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Effects of coagulation on the removal of natural organic matter, genotoxicity, and precursors to halogenated furanones

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ABSTRACT

Natural organic matter (NOM) in drinking water can react with disinfectants to form disinfection by-products (DBPs). Halogenated furanones are a group of emerging DBPs that can account for 20–60% of the total mutagenicity observed in drinking water. This study examined the impacts of bench-scale coagulation and subsequent chlorination on DBP formation as well as genotoxicity using three source waters located in Ontario, Canada. Two halogenated furanones 3-chloro-4-(dichloromethyl)-2(5H)-furanone (MX) and mucochloric acid (MCA) were analyzed; along with trihalomethanes (THMs), haloacetic acids (HAAs), and absorbable organic halides (AOX). NOM was quantified using liquid chromatography–organic carbon detection (LC–OCD). Measured MX and MCA formation was 6.9–15.3 ng/L and 43.2–315 ng/L following optimized coagulation and subsequent chlorination of the three waters tested. DBP formation and speciation were evaluated as a function of the specific NOM fractions present in the source waters. Humics, building blocks, and biopolymers were highly correlated with DBP formation. Correlations between DBPs were also investigated and a potential relationship between MCA and/or MX vs. HAAs was observed. MX was the only measured DBP that contributed to genotoxicity, representing less than 0.001% of AOX by mass but responsible for 40–67% of the genotoxic response in chlorinated Ottawa River water samples. Genotoxic potential decreased with alum dosages, signifying that coagulation was effective at removing genotoxic DBP precursors.

1. Introduction

Disinfection of drinking water effectively reduces the risk of infection due to waterborne pathogens (Richardson, 2005). However, chlorine can react with natural organic matter (NOM) ubiquitous in surface waters (Matilainen et al., 2010) to form disinfection by-products (DBPs), which may be of concern due to potential health risks associated with consumption and exposure (Richardson and Postigo, 2012). Although the two major classes of DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs), are systematically monitored and routinely regulated, these typically account for less than 50% of the total organic halides (AOX) produced in chlorinated drinking waters (Krasner et al., 2006). In addition, recent reports have highlighted relatively low health concerns

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associated with THM/HAA exposure, which questions the use of these DBPs to serve as surrogates (Hrudey, 2009). Studies have also indicated that non-regulated DBPs, including halogenated furanones, may be more cytotoxic and genotoxic than many of the regulated DBPs (Krasner, 2009).

Halogenated furanones gained prominence with the discovery of the highly mutagenic compound 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone, commonly known as Mutagen "X" or MX by Holmbom et al. (1984). Subsequent studies have identified 12 analogs of MX, collectively referred to as halogenated furanones, in a wide range of chlorinated drinking waters (Kronberg et al., 1988; Andrews et al., 1990; Simpson and Hayes, 1993; Krasner et al., 2006) and are usually formed from the reaction of chlorine with humic acid (Kubwabo et al., 2009). Typical observed concentrations of MX (ng/L) are 1000 times lower than THMs or HAAs, however even these levels have been shown to account for 20–60% of the total mutagenicity of treated drinking water (Onstad and Weinberg, 2005). MX has also been shown to be highly genotoxic (Tikkanen and Kronberg, 1990), although other DBPs have also been linked to genotoxicity, mutagenicity, and/or carcinogenicity activity (Onstad et al., 2008).

The toxicological potential of DBPs should be examined in conjunction to their analytical detection in drinking waters. Cell based assay *in vitro* tests bioassays are well suited for monitoring studies and/or initial screenings because they are sensitive, easy to perform, and do not require prior knowledge of the individual constituents in the test mixture (Kocak et al., 2010). Genotoxic agents interact with DNA to induce mutations or pose reproductive harm which may then lead to cancerous transformation of functioning cells or pose reproductive harm (Quillardet et al., 1982). Tests such as the SOS Chromotest offer rapid determination of qualitative and quantitative detection of DNA damaging agents (Wang et al., 2011). Due to these attributes, they can provide a biological context to analytical detection and aid in determining exposure risk.

Halogenated furanones are currently unregulated, in part due to the complex analytical detection techniques required as well as their presence at low ng/L levels in treated drinking waters. While other studies have reported the presence of MX and its analogs in drinking water, few have examined the impact of treatment on MX formation. Andrews et al. (1990) reported efficient removal of MX by activated carbon; Zou et al. (2000) suggested that some aromatic aldehydes and amino acids associated with NOM (humic and fulvic acid fractions) may serve as precursors for MX. No previous studies have directly identified a link between NOM removal, the reduction in MX formation, and its associated genotoxic potential.

This study investigated the relationship between specific NOM fractions and DBP formation, focusing on the formation of halogenated furanones. The specific objectives were to: 1) examine NOM fraction removal and DBP formation following bench-scale coagulation and chlorination, 2) explore correlations between NOM fractions and DBP formation as well as compare the formation of halogenated furanones to monitored DBPs, and 3) examine the relationship between genotoxicity and DBPs.

2. Materials and methods

2.1. Reagents

Aluminum sulfate (alum) was obtained from General Chemical (Parsippany, NJ). Sodium hypochlorite (10–15% chlorine) for chlorination and sulfuric acid for pH adjustment of water and preservation of samples were purchased from Sigma–Aldrich Inc. (St. Louis, MO). 3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) was purchased from Toronto Research Chemicals Inc. (North York, ON). Mucochloric acid (MCA), mucobromic acid (MBA, surrogate standard for MX/MCA analysis), EPA 501/601 trihalomethanes (THMs) calibration mix, EPA 552.2 haloacetic acids (HAAs) mix, 1,2-dibromopropane (1,2-DBP, internal standard for THMs analysis), tetrafluorobenzoic acid (TFBA, internal standard for HAAs analysis) were purchased from Sigma–Aldrich Inc.

2.2. Source waters

Three source waters of differing NOM composition were selected for use in replicated bench-scale coagulation tests. Raw, untreated water was collected from Ottawa River, Otonabee River, and Lake Simcoe all located in Ontario, Canada. Typical raw water characteristics are shown in Table 1.

2.3. Experimental methods

Replicated jar tests were performed for alum coagulation on the three source waters. Aluminum sulfate was selected for coagulation optimization as it represents the most prevalently used chemical coagulant in North America (Matilainen et al., 2010). A wide range of alum dosages was selected to assess a broad range of DBP formation. Raw water was allowed to equilibrate to room temperature (22 °C) in a 100 L stainless steel container while mixing at 100 rpm prior to use. Four replicates for each source water were performed in order to provide sufficient amounts of sample water for all subsequent analyses. Each jar test consisted of six 2 L water samples into which 0, 20, 30, 40, 50, and 60 mg/L of alum (General Chemical, Parsippany, NJ) were added. In the commercial alum, solid alum content was 48.5% and aluminum content comprised 4.3% of the solution. Doses of 0–60 mg/L corresponded to aluminum concentrations of 0–5.45 mg/L as Al. Jar testing consisted of an initial 90 s of rapid mix (100 rpm) followed by 15 min of slow mix/flocculation (30 rpm) and 30 min of settling (Wassink et al., 2011). Settled water was collected and filtered using 1.2 μm glass microfiber filters (42.5 mm diameter,

Table 1 – Raw water characteristics of the three Ontario, Canada source waters.

	DOC (mg/L)	TOC (mg/L)	pH	Alkalinity (mg/L $CaCO_3$)	UV_{254} (cm^{-1})	SUVA (L/mg/m)
Ottawa River	5.9	6.1	7.4	23.5	0.20	3.45
Otonabee River	5.0	4.9	8.4	90.5	0.10	2.05
Lake Simcoe	4.1	4.2	8.5	115.0	0.06	1.32