



Natural solar photolysis of total organic chlorine, bromine and iodine in water



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ABSTRACT

Municipal wastewater has been increasingly used to augment drinking water supplies due to the growing water scarcity. Wastewater-derived disinfection byproducts (DBPs) may negatively affect the aquatic ecosystems and human health of downstream communities during water reuse. The objective of this research was to determine the degradation kinetics of total organic chlorine (TOCl), bromine (TOBr) and iodine (TOI) in water by natural sunlight irradiation. Outdoor solar photolysis experiments were performed to investigate photolytic degradation of the total organic halogen (TOX) formed by fulvic acid and real water and wastewater samples. The results showed that TOX degradation by sunlight irradiation followed the first-order kinetics with half-lives in the range of 2.6–10.7 h for different TOX compounds produced by fulvic acid. The TOX degradation rates were generally in the order of $TOI > TOBr \cong TOCl(NH_2Cl) > TOCl(Cl_2)$. High molecular weight TOX was more susceptible to solar photolysis than corresponding low molecular weight halogenated compounds. The nitrate and sulfite induced indirect TOX photolysis rates were less than 50% of the direct photolysis rates under the conditions of this study. Fulvic acid and turbidity in water reduced TOX photodegradation. These results contribute to a better understanding of the fate of chlorinated, brominated and iodinated DBPs in surface waters.

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1. Introduction

Municipal wastewater has become an increasingly important source of water due to the growing scarcity of potable water supplies worldwide. Water reclamation, recycling and reuse programs have been rapidly developed to mitigate the shortage of drinking water supplies in recent years (Rodriguez et al., 2009). In addition to the planned reuse, unplanned or incidental use of treated wastewater has taken place for several decades. Although the benefits of using wastewater to augment drinking water supplies have been well recognized, water reuse practices have also drawn serious concerns about potential health risks associated with the contaminants in treated effluents (Snyder et al., 2003).

Chlorine disinfection is a common process used by wastewater treatment plants (WWTPs) to inactivate pathogenic microorganisms before the effluent discharge. During the disinfection process, chlorine can react with effluent organic matter and bromide and iodide ions to form a variety of disinfection byproducts (DBPs),

including trihalomethanes (THMs), haloacetic acids (HAAs), chloral hydrate, haloacetonitriles, nitrosamines and others (Mitch and Sedlak, 2002; Yang et al., 2005; Krasner et al., 2009). Toxicological and epidemiological studies have linked carcinogenic and developmental effects to exposure to DBPs in drinking water (Richardson et al., 2007). The United States Environmental Protection Agency currently regulates four THMs and five HAAs in drinking water in an effort to reduce the health risks associated with DBPs. Therefore, wastewater-derived DBPs may negatively affect the aquatic ecosystems and human health of downstream communities during water reuse.

The fate and transport of wastewater-derived DBPs in aquatic environments can be affected by several major biogeochemical processes including sorption, hydrolysis, biodegradation, volatilization and photolysis (Plumlee and Reinhard, 2007; Chen et al., 2008; Jin et al., 2012). Hydrolysis, biodegradation and volatilization can selectively remove certain species of DBPs such as haloacetones (hydrolysis), dihalogenated acetic acids (biodegradation), and trihalomethanes (volatilization). Previous studies on solar photolysis of DBPs have focused on the degradation kinetics of specific DBPs (Lifongo et al., 2004; Chen et al., 2010). Nitrosamines

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were found to be highly photodegradable and the half-lives were less than 16 min under sunlight irradiation (Plumlee and Reinhard, 2007; Chen et al., 2010). Chlorinated THMs and HAAs were generally resistant to solar photolysis. Brominated and iodinated DBPs were more photosensitive than their chlorinated analogues based on solar irradiation experiments and quantitative structure–activity relationship analysis (Chen et al., 2010).

It has been recognized that a large portion of the DBPs formed by chlorine and chloramines have not been chemically identified yet. THMs, HAAs and other specific DBPs collectively accounted for less than 50% of the total organic halogen (TOX) formed by chlorine. When chloramine was used, more than 80% of the TOX remained unknown (Zhang et al., 2000; Hua and Reckhow, 2008a). The unidentified DBPs may contain many toxicologically important compounds that contribute substantially to the observed adverse health effects associated with drinking water DBPs (Bull et al., 2001; Richardson et al., 2007). Little is known about the impact of sunlight on unidentified DBPs in surface waters. Moreover, brominated and iodinated DBPs are likely present in WWTP effluents at relatively high levels because of the contamination from industrial wastewater, hospital wastewater and other anthropogenic activities (Krasner et al., 2009; Duirk et al., 2011; Parker et al., 2014). The bromine and iodine containing DBPs are more cytotoxic and genotoxic than their chlorinated analogues according to toxicity studies (Plewa and Wagner, 2009). The unregulated and unidentified DBPs derived from wastewater treatment may pose significant risks to public health during water reuse practices because these DBPs are typically not monitored by water utilities.

With the rapid development of water reuse programs, we need to acquire a better understanding about the fate and transport of wastewater-derived DBPs (especially unregulated and unidentified species) in surface waters. The primary objective of this research was to determine the degradation kinetics of total organic chlorine (TOCl), bromine (TOBr) and iodine (TOI) under natural sunlight irradiation conditions. In this study, we used fulvic acid and real water and wastewater samples as precursors to produce TOX compounds for outdoor photolysis experiments. The impact of pH, dissolved organic matter, nitrate, sulfite, turbidity and molecular weight fractions on solar photolysis of TOX was evaluated. The results of this research provide information about the photolytic degradation kinetics of total halogenated organic DBPs by natural sunlight irradiation. This knowledge can help us better understand the fate of chlorinated, brominated and iodinated DBPs in surface waters and develop strategies to reduce the health risks associated with wastewater-derived DBPs during water reuse.

2. Experimental methods

2.1. Preparation of TOX samples

The samples used for TOX formation during this study included solutions of Suwannee River Fulvic Acid (SRFA), a wastewater sample collected from the filter effluent of the Brookings WWTP, SD, and a drinking water sample collected from the filter effluent of the Brookings Water Treatment Plant (WTP), SD. All solutions used in this study were prepared with ultrapure water (18 M Ω -cm) produced by a Barnstead NANOpure system. The chemicals used in this study were of American Chemical Society reagent grade and were purchased from Fisher Scientific (Fairlawn, NJ) unless otherwise noted. The SRFA was obtained from the International Humic Substances Society and dissolved in water at a dissolved organic carbon (DOC) concentration of 3 mg C/L. The SRFA solutions were treated with chlorine (3 mg/L as Cl₂), monochloramine (0.4 mg/L as Cl₂), bromine (2 mg/L as Br₂) and iodine (1 mg/L as I₂), respectively, to produce TOCl(Cl₂), TOCl(NH₂Cl), TOBr and TOI for subsequent

solar photolysis experiments. The SRFA oxidation experiments were conducted with 300 mL chlorine-demand free glass bottles on samples buffered with 1 mM phosphate at pH 7. After being dosed with each oxidant, the SRFA samples were stored head-space free at 20 °C in the dark for 72 h. These experimental conditions were chosen so that each oxidant was completely consumed and no residual was found at the end of 72-h incubation time. No quenching chemicals were used in this study to avoid their potential impact on photodegradation of TOX. Relatively high bromine and iodine doses were used in this study to produce large amounts of TOBr and TOI for better quantification of the degradation kinetics by solar photolysis (Moran et al., 2002; Magazinovic et al., 2004; Hua et al., 2006). The resulting TOX concentrations before photolysis experiments were 464 ± 21 µg Cl/L for TOCl(Cl₂), 47 ± 2 µg Cl/L for TOCl(NH₂Cl), 278 ± 10 µg Br/L for TOBr and 144 ± 6 µg I/L for TOI, respectively, for a total of five sets of experiments.

The experimental conditions for TOX formation from fulvic acid were kept the same during this study to produce similar TOX compounds for evaluating the impact of different factors on TOX photolysis. It should be noted that variations in the oxidation conditions (e.g., dose, pH, reaction time, temperature and others) would affect the TOX concentrations and properties, which may subsequently impact the natural photolysis of these compounds. It is recommended that further studies be done on TOX compounds produced by different treatment conditions.

The stock solutions of chlorine, bromine and iodine were prepared by diluting a sodium hypochlorite solution (4–6%, Fisher Scientific) and a bromine solution (>99.5%, Sigma Aldrich, St Luis, MO), and by dissolving solid iodine (>99.8%, Sigma Aldrich) in water, respectively. The stock monochloramine solution was created by mixing aqueous ammonium sulfate and sodium hypochlorite solutions at a Cl₂/N molar ratio of 0.8:1. The pH of both solutions was adjusted to 8.5 using sulfuric acid or sodium hydroxide before mixing. The halogen stock solutions were standardized by the DPD ferrous titrimetric method (APHA et al., 2012).

Chlorination and chloramination were performed for the wastewater and drinking water samples to produce TOX solutions for solar photolysis experiments. The chlorine and chloramine doses were 8 mg/L and 0.8 mg/L, respectively, for Brookings wastewater sample, and 2.5 mg/L and 0.35 mg/L, respectively, for Brookings drinking water sample. These doses were determined through preliminary demand tests such that all chlorine and chloramine were completely consumed and no residual was found at the end of 72-h incubation time. Other experimental conditions were kept the same as the SRFA oxidation experiments.

2.2. Natural solar photolysis experiments

Natural solar photolysis experiments were performed using 60 mL quartz tubes with an outside diameter of 25 mm and a length of 150 mm. The thickness of the tube wall is 1.5 mm. The quartz tubes were capped to prevent the volatilization and evaporation of TOX samples during the photolysis experiments. The sample tubes were placed on fabricated platforms at a 30° angle. The outdoor solar photolysis experiments were conducted between May and September 2014, in an open space adjacent to the Water and Environmental Engineering Research Center in Brookings, SD, USA (44°18'53.5"N, 96°47'09.7"W). Each set of photolysis experiments was started at 11:30 am on the testing day and extended for a total of 6 h of sunlight exposure. The solar radiation intensity (W/m²) was recorded on-site every 30 min using a photometer (Seaward 396A916, Tampa, FL). The average solar radiation intensities varied between 1052 and 1140 W/m² and the average temperatures varied between 25 and 28 °C during a total of 6 sets of photolysis experiments. The cloud cover was also monitored throughout the

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