Trihalomethanes formation in point of use surface water disinfection with chlorine or chlorine dioxide tablets

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Abstract
In remote or underdeveloped areas, natural disaster emergencies and armed conflict zones, point-of-use surface water disinfection with chlorine tablets provides microbiologically safe water, but disinfection by-products such as trihalomethanes (THMs) are formed. While the health risks from THMs are much less than the risks from consuming microbiologically unsafe water, it is nonetheless desirable to understand and minimise THM formation. We show that THM concentrations in surface water samples from the Northern British Isles disinfected with chlorine tablets increased with contact time, in some cases to significantly exceed EU, US EPA and WHO drinking water guidance values after more than an hour. More stagnant water from ponds and lochs had higher THM formation than river water. Doubling the chlorine tablet dose slightly enhanced THM formation, and passing water through coffee filter paper reduced it. Chlorine dioxide tablets produced minimal amounts of THMs.

Introduction
In the absence of a piped potable water supply, for instance in natural disaster emergencies, in remote or underdeveloped areas, and in armed conflict zones, water from rivers, streams, ponds and lakes is often used as a drinking water source. If used for human consumption, surface water should as a minimal treatment first be disinfected to destroy the pathogens contained. Without water disinfection, serious waterborne diseases such as diarrhoea, typhoid and cholera can quickly spread and infect large populations (Walton & Ivers 2011). Chlorinating water at the household level has been shown to be one of the most cost-effective means of preventing diarrhoea in settings where it is endemic and deadly (Hutton & Haller 2004). Chlorine tablets are therefore at times distributed in response to the outbreak of waterborne diseases, and have for example been distributed to thousands of households as an emergency response to a large typhoid fever outbreak in Harare, Zimbabwe (Imanishi et al. 2014). The antimicrobial effectiveness and social acceptance of sodium or calcium hypochlorite and various other point-of-use water treatments such as boiling, ceramic filtration and solar disinfection has been studied extensively (Clasen & Edmondson 2006; Loo et al. 2012; Poulos et al. 2012; Levy et al. 2014).

On the other hand, much less is known about the effect of point-of-use disinfection on chemical water quality, for instance regarding the formation of undesirable disinfection by-products (DBPs) (Lantagne et al. 2010; Smith et al. 2010). Several chlorinated DBPs such as trihalomethanes (THMs) are formed when dissolved organic matter and other precursors in water react with chlorine (Serodes et al. 2003). Long-term exposure to THMs is of concern due to possible cancer risks and other chronic health effects (WHO 2005). While the health risks from THMs are much less than the risks from consuming microbiologically unsafe water, it is nonetheless desirable to minimise their occurrence. The 1998 European Union Drinking Water Directive (Council of the European Union 1998) defines 100 µg/L as the allowable maximum concentration of total THMs (comprising chloroform, bromodichloromethane, dibromochloromethane and bromoform) in drinking water. The US EPA regulates THMs at a maximum allowable annual average level of 80 µg/L (USEPA 1998). Where possible without compromising disinfection, European Union as well as US water providers should strive to minimise THM formation. The World Health Organisation (WHO) has also defined guidance values, but for the individual THM compounds. WHO guidance values are 300 µg/L for chloroform (HCCl3), 100 µg/L for dibromochloromethane (HBr2Cl) and bromoform (HCBr3) and 60 µg/L for bromodichloromethane (HBrCl2) (WHO...
Formation of THMs in conventional water treatment systems has been studied extensively to help suppliers comply with national drinking water standards (Serodes et al. 2003). THMs formation in point of use water disinfection is less well investigated (Lantagne et al. 2010; Smith et al. 2010). Because conventional treatment systems reduce THM precursor concentrations in water prior to disinfection using processes like coagulation and flocculation, sand, activated carbon and membrane filtration, much greater THM formation is anticipated in the absence of such pretreatment. The aim of this study was therefore to quantify THMs concentrations in surface waters disinfected at the point of use with chlorine or chlorine dioxide water purification tablets, and to study the effects on THMs formation of variables such as source water and disinfectant type, disinfectant contact time and dose, and rudimentary pretreatments such as passing water through coffee filter paper.

### Experimental procedure

#### Chemicals

Chlorine and chlorine dioxide water purification tablets releasing according to their manufacturers 17 mg chlorine, or a minimum of 1.5 mg chlorine dioxide, when dissolved in water, were purchased from Lifemarque, Aldermaston, UK. Ammonium chloride, mono and di potassium phosphate salts were purchased from VWR, BHD, Poole, England, with >99% purity. Sodium sulphate salt with >99% purity was purchased from Sigma-Aldrich, Sigma-Aldrich. A THMs calibration mix, 2000 μg/mL each compound in methanol was purchased from Supelco, Belleford, PA, USA.

#### Choosing locations and water sampling

Surface water samples were obtained from four locations in Scotland and three locations in Northumberland, Northeast of England, which together comprised pond, loch (lake) and river water. While public water supply is wide-spread in Scotland and Northeast England, water purification tablets are being used by campers and hikers and others enjoying the outdoors. Surface waters in Scotland and Northeast England tend to be very rich in THMs precursors such as dissolved organic carbon and halides because of the abundance of organic rich soils such as peat, and the coastal influence, and surface waters in this region tend to have a high THMs formation potential (Goslan et al. 2009; Gough et al. 2014). Basic catchment characteristics of the water sources investigated in this study are summarised in Table 1. Water samples were collected in 1 or 2 L DURAN® (Wertheim, Germany), borosilicate glass bottles with Teflon-lined caps purchased from VWR, BHD, Poole, England, and stored in the cold room at 3°C until use. De-ionised water from a MilliQ water filter was used as blank control.

#### Water characterization

Dissolved organic carbon (DOC) was determined by passing the water samples through a 0.45 μm polycarbonate membrane filter (VWR, Poole, England) to remove particulate organic carbon, followed by injection through a TOC-5050A Total Organic Carbon Analyzer coupled with an ASI-5000A Autosampler (Shimadzu, Japan). Conductivity and pH were monitored with a HQ40d Hach-Lange pH meter (Loveland, CO, USA). Alkalinity was measured using APHA standard methods (APHA 2005). Samples for anions determination were filtered through 0.2 μm cellulose acetate syringe filters (VWR, Poole, England) prior to injection into an ICS-1000 Ion Chromatography System (Dionex, CA, USA). Measured

#### Table 1 Sampling location characteristics and sampling dates

| Sampling location | Description                                                                 |
|-------------------|------------------------------------------------------------------------------|
| Exhibition Park Pond, March 2013 | This boating pond in Northumberland is fed by water running off a large meadow mainly used for cattle grazing. |
| Exhibition Park Pond, August 2014 | Same as above, sample taken in August 2014 during a green algae bloom. |
| Mill Loch, May 2014 | This Scottish loch is surrounded by bracken vegetation, peatland, marshes and bogs with low sheep grazing areas. The loch is fed by an aquifer and runoff mainly during autumn months. |
| Loch Gearach, May 2014 | This Scottish loch is surrounded mainly by heather vegetation, peatland and manmade forestry. It also has some farms with low sheep and cattle grazing. |
| Lochs Craigenputton, May 2014 | Scottish lochs located in a peaty area with heather vegetation and man-made forestry. |
| River Ouseburn, March 2013 | Small river in Northumberland which flows through peri-urban areas and a wooded park. |
| River Ugie, May 2014 | River in Scotland, with a mainly agricultural catchment area. |
| River Tyne, March 2013 | Major river in Northumberland with upland sources and flowing through agricultural and urban areas. |
chemical characteristics of the water sources investigated in this study are summarised in Table 2.

**Water disinfection**

Unless otherwise noted, 1 L DURAN®, borosilicate glass bottles with Teflon-lined caps were filled with 1 L of water, leaving a headspace volume of about 100 mL. One chlorine or chlorine dioxide water purification tablet was added and dissolved by repeated shaking. After a minimum 20 min disinfectant contact time, triplicate subsamples of the disinfected water were used for total coliform counts by membrane filtration or preserved for THMs analysis. Variations on this experimental procedure were (i) adding two tablets per litre of surface water to investigate the effect of doubling the disinfectant dose; (ii) storing the disinfected water bottles for up to three days on the laboratory bench at room temperature prior to sampling for THMs analysis to investigate the effect of the disinfectant contact time; (iii) passing the surface water through a coffee filter paper (Melitta, 1 × 4) prior to disinfection to investigate the effect of rudimentary pretreatment.

**Total coliform count**

Total coliform counts were determined by passing 100 mL of disinfected water through a membrane filter (Oxoid, Hampshire, UK, 47 mm diameter, 0.45 µm pore size). Membranes were incubated in plates on Membrane Lauryl Sulphate Broth soaked pads at 37°C for 18 h before counting the colonies.

**THMs analysis**

THMs analysis was based on standard operating protocols published by the University of Massachusetts (Reckhow 2012). To preserve disinfected water samples, 40 mg of ammonium chloride (NH₄Cl) crystals to quench free chlorine and 1 g of buffer salt mix (97.5% by weight KH₂PO₄ and 2.5% Na₂HPO₄) to adjust pH were added to 40 mL glass vials (VWR, Poole, England). These vials were then filled with disinfected water to slightly beyond the rim taking advantage of the convex water-air interface created by surface tension. The vials were immediately tightly capped with a Teflon lined rubber seal cap (VWR, Poole, England). These vials were then filled with disinfected water through a coffee filter paper (Melitta, 1 × 4) prior to disinfection to investigate the effect of rudimentary pretreatment.

| Parameter                  | Exposition Park Pond, March 2013 | Exposition Park Pond, August 2014 | Mill Loch, May 2014 | Lochs Craigendunton, May 2014 | River Ugie, May 2014 | River Tyne, March 2013 |
|----------------------------|----------------------------------|-----------------------------------|---------------------|-----------------------------|---------------------|------------------------|
| Bromide (mg/L)             | 0.2±0.1                          | 0.16±0.01                         | n.d.                | 0.04±0.01                   | 0.1±0.1             | 0.04±0.01              |
| Chloride (mg/L)            | 17.3±3                           | 13.5±0.8                          | 14.0±0.5            | 9.7±0.8                     | 14.3±0.7            | 12.7±0.4               |
| Fluoride (mg/L)            | 0.3±0.01                         | 0.33±0.01                         | n.d.                | 0.04±0.01                   | 0.04±0.01           | 0.04±0.01              |
| TOC (mg/L)                 | 24.3±3                           | 9.07±0.05                         | n.d.                | 11.4±0.05                   | 17.1±0.17           | 19.7±0.05              |
| Conductivity (μS/cm)       | 62±2                            | 6.3±1.2                           | 6.3±1.2             | 4.4±0.1                     | 4.4±0.1             | 3.3±0.2                |
| Alkalinity (mEq/L)         | 0.1±0.04                         | 6.5±2.0                           | 6.5±2.0             | 8.0±0.04                    | 8.0±0.03            | 7.6±0.3               |
| pH                         | 8.3±0.2                          | 7.7±0.1                           | 7.7±0.1             | 7.6±0.1                     | 8.0±0.3             | 7.7±0.1               |

Table 2: Surface Water Parameters
was sealed with a Teflon-lined cap. After 1 min of intensive mixing by hand and 15 min of mixing at 200 rounds per minute on an orbital shaker, the water-pentane mixture in the vials was allowed to density-separate into two layers, before 1 mL of the pentane layer was transferred into an auto sampler vial for GC analysis. The GC-vials capped with Teflon-lined septa lids were frozen for at least 3 h. If ice crystals were detected in the vials, the pentane was transferred into a new vial before the ice defrosted.

THMs were analysed on an Agilent gas chromatograph equipped with an electron capture detector (GC-ECD). Sample injection (1 μL) was done with an autosampler in splitless mode. The THMs were separated on a 60 m HP-5 capillary column with the following temperature programme: 30°C for 10 min, 3°C per min to 41°C, 6 min hold, 5°C per min to 81°C, 25°C per min to 180°C, 10 min hold. The carrier gas was hydrogen at a constant flow of 1 mL per min. Nitrogen was used as make-up gas for the ECD (30 mL per min) and the detector temperature was 300°C. Calibration standards were prepared fresh for each GC run by diluting the THMs calibration mix in internal standard amended pentane for a four point instrument calibration.

Results and discussion

Total coliform count

According to the manufacturer, chlorine tablets release 17 mg of chlorine, and chlorine dioxide tablets a minimum of 1.5 mg free chlorine dioxide, if dissolved in water. For the use of one tablet per litre and 20 min contact time this corresponds to a maximum concentration time (C-t) product of 340 and 30 (mg/L-min), respectively. There was no coliform growth on disinfected water samples after 20 min contact for both chlorine and chlorine dioxide tablets and for both, one or two tablet per litre dosages, indicating good antimicrobial effectiveness. For an assessment of the relative effectiveness of chlorine and chlorine dioxide against different waterborne pathogens at different dosages and contact times we refer the reader to the literature (Association 1999; USEPA 1991).

THM levels after 20 min contact time for different surface water types

Figure 1 compares the concentration of total THMs for different surface water types in Northeast England and Scotland after 20 min contact time with chlorine. With the exception of one loch sample, total THMs were below both EU and US EPA guidance values of 100 and 80 μg/L, respectively. The highest measured individual compound concentrations after 20 min contact time were 79.6 ± 35.8 μg/L chloroform in Loch Gearach water, and 17.1 ± 0.8 μg/L bromodichloromethane, 6.7 ± 0.2 μg/L dibromochloromethane and 1.4 ± 0.8 μg/L bromoform in Mill Loch water. These individual compound concentrations are all well below WHO guidance values, and also compliant with WHO guidance for total THMs using the fractioning approach (the sum of fractions according to Eq. (1) were all <1). An interesting observation is that the total THMs concentrations in each of the four more stagnant waters (ponds/lochs) significantly exceeded those in all of the river waters (t-tests, two-tailed, all P < 0.05). In pond water, total THMs levels were significantly higher for the sample taken in August 2014, during a green algae bloom, as compared to the sample taken in March 2013 (t-test, two-tailed, P < 0.05).

THM levels as a function of disinfectant contact time

Figure 2(a) illustrates how the total THMs concentration in pond water sampled in August 2014 rapidly increased with chlorine contact time to surpass EU and US EPA guidance values within 2 h, before it stabilised at just below 350 μg/L from 20 h contact time onwards. Individual THMs compounds showed similar trends with contact time, and chloroform and bromodichloroform concentrations in particular rose to reach levels just below the WHO guidance values of 300 μg/L and 60 μg/L for these individual compounds, respectively (Fig. 2b), which meant, however, that WHO guidance for total THMs using the fractioning approach was exceeded (the sum of fractions after 21 h equals 1.9 according to Eq. (1), and thus is >1). The effect of a long chlorine contact time was also investigated for water from Loch Gearach and the total THM concentration rose again significantly from 95.0 ± 39.5 μg/L after 20 min contact time to
224.4 ± 3.2 μg/L after 3 days, thus surpassing EU and US EPA guidance values at long contact time, while individual compound concentrations of 196.6 ± 2.7 μg/L chloroform, 24.2 ± 0.5 μg/L bromodichloromethane, 3.6 ± 0.1 μg/L dibromochloromethane and 0.1 ± 0.1 μg/L bromoform meant that WHO guidance values for total THMs were also exceeded (the sum of fractions after 3 days equals 1.1 according to Eq. (1), and thus is >1). These examples show that THMs levels in chlorinated surface water initially significantly increase with disinfected water storage time. When interpreting these measured exceedances of regulatory guidance values, it is important to consider that the guidance values were derived to protect consumers based on life-time exposure, and refer in some cases to average annual values. The WHO stresses that adequate water disinfection should never be compromised because of concerns about THM formation. Nonetheless, it is desirable to minimise by-product formation in water disinfection as far as possible with these caveats.

**Effects of changes in point-of-use disinfection practice on THM levels**

Figure 3 illustrates, how doubling the chlorine tablet dose slightly, but statistically significantly enhanced total THMs levels in pond water sampled in March 2013 from 35.8 ± 1.4 μg/L to 41.7 ± 1.2 μg/L after 20 min chlorine contact time (t-test, two sided, P-value < 0.01), while passing the same water through coffee filter paper prior to disinfection significantly reduced total THMs levels by 28 percent to 25.6 ± 2.3 μg/L (t-test, two-tailed, P-value < 0.01). In comparison with chlorine water purification tablets, THMs formation was significantly lower and in the range of the analytical detection limit, when using chlorine dioxide tablets as an alternative disinfectant (t-test, pairwise comparisons, two-tailed, all P-values < 0.01). Chlorine dioxide water purification tablets, as expected (Li et al. 1996; Zhao et al. 2006), produced only minimal THMs concentrations.

**Conclusions**

(1) Total THM concentrations in surface water after point of use disinfection with chlorine tablets may significantly exceed EU and US EPA and WHO guidance values, especially for more stagnant waters (from ponds/lochs) and after more than one hour chlorine contact time.
Considering that regulatory values were derived to protect consumers based on life-time exposure, the occasional users of chlorine tablets such as recreational hikers and backcountry campers, or those relying on water purification tablets in an emergency of short duration, would nonetheless appear to have low risks of suffering THM related adverse health effects.

Those concerned about THMs should not compromise adequate water disinfection, but can minimise their exposure by using alternative water disinfection methods such as water boiling, ceramic filtration or chlorine dioxide disinfection tablets.

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