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Nitrogenous disinfection byproducts in English drinking water supply systems: Occurrence, bromine substitution and correlation analysis

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ABSTRACT

Despite the recent focus on nitrogenous disinfection byproducts in drinking water, there is limited occurrence data available for many species. This paper analyses the occurrence of seven haloacetonitriles, three haloacetamides, eight halonitromethanes and cyanogen chloride in 20 English drinking water supply systems. It is the first survey of its type to compare bromine substitution factors (BSFs) between the haloacetamides and haloacetonitriles. Concentrations of the dihalogenated haloacetonitriles and haloacetamides were well correlated. Although median concentrations of these two groups were lower in chloraminated than chlorinated surface waters, median BSFs for both in chloraminated samples were approximately double those in chlorinated samples, which is significant because of the higher reported toxicity of the brominated species. Furthermore, median BSFs were moderately higher for the dihalogenated haloacetamides than for the haloacetonitriles. This indicates that, while the dihalogenated haloacetamides were primarily generated from hydrolysis of the corresponding haloacetonitriles, secondary formation pathways also contributed. Median halonitromethane concentrations were remarkably unchanging for the different types of disinfectants and source waters: 0.1 $\mu g \cdot mgTOC^{-1}$ in all cases. Cyanogen chloride only occurred in a limited number of samples, yet when present its concentrations were higher than the other N-DBPs. Concentrations of cyanogen chloride and the sum of the halonitromethanes were not correlated with any other DBPs.

1. Introduction

Nitrogenous disinfection byproducts (N-DBPs), including the haloacetonitriles (HANs), haloacetamides (HAcAms), halonitromethanes (HNMs), cyanogen halides and nitrosamines, have received much research attention in recent years (Mitch et al., 2009; Bond et al., 2011; Shah and Mitch, 2011). While these species typically occur at lower concentrations in drinking water than trihalomethanes (THMs, four of which are regulated in the USA, EU and China) and haloacetic acids (HAAs, five of which are regulated in the USA), there are concerns that this may be offset by their higher cytotoxicity and genotoxicity (Plewa and Wagner, 2009). One option for water utilities aiming to reduce the formation of THMs and HAAs is to use chloramines rather than chlorine as the final disinfectant, however, this change can have the effect of increasing the formation of some N-DBPs, notably cyanogen chloride (CNCl) (Krasner et al., 1989) and N-nitrosodimethylamine (NDMA) (Choi and Valentine, 2002). Another pertinent factor is that drinking water providers are increasingly relying on algal- and wastewater-impacted sources, which tend to be enriched in organic nitrogen compounds known to act as precursor material for many N-DBPs (Mitch et al., 2009). In general, there is a limited extent of published occurrence data for many N-DBPs in drinking water, especially the brominated species. The presence of brominated DBPs is of specific interest because brominated DBPs are typically more cytotoxic and genotoxic than their chlorinated analogues (Richardson et al., 2007; Yang and Zhang, 2013).

The dihaloacetonitriles (DHANs) have been reported from chlorinated water supplies since at least the early 1980s (Oliver, 1983; Trehy et al., 1986). A survey of 35 water treatment facilities later that decade included four HANs (DCAN, BCAN, DBAN and TCAN, collectively HAN_4; see Table 1 for abbreviations used), chloropicrin (trichloronitromethane) and cyanogen chloride

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Table 1
DBPs monitored and abbreviations used.

N-DBPs name	Abbreviation	Name	Abbreviation
Haloacetonitriles	**HANs**	**Halonitromethanes**	**HNMs**
Chloroacetonitrile	CAN	Chloronitromethane	CNM
Bromoacetonitrile	BAN	Bromonitromethane	BNM
Dichloroacetonitrile	DCAN	Dichloronitromethane	DCNM
Bromochloroacetonitrile	BCAN	Bromochloronitromethane	BCNM
Dibromoacetonitrile	DBAN	Dibromonitromethane	DBNM
Trichloroacetonitrile	TCAN	Chloropicrin (trichloronitromethane)	TCNM
Dibromochloroacetonitrile	DBCAN	Bromodichloronitromethane	BDCNM
		Dibromochloronitromethane	DBCNM
Haloacetamides	**HAcAms**	**Cyanogen chloride**	**CNCl**
2,2-Dichloroacetamide	DCAcAm		
2,2-Dibromoacetamide	DBAcAm		
2,2,2-Trichloroacetamide	TCAcAm		
Other DBPs			
Four regulated trihalomethanes: trichloro-, dichlorobromo-, bromodichloro- & tribromo-	**THM_4**	Nine chloro- and/or bromo- haloacetic acids: chloro-, bromo-, dichloro-, chlorobromo-, dibromo-, trichloro-, chlorodibromo-, dibromochloro- & tribromo-	**HAA_9**
Other selected abbreviations			
Bromine substitution factor	BSF	DCAN, BCAN, DBAN and TCAN	HAN_4
Dihaloacetonitriles	DHANs	Minimum detection limit	MDL
Dihaloacetic acids	DHAAs	N-nitrosodimethylamine	NDMA
Dihaloacetamides	DHAcAms	Pearson moment correlation coefficient	r
Drinking water treatment plant	DWTP	Total organic carbon	TOC
		Trihaloacetic acids	THAAs

(Krasner et al., 1989). These N-DBPs were also monitored in 1997–1998 during a survey of USA drinking water treatment plants (DWTPs) undertaken as part of the Information Collection Rule (ICR) (McGuire et al., 2002).

The HAcAms are a group of DBPs known to be produced from hydrolysis of the HANs, and can themselves degrade to the corresponding HAA (Glezer et al., 1999; Reckhow et al., 2001), as shown below for the dihalogenated species (i.e. the DHANs, DHAcAms and DHAAs, with X representing a halogen):

$$X_2C-CN\ (DHAN) \rightarrow X_2C-C(O)NH_2\ (DHAcAm) \rightarrow X_2C-C(O)OH(DHAA) \quad (1)$$

The HAcAms were first reported in drinking water during the USA survey of 2000–2002 (Weinberg et al., 2002; Krasner et al., 2006). Up to nine HAcAms have also been investigated in Chinese raw and treated waters (Chu et al., 2013, 2014). Further, a laboratory study used isotopically-labelled monochloramine and model precursors to show that HAcAm formation pathways exist which are separate from HAN hydrolysis and that HAcAm formation was promoted by chloramination (Huang et al., 2012). It has also been demonstrated that monochloramine reacts with chloroacetaldehyde to form N,2-dichloroacetamide (Kimura et al., 2013). Nonetheless, owing to the paucity of literature comparing concentrations of HAcAms and HANs in real drinking water samples there is still uncertainty regarding whether HAcAms are primarily produced from HAN hydrolysis, or to what extent these, and perhaps other, independent formation pathways also contribute.

Chloropicrin (trichloronitromethane) has been observed in drinking water since the early days of DBP research (Merlet et al., 1985). In the 2000–2002 USA nationwide DBP survey, which sampled 12 DWTPs receiving high precursor loads (measured in terms of high bromide and/or total organic carbon (TOC)), a total of eight HNMs were monitored, though typically only 4–5 at individual DWTPs (Weinberg et al., 2002; Krasner et al., 2006). Six HANs, five HNMs and CNCl were also included in a survey of 11 USA DWTPs receiving waters which were algal and/or wastewater impacted (Mitch et al., 2009). In their study, Hu et al. (2010) included all nine HNM group members, while investigating the formation potential of five natural waters under laboratory conditions. They found chloropicrin and bromodichloronitromethane (BDCNM) were the most commonly encountered species. There have been fewer surveys to investigate the occurrence of N-DBPs in drinking waters outside of North America, although four HANs have been monitored in various parts of Europe (Goslan et al., 2009, 2014).

This paper presents the results of a survey of N-DBPs in 20 English drinking water supply systems. In contrast to many previous DBP surveys, samples were taken from downstream distribution systems as well as from the DWTP itself, allowing for an assessment of N-DBP speciation and concentration trends in distribution. The N-DBPs quantified comprised seven HANs, three HAcAms, eight HNMs and CNCl (Table 1). The selected water supply systems included a variety of disinfection methods and source water types (Table S1). THM_4 and HAA_9 were measured in two and one of the four seasonal sampling rounds, respectively. NDMA and other nitrosamines were excluded, as this group has previously been the subject of separate surveys in the UK (Dillon et al., 2008; Templeton and Chen, 2010).

2. Methods

2.1. Sampling approach

Water supply systems selected for sampling included those with DWTPs using ozone, UV disinfection, chlorine and chloramines for disinfection (Table S1). Six supply systems applied chloramination in the distribution system, while the rest applied chlorination. Eight treatment works received water from a lowland catchment, five from an upland catchment and seven treated groundwater. Twelve treatment works received water from eutrophic sources (a possible source of organic nitrogen), five had an elevated bromide concentration in the source waters (defined as >150 $\mu g\ L^{-1}$, which is considered high in the context of England), and five had elevated THM levels (defined as >50 $\mu g\ L^{-1}$ in finished water).

Sampling was undertaken quarterly from December 2011 to December 2012. Samples were collected at two locations in each DWTP (pre-disinfection and final treated water) plus three sites from within the distribution system, chosen to represent near,