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Behaviour of I/Br/Cl-THMs and their projected toxicities under simulated cooking conditions: Effects of heating, table salt and residual chlorine

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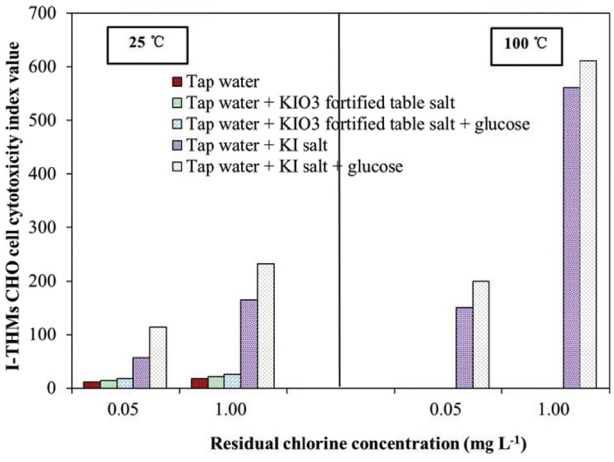
HIGHLIGHTS

- Additions of KI and KIO_3-fortified table salt cause I-THMs to increase.
- $CHCl_2I$ is the predominant I-THM formed in the presence of KIO_3-fortified table salt.
- >90% of $CHCl_2I$ is removed by heating, but concentrations of the other I-THMs increase.
- Additions of KI or KIO_3-fortified salt increase the cytotoxicity due to I-THM formed.
- Heating causes cytotoxicity to decrease for KIO_3-fortified salt but increase for KI.

GRAPHICAL ABSTRACT



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ABSTRACT

This study examined the effects of heating, residual chlorine and concentration of table salt on the generation of iodine-, bromine- and chlorine-containing trihalomethanes (THMs) under simulated cooking conditions. In the case of addition of either KI- or KIO_3-fortified salt, total I-THM concentrations increased with increasing iodine concentration, while total Cl/Br-THM concentrations decreased. $CHCl_2I$, CHBrClI, $CHBrI_2$, $CHBr_2I$ and CHI_3 were formed in the presence of KI salt, while only $CHCl_2I$ was formed in the presence of KIO_3 salt. $CHCl_2I$ was unstable under cooking conditions, and >90% of this DBP was removed during heating, which in some cases increased the concentrations of the other I-THMs.

The calculated cytotoxicity increased with addition of KI- or KIO_3-fortified salt due to the generation of I-THMs, whose impact on the cytotoxicity at room temperature was equal to or five times higher, respectively, than the cytotoxicity of the simultaneously formed Cl/Br-THMs for the cases of salts. Heating decreased the cytotoxicity, except for the case of addition of KI salt, in which the calculated cytotoxicity of I-THMs increased above 150% as the temperature was increased up to 100 °C.

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The reported results may have important implications for epidemiologic exposure assessments and, ultimately, for public health protection.

1. Introduction

Chlorine has been widely used as a disinfectant in water treatment due to its lasting ability to inactivate most harmful microorganisms [1,2]. As an unintended consequence, chlorine reacts with the natural organic matter (NOM), bromide and iodide present in many source waters to produce multiple disinfection by-products (DBPs) [3–8]. Since DBPs were first discovered over 40 years ago [9,10], >600 individual DBPs have been identified and shown to have pronounced toxicity, genotoxicity and carcinogenicity [11–15].

In addition to its use in water treatment plants, residual chlorine is maintained in drinking water distribution systems to prevent the regrowth of microorganisms in them, and as a result, it is present in tap water. When this tap water is used for cooking, chlorine interacts with organic substrates present in foodstuffs, e.g., lipids, glutens and glucose, to produce DBPs [16–25]. DBPs in general and specifically the group of four regulated trihalomethanes (THMs) have been found in beverages and foods that were prepared with chlorinated drinking water [17,26,27]. Chloroform appears to be the most common DBP detected in food, especially in the case of fat-rich products [26]. It is estimated that 50–70% of the cancer risks assignable to regulated THMs are associated with the ingestion of tap water and tap water-based beverages [19,28,29].

Exposures to DBPs via water ingestion are significantly affected by traditional practices and cultural preferences. In many Western countries, notably in the United States, tap water may be iced and/or drunk directly. In many Asian countries, notably China, water is always ingested after boiling and used to prepare hot tea or soups. Hence, the reactions between residual chlorine in tap water and DBP precursors present in foods and the stabilities of DBPs formed are significantly different from those at temperatures of 5–30 °C [25,30]. Boiling has been shown to reduce the concentration of most THMs in water, but it can increase the formation of HAAs and some other DBPs [18,21,25,31]. Loss of THMs and other DBPs caused by heating is attributed to volatilization and decomposition reactions, but such reactions can simultaneously generate other DBPs [19,20].

Food additives universally used in cooking, notably table salt, frequently contain KIO_3 or KI, which can influence the formation of DBPs. Becalski et al. [24] have observed that iodoacetic acid was formed when chloraminated water containing iodized table salt was boiled or stored for prolonged durations at room temperature. Pan et al. [19] have found new iodine- and bromine-DBP species formed in simulated cooking conditions.

Compared to the depth of studies of DBP formation in drinking water treatment and distribution system conditions, the extent of exploration of DBP generation during cooking is relatively limited, and in particular, little information is available about the formation under these conditions of iodinated DBPs that have conspicuously high toxicity [3,32,33]. As table salt fortified with iodine compounds is widely used for cooking in China and globally [34], cooking is likely to be accompanied by interactions between the iodine compound present in table salt, residual chlorine present in tap water and organic substrates in foodstuffs, resulting in the formation of I-DBPs.

This study focused on these processes and quantified the effects of varying residual chlorine levels, concentrations of table salt in the presence of a typical food component (glucose), and heating temperature on the concentrations of I-THMs and the concentrations of the currently regulated Br/Cl-containing THMs formed in simulated cooking conditions. The toxicity of DBPs formed in the examined systems was estimated using data from the Chinese hamster ovary (CHO) cell cytotoxicity database [11,35]. The results of this study may be important for epidemiological exposure assessments, public health protection in general and the general goals of improving drinking water quality, optimization of water treatment processes and the guidelines for the use of drinking water for cooking and other activities.

2. Materials and methods

2.1. Chemicals

Standards for six I-THMs (bromochloroiodomethane ($CHClBrI$), bromodiiodomethane ($CHBrI_2$), chlorodiodomethane ($CHClI_2$), dibromoiodomethane ($CHBr_2I$), dichloroiodomethane ($CHCl_2I$) and iodoform (CHI_3)) were purchased from Orchid Cellmark, Canada. Bromochloromethane and 1,2-dibromopropane, which were used as internal and surrogate standards, respectively, were purchased from J&K Company (China), Beijing, China. Extractions were performed with chromatographically pure methyl-*t*-butyl-ether (MTBE), hexane and methanol purchased from J.T. Baker Company (China), Beijing, China. A calibration mix solution for determination of regulated THMs ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$) was purchased from Sigma-Aldrich (China), Beijing, China (2 g L^{-1} of each component in methanol). Other chemical reagents such as KI, NaOCl, Na_2SO_3, glucose and others were purchased from Enterprise Group Chemical Reagent Co., Ltd., Beijing, China. The potassium iodate-fortified table salt (as stated on the label, referred to henceforth as KIO_3-salt) used in the study was purchased from a major supermarket in Beijing, China. Nominally, the salt is fortified by iodate only, and the concentration of this compound was determined to be 28.6 mg kg^{-1} (as I). Because iodide-fortified table salt was not available, potassium iodide salt additions in amounts equivalent to those used in the case of iodate-fortified table salt were used to represent additions of iodide-fortified table salt (KI-salt).

Tap water was collected on campus at Peking University, Beijing, China, during May to July in 2014. General chemistry parameters of that water are presented in Table S1. The concentration of residual chlorine in the water was determined using the DPD method [36]. The concentration of iodate in table salt was determined by titration, as described by Eaton et al. [36].

2.2. THMs analyses

Br/Cl-THMs were quantified according to EPA methods 551.1. Analyses for these compounds were performed with an Agilent 6890 gas chromatograph equipped with an ECD detector. A DB-5 fused silica capillary column (30 m × 0.53 mm i.d., 1.5 μm film thickness) was used. The initial temperature of the column was 35 °C. The column was held at this temperature for 12 min, after which the temperature was increased at a rate of 8 °C min^{-1} to 190 °C, and this temperature as maintained for 3 min. The temperatures of the injector and detector were 200 and 350 °C, respectively.