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Predicting the formation of haloacetonitriles and haloacetamides by simulated distribution system tests

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Abstract

Unintended chemical reactions between disinfectants and natural organic matter (NOM) or anthropogenic compounds in natural waters result in the formation of disinfection by-products (DBPs) during drinking water treatment. To date, numerous groups of disinfection by-products have been identified in drinking water, some of which are suspected to be of public health importance and thus are regulated in the water industry. Recent studies have suggested that some unregulated nitrogen-containing DBPs, such as haloacetonitriles (HANs) and haloacetamides (HAcAms), may have greater toxicity than the currently regulated groups (trihalomethanes, THMs, and haloacetic acids, HAAs). There is only sparse information on the behaviour of the HANs and HAcAms in distribution systems. It is however known that HANs can be hydrolysed to the HAcAms, which in turn can hydrolyse to form dihaloacetic acids (DHAAs).

Simulated distribution systems tests (SDS) have been successfully applied to predict the formation of THMs and HAAs using a simple and inexpensive lab-based technique, and have been recommended by the US Environmental Protection Agency (EPA) to American water utilities for collecting information about the levels of DBPs occurring in their distribution systems. SDS tests aim to simulate the water quality, disinfectant residuals, and water ages of a real distribution system, allowing easy sampling at prescribed time intervals for analysis of DBP formation. These tests are also a useful tool for considering the impact of potential changes to distribution practices, such as switching from chlorination to chloramination, for example.

Therefore, a sampling survey was conducted in four surface water treatment plants in the UK to examine the formation of HANs and HAcAms in both real distribution systems and SDS tests. The samples were extracted using liquid-liquid extraction and analysed by gas chromatography with electron capture detection (GC-ECD). The research sought to determine whether SDS can be a useful predictive tool for HANs and HAcAms in distribution systems and what levels of prediction error are to be expected.

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1. Introduction

Unintended chemical reactions in water distribution systems result in the formation of disinfection by-products (DBPs), as a result of the reaction between the disinfectant and natural organic matter (NOM) or other anthropogenic compounds present [1]. To date, research has mainly focused on identifying, modeling and controlling DBPs, predominantly THMs and HAAs, during water treatment and distribution, as these compounds are regulated in the water industry in many countries. However, knowledge regarding the fate and behavior of the all the identified DBP compounds to-date (currently numbering over 700 [2]) within distribution is incomplete.

Simulated distribution system (SDS) tests are standardized tests that are used to simulate the formation of disinfection by-products in real water distribution systems [3]. The aim of the SDS test is to apply the equivalent water quality conditions, including temperature, disinfectant residual, and water age, as in an actual water distribution system [4, 5], allowing the collection of abundant information about the levels of DBPs. SDS tests have been previously shown to estimate the levels of THMs and HAAs well [6, 7, 8] and therefore are recommended by the US EPA to water utilities [4]. However, the SDS test is unable to fully replicate all the in-situ conditions of a distribution network, such as metallic pipe corrosion products, biofilm slime or mixing conditions [6, 9].

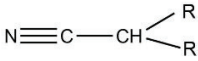
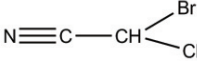
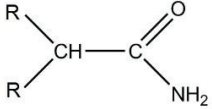
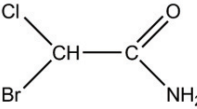
Haloacetonitriles (HANs) and haloacetamides (HAcAms) are a relatively new class of nitrogenous disinfection by-products (N-DBPs), characterized by higher cytotoxicity and genotoxicity than the corresponding THM or HAA [10, 11]. There are concerns this may offset the relatively low concentrations at which the HANs and HAcAms typically occur in drinking water. Yet there is only sparse information about their typical concentrations in drinking water, their potential precursors and the mechanisms by which they are formed during water treatment and distribution. Previous studies have suggested HAcAms are primarily present in distribution networks as hydrolysis degradation products of haloacetonitriles (HANs) [12]. However more recent studies have suggested that HAcAms may also be generated independently by other precursors [13, 14].

In this study, nine haloacetamides (HAcAms) and their relative nine haloacetonitriles (HANs) were measured during SDS tests and real distribution system sampling (*Table 1*). In addition, four THMs and nine relative haloacetic acids (HAAs) were also quantified for comparison. The objective was to evaluate the concentration and speciation of the N-DBPs in distribution and the extent to which the same trends can be identified in SDS tests.

Nomenclature

DBPs	disinfection by-products
NOM	natural organic matter
N-DBPs	nitrogenous disinfection by-products
HANs	haloacetonitriles
HAcAms	haloacetamides
THMs	trihalomethanes
HAAs	haloacetic acids
SDS	simulated distribution system
GC-ECD	gas chromatography electron-capture detection
TOC	total organic carbon
DOC	dissolved organic carbon

Table 1. The structures of the haloacetonitriles (HANs) and haloacetamides (HAcAms) considered in this study.

Compound/Formula	Structure	Speciation	Structure
Haloacetonitriles (HANs) R_3C_2N		Monochloroacetonitrile (CAN)	
		Monobromoacetonitrile (BAN)	
		Dichloroacetonitrile (DCAN)	
		Trichloroacetonitrile (TCAN)	
		Dibromoacetonitrile (DBAN)	
		Bromochloroacetonitrile (BCAN) (right)	
		Bromodichloroacetonitrile (BDCAN)	
		Dibromochloroacetonitrile (DBCAN)	
		Tribromoacetonitrile (TBAN)	
Haloacetamides (HAcAms) $R_3C_2H_2NO$		Monochloroacetamide (CAcAm)	
		Monobromoacetamide (BAcAm)	
		Dichloroacetamide (DCAcAm)	
		Trichloroacetamide (TCAcAm)	
		Dibromoacetamide (DBAcAm)	
		Bromochloroacetamide (BCAcAm) (right)	
		Bromodichloroacetamide (BDCAcAm)	
		Dibromochloroacetamide (DBCAcAm)	
		Tribromoacetamide (TBAcAm)	

R is commonly a halogen (Cl, Br etc.)

2. Materials & Methods

2.1. Water Samples

Treated water samples were collected during two sampling rounds in autumn 2015 and winter 2016 from four surface water treatment works located in England. The selected water treatment plants apply different disinfection practices: A and B are chlorination; C and D chloramination. Samples were collected prior to disinfection in amber glass bottles or polyethylene bottles, preserved in portable coolers (4°C) and transported to the Roger Perry Environmental Engineering Laboratory at Imperial College London for analysis. The samples were analysed for several water quality parameters, including pH, bromide, total organic carbon (TOC), and ultraviolet (UV) absorbance at 254 nm. Specific ultraviolet absorbance (SUVA) was calculated as the ratio of UV absorbance at 254 nm (m^{-1}) to TOC ($mg\ C\ L^{-1}$). Water distribution samples were also collected from various sampling locations (reservoirs, water towers), which were representative of specific water age ranges, so that a comparison between the SDS test samples and the actual distribution samples could take place.

2.2. Sample Preparation

For the water samples used for the SDS tests, a chlorine solution was prepared from a sodium hypochlorite solution and the monochloramine solution was prepared with controlled addition of chlorine solution to an ammonia solution (N/Cl ratio: 1.4/1), with concentrations of these oxidants determined and monitored by DPD-FAS titration [15]. In order to achieve the same disinfectant residual ($\sim 1 \text{ mg L}^{-1}$) as in the real water distribution systems, tests were conducted to determine the necessary disinfectant doses separately beforehand. For both chlorinated and chloraminated samples, 1 L amber bottles were partially filled with water and spiked with the calculated disinfectant dose. Each bottle was filled to the top and capped headspace free with PTFE-lined cap. Duplicate samples were then incubated under mixing conditions in the dark for 12, 48 and 72 hours at the same temperature at which the real distribution systems samples were collected.

After the incubation periods, ammonium chloride, at a concentration of 100 mg L^{-1} , and ascorbic acid, at a concentration of 50 mg L^{-1} , were used to quench the chlorine and monochloramine residuals in the water samples, respectively. Previous research suggested that ammonium chloride is a most suitable quenching agent for preserving the target N-DBPs, HANs [16] and HAcAms [17], as well as the confirmatory DBPs of this project, THMs and HAAs [16, 18], when chlorination is the disinfectant. When chloramination is applied though, ascorbic acid is selected for eliminating monochloramine residual, since previous studies has shown good preservation of N-DBPs [16, 17].

2.3. DBPs Methods & Materials

SDS test samples and real distribution samples, were extracted by two different methods: EPA Method 551.1 [19] and EPA Method 552.3 [18]. In the first method, in which the target analytes HANs and HAcAms were quantified, 30 mL of sample was extracted by liquid-liquid extraction into methyl tertiary-butyl ether (MTBE), after being acidified with H_2SO_4 and enriched with 10 g pre-baked sodium sulphate and 1 g of copper sulphate [19]. HANs, HAcAms and THMs were then quantified by a modified version of EPA Method 551.1 by gas chromatography coupled with electron-captured detection (GC-ECD) (Clarus 500, Perkin Elmer, UK) using a Restek Rxi-5 Sil MS column. EPA Method 552.2 [18] was implemented to quantify HAAs, during which they were converted to their methyl esters then analysed by GC-ECD with the aid of a different capillary column (DB-170, Thames Restek Ltd, UK) in Brunel University. Method detection limits for HAcAms, BAN, DCAN, and TCAN were $0.1 \mu\text{g L}^{-1}$, for DBAN, BCAN were $0.2 \mu\text{g L}^{-1}$ and for BDCAN, DBCAN, TBAN were $0.5 \mu\text{g L}^{-1}$. In the case of THMs, method detection limits for chloroform and bromoform were $0.4 \mu\text{g L}^{-1}$ while for BDCM and DBCM were $0.3 \mu\text{g L}^{-1}$. Detection limits for HAAs ranged between $0.1 - 1 \mu\text{g L}^{-1}$.

The analytical standards, containing THMs (Supelco 48045), 4 HANs (Supelco 48046) and HAAs (Supelco 49107-U) were available as mixtures by Sigma Aldrich (UK), whereas the rest of the HANs were supplied separately by Toronto Research Chemical Inc. or Sigma-Aldrich and the HAcAms were supplied by Orchid Cellmark or Alfa Aesar. All the chemicals used, including quenching agents, extraction salts, extraction solvent, and internal standards, were obtained at high purity (analytical grade) from Sigma Aldrich or VWR International and all solutions were prepared in ultra-pure water treated via reversed osmosis (RO water).

3. Results and Discussion

The results of the SDS tests conducted on the selected water treatment plants were compared with the results of the samples of similar water ages collected from the relevant distribution system. The pH ranged from 7 to 7.6, with higher values in plants A and B. Bromide levels in plants A, B and D were relatively low in comparison with plant C, with concentrations ranging around $15\text{--}20 \mu\text{g L}^{-1}$ and 80, respectively. All four treatment plants had consistent TOC values in the two sampling rounds with the highest value reported in plant B (3.8 mg L^{-1} C) and the lowest value in plant C (2.8 mg L^{-1} C). SUVA values ranged from $1.0 \text{ m} \cdot \text{mg C L}^{-1}$ (plant D) to $2.4 \text{ m} \cdot \text{mg C L}^{-1}$ (D).

3.1. Haloacetonitrile formation

The total HAN concentrations of this study were $< 8 \mu\text{g L}^{-1}$ with a mean value of $2.9 \mu\text{g L}^{-1}$, which agrees with the occurrence data of a recent nationwide N-DBPs survey in England (mean value = $3.2 \mu\text{g L}^{-1}$) [20, 21]. Figure 1 (a, b) shows the HANs concentrations reported during the SDS tests in comparison with those from the distribution sampling. The HANs are not characterized by seasonal variability, but lower concentrations were observed in the distribution systems where chloramination was applied (C and D) during both rounds. The deviation between the SDS and real distribution values was minimal from a practical viewpoint, with the largest difference being $1.9 \mu\text{g L}^{-1}$.

HAN speciation was also well predicted by the SDS tests, both in terms of their concentrations and their occurrence at different contact times. The most prominent HAN in all the water samples was DBAN, followed by BCAN, DCAN and TCAN. All the other species were either below the method detection limits or not detected at all.

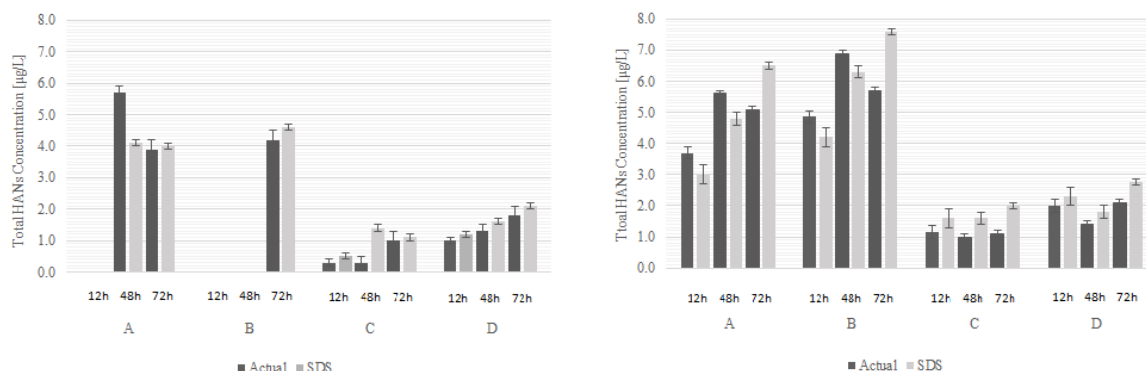


Fig. 1. Total HAN concentrations in SDS tests and actual distribution water samples in (a) Round 1 and (b) Round 2. Systems A and B are chlorinated, whereas systems C and D are chloraminated.

3.2 Haloacetamide formation

The total HAcAms concentrations identified in this study were all $< 7 \mu\text{g L}^{-1}$ with a mean value of $3.7 \mu\text{g L}^{-1}$ which is comparable with earlier reports of HAcAms occurrence ($2\text{--}5 \mu\text{g L}^{-1}$) in the UK [20, 21]. The total HAcAm concentrations were not characterized by seasonal variability and similar concentrations were identified regardless of the disinfection method.

Figure 2 (a, b) shows the total HAcAm concentrations reported during the SDS tests in comparison with those in the real water distribution samples in both sampling rounds. The SDS tests generally slightly underestimated HAcAms formation, though this trend was not observed in the second round. In general, the SDS test illustrated similar trends of formation and potential decay of HAcAm species as in the real distribution system samples, suggesting that the test is a useful prediction tool for HAcAms as well.

All the HAcAms except CAcAm were detected, of which the most abundant these were DCACAm, BCACAm and DBACAm.

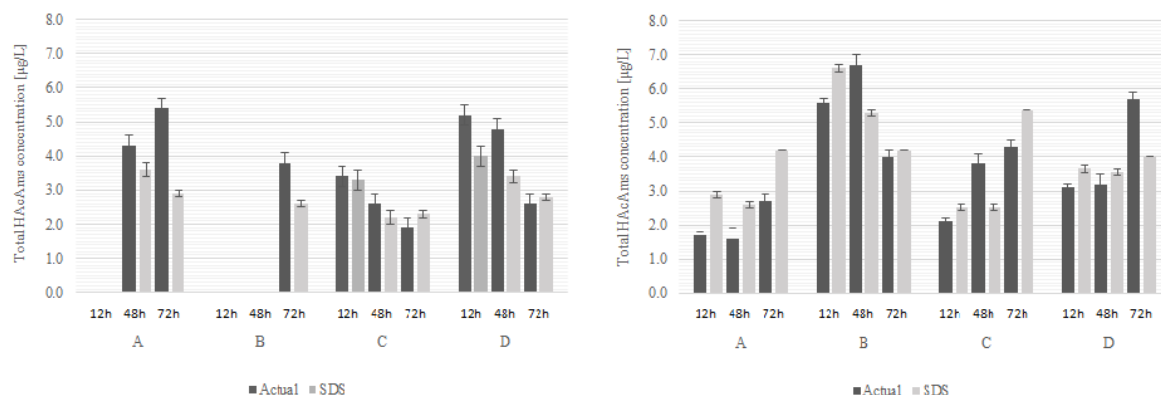


Fig. 2. Total HAcAm concentrations in SDS tests and actual distribution water samples with standard deviations in (a) Round 1 and (b) Round 2. Systems A and B are chlorinated, whereas systems C and D are chloraminated.

3.3 Other DBPs

THMs and HAAs were also measured during these sampling rounds to validate the SDS test methods being applied, since SDS tests have been previously reported to provide good correlations for these DBPs with values in real samples. Indeed, their concentrations and speciation showed a very good agreement between the SDS tests and the real distribution samples. The minimal deviation observed between SDS tests and real distribution samples was in average 2 µg L⁻¹ during short retention times and would increase up to 4.5 µg L⁻¹ during longer retention times, in total concentrations ranging between 20-50 µg L⁻¹ and 20-40 µg L⁻¹ for THMs and HAAs, respectively.

4. Conclusions

This study examined the ability of simulated distribution system (SDS) tests to predict the formation of HANs and HAcAms in water distribution networks. The initial findings are helpful in understanding the benefits and complications of such an analysis for both chlorinated and chloraminated systems. The main findings to-date are:

- The SDS test can be used effectively to estimate the formation and degradation of HANs and HAcAms in a distribution system, both in chlorinated and chloraminated systems. The test is not only a useful prediction tool for the concentrations of total HANs and HAcAms but also their speciation.
- Deviations observed between the SDS tests and real water distribution samples concentrations are likely to be considered small, from a practical viewpoint, in most cases, and are likely associated with chemical and biological processes occurring in the real water distribution systems which are not possible to be accurately simulated in the SDS test (e.g. degradation of some DBP species by biofilms) and require further research.
- SDS tests also captured the species transformations of HANs and HAcAms during the various reaction times of both chlorinated and chloraminated systems.
- The setup parameters of this test are adjustable and therefore SDS test is a useful and low-cost tool for water utilities to estimate N-DBPs formation in their own distribution systems.

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