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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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Keywords: Simulated distribution systems; disinfection by-products; haloacetonitriles, haloacetamides.

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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