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Formation of trichloromethane in chlorinated water and fresh-cut produce and as a result of reaction with citric acid☆

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ABSTRACT

Chlorine (sodium hypochlorite) is commonly used by the fresh produce industry in the U.S. to sanitize wash water, fresh and fresh-cut fruits and vegetables. However, possible formation of harmful chlorine by-products is a concern. The objectives of this study were to compare chlorine and chlorine dioxide in trichloromethane formation, determine trichloromethane levels in chlorinated wash water, cut-lettuce and diced onions, and evaluate the reaction of chlorine with citric acid, a chemical often used to adjust pH of chlorine solution. Results showed that little trichloromethane ($\leq$3 $\mu g\,L^{-1}$) was produced from chlorine dioxide solution even at concentrations up to 200 $mg\,L^{-1}$ compared with the trichloromethane level ($\sim$40 $\mu g\,L^{-1}$) in solutions of chlorine mixed with lettuce extract. The formation of trichloromethane in 1 L of 100 $mg\,L^{-1}$ chlorine wash water increased from 155 to 284 $\mu g\,L^{-1}$ after repeated use of the wash water to wash six batches of 100 g cut lettuce. Levels of trichloromethane in the washed cut lettuce were in the range of 14–22 $\mu g\,kg^{-1}$, and were reduced to less than 8 $\mu g\,kg^{-1}$ after being rinsed with water. Chlorine solution used to wash diced onions produced much less trichloromethane (32 $\mu g\,L^{-1}$) compared with that for washing cut lettuce despite higher chemical oxygen demand and turbidity in the wash water. Citric acid reacted with chlorine and produced trichloromethane. Over 1000 $\mu g\,L^{-1}$ trichloromethane was produced after 30 min reaction with chlorine at 22 °C, while less than 35 $\mu g\,L^{-1}$ trichloromethane was produced when Na-phosphate was used to adjust pH of chlorine. The amount of trichloromethane increased with reaction time and concentration of citrate. Our results demonstrated that formation of trichloromethane in wash water depended on type of cut-vegetables, and citric acid contributed to a significant amount of trichloromethane formation.

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1. Introduction

A number of outbreaks of foodborne diseases have been linked with fresh and fresh-cut fruits and vegetables in recent years, prompting concerns about the microbial safety of these products (AFF (Alliance for Food and Farming), 2010; Gould et al., 2013). Washing (with or without solutions of sanitizers) is commonly used by the produce industry to remove dirt and microorganisms as well as for rapid cooling of the products (Gil et al., 2009). To further reduce the population of microorganisms in the products/water and to minimize cross contamination, disinfectants (sanitizers) are often used in the wash water. Washing with sanitizers is one of the critical processing steps for fresh and fresh-cut produce. The most common sanitizers used by the fresh produce industry in the U.S. are chlorine-based compounds, such as sodium hypochlorite (chlorine) and chlorine dioxide (ClO_2), even though the efficacy of the chlorine-based sanitizers in reducing population of microorganisms on fresh produce is very limited (1–2 logs at the most) (Beuchat et al., 2004). Ease of use and relatively low cost make chlorine a very common water disinfectant throughout the fresh produce industry in the U.S. Chlorine is used in the concentration range of 50–200 $mg\,L^{-1}$, although recent studies (Luo et al., 2011; Shen et al., 2012) indicated that lower concentrations of free chlorine were sufficient to inactivate pathogenic bacteria in water and to avoid cross-contamination. However, there is a concern about the use of chlorine in the fresh produce industry and other industries due to potential environmental and health risks associated with the formation of carcinogenic halogenated disinfection by-products (DBPs)

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(Ölmez and Kretzschmar, 2009). Chlorine reacts with organic matter and forms carcinogenic halogenated DBPs, such as trichloromethane (Hua and Reckhow, 2007; Singer, 1994). Partly due to the possible generation of halogenated DBPs in the water, the use of chlorine in fresh-cut produce washing is prohibited in European countries (Van Haute et al., 2013). ClO_2 produces fewer potentially carcinogenic halogenated DBPs and is less corrosive than chlorine (Hua and Reckhow, 2007), and is allowed at a maximum concentration of 3 mg L^{-1} in the U.S. (CFR (Code of Federal Regulations), 2007).

The antimicrobial efficacy of chlorine largely depends on the pH and the amount of organic material in the water, and to a limited extent, on the temperature of water (Suslow, 2001). At pH values above 7.5, a very low percentage of chlorine exists in the active HClO form. At pH values below 6.0, off-gas (probably as di- and trichloramines) may occur and irritate workers (Black & Veatch Corporation, 2009). In addition, low pH may increase equipment corrosion. Therefore, it is desirable in the management of chlorine that the pH of water be adjusted and maintained at values of 6.5–7.0 to maximize the HClO level and minimize off-gas (Suslow, 2001). Chlorine (sodium hypochlorite) solution at pH 6.5 is currently the most common sanitizer used in the fresh-cut produce industry in the U.S. (Shen et al., 2012). To adjust the pH of chlorine solution, citric acid is commonly used by the industry (Suslow, 1997; Herdt and Feng, 2009; Shen et al., 2012).

Maintaining appropriate levels of effective chlorine in washing solutions with fresh-cut produce is a challenge due to the release of copious amount of juices from fresh-cut products into wash water (Shen et al., 2012). In addition, other organic materials from soil and microorganisms may accumulate during produce washing (Allende et al., 2008). Replenishing chlorine including continual fixed dosing, automated demand-based injection systems, and manual demand-based periodic dosing is a common practice in fresh-produce processing. With increasing organic loads originated from fresh produce in the recirculated water, and the need to maintain a certain level of chlorine, the levels of chlorine-by-products in the water would increase over-time. As a result, the production of large amounts of wastewater with high levels of biological oxygen demand and chlorine-by products may become a concern (Ölmez and Kretzschmar, 2009). To reduce water consumption and conserve energy associated with cooling or heating during processing of fresh-cut produce, most postharvest processes recirculate used water. The amount of water lost during transfer and transport of the products is replaced with fresh water, and chlorine concentration is constantly adjusted to targeted levels.

While information about chlorine by-product formation in drinking water is available (Richardson et al., 2000; Gopal et al., 2007; Hua and Reckhow, 2007), there is limited research about trichloromethane formation in process water and in the fresh produce that have been washed with chlorine (Klaiber et al., 2005; COT (Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment, 2006; López-Gálvez et al., 2010; Gómez-López et al., 2013). Klaiber et al. (2005) determined that the by-product formation due to chlorination of minimally processed carrots with tap water containing 200 mg L^{-1} free chlorine was negligible (<0.2 μg L^{-1}). There have been no studies dealing with accumulation of chorine by-products in re-used chlorine water with a fixed chlorine concentration during washing. It is unknown whether citric acid, which is commonly used for pH adjustment, would affect the formation of trihalomethanes. The objectives of the present study were therefore to investigate the formation of trichloromethane in wash water, cut lettuce and diced onions, to compare sodium hypochlorite with chlorine dioxide in producing trichloromethane, and to evaluate the impact of citric acid on trichloromethane formation.

2. Materials and methods

2.1. Chemicals

Trichloromethane (chloroform, high purity) was purchased from American Burdick and Jackson (Muskegon, MI). Citric acid (99%), 1-bromo-3-chloropropane (99%) and sodium phosphate were from Sigma–Aldrich (St. Lois, MO). Sodium citrate, NaOH and hydrochloric acid (36.5–38%) were from J.T. Baker (Phillipsburg, NJ). Ultrapure water from a Barnstead E-pure (Dubuque, IA) water purification system was used as wash water and for preparing solutions. The deionized water in the laboratory was found to contain about 2 μg L^{-1} trichloromethane. The purified water contained less than 0.5 μg L^{-1} trichloromethane. Solutions of sodium hypochlorite were prepared by diluting 8.25% sodium hypochlorite (Clorox, Oakland, CA). The pH of the solutions was maintained at ~6.5 using 50 mmol L^{-1} Na-phosphate buffer unless otherwise stated.

2.2. Plant materials

Whole heads of iceberg lettuce, onions, and fresh-cut produce including iceberg lettuce, fresh salsa, coleslaw, shredded carrots and shredded red cabbage were purchased from local supermarkets. The ingredients for fresh salsa were tomato, cucumber, green pepper, red pepper, red onion, cilantro, lime juice, tomato juice, garlic, poblano pepper, serrano pepper and salt.

2.3. Establishment of trichloromethane standard and analysis of trichloromethane

A series of trichloromethane and 1-bromo-3-chloropropane (as an internal standard) concentrations (0–500 μg L^{-1}), prepared in 7 mL glass vials, were equilibrated at 35 °C on a heating block for 25 min before the carboxen/polydimethylsiloxane solid phase microextraction (SPME) fiber (85 μm coating, Stableflex, Sigma–Aldrich) was inserted into the headspace of the vials through PTFE-faced septa. Previous studies suggested that carboxen/polydimethylsiloxane fiber was the best option for analysis of trihalomethane, particularly for trichloromethane (Allard et al., 2012; Antoniou et al., 2006; San Juan et al., 2007). The SPME fiber was lowered into the headspace of the vials for 20 min. During incubation and absorption period, the samples in the vials were mixed using a mini magnet stir bar inside of the vial on a stirrer/heater at a speed of 11.7 s^{-1} (model number SP133835, Barnstead Intern., Dubuque, IA). The fiber was retrieved from the vials and inserted into the injection port (temperature: 250 °C) of gas chromatograph (GC) with a desorption time of 4 min. Separation was achieved using DB-5MS (30 m, 0.32 mm ID and 1 μm film thickness) capillary column (Agilent Technology, Santa Clara, CA) coupled with an Agilent 6890 GC and 5973 MSD. Column flow was set at a constant flow of 1 mL/min. Temperature program for oven was 40 °C for 1 min, increased to 70 °C at 5 °C/min, then to 250 °C at 25 °C/min and held at 250 °C for 6 min. MS source temperature was 230 °C. Mass spectra were recorded in full scan mode. The identification of trichloromethane and the internal standard was based on the retention times of the authentic compounds with the assistance of the NIST version 02 library. In addition, the m/z 83 and 85 ions and the ratio of 83/85 were used for the confirmation of trichloromethane while m/z 158 and 77 ions and the ratio of 158/77 were used for the confirmation of 1-bromo-3-chloropropane. Ions 83 and 158 were used as the quantifiers for trichloromethane and 1-bromo-3-chloropropane, respectively.

The effect of salt addition on the SPME extraction efficiency of trichloromethane was studied. Addition of salt at amounts up to 0.5 kg L^{-1} did not significantly increase extraction efficiency of