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17β-estradiol as precursors of Cl/Br-DBPs in the disinfection process of different water samples☆

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ABSTRACT

During chlorine disinfection process, reactions between the disinfectant and 17β-estradiol (E2) lead to the formation of halogenated disinfection byproducts (DBPs) which can be a risk to both ecosystem and human health. The degradation and transformation products of E2 in sodium hypochlorite (NaClO) disinfection processes of different water samples were investigated. The reaction kinetics research showed that the degradation rates of E2 were considerably dependent on the initial pH value and the types of water samples. In fresh water, synthetic marine aquaculture water and seawater, the reaction rate constant was 0.133 min^{-1}, 2.067 min^{-1} and 2.592 min^{-1}, respectively. The reasons for the above phenomena may be due to the different concentrations of bromide ions (Br^-) in these three water samples which could promote the reaction between NaClO and E2. Furthermore, Br^- could also cause the formation of brominated DBPs (Br-DBPs). The main DBPs, reaction centers and conceivable reaction pathways were explored. Seven halogenated DBPs have been observed including three chlorinated DBPs (Cl-DBPs) and four Br-DBPs. The active sites of E2 were found to be the pentabasic cyclic ring and the ortho position of the phenol moiety as well as C9-C10 position. The identified Cl/Br-DBPs were also confirmed in actual marine aquaculture water from a shrimp pond. The comparison of bio-concentration factors (BCF) values based on calculation of EPI-suite showed that the toxicities of the Br-DBPs were stronger than that of their chloride analogues. The absorbable organic halogens (AOX) analysis also suggested that the DBPs produced in the marine aquaculture water were more toxic than that in the fresh water system.

1. Introduction

For the sake of control aquatic reproduction, monosex aquaculture has emerged as a popular practice in aquaculture systems (Beardmore et al., 2001; Rodgers et al., 2006). A higher growth rate could be achieved through the application of monosex aquaculture. At the same time, it could also reduce variation in harvest size sexual, territorial behaviors and risk of environmental impact resulting from escapes of exotic species (Sagi and Aflalo, 2015). Hormonal induction of sex reversal is usually served as a valuable approach to achieve monosex aquaculture (Pandian and Sheela, 1995). For example, Yamazaki reported that endogenous estrogen could act as an ovarian inducer which leading to protogynous sex change of three-spotted wrasse and saddleback wrasse (Yamazaki, 1983). 17β-estradiol (E2) is an effective feminization hormone because it can induce the sex reversal in aquaculture (Carvalho et al., 2014; Nakamura et al., 2003; Wang and Croll, 2004). However, a number of papers have reported the potentially detrimental effects of E2 on aquatic organism and especially the carcinogenicity on humans (Ahmad et al., 2000; Bradley et al., 2009; Pedram et al., 2006). Through the investigation of the genotoxic effect of E2 on human chromosomes in lymphocytes aquacultures in vitro, E2 was found to associate with chromosomal aberrations and sister chromatid exchanges(Pedram et al., 2006). Estrogens including E2 have been detected in seawater with concentrations about

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8.8 ± 0.7 ng L^{-1} (Heub et al., 2015). For marine aquaculture water, there is no reference reported and about 350 ng L^{-1} of E2 was detected in a shrimp pond in FangChengGang breeding base. Therefore, the residual E2 is still a special pollutant in marine aquaculture water and a matter of continuing concern (Janer et al., 2004). The transformation of E2 in marine aquaculture water should be also researched.

On the other hand, chlorination disinfection is a universal procedure as water quality is very important for the intensive marine aquaculture systems (Boyd, 1996; Sanawar et al., 2017). However, chlorination treatment of water has been shown to generate unintended disinfection byproducts (DBPs) as chlorine-containing disinfectant would react with the natural or artificial organic matter in water (Liu et al., 2012; Teixeira et al., 2011). DBPs, halogenated DBPs in particular, have received a growing concern because of their significant toxicity and environmental risks (Hrudey, 2009; Moudgal et al., 2000; Nikolaou et al., 2004; Zamyadi et al., 2012). Since the 1970's, trihalomethanes (THMs) as the chlorination DBPs were first reported in drinking water, the original halogenated DBPs has been expanded to more than 600 different types (Chu et al., 2011; Liviac et al., 2011). A lot of studies suggested that the halogenated DBPs such as THMs, haloacetic acids (HAAs) and haloacetonitriles (HANs) possess cytotoxicity and genotoxicity (Bekbolet et al., 2005; Sadiq et al., 2004). It is worth noting that brominated DBPs (Br-DBPs) which are substantially more toxic than their chloro-analogues will be generated once the water contains bromide ions (Br^-) such as the marine aquaculture water (Qiang et al., 2014; Abdelwahab et al., 2010; Ged and Boyer, 2014; Parinet et al., 2012; Saidan et al., 2015). Through the studies of the microplate cytotoxicity assay and single-cell gel electrophoresis assay on Chinese hamster, brominated HAAs were found to be 18.4 and 89.8 times more cytotoxic and genotoxic than their chlorinated products (Plewa et al., 2002). The formation of Br-DBPs was due to that the strong oxidizing agent of hypochlorous acid can oxidize the Br^- to hypobromite which is a stronger halogenating agent than hypochloric acid (Sun et al., 2009; Zhang et al., 2017). As reported, under the same condition, the reaction rate constant of hypochlorite with DBPs organic precursors was 0.7–5.0 L $(mol \cdot s)^{-1}$, while the reaction rate constant of hypobromite with DBPs organic precursors could up to 15–167 L $(mol \cdot s)^{-1}$ (Ichihashi et al., 1999).

Researches on the halogenated DBPs were traditionally focused on the reaction product of chlorine-containing disinfectant with natural organic matter such as humic acid presented in water sources, while limited studies has focused on the reaction of disinfectant with other man-made organic compounds (Ichihashi et al., 1999; Jiang et al., 2017; Lu et al., 2009). Some special organic substances are not only pollutants themselves in water sources, but also can react with chlorine-containing disinfectant to form novel halogenated DBPs. Only recently, the related research has aroused concern. For example, an antibiotic oxytetracycline has been reported to react with chlorine disinfectant and six chlorinated DBPs (Cl-DBPs) were detected (Bi et al., 2013). The reaction kinetics, mechanisms and pathways of sulfamethoxazole with free available chlorine were investigated. The results showed that direct reactions were very quickly, two DBPs were found. The formation of DBPs indicated that S-C cleavage, polymerization, S-N hydrolysis, chlorine substitution and desulfonation reactions was occurred (Dodd and Huang, 2004). Hu et al. reported that E2 could react with sodium hypochlorite (NaClO) and seven products including 2,4-dichloro-17β-estradiol, monochloroestrone, 2,4-dichloroestrone, and other four byproducts were identified (Hu et al., 2003). However, compared with fresh water, marine aquaculture water which was a mix of seawater with fresh water with a proportion of 1:2 contains Br^- with a concentration of up to 22 mg L^{-1}, Br-DBPs will be produced consequently (Dorji et al., 2018).

As discussed above, E2 in the marine aquaculture water was not only a pollution but could also act as a special precursor of halogenated DBPs including Br-DBPs. In this paper, the research priority will be mainly focused on the kinetics, pathways and the final products especially the Br-DBPs of the reaction between chlorine-containing disinfectant and E2 in the marine aquaculture water. The fates of E2 in fresh water, marine aquaculture water and seawater samples were analyzed respectively to emphasize the effect of Br^- on the formation of reaction products. NaClO which is often used as an effective disinfectant to control marine aquaculture disease was selected as the chlorine-containing disinfectant. The activity and potential health risk of Br-DBPs brought by E2 during the chlorination disinfection process of marine aquaculture water will be primarily explored.

2. Materials and methods

2.1. Chemicals

Analytical grade E2 was purchased from the Shanghai Yuanye biological technology company (98% purity or higher) and without further purification in use. Both sodium chloride (NaCl) and sodium bromide (NaBr) were of analytical grade and were obtained from Guangzhou Chemical Reagent Company. Sodium sulfite (Na_2SO_3) was purchased from the Chengdu Jinshan Chemical Reagent Company, China. Formic acid was obtained from Chengdu Kelong Chemical Reagent Company, China. Analytical grade NaClO was obtained from Tianjin Damao Chemical Reagent Company at 10% purity. High performance liquid chromatography (HPLC) grade methanol was purchased from Anhui Fulltime Specialized Solvents & Reagents.Co., LTD. The stock solutions of humic acid (HA) which was selected as a surrogate of dissolved organic matter (DOM) were purified by filtration and precipitation and its concentration was measured in mgC L^{-1} (Gao et al., 2016). All reagent solutions were prepared using water from a Millipore Milli-Q Ul-trapure Gradient A10 purification system. Real marine aquaculture water samples of shrimp ponds were obtained from FangChengGang, GuangXi province, China.

2.2. Analytical methods

Liquid chromatography was performed on an ultra-performance liquid chromatography (UPLC) system which equipped with an Acquity UPLC QSM (Waters, USA), a quaternary gradient pump, fluorescence detector, and UV diodearray detector was used to monitor the content of E2. The detection wavelength for E2 was set at 280 nm. The mobile phase used was ultrapure water and acetonitrile at a flow rate of 0.30 ml min^{-1}. All solutions used for UPLC analysis were degassed by sonication for more than 20 min. Adsorbed organic halogen (AOX) was measured with the microcoulometric titration method using a total organic halogen analyzer (XPLORER; TE Instruments B.V.).

2.3. Preparation of synthetic water samples

The synthetic fresh water was obtained by Milli-Q pure water system. The synthetic seawater was prepared by adding NaCl and NaBr to the fresh water (Cl^-: 19 g L^{-1}, Br^-: 65 mg L^{-1}). The inorganic cations such as Na^+, Ca^{2+}, Mg^{2+}, K^+ and inorganic anions including SO_4^{2-} and HCO_3^- which concentrations are high in the seawater were added according to their actual concentration. The marine aquaculture water was a mixture of seawater and fresh water with proportion of 1:2 as in the actual breeding process. The concentration for Cl^- and Br^- in the synthetic marine aquaculture water was about 6.6 g L^{-1} and 22 mg L^{-1}, respectively. The pH