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Transformation of methylparaben during water chlorination: Effects of bromide and dissolved organic matter on reaction kinetics and transformation pathways

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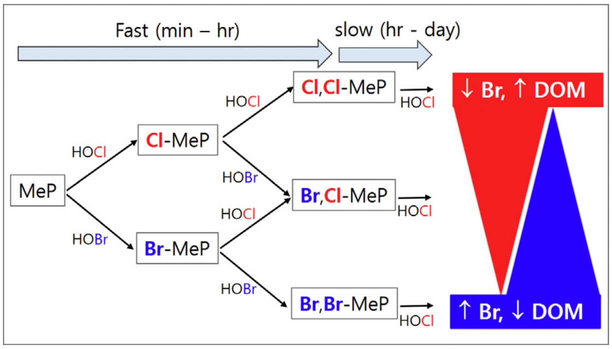
HIGHLIGHTS

- Transformation kinetics and pathways of methylparaben during chlorination are studied.
- Second-order rate constants for chlorine/bromine with methylparabens are reported.
- Brominated methylparabens are dominant over chlorinated ones with increasing bromide.
- Bromide effect on methylparaben transformation diminishes by dissolved organic matter.
- The developed kinetic model can simulate the paraben transformation in chlorination.

GRAPHICAL ABSTRACT



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ABSTRACT

The reaction kinetics, products, and pathways of methylparaben (MeP) during water chlorination with and without bromide (Br^-) were investigated to better understand the fate of parabens in chlorinated waters. During the chlorination of MeP-spiked waters without Br^-, MeP was transformed into mono-Cl-MeP and di-Cl-MeP with apparent second-order rate constants (k_{app}) of 64 $M^{-1}\ s^{-1}$ and 243 $M^{-1}\ s^{-1}$ at pH 7, respectively, while further chlorination of di-Cl-MeP was relatively slower ($k_{app} = 1.3\ M^{-1}\ s^{-1}$ at pH 7). With increasing Br^- concentration, brominated MePs, such as mono-Br-MeP, Br-Cl-MeP, and di-Br-MeP, became major transformation products. The di-halogenated MePs (di-Cl-MeP, Br,Cl-MeP, and di-Br-MeP) showed relatively low reactivity to chlorine at pH 7 ($k_{app} = 1.3$–$4.6\ M^{-1}\ s^{-1}$) and bromine ($k_{app} = 32$–$71\ M^{-1}\ s^{-1}$), which explains the observed high stability of di-halogenated MePs in chlorinated waters. With increasing pH from 7 to 8.5, the transformation of di-halogenated MePs was further slowed due to the decreasing reactivity of di-MePs to chlorine. The formation of the di-halogenated MePs and their further transformation become considerably faster at Br^- concentrations higher than 0.5 μM (40 μg/L). Nonetheless, the accelerating effect of Br^- diminishes in the presence of dissolved organic matter (DOM) extract (Suwannee River humic acid (SRHA)) due to a more rapid consumption of bromine by DOM than chlorine. The effect of Br^- on the fate of MeP was less in the tested real water matrices, possibly due to a more rapid bromine consumption by the real water DOM compared to SRHA. A kinetic model was developed based

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on the determined species-specific second-order rate constants for chlorination/bromination of MeP and its chlorinated and brominated MePs and the transformation pathway information, which could reasonably simulate the transformation of MePs during the chlorination of water in the presence of Br^- and selected DOM.

1. Introduction

Parabens, the esters of *para*-hydroxybenzoic acid, are widely used as antimicrobial preservatives in cosmetics, foodstuffs, and pharmaceuticals (Dodge et al., 2015; Guo and Kannan, 2013; Liao and Kannan, 2014). Due to their extensive and frequent use in everyday life, parabens are commonly found in various water environments, such as wastewater, surface water, and swimming pool water, at a concentration range of ng/L–μg/L (Evans et al., 2016; Haman et al., 2015; Wang and Kannan, 2016). Parabens are known to be practically non-toxic based on acute and chronic studies with rodents (Soni et al., 2005). Even though some parabens are found to have estrogenic activity in in vitro and in vivo assays (Routledge et al., 1998), studies have shown that the estrogenic potency of parabens is too low to cause adverse estrogen-related effects in humans in typical exposure scenarios (Golden et al., 2005). Nonetheless, it has been shown that parabens can potentially exert various other adverse effects on humans (e.g., anti-androgenicity and genotoxicity) and aquatic organisms (e.g., acute toxicity in *Daphnia magna* and *Vibrio fischeri*) (Darbre and Harvey, 2008; Ding et al., 2017; Terasaki et al., 2009a). Furthermore, chronic toxicity of parabens has been reported, which warrants further investigation. For instance, an association between the urinary concentration of parabens in females and the reduced fecundity of couples has recently been reported (Smarr et al., 2017).

Halogenated parabens at their phenolic moiety, such as mono-Cl-, mono-Br-, di-Cl-, Br, Cl-, and di-Br-parabens, have been detected in municipal wastewater, river water, and swimming pool water (Canosa et al., 2006; González-Marino et al., 2011; Terasaki and Makino, 2008; Terasaki et al., 2012). The presence of these halogenated parabens, sometimes having higher concentrations than their parent parabens, can be explained by the fact that chlorine (hereafter indicating HOCl/OCl^-) is a common disinfectant for municipal water and reacts readily with phenolic compounds (Deborde and von Gunten, 2008; Lee and von Gunten, 2010). In addition, bromine (hereafter indicating HOBr/OBr^-) is rapidly formed from the reaction of chlorine (HOCl) with bromide (Br^-) (Eq. (1)).

$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad k_1 = 1.55 \times 10^3\ M^{-1}\ s^{-1} \tag{1}$$

Br^- is ubiquitously present in drinking water and wastewater in the concentration range of a few tens to thousands of μg/L (Soltermann et al., 2016 and references therein). Furthermore, bromine is about three orders of magnitude more reactive to phenols than chlorine (Criquet et al., 2015; Heeb et al., 2014). These facts also explain the occurrence of various halogenated phenolic contaminants in chlorinated wastewater effluents (Bulloch et al., 2015; Fan et al., 2013).

The transformation of parabens into their halogenated forms may significantly affect their physicochemical and biological properties and consequently their fate and adverse biological effects in built and natural water systems. Halogen substitutions can increase the lipophilicity and hydrophobicity of parabens while making the parabens' phenolic moiety more acidic and electron-deficient (Schwarzenbach et al., 2016). These changes in physicochemical properties can affect various partitioning and transformation processes of parabens in aquatic environments. Chlorinated parabens have shown reduced biodegradability compared to their parent parabens in biological wastewater treatment processes (González-Marino et al., 2011; Li et al., 2015). Chlorinated parabens have shown higher acute toxicity in *Daphinia* and *Vibrio* (Terasaki et al., 2009a) while lower chronic toxicity in water fleas (Terasaki et al., 2015a). Estrogenic activity is usually reduced upon the chlorination of parabens (Terasaki et al., 2009b). Aryl hydrocarbon receptor activity has been found to increase for mono-chlorinated parabens but to decrease for di-chlorinated parabens (Terasaki et al., 2015b). Overall, it is important to consider chlorinated and brominated parabens in assessing the fate and behavior of and risk associated with parabens in the environment.

The objective of this study was to better understand the fate of parabens during water chlorination in the absence and presence of Br^- and at various pH and dissolved organic matter (DOM) levels. A kinetic modeling approach was applied to quantitatively describe the transformation of parabens, an approach that has been successfully applied to investigate similar reaction systems (Abdallah et al., 2015; Lee and von Gunten, 2009; Langsa et al., 2017). Even though some kinetic parameters have been reported for the reaction of chlorine with parabens (Canosa et al., 2006; Mao et al., 2016; Terasaki et al., 2012), they were mostly empirical rate constants and therefore showed limited applicability to other systems. In addition, principle-based kinetic parameters (i.e., second-order rate constants) to describe the full transformation pathways of parabens by chlorine and bromine are still lacking.

In this study, methylparaben (MeP) was selected as a model paraben considering its frequent occurrence in various water environments (Haman et al., 2015). In the first step, the transformation pathways of MeP were investigated, and unknown second-order rate constants were determined as a function of pH for each of the steps involved in the transformation of MeP by chlorine and bromine. A kinetic model was constructed based on the identified transformation pathways of MeP and the corresponding second-order rate constant information. The kinetic model includes the reactions of chlorine and bromine with selected DOM. The established kinetic model was then validated with experimental data for the transformation of MeP and the chlorine consumption obtained from various conditions for pH, Br^-, and DOM. Finally, the transformation of MeP and its product evolution were determined after the chlorination of real water matrices.

2. Materials and methods

2.1. Standards and reagents

All chemicals and solvents were purchased from various commercial suppliers and used as received (Supplementary Information, SI-Text-1). Stock solutions of chlorine (5 mM–100 mM) were prepared by diluting the commercial solution of NaOCl (4%–5%, Sigma-Aldrich Korea, Yongin-Si, Korea). The chlorine stock solution was standardized spectrophotometrically using the molar absorption coefficient of OCl^-: $\varepsilon = 350\ M^{-1}\ cm^{-1}$ at 292 nm (Deborde and von Gunten, 2008). Stock solutions of bromine (10 mM) were prepared by reacting 10 mM of NaOCl with 10.5 mM of Br^- at pH 11 (adjusted by using 1 M NaOH) for 3 days (Lei et al., 2004). The bromine stock solution was standardized spectrophotometrically using the molar absorption coefficient of OBr^-: $\varepsilon = 332\ M^{-1}\ cm^{-1}$ at 329 nm (Heeb et al., 2014). MeP was purchased from Sigma-Aldrich Korea. Chloro-methylparaben (Cl-MeP), 3,5-dichloro-methylparaben (Cl,Cl-MeP), and bromo-methylparaben (Br-MeP) were purchased from Fluorochem Ltd. (Hadfield, UK). 3-Bromo, 5-chloro-methylparaben (Br,Cl-MeP) was purchased from FCH Group (Chernigiv, Ukraine). 3,5-Dibromo-methylparaben (Br,Br-MeP) was