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Breakpoint chlorination and free-chlorine contact time: Implications for drinking water N-nitrosodimethylamine concentrations

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ABSTRACT

North American drinking water utilities are increasingly incorporating alternative disinfectants, such as chloramines, in order to comply with disinfection by-product (DBP) regulations. *N*-Nitrosodimethylamine (NDMA) is a non-halogenated DBP, associated with chloramination, having a drinking water unit risk two to three orders of magnitude greater than currently regulated halogenated DBPs. We quantified NDMA from two full-scale chloraminating water treatment plants in Alberta between 2003 and 2005 as well as conducted bench-scale chloramination/breakpoint experiments to assess NDMA formation. Distribution system NDMA concentrations varied and tended to increase with increasing distribution residence time. Bench-scale disinfection experiments resulted in peak NDMA production near the theoretical monochloramine maximum in the sub-breakpoint region of the disinfection curve. Breakpoints for the raw and partially treated waters tested ranged from 1.9:1 to 2.4:1 (Cl_2:total NH_3-N, M:M). Bench-scale experiments with free-chlorine contact (2 h) before chloramination resulted in significant reductions in NDMA formation (up to 93%) compared to no free-chlorine contact time. Risk-tradeoff issues involving alternative disinfection methods and unregulated DBPs, such as NDMA, are emerging as a major water quality and public health information gap.

1. Introduction

Disinfection of drinking water is one of the greatest advances in public health protection. During drinking water treatment, unintended chemical disinfection by-products (DBPs) are produced by complex reactions between oxidants used for disinfection (e.g. chlorine, chloramine, ozone, or chlorine dioxide) and diverse groups of precursors such as: humic materials (Reckhow et al., 1990; Singer, 1999), bromide, iodide (Plewa and Wagner, 2004), and some amine-based coagulant aids (Wilczak et al., 2003; Kohut and Andrews, 2003). Although drinking water is a complex mixture of chemical constituents, with over 500 individual DBP species identified to date (Richardson, 1998), DBP research and regulatory agendas have primarily focused on chlorinated and brominated analogs of the two most abundant DBP classes: trihalomethanes (THMs) and haloacetic acids (HAAs).

Public concerns regarding adverse health outcomes resulting from increased exposure to drinking water DBPs stem from several epidemiology studies that demonstrated elevated risks of developing urinary bladder cancer (Mills et al., 1998; Villanueva et al., 2004) or adverse reproductive outcomes (Nieuwenhuijsen et al., 2000). However, in spite of significant DBP research efforts, identification of (a) plausible

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DBP agent(s) and mechanism of action leading to bladder cancer are yet to be elucidated (Bull, 2001). Low epidemiology cancer risk estimates from lifetime exposures to DBPs are still relevant because they could translate into a significant number of cases at the population level because exposure is widespread. Given considerable uncertainties in understanding adverse health effects attributed to DBPs, drinking water research requires refocusing toward DBPs that are biologically capable of producing the observed adverse outcomes measured in epidemiology and toxicology studies, particularly with respect to cancer endpoints.

N-Nitrosodimethlyamine (NDMA) is a non-halogenated DBP occurring in drinking water and treated wastewater (Mitch et al., 2003). *N*-Nitrosopyrrolidine and *N*-nitrosomorpholine have also been identified in drinking water (Charrois et al., 2004). As a chemical group, *N*-nitroso compounds have caused cancer in every vital tissue tested (Shank and Magee, 1981) and NDMA is a probable human carcinogen (USEPA, 1987). Additionally, the bladder is the site of action for several *N*-nitroso compounds in humans and rodent models (International Agency for Research on Cancer (IARC), 1978; Shank and Magee, 1981). Thus, *N*-nitrosamines offer a more biologically plausible basis from which to investigate correlations between cancer endpoints and DBP exposures, compared to THMs and HAAs.

A trend amongst North American drinking water utilities is the incorporation of alternative disinfectants, such as chloramines, in order to comply with current and upcoming DBP regulations. Though alternative disinfectants generally produces lower concentrations of THMs and HAAs (Kirmeyer et al., 2004), switching to chloramination still requires informed decision-making that considers risk trade-offs. Growing evidence suggests NDMA occurs more frequently and at higher concentrations in drinking water systems that chloraminate compared to chlorination-only systems (Najm and Trussell, 2001; Wilczak et al., 2003; Charrois et al., 2007). Additionally, chloramination can produce other unregulated DBP classes. Some, such as the halonitromethanes or certain iodoacid species have been shown more genotoxic or cytotoxic compared to regulated DBPs (Plewa and Wagner, 2004; Plewa et al., 2004). Moreover, switching from chlorine-only to chloramination can result in the release of lead into drinking water from distribution system pipes, solder and brass fittings (Edwards and Dudi, 2004) creating additional public health challenges for utilities. Chloramination risk-tradeoff considerations are emerging as a critical research gap that warrants increased scrutiny and must be addressed prior to utilities adopting changes to full-scale disinfection practices.

N-Nitrosamine monitoring efforts in drinking water continue to increase. With the inclusion of NDMA and five other *N*-nitrosamines in the Unregulated Contaminant Monitoring Regulation 2 (UCMR 2) (USEPA, 2005), it is reasonable to anticipate that additional utilities will begin to be identified as having elevated *N*-nitrosamine concentrations, when more systems start analyzing for them. With this in mind, a series of bench-top experiments was designed using raw source waters as well as partially treated waters collected prior to disinfection, but after full-scale coagulation, flocculation, sedimentation, and filtration from two treatment plants. Chloramination/breakpoint experiments were conducted, followed by extraction and analysis for NDMA. The main objectives of this study were to: (1) investigate NDMA drinking water formation within two full-scale chloraminating drinking water treatment plants; (2) explore the influence of Cl_2: total NH_3-N ratios on the production of NDMA at the bench-scale; and (3) identify potential treatment process options for drinking water utilities experiencing elevated NDMA concentrations, specifically by varying free-chlorine contact time prior to ammonia application.

2. Materials and methods

2.1. Reagents and standards

Methanol (AnalaR®) and dichloromethane (DCM; Omni-Solv®) were acquired from VWR Canlab (Mississauga, Ont., Canada). Hexane and reagent water (Optima Grade) as well as sodium bicarbonate and L-ascorbic acid (ACS reagent grade) were obtained from Fisher Scientific (Nepean, Ont., Canada). Additionally, sodium hypochlorite (purified grade; 4–6%) and ammonium hydroxide (ACS *Plus;* 14.8 M) were obtained through Fisher Scientific. Solid-phase extraction (SPE) materials, Ambersorb® 572 (Rohm and Haas; Philadelphia, PA, USA) and LiChrolut® EN (Merck; Darmstadt, Germany) were supplied through Supelco (Oakville, Ont., Canada) and VWR Canlab, respectively. A standard solution containing nine *N*-nitrosamines, including NDMA, was purchased from Supelco. Isotopically labeled standards, (98%) ([6-^{2}H] NDMA, NDMA-*d*6 and [14-^{2}H] *N*-nitrosodi-*N*-propylamine, DPNA-*d*14) were from Cambridge Isotope Laboratories (Andover, MA, USA).

2.2. Alberta water treatment plants and sample collection

2.2.1. City A

City A employs conventional treatment consisting of: powdered activated carbon, aeration, alum with cationic polymer (diallyldimethylammonium chloride; poly-DADMAC), clarification, lime softening, CO_2 (pH control), filtration (anthracite/sand/gravel), disinfection, and fluoride. Disinfection occurs after filtration in the following order: chlorine (gas), medium pressure UV (Sentinel® UV Disinfection System; Calgon Carbon Corporation, Pittsburgh, PA, USA), followed immediately by aqua ammonia to form chloramines. The amount of free-chlorine contact time (and UV exposure) before ammonia addition is nominal (<30 s). Prior to February 2004 chlorine and ammonia were added simultaneously prior to UV exposure.

2.2.2. City B

City B employs conventional treatment consisting of: potassium permanganate, alum with cationic polymer (poly-DADMAC) and anionic polymer, clarification, filtration (granular-activated carbon/sand), disinfection, and fluoride. Chlorine (gas) is added immediately after filtration but aqua ammonia is only added prior to water entering the distribution system. The time between chlorine and ammonia additions is approximately 2–4 h depending on seasonal flow