

Disinfection by-product formation and mitigation strategies in point-of-use chlorination of turbid and non-turbid waters in western Kenya

D. S. Lantagne, B. C. Blount, F. Cardinali and R. Quick

ABSTRACT

Over 1.1 billion people in the world lack access to improved drinking water. Diarrheal and other waterborne diseases cause an estimated 2.2 million deaths per year. The Safe Water System (SWS) is a proven household water treatment intervention that reduces diarrheal disease incidence in users in developing countries. Because the SWS recommends the addition of sodium hypochlorite to unfiltered water sources, concerns have been raised about the potential long-term health effects of disinfection by-products to SWS users. This study investigated the production of trihalomethanes (THMs) in water treated with sodium hypochlorite from six sources used for drinking water in western Kenya. The turbidity values of these sources ranged from 4.23 NTU to 305 NTU. THM concentrations were analysed at 1, 8, and 24 hours after addition of sodium hypochlorite. No sample exceeded the World Health Organization (WHO) guideline values for any of the four THMs: chloroform, bromodichloromethane, dibromochloromethane, or bromoform. In addition, no sample exceeded the WHO additive total THM guideline value. These results clearly show that point-of-use chlorination of a variety of realistic source waters used for drinking did not lead to THM concentrations that pose a significant health risk to SWS users.

Key words | developing countries, disinfection by-products, drinking water, household water treatment, point-of-use chlorination, Safe Water System

D. S. Lantagne (corresponding author)

R. Quick

Enteric Diseases Epidemiology Branch, M/S A-38,
Centers for Disease Control and Prevention,
1600 Clifton Road NE, Atlanta GA 30333,
USA

Tel.: 404 639 0231

Fax: 404 639 2205

E-mail: dlantagne@cdc.gov

B. C. Blount

F. Cardinali

Division of Laboratory Sciences,
National Center for Environmental Health,
U.S. Centers for Disease Control and Prevention,
Atlanta, GA 30341,
USA

INTRODUCTION

Point-of-use water treatment and the Safe Water System

An estimated 1.1 billion people lack access to improved water supplies and 2.4 billion people are without adequate sanitation (WHO/UNICEF 2000). The health consequences of inadequate water and sanitation services include an estimated 4 billion cases of diarrhea and 2.2 million deaths each year, mostly among young children in developing countries (WHO/UNICEF 2000). In addition, waterborne diarrheal diseases lead to decreased food intake and nutrient absorption, malnutrition, reduced resistance to infection (Baqui *et al.* 1993), and impaired physical growth and cognitive development (Guerrant *et al.* 1999). Recently, point-of-use drinking

water treatment and safe storage options have been recognized as approaches which can accelerate the health gains associated with improved water until the longer term goal of universal access to piped, treated water can be attained (Fewtrell & Colford 2004). Household water treatment and storage practices can prevent disease, and thereby support poverty alleviation and development goals.

Chlorination was first used for disinfection of public water supplies in the early 1900s, and is one factor that contributed to dramatic reductions in waterborne disease in cities in the United States (Cutler and Miller 2005). Although small trials of point-of-use chlorination had been implemented in the past (Mintz *et al.* 1995), larger scale trials began in the 1990s, as part of the Pan American

doi: 10.2166/wh.2007.013

Health Organization (PAHO) and the U.S. Centers for Disease Control and Prevention (CDC) response to epidemic cholera in Latin America (Tauxe 1995). The Safe Water System (SWS) strategy devised by CDC and PAHO includes three elements: water treatment with dilute sodium hypochlorite at the point-of-use, storage of water in a safe container, and behavior change communication to improve hygiene and water and food handling practices. The sodium hypochlorite solution is packaged in a bottle with directions instructing users to add one full bottle cap of the solution to clear water (or 2 caps to turbid water) in a standard sized storage container, agitate, and wait 30 minutes before drinking. In five randomized controlled trials, the SWS has resulted in reductions in diarrheal disease incidence ranging from 26–84% (Semenza 1998; Quick 1999; Quick 2002; Luby 2004; Crump *et al.* 2005).

The standard Safe Water System sodium hypochlorite dosage provides a maximum CT factor of 56.25 mg-min/L. A CT factor of 56.25 is sufficient to inactivate most bacteria, viruses, and some protozoa (such as giardia) which cause waterborne diseases (CDC 2006). It will not inactivate *Cryptosporidium* and populations at risk for *Cryptosporidium* infection should consider a filtration step prior to chlorination to remove the oocysts.

This well-documented reduction of diarrheal disease incidence in SWS users has encouraged non-governmental organizations (NGOs) and governments to broadly disseminate the program. National, regional, and local SWS projects have been implemented with NGO and government partners in over 20 countries since 1998. As access to the SWS has expanded in developing countries, where many water sources contain suspended organic material, some health officials and implementing organizations have expressed concern about the formation of disinfection by-products in treated water and the attendant risk to users.

Trihalomethanes

In 1974, Rook discovered that hypochlorous acid and hypobromous acid react with naturally occurring organic material to create four compounds with potential human health effects: chloroform (CHCl₃), bromoform (CHBr₃), bromodichloromethane (CHCl₂Br), and dibromochloromethane (CHClBr₂) (Rook 1974). These four compounds

are collectively termed trihalomethanes (THMs). Initially, research focused on the long-term health effects of chloroform and the other trihalomethanes, however, further research has shown that chlorination of drinking water leads to the formation of numerous compounds that may or may not have mutagenic activity. Richardson *et al.* (2002) identified greater than 600 water disinfection byproducts in chlorinated tap water, including haloacetic acids (HAAs), THMs, and to a lesser extent HAAs, are currently used by regulatory agencies as indicator chemicals for all potentially harmful compounds formed by the addition of chlorine to water.

The World Health Organization (WHO) has established guideline values for trihalomethane exposure, based on epidemiological and laboratory studies. The guideline values are based on an allowable risk of one extra cancer attributable to THM exposure in 100,000 people who ingest two litres of chlorinated water per day with trihalomethane concentrations at the guideline value for a lifetime period of 70 years.

Chloroform has been classified as possibly carcinogenic to humans, based on sufficient evidence for carcinogenicity in experimental animals but inadequate evidence in humans (IARC 1999). The WHO guideline value for chloroform is 300 µg/L (300 parts per billion (ppb)) (WHO 2005). Bromodichloromethane (BDCM) has been classified as probably carcinogenic to humans, with sufficient evidence in animals and inadequate evidence in humans (IARC 1991). The WHO guideline value for BDCM is 60 µg/L (WHO 2004). Both dibromochloromethane (DBCM) and bromoform have been classified as not classifiable in humans for carcinogenicity (IARC 1991), and the WHO guideline values for both are 100 µg/L (WHO 2004)¹.

WHO also proposes the use of an additive toxicity guideline value, using the fractionation equation that the sum of the four THMs' actual concentration (C) divided by their guideline value (GV) should not be greater than

¹Note that the publication *Trihalomethanes in Drinking-Water* (WHO 2005) supersedes the 3rd Edition of the *Guidelines for drinking-water quality* (WHO 2004) with an updated chloroform guideline value. The chlorine guideline value has been increased from 200 µg/L in 1993 to 300 µg/L in 2006 due to an increase in the proportion of chloroform exposure attributed to drinking water (with low chloroform concentrations) and a decrease in the proportion of chloroform exposure from other mechanisms (with higher chloroform concentrations). This updated guideline value will be formalized in an addendum to the *Guidelines for drinking-water quality* anticipated in early 2007 (Bartram personal communication 2006).

one (WHO 2004).

$$\frac{C_{\text{Chloroform}}}{GV_{\text{Chloroform}}} + \frac{C_{\text{BDCM}}}{GV_{\text{BDCM}}} + \frac{C_{\text{DBCM}}}{GV_{\text{DBCM}}} + \frac{C_{\text{Bromoform}}}{GV_{\text{Bromoform}}} \leq 1 \quad (1)$$

In addition, the WHO Guidelines specifically state that: 'Where local circumstances require that a choice must be made between meeting either microbiological guidelines or guidelines for disinfectants or disinfectant by-products, the microbiological quality must always take precedence, and where necessary, a chemical guideline value can be adopted corresponding to a higher level of risk. Efficient disinfection must never be compromised' (WHO 1993).

In contrast to the health-based WHO THM guidelines, the USEPA and other developed country regulatory agencies regulate the reduction of trihalomethane concentrations in drinking water through technology improvements to 'provide an incremental step towards mitigating potential risks' and 'potential health concerns' (USEPA 2006). The USEPA maximum contaminant level (MCL) for total trihalomethanes (there are no individual analyte trihalomethane USEPA MCLs) is currently 80 µg/L. In response to these regulations, the majority of the trihalomethane literature has analyzed trihalomethane formation potential of source waters and mitigation strategies such as the use of alternate disinfectants in centralized water treatment plants in developed countries.

No known research to date has examined the formation of trihalomethanes consequent to household water treatment with sodium hypochlorite, which is the most practical form of treatment in many parts of the world lacking piped water supplies. In September 2003, we conducted research on trihalomethane formation resulting from the chlorination of stored water from a variety of sources with varying turbidity levels, and the effectiveness of several potential mitigation strategies, in rural Western Kenya, where CDC and the NGOs CARE International and Population Services International operate an SWS program which began in 1999.

METHODS

Setting

This study was conducted in September 2003 in areas surrounding Homa Bay, which is south of Kisumu on Lake Victoria in rural western Kenya. Previous studies have found that SWS users in this region access a wide variety of

drinking water sources, with low to extremely high turbidity levels (Ogutu *et al.* 2001; Crump *et al.* 2004). In one study that examined 30 samples from a variety of surface and borehole water sources in Western Kenya, the mean turbidity was 331.9 Nephelometric Turbidity Units (NTUs), with a range of 0.3 to 1724 NTUs (Crump *et al.* 2004). The addition of sodium hypochlorite in the household to this water led to a 26% reduction in diarrheal disease risk among users as compared to controls who implemented safe storage practices only (Crump *et al.* 2005).

Study design

We analyzed THM concentrations after chlorination in six different water sources which were used for drinking by local communities: lake, river, earth pond, protected well, open well, and rainwater catchment system (Figure 1).

To assess whether use of different types of water storage containers led to different THM exposure risk, water treatment procedures were conducted in water stored in both 20-litre HDPE plastic jerry cans and locally purchased ceramic pots. The jerry cans were cleaned, recycled vegetable oil containers which are widely used as water storage containers throughout Africa. The ceramic water storage pots are the preferred storage container in many parts of Africa because they are locally available from potters, inexpensive, and the stored water is cooled by transpiration through the ceramic pores.

For each of the six water sources, THM concentrations were measured after three different treatment procedures were used in plastic jerry cans and in ceramic pots (Table 1): 1) after the addition of sodium hypochlorite solution; 2) after filtration of sample water through a commonly available local cloth before adding sodium hypochlorite; and 3) after settling of the water for 24 hours and decanting supernatant water before adding sodium hypochlorite. In addition, samples in plastic jerry cans were treated with the alternate point-of-use water treatment product PuR[™] (Procter & Gamble Company, Cincinnati, OH, USA), and samples in ceramic pots were pre-treated with the natural flocculant moringa seeds. PuR[™] and moringa seeds were not tested in both plastic and ceramic containers due to sample number limitations, and thus it was decided to test the commercial PuR[™] product

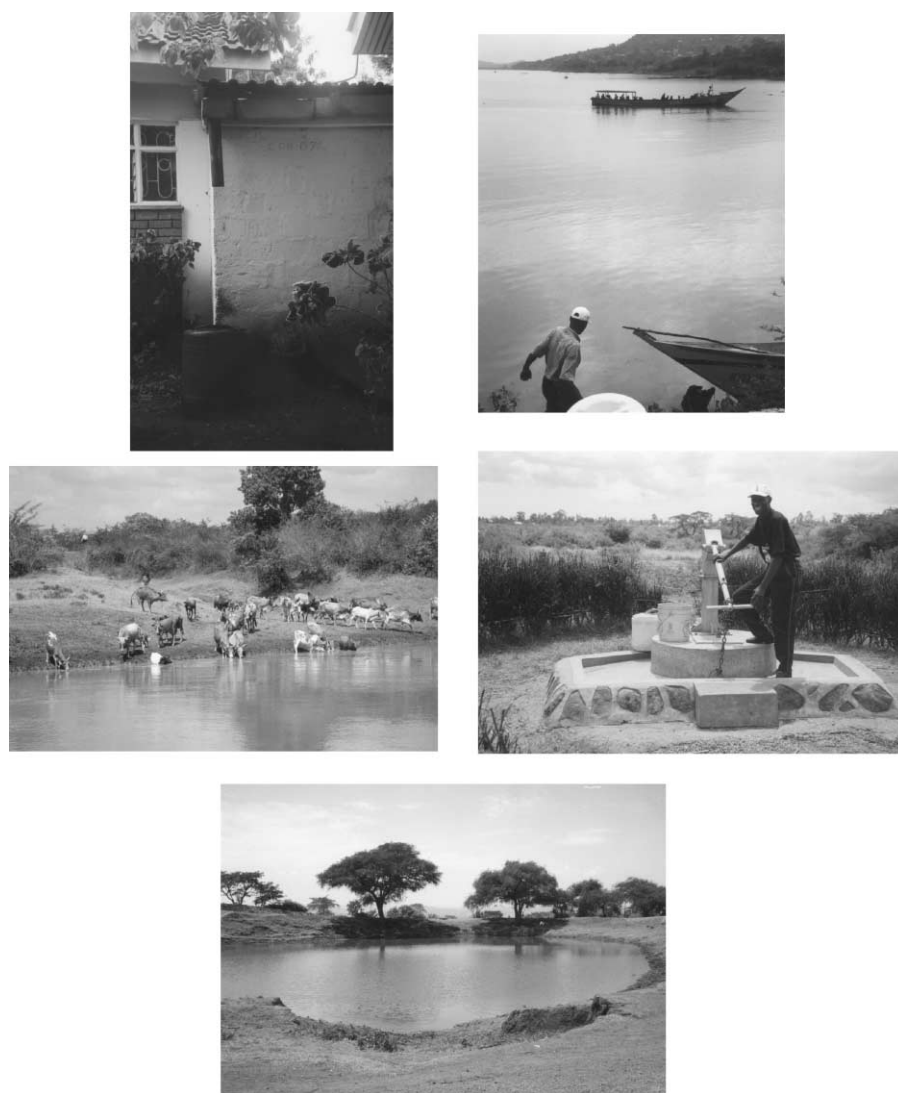


Figure 1 | Water sources used in study (Clockwise from top left: rainwater catchment, lake, protected well, earth pond, river). Note the open well source was not photographed.

in plastic jerry cans and the local moringa seeds, normally used in rural areas, in the locally-made ceramic pots.

A 1% sodium hypochlorite solution, marketed under the brand name WaterGuard by Population Services International (PSI) (Figure 2), was used in the study. Two 500 ml bottles of WaterGuard were purchased locally, and each was tested to ensure correct concentration with a Hach (Loveland, CO) Method 8209 portable iodimetric digital titration kit for high-range total chlorine. The sodium hypochlorite concentration of the two bottles was 0.96% and 1.02%, respectively, which reflects non-concerning variation of concentration in the production process. An 8 ml (1 capful) volume from one of

the two containers was added to water in plastic containers from all sources except the river water, to which 16 ml (two capfuls) was added. For the ceramic pots, 8 ml (1 capful) of 1.02% WaterGuard sodium hypochlorite solution was added to earth pond water; 16 ml (two capfuls) of 0.96% or 1.02% sodium hypochlorite solution was added to rainwater, open well water, protected well water, and lake water; and 24 ml (three capfuls) of 1.02% solution was added to the river water. This dosing regime, and the difference from the dosing in the plastic containers, was developed by Ogutu *et al.* (2001) in response to concern that organic material in the ceramic pots would exert additional chlorine demand than in plastic

Table 1 | Water storage, clarification, and treatment procedures completed for each of six water sources

	Container type	Water clarification procedure	Disinfection procedure
1	Plastic	None	Sodium hypochlorite
2	Plastic	Filtered through cloth	Sodium hypochlorite
3	Plastic	Settled for 24 hours and decanted	Sodium hypochlorite
4	Plastic	PuR [®] (ferrous sulphate)	PuR [®] (Calcium hypochlorite)
5	Ceramic	None	Sodium hypochlorite
6	Ceramic	Filtered through cloth	Sodium hypochlorite
7	Ceramic	Settled for 24 hours and decanted	Sodium hypochlorite
8	Ceramic	Moringa addition for 24 hours and decanted	Sodium hypochlorite

containers. This dosage is double the amount of chlorine recommended currently in Safe Water System programs, including in Kenya. Based on additional chlorine demand testing in both plastic and ceramic containers, the new recommended dose for Kenya is 1.875 mg/L of chlorine in clear sources, and 3.75 mg/L in turbid sources in both plastic and ceramic containers. The utilization of this older dosing regime provides a worst-case scenario of trihalomethane formation potential for Safe Water System programs.

A sachet of the Procter & Gamble point-of-use treatment product, PuR[®], includes a proprietary mixture of the flocculant ferrous sulphate and the disinfectant calcium hypochlorite. PuR[®] sachets are now marketed in Kenya by PSI, but for this study sachets were obtained in the United States. A sachet was added to 10 litres of water, which was stirred for five minutes, allowed to settle, and then poured through a locally-available cloth to remove the floc.

The natural flocculant *Moringa oleifera* pods were obtained locally. Pods were opened to remove the seeds, which were peeled and crushed into a powder using a mortar and pestle. Two grams of the powder was measured on a digital scale and were added to 20 litres of water (Madsen *et al.* 1987), stirred for 5 minutes, and allowed to settle for 24 hours before supernatant water was decanted off and treated with sodium hypochlorite. The coagulation properties of moringa are attributed to polypeptides acting as cationic polymers (Madsen *et al.* 1987).

Water collection

Water from each of the six sources was collected in eight clean 20 litre plastic jerry cans and transported to the lab the day before analysis occurred.

Water testing procedures

On each day of analysis, each source water sample was tested for chemical and bacteriological water quality parameters before treatment began to characterize the source water, ensure samples with well differentiated water quality characteristics were collected, and provide appropriate data for regression analysis.

Each water sample was analyzed for turbidity, pH, ammonia, conductivity, temperature, free and total chlorine, and total coliform and *Esherichia coli* colony counts. In addition, a water sample was collected for later analysis for total organic carbon (TOC) in a glass container, acidified to a pH below 2.0, and stored on ice below 6°C for later analysis in the United States. Total organic carbon samples were delivered to Analytical Services, Incorporated (Norcross, GA, USA) within two weeks of collection. EPA Method 9060 was used to analyze the samples, and all laboratory quality control guidelines were met.

Turbidity was measured after agitation of the sample water with a Lamotte 2020 turbidimeter (Cherstertown, MD,

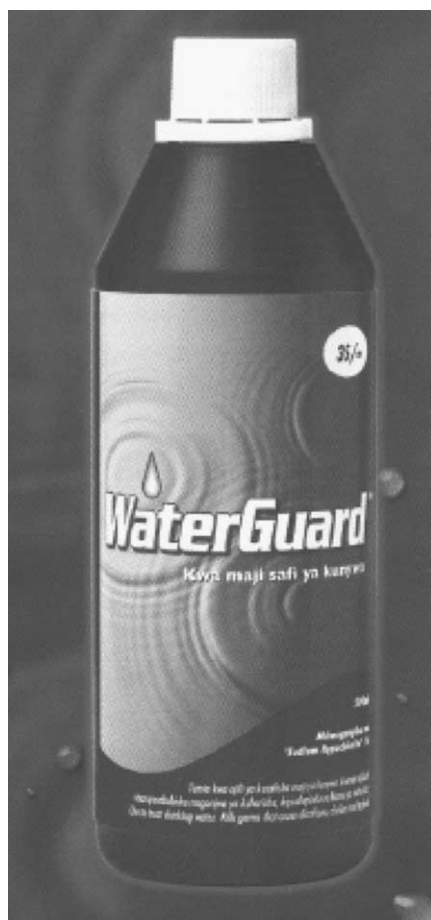


Figure 2 | The PSI Kenya WaterGuard product.

USA) calibrated weekly with non-expired stock calibration solutions. pH and conductivity were measured with a Hanna multimeter (Bedfordshire, UK) calibrated weekly with non-expired stock calibration solutions. Temperature was measured with an EnviroSafe® non-mercury thermometer (Ben Meadows Company, Jainsville, WI, USA). Ammonia was measured with an Aquarium Pharmaceuticals, Inc. Ammonia NH_3/NH_4 test kit (Oxfordshire, UK).

Free and total chlorine were measured immediately after sample collection using a Lamotte 1200 single wavelength chlorine colorimeter and DPD-1 and DPD-3 tablets (Chestertown, MD, USA). The meter was calibrated daily using non-expired stock calibration solutions at 0, 0.1, 1.0, and 2.65 mg/L free chlorine.

Total coliform and *E. coli* were measured using a portable Millipore (Billerica, MA, USA) filtration stand and

mColiBlue24 media. Samples were diluted appropriately with sterile buffered water, filtered aseptically through a 45-micron filter, placed in a petri-dish with a media soaked pad, and incubated for 24 hours at 35°C following *Standard Methods* (1998). Negative controls were included within each daily run.

For each of the six water sources, at 1 hour, 8 hours, and 24 hours after each treatment procedure was completed in the plastic jerry cans and the ceramic containers, three water quality testing procedures were completed: 1) Free and total chlorine were measured using the procedures detailed above; 2) Total coliform and *E. coli* samples were collected and analyzed on site using the procedures detailed above; and 3) An THM sample was collected and stored on ice for later analysis in the United States.

Trihalomethane sampling

Samples for THM testing were collected by using a pre-cleaned 40 ml VOA vial to transfer liquid into a pre-cleaned 12 ml glass vial containing 125 μl of a bufferquench solution (Cardinali et al. 2004). The 12 ml vial was slightly overfilled to create an inverted meniscus and avoid air bubbles. The sample vials were then sealed with Teflon-lined silicone septa and stored in a cool (4–8°C temperature range) and dark location. Samples were stored no longer than two weeks before delivery to the Division of Laboratory Sciences at the National Center for Environmental Health, CDC, for analysis of trihalomethanes (THMs).

Water samples were analyzed for THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) using stable isotope dilution headspace SPME GC-MS (Cardinali et al. 2004). Briefly, water vials were removed from refrigerated storage and allowed to equilibrate to room temperature before analysis. Immediately after removal of the vial cap, water (5.0 ml) was removed using a pre-cleaned gas-tight syringe and transferred into an SPME headspace vial. Stable isotope labeled analog solution was added to the sample and the SPME vial immediately crimp-sealed using Teflon-lined septum.

We analyzed samples using SPME/GC-MS on a ThermoFinnigan TraceMS (ThermoFinnigan, Austin, TX, USA) attached to a Trace 2000 gas chromatograph equipped with a split/splitless injector and operated in the

splitless mode. Because of the volatility of THMs, a cryo-trap (model 961, Scientific Instrument Services, Ringoes, NJ, USA) was used to cryofocus the analytes at the head of the GC column. VOCs were chromatographically separated on a VRX capillary column (20 m × 0.18 mm i.d. × 1.0 μm film, Restek, Bellefonte, PA, USA) during a thermal gradient from 20°C to 200°C. Automated sampling was done using a CombiPAL autosampler (CTC Analytics AG, Zwingen, Switzerland) equipped with a 75-μm Carboxen/PDMS SPME fiber assembly (Supelco, Bellefonte, PA, USA) and heated/agitated headspace extraction (8 min, 500 rpm, 50°C). The fiber was promptly desorbed by insertion into the hot GC inlet (200°C). The mass spectrometer was equipped with an electron impact source and run in the selected ion monitoring (SIM) mode at unit mass resolution. Xcalibur Quan software (ThermoFinnigan, Austin, Texas, USA) was used for peak integration, calibration, and quantification. We performed peak integrations with ICIS integrator and confirmed by visual inspection. We calculated relative response factors on the basis of the relative peak areas of analyte quantitation ion and labeled analog ion. Quality control consisted of daily analysis of blind quality control material and pure water blanks. Trihalomethanes were quantified by comparing the ratios of analyte peak areas with labeled analog areas for both unknowns and freshly prepared calibrators.

Data analysis

All data were entered into Microsoft Excel, and the Analysis ToolPak regression tools were utilized to analyze the data.

RESULTS

Source water quality

Results of the water quality testing are presented in Table 2. A wide range of turbidity (4.2–305 NTU) and TOC (0–7 mg/L) values were found in water from the six sources. Turbidity and TOC values, however, were not related ($R^2 = 0.03$). The lowest and highest turbidity values were seen in rainwater catchment and river water, respectively. The lowest and highest TOC values were seen in the open well water and earth pond water, respectively.

The WHO has established a maximum recommended pH value for chlorination of water of 8.0, as chlorine is less effective at inactivating microorganisms at higher pH values (WHO 2004). The only pH value that exceeded this recommendation in source waters in this study was obtained from earth pond water. Conductivities were well differentiated (10–770 μmhos/cm). Conductivity is a measure of the ionic material dissolved in the water,

Table 2 | Source water physical and chemical characteristics and microbiological water quality

	Source 1: Rainwater catchment	Source 2: Lake	Source 3: Protected well	Source 4: Earth pond	Source 5: River	Source 6: Open well
Turbidity (NTU)	4.2	28.2	40.4	59.6	305	8.4
TOC (mg/L)	2	4	1	7	3	<1
pH	6.9	8.0	6.7	8.6	7.2	7.2
Conductivity (μmhos/cm)	10	160	260	200	70	770
Temperature (°C)	19.5	23.5	22	23.5	23.0	23.5
Ammonia (mg/L)	0–0.25	0–0.25	0–0.25	0–0.25	0–0.25	0–0.25
Total coliform (col/100 ml)	3,550	10,600	6,700	5,200	57,000	>4,000
<i>E. coli</i> (col/100 ml)	350	285	220	700	2,700	50

including chloride. Chlorine and bromide are often closely related, and thus conductivity is potentially related to bromide concentration. The lowest and highest conductivity values were seen in rainwater catchment and open well water, respectively.

Source water temperatures were normal for the Western Kenya region, ranging from 19.5–23.5°C. Ammonia values in all samples were at a similarly low, undifferentiated level. No source had detectable free or total chlorine before treatment. All sources, whether protected or not, were contaminated with total coliform (range 3,550–57,000 col/100 ml) and *E. coli* (range of 50–2,700 col/100 ml) at concentrations that far exceed the WHO drinking water guideline values of <1 col/100 ml for both total coliform and *E. coli* (WHO 2004).

Water quality characterization of the six source waters demonstrated that they were well differentiated in terms of TOC, turbidity, and conductivity, and therefore provided appropriate data for regression analysis.

Quality control

Duplicate sampling was conducted for each water quality parameter tested. All data met high quality control standards (Table 3). The relative percent difference (RPD) of duplicated samples was 5.3% for turbidity, 1.76% for pH, 0.0% for conductivity, 0.0% for temperature, and 0.0% for ammonia. On average, the RPD of duplicated free chlorine samples was 12.6%, and of duplicated total chlorine samples was 5.7%.

For quality control of microbiologic testing, an R^2 value was calculated in place of RPD to account for readings of 0 col/100 ml. Results for original and duplicate water samples were highly correlated for *E. coli* ($R^2 = 0.997$) and total coliform ($R^2 = 0.943$).

All THM quality control materials were evaluated using Westgard rules (Westgard 1981). Of 143 total samples analyzed for THM concentration, 47 (32.9%) were duplicated. Each of the duplicate samples was analyzed for all

Table 3 | Quality control for water quality parameters

	Total samples collected	Number and percent of duplicated samples	Relative percent difference	R^2
Free chlorine	144	28 (19.4%)	12.6%	
Total chlorine	144	22 (15.3%)	5.7%	
<i>E. coli</i>	131	41 (31.3%)	–	0.997
Total Coliform	131	33 (25.2%)	–	0.943
Turbidity	57	6 (10.5%)	5.3%	
pH	6	3 (50%)	1.76%	
Conductivity	6	3 (50%)	0%	
Temperature	6	1 (16.7%)	0%	
Ammonia	6	1 (16.7%)	0%	
Trihalomethanes	572	188 (32.9%)	3.59%	
Chloroform	143	47 (32.9%)	2.76%	
Bromodichloromethane	143	47 (32.9%)	2.42%	
Dibromochloromethane	143	47 (32.9%)	1.32%	
Bromoform	143	47 (32.9%)	7.85%	

four THMs, for a total of 188 duplicate trihalomethane results, 47 for each analyte. The average RPD of the 188 samples was 3.89%, with only 5 (2.7%) of the 188 individual analyte duplicate samples exceeding a 10% RPD. The individual RPDs for chloroform, bromodichloromethane, dibromochloromethane, and bromoform were 2.76%, 2.42%, 1.32%, 7.85%, respectively (Table 3).

Overall THM data

Results from all 143 samples analyzed for the four individual THMs are presented in Table 4. One sample broke in transit. No sample exceeded the WHO guideline values for any of the four individual THMs.

The WHO additive ratio guideline values ranged from 0.004 to 0.997, with a mean of 0.285 and a standard deviation of 0.199. Thus, all samples also met the additive guideline value: the sum of the four THMs' actual values divided by their guideline value should not be greater than one.

The average relative percentage for all treatment types of the individual THM analytes and the average concentration of individual THM analytes by source is presented in Table 5. There was no significant difference seen in individual analyte percentage between the plastic and ceramic containers. Chloroform was the dominant analyte in the rainwater, lake water, protected well water, earth pond water, and river water (74.9–95.2% of the total trihalomethanes (TTHM)), with correspondingly low percentages of the DBCM and bromoform analytes. In the open well water source, there was substantially lower chloroform (47.9%), and correspondingly higher BDCM and DBCM percentages.

The percent chloroform was related to the conductivity of the source water as shown in Equation 2:

$$\begin{aligned} \text{Percent Chloroform} = & -0.0565 \times \text{Conductivity} (\mu\text{mhos/cm}) \\ & + 91.1 \end{aligned} \quad (2)$$

$$R^2 = 0.9414, p\text{-value } 0.0013$$

Conductivity is inversely related to the percent chloroform, accounting for 94% of the variance in the percent chloroform in the six samples, and can therefore be considered a good indicator of bromide concentration in these waters. Sources with higher bromide concentrations (with corresponding increases in the conductivity due to the presence of the dissolved ionic chloride and thus bromide), such as open well water, will have a lower chloroform percentage, and higher percentage of the brominated trihalomethanes, in the treated water. Presence of bromine impacts the additive guideline value results as well, as the individual guideline value for chloroform is higher than the individual guideline values for the brominated trihalomethanes.

No significant variation was seen in the individual THM percentages between plastic and ceramic containers. Because of this lack of variation in individual THM percentages, in the following analysis by treatment methodology, all results will be presented as TTHMs, which is the summation of the four individual trihalomethane analytes. The analysis will focus on samples collected at 24 hours after chlorine addition, as this is the highest TTHM value seen in the samples. Supplementary analysis by individual analyte is available from the authors.

Sixteen of the 48 samples (33%) taken at 24 hours after chlorine addition exceeded the USEPA MCL for TTHM. Two of the twelve total chlorination only samples exceeded the

Table 4 | Individual analyte trihalomethane results, all samples

	Average (ppb)	Minimum (ppb)	Maximum (ppb)	Standard deviation (ppb)	WHO guideline value (ppb)
Chloroform	43.4	0.6	160	36.4	300
Bromodichloromethane	7.2	0.1	33.0	5.6	60
Dibromochloromethane	2.0	0.0	8.1	1.9	100
Bromoform	0.1	0.0	1.1	0.2	100

Table 5 | Average individual THM percentage and concentration by source

Source	Chloroform	Bromodichloromethane	Dibromochloromethane	Bromoform
1: Rainwater	95.2%	4.5%	0.3%	0%
	42.88 µg/L	2.13 µg/L	0.17 µg/L	< 0.1 µg/L
2: Lake water	78.4%	18.2%	3.4%	0%
	45.63 µg/L	9.26 µg/L	1.70 µg/L	< 0.1 µg/L
3: Protected well water	75.2%	17.4%	7.0%	0.4%
	16.71 µg/L	3.99 µg/L	1.57 µg/L	0.09 µg/L
4: Earth pond water	74.9%	19.6%	5.2%	0.3%
	56.46 µg/L	14.10 µg/L	3.50 µg/L	0.18 µg/L
5: River water	90.1%	9.1%	0.8%	0.0%
	84.02 µg/L	7.4 µg/L	0.53 µg/L	< 0.1 µg/L
6: Open well water	49.7%	26.6%	20.8%	2.9%
	13.50 µg/L	6.08 µg/L	4.40 µg/L	0.57 µg/L

USEPA MCL for TTHM, from the river water in plastic and ceramic containers.

Chlorination only in plastic containers

Free chlorine residual was maintained in water from all sources for 24 hours (range 0.07–3.64 mg/L). Water samples from all sources had no detectable *E. coli* colonies at 1 and 8 hours after treatment, however, at 24 hours in the lake water and the earth pond water, there was slight regrowth of *E. coli* (12 and 32 col/100 ml, respectively). The chlorine residual levels in these sources at 24 hours were low, at 0.10 and 0.33 mg/L, respectively.

No sample using treatment with sodium hypochlorite solution only in plastic containers exceeded any of the WHO guideline values for the four individual THMs. TTHM results over time for these samples are presented in Figure 3. TTHM at 24 hours was strongly correlated with turbidity, according to the equation:

$$\text{TTHM } (\mu\text{g/L}) = 0.3692 \times \text{Turbidity (NTU)} + 40.2 \quad (3)$$

$$R^2 = 0.8907, p - \text{value } 0.0084$$

Turbidity accounted for 89% of the variance in the TTHM concentration at 24 hours. In the regression analysis, there were no statistically significant correlations between the other source water quality parameters, including TOC, and TTHM concentrations at 24 hours.

The WHO additive ratio guideline value results at 24 hours ranged from 0.182 to 0.674, well below the WHO guideline value of less than one, with the protected well water lowest and the river water highest. The open well water had relatively higher additive guideline values due to the higher proportion of bromodichloromethane, which has a lower guideline value than the other trihalomethanes.

Potential mitigation strategies: Filtration, settling & decanting, and PuR[™] in plastic containers

Neither filtration nor settling & decanting showed any statistically significant reduction of THM levels at 1, 8, or 24 hours after chlorine addition, indicating that the THM precursors are smaller particles than are removed by filtration or settling & decanting. In fact, there was little difference in the resultant TTHM values when the chlorination only

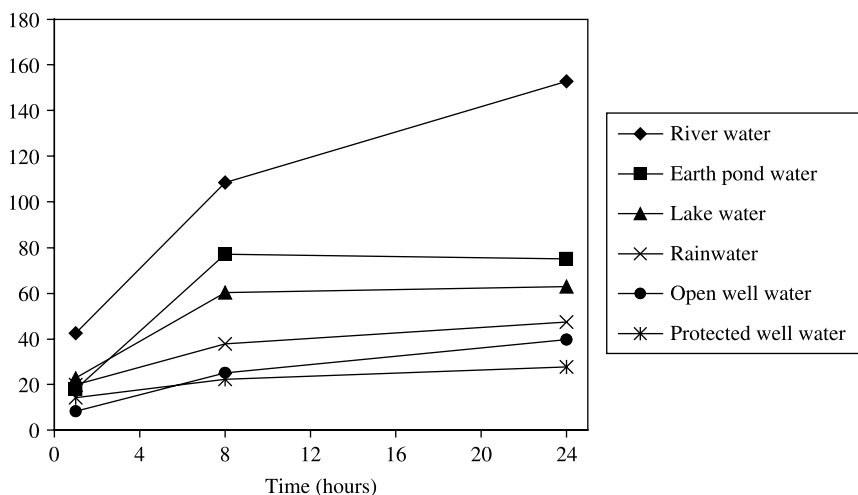


Figure 3 | TTHM versus time in plastic containers, chlorination only.

results are compared with these two potential mitigation strategies (Figure 4). The rainwater results presented in Figure 4 are similar to the other five sources tested. The use of these two pretreatments did not consistently reduce turbidity and maintain higher chlorine residuals at 24 hours after chlorine addition as compared to the chlorination only samples, and this accounts for the lack of statistically significant TTHM reduction.

In contrast, PuR[™] was a very effective mitigation strategy. After the use of PuR[™], turbidity in the samples dropped from a range of 4.23–305 NTU to a range of 0.93–2.1 NTU. On average, in the six different source samples when compared with the chlorine only samples, TTHM levels were 26.1% lower at 1 hour after treatment, 65.0% lower at 8 hours, and 73.1% lower at 24 hours in PuR[™] treated samples. All individual and TTHM values were very low (Figure 5), and the WHO additive ratio guideline value results at 24 hours ranged from 0.015–0.183. No significant relationship was seen between TTHM and any of the water quality variables. Low levels of free chlorine residual were maintained using PuR[™] in all six water sources after 24 hours, ranging from 0.08–0.32 mg/L, and there was no regrowth of *E. coli*.

Chlorination only in ceramic containers

Free chlorine residual was maintained in all stored water samples from all sources for 24 hours after chlorine addition

(range 0.28–3.5 mg/L). All *E. coli* were removed in the six sources and all sources remained *E. coli* free at 24 hours.

No chlorination only samples in ceramic containers exceeded any of the WHO guideline values for the four individual THMs. TTHM results over time for these samples are presented in Figure 6. TTHM at 24 hours was correlated with turbidity using the following equation:

$$\text{TTHM } (\mu\text{g/L}) = 0.2925 \times \text{Turbidity (NTU)} + 48.7 \quad (4)$$

$$R^2 = 0.6648, p - \text{value } 0.0606$$

Turbidity of the source water accounted for 66% of the variability in the TTHM concentrations at 24 hours. In the regression analysis, there were no statistically significant

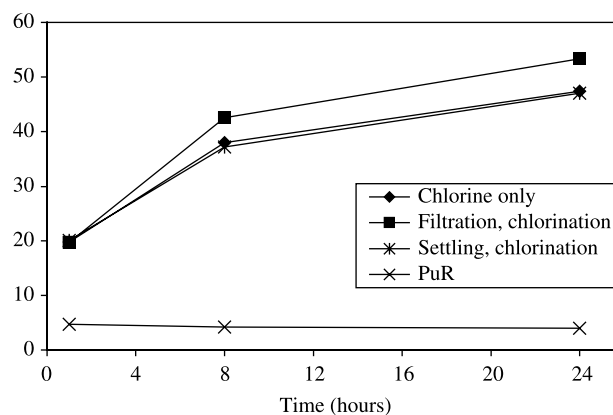


Figure 4 | TTHM versus time in rainwater using plastic containers and four treatments.

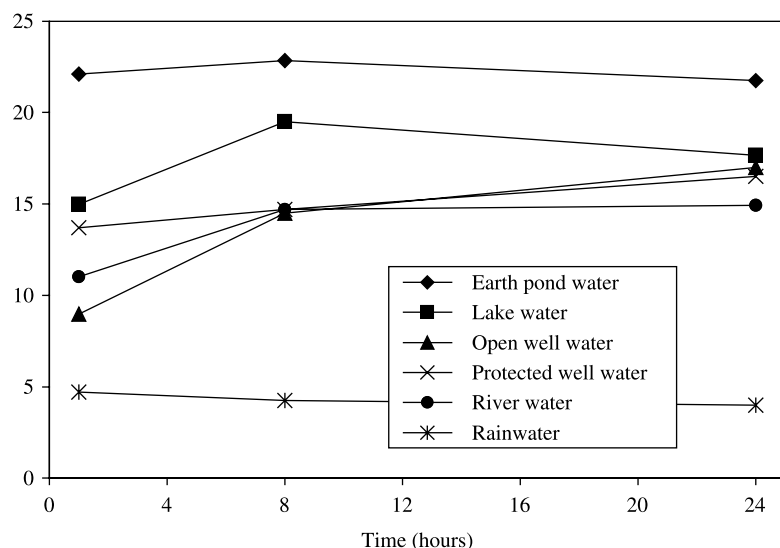


Figure 5 | TTHM versus Time in Plastic Containers using PuR.

correlations between the other source water quality parameters, including TOC, and TTHM concentration at 24 hours. These findings were similar to those obtained in water stored in plastic containers. The reason for the low TTHM value in the 24-hour earth pond water sample is unknown (Figure 6). This value is considered an outlier and was excluded from the regression analysis due to this unexplained TTHM drop over time, which might be attributable to sampling error.

The WHO additive ratio guideline value results at 24 hours were 0.142 to 0.607 (as compared with the chlorination only values in the plastic containers of 0.182 to 0.674), with

the protected well water lowest and the river water highest (the same as in the chlorination only samples in plastic containers). These results were strikingly similar to the chlorination only values in the plastic containers (Table 6).

Potential mitigation strategies: Filtration, settling & decanting, and moringa in ceramic containers

Both filtration and settling and decanting showed no statistically significant reduction of TTHM levels at 1, 8, or 24 hours after chlorine addition. In fact, in ceramic pots, as in the plastic containers, there was little difference in the

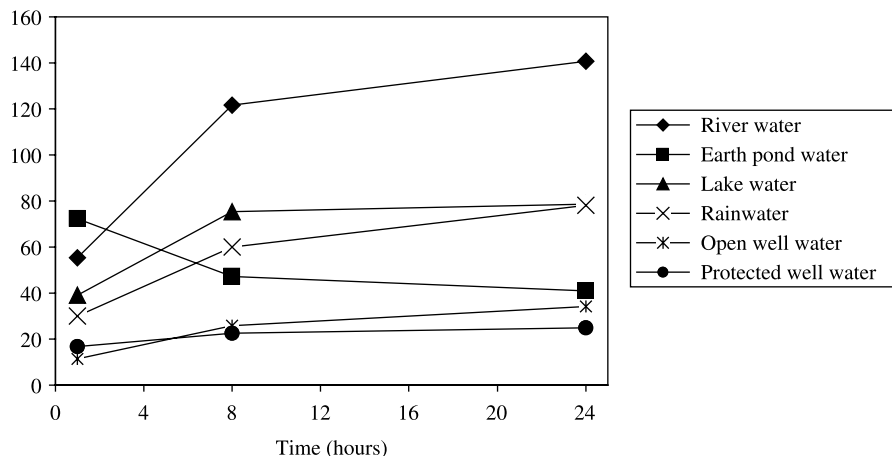


Figure 6 | TTHM versus time in ceramic containers, chlorination alone.

resultant TTHM values between samples treated with chlorination only and samples pre-treated with the two potential mitigation strategies.

Moringa was also an ineffective THM formation mitigation strategy. The 2-gram dose of moringa reduced turbidity in medium turbidity source waters (lake, protected well, and earth pond) (Table 7), but had less effect in river water, and was ineffective in low turbidity rain water.

The use of moringa seeds as a flocculant resulted in little or no reduction in TTHM concentration in treated water as compared with the chlorination only samples. In fact, there was a slight increase in TTHM concentration in five of the six source samples at 24 hours as compared to the chlorination only in ceramic container samples. The WHO additive ratio guideline value results at 24 hours were 0.200 to 0.997, as compared to the chlorination only values in the ceramic containers of 0.142 to 0.607. The protected well water had the lowest additive guideline value. The earth pond water had the highest additive guideline value seen in the study, at 0.997.

DISCUSSION

No point-of-use treatment method, alone or in combination with any pre-treatment method, yielded any samples that exceeded WHO guideline values for any of the four individual THMs or the additive TTHM ratio guideline value irrespective of the water source or storage container. This is not a surprising result, although the relatively low percentage of samples that exceeded the USEPA MCL (33% of samples at 24 hours after chlorine addition) is of note. In

contrast to public utilities in the United States and Europe, which devote considerable expense to reducing trihalo-methane concentrations in their treated water through technology improvements as part of balancing the risk of waterborne disease and reducing disinfection by-products to “mitigate potential risks” (USEPA 2006), WHO simply considers health effects and health risk to potential users from exposure to a certain compound when developing guideline values (WHO 2005). WHO has defined the acceptable risk from the individual THMs as one extra cancer in every 100,000 people who drink two litres of chlorinated water for 70 years. WHO guidelines, which are considered separately from the goal of providing highly treated water through infrastructure, are applicable to the Safe Water System, and other health-based point-of-use water treatment interventions.

A significant difference in THM concentrations in water stored in ceramic and plastic storage containers was not seen. We added ceramic pots to the study to test whether the ceramic would either absorb THMs, or add THM precursors to stored water. The data clearly showed neither significant gains nor losses of TTHMs in the ceramic container, suggesting that TTHMs were not absorbed into the ceramic, and that organic material with TTHM formation potential did not leach from the ceramic containers into the stored water. It is likely that organic material that would lead to THM formation potential was burned off in the firing process of the ceramic.

The majority of TTHMs were formed within 8 hours after chlorine addition, indicating that as chlorine residual decays during storage, there is less TTHM production.

Pretreatment of water by filtration through a cloth or settling for 24 hours and decanting supernatant water before chlorination did not appear to be effective THM mitigation strategies. Neither procedure reduced TTHM concentrations in chlorinated water as compared to chlorination only. These are not unexpected results, as THM precursor compounds have been identified as primarily organic carbon particles smaller than 0.45 microns in size (Chow *et al.* 2005). It is unlikely that such gross filtration mechanisms as tested in this study would remove such small particles. It was, however, important to test these potential mitigation strategies, as they are practical and inexpensive strategies available to and used by the populations who are targeted by point-of-use water treatment intervention programs like the Safe Water System.

Table 6 | Comparison of plastic and ceramic results, chlorination only treatment

Source	TTHM (ppb) in chlorination only treatment at 24 hours after chlorine addition	
	Plastic containers	Ceramic containers
1: Rainwater	47.4	78.2
2: Lake water	62.9	78.6
3: Protected well water	27.9	24.9
4: Earth pond water	75.1	47.3
5: River water	152.8	121.7
6: Open well water	39.8	34.1

Table 7 | Turbidity reduction using moringa powder

Source	Source water turbidity (NTU)	After addition of 2 grams moringa and 24 hours of settling (NTU)	Percent reduction (%)
1: Rainwater	4.2	7.4	-76.2
2: Lake water	28.2	3.1	89.0
3: Protected well water	40.4	2.9	92.8
4: Earth pond water	59.6	7.4	87.6
5: River water	305.0	211.0	30.8
6: Open well water	8.4	6.0	28.6

There were inconclusive results as to whether the use of these two pretreatment mechanisms increases the chlorine residual present in stored water at 24 hours after chlorination because of reduction in chlorine demand. It is recommended that the impact of these pretreatment mechanisms on free chlorine residual over time, as compared to chlorination only, be further investigated to fully characterize their potential effectiveness in maintaining free chlorine residual.

The use of PuR[™] led to significantly lower TTHM concentrations at 24 hours after treatment than the use of chlorination only and was thus an effective TTHM mitigation strategy. This finding was expected because PuR[™] has been proven to reduce turbidity (Crump *et al.* 2004). PuR[™] is marketed by PSI for sale in Kenya at a product cost-recovery price of 7 Kenya Shillings (9.7 US cents) to treat 10 litres of water (0.97 cents per litre). In contrast, the Safe Water System product, WaterGuard (Figure 2), is marketed by the NGO Population Services International (PSI) in Kenya at a product cost-recovery price of 20 Kenya Shillings (27.8 US cents) to treat 1,000 litres of water (0.0278 cents per litre). As both are available to the Kenyan population, variables such as disposable income and user preference will impact each family's choice of which household water treatment product to utilize.

Our findings suggest that the use of ground moringa seeds increases TTHM concentrations as compared to chlorination alone, particularly at 24 hours after the addition of sodium hypochlorite solution. It is postulated that the addition of the moringa resulted in an increase of THM precursors in the water, which led to a corresponding higher THM formation potential than would be expected in water chlorinated without moringa pre-treatment. In addition, the dose of moringa necessary to

remove turbidity varied depending on the turbidity of the source water. It is recommended that organizations promoting moringa seed use for flocculation followed by chlorination for disinfection consider the potential impacts of this combined use on TTHM concentrations. Further research should be conducted to determine more appropriate use of moringa in waters of different turbidity levels.

In this study, conductivity was identified as a surrogate for bromide concentration to predict THM speciation ($R^2 = 0.94$), and turbidity was significantly related to TTHM concentration at 24 hours after chlorine addition in both plastic ($R^2 = 0.89$) and ceramic containers ($R^2 = 0.66$). The relationship between conductivity and bromide is clear, as increases in the dissolved ionic chloride concentration, which is related to bromide, will lead to corresponding increases in the conductivity. Other minerals and sodium chloride can also cause increases in conductivity, so this result cannot be generalized. Turbidity has traditionally been used in drinking water treatment as a surrogate parameter for particle concentrations. While UV₂₅₄ absorbance has been identified as a surrogate indicator of THM formation potential (Chow *et al.* 2005), it is more difficult to measure in areas without access to a spectrophotometer (Standard Methods 1998). It is recommended that, in situations in which access to laboratory facilities is limited, further research should consider using water quality parameters of conductivity and turbidity as indicators for bromide concentration and THM formation potential, respectively, because they can be accurately measured in the field.

Source waters tested in this study represent a wide range of drinking waters typically used by populations who would benefit from chlorine-based household water treatment

products to improve water quality. Although further testing of THM formation in additional water sources is warranted, this study provides strong evidence that use of the Safe Water System in both turbid and non-turbid waters does not cause the formation of trihalomethanes in excess of WHO drinking water guideline values. Thus, it is recommended that, when microbiologic water quality cannot be assured; households adopt or continue to use the Safe Water System or PuR[®] in both turbid and non-turbid waters in western Kenya.

CONCLUSIONS

Diarrheal diseases kill an estimated 2.2 million people each year, and point-of-use chlorination options, including both the Safe Water System and PuR[®], are proven interventions that can reduce diarrheal disease incidence and protect health in developing countries. Because the SWS includes the addition of sodium hypochlorite to unfiltered water sources, concerns have been raised about the potential long-term health effects of disinfection by-products to SWS users. The data presented herein clearly show that chlorination of turbid and non-turbid waters does not lead to trihalomethane concentrations that exceed the WHO guideline values. Proper chlorination of household water with the Safe Water System does not form harmful levels of disinfection by-products. This approach to water quality improvement and disease prevention merits wider promotion and use.

ACKNOWLEDGEMENTS

The authors thank Philip Makutsa, Sam Ombeki, Alex Mwaki, John Migele, Charles Komolleh, Charles Ndinya, Mary Ayalo, and Meshak Ajode of CARE/Kenya in Homa Bay, and Bill Gallo, Sr. for their assistance in sample collection and logistical coordination.

DISCLAIMER

The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the Centers for Disease Control and Prevention.

REFERENCES

- Baqui, A. H., Black, R. E., Sack, R. B., Chowdhury, H. R., Yunus, M. & Siddique, A. K. 1993 Malnutrition, cell-mediated immune deficiency and diarrhea: A community-based longitudinal study in rural Bangladeshi children. *Am. J. Epidemiol.* **137**(3), 355–365.
- Bartram, J. 2006 *Personal Communication via Email*. World Health Organization, Geneva, Switzerland.
- Cardinali, F. L., Ashley, D. L., Morrow, J. C., Moll, D. M. & Blount, B. C. 2004 Measurement of trihalomethanes and methyl tertiary-butyl ether in tap water using solid-phase microextraction GC/MS. *J. Chromatogr. Sci.* **42**(4), 200–206.
- CDC 2006 *Effect of chlorine in inactivating selected microorganisms*. http://www.cdc.gov/safewater/about_pages/chlorinationtable.htm, Accessed January 8, 2007.
- Chow, A. C., Guo, F., Gao, S., Breuer, R. & Dahlgren, R. 2005 Filter pore size selection for characterizing dissolved organic carbon and trihalomethane precursors from soils. *Water Res.* **39**(7), 1255–1264.
- Crump, J. A., Okoth, G. O., Slutsker, L., Ogaja, D. O., Keswick, B. H. & Luby, S. P. 2004 Effect of point-of-use disinfection, flocculation and combined flocculation-disinfection on drinking water quality in western Kenya. *J. Appl. Microbiol.* **97**, 225–231.
- Crump, J. A., Otieno, P. O., Slutsker, L., Keswick, B. H., Rosen, D. H., Hoekstra, R. M., Vulule, J. M. & Luby, S. P. 2005 Household based treatment of drinking water with flocculant-disinfection for preventing diarrhoea in areas with turbid source water in rural western Kenya: Cluster randomized controlled trial. *Br. Med. J.* **331**(7515), 478–483.
- Cutler, D. & Miller, G. 2005 The role of public health improvements in health advances: The twentieth-century United States. *Demography* **42**(1), 1–22.
- Fewtrell, L. & Colford, J. 2004 *Water, Sanitation and Hygiene: Interventions and Diarrhoea: A Systemic Review and Meta-analysis*. Health, Nutrition, and Population Family of the World Bank Human Development Network, Washington, DC.
- Guerrant, D. I., Moore, S. F., Lima, A. A., Patrick, P. D., Schorling, J. B. & Guerrant, R. L. 1999 Association of early childhood diarrhoea and cryptosporidiosis with impaired physical fitness and cognitive function four-seven years later in a poor urban community in northeast Brazil. *Am. J. Trop. Med. Hyg.* **61**(5), 707–713.
- International Agency for Research on Cancer, World Health Organization 1991 *IARC monographs on the evaluation of carcinogenic risks to humans, Volume 52: Chlorinated drinking-water; chlorination by-products; some other halogenated compounds; cobalt and cobalt compounds*. WHO, Lyon, France. Available online: <http://monographs.iarc.fr/ENG/Monographs/vol52/volume52.pdf>.
- International Agency for Research on Cancer, World Health Organization 1999 *IARC monographs on the evaluation of carcinogenic risks to humans, Volume 73: Some chemicals that cause tumours of the kidney or urinary bladder in rodents*

- and some other substances. WHO, Lyon, France. Available online: <http://monographs.iarc.fr/ENG/Monographs/vol73/volume73.pdf>.
- Luby, S. P., Agboatwalla, M., Hoekstra, R., Rahbar, M., Billhimer, W. & Keswick, B. 2004 Delayed effectiveness of home-based interventions in reducing childhood diarrhea, Karachi, Pakistan. *Am. J. Trop. Med. Hyg.* **71**(4), 420–427.
- Madsen, M., Schlundt, J. & Omer, E. F. E. 1987 Effect of water coagulation by seeds of *Moringa oleifera* on bacterial concentrations. *Am. J. Trop. Med. Hyg.* **90**(3), 101–109.
- Mintz, E., Reiff, F. & Tauxe, R. 1995 Safe Water treatment and storage in the home: A practical new strategy to prevent waterborne disease. *JAMA* **273**(12), 948–953.
- Ogutu, P., Garrett, V., Baras, P., Ombeki, S., Mwaki, A. & Quick, R. E. 2001 Seeking safe storage: A comparison of drinking water quality in clay and plastic vessels. *Am. J. Public Health* **91**(10), 1610–1611.
- Quick, R., Venczel, L., Mintz, E., Soletto, L., Aparicio, J., Gironaz, M., Hutwagner, L., Greene, K., Bopp, C., Maloney, K., Chavez, D., Sobsey, M. & Tauxe, R. 1999 Diarrhea prevention in Bolivia through point-of-use disinfection and safe storage: A promising new strategy. *Epidemiol. Infect.* **122**(1), 83–90.
- Quick, R. E., Kimura, A., Thevos, A., Tembo, M., Shamputa, I., Hutwagner, L. & Mintz, E. 2002 Diarrhea prevention through household-level water disinfection and safe storage in Zambia. *Am. J. Trop. Med. Hyg.* **66**(5), 584–589.
- Richardson, S. D., Simmons, J. E. & Rice, G. 2002 Disinfection byproducts: The next generation. *Environ. Sci. Technol.* **36**(9), 198A–205A.
- Rook, J. J. 1974 Formation of haloforms during chlorination of natural waters. *Water Treat. Exam.* **23**(2), 234–243.
- Semenza, J., Roberts, L., Henderson, A., Bogan, J. & Rubin, C. 1998 Water distribution system and diarrheal disease transmission: A case study in Uzbekistan. *Am. J. Trop. Med. Hyg.* **59**(6), 941–946.
- Standard Methods for the Examination of Water and Wastewater* 1998 20th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC.
- Tauxe, R. 1995 Epidemic cholera in the new world: Translating field epidemiology into new prevention strategies. *Emerg. Infect. Dis.* **1**(4), 141–146.
- USEPA (United States Environmental Protection Agency) 2006 *Stage 2 Disinfectants and Disinfection Byproduct Rule (Stage 2 DBP rule): Basic Information*. <http://www.epa.gov/safewater/disinfection/stage2/basicinformation.html>. Accessed January 9, 2007.
- Westgard, J. O., Barry, P. L., Hunt, M. R. & Groth, T. 1981 A multi-rule Shewhart chart for quality control in clinical chemistry. *Clin. Chem.* **27**(3), 493–501.
- WHO (World Health Organization) 1993 *Guidelines for Drinking-Water Quality, 2nd Edn, Volume 1: Recommendations*. WHO, Geneva, Switzerland.
- WHO (World Health Organization) 2004 *Guidelines for Drinking-Water Quality, 3rd Edn, Volume 1: Recommendations*. WHO, Geneva, Switzerland.
- WHO (World Health Organization) 2005 *Trihalomethanes in Drinking-Water: Background Document for Development of WHO Guidelines for Drinking-Water Quality*. WHO, Geneva, Switzerland.
- WHO/UNICEF (World Health Organization/United Nations Children's Fund) 2000 *Global Water Supply and Sanitation Assessment 2000 Report*. Water Supply and Sanitation Collaborative Council. WHO/UNICEF, Geneva, Switzerland.

First received 15 May 2006; accepted in revised form 12 January 2007. Available online November 2007.