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The comparative formation of trihalomethanes using chlorine-based disinfectants within a model system

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Abstract:
Point-of-use [POU] drinking water treatment systems can provide alternative solutions to communities where access to centralised facilities are not available. Chlorination processes in water treatment can lead to the formation of disinfection by-products [DBPs], such as trihalomethanes [THMs], through reactions with organic matter over time. This study compared the formation of total THMs in model water (4 mg L^{-1} humic acid) when treated with three disinfectants (electrochemically activated solutions [ECAS], NaOCl and HOCl) as a function of contact time and free chlorine, with respect to their potential to produce THMs within POU drinking water treatment systems. All disinfection treatments were matched to free chlorine concentrations of 1, 3, and 5mg L−1, using reaction times of 1, 5, and 10min. THMs. ECAS or HOCl, resulted in the formation of significantly lower total THM concentrations across all reaction times and free chlorine concentrations, compared to NaOCl.

Keywords: Electrochemically activated solutions; Point-of-use drinking water production; Trihalomethane formation management

Introduction

For the past century, chlorine has been critical in ensuring the production of biologically safe drinking water, and is the most widely used disinfectant for drinking water treatment. However, the interaction between chlorine and natural organic matter [NOM] can result in the formation of disinfection by-products, including trihalomethanes [THMs] (World Health Organization, 2000), which are known to be hazardous to human health (Liang and Singer, 2003).

Alternative disinfection techniques that can be implemented as part of POU drinking water treatment systems to ensure biological safe water production and minimal THM formation require investigation. Electrochemically activated solutions [ECAS] are generated by passing a weak NaCl solution (e.g. 1% [w/v]) through an electrochemical cell containing separate anodic and cathodic chambers. Anodic solutions are highly oxidative [> + 1000 mV], resulting in the generation of hydroxyl radicals and transient oxidative functional groups which are highly reactive and exhibit rapid antimicrobial kinetics (e.g. between 2 – 10 seconds) (Robinson et al., 2011).

This study compared the formation of total THMs in model water (4 mg L^{-1} humic acid) when treated with three disinfectants (electrochemically activated solutions [ECAS], NaOCl and HOCl) as a function of contact time and free chlorine, with respect to their potential to produce THMs within POU drinking water treatment systems

Methods

Three chlorine-based disinfectants were used throughout this study; sodium hypochlorite [NaOCl], hypochlorous acid [HOCl] and electrochemically activated solutions [ECAS].

Disinfectants were added to standard NOM solution (4mg L^{-1} IHSS Suwannee River Humic acid), maintaining a total reaction volume of 30 mL, to achieve free chlorine concentrations of 0, 1, 3, and 5mg L^{-1}. Reaction times (1, 5, or 10 mins) were controlled by taking a 20 mL sample from the test reaction vial, and injected into a test extraction vial. Test extraction vials (30 mL sterile extraction glass universals) contained 6 g laboratory grade NaCl, 5 g L^{-1} sodium thiosulfate and the internal standard, fluorobenzene, at a final concentration of 100 µg L^{-1}. Prior to headspace extraction all samples were incubated at 40°C for 20 mins, inclusive of 10 min headspace extraction (fiber exposed). After the 10-min fiber exposure period, the CAR/PDMS fiber was retracted into the manual SPME holder and inserted into the GC/MS inlet (< 30 s). All sample fibers had a desorption period of 2-min prior to analysis.

Results and Discussion:

The reaction of the three disinfectants with standard NOM solution resulted in tTHM formation at free chlorine concentrations of 3 and 5 mg L^{-1} at reaction times of 5 and 10 minutes (see Figure 1). At the lowest free chlorine concentration tested, 1 mg L^{-1}, the observed production of tTHMs for all disinfectants was low (< 14.237 ± 3.751 µg L^{-1}) or below the LoD (0.86 µg L^{-1}). A 10-minute reaction time in the presence of NaOCl resulted in the greatest tTHM formation at the lowest free chlorine concentration tested.

Increasing the free chlorine concentrations of the disinfectants to 3 and 5 mg L^{-1} resulted in significant differences between the reaction times. Peak tTHM formation was achieved after 10 minutes for HOCl and ECAS at the highest free chlorine concentration tested: 5 mg L^{-1} (Figure 1C). However, the maximum observed concentration of tTHMs was observed for NaOCl after 5 minutes at a free chlorine concentration of 5 mg L^{-1} (Figure 1B). Surprisingly, the mean level of tTHMs decreased between 5 and 10-minute reaction times at free chlorine concentrations of 3 and 5 mg L^{-1}. This contradicts other published studies, therefore, it is postulated that this decrease is due to the hydrolysis or dehalogenation of already formed tTHMs present in solution.

The reaction between NOM, and ECAS or HOCl, formed comparable tTHM concentrations, significantly lower than NaOCl at all free chlorine concentrations and contact times. No tTHMs were detected after a 1-minute contact time for ECAS or HOCl, and only low concentrations of tTHMs were detected after 5 and 10 minutes, which were considerably lower than the maximum guideline value permissible in drinking water. Therefore, ECAS and HOCl could be considered a safe alternative to conventional chorine disinfection for decentralised point-of-use water treatment systems, as free chlorine concentrations can be lower compared to conventional chlorination solutions due to comparative higher efficacy. This reduces an integral THM precursor, decreasing the formation potential.

This study focussed on the quantification of four specific THMs (chloroform, BDCM, DBCM, and bromoform). Other associated THM derivatives or DBPs that formed throughout the experimental design were not identified. Further work is required to identify other DBP derivatives that may form in place of, or in addition to, THMs.

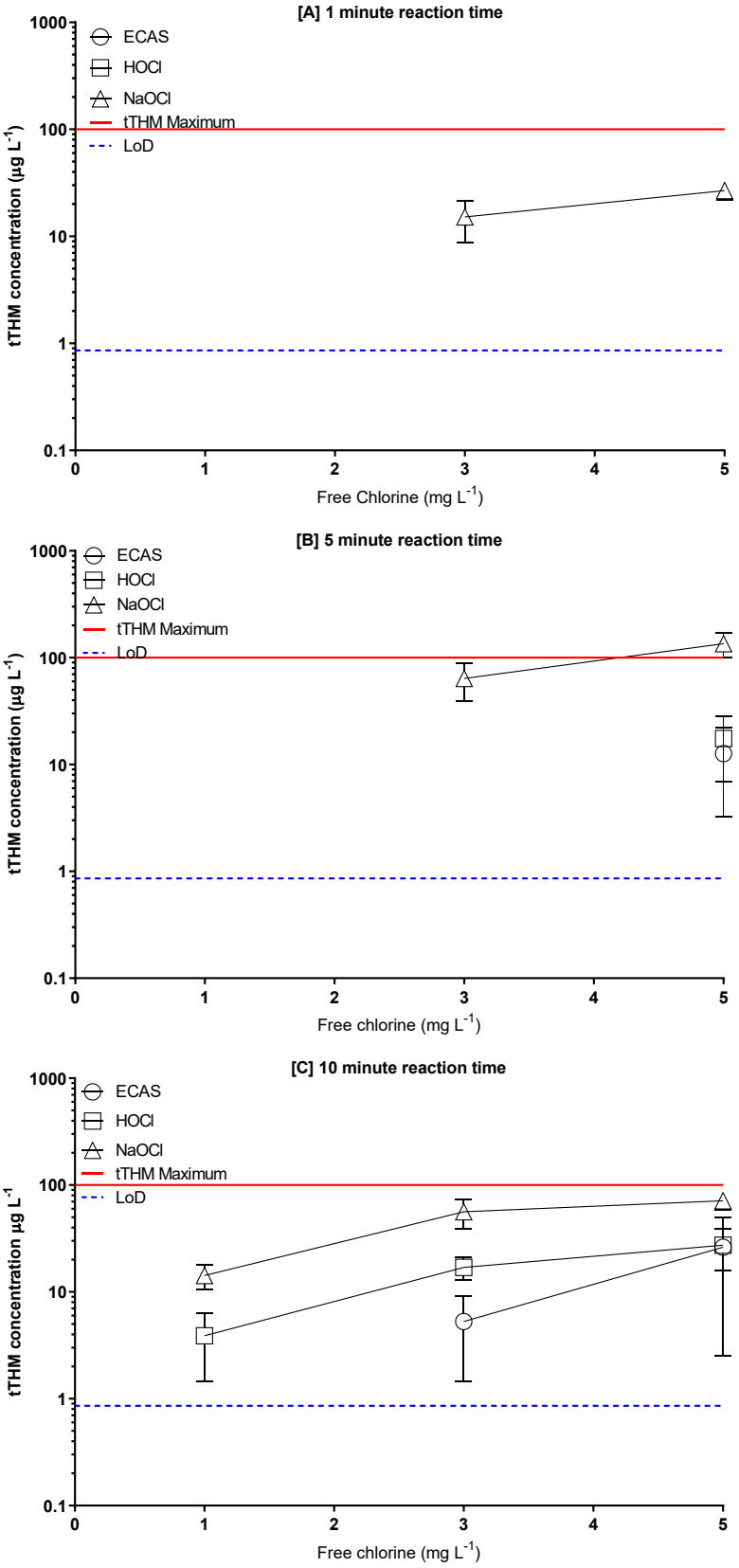

Figure 1.1 Total THM formation with disinfectants NaOCl (△), HOCl (□), or ECAS (○) at free chlorine concentrations between 1, 3 (gray), and 5mg L^{-1}. Contact times were [A] 1, [B] 5, and [C] 10 minutes (n = 6 ± SD). tTHM Maximum (horizontal dashed line) refers to the maximum guideline value permissible in drinking water (within the UK). tTHMs concentrations below the limit of detection (*).

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