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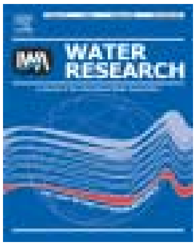

Factors affecting formation of haloacetonitriles, haloketones, chloropicrin and cyanogen halides during chloramination

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abstract

Effects of contact time, monochloramine doses, monochloramine application modes, pH, temperature and bromide ion concentrations on formation of disinfection by-products (DBPs), including haloacetonitriles, haloketones, chloropicrin, cyanogen halides and trihalomethanes, during chloramination were investigated using model solutions containing 5 mg/L (as DOC) Suwannee River natural organic matter (NOM). Chloramine speciation and some DBPs were measured using membrane introduction mass Spectrometer (MIMS). Longer reaction times led to continued formation over time for dichloroacetonitrile (DCAN), 1,1-dichloro-2-propanone (1,1-DCP) and chloroform. Cyanogen chloride (CNCl) formation occurred over time, but after reaching a peak concentration CNCl concentrations decreased over longer time periods. Linear relationships were observed between the formation of DCAN, 1,1-DCP, CNCl or chloroform and the dosage of monochloramine. Chloramination modes (addition of preformed monochloramine or variable sequential additions of free chlorine and ammonium salts) exhibited the largest impact on chloroform formation but displayed little effect on the formation of DCAN, 1,1-DCP and CNCl. Over the range in pH from 4 to 9 profound differences in DBP formation were observed; pH values between 5 and 6 resulted in the highest DBP concentrations. An increase in temperature enhanced the formation of chloroform but did not affect DCAN, 1,1-DCP and CNCl formation. Chloropicrin concentrations were always low (around detection limits) under all conditions. Increasing the concentrations of bromide ions enhanced the formation of bromine-substituted DBPs.

1. Introduction

Monochloramine (NH_2Cl) has gained popularity as an alternative disinfectant to chlorine because of reduced disinfection by-product (DBP) formation and ability to provide residuals in water distribution systems. The amount of total organic halogen (TOX) generated during chloramination ranges from 9% to 49% of that in chlorination of the same types of water under the same water quality conditions (Speitel, 1999). DBPs, such as trihalomethanes (THMs) and haloacetic acids (HAAs), regulated by the USEPA and other national agencies are present at lower concentrations in chloraminated water samples than in chlorinated ones (Krasner et al., 1989; Cowman and Singer, 1996). Other DBPs including haloacetonitriles (HANs), haloketones (HKs), chloropicrin and cyanogen halides (CNX) are also found in

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chloraminated water (Zhang et al., 2000). Common HANs compounds observed in chlorinated or chloraminated water consist of dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroaceontrile (BCAN) and dibromoacetonitrile (DBAN), and major HKs identified as chlorinated DBPs are 1,1-dichloro-2-propanone (1,1-DCP) and 1,1,1-trichloro-2-propanone (1,1,1-TCP) (Krasner et al., 1989). CNX include cyanogen chloride (CNCl) and cyanogen bromide (CNBr). CNCl has been found in higher quantity in chloraminated water than in chlorinated water (Krasner et al., 1989). With respect to their adverse effects, DCAN leads to mutagenicity in bacterial assays (Oliver, 1983) and DBAN, BCAN, 1,1-DCP and 1,1,1-TCP exert carcinogenic or mutagenic effects in mice (Bull and Robinson, 1986). CNCl is a highly toxic compound (Kononen, 1988). Due to their potential health effects and unclear exposure doses, DBPs including the above-listed HANs, HKs, chloropicrin and CNCl were included in the United States Environmental Protection Agency Information Collection Rule (ICR) (USEPA, 1996) and they may be considered in future regulation.

Many factors affect the formation of DBPs, including reaction time, pH, temperature, disinfectant doses and application modes, bromide ion concentrations and precursor properties. DBP formation during chlorination has been extensively studied. THMs and HAAs, the two major groups of DBPs, formed higher amounts with longer reaction times and higher chlorine doses (Pourmoghaddas and Stevens, 1995; Reckhow and Singer, 1985). Increasing pH enhanced THM formation but reduced HAA formation (Pourmoghaddas and Stevens, 1995). Increasing the bromide concentration shifted DBPs from chlorinated compounds to brominated compounds (Pourmoghaddas and Stevens, 1995; Cowman and Singer, 1996). HAN, HK and CNX formation followed different trends. DCAN, 1,1,1-TCP and CNBr formation decreased with increasing pH (MacNeill, 1994; Heller-Grossman et al., 1999). Increasing the reaction time and chlorine dose did not necessarily lead to increasing formation of these DBPs, due to their hydrolysis and decomposition in the presence of chlorine (Reckhow et al., 2001; MacNeill, 1994; Na and Olson, 2004).

Some results on DBP formation during chloramination are available in the literature. Diehl et al. (2000) reported that formation of THMs, HAAs and CNX decreased with an increase in the pH from 6 to 10 and with a decrease in the chlorine-to-ammonia nitrogen (Cl:N) ratio while increasing the bromide concentration increased the production of brominated compounds. Similar results on pH, Cl:N ratios and bromide on the formation of HAAs (Wu et al., 2003; Qi et al., 2004; Cowman and Singer, 1996) and THMs (Wu et al., 2003; Stevens et al., 1989) during chloramination were also reported. CNCl formation had a maximum yield when chlorine was added to water containing humic acid and ammonium ions at Cl:N weight ratios of 8–9:1 and further increases of free chlorine dosages reduced CNCl formation (Ohya and Kanno, 1985). Our previous study showed that CNCl concentrations increased with increasing glycine concentrations when 8 mg/L (as Cl_2) free chlorine was added to solutions containing 5 mg/L humic acid (Aldrich), 2 mg/L N ammonium ions and varied amounts (0.067–2 mg/L N) of glycine (Yang and Shang, 2004). In practice, monochloramination can be achieved by adding preformed monochloramine or adding free chlorine and ammonium salts in different orders. These different orders of addition have been reported to affect DBP formation, including the formation of THMs, HAAs, CNX and NDMA (Yang and Shang, 2004; Qi et al., 2004; Schreiber and Mitch, 2005). However, little information is available about the effects of these factors on the formation of HANs, HKs and chloropicrin during chloramination. Their formation during chloramination is expected to be different from that during chlorination, since HANs, HKs and CNX react with free chlorine but they can be stable in monochloramine solutions. For example, CNCl has been confirmed to be stable at pH 7 in monochloramine solutions (Na and Olson, 2004). Also, monochloramine undergoes self-decomposition and hydrolysis to form dichloramine and free chlorine (Jafvert and Valentine, 1992). The chloramine-natural organic matter (NOM) chemistry to yield DBPs involves monochloramine, dichloramine and free chlorine. Factors, such as pH and chloramination modes, affect the relative amounts of these compounds.

Concomitant with changes from free chlorine to monochloramine are changes in water quality (e.g., higher pH levels) and treatment conditions (e.g., selection of monochloramine addition or sequential addition of chlorine/ammonia). A further potential impact of switching from free chlorine to monochloramine is the formation of nitrogenous DBPs (N-DBPs) of potentially greater health concern than THMs or HAAs. The objectives of the study are, therefore, to investigate the effects of reaction time, pH, chloramine doses, chloramination modes, temperature and bromide ion concentrations on the formation of HANs, HKs, chloropicrin and CNX during chloramination of synthetic water prepared from Suwannee River reverse osmosis (RO) NOM isolate (purchased from the International Humic Substances Society (IHSS)). This NOM is chosen because it is commercially available and more representative than soil humic acids commonly used in other studies. To complement the suite of nitrogeneous DBPs (N-DBPs) of emerging concern with the shift towards chloramination, THMs are monitored as a surrogate of free-chlorine carbonaceous DBPs of current regulatory concern.

2. Materials and methods

2.1. Chemicals and materials

Ultrapure water was produced by a Barnstead NANOpure Diamond system. Monochloramine (NH_2Cl) solutions were prepared daily by reacting equal volumes of ammonium chloride and sodium hypochlorite solutions at a weight ratio of 4 mg/L Cl_2 to 1 mg/L N-NH_4^+. Dichloramine ($NHCl_2$) solutions were prepared by quickly adding acetic acid (1 M) to the monochloramine solution to adjust the pH to 4, followed by allowing it to sit overnight in the dark to complete the reactions (Hand and Margerum, 1983). The resulting solutions were standardized by DPD/FAS titration (Standard Method 4500-Cl, 1998). A NOM stock solution was prepared by dissolving an aliquot of Suwannee River RO NOM isolate (Cat. No. 1R101N, International Humic Substances Society)