^+, and the abbreviation is Av Cl_2. However, since only one of the chlorine atoms in Cl_2 has a valence of +1, the available chlorine in any chlorine compound is twice the amount of Cl^+ that is present.

Available chlorine can be thought of as the oxidizing percentage of the mass of a disinfectant. In the case of sodium hypochlorite, the following calculation can be carried out to determine this percentage:

$$\frac{\text{Molecular Weight of } Cl^+ * 2}{\text{Molecular Weight of NaOCl}} = \frac{35.5 * 2}{74.5} = 95.4\% \qquad \textbf{Eq. 6}$$

where the 2 is intended to account for two chlorine atoms in one molecule of elemental chlorine.

2.4 Chlorine Demand

Metcalf & Eddy (1991) defines chlorine demand as "the amount of chlorine that must be added to reach a desired level of residual." Aside from reactions with ammonia species, sodium hypochlorite reacts with many other substances in water. These reactions reduce the amount of chlorine residual available for disinfection, which in turn increases the amount of sodium hypochlorite that must be added to water in order to meet the chlorine demand of the system.

Turbidity can have a great effect on the chlorine demand of the system as it is composed of both inorganic and organic matter. Turbidity can reduce the effectiveness of chlorination through absorption of chlorine species (Metcalf & Eddy, 1991). Also, microorganisms are somewhat protected when attached to particulate matter and are more resistant to disinfection than microorganisms that are freely suspended in water (Bitton, 1999). United States Environmental Protection Agency standards allow only 1 nephelometric turbidity unit (NTU) in drinking water.

Total organic carbon (TOC), which is associated with turbidity, exerts a very large chlorine demand (Bitton, 1999). The presence of dissolved organic compounds can result in lowered disinfection efficiency. In addition, organic matter is responsible for reacting with chlorine to produce harmful chlorination-by-products, such as trihalomethanes.

A subset of TOC, those organic compounds with unsaturated bonds, may pose another problem when studying chlorine demand. These compounds, as well as those with polycyclic rings containing hydroxyl groups and those containing sulfur groups, react readily with chlorine to produce substances that appear as chlorine residual and cause falsely high readings when tests are conducted (Metcalf & Eddy, 1991). However, Metcalf & Eddy states that these compounds are assumed to have little or no germicidal ability.

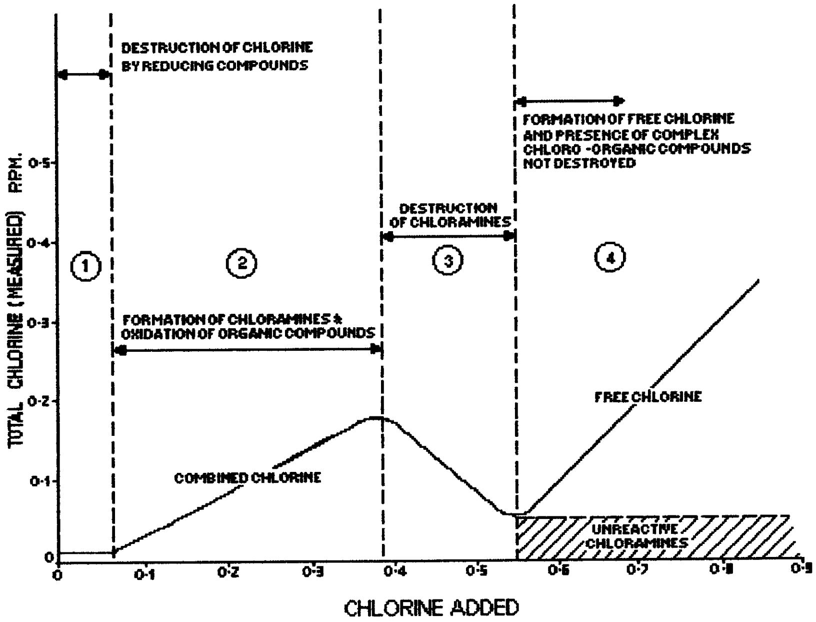
Other substances that can create a significant chlorine demand are hydrogen sulfide, iodine, nitrite, and heavy metals, particularly iron and manganese (Bitton, 1999; Gordon et al., 1987).

2.5 Breakpoint Chlorination

Breakpoint chlorination refers to the process by which chlorine reacts with all oxidizable species in a water sample up until the point where the reactions do not further consume chlorine that is added to the water. The point at which all additional chlorine added becomes free residual is called the breakpoint.

Chlorine has four stages of chemical reactions in a water sample (Figure 5). The length of each stage is dependent upon what other chemicals are present. Ammonia content has the greatest affect on the breakthrough curve due to the production of chloramines through the reactions of ammonia and chlorine. The first stage of chemical reactions occurs just after chlorine is added to a water sample. Chlorine is a strong oxidant and will react with reducing compounds, such as ferrous and manganous, which destroy the germicidal ability of the chlorine by reducing it to chloride ion, which has a valence of -1 (Metcalf & Eddy, 1991). Compounds produced during this stage are not included in the calculations of residual chlorine. The chlorine that is used in this stage is considered the initial chlorine demand of the water (*Emergency Treatment Methods*, 2002).

During stage 2, chlorine reacts with ammonia to create combined residual, mostly monochloramines, which has significantly less germicidal potency than hypochlorous acid, but is still considered an effective disinfectant. Chlorine will also begin oxidizing organic compounds, again destroying the germicidal potential of some of the chlorine added to a water sample. The residual during this stage is predominantly composed of chloramines, but there is some free residual present.



(Department of Education of the State of Queensland, Australia, 2002)

Figure 5 Breakpoint Chlorination Curve

Stage 2 ends and stage 3 commences when free residual that is present in the water begins to further oxidize the chloramines and any remaining oxidizable material. Monochloramines are oxidized again to become dichloramines, which can further be oxidized to form nitrogen trichloride, a non-germicidal compound. The hump in the breakpoint curve between stages 2 and 3 generally occurs when the molar concentrations of chlorine and ammonia are equivalent (Chungrok ENC Company, 2002). As chlorine is added and the molar ratio of chlorine to ammonia exceeds 1:1, dichloramines are formed. Further oxidation occurs as chloramines are oxidized to nitrogen gas, nitrate, nitrogen trichloride and other compounds. The complete oxidation of chloramines is shown in the following equation:

$$2NH_3 + 3HOCl \rightarrow N_2 + 3H_2O + 3HCl \qquad \textbf{Eq. 7}$$

This reaction generally takes place when the molar ratio of chlorine to ammonia is between 7.5:1 and 11:1 (Bitton, 1999).

Once the breakpoint is reached and all ammonia compounds are completely oxidized, any further chlorine added to the water can form and remain as free residual because there is no longer any chlorine demand. (This assumption does not account for compounds that might react with chlorine over a longer timescale. Therefore the free residual might still have a slight chlorine demand.) This portion of the breakthrough curve has a 45° slope because the amount of free residual created is directly proportional to the amount of chlorine added in a one-to-one relationship.

If the amount of chlorine used in disinfection does not surpass the breakpoint, it is important to account for the presence of the less germicidal species in combined chlorine residual when determining a contact time. It is also important to account for pH's effect on the ratio of hypochlorous acid to hypochlorite ion.

The breakpoint curve is a good indicator of the manner in which chlorine reacts with substances and produces germicidal residuals or non-germicidal compounds. Chlorine's interactions with these compounds that cause chlorine demand will be investigated in this study, with particular attention paid to ammonia since this interaction produces species that are still germicidal, even though less so than hypochlorous acid.

3 Pathogens

3.1 Pathogens of Concern

There are four categories of pathogens that are of concern when discussing waterborne disease in humans: bacteria, viruses, protozoa, and helminthes (Table 2).

Organism	Disease	Remarks
Bacteria		
Escherichia coli	Gastroenteritis	Diarrhea
Legionella pneumophila	Legionellosis	Acute respiratory illness
Leptospira	Leptospirosis	Jaundice, fever (Weil's disease)
Salmonella typhi	Typhoid fever	High fever, diarrhea, ulceration
Salmonella	Salmonellosis	Food poisoning
Shigella	Shigellosis	Bacillary Dysentery
Vibrio cholerae	Cholera	Extremely heavy diarrhea, dehydration
Yersinia enterolitica	Yersinosis	Diarrhea
Viruses		
Adenovirus (31 types)	Respiratory disease	
Enteroviruses (67 types)	Gastroenteritis, heart anomalies, meningitis	
Hepatitis A	Infectious hepatitis	Jaundice, fever
Norwalk agent	Gastroenteritis	Vomiting
Reovirus	Gastroenteritis	
Rotavirus	Gastroenteritis	
Protozoa		
Balantidium coli	Balanticliasis	Diarrhea, dysentery
Cryptosporidium	Cryptosporidiosis	Diarrhea
Entamoeba histolytica	Amebiasis (amoebic dysentery)	Prolonged diarrhea with bleeding, abscesses of the liver and small intestine
Giardia lamblia	Giardiasis	Mild to sever diarrhea, nausea, indigestion
Helminths		
Ascaris lumbricoides	Ascariasis	
Enterobius vericularis	Enterobiasis	Roundworm infestation
Fasciola hepatica	Fascioliasis	Sheep liver fluke
Hymenolepis nana	Hymenolepiasis	Dwarf tapeworm
Taenia saginata	Taeniasis	Beef tapeworm
Taenia solium	Taeniasis	Pork tapeworm
Trichuris trichiura	Trichuriasis	Whipworm

(Metcalf & Eddy, 1991)

Table 2 Pathogens associated with waterborne disease.

Each class of pathogen contains many infectious species that can cause various illnesses. Viruses are the smallest pathogen in size, and bacteria are the next smallest. Viruses and the smaller bacteria are generally too little to be filtered, as is most likely the case in the Gift of Water, Inc. filter. The polypropylene filter in the top bucket of the filtration system is has a five micron pore size, such that some protozoa and helminthes will be filtered, but not all (Dann, 2002).

Travelers to Haiti are advised to receive inoculations for several waterborne diseases including Polio and Hepatitis A, both of which are caused by viruses, and typhoid fever, which is caused by the bacterium *Salmonella typhi*. As well, *Campylobacter*, *Toxigenic Escherichia coli (E. coli)*, *Shigella, and Vibrio cholerae,* the pathogen that causes cholera, are considered bacteria of concern in Haiti (Tauxe, 2001).

A common ailment, and one of great concern is gastroenteritis. Bacterial gastroenteritis can be caused by *Shigella*, *Salmonella*, *Toxigenic E. coli*, *Campylobacter*, *Vibrio cholerae*, and *Yersinia* (White, 1986; Metcalf & Eddy, 1991). Many viruses and protozoa cause gastroenteritis as well. *Norwalk virus* and *Rotavirus* are believed responsible for 77 percent of acute waterborne gastroenteritis (White, 1986). They are extremely resilient viruses, and it is believed that Rotavirus can survive modern wastewater treatment.

Symptoms of gastroenteritis include diarrhea, stomach cramping, nausea, vomiting, fever, and headaches (Public Health Division of the Government of Victoria, Australia, 2002). Of particular concern are diarrhea and vomiting, which can cause dehydration, a condition that is exacerbated by the fact that the water used for rehydration will most likely contain the same pathogens that caused the illness in the first place. This cycle can only be ended if water is properly disinfected.

The scope of this study has been limited to bacteria that cause gastroenteritis, since this is an extremely common ailment. If there is confidence that the majority of the bacteria that cause gastroenteritis are destroyed, a large percentage of waterborne illness should be eliminated.

3.2 Mechanisms of Pathogen Inactivation

Chlorine works to deactivate pathogens through a variety of mechanisms. Bacterial cells are the easiest targets of chlorination because chlorine causes significant damage to many parts of the bacterial cell (Bitton, 1999). Chlorine can attack the cell wall or membrane, leading to a disruption in cell permeability and other cell functions, such as DNA synthesis and nutrient transport. Chlorine also damages nucleic acids and enzymes, causing a cell to lose survival functions. In multicellular organisms, chlorine must deactivate a large number of cells before inactivation of the organism takes place. A large portion of the organism is shielded by outer layers of cells, which must be significantly damaged before the organism can be destroyed, therefore multicellular organisms are significantly more difficult to inactivate than single-celled bacteria.

Chlorine destroys viruses through two primary mechanisms. Both bacterial phage f2 and poliovirus type 1, for example, are inactivated primarily by damage to nucleic acids. Rotaviruses, on the other hand, are inactivated through attack of the virus' protein coat.

3.3 Ct values

The effectiveness of chlorination on a pathogen can be represented by the Ct value. The "C" in the Ct values represents the chlorine concentration, usually expressed as mg/l, and the "t" in the Ct value represents the contact time, usually expressed in minutes, required to kill a percentage of a population at a specific pH and temperature (Bitton, 1999). This value is often called a k-factor, although in actuality the relationship between k and Ct is expressed by the following:

$$k = C^n t \qquad \textbf{Eq. 8}$$

where n is a factor that determines the relative importance of contact time versus disinfection concentration. When n is less than one, contact time is the more important factor for effective disinfection. When n is greater than one, the chlorine concentration is more important. Often n is close enough to one that k can be considered simply C*t.

Changes in temperature and pH both alter the k-factor for a given organism. As pH increases Ct generally increases, requiring either more disinfectant or a longer contact time (Bitton, 1999). Temperature has the opposite affect; Ct decreases with increases in temperature, requiring lower concentrations and contact times for effective disinfection.

3.3.1 Pathogen specific Ct values

Bacteria are the easiest pathogens to inactivate using chlorine (Table 3). Generally treatment of water with 1 mg/l, or even less, for 30 minutes is sufficient to kill a significant percentage of bacterial cells. The rugose strain of *Vibrio cholerae* is one exception, as it requires twice the concentration, 2 mg/l, over a 30-minute period.

Viruses can be significantly harder to kill. Viruses require a Ct value of at least 15-30 min-mg/l, while only the most hardy of bacteria require Ct values that large. The less resilient bacteria require Ct value in the range of 0.5-3 min-mg/l. After chlorination many viruses are still viable, such as *Norwalk Agent* (Liptak, 1974).

Microorganism	Av Cl_2 Concentration	Time	Ct	pH	Temperature	Reduction
	[mg/L]	[min]			°C	%
Bacteria						
Campylobacter jejuni	0.1	5	0.5	8.0	25	99.99
Escherichia coli	0.2	15	3	7.0	25	99.99
Salmonella typhi	0.5	6	3	?	20	99
Shigella dysenteriae	0.05	10	0.5	7.0	20-29	99.6-100
Vibrio cholerae (smooth strain)	1.0	<1	<1	7.0	20	100
Vibrio cholerae (rugose strain)	2.0	30	60	7.0	20	> 99.99
Yersinia enterolitica	1.0	30	30	7.0	20	92
Viruses						
Norwalk agent	0.5-1.0	30	15-30	7.4	20	Not completely inactivated
Rotavirus	0.5-1.0	30	15-30	7.4	25	100

(Centers for Disease Control and Prevention, 2002a)

Table 3 Known Ct values for the inactivation of pathogens of concern.

In order to eliminate a significant proportion of the risk from the pathogens listed in Table 3 in the half hour contact time used in the Gift of Water, Inc. filter, it is necessary to have an available chlorine concentration of 2 mg/l. If the more virulent strains, such as the rugose strain of *Vibrio cholerae*, are not present in the drinking water source, it is possible to attain reasonable disinfection with a 1 mg/l concentration of available chlorine.

Because a single unit of sodium hypochlorite is equivalent to 95.4 percent of a unit of Av Cl_2, in order to create an available chlorine residual of 1ppm in a system with no chlorine demand, it would be necessary to create a concentration of 1.05 ppm NaOCl. The bleach currently used in the Gift of Water, Inc. filtration system is a 5.25 percent by weight sodium hypochlorite solution. Therefore the five gallon Gift of Water bucket will have 1.05 ppm NaOCl concentration when 0.378 ml of bleach are added. Even if the water contained the rugose strain of *Vibrio cholera*, it would still be possible to use less than 1 ml of bleach to kill the pathogens of concern if the water had no chlorine demand. A safety factor of 2 should be multiplied by this amount in order to account for uncertainties in Ct values or variations in temperature and pH. In a chlorine-demand-free system it would be acceptable to use only 1.5 ml of bleach for adequate disinfection. This number must be increased proportional to the chlorine demand of the system.

4 Methodology

4.1 Field Work in Haiti

Field work for this study took place in Haiti during the month of January 2002. Sites were selected from among the villages within which Gift of Water, Inc. has established filtration programs. Six villages were chosen: Dumay, Fon Veret, Barasa, Karako, Bas Limbe, and Les Palmes. One to four water sources was studied in each village, and the number and type of sources varied from village to village.

(US Central Intelligence Agency, 2001)

Figure 6 Map of Haiti. Red suns indicated cities visited.

There were five different types of water sources examined in this study: groundwater wells, surface water streams, springs, cisterns, and captages. Captages are outputs of water that have been piped down a mountain from a spring. Depending on the climate, geography, and resources available, some villages had only one type of source while others had varying source types. Also, some villages had only one or two sources from which people gathered drinking water during the winter, while others had several sources from which people could choose. This study aimed to examine a representative set of water sources both across each village and across the entire country. Table 4 shows the number and types of sources studied in each village, as well as the date that sampling took place and the local name of the source, so that those familiar with the villages may have an additional reference. Individual sources will further be referred to by location and number, as shown in the table.

Site Location	Number	Type of Source	Date Sampled	Local Name
Dumay	1	Captage	January 15	Kapatage Bò Kay Rodrigue La, Pa Two Lwen Legliz Pastè Nathan
Dumay	2	Captage (same site as 1)	January 27	
Dumay	3	Captage	January 27	Tiyo Santral Dumay
Dumay	4	Groundwater Well	January 27	Pwi Nan Kafou Dival
Dumay	5	Captage	January 29	Bò Bòs Deli, Campêche
Fon Veret	1	Cistern	January 16	Rectory: Sitèn Pè A
Fon Veret	2	Surface Water Stream	January 17	Karetye
Barasa	1	Spring	January 18	Sous Sen Lwi
Bas Limbe	1	Spring into Stream (mixed water)	January 20	Koray
Bas Limbe	2	Captage	January 21	Konti
Karako	1	Groundwater Well	January 22	Basalin
Les Palmes	1	Captage	January 24	Tewouj
Les Palmes	2	Captage	January 25	Senak
Les Palmes	3	Cistern	January 26	Rectory: Sitèn Pè A

Table 4 List of sampling sites, type of water source, date sampled, and local name.

4.1.1 Description of Source Types

Captages were the most common source type sampled in this study. These sources were created mainly by foreign aid organizations that piped water underground from mountainous springs down to lower elevations where people then gathered water from a fountain. Piping the water, rather than allowing it to flow naturally down the mountain in streams, allowed for routing of the water to specific locations, as well as theoretically decreased contamination of the water from animals and other contaminant sources along the path down the mountain because the water is closed off from these sources.

Since captages are based mainly on the gravitational flow of water, much like a continuously running stream, the water from a captage is continuously flowing and always available unless the spring has run dry. In Bas Limbe, however, the captage had been stopped by a faucet that released water only when needed. It is unknown exactly where the water is stored when the faucets are turned off, but most likely it was stored in a concrete structure adjacent to the faucet. Figure 7 shows an example of each type of captage.

Figure 7 Examples of a free flowing captage (Dumay 5) and a fauceted captage (Bas Limbe 2).

Groundwater wells were sampled in two of the villages in which sampling took place. These sources are pumping stations that bring water from the ground to the surface for collection (Figure 8).

Figure 8 An example of a groundwater well (Dumay 4), being pumped by a child.

Streams were found in several villages, but only certain ones were used for drinking. People were conscious of the other uses of surface water, such as bathing and laundry, and, when possible, would hike further upstream than where these activities were taking place in order to collect drinking water.

The sources of the streams are springs, places where groundwater reaches the surface and flows as surface water. In places where springs flow slowly, often drinking water is a mixture of water flowing from the spring and that which has already become part of the stream (Figure 9).

Figure 9 Examples of a stream (Fon Veret 2) and a spring developing into a stream (Barasa 1).

Cisterns were also commonly used for drinking water in Haiti. These sources collect rainwater, often on a roof or in a large freestanding structure. The water is then piped to a faucet for collection, either indoors or outdoors.

4.2 Methods Utilized in Field

Several tests were conducted in the field in order to determine what characteristics of the water affected chlorine demand. I chose six water quality parameters to investigate: ammonia concentration, iron concentration, temperature, pH, conductivity, and turbidity. As well, I sampled for free and total chlorine residuals in each of my water samples.

4.2.1 Experimental Setup

At each site my experimental setup consisted of several Gift of Water, Inc. filter top buckets, containing polypropylene filters, filled with source water. To each bucket a different amount of bleach was added in order to determine how a range of bleach concentrations were affected by the chlorine demand of the water supply. When filled, each bucket held approximately 5 gallons of water. At the majority of sites, 4 top buckets were used with a 1ml addition, 3 ml addition, 5 ml addition, and 10 ml addition of 5.25 percent bleach. The Dumay 1 setup had a 2 ml addition bucket instead of a 3 ml addition bucket. The Dumay 2 and Dumay 4 setups lacked 10 ml buckets.

Each bucket was tested for the six water quality parameters and residual chlorine as described below, with duplicates conducted on every tenth sample. Testing was completed half an hour after the addition of chlorine, which is the amount of time Gift of Water instructs filter owners to wait before allowing the water to pass to the lower bucket. The six tests were also conducted on a raw water sample.

Figure 10 The experimental field setup at Bas Limbe 2, showing the four top buckets being sampled.

In addition to the tests done on each bucket, one sample was chosen at random at each of the first ten sites to be tested for chlorine residual every 10 minutes in order to determine the variation over time of chlorine residual in a sample.

4.2.2 Chlorine Residual Testing

4.2.2.1 DPD Chemistry

The sampling of chlorine residual in my water samples was conducted through a colorimetric method, utilizing N, N diethyl-p-phenylenediamine sulfate (DPD) tablets as the color-producing reagent. Two types of DPD tablets were used, and only DPD-1, which measured the free residual available in the sample, is composed of N, N diethyl-p-phenylenediamine sulfate. DPD-3, the active ingredient of which is potassium iodide, gave a measure of the total residual after addition to a sample already containing DPD-1.

The basis for the ability of this reaction to proceed is chlorine's desire for electrons. Chlorine, a halogen, is extremely electronegative with a value of 3.0 on the Pauling scale (Alberty, 1997). Oxygen, however, is even more electronegative with a value of 3.5. When hypochlorous acid is formed, the oxygen is the atom in the middle with a hydrogen atom and a chlorine atom attached on opposite sides. The oxygen draws the electrons away from the chlorine atom, giving the chlorine a positive polarity. Because of this, the chlorine is willing to accept electrons from another molecule that will give them up, so that when a reducing compound is added, the chlorine will break off from the hypochlorous acid molecule and form a compound with a reducing substance.

The process by which DPD works is as follows. The active ingredient in the DPD-1 tablets, N, N diethyl-p-phenylenediamine sulfate is an organic compound with a benzene ring base. The substances, such as reduced nitrogen compounds, around the benzene ring are available for oxidation by chlorine and will break away from the DPD to form a compound with the more electronegative chlorine. Each DPD must give two electrons in the following reaction:

$$Cl_2 + DPD \rightarrow 2Cl^- + DPD^{+2} \qquad \textbf{Eq. 9}$$

(Total Residual Chlorine LaMotte Method 7916, 1996)

This oxidation causes the DPD to change from colorless to the red or pink color read by the spectrophotometer.

The DPD-3 reaction adds more red color to the solution in proportion to the amount of combined chlorine available in the sample. In chloramines, the chlorine is attached to a nitrogen atom that is equally as electronegative as chlorine. Chlorine therefore wants to combine with something less electronegative than itself, but because it has not given up its electrons like it had to oxygen in hypochlorous acid, the attraction to reducing agents is not so strong that DPD can strip the chlorine from the chloramine molecules. DPD-3 tablets contain potassium iodide. Chloramines oxidize the iodide ion, forming ICl. DPD is able to liberate the iodine from the chlorine atom, similar to the way in which DPD reacted with hypochlorous acid. The reaction between iodine and DPD forms a further red color read by the spectrophotometer (*Total Residual Chlorine LaMotte Method 7916*, 1996).

It should be noted that the addition of potassium iodide would produce a similar reaction with hypochlorous acid and hypochlorite ion, so that it is important to get a free chlorine reading without the presence of iodine in the water or the reading will be inaccurately high. Other compounds that can cause false high readings in the timeframe of the testing procedure include bromine and bromamines, ozone, hydrogen peroxide, oxidized manganese, permanganate, and monopersulfate. Most likely, many of these interferences were not encountered during my sampling in Haiti, although it is possible that oxidized manganese may have led to some false high readings.

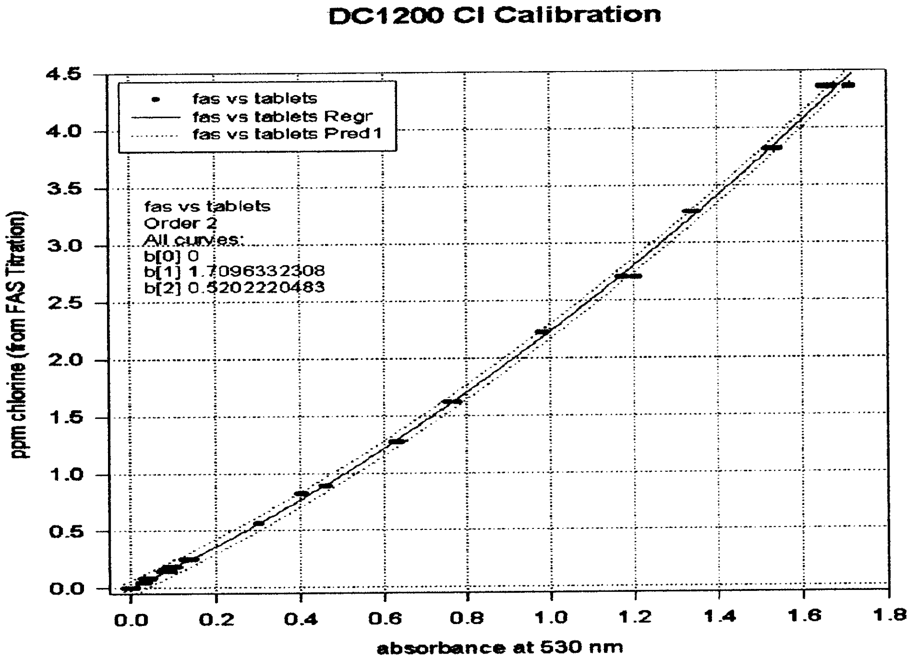
It is also recommended that glassware be acid washed between samples to remove any residues of potassium iodide that might cause combined chlorine to show up in a test for free chlorine. Due to limitations in the field my glassware could only be rinsed thoroughly multiple times with the sampling water or distilled water to remove any residues from previous tests. This may have contributed to falsely high free chlorine readings, however the total chlorine readings should still have read approximately the correct value.

4.2.2.2 LaMotte 1200 Colorimeter

The chlorine residual readings were taken with a LaMotte 1200 Colorimeter, a single wavelength, direct-reading instrument. LaMotte brand DPD-1 and DPD-3 tablets were utilized. The colorimeter comes with 10ml glass colorimeter tubes used in the sampling procedure, a tablet crusher used to dissolve DPD tablets, a wiping cloth, and a water sampling bottle used to collect sample.

The colorimeter has a chlorine residual detection range of 0-4.00 ppm of Cl^+ (LaMotte 1200 Colorimeter Instruction Manual, 2002). Because some samples into which bleach had been added were expected to have readings approaching or higher than the detection limit, all samples were diluted by approximately 19:1 using a 10 ml graduated cylinder. Dilutions were made with distilled water.

The LaMotte 1200 Colorimeter, when calibrated to measure chlorine, utilizes a 530 nm wavelength to detect the intensity of color caused by the reaction of chlorine and the DPD tablets (Figure 11).



(*DC1200 Cl Calibration Curve,* 2002)

Figure 11 Calibration curve for the LaMotte 1200 Colorimeter.

The colorimeter was calibrated once per week using LaMotte's Chlorine Standards for Model 1200. This is a secondary standard kit containing a blank, as well as three standards for low, midrange, and high chlorine calibrations. The instrument had been borrowed from Gift of Water, Inc. and had previously been calibrated with primary standards.

Before collecting a sample, the water sampling bottle was rinsed three times with sample water in order to wash away any residue of previous water samples. The sampling bottle was then filled and only water from this bottle was used in the colorimetric analysis. A colorimeter tube was also rinsed three times with either sample water, or distilled water if the sample had been diluted. The graduated cylinder used for dilutions was rinsed three times with distilled water.

Either 10 ml of pure or diluted sample was placed in a colorimeter tube, which was then capped and wiped down with the wiping cloth. The colorimeter requires no warm-up time, so the sample was placed directly in the machine and the colorimeter was zeroed by holding the zero button for 2 seconds until bLA appeared on the screen (LaMotte 1200 Colorimeter Instruction Manual, 2002). The sample was removed and a DPD-1 tablet was placed in the tube and dissolved as quickly as possible with the aid of the tablet crusher. A reading was taken by pressing the read button on the colorimeter. A DPD-3 tablet was then added and crushed, and a reading was taken in the same manner.

This method of chlorine residual testing was utilized for both the chlorine residual samples taken half an hour after chlorination and samples taken on one bucket per site at ten minute intervals.

4.2.3 Water Quality Parameters

4.2.3.1 Ammonia Concentration Testing

Ammonia testing was completed using Hach's "Test Kit Nitrogen Ammonia, Model NI-8, Mid Range 0-3 mg/l, Color Disc", which uses the Nessler method to determine the amount of ammonia in a sample. In this method, Nessler's reagent reacts with ammonia to form a yellow color in proportion to the concentration of ammonia present in the sample. The reagent is a solution of mercuric iodide, HgI_2, in potassium iodide KI (Clesceri et al., 1989). According to Hach's product information, the typical accuracy of a color disk test kit is ± 10 percent, but this is subject to the color perception of the individual reading the sample (Hach Single-Parameter Test Kits, 2002).

The test kit contained two 5 ml test tubes, a bottle of Nessler's reagent, and a color wheel. Before any samples were taken, the test tubes were rinsed 3 times with the sample water to wash away any residues from previous samples. The tubes were then filled to the 5 ml line with sample water and 3 drops of Nessler's reagent were added to one of the test tubes. The tubes were placed inside the color wheel holder, and the concentration was determined by turning the colored portion of the wheel over the tube containing pure sample (in order to account for color in the sample). When the color of the wheel, when viewed over the pure sample, matched the color of the tube to which the reagent had been added the corresponding concentration could be read off the color wheel.

When not in use the color wheel was stored in a light protective sleeve in order to prevent the colors from fading.

4.2.3.2 Iron Concentration Testing

Iron analysis was conducted using a Hach "Test Kit Iron, Model IR-18, Medium Range 0-5 mg/l, Color Disc", which uses 1,10-phenanthroline to react with ferrous iron (Fe^{2+}) to produce a range of colors proportional to the concentration of Fe^{2+} in a sample. An orange-red complex is formed when three atoms of phenanthroline react with ferrous iron and the intensity of the color varies with concentration (Clesceri et al., 1989). The accuracy of this test kit is subject to the color perception of the test reader, but generally is approximately ± 10% (Hach Single-Parameter Test Kits, 2002).

The iron test kit is very similar to the ammonia test kit described above. The test contains two 5ml test tubes, 100 packets of 1,10-phenanthroline, and a color wheel. The test tubes were rinsed 3 times with sample water to remove residues of previous samples and then filled to the 5 ml line. One packet of 1,10-phenanthroline was added to one of the test tubes, which was capped and shaken to mix the reagent. The tubes were placed in the color wheel holder and a reading was taken by passing the colored part of the wheel over the tube containing only sample water. When the color on the wheel matched the color of the reacted test tube, the concentration could be determined by reading the wheel.

Again, in order to prevent the colors on the wheel from fading, the color wheel was stored in a light protective sleeve when not in use.

4.2.3.3 Temperature Measurements

Temperature measurements were conducted using an Envirosafe Celsius Thermometer, an instrument that requires no calibration. The thermometer was dropped into each sample bucket and left for a minimum of 2 minutes in order to allow the thermometer to reach the sample temperature. This was done after all other tests on a sample were completed in order to avoid possible contamination of the sample from the thermometer directly entering the water.

4.2.3.4 pH/Conductivity Measurements

pH and conductivity measurements were taken with Hanna Instrument's HI-9812 Conductivity, TDS & pH meter. This instrument is temperature compensated for conductivity and pH measurements from 0 to 50°C (HI-9812 Conductivity, TDS & pH meter, 2001). Measurements were conducted by dipping the instrument's probe into the water sample after all other chemical analysis was completed in order to avoid possible contamination. The probe was swirled around in the sample for 15-30 seconds to ensure an accurate reading. The probe read pH or conductivity measurements depending on which setting it was on and to switch back and forth a button on the face of the meter was pressed.

This instrument was calibrated once each week for both pH and conductivity. Generally the instrument read the appropriate value for both pH and conductivity when calibrated, and altering settings was usually unnecessary. pH calibrations were conducted using pH 4 and pH 7 standard solutions and the conductivity calibration used a 1410 µS/cm standard solution.

4.2.3.5 Turbidity Measurements

Turbidity is an indication of the cloudiness of a water sample. It can be caused by suspended and colloidal material, including inorganic and organic matter, microorganisms, clay, and silt (LaMotte 2020 Turbidimeter Instruction Manual, 2002). Some of this material may exert a chlorine demand.

Turbidity measurements were conducted using a LaMotte 2020 Turbidimeter, which comes with 25 ml glass turbidity tubes. The meter was calibrated once each week using 1 Nephelometric Turbidity Units (NTU) and 10 NTU standards.

Before a measurement was taken, the turbidity tube was rinsed three times with sample water in order to remove traces of any previous sample. It was then filled with sample water, capped, and wiped clean and dry with a lint free cloth. A measurement was taken by placing the tube in the holder, aligning the arrow on the turbidity tube with the indexing arrow on the meter, closing the lid, and pressing read.

4.3 Follow-up Laboratory Work

In order to further evaluate the data that was gathered in the field, follow-up laboratory work was conducted. The main purpose was to learn more about the field chlorine data. Three types of experiments were conducted. The first set of experiments utilized LaMotte DPD-1 and DPD-3 tablets to conduct colorimetric experiments on Haitian water samples using a DU Series 600 Spectrophotometer. In the second set of experiments, water was artificially stratified to see how stratification could affect the mixing of bleach. The third experiments involved testing water samples from field sites for total organic carbon (TOC).

4.3.1 Haitian Water Testing

The first lab tests that were conducted utilized Haitian water samples brought to the US in January 2001. The samples were stored in a dark refrigerator at 4°C since the time they were brought back. Each jar of water had been sealed without headspace.

The goal of these tests was to determine through controlled laboratory experiments, based on water samples from the same sites visited during this field study, whether or not the DPD method used in the field was accurate. Although the water was approximately a year old, because it was stored with no headspace, it is assumed that substances that were present in the water upon collection were still present at the time of these experiments.

The experiments were conducted to replicate my field chlorine sampling, however on a smaller scale. Instead of 5 gallon buckets, beakers filled with 100 ml of sample water were used. Each was labeled to correspond to a field bucket: 1 ml, 3 ml, 5 ml, and 10 ml. Six percent Clorox bleach was used instead of 5.25 percent bleach, so a factor was used in calculating how much bleach to add to the samples in order to account for the concentration difference. Also, because the water in the beakers was only about 0.5 percent of the amount of water used in the field, the bleach was diluted 100 times to a 600 ppm sodium hypochlorite solution to make feasible measurements of the amount of bleach added.

The amount of the 600 ppm sodium hypochlorite solution placed in each sample was calculated through the following equation

$$\text{Amount to add} = \frac{(\text{ml added in field})*(52500\text{ ppm NaOCl})*(100\text{ ml})}{(600\text{ ppm NaOCl}) * (5\text{ gallons} * 3780\text{ ml/gallons})} \qquad \textbf{Eq. 10}$$

Table 5 shows how much of the 600 ppm NaOCl solution was added to the beakers corresponding to each field bucket

Field addition	1 ml	3 ml	5 ml	10 ml
Lab addition	0.46 ml	1.4 ml	2.3 ml	4.6 ml

Table 5 Amount of 600 ppm NaOCl solution added to beakers in a laboratory corresponding to buckets used for sampling in the field.

Water samples from both Dumay 1 and Les Palmes 2 were tested using this procedure. 100 ml of each sample was poured into the four beakers. Also, approximately 40 ml were poured into a fifth beaker for raw water testing. The water was brought to room temperature and then the bleach was added to each beaker, staggered by 10 minutes in order to allow for testing of each sample before moving onto the next one. After half an hour, tests were run on the spectrophotometer using the DPD method. All samples were diluted with Q-water in order to assure that chlorine concentrations were not higher than the machine could distinguish. Q-water is reverse osmosis water that is first passed through an Aries Vaponics 110 volt system containing ion-exchange cartridges in series, and then passed through a TOC remover (Lantagne, 2001b). Because this water is highly purified, it is assumed to have little chlorine demand. The amount of dilution depended on the expected bleach concentration in the sample. Ten ml of a sample and Q-water mixture was poured into a beaker in which DPD tablets could be crushed with a glass rod. Raw water was tested without dilution.

Readings were conducted by placing a blank of the sample in the spectrophotometer in order to zero the machine. A DPD-1 tablet was added to the sample and crushed, and some of the sample was poured off into a cuvette and placed in the machine. The DPD-1 sample read by the machine was added back into the beaker in order to have 10 ml of sample, and a DPD-3 tablet was added, crushed, and sampled in a cuvette in the spectrophotometer. A reading of the blank was then taken to check for fluctuations in the machine's accuracy.

Readings were taken at both 515 nm and 650 nm wavelengths. The 515 nm wavelength determines the intensity of the pink color caused by the DPD reactions, while the 650 nm wavelength indicates the amount of light scattering caused by particulate matter in the water (such as non-dissolved particles of DPD) or scratches in a cuvette.

In order to determine what the machine readings corresponded to in terms of concentration, standards were created and tested each day in the same manner as the Haitian water samples, although without further dilution. It is important to note that according to Standard Methods for the Treatment of Water and Wastewater, the DPD method for chlorine testing measures concentration in terms of ppm of Cl, like the LaMotte 1200 Colorimeter used in the field, however the field method utilized a 530 nm wavelength to take readings rather than a 515 nm wavelength (Clesceri et al., 1989; Parent, 2002).

Standards were created using the 600 ppm NaOCl solution and adding specified quantities to 500 ml of Q-water. The standards are in ppm of Cl, so a conversion between the molecular weight of NaOCl and Cl must be accounted for in determining what amount of the 600 ppm NaOCl solution to add to create each standard. The following equation was used:

$$\text{Amount added} = \frac{500\text{ ml} * \text{ppm of standard} * 74.5\text{ g/mol NaOCl}}{600\text{ ppm NaOCl} * 35.5\text{ g/mol Cl}} \quad \textbf{Eq. 11}$$

Standards were created each day that testing was conducted, and ranged from 0.014 ppm to 1.42 ppm.

4.3.2 DU Series 600 Spectrophotometer

The DU Series 600 Spectrophotometer is a microprocessor controlled spectrophotometer that can make measurements in the UV and visible ranges of the electromagnetic spectrum (*DU Series 600 Spectrophotometer Operating Instructions*, 1993). It has three standard routine methods, one of which, "fixed wavelength", was used for the purpose of these tests. All controls are adjusted using a mouse connected to the machine, which displays on a monitor screen.

When using the fixed wavelength method, there is a "Parameters" menu in which the wavelengths of light used in an experiment are set. In order to choose a wavelength, one must click on the "Use" column in that wavelength's row and change the entry to "Yes". To deselect a wavelength, the Use column's entry must be changed to "No". If a desired wavelength does not appear on the list, one must click on one of the unused wavelengths and set the number to the desired wavelength, being sure to change the Use to Yes. There is also a "Factor" column that can be set to multiply by the reading at a given wavelength. For the purpose of my experiments, the Factor was set to 1. The "Units" column was disregarded, as the output for my purposes was independent of the entry in this column.

In order to blank a sample, the <<BLANK>> symbol at the bottom left of the screen must be pressed. To take sample readings, ReadSamples at the top left of the screen must be selected.

The visible source lamp is kept off when not in use and must be turned on and allowed to warm up for at least 30 minutes before any readings are taken (*DU Series 600 Spectrophotometer Operating Instructions*, 1993).

4.3.3 Stratification Experiments

Stratification experiments were also conducted in the laboratory. These experiments involved artificially stratifying water so that a layer of slightly warmer and less dense water lay on top of cooler water. The stratified column was produced by filling a tank with 19-21°C water, and then pouring over the top water that was 10°C warmer. The warm water was passively poured by dribbling the water into a spoon on the surface of the cooler water. This method of adding the warm water to the water column kept the warm from plunging into the cool as would happen if the water were simply dropped onto the water surface in a single plume. The goal for the warmer layer was approximately 1°C warmer over 1 cm of depth or another combination with a product equivalent to 1°C-cm. The volume of 1 cm depth of water in the tank was 530.9 ml, however rather than use 1°C warmer water I used water that was 10°C warmer, so only one tenth of that volume, or approximately 53 ml, of warm water were poured over the top. In order to visually assure that stratification occurred, the warm water was dyed red. A stratified layer of approximately 5 cm was created, (Figure 12, the layer had grown slightly deeper by the time the photograph was taken). There was a roughly 0.2°C change in temperature across the entire stratified layer.

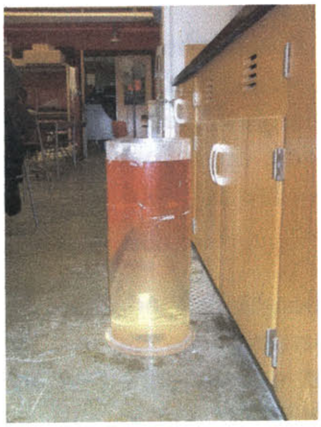


Figure 12 Artificial stratification. Hotter and therefore less dense water is red in color.

A salt water solution, composed of NaCl, blue food coloring, and Q-water was created with the same density as 5.25 percent bleach, 1.076 g/cm^3, in order to emulate field bleach additions without bleaching out the dyes used for visualization purposes. Varying amounts of the bleach substitute were added to the tank either in a single plume release or by carefully spreading the solution across the surface of the water column. Observations were recorded on the behavior of the blue salt solution upon entering the water column, particularly whether or not the solution was held up in the red stratified layer or if it sank to the bottom of the tank.

4.3.4 TOC Measurements

Experiments were also conducted in the laboratory in order to test for the presence of TOC in Haitian water sources. At each site 60 ml glass bottles, pre-filled with 1 ml of hydrochloric acid, were filled with source water and capped at each site. The hydrochloric acid was intended to acidify the samples so that inorganic carbon would be converted to CO2, which could be sparged out of the sample during the testing procedure (Clesceri et al., 1989). Samples were stored in the dark at 4°C from the time of collection to the time of testing.

During transport, the Les Palmes 2 sample bottle broke, so only thirteen samples were available for testing. Of those samples all were tested but Dumay 1, Dumay 3, and Dumay 5. Due to time constraints, not all samples could be tested, and I put priority on testing at least one sample from each village and one of each type of source in a village. As the three samples not tested were all from free flowing captages in Dumay, like the Dumay 2 sample that I did test, these were the three sources I chose not to test.

Concentrations of TOC were determined in the laboratory using the Shimadzu Total Organic Carbon Analyzer Model TOC-5000, which uses the combustion/non-dispersive infrared gas analysis method (Shimadzu Corporation, Date unknown). The instrument can measure total carbon (TC), inorganic carbon (IC) and non-purgeable organic carbon (NPOC, generally referred to as TOC). For my experiments, I tested only for NPOC.

The Shimadzu Total Organic Carbon Analyzer Model TOC-5000's NPOC method works by sparging an acidified water sample with high purity air in order to remove inorganic carbon prior to measuring TOC (Shimadzu Corporation, Date unknown). It then injects 26 μl of sample water into a combustion tube and air carries the combustion products of organic carbon to a non-dispersive infrared gas analyzer (NDIR), which converts the signal from the combustion products to a peak whose area is proportional to the concentration of TOC in the sample.

Sample was poured from the 60 ml glass bottle into a combusted (free of organic matter) glass vial, from which sparging and injections occurred.

The length of time of sparging, the number of times the injection tube is rinsed, and the number of injections per sample are variables set by the user. For the purpose of my experiments, the sparging time was five minutes, the injection tube was rinsed four times, and there were 3 injections per sample.

A calibration curve was found for the instrument by running 0, 1, 2.5, 5, 10, and 50 ppm standards and fitting a linear calibration curve to the data (Figure 13). There were two calibration curves created, one for small concentrations of TOC and one for large concentrations. The reason for this is that the low concentration samples are more properly calculated using a curve fit only to lower concentration standards in case the 50 ppm standard caused the curve to be skewed slightly as there are no intermediate values between 10 and 50 ppm. For the larger samples, including the 50 ppm standard is essential and the error is a smaller percentage of the measurement. The two calibration curves are quite similar. The areas of my measured samples were compared to the calibration curve to determine the equivalent concentration.

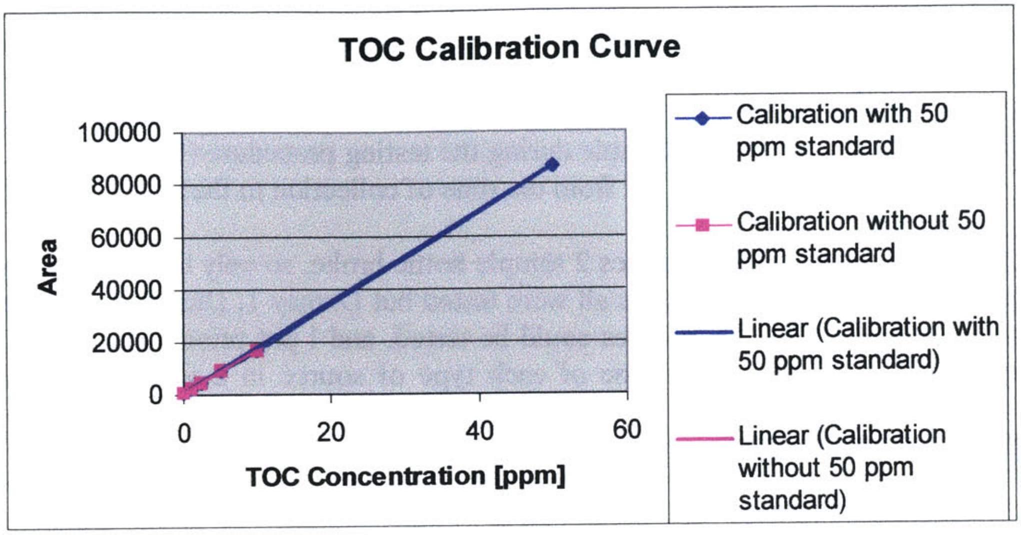


Figure 13 Calibration curve for TOC measurements.

4.4 Discussion of uncertainties

It is important to recognize that there are uncertainties in the data and that all numbers can only be known with a certain confidence. For field chlorine data, the uncertainty was determined by taking duplicates on every tenth sample and finding the percent error on the duplicate measurements. Percent error is calculated through the following equation:

$$\%\text{ error} = \frac{(\text{Reading 1 - Reading 2})}{\text{Average of the Readings}} = \frac{(\text{Reading 1 - Reading 2})}{(\text{Reading 1 + Reading 2})/2} \qquad \textbf{Eq. 12}$$

In the case of a triplicate reading, Reading 1 is the highest reading, Reading 2 is the lowest reading, and the Average of the Readings is actually the sum of all three readings divided by three. The range of percent error on the field chlorine data points was 2.3 percent to 49.7 percent. The average uncertainty was 24%.

Uncertainty in the laboratory residual measurements was determined using the calibration curves derived from standard concentration bleach solutions. The calibration curves were created by comparing known concentration solutions to their spectrophotometer readings and plotting the results (Figure 14). A linear trendline was found and all samples were compared to this trendline to determine their chlorine residual concentrations. The samples can be no more certain than the calibration curve to which they were compared.

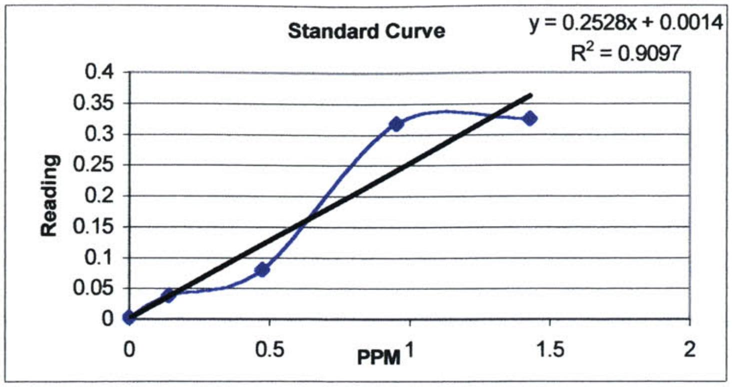


Figure 14 Sample standard curve from laboratory experiments.

The uncertainty of the laboratory data was also computed using the percent error of two data points, this time the known concentration of bleach at a certain absorbance and the concentration of bleach that the trendline would compute for the same absorbance. The equation for percent error in this case was:

$$\%\ \text{error} = \frac{(\text{Actual Concentration - Trendline Concentration})}{\text{Actual Concentration}} \qquad \textbf{Eq. 13}$$

The uncertainty is an average of the percent error from several calibration curves taken over several days of experiments. The value is 21.5 percent, very close to the uncertainty of the field samples.

5 Results

5.1 Water Quality Parameter Data

The results from the five water quality parameters tested were similar across the villages in Haiti (except for temperature), but did vary by the type of source tested (Table 6).

Raw Water	Type	Temp.	pH	Conductivity	Turbidity	Iron	Ammonia	TOC
Site		°C		µS	NTU	ppm	ppm	ppm
Dumay 1	Captage	26	7.2	580	0.05	0.4	0.4	N/A
Fon Veret 1	Cistern	22	8.2	70	0	0.4	0.4	1.72
Fon Veret 2	Surface water Stream	17	8.3	300	2.8	0	0.1	1.26
Barasa 1	Spring	17	7.6	430	10.91	0	0	0.83
Bas Limbe 1	Spring into Stream	26	7.1	540	1.86	0.1	0.1	0.54
Bas Limbe 2	Fauceted Captage	24.5	8.0	200	1.09	0.1	0.4	0.66
Karako 1	Groundwater Well	27.5	7.6	560	0.48	0	0.3	0.97
Les Palmes 1	Captage	20	7.0	110	0.96	0.4	0.1	0.88
Les Palmes 2	Captage	23	7.2	470	0.52	0.2	0.3	N/A
Les Palmes 3	Cistern	20	8.0	40	0.3	0.4	0.2	22.51
Dumay 2	Captage	26	7.3	590	0.26	0	0	0.80
Dumay 3	Groundwater Well	25	7.5	570	0.27	0.4	0.4	N/A
Dumay 4	Captage	26.5	7.3	690	1.3	0.4	0	26.81
Dumay 5	Captage	25.5	7.3	580	0.31	0	0.2	N/A

Table 6 Water quality data for raw water at each site

The water ranged in temperature from 17°C to 27.5°C, with a mean temperature of 23.3°C. The lower temperatures generally occurred in the mountainous areas of Fon Veret, Barasa, and Les Palmes, where the daytime ambient air temperatures can be as high as the temperatures in the lower altitude villages, but the nighttime air temperatures are significantly cooler.

The pH of the water samples ranged from neutral to slightly basic, 7.0-8.3. There does not appear to be a correlation between the village in which the sample was taken and the pH, however pH may be correlated to the type of water source. All free flowing captages had close to neutral pH values ranging from 7.0-7.3. Slightly higher pH values were found in the groundwater wells with a pH range of 7.5-7.6. The cisterns tended to be slightly basic with a range of pH 8.0-8.2. The fauceted captage had a higher pH than the free flowing captages, perhaps affected by the water sitting in a concrete structure until the faucets were turned on. The concrete captages and cisterns had higher pH, most likely due to the limestone in the concrete. Surface water streams and springs ranged in pH values.

Conductivity seemed to vary no matter where the sample was taken or the source type, with one exception. Cistern water had significantly less conductivity than most other water sources. This is logical because conductivity is caused by ions in the water, and a cistern simply collects rainwater and holds it until it is used. The water does not have a chance to mix with the environment and collect ions.

Turbidity ranged from 0.00 NTU to 10.91 NTU. The highest turbidity was in surface water streams and springs. All other sources had a similar range of turbidity, from 0.00 NTU to 1.09 NTU, which did not appear to correlate to the type of source.

Both iron and ammonia readings ranged from 0-0.4 ppm. The error on these readings, however, is large. The color wheel in the test kits for both parameters did not have a noticeable color gradient until 0.5 ppm, and therefore all readings below that amount were largely estimated. Essentially all readings could be considered to indicate a value of iron or ammonia in the range of 0-0.4, regardless of what the reading taken on site was. Depending on who was looking and the angle of the sun behind the color wheel, the values read off varied greatly within that range for a single sample. Therefore iron and ammonia concentrations are considered extremely small and based on these tests, most likely did not contribute greatly to chlorine demand.

TOC concentrations were fairly low in most water sources. The average concentration of TOC was 5.70 ppm. Two samples were significantly larger than all other samples, Les Palmes 3 and Dumay 4, indicating that TOC most likely played a significant role in chlorine demand at those sites. Without the two high samples, the average TOC value was 0.96 ppm. Interestingly, while Les Palmes 3 had the lowest chlorine residual measurements (Section 5.2.2), Dumay 4 had some of the highest total chlorine residual measurements. The high concentrations at Dumay 4, in spite of high TOC concentrations, are due to an undetermined cause.

5.2 Chlorine Data

5.2.1 Contribution of Combined Chlorine to Total Residual

Despite the low readings of ammonia concentrations, chlorine residual measurements indicate that combined chlorine was produced in nearly all samples and on average accounted for 25 percent of the total chlorine residual in a sample half an hour after the addition of bleach. Combined chlorine was calculated by subtracting the free chlorine reading for a sample from the total chlorine reading. Figure 15 shows the relationship between free chlorine residual (DPD 1) and total chlorine residual (DPD 3) at all sites for each of the four buckets. At almost every site, for all buckets, the data points lay above the 1 to 1 line, indicating that the total chlorine residual measured was higher than the free chlorine residual measured. In all cases, the general trendline of the data is above the 1-to-1 line.

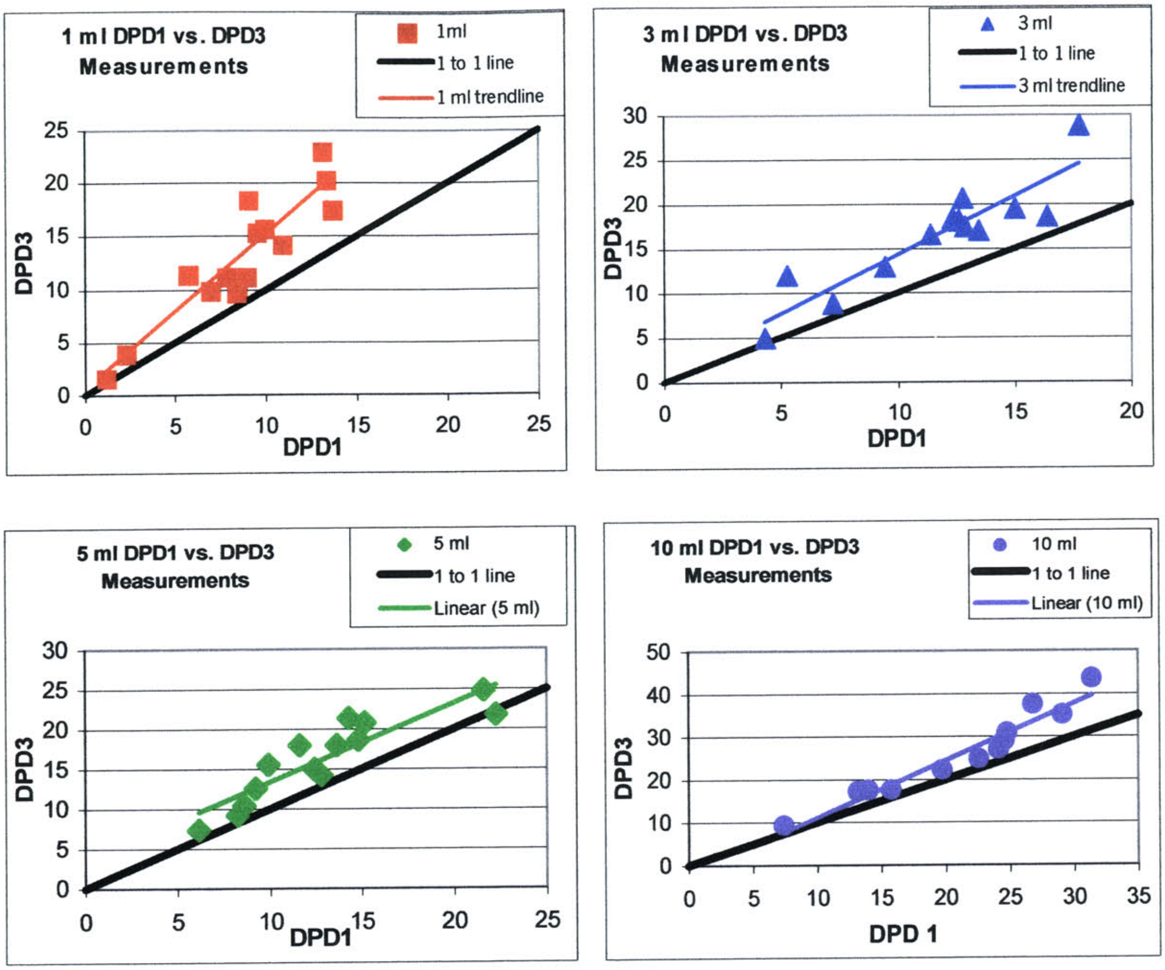


Figure 15 Free chlorine residual vs. total chlorine residual in the 1, 3, 5, and 10 ml buckets.

The presence of chloramines is not fully supported by the ammonia concentration measurements taken at the sites. There could be at most one chloramine created for each ammonia molecule present in the water. Assuming the validity of the results of the chlorine test kit, the greatest ammonia concentration that could have been present in a water sample was approximately 0.4 mg/l. The maximum amount of chloramine that can be produced can be calculated through the following relationship:

$$[\text{Chloramine}] = \frac{0.4\text{ mg Ammonia}}{\text{liter}} * \frac{1\text{ mol}}{17\text{ g Ammonia}} * \frac{\text{MW Chloramine [g]}}{1\text{ mol}} \qquad \textbf{Eq. 14}$$

where,

MW (molecular weight) monochloramine = 51.5g
MW dichloramine = 86 g
MW trichloramine = 120.5 g

Therefore at the extremes of only monochloramine produced or trichloramine produced, the maximum concentration of chloramines in the water would range from 1.2-2.8 ppm. Combined chlorine measurements in the field were generally much larger than this amount (Table 7).

Site	1 ml	2 ml	3 ml	5ml	10 ml
Dumay 1	6	1.6		1.4	2.2
Fon Veret 1	6		6	3.2	6
Fon Veret 2	3.5		1.6	1.8	1.8
Barasa 1	1.47		4.5	2.6	10.8
Bas Limbe 1	3.6		5.2	6.4	6.13
Bas Limbe 2	4		7.8	7.1	4.6
Karako 1	5.83		5.6	5.7	12.2
Les Palmes 1	2.4		3.6	3.4	3.5
Les Palmes 2	1.8		6.8	0.95	4
Les Palmes 3	0.63		0.75	1.17	1.88
Dumay 2	10		4.5	3.8	
Dumay 3	3.125		3.5	4.38	2.83
Dumay 4	9.5		11	5.67	
Dumay 5	7.25		2.25	-0.5	2.5

Table 7 Combined Chlorine Residual Measurements in ppm of Cl^+.

The reason for this discrepancy is unclear, but it may be attributed to many causes, such as residues in the colorimeter tubes or a lack of accuracy in the use of either the ammonia test kit or colorimeter. The uncertainty of the field chlorine residual measurements, ±24 percent, can only account for the difference between measured combined chlorine concentrations and expected combined chlorine concentrations based on the concentration of ammonia, for field measurements up to approximately 3.7 ppm.

5.2.2 High Chlorine Residuals

5.2.2.1 Field Data and Theory

The chlorine residual measurements conducted in Haiti yielded a peculiar trend. In particular, many concentrations were higher than the value expected if the bleach were well mixed and there was no chlorine demand (Table 8). The 10 ml bucket at Les Palmes 3, in bold, is the only sample that did not exceed the expected concentration.

Even if the assumption were made that there was no chlorine demand in any of the water sources, as long as the bleach were adequately mixed in the top bucket within the half hour contact time, the chlorine residual readings should not be higher than the expected value. Therefore most likely there is not complete mixing in the filtration system and more of the bleach than expected remains on the top of the filter, where water for sampling is poured off. This is extremely problematic because it is possible that even with high levels of bleach addition to the filtration system, water in some parts of the bucket may not receive a chlorine residual that is sufficient to destroy all pathogens of concern.

Site	Raw	1 ml	2ml	3ml	5ml	10 ml
Maximum Expected (no chlorine demand)	0*	1.32	2.65	3.97	6.62	13.24
Dumay 1	0.45	15.8	10		14.2	24.8
Fon Veret 1	0.59	15.4		18.4	24.8	35.13
Fon Veret 2	0.58	11.2		8.8	10.4	17.6
Barasa 1	0.69	9.73		17.4	15	37.6
Bas Limbe 1	0.59	14.4		16.6	18	30.93
Bas Limbe 2	0.62	17.6		20.6	21.4	29.2
Karako 1	0.67	11.44		18.2	15.6	43.6
Les Palmes 1	0.63	11.2		13	12.6	17.5
Les Palmes 2	0.69	4		12	9.2	17.2
Les Palmes 3	0.06	1.75		5	7.33	**9.25**
Dumay 2	0.78	23		19.5	18.6	
Dumay 3	0.8	10		17	18	27
Dumay 4	0.82	18.5		28.75	20.83	
Dumay 5	0.78	20.5		18.63	21.75	22.25

Table 8 Total Chlorine Residual Measurements in ppm of Cl^+. Raw water readings greater than 0 are most likely due to interference from Mn^{4+} or non-dissolved pieces of DPD tablet.

If the water to which bleach is added is uniform in temperature and density, bleach should fall directly to the bottom of the bucket. It would mix along the way, but the density of the mixed solution would always exceed the ambient density, and the solution would sink to the bottom. This phenomenon could be used to explain samples with a low chlorine residual because the water sampled was taken from the top of the bucket where the concentration would be fairly low.

However the trend in my data indicates that the opposite is occurring. Large concentrations of bleach are remaining at the top of most of the samples, and while there is no data about the chlorine residuals at the bottom of the samples, it can be assumed that residuals would be lower than the residual if all of the bleach were to fall to the bottom. Certainly the concentrations in various parts of the bucket would be different from the well-mixed concentration.

It is possible to capture a portion or all of the dense bleach that is put into a sample if the water is vertically stratified, meaning that there are layers in water that have a gradient in density. This could occur in two ways: either the initial water density was not completely uniform, or the water became stratified due to warming between the time the bucket was filled and the bleach was added. In the field, the water samples collected most likely would not have been initially stratified because in general they came from a flowing source where mixing occurred. However, in the time between the collection of the water and the addition of bleach to the buckets, it is possible that the ambient heat in the air as well as the sun could have warmed the upper layers of the water enough to create the necessary stratification to hold up a portion of the bleach.

For the purposes of the calculations that follow, a time of three minutes will be used as an estimate between the time of water collection and the time of bleach addition. It is possible that this time was longer for some samples, which would only increase the amount of time in which the air and sun could act to produce stratification in the water samples.

Energy is transferred into and out of water through a combination of several fluxes including solar radiation, atmospheric radiation, back radiation, evaporation, and convection (Ryan, 1974). The sum of these fluxes can be called Φ_{net}, which represents the total energy input to the water per unit area, and can be expressed as the product of a surface heat transfer coefficient, K, multiplied by the difference between the surface water temperature and a so-called equilibrium temperature, the latter being the temperature at which there would be no net heat exchange (Figure 16). This relationship should actually look somewhat curved, where K is the approximate slope. In the absence of more complete meteorological data, the equilibrium temperature can be approximated as the ambient air temperature. For the purpose of these calculations, the ambient air temperature will be estimated as approximately 92°F or 33.3°C.

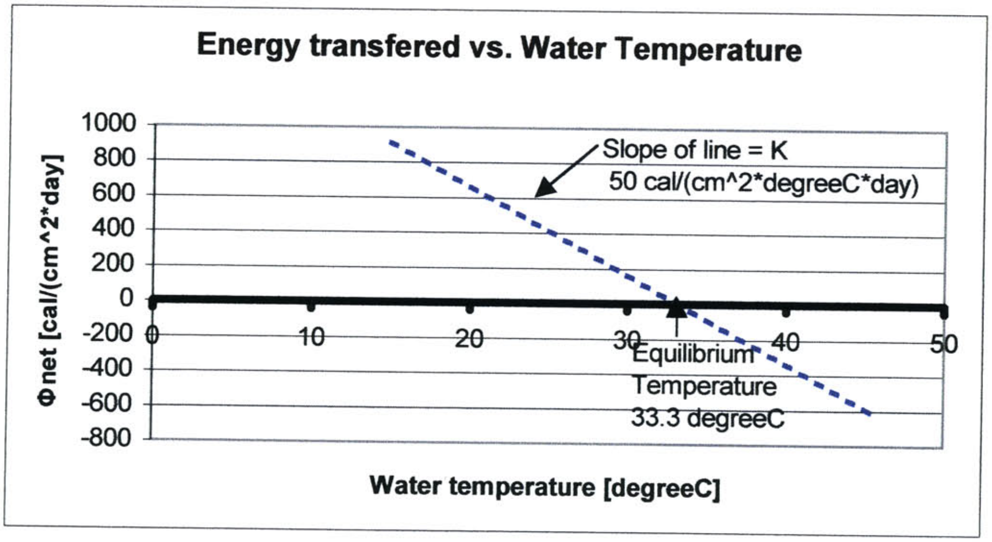


Figure 16 Energy transfer into water vs. water temperature.

If an average K of 50 cal/(cm^2-°C-day) and the average water temperature of my samples, 23.3°C, are used, Φ_{net} is 500 cal/(cm2-day), which is equivalent to 500 °C-cm/day or 0.35 °C-cm/min (Adams, 2002). The units on this number indicate that in 1 minute, 1 centimeter of water can increase in temperature by 0.35°C. In the three minutes estimated between water collection and bleach addition, there could be a 1.05°C change in temperature (ΔT) over the top centimeter of water, or a proportionally smaller fraction of that temperature change over a proportional larger depth, for example 0.21°C over five centimeters.

This heat addition creates a density change in the water. Density (ρ) is related to the temperature (T) of water in °C through the following equation (Adams, 2002):

$$\rho = 1 - 6.3 \times 10^{-6} * (T-4)^2 \text{ [g/cm}^3\text{]} \qquad \textbf{Eq. 15}$$

Therefore the change in density is related to the change in temperature through the following relationship:

$$\Delta\rho = (\partial\rho/\partial T) * \Delta T = -1.26 \times 10^{-5} * (T-4) * \Delta T \text{ [g/cm}^3\text{]} \qquad \textbf{Eq. 16}$$

Using the average temperature of my water samples (23.3°C) and the average temperature change for one centimeter of water (1.05°C), the value for $\Delta\rho$ for this one centimeter of water is 2.6×10^{-4} g/cm^3. As indicated below, this is a large enough density gradient to "hold up" the bleach added to many of the samples.

The density change needed to hold up a volume of bleach can be approximated by the following relationship:

$$|\Delta\rho| \geq \rho_{mixed} - \rho_w = \frac{(V_b * \rho_b + V_w * \rho_w)}{(V_b + V_w)} - \rho_w \qquad \textbf{Eq. 17}$$

where,

V_b = Volume of bleach added

V_w = Volume of water over which the density change takes place

ρ_b = Density of 5.25% bleach $\approx$ 1.076 g/cm^3

ρ_w = Density of water $\approx$ 1 g/cm^3 at 23.3°C

ρ_{mixed} = Density of mixed bleach and water solution

A comparison of the mass deficit of stratified water and the mass surplus of bleach can be made by the following equation:

$$\frac{|\Delta\rho|}{\rho_w} * V_w \geq \frac{(\rho_b - \rho_w)}{\rho_w} * V_b \qquad \textbf{Eq. 18}$$

In order for all of the bleach to be held up, the product of the volume of water that is warmed and the density change in that water must be greater than the product of the volume of bleach added and the increase in the density of bleach over the density of water. Based on the water density change calculated above, 2.6×10^{-4} g/cm^3, and a bucket diameter of 28 cm, the left side of this equation is equal to 0.16 cm^3. Therefore the maximum volume of bleach that can be held up due to stratification under average temperature conditions would be 2.0 ml.

Therefore based on theory, all the bleach additions less than or equal to 2 ml should be fully held up. When more bleach is added, a fraction of the volume of bleach can still be held up, at maximum 2 ml, and the rest will settle to the bottom of the bucket. This possibility is maximized if bleach is not simply poured into the water in a single plume, but spread around, so that not all of the bleach would sink to the bottom and that some would get caught up in the stratified layer.

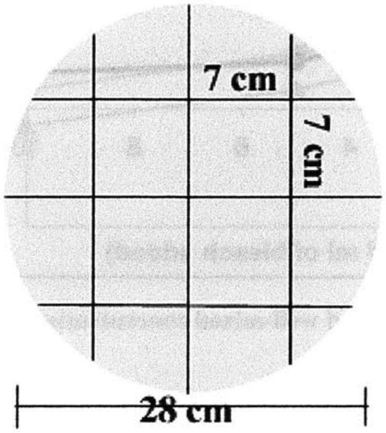


Figure 17 Example of the way bleach that may have been spread over the surface area of a bucket.

Figure 17 shows an idealized representation of the surface of a Gift of Water top bucket. The grid represents sections of the surface into which a volume of bleach can be poured. The total surface area of the bucket is approximately 615 cm^2. Each section of the grid should hold up an amount of bleach equivalent to 2 ml multiplied by the area of that section and divided by the total surface area. So one of the 7 cm by 7 cm squares on the grid should hold approximately 0.16 ml of bleach. If the bleach were unevenly distributed, some sections of the grid could receive less bleach than the maximum it can hold up and therefore not all of the bleach will sink to the bottom. This may account for the somewhat higher than well mixed concentration levels in the 3 ml, 5 ml, and 10 ml buckets.

Although the theoretical ability of the mixed layer to hold up the bleach is independent of the layer volume or depth, the depth will have an effect on how concentrated chlorine residuals are in the layer (Figure 18). Based on the average measured concentrations for each bucket, in relation to the theoretical chlorine-demand-free concentrations, the stratified layer would have been between 5 and 10 centimeters. If there were significant chlorine demand in the water, the stratified layer could have been smaller while still achieving the same concentrations of chlorine residual.

These calculations were completed for average temperature conditions and for a typical value of K. In the field, some samples may have had less stratification because the water temperature was warmer when compared to the ambient air temperature, and in other cases more stratification may have occurred in cooler water. Reasonable values of K can range from 50-75 cal/(cm^2-°C-day) (Adams, 2002). If a lower value of K is appropriate, the density change in the water would be smaller and less bleach would be held up. Vice-versa, a higher value of K could account for more bleach being held up.

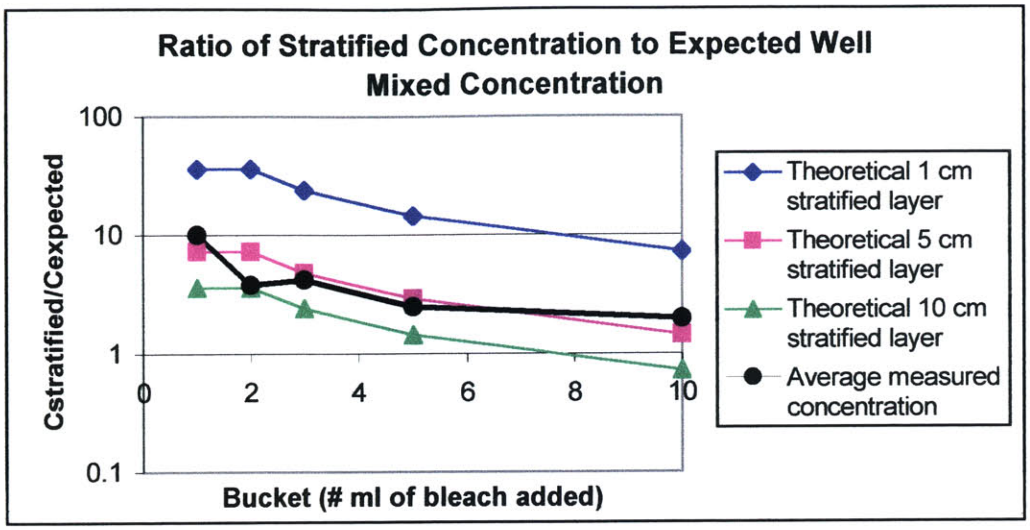


Figure 18 Comparison of stratified and well-mixed concentrations for varying depths of stratification.

5.2.2.2 Laboratory Stratification Experiments

The stratification experiments conducted in the laboratory supported the conclusion that 1 ml of bleach can be held up if there is approximately a 0.2°C change over a 5 cm depth of water (Figure 19). The red colored water is the artificially warmed water layer, where the blue colored salt solution (the plume) appeared to remain rather than settling to the bottom of the water column.

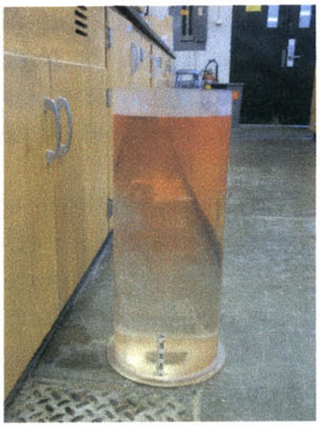


Figure 19 Mixing of 1 ml of bleach in a stratified water column.

As shown by a subsequent laboratory stratification experiment, in which 10 ml of bleach were dispersed into an artificially stratified water column, the way in which bleach is dispensed can have an effect on how much bleach is held up (Figure 20). If 10 ml of bleach are added to the water in a single plume the stratification layer is quickly penetrated and mixing occurs throughout the water column as the bleach falls straight to the bottom of the column. In this case, relatively little of the bleach will be held up within the mixed layer. Alternatively, if the 10 ml of bleach is spread around the water surface, much more can get caught up in the stratified layer. It may be difficult to distinguish in Figure 20b, however in the laboratory, there was a clear darker blue color within the stratification layer than outside of it when the bleach is distributed across the surface.

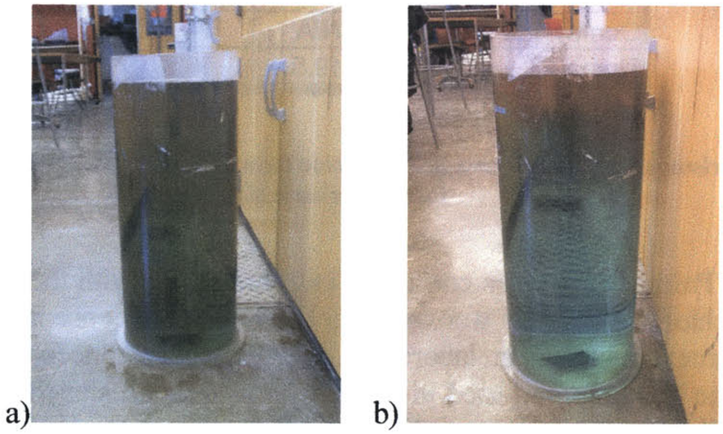


Figure 20 Mixing of 10 ml of bleach in a stratified water column if added in a single plume (a) or spread around the water surface (b).

5.2.2.3 Laboratory Experiments on Haitian Water Samples

The conclusion that the high concentrations of chlorine residual in the field were caused by stratification also appears to be supported by laboratory experiments that emulated, on a smaller scale, my field experiments on water samples brought back from Haiti a year earlier.

In the laboratory, varying volumes of bleach were added to 100 ml of water from Dumay 1/Dumay 2 and Les Palmes 2. Since the bleach was added in a quantity proportional to the scale of the experiment, the expected concentrations of bleach would have been the same. A main difference between the laboratory setup and the field setup was that in the laboratory there was no sun, only fluorescent lighting, and the ambient temperature was significantly cooler, around 23°C. There was still some energy transfer, particularly because the volume of water that had to be warmed to create stratification was less. However, most likely the flux of energy into the water was also less, so that a smaller volume of bleach could be held up.

The Dumay samples had concentrations somewhat less than those in the field, supporting the theory that with a smaller energy flux, less bleach is held up (Table 9). The concentrations were higher than the expected concentrations, indicating that some stratification likely occurred.

Dumay	1 ml	3 ml	5 ml	10 ml
Expected	1.32	3.97	6.62	13.24
Laboratory	2.36	7.94	10.07	18.99
Dumay 1	15.8	N/A	14.2	24.8
Dumay 2	23	19.5	18.6	N/A

Table 9 Comparison of laboratory and field chlorine data from Dumay. Measurements are in ppm of total chlorine residual.

The Les Palmes 2 samples correlated extremely well with the stratification theory. In the laboratory, chlorine residuals were extremely close to the concentrations expected, with at most a 13.9 percent increase in laboratory over expected concentration (Table 10). The uncertainty of the DPD method used in the laboratory was greater than 13.9 percent (Section 4.4), indicating that the laboratory readings are in the range of values that can be considered expected.

Les Palmes	1 ml	3 ml	5 ml	10 ml
Expected	1.32	3.97	6.62	13.24
Laboratory	1.33	4.52	5.66	13.09
Percentage over expected	0.75	13.9	-14.4	-1.1
Les Palmes 2	4	12	9.2	17.2

Table 10 Comparison of laboratory and field chlorine data from Les Palmes 2. Measurements are in ppm of total chlorine residual.

The fact that the Dumay laboratory measurements were higher than the Les Palmes measurements might be explained by the chlorine demand of the water. In general, the Les Palmes samples had lower chlorine residual measurements than the other field samples, and it is likely that chlorine demand played a role.

5.2.2.4 The Experience of Gift of Water, Inc.

Gift of Water, Inc. most likely encountered the problem of poor mixing due to stratification when the filtration program was first implemented. Lab work conducted by Phil Warwick determined that a safe level of chlorine addition to the filter was 3 ml of 5.25 percent bleach (Warwick, 2002). However, once the filter was utilized in Haiti, Gift of Water, Inc. observed that pathogens were surviving in the finished water. The amount of bleach added to the filter was raised to 5 ml and it was found that this level of chlorination provided sufficient disinfection.

A possible explanation is that more bleach breaks through the stratified layer and falls to the bottom of the bucket with a 5 ml addition of bleach rather than 3 ml. Mixing occurs as the bleach falls. In the laboratory, the stratification would not have been as great, and more of the 3 ml addition of bleach would have fallen to the bottom of the bucket and mixed with the water throughout the bucket. Therefore, chlorine residual levels from a 3 ml bleach addition would have appeared sufficient to destroy pathogens in the laboratory, but would not have been adequate under field conditions.

5.2.3 Lower Chlorine Residuals

As noted, the Les Palmes field samples generally produced lower chlorine residuals than other samples (Table 11). Les Palmes 3 samples had lower chlorine residuals than any other samples, and Les Palmes 2 had the next lowest chlorine residuals. The Les Palmes 3 10 ml bucket was the only sample to have a lower chlorine residual than the expected chlorine-demand-free concentration. The Les Palmes 1 samples' total residual concentrations were smaller than the concentrations in all samples in villages other than Les Palmes for the 3 ml, 5ml, and 10 ml buckets. The 1 ml bucket produced a chlorine residual concentration that, although not the lowest, was among the lowest values measured.

Site	1 ml	3 ml	5 ml	10 ml
Average	13.18	16.45	16.27	26.00
Les Palmes 1	11.2	13	12.6	17.5
Les Palmes 2	4	12	9.2	17.2
Les Palmes 3	1.75	5	7.33	9.25

Table 11 Les Palmes total chlorine residual measurements (ppm) compared to the average residual values for all field samples.

The data indicate that there are two possible processes occurring, either separately or in combination. It is possible that there is something in the water in Les Palmes that is causing a significantly higher chlorine demand than other water sources have. There was nothing out of the ordinary in any of the water quality parameters, except TOC, however there may be another source of chlorine demand for which tests were not conducted, such as manganese (or TOC in the case of the Les Palmes 2 sample). The characteristic black color that typically accompanies manganese was not present at any sites in the field study, however manganese cannot be ruled out completely. TOC most likely played a large role in the low chlorine residual measurements of the Les Palmes 3 samples, as this site had a TOC concentration of 22.51 ppm, significantly higher than most other sampling locations.

Another possibility is that the Les Palmes samples were less stratified than samples from other villages due to differences in ambient temperature and solar radiation. There is reason to suspect that Les Palmes 3 has concentrations so much lower than other samples due to a difference in stratification, however there is no apparent reason why this would be so with the other two Les Palmes samples. Daytime sun and heat in Les Palmes seemed comparable to the sun and heat in other Haitian villages. Les Palmes 3, however, was sampled at 5AM, before the sun had risen and before the air had warmed to daytime temperatures (although the ambient temperature was still warmer than the water temperature). For this reason, there would not have been much stratification and more of the bleach would have fallen to the bottom of the bucket than in other samples.

5.2.4 Time of Residual Formation

At each of the first 10 field sites, chlorine residual measurements were taken at 10-minute intervals in one bucket, chosen at random, to learn how time affects the formation of free and combined residuals. In all samples, except the 10 ml bucket at Bas Limbe 2, the 1 ml bucket at Fon Veret 1, and the 5 ml bucket at Les Palmes 3, free chlorine residuals increased over the first 20 minutes and then began to level off or decreased between twenty and thirty minutes (Figure 21). In the Fon Veret 1 and Les Palmes 3 samples, free residual continued to increase throughout the full thirty-minute contact time. Bas Limbe 2 actually began decreasing between ten and twenty minutes, earlier than most samples.

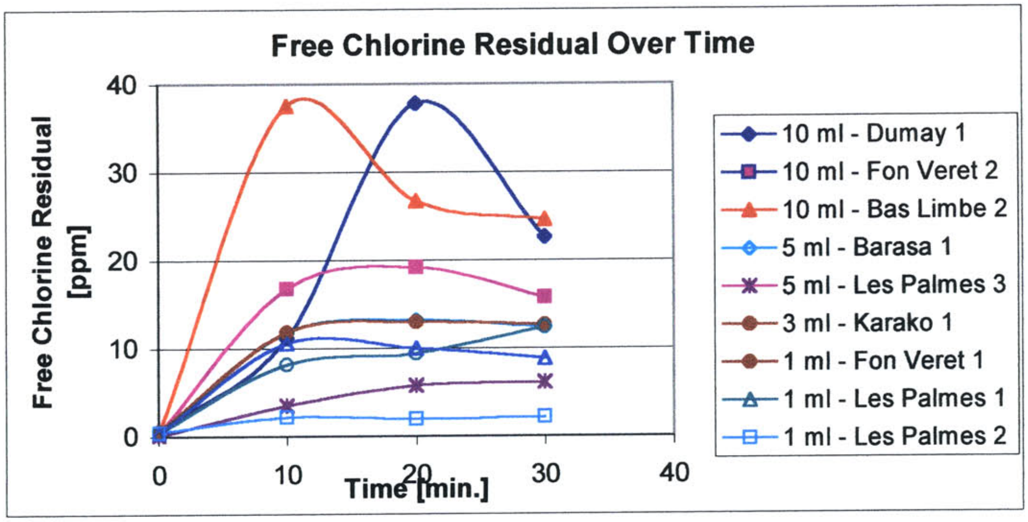


Figure 21 Free chlorine residual measurements at 10-minute intervals.

It is important to note that the residual measurements are very likely, in an undetermined way, affected by the fact that the water in the field samples was stratified.

Combined residual generally increased until somewhere between ten and twenty minutes, when the concentration began decreasing, severely in some samples (Figure 22). In most cases, the concentration of combined chlorine continued to decrease through thirty minutes, however this is not the case in the Fon Veret 1, Les Palmes 3 or Dumay 1 samples. The twenty-minute data point for Dumay 1 may be considered an outlier or subject to experimental uncertainty, as might the 30-minute data points for Fon Veret 1 and Les Palmes 3, which are inconsistent with the general trends for both free and combined residuals.

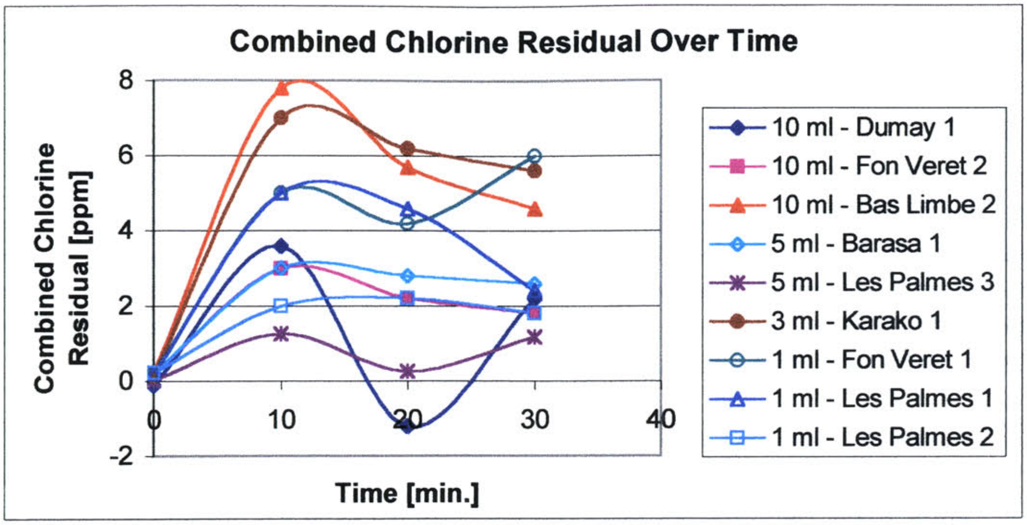


Figure 22 Combined chlorine residual measurements at 10-minute intervals.

The changes in the concentrations of free residual and combined residuals over time seem related to the oxidation reactions that take place between free residual and chloramines. The curves in Figure 21 and Figure 22 resemble the breakpoint curve, discussed in Chapter 2. Initially there is the formation of chloramines as well as free residual, however after a certain amount of time, free residual reaches a large enough concentration that it begins to further oxidize chloramines, which reduces the concentration of both types of residuals. In general, chloramines concentrations continue to be reduced over time, while free residual concentrations continue to be reduced (a sign of the oxidation reaction with combined chlorine) or stay stable indicating that most oxidation reactions have taken place, and free residual is no longer used up. Based on this data, it appears that free residual generally does not react to fully oxidize combined residual in the half hour contact time used in the Gift of Water, Inc. filter.

6 Conclusions and Recommendations

It appears that there may be a significant chlorine demand in some of the drinking water sources that are gathered by users of the Gift of Water, Inc. filtration system. This is evidenced by the lower than average chlorine residuals in the Les Palmes samples, as well as the comparison of free residual to combined and total residual in all villages, both after thirty minutes and over ten-minute intervals. Chlorine demand will most likely play an important role in determining how much of a reduction in bleach addition Gift of Water, Inc. can afford without sacrificing adequate disinfection.

Unfortunately, the fact that the bleach apparently did not mix uniformly in the top bucket means that I cannot provide an answer to how much chlorine demand is present in Haitian drinking water supplies, nor can I recommend lowering the amount of bleach added to the Gift of Water, Inc. filter without further studies being conducted. In the absence of well-mixed field samples, it is not possible to determine how much chlorine residual is present throughout the water samples during the thirty-minute contact, and therefore the residuals cannot be compared to the Ct values of the pathogens of concern.

The primary recommendation of this study is that Gift of Water, Inc. implement mixing in the top bucket. This could be achieved in one of two ways. One solution is to create a small paddle, which would be used to stir like a spoon, and would be sold with the filtration system. It would be best if the paddle were of the same plastic as the buckets so as not to introduce a new material that might react with chlorine or other substances in the water. This paddle should be for explicit use with the filtration system.

Another possible solution is to require the use of a third bucket, which would carry the water from the source, but not be the bucket in which disinfection takes place. Bleach should be placed in the Gift of Water, Inc. top bucket prior to pouring the water from the third bucket into the top bucket. The momentum of the water falling onto the bottom of the bucket should be sufficient to mix the bleach.

Although there might be concern about contamination of the water from the paddle, if stirring occurred immediately after adding bleach to the top bucket, any pathogenic contamination would most likely get destroyed in the thirty-minute contact time along with the pathogens already present in the water.

Mixing is the only way to assure that enough chlorine residual is present in all areas of the water that pathogens might be, and should be implemented as soon as possible. After mixing is employed, it will be possible to run a series of tests to determine the chlorine demand of the Haitian water supplies. A future study is recommended in order to achieve the initial goal of this study, reducing the amount of chlorine used in the Gift of Water, Inc. filter.

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8 Appendix - Complete Chlorine Data

The following is complete record of chlorine residual measurements from the field. All values are reported in ppm of Cl^+.

Raw Water Data

Site	Total Residual	Free Residual	Combined Residual
Dumay 1	0.55	0.45	-0.10
Fon Veret 1	0.41	0.59	0.18
Fon Veret 2	0.40	0.58	0.18
Barasa 1	0.47	0.69	0.22
Bas Limbe 1	0.41	0.59	0.18
Bas Limbe 2	0.42	0.62	0.20
Karako 1	0.52	0.67	0.15
Les Palmes 1	0.43	0.63	0.20
Les Palmes 2	0.47	0.69	0.22
Les Palmes 3	0.05	0.06	0.01
Dumay 2	0.54	0.78	0.24
Dumay 3	0.57	0.80	0.23
Dumay 4	0.58	0.82	0.24
Dumay 5	0.60	0.78	0.18

1 ml Bucket Data

Site	Total Residual	Free Residual	Combined Residual
Dumay 1	15.80	9.80	6.00
Fon Veret 1	15.40	9.40	6.00
Fon Veret 2	11.20	7.70	3.50
Barasa 1	9.73	8.26	1.47
Bas Limbe 1	14.40	10.80	3.60
Bas Limbe 2	17.60	13.60	4.00
Karako 1	11.44	5.61	5.83
Les Palmes 1	11.20	8.80	2.40
Les Palmes 2	4.00	2.20	1.80
Les Palmes 3	1.75	1.13	0.63
Dumay 2	23.00	13.00	10.00
Dumay 3	10.00	6.88	3.12
Dumay 4	18.50	9.00	9.50
Dumay 5	20.50	13.25	7.25

2 ml Bucket Data

Site	Total Residual	Free Residual	Combined Residual
Dumay 1	10	8.40	1.60

3 ml Bucket Data

Site	Total Residual	Free Residual	Combined Residual
Fon Veret 1	18.40	12.40	6.00
Fon Veret 2	8.80	7.20	1.60
Barasa 1	17.60/17.20	13.20/12.60	4.40/4.60
Bas Limbe 1	16.60	11.40	5.20
Bas Limbe 2	20.60	12.80	7.80
Karako 1	18.20	12.60	5.60
Les Palmes 1	13.00	9.40	3.60
Les Palmes 2	12.00	5.20	6.80
Les Palmes 3	5.00	4.25	0.75
Dumay 2	19.50	15.00	4.50
Dumay 3	17.00	13.50	3.50
Dumay 4	28.75	17.75	11.00
Dumay 5	14/23.25	12.50/20.25	1.50/3.00

5 ml Bucket Data

Site	Total Residual	Free Residual	Combined Residual
Dumay 1	14.20	12.80	1.40
Fon Veret 1	24.80	21.60	3.20
Fon Veret 2	10.40	8.60	1.80
Barasa 1	15.00	0.80	14.20
Bas Limbe 1	18.00	11.60	6.40
Bas Limbe 2	19.40/23.40	13.80/14.80	5.60/8.60
Karako 1	15.60	9.90	5.70
Les Palmes 1	12.60	9.20	3.40
Les Palmes 2	9.20	8.25	0.95
Les Palmes 3	7.33	6.17	1.16
Dumay 2	18.60	14.80	3.80
Dumay 3	18.00	13.63	4.37
Dumay 4	20.83	15.17	5.66
Dumay 5	21.75	22.25	-0.50

10 ml Bucket Data			
Site	**Total Residual**	**Free Residual**	**Combined Residual**
Dumay 1	24.80	22.60	2.20
Fon Veret 1	29.20/38.60/37.60	24.80/31.20/31.40	4.40/7.40/6.20
Fon Veret 2	17.60	15.80	1.80
Barasa 1	37.60	26.80	10.80
Bas Limbe 1	30.93	24.80	6.13
Bas Limbe 2	29.20	24.60	4.60
Karako 1	43.60	31.40	12.20
Les Palmes 1	16.40/18.60	11.8/16.20	4.60/2.40
Les Palmes 2	17.20	13.20	4.00
Les Palmes 3	9.25	6.25	3.00
Dumay 3	27.00	24.17	2.83
Dumay 5	22.25	19.75	2.50