Chloramination of wastewater effluent: Toxicity and formation of disinfection byproducts

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ABSTRACT

The reclamation and disinfection of waters impacted by human activities (e.g., wastewater effluent discharges) are of growing interest for various applications but has been associated with the formation of toxic nitrogenous disinfection byproducts (N-DBPs). Monochloramine used as an alternative disinfectant to chlorine can be an additional source of nitrogen in the formation of N-DBPs. Individual toxicity assays have been performed on many DBPs, but few studies have been conducted with complex mixtures such as wastewater effluents. In this work, we compared the cytotoxicity and genotoxicity of wastewater effluent organic matter (EfOM) before and after chloramination. The toxicity of chloraminated EfOM was significantly higher than the toxicity of raw EfOM, and the more hydrophobic fraction (HPO) isolated on XAD-8 resin was more toxic than the fraction isolated on XAD-4 resin. More DBPs were also isolated on the XAD-8 resin. N-DBPs (i.e., haloacetonitriles or haloacetamides) were responsible for the majority of the cytotoxicity estimated from DBP concentrations measured in the XAD-8 and XAD-4 fractions (99.4% and 78.5%, respectively). Measured DBPs accounted for minor proportions of total brominated and chlorinated products, which means that many unknown halogenated compounds were formed and can be responsible for a significant part of the toxicity. Other non-halogenated byproducts (e.g., nitrosamines) may contribute to the toxicity of chloraminated effluents as well.

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Introduction

The disinfection of waters impacted by human activities (e.g., agriculture or wastewater effluent discharges) has been associated with the formation of nitrogenous disinfection byproducts (N-DBPs) due to their enrichment in nitrogen-containing compounds (e.g., ammonia or organic nitrogen such as amino acids and peptides) (Bond et al., 2011; Westerhoff and Mash, 2002). N-DBPs generally form in lower concentrations than non-nitrogenous regulated DBPs (i.e., trihalomethanes, THMs, and haloacetic acids, HAAs), but may present a higher health risk (Muellner et al., 2007; Plewa et al., 2004). In vitro mammalian cell assays have demonstrated that N-DBPs such as haloacetonitriles (HANs) (Muellner et al., 2007), halonitromethanes (HNMs) (Plewa

et al., 2004) and haloacetamides (HAcAms) (Plewa et al., 2007) exhibit orders of magnitude higher levels of cytotoxicity and genotoxicity than THMs and HAAs (Plewa et al., 2008). Reclaiming wastewater for various agricultural, industrial or municipal applications is of growing interest but requires the practice of disinfection to prevent outbreaks of waterborne diseases. Dissolved organic matter isolated from wastewater effluent (EfOM) was found to be significantly more enriched in nitrogen (i.e., to be a potential source of N-DBPs) than organics recovered from surface waters (e.g., N/C mass ratios up to 0.17 compared to 0.01–0.06 for river waters) (Drewes and Croue, 2002; Le Roux et al., 2016; Zheng et al., 2014).

Moreover, the presence of bromide and iodide ion in wastewater (especially at locations where potable water is produced through the desalination of seawater or brackish water) favors the formation of brominated and iodinated byproducts that are often more toxic than their chlorinated analogues (Plewa et al., 2008; Richardson et al., 2007, 2008). Brominated and iodinated N-DBPs are among the most cytotoxic/genotoxic disinfection by-products known today (Muellner et al., 2007; Plewa et al., 2008). Water utilities, especially in the USA, have been increasingly switching chlorine disinfection to monochloramine to reduce the concentration of regulated THMs and HAAs (U.S. Environmental Protection Agency, 2006), however, monochloramine can be an additional source of nitrogen in the formation of N-DBPs (Kimura et al., 2013; Le Roux et al., 2016). Chloramines can also be formed unintentionally from the reaction between free chlorine and ammonia during chlorination, which may increase the risk of N-DBP formation when high ammonia concentrations are present.

While toxicity assays have been conducted for many individual DBPs, few studies have been performed with complex mixtures such as natural waters, drinking waters or wastewater effluents. Many of the >500 DBPs reported in the literature were not analyzed for toxicological effects (Richardson and Postigo, 2015). Similarly, many studies characterized DBP occurrence from various sources and their formation conditions, but the evaluation of DBP formation in conjunction with toxicity assays has not been extensively explored. Richardson et al. (2011) published a protocol for DBP extraction, analysis and toxicity assessment, consisting in the extraction of disinfected waters by XAD resins (XAD-8 and XAD-2 in series), followed by an elution with ethyl acetate. The extract is then either directly analyzed by gas chromatography coupled with mass spectrometer (GC–MS) or evaporated and exchanged to dimethylsulfoxide (DMSO) for further genotoxicity/cytotoxicity analyses. This method has been used for swimming pool waters (Liviac et al., 2010; Plewa et al., 2011; Richardson et al., 2010) and drinking waters disinfected with chlorine, ozone or chlorine dioxide (Jeong et al., 2012) and was recently applied to disinfected (i.e., chlorinated and ozonated) wastewater effluents (Dong et al., 2016). N-DBPs are compounds of interest because of their potential toxicity, and the chloramination of EfOM is expected to favor the production of this class of DBPs because nitrogen can be incorporated both from monochloramine and from the nitrogenous moieties present in EfOM.

As a result, the aim of this work was (i) to compare the cytotoxicity and genotoxicity of EfOM resin isolates recovered before and after chloramination, (ii) to analyze the toxicity of resin extracts obtained from chloraminated wastewater effluent in relation with the formed DBPs, and (iii) to estimate the contribution of N-DBPs to the toxicity of chloraminated wastewater effluents.

1. Materials and methods

1.1. Materials

Analytical or laboratory grade reagents and were used without further purification. MilliQ water was produced with a Millipore system (18.2 MΩ/cm). Sodium hypochlorite (NaOCl, 5.65–6%, Fisher Scientific) and ammonium chloride (Acros Organics, 99.6%) were used to prepare chloramine solutions. Methyl tert-butyl ether (MTBE) and ethyl acetate (>99%, Fisher Scientific) were used for DBP extractions without further purification. A THM calibration mix (chloroform — TCM, dichlorobromomethane — $CHCl_2Br$, chlorodibromomethane — $CHClBr_2$, and bromoform — TBM), a mixed standard (EPA 551B Halogenated Volatiles Mix) containing HANs, trichloro-nitromethane (TCNM, or chloropicrin) and haloketones (HKs), and a mixed standard containing 9 HAAs (EPA 552.2 Methyl Ester Calibration Mix) were supplied from Supelco (Sigma-Aldrich). Chloro-, bromo-, dichloro-, and trichloroacetamide (CAcAm, BAcAm, DCAcAm and TCAcAm, respectively) were obtained from Sigma-Aldrich. Other HAcAms (i.e., dibromoacetamide — DBAcAm, tribromoacetamide — TBAcAm, bromochloroacetamide — BCAcAm, chloroiodoacetamide — CIAcAm, bromoiodoacetamide — BIAcAm and diiodo-acetamide — DIAcAm) were purchased from Cansyn Chem. Corp. Haloacetaldehydes (HAcAls) were obtained from TCI America, Cansyn Chem. Corp. and Sigma-Aldrich. Deca-fluorobiphenyl (99%, Sigma-Aldrich, Supelco) was used as a surrogate standard. 2 bromopropionic acid (Fluka Analytical) was used as a surrogate for HAA extractions and analyses.

1.2. Analytical methods

Total organic carbon (TOC) and total nitrogen (TN) concentrations were measured using a TOC analyzer equipped with a TN detection unit (TOC-VCSH, Shimadzu). Three-dimensional fluorescence excitation–emission matrices (EEMs) were obtained by a Fluoromax fluorometer (Horiba Scientific, Japan). Samples for Adsorbable Organic Halide (AOX) analyses were processed through adsorption on activated carbon columns using a TOX sample preparatory unit (TXA-03, Mitsubishi Chemical Analytech Co., Ltd., Japan). AOX were then transformed into hydrogen halides by combustion (950°C) of the activated carbon for at least 30 min via an AOX-200 adsorbable halogen analyzer and then collected in Milli-Q water as chloride and bromide ions. Offline quantification of chloride and bromide ions was performed by a Dionex 1600 reagent free ion chromatograph (IC) equipped with a conductivity detector and a Dionex IonPac AS-15 column (2 × 250 mm) and using an online KOH eluent (30 mM) generator at a flow rate of 0.4 mL/min. AOCl and AOBr concentrations were determined from the respective Cl⁻ and Br⁻ concentrations. Free chlorine and total chlorine concentrations in the sodium hypochlorite stock solutions were determined by spectrophotometric