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Halonitromethanes formation in wastewater treatment plant effluents

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ABSTRACT

Halonitromethanes (HNMs) constitute one class of emerging disinfection by-products with high potential health risks. This study investigated the formation and occurrence of HNMs under different disinfection scenarios and the presence of their precursors in municipal wastewater treatment plant (WWTPs) effluents. Formation potential tests performed on WWTP effluents revealed that HNM formation occurred in the order of ozonation–chlorination $\gg$ ozonation–chloramination > chlorination > chloramination. Ozonation alone did not produce any HNM. Municipal WWTP effluents contained some reactive HNM precursors, possibly the by-products of biological treatment processes and/or some moiety of industry or household origin. No effects of nitrate on the formation of HNMs were observed in this study, and nitrification in WWTPs appears to remove appreciable portion of HNM precursors, especially those reactive to chlorine. UV disinfection using low pressure lamps in municipal WWTPs had negligible impact on HNM formation potential. HNM concentrations in the effluents of selected WWTPs were either non-detectable or less than minimum reporting level, except for one WWTP that gave trichloronitromethane concentrations in the range of 0.9–1.5 $\mu g\ L^{-1}$. No HNMs were observed in the effluents disinfected with UV radiation. Therefore, it appears the typical wastewater disinfection processes involving chlorination or UV treatment in WWTPs do not produce significant amounts of HNMs.

1. Introduction

Since the discovery of chloroform as a disinfection by-product (DBP) in drinking water in the early 1970s (Rook, 1974), significant research efforts have been made to improve our understanding of DBP formation and control. To date, more than 600 DBPs have been identified in drinking waters (Richardson, 2003). Despite this daunting number, only 11 DBPs (4 trihalomethanes (THMs), 5 haloacetic acids (HAAs), bromate, and chlorite) are currently regulated in the United States under the US Environmental Protection Agency's (USEPA's) Disinfectants/DBP Rule (USEPA, 2006). Additional DBP regulations may be proposed and implemented as potential health risks of many unregulated DBPs are determined (Richardson et al., 2007).

In a nationwide occurrence study funded by the USEPA, approximately 70 unregulated DBPs that were identified to cause the highest potential human health risks were selected and monitored in 12 water utilities across the US in 2000–2002 (Woo et al., 2002; Krasner et al., 2006). Among those DBPs, halonitromethanes (HNMs) received special attention because of their potential high toxicity and the level of occurrence in finished waters at some treatment facilities (Plewa et al., 2004; Krasner, 2006; Krasner et al., 2006). The toxicology studies on emerging DBPs conducted in recent years indicate that HNMs are one of the most cytotoxic and genotoxic classes among the emerging DBPs, and have orders of magnitude higher toxicity than the regulated THMs and HAAs (Plewa et al., 2004).

There are a total of nine species of chorine and bromine substituted HNMs, including chloro- (CNM), dichloro- (DCNM), trichloro- (TCNM), bromo- (BNM), dibromo- (DBNM), tribromo- (TBNM), bromochloro- (BCNM), bromodichloro- (BDCNM), and dibromochloronitromethane (DBCNM). Most of the previous HNM studies focused on TCNM formation due to unavailable chemical standards for all other HNM species, which became available in early 2000s. A general observation in those studies is that TCNM formation substantially increased when ozonation was used prior to chlorination (Merlet et al., 1985; Hoigné and Bader, 1988; Choi and Richardson, 2004), although the work by Choi and Richardson (2004) also addressed the formation of other HNM species.

In recent years, many countries have been experiencing drought and water shortage problems, and as a result, wastewater reclamation has been gaining more attention as a way to cope with the increasing water demand. In the US, the volume of wastewater reused grew by 15% from 2002 to 2006, and in 2006, wastewater reuse increased to $98 \times 10^6\ m^3\ d^{-1}$ for various purposes, such as irrigation, process cooling, and groundwater recharge (Miller, 2006). When a wastewater treatment plant (WWTP) discharges

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upstream from a drinking water treatment plant (DWTP), the source water of the DWTP is impacted by the effluent, which is known as unplanned indirect potable reuse (Krasner et al., 2008, 2009; Mitch et al., 2008). In the case where high quality source water is not available or economically viable, wastewater effluents may become the major contributor to influent flow of the DWTP. For example, effluent discharges from WWTPs contributed at least 70% of the total volume of a river in South Carolina during low flow drought years (Anderson et al., 2004). One major concern about WWTP effluent discharge is the introduction of DBPs and DBP precursors to the receiving waters. Because WWTP effluents contain relatively higher concentrations of nitrogenous compounds (e.g., organic nitrogen and ammonia), which may serve as precursors for various nitrogenous DBPs, there is a greater possibility of public health risk when a DWTP treats a wastewater–impacted source water (Plewa et al., 2008). A recent study by Krasner et al. (2008) showed that WWTP effluents contain significant amount of dissolved organic nitrogen (DON) that could be a source of precursors for nitrogenous DBPs such as HNMs, haloacetonitriles (HANs) and N-nitrosodimethylamine (NDMA). It has been reported that nitrogenous DBPs are far more toxic than carbon-only based DBPs (Plewa et al., 2008). The study by Krasner et al. (2008) showed the presence of HNMs and their precursors in various WWTP effluents and downstream of WWTPs. The researchers reported that the reduction of TCNM precursors through nitrification at WWTPs was relatively small as compared to other DBPs (e.g., HANs and haloacetaldehydes). The precursor removal during nitrification may be attributed to oxidation of inorganic nitrogen to nitrate (the most oxidized nitrogen), leaving less amounts of reduced nitrogen species to be oxidized by disinfectants and incorporated into DBP molecules.

The objectives of this study were to (i) investigate the formation potentials (FP) (i.e., total amount of HNM precursors available) of HNMs in municipal WWTP effluents under different oxidation conditions, (ii) examine the effect of UV disinfection in WWTPs on HNM FP, and (iii) to measure actual HNM concentrations at the effluents of selected WWTPs to obtain some information about the occurrence of HNMs in wastewater effluents. Unlike most of the previous HNM research, the samples were analyzed for all nine HNM species in this study. Furthermore, correlations between the HNM formation and various water quality parameters were examined to assess the capabilities of some simple water quality parameters in predicting HNM FP in a wastewater sample.

2. Materials and methods

2.1. Wastewater effluent samples

HNM FP experiments were performed using effluent samples from six municipal WWTPs in the US: Denver South Complex in Colorado (CO), Nogales International in Arizona (AZ), five plants in South Carolina (SC) (Mauldin, Pelham, Lower Reedy, Gilder Creek, and Piedmont). While Denver South Complex and Nogales International plants do not perform nitrification, five SC plants are designed and operated to achieve nitrification. Samples were taken from the SC plants in April and September, 2007, except the Lower Reedy facility which was sampled only in the fall due to construction in the spring. The samples from the AZ and CO facilities were taken in September and October, 2007. At each facility, samples were collected from the weir of secondary clarifier before contacting with any disinfectant. Samples were filtered with pre-washed 0.2 μm Supor membrane filters immediately after arrival at the laboratory to eliminate the biological activity, and were stored in a constant temperature room (4 °C) until the experiments were performed.

2.2. HNM FP tests

HNM FP tests were performed for different disinfection scenarios including chlorination, chloramination, ozonation, ozone-chlorination, and ozone-chloramination. The dosage of chlorine was determined using the method developed by Krasner and co-workers studying the presence of DBP precursors in treated wastewaters, reclaimed water and drinking waters from various sources with different compositions (Krasner et al., 2004, 2008). Detailed information about FP tests is provided in Supplementary materials (SM).

2.3. HNM determination at the WWTPs

HNM levels in the WWTP effluents were determined by performing onsite extraction of the effluent samples. Two more nitrifying WWTPs in SC, Georges Creek and Grove Creek, were included in the tests in addition to the five facilities examined in the FP tests. Samples were taken after UV contact chambers in Lower Reedy, Pelham, and Gilder Creek WWTPs, and after the chlorine contact chamber at the Mauldin, Piedmont, Georges Creek, and Grove Creek plants. The extractions were performed on-site immediately after the samples were collected. Samples were immediately analyzed for HNMs upon arrival at the laboratory.

2.4. HNM analysis

HNMs were measured using USEPA Method 551.1 with minor modifications (USEPA, 1995). Sodium sulfate (3 g) and cupric sulfate (1 g) was added to a 10 mL sample, followed by addition of 10 mL of methyl tert-butyl ether (MTBE, Sigma–Aldrich). The samples were then placed on a shaker table at 300 rpm for 30 min. The MTBE extract was analyzed with a HP 6850 gas chromatograph (GC) equipped with a DB-5 column (J&W Scientific, 30 m, 0.25 mm, 1.8 μm) and an electron capture detector. HNM standards were obtained from Orchid Cellmark (New Westminster, Canada, CNM 93.6%, DCNM 99+%, BCNM 91.9%, BDCNM 93.9%, DBNM 91.4%, DBCNM 94.1%, TBNM 99+%) and Sigma–Aldrich (TCNM 99+%, BNM 99+%). The GC temperature program used was 35 °C for 6 min, 30 °C min^{-1} to 190 °C and held for 1.5 min. The sample (2 μL) was injected in splitless mode. The carrier and make-up gas were ultra-high purity (UHP) He at 2.3 mL min^{-1} and UHP nitrogen at 60 mL min^{-1}, respectively. The injector temperature was set at 117 °C in order to minimize the thermal decomposition of HNM species (Chen et al., 2002), and the detector temperature was set at 297 °C. The extraction efficiencies were determined by fortifying ~10 μg L^{-1} HNM species to Pelham WWTP secondary clarifier effluent before any disinfectant addition, and they ranged 95–108%. Minimum reporting levels (MRLs) for HNMs were determined to be 0.7 μg L^{-1}.

2.5. Analytical methods

The effluent samples were analyzed for dissolved organic carbon (DOC), total nitrogen (TN), UV absorbance, Br^-, NO_3^-, NO_2^-, NH_3, and pH. The reacted samples were also measured for O_3 and residual free and combined chlorine. The analytical methods for the measurements are listed in Table S1 (SM) along with the MRLs.

3. Results and discussion

3.1. HNM FP in WWTPs effluents

A total of thirteen FP tests were performed to examine the extent of HNM formation in WWTPs effluents under different oxida-