

CRITICAL REVIEW OF DISINFECTION BY-PRODUCTS (DBPS)
IN FRESH PRODUCE AND PROCESS WATER

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LIST OF SYMBOLS AND ABBREVIATIONS

DBP	Disinfection by-product
THM	Trihalomethane
TTHM	Total trihalomethane
CF	Chloroform
BDCM	Bromodichloromethane
DBCM	Dibromochloromethane
BF	Bromoform
HAA	Haloacetic acid
MCAA	Monochloroacetic acid
DCAA	Dichloroacetic acid
TCAA	Trichloroacetic acid
MBAA	Monobromoacetic acid
DBAA	Dibromoacetic acid
TBAA	Tribromoacetic acid
BCAA	Bromochloroacetic acid
BDCAA	Bromodichloroacetic acid
DBCAA	Dibromochloroacetic acid
NDMA	<i>N</i> -Nitrosodimethylamine
NPIP	1-Nitrosopiperidine
NPYR	1-Nitrosopyrrolidine
GC	Gas chromatography
MS	Mass spectrometry
ECD	Electron capture detector

HS	Head space
HPLC	High performance liquid chromatography
USEPA	U.S. Environmental Protection Agency
USFDA	U.S. Food and Drug Administration
WHO	World Health Organization
IARC	International Agency for Research on Cancer
COD	Chemical oxygen demand
BOD	Biological oxygen demand
TOC	Total organic carbon
UF	Ultra filtration
NF	Nano filtration

SUMMARY

Disinfection is one of the most significant steps to guarantee the quality, safety, and shelf-life of fresh and fresh-cut produce in food processing industry. However, the disinfectant can react with the organic matter in produce and water, leading to the formation of disinfection byproducts (DBPs), which pose potential carcinogenic risks to human health. Despite the common use of disinfectants in produce processing and extensive research of DBPs in the drinking water field, studies investigating the DBP levels in fresh produce are quite limited. The research objectives of this thesis are to conduct a critical literature review regarding DBP occurrence and formation potential in fresh produce and produce process water, summarize the analytical methods, assess DBP exposure and risks, explore the current knowledge status, identify major information gaps, and provide recommendations for future research. It has been found that the majority of the existing studies focused on investigation of THM residues in fresh produce and associated process water. Process water contains significant levels of DBPs due to high organic load, indicating that more challenges can arise in treating and recycling process water. Future research should look into gathering more comprehensive data on DBPs in food, particularly for emerging nitrogenous DBPs, developing disinfection strategies alternative to chlorine with both disinfection efficacy and DBP minimization in consideration, and improving the risk assessment methods for DBPs in food.

CHAPTER 1

INTRODUCTION

In the food processing industry, washing with disinfectants is one of the most important techniques to reduce microorganisms, maintain food safety and extend the shelf-life of fresh food. When the disinfectant plays its role in inactivating pathogens, simultaneously it can react with the naturally-occurring organic substances in the water or food to generate unintended by-products. This chapter will introduce the typical disinfectants used in food industry and various classes of DBPs that tend to generate.

1.1 Food Safety

Food safety has always been a critical issue. Foodborne disease outbreaks would cause huge health and economic losses. According to the report of the U.S. Department of Agriculture, around 9,000 deaths and 6.5-33 million cases of illness were caused by microbial pathogens in food per year (Buzby et al., 1996). The cost was estimated to be \$9.3-\$12.9 billion each year for 6 bacterial pathogens out of over 40 various types of pathogens. Though the numbers appeared to be high, Wilcock et al. (2004) questioned the statistics had underestimated the actual cases. Bacteria and fungi have great ability to reproduce in food. Improper handling of food processing, product transportation and storage can even aggravate the situation. How to control the pathogenic microorganisms in foodstuffs and prevent foodborne disease is therefore of paramount importance to guarantee food safety. Washing produce by disinfectants is a desirable means to achieve that.

1.2 Typical Disinfectants

Disinfectants used in the food industry are required to have these characteristics: high efficacy against pathogenic microorganisms, easy to use, and relatively low cost to satisfy the industrial demand. Gil et al. (2009) summarized that 2 to 3 log reduction of natural microorganisms were achieved in many studies after washing with disinfectants or water. Common disinfectants used in food industry include chlorine, chlorine dioxide, electrolyzed oxidizing (EO) water, and peracetic acid (PAA).

1.2.1 Chlorine

Chlorine (Cl_2) or sodium hypochlorite (NaOCl) is the most widely used disinfectant in the washing of fresh and fresh-cut produce due to its high efficacy against pathogens, simple use and low cost. In an industry survey, nearly 76% of respondents reported the use of hypochlorite (Seymour et al., 1999). Liquid chlorine and hypochlorite are commonly used at the concentration of 50–200 mg L^{-1} with 1 or 2 min contact time (USFDA, 2014). The antimicrobial efficacy is dependent on pH. When pH is lower than 7.5, hypochlorous acid (HOCl) is the dominant species. Since hypochlorous acid (HOCl) has much more killing power than hypochlorite (OCl^-), pH less than 7.5 is desired. Additionally, to reduce the risk of metallic corrosion of processing equipment, the pH should be kept in the range of 6.5–7.5 (Artés et al., 2009). Chlorine has been extensively applied for produce disinfection such as lettuce, spinach, carrots, apples, strawberries, and cantaloupe (Gómez-López et al., 2013; Klaiber et al., 2005; Rodgers et al., 2004).

1.2.2 Chlorine Dioxide

Chlorine dioxide (ClO_2), a gas with great water solubility, has higher oxidizing and penetrating power than NaOCl . It is highly effective to inactivate pathogenic

microorganisms like *Legionella*, amoebal cysts, *Giardia* cysts, *Escherichia coli*, and *Cryptosporidium* (Xie, 2003). Chlorine dioxide generates less chlorinated by-products such as trihalomethanes in comparison with sodium hypochlorite (López-Gálvez et al., 2010). Nevertheless, it may yield other by-products: chlorite (ClO_2^-) and chlorate (ClO_3^-). ClO_2 can be employed with a wide range of pH (Artés et al., 2009). The main drawback is that it has to be generated on site since it can be explosive when concentrations reach 10% or more in air (Betts et al., 2005).

1.2.3 Electrolyzed Oxidizing (EO) Water

Electrolyzed oxidizing (EO) water is a novel antimicrobial agent that was initially developed in Japan (Shimizu & Hurusawa, 1992). It is generated by electrolysis of water containing a low concentration of sodium chloride. Normally acidic EO water has an oxidation-reduction potential greater than 1,100 mV, a pH lower than 2.7, and a free chlorine concentration of 10–80 ppm (Shimizu & Hurusawa, 1992). Thus, EO water can be viewed as another type of chlorine-containing disinfectant. Studies have shown that EO water is highly effective against *E. coli* O157:H7, *Salmonella* enteritidis, and *Listeria monocytogenes* (Venkitanarayanan et al., 1999), and applications are promising in various produce such as tomatoes, apples, peaches, and food contact surfaces (Huang et al., 2008).

1.2.4 Peracetic Acid (PAA)

Peracetic acid ($\text{CH}_3\text{C}(\text{O})\text{OOH}$), also known as peroxyacetic acid, has been widely used in meat and produce washing process because it is tolerable to several factors such as pH and temperature (Artés et al., 2007). PAA has been reported effective to control *E. coli* O157:H7 and *L. monocytogenes* on produce (Rodgers et al., 2004).

1.3 Disinfection By-products (DBPs)

1.3.1 Trihalomethanes (THMs)

Trihalomethanes are a group of compounds in which three of the four hydrogen atoms in methane are replaced by halogens, as shown in Figure 1.1. Trihalomethane is identified as the most prevalent class of DBPs in chlorinated water. Common trihalomethanes includes trichloromethane (TCM, or chloroform), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM, or bromoform). The complex reaction between chlorine and the natural organic matter (NOM) in water such as humic or fulvic substances leads to THM formation. If bromide is present, brominated THMs can be generated.

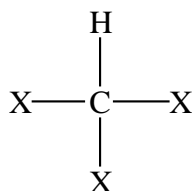


Figure 1.1: Molecular Structure of THMs (X represents halogens)

1.3.2 Haloacetic acids (HAAs)

Haloacetic acids, the second largest class of DBPs found in chlorinated water, are carboxylic acids where halogen atoms take the place of one, two, or three hydrogen atoms of the acetic acids, generating mono-, di-, tri-haloacetic acids. Figure 1.2 illustrates the molecular structure of them. Common haloacetic acids include monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetic acid

(TCAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), and tribromoacetic acid (TBAA). Similar to THM, the reaction between NOM and chlorine results in the formation of HAA. Apart from chloro- and bromo-HAAs, iodo-HAAs have also been reported if the water contains iodide. It is worth noting that the formation mechanism of dihaloacetic acids and trihaloacetic acids is not due to the further chlorination of monohaloacetic acids and dihaloacetic acids in chlorinated water. Di- and tri-haloacetic acids can be generated by the hydrolysis reactions of halopropanones (Xie, 2003).

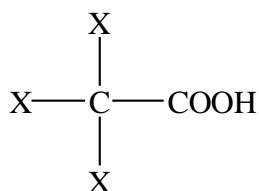


Figure 1.2: Molecular Structure of HAAs (X can be hydrogen or halogen)

1.3.3 Haloacetaldehydes

Haloacetaldehydes are another major class of DBPs detected after chlorine treatment. The commonly reported compound within this class is trichloroacetaldehyde, or its hydrate form (chloral hydrate), because mono-, and di-haloacetaldehydes can be further oxidized to trihaloacetaldehydes and brominated haloacetaldehydes are unstable or difficult to get commercial standards (Xie, 2003). Figure 1.3 shows the structure of trichloroacetaldehyde and chloral hydrate. The formation of trichloroacetaldehyde is mainly due to the reaction between chlorine and acetaldehyde.

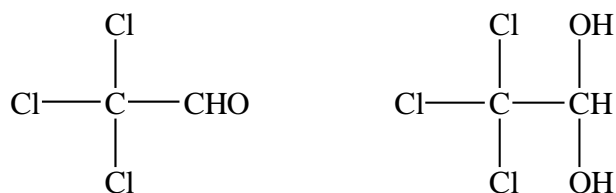


Figure 1.3: Molecular Structure of Trichloroacetaldehyde and Chloral Hydrate

1.3.4 Halopropanones (HPNs)

Halopropanones, also called haloacetones or haloketones, are formed by the reaction of chlorine and propanones. Propanones contain six hydrogen atoms that can be partially or fully substituted by halogen atoms, leading to the generation of mono-, di-, tri-, tetra-, penta-, and hexa-halopropanones. The molecular structure of halopropanone is shown in Figure 1.4. Again, monohalopropanones can be subsequently oxidized into di- and tri-halopropanones. Tetra-, penta-, and hexa-halopropanones are not stable and will degrade at neutral or higher pH (Xie, 2003).

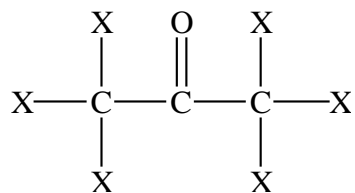


Figure 1.4: Molecular Structure of Halopropanone (X can be hydrogen or halogen)

1.3.5 Haloacetonitriles (HANs)

Haloacetonitriles can be formed by acetonitrile reacting with chlorine. Typical haloacetonitriles include dihaloacetonitriles and trihaloacetonitriles, which means two or three hydrogen atoms at the α position are replaced (see Figure 1.5). Considering all the

chlorinated and brominated cases, there are three types of dihaloacetonitriles (dichloroacetonitrile, bromochloroacetonitrile, and dibromoacetonitrile) and four types of trihaloacetonitriles (trichloroacetonitrile, bromodichloroacetonitrile, dibromochloroacetonitrile, and tribromoacetonitrile).

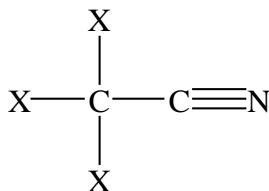


Figure 1.5: Molecular Structure of Haloacetonitrile (X represents hydrogen or halogen)

1.3.6 Nitrosamines

Nitrosamines are primarily formed by chloroamination. Although the typical reported levels are at low ng L^{-1} in drinking water, most nitrosamines are carcinogenic and have raised wide concerns. The chemical structure is shown in Figure 1.6. Common nitrosamines include *N*-nitrosodimethylamine (NDMA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosoethylmethylaniline (NEMA), *N*-nitrosopyrrolidine (NPYR), and *N*-nitrosomorpholine (NMOR).

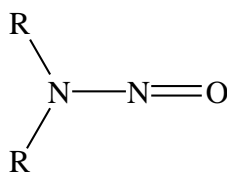


Figure 1.6: Molecular Structure of Nitrosamines (R represents aliphatic or aromatic group)

1.3.7 Halonitromethanes (HNMs)

Halonitromethanes are nitrogenous DBPs that may be present at $\mu\text{g L}^{-1}$ in drinking water systems. Halonitromethanes can be generated by ozonation, chlorination, or chloramination (Hu et al., 2010) and they are potent mammalian cell cytotoxins and genotoxins (Plewa et al., 2004). Figure 1.7 shows the structure of halonitromethanes. The most commonly detected species is trichloronitromethane, also called chloropicrin.

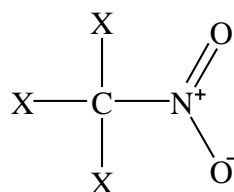


Figure 1.7: Molecular Structure of halonitromethanes (X represents halogen or hydrogen)

1.3.8 Haloacetamides (HAcAms)

Haloacetamides, an emerging class of highly cytotoxic and genotoxic nitrogenous DBPs (Plewa et al., 2007), were first detected in the 2000-2002 US survey of drinking water (Bond et al., 2011). Chloro-, bromo-, dichloro-, dibromo-, and trichloro-acetamide were found at $\mu\text{g L}^{-1}$ levels in the finished drinking water treated with chlorine dioxide-chlorine-chloramines (Krasner et al., 2006). The structure of haloacetamides is shown in Figure 1.8.

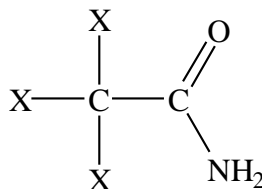


Figure 1.8: Molecular Structure of haloacetamides (X represents halogen or hydrogen)

1.4 Objective

The primary objective of this thesis is to perform a critical literature review of DBP occurrence and formation potential in fresh produce and process water. Specifically, several study aims include: 1) summarizing reported DBP levels in fresh vegetables, fruits and juices, and analyzing the DBP sources and factors that can influence the concentration; 2) assessing if any particular trends of DBPs exist, such as the correlation between certain DBP occurring frequency or concentration and food types; 3) identifying the limitations and information gaps of the existing studies; 4) investigating the possibility of water reuse in food processing industry; and 5) evaluating the health risks of DBPs from food consumption and integrating the available regulatory information.

CHAPTER 2

OCCURRENCE AND FORMATION POTENTIAL OF DBPS IN FRESH PRODUCE

Different types of DBPs with different concentrations have been detected in various fresh produce. Several studies also tested DBP formation potential resulting from disinfectant washing. Distinct conditions during disinfection can lead to diverse consequences. Thus, this chapter will summarize the DBP levels occurring or forming in fresh produce, and discuss their relation with disinfectant type, dosage, and contact time.

2.1 DBP Levels in Fresh Produce

Fresh and fresh-cut produce includes both vegetables and fruits. Fruit juices are considered to be the closely related products of fruits, so fruit juices are also taken into account in this study. Cooked vegetables and infant food are excluded from the scope of this thesis. The levels of DBPs are usually expressed in the range of ppb ($\mu\text{g kg}^{-1}$ or $\mu\text{g L}^{-1}$ based on the state of the food). Though DBP concentrations are strongly dependent on the disinfection procedures and produce type, Table 2.1 exhibits a general summary of the range of DBPs that would be possibly occurring in fresh produce according to the published studies after an extensive search of the literature. Complete information of the published studies shown in Table 2.1 is compiled in Appendix Tables A.1–A.3.

2.1.1 THMs

The majority of the studies on the DBPs in food have been focused on THM formation, particularly trichloromethane (Fan et al., 2015; Gómez-López et al., 2013; Huang & Batterman, 2009; López-Gálvez et al., 2010; Van Haute et al., 2013). This can

Table 2.1: Ranges of DBP Levels Reported in Fresh Produce

DBP Type	Food Type	Concentration Range (ppb)	References
CHCl ₃	Leafy Vegetables	ND–87.9	3, 4, 5, 7, 8, 10
	Non-leafy vegetables	ND–320	4, 5, 8, 9, 11, 13
	Fruits	ND–30.0	3, 4, 6, 13
	Juices	ND–12.0	1, 2, 8, 9, 11, 12, 13
CHCl ₂ Br	Leafy Vegetables	<0.30	8
	Non-leafy vegetables	ND–14.0	8, 9, 13
	Fruits	ND–14.0	13
	Juices	ND–33.0	1, 8, 9, 13
CHClBr ₂	Leafy Vegetables	0.7–1.5	7
	Non-leafy vegetables	ND–7.1	11
	Juices	ND–1.4	
CHBr ₃	Leafy Vegetables	0.9–1.7	7
	Juices	2.4–4.6	1
TTHMs	Leafy Vegetables	<6.3–90.8	3, 7, 14
DCAA	Leafy Vegetables	ND–32	3, 15, 16
	Non-leafy vegetables	5.8–6.8	
	Juices	ND–15	
TCAA	Leafy Vegetables	0.4–51.3	
	Non-leafy vegetables	0.6–14	
	Juices	ND–15	
BCAA	Leafy Vegetables	ND–4.4	
	Non-leafy vegetables	1.1–1.3	
	Juices	ND–4.0	
DBAA	Leafy Vegetables	ND–1.5	
	Non-leafy vegetables	0.7–0.9	
	Juices	ND–1.9	
BDCAA	Leafy Vegetables	ND–5.1	
	Non-leafy vegetables	<2	
	Juices	ND–1.5	
MCAA	Juices	ND–4.3	
MBAA	Juices	ND–1.04	

1: Campillo et al., 2004; 2: Chang et al., 1988; 3: COT, 2006; 4: Daft, 1988; 5: Fan et al., 2015; 6: Fleming-Jones & Smith, 2003; 7: Gómez-López et al., 2013; 8: Huang & Batterman, 2009; 9: Klaiber et al., 2005; 10: López-Gálvez et al., 2010; 11: Miyahara et al., 1995; 12: McNeal et al., 1995; 13: USFDA, 2006; 14: Van Haute et al., 2013; 15: Cardalor & Gallego, 2012; 16: Cardalor & Gallego, 2015.

be attributed to the fact that THMs are the most prevalent class of DBPs detected in drinking water and THMs have been regulated by the USEPA. Therefore, knowledge of THMs is more abundant than the other classes of DBPs.

2.1.1.1 Trichloromethane (CHCl_3)

Lettuce is one of the most frequently studied vegetables due to its relatively large consumption in daily life. Trichloromethane levels in chlorine-washed cut lettuce were found from 14 to 22 $\mu\text{g kg}^{-1}$ after 6 batches of 1 min treatment with 100 mg L^{-1} chlorine (Fan & Sokorai, 2015). If the chlorine-washed lettuce was rinsed with purified water, the trichloromethane concentration was less than 8 $\mu\text{g kg}^{-1}$. As for lettuce juice, trichloromethane concentration ranged from 0–40 $\mu\text{g L}^{-1}$ with a series of 0–200 mg L^{-1} sodium hypochlorite treatment for 5 min, whereas the levels were around 3 $\mu\text{g kg}^{-1}$ if the disinfectant was chlorine dioxide under the same conditions. Another study by López-Gálvez et al. (2010) also compared the formation potential of trichloromethane by chlorine versus chlorine dioxide. The authors detected less than 5 $\mu\text{g kg}^{-1}$ trichloromethane in lettuce after washing by process water for 1 min. It is worth noting that the process water was generated by adding 100 mg L^{-1} NaClO or 3.7 mg L^{-1} ClO_2 to water containing certain amount of microorganisms as well as organic matter and remained in constant agitation for 30 min. Daft (1988) reported that trichloromethane was present in fresh lettuce obtained from groceries in the U.S. at a concentration of 30 $\mu\text{g kg}^{-1}$.

For other leafy vegetables, spinach showed the trichloromethane level less than 5 $\mu\text{g kg}^{-1}$ after contacting with 6 mg L^{-1} chlorine for 5 min (Huang & Batterman, 2009). Gómez-López et al. (2013) reported a similar level ($3.9 \pm 0.7 \mu\text{g kg}^{-1}$) of trichloromethane

in baby spinach with 3.8 mg L^{-1} chlorine treatment for 1 min. Additionally, a slightly higher amount of trichloromethane ($6.4 \pm 1.0 \text{ } \mu\text{g kg}^{-1}$) was generated if EO water (whose concentration was 1.9 mg L^{-1} as free chlorine) was used. Furthermore, EO water with 1 g L^{-1} NaCl would generate a much higher amount of trichloromethane at $70.6 \pm 17.3 \text{ } \mu\text{g kg}^{-1}$ in baby spinach. In this case, the active chlorine was around 4.4 mg L^{-1} .

Trichloromethane was detectable in shredded red cabbage; however, the concentration ($2.5 \text{ } \mu\text{g kg}^{-1}$) was below the detection limit of $4 \text{ } \mu\text{g kg}^{-1}$ (Fan & Sokorai, 2015). In raw celery, the trichloromethane level was $14 \text{ } \mu\text{g kg}^{-1}$ (Daft, 1988). COT (2006) detected $<10\text{--}16 \text{ } \mu\text{g kg}^{-1}$ trichloromethane residue in prepared salad.

In terms of non-leafy vegetables, a variety of species such as potatoes, carrots, and radish have been studied. Miyahara et al. (1995) found that in tofu (soybean curd) and moyashi (bean sprout), the trichloromethane levels were at the range of $1.1\text{--}36$ and $0.8\text{--}320 \text{ } \mu\text{g kg}^{-1}$, respectively. Miyahara et al. (1995) interpreted that higher levels in moyashi may result from the production process, where moyashi is produced in high humidity as well as high temperature. So the product must be disinfected with sodium hypochlorite to reduce the bacteria in and on it. Besides, trichloromethane source in soybeans may come from the water used for production, which could be disinfected by chlorination. Huang and Batterman (2009) detected trichloromethane at less than $0.2 \text{ } \mu\text{g kg}^{-1}$ in potato and $1.0\text{--}1.6 \text{ } \mu\text{g kg}^{-1}$ in corn. In the report published by the USFDA (2006), the highest trichloromethane level in black olives was $11.0 \text{ } \mu\text{g kg}^{-1}$ among the tested samples above the detection limit. Daft (1988) reported trichloromethane level in raw green sweet pepper at $31 \text{ } \mu\text{g kg}^{-1}$, and in raw radish at $24 \text{ } \mu\text{g kg}^{-1}$. Carrots washed by warm chlorinated water ($50 \text{ }^{\circ}\text{C}$) formed $2.5 \text{ } \mu\text{g kg}^{-1}$ trichloromethane, whereas carrots

washed by cold chlorinated water formed trace amounts of trichloromethane (Klaiber et al., 2005). Diced onions and salsa were found with approximately 2.8–3.8 and 2.4 $\mu\text{g kg}^{-1}$ of trichloromethane, respectively, although these concentrations were below the detection limit of 4 $\mu\text{g kg}^{-1}$ reported by those authors in their study (Fan & Sokorai, 2015).

The USFDA (2006) determined the trichloromethane residue in a lot of fruits: raw apple, orange, banana, pear, strawberries, sweet cherries, and avocado. Not each individual sample showed trichloromethane detection. But for those detected, tomato and avocado formed the highest concentration (up to 30.0 $\mu\text{g kg}^{-1}$), followed by bananas (up to 20.0 $\mu\text{g kg}^{-1}$), sweet cherries (up to 11.0 $\mu\text{g kg}^{-1}$), and raw pear (up to 10.0 $\mu\text{g kg}^{-1}$). The related detailed information is included in Appendix Table A.1. Fleming-Jones and Smith (2003) also analyzed trichloromethane as one of the volatile organic compounds in various kinds of foods. Up to 15.0 $\mu\text{g kg}^{-1}$ of trichloromethane was detected in avocado, up to 8.0 $\mu\text{g kg}^{-1}$ in banana, and up to 6.0 $\mu\text{g kg}^{-1}$ in orange. From the study of Daft (1988), 10 $\mu\text{g kg}^{-1}$ and 12 $\mu\text{g kg}^{-1}$ of trichloromethane were found in raw tomatoes and avocado, respectively.

The trichloromethane results found in fruit juice are relatively consistent from several recent studies; namely, in the range of from non-detectable (ND) to 10 $\mu\text{g L}^{-1}$ or so. Huang and Batterman (2009) detected 3.9–9.1 $\mu\text{g L}^{-1}$ of trichloromethane in orange flavor concentrated juice and 3.9–4.7 $\mu\text{g L}^{-1}$ in apple flavor concentrated juice, from their screening experiments. The USFDA (2006) found up to 11.0 $\mu\text{g L}^{-1}$ and 12.0 $\mu\text{g L}^{-1}$ CHCl_3 in the orange juice and apple juice, respectively. Reconstituted orange juice showed a little lower CHCl_3 than the bottled or carton one. For fruit juice blend, ND–6.0 $\mu\text{g L}^{-1}$ of trichloromethane was detected. Miyahara et al. (1995) found up to 8.2 $\mu\text{g L}^{-1}$

trichloromethane in juice, which contains water as a main component. However, the authors stated it was not clear whether water was the source of the contaminants. Chang et al. (1988) reported trichloromethane detection in various types of juices including orange, grape, apple, pineapple, and grapefruit juice after chlorine treatment for one week, but the levels were not quantified. From Campillo et al. (2004), 0.9–3.1 $\mu\text{g L}^{-1}$ of trichloromethane was detected in four juices.

2.1.1.2 Bromodichloromethane (CHCl_2Br)

A few studies investigated THMs other than trichloromethane such as CHCl_2Br or CHClBr_2 . No detection of CHCl_2Br was found in baby spinach after 2–4 mg L^{-1} free chlorine washing for 1 min regarding three different disinfectant scenarios (NaOCl , EO water, and EO water + NaCl), whereas CHCl_3 , CHClBr_2 , and CHBr_3 were all present (Gómez-López et al., 2013). Trace amounts of CHCl_2Br was detected in corn and potato ($<0.06 \mu\text{g kg}^{-1}$) and spinach showed slightly higher level of CHCl_2Br ($<0.30 \mu\text{g kg}^{-1}$) (Huang & Batterman, 2009). Up to $7.1 \mu\text{g kg}^{-1}$ of CHCl_2Br was found in tofu and up to $0.5 \mu\text{g kg}^{-1}$ in moyashi (bean sprout) (Miyahara et al., 1995). Raw green sweet pepper, orange, tomato, and strawberries were detected with 14.0, 14.0, 11.0, and $3.0 \mu\text{g kg}^{-1}$ of CHCl_2Br at the highest value (USFDA, 2006). In the same study, apple juice showed the highest concentration of CHCl_2Br (up to $33 \mu\text{g L}^{-1}$), followed by pineapple juice (up to $14 \mu\text{g L}^{-1}$). Reports of CHCl_2Br in several other types of juice are included in Appendix Table A.1.

2.1.1.3 Dibromochloromethane (CHClBr_2)

Only a couple of studies had tried to evaluate CHClBr_2 in fresh produce. Miyahara et al. (1995) reported CHClBr_2 residue in tofu, moyashi (bean sprout), and

juice. Their concentrations were 2.3–7.1, ND–3.6, and ND–1.4 $\mu\text{g kg}^{-1}$, respectively.

Gómez-López et al. (2013) detected 0.7–1.5 $\mu\text{g kg}^{-1}$ of CHClBr_2 in baby spinach after washing by three types of chlorine-based disinfectant, NaOCl , EO water, and EO water + NaCl .

2.1.1.4 Tribromomethane (CHBr_3)

Few studies have conducted experiments of measuring tribromomethane formation potential in fresh produce. Tribromomethane was found at the level of 0.9–1.7 $\mu\text{g kg}^{-1}$ in baby spinach with 2–4 mg L^{-1} chlorine-based treatment for 1 min (Gómez-López et al., 2013).

2.1.1.5 Total THMs

The total THMs is the sum of CHCl_3 , CHCl_2Br , CHClBr_2 , and CHBr_3 . In the COT (2006) statement, the levels of total THMs were comparable to the trichloromethane levels, namely, <10–16 $\mu\text{g kg}^{-1}$ in prepared salads. Gómez-López et al. (2013) found that after being immersed in EO water + NaCl for 1 min, baby spinach showed $73.4 \pm 17.4 \mu\text{g kg}^{-1}$ of total THM formation, which was one order of magnitude higher compared to being treated with NaOCl or EO water alone. No THM was present if the sanitized baby spinach was rinsed with tap water for 1 min. The authors explained that probably THMs were weakly absorbed to the surface of spinach and thus easily removed by rinse water. In contrast, Van Haute et al. (2013) reported no measurable amounts of total THMs (< 6.3 $\mu\text{g kg}^{-1}$) in the lettuce after washing and rinsing. In their study, washing bath was carried out by placing 50 g lettuce into 4 L tap water or standardized process water with 500/1000 mg L^{-1} of COD for 1 min below 7 °C. During the consecutive washing process, chlorine was added to maintain the level of free chlorine at 1 mg L^{-1} .

2.1.2 HAAs

Cardador & Gallego (2012) established the first method to study the genuine presence of nine HAAs in several minimally processed vegetables (MPVs) including carrot, chicory, green pepper, lettuce, spinach, and mixed salad (see Appendix Table A.2). Green pepper seemed to contain the least amount of HAAs in this study. DCAA ($<0.4\text{--}24\ \mu\text{g kg}^{-1}$) and TCAA ($0.4\text{--}26\ \mu\text{g kg}^{-1}$) were present in almost all the samples that showed positive results (23% of the total). However, brominated HAAs such as BCAA, DBAA, and BDCAA were occasionally found and at six times lower concentrations than the chlorinated ones. In order to interpret why HAAs were found in MPV samples, whole vegetables (that were directly collected from the field and without any industrial process) were analyzed as comparison. No HAAs were detected in all of the whole vegetables, suggesting that chlorine solution might be used in the washing step of MPV production. The authors also looked into the stability of these DBPs spiked in iceberg lettuce. It was found that DCAA, TCAA, BCAA, DBAA, and BDCAA remained constant up to 3 days, after which they decreased slightly. In contrast, other compounds like MCAA, MBAA, CDBAA, and TBAA only remained constant up to 36 h. Additionally, the authors employed some home friendly use products to test whether they can help clean MPVs. The rinse with salted tap water showed the best removal rate (70–80% of the total HAAs), followed by tap water and tap water with vinegar (50–60%) and then tap water with sodium hypochlorite (45–55%).

Cardador & Gallego (2015) also determined HAA contents in fruit juices and soft drinks by static head space gas chromatography mass spectrometry (HS-GC-MS). Likewise, DCAA and TCAA were found in all the juice samples and at higher

concentrations, followed by BCAA and MCAA. BDCAA, MBAA, and DBAA were occasionally detected. Other HAA species like MIAA, CDBAA, and TBAA were not present in all the analyzed samples or at levels below the detection limit. Average total HAA levels in nectar juices ($6.7 \mu\text{g L}^{-1}$) were higher than those in reconstituted juices ($4.5 \mu\text{g L}^{-1}$) because of more treated water in their composition. No significant variation was observed among different juice types (apple, grape, orange, peach, etc.). Moreover, different containers (can, cardboard boxes, glass bottles, or PET) had little influence on the total HAA levels regarding the same kind of beverage. Furthermore, the HAA stability in orange juice was tested at room temperature or in a refrigerator. Three chlorinated HAAs (MCAA, DCAA, and TCAA) were almost unaffected for 2–3 months, whereas MBAA, MIAA, and BCAA remained constant for about 4–6 weeks, and the rest of the HAAs were even less stable. Notably, TBAA and CDBAA only remained constant for 2–4 days, after which they were degraded to their corresponding THMs. In addition, another reason for TCAA's presence can be the use as herbicide in fruit growing (McCulloch, 2002).

2.1.3 Other DBPs

The occurrence of other DBPs in produce-based foodstuffs has remained an almost totally uninvestigated area of research. To the author's best knowledge, very few publications can be found that discuss the issue of DBPs other than THMs and HAAs generated in the fresh and fresh-cut produce.

Chang et al. (1988) investigated the interaction of chlorine with a number of fruit juices (orange, grape, apple, pineapple, and grapefruit) and observed that 1,1,3,3-tetrachloropropanone and pentachloropropanone were present in all five fruit juices.

Other types of chloropropanones, dichloroacetonitrile and trichloroacetaldehyde were occasionally detected in these five juices. The authors also tried to elucidate the DBP formation mechanism by discussing the chlorination and decarboxylation of malic acid. The generation of major chlorinated products, could be ascribed to the reactions of chlorine with fruit acids (citric acid or malic acid) primarily and with trace amounts of acetaldehyde and acetone in the juices. While for the minor products, such as dichloroacetonitrile, they were possibly derived from the chlorination of certain amino acids such as aspartic acid. Notwithstanding a much wider diversity of DBPs were reported by Chang et al. (1988) to form in the produce, the main drawback of this study is that these DBP concentrations were not quantified.

N-nitrosamines are typically present at low levels in cooked, smoked and cured meat products, spices, and beer. As to fresh vegetables and fruits, *N*-nitrosodimethylamine (NDMA), *N*-nitrosopiperidine (NPIP), and *N*-nitrosopyrrolidine (NPYR) were not found in them. However, preserved vegetables were detected with a trace level of NDMA (ND=0.1 ppb) (Tricker et al., 1991). Sen et al. (2006) detected 0.086–5.51 ng g⁻¹ of NDMA in various contaminated samples of fruit drinks/juices from a food processing plant, but for those purchased from local retail outlets, NDMA was not detected.

As to inorganic DBPs, COT (2006) reported <6.0 µg kg⁻¹ of bromate and <200 µg kg⁻¹ of chlorite in prepared salads.

2.2 Factors Affecting DBP Levels

Raymer et al. (2000) stated that the types and concentrations of DBPs in food and beverage would depend on three factors: the disinfection process used to produce tap

water, the chemical components of the source water, and the dynamics of the water in the distribution system. But the authors only considered the reasons from the viewpoint of water; that is to say, the DBPs in foodstuffs come from the constituent—disinfected water that already contains DBPs. For DBPs detected in fresh or fresh-cut produce, washing with the disinfectant can be the more significant and direct causation. During this process, disinfectant type and dosage, produce type, contact time, and organic load in wash water play a vital role in affecting DBP levels.

2.2.1 Disinfectant Type & Dosage

Research has found that THM generation from the lettuce juice was linearly correlated well with the free chlorine concentration (Fan & Sokorai, 2015; Shen et al., 2016). Although an extreme condition was adopted, levels of THMs in washed lettuce increased with a higher concentration of NaOCl and longer contact time (López-Gálvez et al., 2010). In the same study, ClO₂ generated far less THMs (actually below detection limit) than NaOCl, but still demonstrated equal efficacy against pathogens.

2.2.2 Organic Load

Organic load is a critical factor to DBP formation. Higher organic loads result in faster chlorine consumption, which leads to less chlorine in contact with the target pathogens, thus lowering the disinfection efficiency and generating more DBPs at the same time. A lot of the studies have confirmed that formation of THMs increases with the increasing chlorine dose and organic load (López-Gálvez et al., 2010; Van Haute et al., 2013), in both wash water and fresh produce. As the washing process goes on, organic matter in the water tends to accumulate with the increasing volume of produce being washed. It has been found that COD and turbidity increased linearly ($R^2 = 0.99$) with the

increasing number of lettuce batch, indicating that organic material leaked out into the chlorine solution, and the leaked material reacted with chlorine to form THMs (Fan & Sokorai, 2015). Likewise, total HAA concentrations would increase with the increasing organic load and the amount of chlorine (Shen et al., 2016).

2.2.3 Storage Time

The relationship between DBP levels and storage time may depend upon different circumstances. For example, contaminants levels in tofu are indifferent to the storage periods. In contrast, trichloromethane levels in juice are related to storage periods (Miyahara et al., 1995). This variation may be caused by the different stability of DBPs.

CHAPTER 3

ANALYTICAL METHODS

3.1 Sample Preparation

Fresh or fresh-cut produce is usually purchased from local grocery stores or supermarkets, transported and stored under refrigerated conditions. Before processing, produce may be peeled, cut, chopped, or shredded. Sometimes certain weight of produce would be homogenized with water in a stomacher for about 2 min to make produce juices. The produce-to-water ratio can make a big difference of the DBP concentration in the final results.

The next step is the simulated disinfection/washing. Prepared produce samples are immersed in water containing different types of disinfectants at varying doses. After several minutes, sodium thiosulfate is added to quench the reaction. Then samples are undergoing future analytical procedure. Typically, washing process can be categorized into two types: 1) one-time event, meaning that studies determined the THM levels after washing produce only once; 2) dynamic change event, which includes repeated supplement of produce (juice) and disinfectant (Fan & Sokorai, 2015; Shen et al., 2016; Van Haute et al., 2013).

3.2 Extraction

In light of the fact that publications are highly focused on THMs and HAAs, analytical methods in this thesis will only cover these two classes of DBPs. The majority of them are modified on the basis of the well-established USEPA Methods. Though these

analytical methods are originally developed for drinking water, they are applicable for produce wash water. Extraction methods that are often used in the literature include purge-and-trap, liquid-liquid extraction, and solid phase extraction.

3.3 Analysis

Some of the studies on produce focused on the detection of DBPs only, while others investigated the occurrence of DBPs along with other types of contaminants. If the DBPs were among multiple groups of contaminants monitored, the analytical methods chosen needed to be capable of measuring multiple classes of chemicals simultaneously, some of which were significantly different from DBPs. In those studies, the data associated with DBPs were less precise or accurate compared to those that specifically focused on DBPs.

Gas chromatography with electron capture detection (GC-ECD) and gas chromatography with mass spectrometry (GC-MS) are two of the most frequently used instrument to determine the DBP concentrations. Methods of selected literature are summarized as follows:

THMs – EPA Method 555.1 (GC-ECD): (Huang & Batterman, 2009), (Shen et al., 2016); HS-GC-ECD: (Klaiber et al., 2005); EPA Method 524.2 (GC-MS): (McNeal et al., 1995)

HAAs – EPA Method 552.3 (GC-ECD) (Shen et al., 2016); HS-GC-MS, (Cardalor & Gallego, 2012; 2015)

Purge-and-trap GC-MS has been used to analyze THM residues in juices and other foods (Fleming-Jones & Smith, 2003; McNeal et al., 1995). Similarly, Campillo et

al. (2004) developed purge-and-trap followed by GC with atomic emission spectrometry (AED) to determine 4 THMs among 10 halogenated VOCs in juices.

Other approaches of analyzing THMs include solid phase micro-extraction (SPME) coupled with GC-MS (Fan et al., 2015), or HS-GC-MS (Gomez-Lopez et al., 2015; Lopez-Galvez et al., 2010; Van Haute et al., 2013).

Free chlorine and COD is typically measured by *N,N*-diethyl-*p*-phenyldiamine (DPD) method and the standard photometric method, respectively (APHA, 1998).

3.4 Recovery & Detection Limit

Recovery and detection limit are two significant factors in evaluating the robustness of the analytical methods. In screening experiments or control groups, standards need to be spiked into the tested samples to calculate the recovery. The recoveries of HAAs were better when leaching and derivatization process was carried out simultaneously than sequentially (Cardador & Gallego, 2012).

Several studies reported the detection limit for THMs was around 1–6.3 ppb (Fan et al., 2015; López-Gálvez et al., 2010; Van Haute et al., 2013). From the recent paper of Shen et al. (2016), detection limits were less than 0.2 ppb for both THMs and HAAs. Moreover, some publications have achieved an even lower detection limit. For instance, McNeal et al. (1995) reported the quantification limits of purge-and-trap GC-MSD method were 0.04–0.05 ppb for CHCl_3 in water, 0.1 ppb for CHBrCl_2 and CHBr_2Cl , and 0.2 ppb for CHBr_3 . Huang & Batterman (2009) found the detection limits for CHCl_3 , CHCl_2Br , CHClBr_2 , and CHBr_3 were 0.1, 0.03, 0.04, and 0.5 ppb, respectively. For the HS-GC-MS method to analyze HAAs proposed by Cardador & Gallego (2012), more

precise detection limit (0.1–2.4 ppb) has been achieved compared with the EPA Method 552.2 or the ultrasonic-assisted leaching method.

3.5 Statistical Analysis

Experiments are usually conducted with several replications so the mean value and standard deviations can be calculated. The majority of the studies have used Pearson product-moment correlation to describe the relation between DBPs and another factor. Besides, Miyahara et al. (1995) applied principal component analysis (PCA) to identify the most significant component or contaminant in food. For PCA results, main contaminants varied with the foods. Trihalomethanes were the main contaminants in tofu and moyashi.

CHAPTER 4

DBPS IN PRODUCE PROCESS WATER

DBPs can be generated not only in the fresh produce, but also in the process water, with much higher concentrations. In addition, the large quantity of water usage in food processing has raised wide concerns in the recent decades. Chapter 4 will discuss the water issue from the viewpoint of food processing, mainly produce processing. To address the problem of DBPs in produce process water, typical treatment techniques for process water and the possibility to reuse the process water will be explored.

4.1 Quantity of Water Usage in Produce Processing

Before taking a look at the DBP levels in process water, a more basic and challenging problem will be discussed first—tremendous water consumption in food processing industry. Water is used for many purposes including cooling and heating, washing and rinsing, sanitation, transport, etc. Table 4.1 shows what percentage water use for food processing accounts for the total freshwater withdrawals in different countries. To better demonstrate the quantity, domestic water use is also presented to make a comparison. However, due to limited studies, data are incomplete to be compared in the same year.

The water consumption for the food processing industry in Australia is close to 215 Mm³ per year, which constitutes 1% of the overall water usage (Wallis et al., 2007). In Canada, the food and beverage industry consumes 6% of the water withdrawn and it is among the largest producers of commercial/industrial waste (Maxime et al., 2006). In Europe, food and drink manufacturing industry takes 8%–15% of overall industrial water

use, which has a share of around 1%–1.8% of total water use (CIAA, 2007). The annual water use of the food industry is 455 Mm³ in Germany, with 5–10 m³ specific wastewater generated averagely for each ton of product (Fähnrich et al., 1998). The total annual water use of the food processing industry is approximately 32 Mm³ in Norway (Stave, 2006). The water consumption for the food and drink industry has been estimated to be 3,000 Mm³ annually in the UK (Cheeseborough, 2000). The actual years when the data were retrieved are shown in parentheses in Table 4.1. Total freshwater withdrawal and domestic water use is from the UNFAO dataset (2015). Moreover, washing and sanitation is responsible for 42% of the total water usage at food processors, which is the dominant category (NCDENR, 2009).

Table 4.1: Water Usage Comparison between Food Processing & Domestic Use

Country	Total freshwater withdrawals ($\times 10^9 \text{ m}^3$) (year)	Water use for food processing (% of total) (year)	Water use for domestic (% of total) (year)
Australia	22.6 (2002)	1.0 (2004)	15.6 (2002)
Canada	42.2 (1996)	6.0 (1996)	12.3 (1996)
Germany	45.2 (1995)	1.0 (1995)	12.8 (1995)
Norway	2.94 (2006)	1.1 (2004)	28.3 (2006)
UK	15.6 (2002)	19.2 (2000)	45.5 (2002)

Food processing plants make use of fresh water resources; in the meantime they generate a huge amount of wastewater that may be discharged to surface water systems with or without treatment. As can be seen from Table 4.2, water consumption and

wastewater generation in each food sub-industry are listed. Manufacturing one ton of produce would consume 2.4–11 m³ clean water and generate 11–23 m³ wastewater. Table 4.3 gives some examples of the average wastewater flow based on the produce type. Processing per ton of asparagus can bring about up to 29,000 gallon of wastewater (NCDENR, 2009).

Table 4.2: Water Consumption & Wastewater Generation in Food Industry
(FDM-BREF, 2006)

Sub-industry	Water consumption (m³/t)	Wastewater generation (m³/t)
Fruit and vegetable	2.4–11	11–23
Meat and poultry	2–20	10–25
Dairy	0.6–60	0.4–60
Fish and seafood	3.3–32	2–40

* /ton of production

Table 4.3: Representative Wastewater Loadings in Produce Processing (NCDENR, 2009)

Products	Minimum flow (1000 gallon/ton)	Mean flow (1000 gallon/ton)	Maximum flow (1000 gallon/ton)
Apple	0.2	2.4	13.0
Berry	1.8	3.5	9.1
Peach	1.4	3.0	6.3
Cauliflower	12.0	17.0	24.0
Tomato	1.1	1.6	2.4
Spinach	3.2	8.8	23.0

4.2 DBP Levels in Produce Process Water

4.2.1 THMs

During the produce washing process, the released organic matter reacts with the chlorine or EO water, generating considerable amounts of THMs. Table 4.4 lists the general DBP levels found in process water. Process water used for washing leafy-vegetables such as lettuce and spinach has been studied extensively, whereas limited studies have been conducted for non-leafy vegetables or fruits. Again, the concentrations are highly dependent on the type of disinfectants and disinfectant application conditions. Comprehensive information related to the studies shown in Table 4.4 is summarized in Appendix Table A.4.

Table 4.4: Ranges of DBP Levels Reported in Produce Processing Water

DBP Type	Food type of processing water	Concentration Range (ppb)	References
CHCl ₃	Leafy Vegetables	ND–858.0	1, 2, 4, 5, 6
	Non-leafy vegetables	ND–32	1, 3
CHCl ₂ Br	Leafy Vegetables	ND–16.3	2, 5, 6
CHClBr ₂		13.6–72.6	2
CHBr ₃		2.6–15.1	
TTHMs		20.79–859.47	2, 5, 6

1: Fan et al., 2016; 2: Gómez-López et al., 2013; 3: Klaiber et al., 2005; 4: López-Gálvez et al., 2010; 5: Shen et al., 2016; 6: Van Haute et al., 2013.

Trichloromethane levels in chlorine solution used for washing lettuce ranged from 155 to 284 µg L⁻¹, and the concentration increased during the first 4 batches of adding lettuce, while almost no increase was found during the 5th and 6th batches (Fan & Sokorai, 2015). Trichloromethane in the water used for rinsing the lettuce was in the

range of 2–4.5 $\mu\text{g L}^{-1}$. In the chlorine solutions that were used to wash diced onions, trichloromethane increased from 0 to 32 $\mu\text{g L}^{-1}$ with the initial chlorine concentration increasing from 0 to 100 mg L^{-1} . Similar to lettuce, further increase in chlorine concentration did not lead to additional increase in the THM level.

Van Haute et al. (2013) evaluated the total THMs in lettuce wash water. The process water was prepared by homogenizing 67 g of butterhead lettuce with 200 mL tap water and further diluting to targeted COD. 27.8 \pm 5.4 $\mu\text{g L}^{-1}$ of total THMs were found in the simulated process water containing 500 mg L^{-1} COD after 1 h continuous washing with chlorine addition. If the process water initially had a COD value around 1,000 mg L^{-1} , the total THM levels could be up to 124.5 \pm 13.4 $\mu\text{g L}^{-1}$, of which most was trichloromethane and the rest was bromodichloromethane (13.4 \pm 2.9 $\mu\text{g L}^{-1}$).

For another lettuce-derived water matrix, 217 \pm 38 $\mu\text{g L}^{-1}$ of trichloromethane was detected in the process wash water treated with 100 mg L^{-1} sodium hypochlorite for 30 min. In contrast, the trichloromethane level was below detection limit ($\leq 5 \mu\text{g L}^{-1}$) in the process water where 3.7 mg L^{-1} aqueous chlorine dioxide was added for the same contact time (López-Gálvez et al., 2010).

Shen et al. (2016) evaluated the dynamic impact of organic load and free chlorine on THM formation. In order to simulate the commercial washing process, aliquots of 60 mL iceberg lettuce juice (100 g lettuce homogenized with 200 mL distilled water) was sequentially added to represent the increasing organic load and sodium hypochlorite was periodically replenished. The initial free chlorine concentration was approximately 80 mg L^{-1} . Samples were collected 1 min after each lettuce juice addition. Throughout the whole process, 20.79–859.47 $\mu\text{g L}^{-1}$ of total THMs were detected after adding 13 rounds of

lettuce juice and chlorine replenishment for twice, in which trichloromethane was the most predominant species generated ($20.12\text{--}858.0\ \mu\text{g L}^{-1}$) and a trace amount of BDCM was found at $0.2\text{--}1.47\ \mu\text{g L}^{-1}$, but no DBCM or tribromomethane was detected.

Gómez-López et al. (2013) reported that NaOCl brought about the highest total THM formation ($194.0\pm29.6\ \mu\text{g L}^{-1}$) in the process water used for washing baby spinach, followed by EO water + NaCl treatment ($125.9\pm15.4\ \mu\text{g L}^{-1}$) and EO water alone ($50.2\pm2.1\ \mu\text{g L}^{-1}$). Four individual THMs also followed the same tendency. Notably, trichloromethane accounted for more than 60% of the total THMs, no matter which disinfectant was used. CHClBr_2 was observed to be the second highest compound generated among all THM types. Appendix Table A.4 shows their detailed concentrations.

Negligible trichloromethane formation was found in cold chlorinated water after washing carrots and up to $0.2\ \mu\text{g L}^{-1}$ was detected in warm chlorinated water (Klaiber et al., 2005). This can be ascribed to the low COD level (less than 10 mg/L) monitored in a comparable processing design (Klaiber et al., 2004). Thus, slight THM formation was expected.

The above studies have demonstrated that considerable levels of THMs can be generated in the water during the produce washing process, because the organic substances can easily leach out from produce and participate in the reaction with disinfectant. Moreover, most of the total THM levels in the produce process water exceeded the USEPA regulatory maximum contaminant level (MCL) ($80\ \mu\text{g L}^{-1}$) of drinking water (EPA, 2010).

4.2.2 HAAs

As reported by Shen et al. (2016), the total HAAs were found at the level of 88–2,103 $\mu\text{g L}^{-1}$ during the dynamic adding process of lettuce juice and NaOCl. The major HAA components included MBAA (19.5–1348.9 $\mu\text{g L}^{-1}$), TBAA (6.7–529.7 $\mu\text{g L}^{-1}$), TCAA (2.3–148.6 $\mu\text{g L}^{-1}$), and CDBAA (36.5–89.2 $\mu\text{g L}^{-1}$), whereas other four HAAs showed very low concentrations: BDCAA (1.4–13.1 $\mu\text{g/L}$), DCAA (0.0–6.8 $\mu\text{g/L}$), DBAA (0.1–5.1 $\mu\text{g/L}$), and MCAA (0.0–1.5 $\mu\text{g/L}$). The relative abundance of HAAs in the processing solution was different from that found in vegetables (Cardador & Gallego, 2012) and fruit juices (Cardador & Gallego, 2015). In vegetables and fruit juices, DCAA and TCAA were the two primary HAAs.

Some studies reported unusual high concentrations (up to ppm level) of THMs or HAAs in the process water (Gómez-López et al., 2014; Gomez-Lopez et al., 2015). This was likely because the produce was homogenized with water by a stomacher and the highly soluble produce juice directly reacted with the disinfectant for a long contact time (60 min or even 90 min). Such stimulated processes are considered as not close to industrial practice, so their reported values are not included in Table 4.4 or Appendix Tables.

4.3 Process Water Reusability

In view of the huge fresh water consumption by food processors, it is of vital importance to enhance the water use efficiency and consider the possibility of water reuse. First, characteristics of the process water should be considered.

Water emitted from food and beverage manufacturing sectors contains a large amount of organic matter such as carbohydrates, proteins, and lipids, and exhibits high variation in pH as well as high nitrogen concentration (Kroyer, 1995). Generally, the

biological oxygen demand (BOD) and COD levels in untreated food processing wastewater can be 10–100 times higher than those in municipal wastewater (FDM-BREF, 2006). Different sub-industries like fruit and vegetable processing, meat processing, fish and seafood processing, and dairy processing may display a diverse range of compositions in the wastewater, as indicated by Kroyer (1995) (see Table 4.5). But in all, they impose heavy burden on the environment. For water in fruit and vegetable processing plants, the major concerns in common are BOD, suspended solids, and residues of pesticides (FDM-BREF, 2006; Kroyer, 1995). Occasionally, high concentrations of inorganic salts, sugars and starches would show up. DBPs were not traditionally considered as pollutants of concerns in the process water due to limited data, but need to be taken into account due to their toxicity.

Another concern of the process water reuse is potential pathogen cross-contamination deriving from continuous input of produce, which brings soil debris and exudate of produce into the wash water system. They can consume a portion of the disinfectant and increase the risk of food-borne disease outbreaks. Thus, assessing the dosage of disinfectant and keeping track of its depletion process is crucial to ensure the safety. In a recent paper by Weng et al. (2016), chlorine demand and chlorine decay kinetics over 90 min were evaluated during the washing of four vegetables (romaine lettuce, iceberg lettuce, carrot and baby spinach). It was found that COD and total organic carbon (TOC) were well correlated with chlorine demand, and these two parameters could be used as the indicators of chlorine demand when establishing a real-time monitoring system for water quality. Furthermore, constituents that are small dissolved molecules (<3400 Da) contributed primarily to chlorine demand based on the high

Table 4.5: Wastewater Characteristics in Different Types of Food Processing

Characteristics	Fruit and Vegetable	Meat	Fish	Dairy
High BOD/COD	Highly variable	✓		✓
High N, P	✗			
Inorganic salts	✓			
pH	Most neutral/alkaline, quickly turn acid on standing			
Bad odor		✓		
Floating scum		✓		
Suspended solids	✓		✓	
Residues of pesticides	✓			
Proteins and oil			✓	

performance liquid chromatography-size exclusion chromatography (HPLC-SEC) results. This information is highly valuable for the development of process water reuse because treatment method can be targeted to the compounds within this range. For instance, to apply membrane filtration with certain molecular weight cutoffs may be an option.

Typically, produce process water treatment techniques are similar to the approaches in domestic wastewater treatment, following the sequence of preliminary – primary – secondary – tertiary/advanced/specific treatment. Casani et al. (2005) reviewed some treatment methods of process water to be used in different types of produce processing. For washing water, settling + filtration or sedimentation was employed.

Blöcher et al. (2002) studied the recycling of process water at a fruit juice production plant by using membrane supported bioreactor and combined nanofiltration/ultraviolet light (NF/UV) technology. After treatment, COD, decreasing from 1,770-6,620 mg/L to less than 5 mg/L, along with other chemical and biological parameters, all met the standards of the German Drinking Water Act. Some studies also applied advanced oxidation processes (AOPs) to remove the organics from fruit and vegetable processing wastewater. Beltran et al. (1997b; 1997a) compared UV, UV/H₂O₂, O₃, O₃/H₂O₂ and O₃/UV to treat the wastewater from a tomato processing plant. The authors found that O₃/UV system achieved the highest removal rate (90%) of COD, and they also recommended studying the feasibility of adding biological treatment after AOP, in this way BOD parameter could be measured. Caudo et al. (2008) used copper-pillared clays (Cu-PILC) catalyzed wet H₂O₂ oxidation to treat the wastewater from citrus juice manufacture (processing oranges, tangerines, and lemons), which showed alkaline pH, low biodegradability (BOD₅/COD=0.05), 40–250 mg L⁻¹ of polyphenolic compounds and 4000–8000 mg L⁻¹ of COD. The results demonstrated that TOC decreased by 50% and the biodegradability index (BOD₅/COD) increased from 0.05 to around 0.3–0.4 after 4 h of reaction. In terms of the wash water intended for disinfection, Gil et al. (2009) proposed a promising water recirculation system within a produce disinfection process. This system, consisting of pre-washing (showering), sanitizing, and optional rinsing, made the water flow oppositely to the movement of the produce. On one hand, the water dropping from the produce in rinsing step could be collected, and go through sanitizing tank so it can be reused in pre-washing step. On the other hand, the water dropping from prewashing step could be recirculated for rinsing after disinfection equipment. In addition,

on-line monitoring devices should be installed to guarantee the water quality such as pH, turbidity, and total coliforms. In this way, wash water can be efficiently and safely reused.

Treated water can be reused for many purposes such as cooling water, cleaning water or boiler make-up water. Before deciding on the options of water reuse techniques to be employed, it is essential to have clear information on where the reclaimed water will be used and the required purity standards accordingly. Apart from that, economic factors can significantly influence the practical application of water reuse in the food industry. On one hand, the increasing costs for fresh water and wastewater discharge may encourage the manufacturer to adopt water reuse (Casani et al., 2005); on the other hand, implementation of water treatment and reuse systems will bring extra installation and maintenance fees, while companies want short pay back times, which may hinder the decision making. The solution, pointed out by Casani et al. (2005), is to calculate and analyze based upon the real costs of water. An in-depth cost analysis was performed by Blöcher et al. (2002) based on the one-year operation of recycling process water. In this case, amortization time was likely to be less than 3 years and annual savings amounted to nearly 90,000 euros provided that the reuse potential was 5 m³/h. In addition to environmental and economic factors, other aspects like legislation and safety issues need to be carefully examined regarding the water reuse.

CHAPTER 5

HEALTH RISKS AND REGULATION OF DBPS

5.1 Estimate of DBP Exposure from Food Consumption

In order to assess the hazard of DBPs detected, daily personal intake through food was estimated by many studies. Based on the comprehensive study by the USFDA published in 2006 (USFDA, 2006), the mean and maximum daily intakes of trichloromethane (TCM) as well as bromodichloromethane (BDCM) from several kinds of produce/juice are calculated and shown in Table 5.1. The calculation was also compared with the estimated daily intake from tap water. It can be concluded that generally the exposure to TCM and BDCM from certain produce is quite low; however, this estimate does not preclude the possibility of significant amounts of DBP intake in selected cases where contamination of food by DBPs may be exacerbated by special conditions. Furthermore, the estimated values in Table 5.1 are also compared with the estimation by Huang (2005), the computed values in this study are nearly one order of magnitude lower than those by Huang (2005). This may be due to the different interpretation of the mean DBP concentrations and use of data from different versions of USFDA reports by the two studies. The estimation by Huang (2005) was based on data from an earlier USFDA report (1999).

Cardador & Gallego (2012) estimated a person might take in 8 μg of HAAs per day by assuming that this person could ingest around 150 g vegetables and the most contaminated salad contained 55 $\mu\text{g kg}^{-1}$ of total HAAs. In comparison, the daily exposure of HAAs via drinking water could be up to 30–50 μg , provided that this

Table 5.1: Estimated Daily Personal Intake (ng/d) of Trichloromethane (TCM) & Bromodichloromethane (BDCM) through Produce and Water

Food	^aConsumption of food (g/d)	^aMean CHCl₃ concentration (ng/g)	^bMean daily intake	^aMax CHCl₃ concentration (ng/g)	^bMax daily intake
Apple (red), raw (w/ peel)	13.91	0.27	3.76	6	83.46
Apple juice, bottled	15.72	0.27	4.24	12	188.64
Avocado, raw	0.59	3.64	2.15	30	17.7
Banana, raw	15.88	0.91	14.45	20	317.6
Black olives	0.37	0.25	0.09	11	4.07
Fruit juice blend (100% juice), canned/bottled	6.07	2.75	16.69	6	36.42
Orange (navel/Valencia), raw	7.01	0.55	3.86	6	42.06
Orange juice, bottled/carton	35.25	5.25	185.06	11	387.75
Orange juice, frozen conc, reconstituted	18.85	1	18.85	8	150.8
Pear, raw (w/ peel)	2.22	0.23	0.51	10	22.2
Strawberries, raw/frozen	2.8	0.12	0.34	3	8.4
Tomato, raw	11.49	1.32	15.17	30	344.7
Sum			265.16		1603.8
Tap water	2000	6.53	13060	53	106000
Food	Consumption of food (g/d)	Mean CHCl₂Br concentration (ng/g)	Mean daily intake	Max CHCl₂Br concentration (ng/g)	Max daily intake
Apple juice, bottled	15.72	0.75	11.79	33	518.76
Orange (navel/Valencia), raw	7.01	0.32	2.24	14	98.14
Orange juice, bottled/carton	35.25	0.75	26.44	3	105.75
Pepper, sweet, green, raw	1.99	0.32	0.64	14	27.86
Pineapple juice, frozen conc, reconstituted	2.15	0.32	0.69	14	30.1
Strawberries, raw/frozen	2.8	0.07	0.20	3	8.4

Table 5.1 (continued)

Tomato, raw	11.49	0.25	2.87	11	126.39
Sum			44.86		915.4
Tap water	2000	1.62	3240	30	60000

^a Data are from USFDA (2006).

^b Calculated values in this study.

person consumes 2 L of tap water every day and the average total HAA concentrations are 15–25 $\mu\text{g L}^{-1}$ (Cardador et al., 2008; Sarrión et al., 2000; Varanusupakul et al., 2007; Wang & Wong, 2005).

In addition, humans can be exposed to HAAs through drinking juices or soft drinks. Cardador & Gallego (2015) estimated that a pack of juice or soft drink contained 1–4 μg HAAs based on the assumption of the volume (0.2–0.33 L) and the average HAA concentration (4.5–12 $\mu\text{g L}^{-1}$ found in this study). If a person took in 2–3 packs of juices or soft drinks, it wouldn't cause significant health risk compared to the established MCL in drinking water.

The World Health Organization (WHO) (2006) evaluated a number of disinfectants and disinfection by-products in the 3rd edition of the Guidelines for Drinking Water Quality. As seen in Table 5.2, tolerable daily intakes (TDI) ($\mu\text{g/kg}$ body weight/day) have been derived for chlorite, chlorate, total chlorine, chloramine, chloroform, bromoform, DBCM, TCAA, MCAA, and chloral hydrate. Note that the basis of how the TDI was formulated can be different. The TDI may give us some ideas about the upper limit of DBPs ingested in an extreme case.

Table 5.2: Tolerable Daily Intakes (TDI) of Some DBPs from the WHO Guidelines

Compounds	TDI ($\mu\text{g/kg}$ body weight/day)
Chlorite	30
Chlorate	30
Chlorine	150
Chloramine	94
Chloroform	15
Bromoform	17.9
DBCM	21.4
TCAA	32.5
MCAA	3.5
Chloral hydrate	4.5

5.2 Toxicity Studies of DBPs

Some studies claimed that the low DBP levels in food do not merit attention, but toxicity results proved some agents to be cytotoxic, genotoxic, or carcinogenic when reaching to the critical concentration. Plewa and Wagner (2009) have conducted a series of experiments to estimate the cytotoxicity and genotoxicity of different classes of DBPs based on the Chinese hamster ovary (CHO) cells. The authors found that the emerging and nitrogen-containing DBPs such as haloacetaldehydes, haloacetamides, halonitromethanes, and haloacetonitriles could be much more toxic than the regulated haloacetic acids and halomethanes. Besides, the toxicity generally follows this order: iodinated > brominated > chlorinated DBPs. Detailed information about toxicological

review of DBPs is available in the WHO guidelines for drinking water quality (WHO, 2006).

As to risk assessment, Huang (2005) calculated cancer risk and non-cancer risks of THMs from ingesting food, beverages and drinking water. The cancer risk of trichloromethane from the food exposure pathway for adults was equal to 3.2×10^{-6} , meaning that there is an additional 3.2 in a million probability of an individual developing a cancer from lifetime exposure to trichloromethane by this exposure pathway. For BDCM, the cancer risk was 0.53×10^{-6} . In risk-based decision making, benchmark values for acceptable risk are typically 10^{-6} to 10^{-4} (Risk & Commission, 1997). Since cancer risk of THMs is within this range, future studies can look into the risks of other DBPs.

Grellier et al. (2015) conducted a critical review of many concepts and methods in terms of evaluating the human health impacts of exposure to DBPs. It was concluded that the majority of the existing studies tended to overestimate the lifetime cancer risk (LECR), had large uncertainties in the data and models, and lacked conclusive evidence of the causation of health outcomes regarding human exposure to DBPs.

The International Agency for Research on Cancer (IARC) has evaluated a number of drinking water disinfectants and contaminants and classified them into different groups (1991, 1999, 2004). As seen in Table 5.3, Group 2B indicates the agent (mixture) is possibly carcinogenic to humans and Group 3 means the agent (mixture) is not classifiable as to their carcinogenicity to humans. It should be clarified that Group 3 doesn't suggest these compounds are not carcinogenic to humans. An agent is classified into this group when the evidence of its carcinogenicity is inadequate in humans as well

as in experimental animals. Hence, more studies are needed to investigate the carcinogenicity of these DBPs.

Table 5.3: DBP Classification Regarding Carcinogenicity

Group 2B	Group 3
CF	BF
BDCM	DBCM
MX	Chloramine
DCAA	TCAA
Potassium bromate	Sodium chlorite
	CH
	HAN ¹

¹ HAN includes BCAN, CAN, DBAN, DCAN, and TCAN.

5.3 Regulation

5.3.1 Regulatory Description for DBPs in food

There are currently no regulated levels of DBPs in food in the U.S. The U.S. allows sanitizing with hypochlorite solutions up to a concentration of 200 mg/L or dichloroisocyanurate up to 100 mg/L with adequate draining (Fleming-Jones & Smith, 2003). Rinsing after sanitization can reduce the DBP levels in fresh produce to some degree (Fan et al., 2015) or even completely to non-detection (Gómez-López et al., 2013). Rinsing is required under the German law, but is not required in the U.S. (Fleming-Jones & Smith, 2003)

The COT (2006) reported that chlorine washes can currently be used for non-organic fruits and vegetables in the United Kingdom (UK) provided that they meet the legal definition of a processing aid. However, some other European countries including Germany, The Netherlands, Switzerland, Belgium, and Denmark have prohibited the use of chlorine in ready-to-use products (Artés et al., 2009; Betts et al., 2005; Rico et al., 2007). Legislation on processing aids has not yet been harmonized in the European Union (EU).

Although chlorine may still be the most commonly used disinfectant so far, future regulatory restrictions are likely to be put in force and will require the development of new alternative disinfectants (Oms-Oliu & Soliva-Fortuny, 2010).

5.3.2 Regulation and Guidelines on DBPs in Drinking Water

The USEPA announced the Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules in 1998 and 2006, respectively, so as to improve the public health protection by reducing the exposure to DBPs (EPA, 2010). The Rules established the maximum residual disinfectant level goals (MRDLGs) and maximum residual disinfectant levels (MRDLs) for chlorine, chloramine and chlorine dioxide; and also established maximum contaminant level goals (MCLGs) and maximum contaminant levels (MCLs) for total THMs (TTHMs), 5 HAAs, chlorite, and bromate (see Table 5.4).

The WHO (2006) suggested different guideline values for DBPs in drinking water (see Table 5.5). For compounds that are both included in the USEPA regulation and WHO guidelines, the former one seems to be stricter with respect to most HAAs and all THMs. Nevertheless, the latter one considers a wider variety of DBP classes such as haloacetonitriles.

Table 5.4: EPA Stage 2 Disinfectants and Disinfection Byproducts Rule

Disinfectant Residual	MRDLG (mg/L)	MRDL (mg/L)	Compliance Based On
Chlorine	4 (as Cl ₂)	4.0 (as Cl ₂)	RAA ¹
Chloramine	4 (as Cl ₂)	4.0 (as Cl ₂)	RAA
Chlorine Dioxide	0.8 (as Cl ₂)	0.8 (as Cl ₂)	Daily Samples
Disinfection Byproducts	MCLG (µg/L)	MCL (µg/L)	Compliance Based On
TTHM		80	LRAA ²
-CF	70		
-BDCM	0		
-DBCM	60		
-BF	0		
5 HAAs		60	LRAA
-MCAA	70		
-DCAA	0		
-TCAA	20		
-BAA	N.A.		
-DBAA	N.A.		
Chlorite	800	1000	Monthly Average
Bromate	0	10	RAA

¹RAA stands for running annual average, of all samples from all monitoring locations across the system.

²LRAA stands for locational running annual average, for each monitoring location in the distribution system.

Table 5.5: WHO Guideline Values for DBPs in Drinking Water

Compounds	Guideline values (µg/L)
CF	300
BDCM	60
BF	100
DBCM	100
MCAA	20
DCAA	50 ^a
TCAA	200
Bromate	10 ^a
Chlorite	700 ^a
Chlorate	700 ^a
Chloral hydrate (trichloroacetaldehyde)	10 ^a
Dichloroacetonitrile	20 ^a
Dibromoacetonitrile	70
Cyanogen chloride	70
2,4,6-Trichlorophenol	200

^a Provisional guideline values.

CHAPETER 6

CONCLUSIONS AND RECCOMENDATIONS

6.1 Conclusions

From all the aspects discussed above, several conclusions can be drawn.

Extensive research has investigated the DBPs resulting from produce washing by sodium hypochlorite, while only a small number of studies have explored other disinfectants like chlorine dioxide or EO water.

DBP levels are strongly affected by the disinfectant type and dosage, organic matter, contact time, and other reaction conditions. Generally, THM and HAA concentrations are found at several to tens of ppb in fresh produce, and can be at several hundreds of ppb in produce process water. The DBP concentration seems to be higher in leafy vegetables (lettuce, spinach) than non-leafy vegetables (carrot, potato), so does in the process water.

The majority of the studies looking for alternative disinfectants are basically from the microbial point of view, i.e., the efficacy of killing pathogenic microorganisms. Only a small portion of them have considered the DBP formation potential.

Published data are quite limited with respect to addressing the various DBP types, and most of them focused on THMs, particularly trichloromethane. Since the emerging DBPs such as haloacetonitriles and haloacetamides have been detected in drinking water, and food processing involves higher organic load as DBP precursors and use of tap water in which some DBPs may already exist, chances are high that the emerging DBPs may be present in food and associated process water.

Most experiments reported in the published studies thus far were conducted in a one-time static way, i.e. measuring the DBP formation in a chlorinated solution under a set of fixed conditions, which ignored the fact that water quality was gradually deteriorated as organic matter was continuously released from the produce to water. More recent studies, including those by Fan & Sokorai (2015) and Shen et al. (2016), simulate commercial practice by sequentially adding produce/juice and chlorine. However, the methods of how these studies wash fresh produce and generate process water are inconsistent and could be unrealistic. Due to the testing inconsistency, the DBP concentrations found within the same type of produce cannot be compared fairly among different studies.

Studies that have shown effective microbial reduction are primarily based on the experimental results but neglected the industrial practical conditions to some degree (Fonseca, 2006; Gil et al., 2009). Furthermore, the lab, pilot, and/or factory scales can influence the sanitizing performance significantly (Beuchat et al., 2004; Sapers, 2001).

6.2 Recommendations

On the basis that chlorine is still the major disinfectant in the food processing industry in the U.S., there appear to be major data gaps in terms of the types and concentrations of DBPs that could be formed in fresh produce and process water. The data is particularly scarce for emerging classes of DBPs other than THMs and HAAs. More research is needed to obtain the information to properly assess the potential risks of DBPs in food. Since chlorine is still widely used in produce processing, research should be conducted to maintain the antimicrobial efficacy but optimize the chlorine dose to ensure microbial safety and control DBP formation across various produce processing

conditions. In order to provide safe and high quality fresh fruits and vegetables, the produce industry needs to develop and implement improved or alternative disinfection strategies.

At the produce processing plants, it may be possible to reduce DBP formation through modifications in the processing procedures. Although cutting followed by chlorine washing is the traditional design for fresh-cut leafy processing plants, Nou and Luo (2010) proposed that washing whole-leaf produce prior to cutting would release less organic substances and consequently enhance the disinfection efficacy by around 1 log unit as well as significantly reduce the potential of microbial cross-contamination.

In addition, the advanced technology and design can be applied in produce washing system. To limit the amount of DBPs generated, filtration steps can be useful to reduce the organic matter during the produce washing process (Shen et al., 2016). Future design of washing and decontamination process can be made up of multiple stages. For instance, produce goes through the pre-wash shower device first to remove the soil dirt or liquid exudate. Then produce can be washed by disinfectants at pre-determined optimal dosage and conditions to balance the effectiveness of pathogen inactivation and minimal generation of the detrimental by-products. Moreover, real-time water quality monitoring systems and water treatment techniques should be incorporated to facilitate the water reuse in food processing.

Furthermore, considering that various agents and methods have been used to simulate the washing process of fresh produce, future research will be needed to develop standardized procedures and validated approaches to evaluate and compare results from different studies meaningfully.

Finally, the data basis of food DBPs for the risk assessment is quite limited and many other types of DBPs, albeit their higher toxicity, are completely neglected. Overall, more research on the DBP occurrence in produce and toxicity evaluation is highly necessary to support proper risk assessment and facilitate development of appropriate regulatory measures and guidance.

APPENDIX A

TABLES OF DBP LEVELS

Table A.1: THMs in Fresh Produce

Compound	Food Type	Concentration ppb ($\mu\text{g kg}^{-1}$ for produce) ($\mu\text{g L}^{-1}$ for juice)	Disinfectant	Disinfectant Dosage (mg L^{-1})	Contact Time	Reference
CHCl_3	Forest fruits juice	1.1 ± 0.1	N.A.	N.A.	N.A.	Campillo et al., 2004
	Lemon juice	2.1 ± 0.2				
	Orange juice	3.0 ± 0.1				
	Pineapple juice	1.0 ± 0.1				
	Apple juice	N.A.	Chlorine	N.A.	~1 week	Chang et al., 1988
	Grape juice					
	Grapefruit juice					
	Orange juice					
	Pineapple juice					
	Prepared salads	<10–16	Possible hypochlorite wash	N.A.	N.A.	COT, 2006
	Avocado, raw	12	N.A.	N.A.	N.A.	Daft, 1988
	Celery, raw	14				
	Lettuce, raw	30				
	Radish, raw	24				
	Sweet pepper, green, raw	31				

Table A.1 (continued)

Tomatoes, raw	10				
Lettuce juice	0–40	Sodium hypochlorite	0–200	5 min	Fan et al., 2015
	~3	Chlorine dioxide			
Lettuce	14–22	Sodium hypochlorite	100	1 min each, six batches	
Lettuce treated, rinsed	8	N.A.	N.A.	N.A.	
Onions	2.8–3.8 ^a	Sodium hypochlorite	0–200	1 min	
Red cabbage	2.5 ^a		100	1 min each, six batches	
Salsa	2.4 ^a				
Avocado, raw	ND–15.0	Possible chlorine use	N.A.	N.A.	Fleming-Jones & Smith, 2003
Banana, raw	ND–8.0				
Orange, raw	ND–6.0				
Baby Spinach (7 °C)	3.9±0.7	Sodium hypochlorite	3.8 (as free Cl ₂)	1 min	Gómez-López et al., 2013
	6.4±1.0	EO Water	1.9 (as free Cl ₂)		
	70.6±17.3	EO Water + 1 g L ⁻¹ NaCl	4.4 (as free Cl ₂)		
Concentrated juice, apple flavor	3.9–4.7 ^b	Chlorine	6	5 min	Huang & Batterman, 2009
Concentrated juice, orange flavor	3.9–9.1 ^b				
Corn	1.0–1.6 ^b				
Potato	<0.2 ^b				
Spinach	<5.0 ^b				
Carrots washed by warm (50 °C) chlorinated water	2.5	Sodium hypochlorite	200	2 min	Klaiber et al., 2005

Table A.1 (continued)

Carrots washed by cold (4 °C) chlorinated water	Trace amounts				
Lettuce washed	<5	Sodium hypochlorite	100	(30) +1 min ^c	López-Gálvez et al., 2010
Lettuce washed and rinsed					
Lettuce washed	<5	Chlorine dioxide	3.7		
Lettuce washed and rinsed					
Juice	ND–8.2	Possible chlorinated water use	N.A.	N.A.	Miyahara et al., 1995
Moyashi (bean sprout)	0.8–320				
Tofu (soybean curd)	1.1–36				
Apple juice	ND-1	N.A.	N.A.	N.A.	McNeal et al., 1995
Apple (red), raw (w/peel)	ND–6.0	N.A.	N.A.	N.A.	USFDA, 2006
Apple juice, bottled	ND–12.0				
Avocado, raw	ND–30.0				
Banana, raw	ND–20.0				
Black olives	ND–11.0				
Cherries, sweet, raw	ND–11.0				
Fruit juice blend (100% juice), canned/bottled	ND–6.0				
Orange (navel/Valencia), raw	ND–6.0				
Orange juice, bottled/carton	ND–11.0				
Orange juice, frozen conc, reconstituted	ND–8.0				
Pear, raw (w/ peel)	ND–10.0				
Strawberries, raw/frozen	ND–3.0				
Tomato, raw	ND–30.0				

Table A.1 (continued)

CHCl ₂ Br	Pineapple juice	2.1 ±0.2	N.A.	N.A.	N.A.	Campillo et al., 2004
	Concentrated juice, apple flavor	3.5–5.5 ^b	Chlorine	6	5 min	Huang & Batterman, 2009
	Concentrated juice, orange flavor	0.8–1.6 ^b				
	Corn	<0.06 ^b				
	Potato	<0.06 ^b				
	Spinach	<0.30 ^b				
	Juice	ND–2.9	Possible chlorinated water use	N.A.	N.A.	Miyahara et al., 1995
	Moyashi (bean sprout)	ND–0.5				
	Tofu (soybean curd)	ND–7.1				
	Apple juice, bottled	ND–33.0	N.A.	N.A.	N.A.	USFDA, 2006
	Orange (navel/Valencia), raw	ND–14.0				
	Orange juice, bottled/carton	ND–3.0				
	Pepper, sweet, green, raw	ND–14.0				
	Pineapple, canned in juice	ND–14.0				
	Strawberries, raw/frozen	ND–3.0				
	Tomato, raw	ND–11.0				
CHClBr ₂	Baby Spinach (7 °C)	1.4 ±0.1	Sodium hypochlorite	3.8 (as free Cl ₂)	1 min	Gómez-López et al., 2013
		0.7 ±0.0	EO Water	1.9 (as free Cl ₂)		
		1.5 ±0.0	EO Water + 1 g L ⁻¹ NaCl	4.4 (as free Cl ₂)		

Table A.1 (continued)

	Juice	ND–1.4	Possible chlorinated water use	N.A.	N.A.	Miyahara et al., 1995
	Moyashi (bean sprout)	ND–3.6				
	Tofu (soybean curd)	2.3–7.1				
CHBr ₃	Apple juice	3.5 ±0.1	N.A.	N.A.	N.A.	Campillo et al., 2004
	Forest fruits juice	2.5 ±0.1				
	Pineapple juice	4.2 ±0.4				
	Baby Spinach (7 °C)	1.5 ±0.2	Sodium hypochlorite	3.8 (as free Cl ₂)	1 min	Gómez-López et al., 2013
		1.0 ±0.1	EO Water	1.9 (as free Cl ₂)		
		1.5 ±0.1	EO Water + 1 g L ⁻¹ NaCl	4.4 (as free Cl ₂)		
Total THMs	Prepared salads	<10–16	Possible hypochlorite wash	N.A.	N.A.	COT, 2006
	Baby Spinach (7 °C)	6.8 ±1.0	Sodium hypochlorite	3.8 (as free Cl ₂)	1 min	Gómez-López et al., 2013
		8.1 ±1.2	EO Water	1.9 (as free Cl ₂)		
		73.4 ±17.4	EO Water + 1 g L ⁻¹ NaCl	4.4 (as free Cl ₂)		
	Lettuce washed and rinsed (7 °C) ^d	< 6.3	Chlorine	1 (as free chlorine)	1 min	Van Haute et al., 2013

^a These values are below the detection limit (4 µg kg⁻¹).

^b These concentrations are calculated from CHCl₃ levels in solution divided by the food concentration in solution.

^c Wash water containing COD=700 mg L⁻¹ contacted with disinfectant for 30 min, and then this process water washed lettuce for 1 min. Rinse took 1 min by tap water.

^d Lettuce was washed by tap water or standardized process water with 500/1000 mg L⁻¹ COD. Tap water was used for rinsing.

Table A.2: HAAs in Fresh Produce

Compound	Food Type	Concentration ppb ($\mu\text{g kg}^{-1}$ for produce) ($\mu\text{g L}^{-1}$ for juice)	Disinfectant Source	Disinfectant Dosage	Contact Time	Reference
DCAA	Carrot	5.8–6.8	Chlorinated Washing	N.A.	N.A.	Cardalor & Gallego, 2012
	Chicory	<0.4				
	Iceberg lettuce	1.3–16				
	Mixed salad	0.4–24				
	Romaine lettuce	2.0–3.8				
	Spinach	ND–17				
	100% mango juice	0.07–0.09	Contamination through cleaning and disinfection equipment	N.A.	N.A.	Cardalor & Gallego, 2015
	100% orange juice	0.06–0.08				
	Apple nectar juice	0.26–6.5	Use of treated water either from distribution network or water disinfected by the food factory			
	Apple reconstituted juice	0.54–4.2				
	Cranberry reconstituted juice	0.90–3.0				
	Grape reconstituted juice	5.2–6.0				
	Grapefruit nectar juice	3.3–4.5				
	Guava nectar juice	8.0–9.0				
	Mix nectar juice	0.19–15				
	Mix reconstituted juice	0.27–9.5				
	Orange nectar juice	1.5–8.7				
	Orange reconstituted juice	ND–12				
	Passion fruit nectar juice	4.3–4.9				
	Peach nectar juice	1.7–1.9				
	Peach reconstituted juice	0.12–1.8				

Table A.2 (continued)

	Pear nectar juice	6.0–6.8				
	Pineapple nectar juice	0.28–6.8				
	Pineapple reconstituted juice	1.6–2.3				
	Prepared Salads	<4.0–32	Possible hypochlorite wash	N.A.	N.A.	COT, 2006
TCAA	Carrot	12–14	Chlorinated Washing	N.A.	N.A.	Cardalor & Gallego, 2012
	Chicory	1.5–1.7				
	Green pepper	0.6–0.8				
	Iceberg lettuce	3.4–19				
	Mixed salad	0.4–26				
	Romaine lettuce	1.8–5.6				
	Spinach	0.4–20				
	100% orange juice	<0.1	Contamination through cleaning and disinfection equipment	N.A.	N.A.	Cardalor & Gallego, 2015
	Apple nectar juice	0.07–3.8	Use of treated water either from distribution network or water disinfected by the food factory			
	Apple reconstituted juice	0.18–1.4				
	Cranberry reconstituted juice	0.17–0.66				
	Grape reconstituted juice	0.87–1.01				
	Grapefruit nectar juice	0.57–1.9				
	Guava nectar juice	1.4–1.6				
Mix nectar juice	ND–5.6					
Mix reconstituted juice	0.08–6.5					
Orange nectar juice	0.18–6.0					
Orange reconstituted juice	0.09–15					

Table A.2 (continued)

	Passion fruit nectar juice	0.59–0.69				
	Peach nectar juice	3.1–3.5				
	Peach reconstituted juice	0.24–1.2				
	Pear nectar juice	2.4–2.8				
	Pineapple nectar juice	0.23–4.5				
	Pineapple reconstituted juice	0.35–0.90				
	Prepared salads	<2.4–51.3	Possible hypochlorite wash	N.A.	N.A.	COT, 2006
BCAA	Carrot	1.1–1.3	Chlorinated Washing	N.A.	N.A.	Cardalor & Gallego, 2012
	Iceberg lettuce	0.4–4.2				
	Mixed salad	ND–3.4				
	Romaine lettuce	ND–0.6				
	Spinach	ND–4.4				
	Apple nectar juice	ND–0.65	Use of treated water either from distribution network or water disinfected by the food factory	N.A.	N.A.	Cardalor & Gallego, 2015
	Apple reconstituted juice	ND–0.26				
	Grapefruit nectar juice	ND–0.54				
	Mix nectar juice	ND–0.65				
	Mix reconstituted juice	ND–1.8				
	Orange nectar juice	ND–2.9				
	Orange reconstituted juice	ND–4.0				
	Pineapple nectar juice	ND–0.66				
	Pineapple reconstituted juice	0.08–0.34				
DBAA	Carrot	0.7–0.9	Chlorinated Washing	N.A.	N.A.	Cardalor & Gallego, 2012
	Iceberg lettuce	ND–1.4				
	Mixed salad	ND–1.5				
	Romaine lettuce	ND–0.8				

Table A.2 (continued)

	Spinach	ND–0.8	Use of treated water either from distribution network or water disinfected by the food factory	N.A.	N.A.	Cardalor & Gallego, 2015
	Mix nectar juice	ND–0.27				
	Orange nectar juice	ND–1.9				
	Pineapple reconstituted juice	ND–0.65				
BDCAA	Carrot	<2	Chlorinated Washing	N.A.	N.A.	Cardalor & Gallego, 2012
	Iceberg lettuce	ND–3.4				
	Mixed salad	ND–5.1				
	Romaine lettuce	ND–2				
	Apple nectar juice	ND–<0.5	Use of treated water either from distribution network or water disinfected by the food factory	N.A.	N.A.	Cardalor & Gallego, 2015
	Mix nectar juice	ND–<0.5				
	Orange nectar juice	ND–1.5				
	Pineapple nectar juice	ND–<0.5				
MCAA	Pineapple reconstituted juice	0.49–0.53	Use of treated water either from distribution network or water disinfected by the food factory	N.A.	N.A.	Cardalor & Gallego, 2015
	Apple nectar juice	ND–1.9				
	Grapefruit nectar juice	ND–0.62				
	Guava nectar juice	<0.5				
	Mix nectar juice	ND–2.0				
	Mix reconstituted juice	1.2–1.8				
	Orange nectar juice	ND–1.8				
	Orange reconstituted juice	ND–4.3				
	Pineapple nectar juice	ND–1.05				

Table A.2 (continued)

	Pineapple reconstituted juice	<0.5–0.68				
MBAA	Mix reconstituted juice	ND–1.04	Use of treated water either from distribution network or water disinfected by the food factory	N.A.	N.A.	Cardalor & Gallego, 2015
	Orange nectar juice	ND–0.68				
	Pineapple nectar juice	ND–<0.5				
	Pineapple reconstituted juice	ND–0.61				

DCAA was not detected in green pepper (Cardador & Gallego, 2012).

TCAA was not detected in 100% mango juice (Cardador & Gallego, 2015).

BCAA was not detected in chicory, green pepper; 100% mango/orange juice; guava/passion fruit/peach/pear nectar juice; cranberry/grape/peach reconstituted juice (Cardador & Gallego, 2012, 2015).

DBAA was not detected in chicory, green pepper; 100% orange/mango juice; apple/grapefruit/guava/passion fruit/peach/pear/pineapple nectar juice; apple/cranberry/grape/mix/orange/peach reconstituted juice (Cardador & Gallego, 2012, 2015).

BDCAA was not detected in chicory, green pepper, spinach; 100% orange/mango juice; grapefruit/guava/passion fruit/peach/pear nectar juice; apple/cranberry/grape/mix/orange/peach reconstituted juice (Cardador & Gallego, 2012, 2015).

MCAA was not detected in 100% mango/orange juice; passion fruit/peach/pear nectar juice; apple/cranberry/grape/peach reconstituted juice (Cardador & Gallego, 2015).

MBAA was not detected in 100% mango/orange juice; apple/grapefruit/guava/mix/passion fruit/peach/pear nectar juice; apple/cranberry/grape/orange/peach reconstituted juice (Cardador & Gallego, 2015).

Table A.3: Other DBPs in Fresh Produce

Compound	Food Type	Concentration ppb ($\mu\text{g kg}^{-1}$ for produce) ($\mu\text{g L}^{-1}$ for juice)	Disinfectant Source	Disinfectant Dosage	Contact Time	Reference
Bromate	Prepared salads	<6.0	Possible hypochlorite wash	N.A.	N.A.	COT, 2006
Chlorite		<200				
Chloropropanone	Grape juice	N.A.	Chlorine	N.A.	~1 week	Chang et al., 1988
1,3- Dichloropropanone	Grapefruit juice					
	Pineapple juice					
1,1,3- Trichloropropanone	Grape juice					
	Grapefruit juice					
	Pineapple juice					
1,1,1,3- Tetrachloropropanone	Grapefruit juice					
	Pineapple juice					
1,1,3,3- Tetrachloropropanone	Apple juice					
	Grape juice					
	Grapefruit juice					
	Orange juice					
	Pineapple juice					
Pentachloropropanone	Apple juice					
	Grape juice					
	Grapefruit juice					
	Orange juice					
	Pineapple juice					
Hexachloropropanone	Grape juice					
	Pineapple juice					
Dichloroacetonitrile	Grapefruit juice					

Table A.3 (continued)

Trichloroacetaldehyde	Orange juice	0.086–5.51	N.A.	N.A.	N.A.	Sen et al., 2006
	Pineapple juice					
	Apple juice					
	Grape juice					
	Grapefruit juice					
	Orange juice					
NDMA	Contaminated fruit drinks or juices					

Table A.4: THMs in Wash Water/Process Water

Compound	Wash Water	Concentration ($\mu\text{g L}^{-1}$)	Disinfectant	Disinfectant Dosage (mg L^{-1})	Contact Time	Reference
CHCl_3	Chlorine solution used to wash cut lettuce	155–284	Chlorine	100	1 min each, 6 batches	Fan et al., 2015
	Chlorine solution used to wash diced onions	0–32	Chlorine	0–100	1 min	
	Rinse water to wash lettuce after chlorine treatment	2–4.5	N.A.	N.A.	N.A.	
	Process water used to wash baby spinach ($7\text{ }^{\circ}\text{C}$) (COD = 474 mg L^{-1})	119.1 ± 21.1	Sodium hypochlorite	3.8 (as free Cl_2)	1 min	Gómez-López et al., 2013
		31.5 ± 2.4	EO Water	1.9 (as free Cl_2)		
		90.8 ± 12.6	EO Water + 1 g L^{-1} NaCl	4.4 (as free Cl_2)		
	Warm ($50\text{ }^{\circ}\text{C}$) chlorinated water used to wash carrots	0.2	Sodium hypochlorite	200	2 min	Klaiber et al., 2005
	Process water used to wash lettuce (COD = 700 mg L^{-1})	217 ± 38	Sodium hypochlorite	100	30 min	López-Gálvez et al., 2010
	Process water used to wash lettuce (COD = 700 mg L^{-1})	<5	Chlorine dioxide	3.7	30 min	
	Process water sequentially added with iceberg lettuce juice (13 rounds) and chlorine replenishment (twice)	20.12–858.0	Sodium hypochlorite	80 (initial)	1 min each, 13 rounds	Shen et al., 2016

Table A.4 (continued)

	Process water used to wash lettuce (7 °C) (COD = 500 mg L ⁻¹)	27.8±5.4	Chlorine	235.8±23.6 (cumulative dose)	1 h	Van Haute et al., 2013
	Process water used to wash lettuce (7 °C) (COD = 1000 mg L ⁻¹)	111.1±17.3		609.0±59.4 (cumulative dose)		
CHCl ₂ Br	Process water used to wash baby spinach (7 °C) (COD = 474 mg L ⁻¹)	9.9±0.3	Sodium hypochlorite	3.8 (as free Cl ₂)	1 min	Gómez-López et al., 2013
		2.1±0.1	EO Water	1.9 (as free Cl ₂)		
		3.9±0.5	EO Water + 1 g L ⁻¹ NaCl	4.4 (as free Cl ₂)		
	Process water sequentially added with iceberg lettuce juice (13 rounds) and chlorine replenishment (twice)	0.2–1.47	Sodium hypochlorite	80 (initial)	1 min each, 13 rounds	Shen et al., 2016
	Process water used to wash lettuce (7 °C) (COD = 500 mg L ⁻¹)	<6.3	Chlorine	235.8±23.6 (cumulative dose)	1 h	Van Haute et al., 2013
	Process water used to wash lettuce (7 °C) (COD = 1000 mg L ⁻¹)	13.4±2.9		609.0±59.4 (cumulative dose)		
CHClBr ₂	Process water used to wash baby spinach (7 °C) (COD = 474 mg L ⁻¹)	54.0±18.6	Sodium hypochlorite	3.8 (as free Cl ₂)	1 min	Gómez-López et al., 2013
		13.9±0.3	EO Water	1.9 (as free Cl ₂)		
		26.2±2.3	EO Water + 1 g L ⁻¹ NaCl	4.4 (as free Cl ₂)		

Table A.4 (continued)

CHBr ₃	Process water used to wash baby spinach (7 °C) (COD = 474 mg L ⁻¹)	11.0±4.1	Sodium hypochlorite	3.8 (as free Cl ₂)	1 min	Gómez-López et al., 2013
		2.7±0.1	EO Water	1.9 (as free Cl ₂)		
		5.0±0.3	EO Water + 1 g L ⁻¹ NaCl	4.4 (as free Cl ₂)		
Total THMs	Process water used to wash baby spinach (7 °C) (COD = 474 mg L ⁻¹)	194.0±29.6	Sodium hypochlorite	3.8 (as free Cl ₂)	1 min	Gómez-López et al., 2013
		50.2±2.1	EO Water	1.9 (as free Cl ₂)		
		125.9±15.4	EO Water + 1 g L ⁻¹ NaCl	4.4 (as free Cl ₂)		
	Process water sequentially added with iceberg lettuce juice (13 rounds) and chlorine replenishment (twice)	20.79–859.47	Sodium hypochlorite	80 (initial)	1 min each, 13 rounds	Shen et al., 2016
	Process water used to wash lettuce (7 °C) (COD = 500 mg L ⁻¹)	27.8±5.4	Chlorine	235.8±23.6 (cumulative dose)	1 h	Van Haute et al., 2013
	Process water used to wash lettuce (7 °C) (COD = 1000 mg L ⁻¹)	124.5±13.4		609.0±59.4 (cumulative dose)		

REFERENCES

- APHA. (1998). *Standard methods for the examination of water and wastewater (20th ed.)* Washington DC: America Public Health Association.
- Artés, F., Gómez, P., Aguayo, E., Escalona, V., & Artés-Hernández, F. (2009). Sustainable sanitation techniques for keeping quality and safety of fresh-cut plant commodities. *Postharvest Biology and Technology*, 51(3), 287-296.
- Artés, F., Gómez, P., Artés-Hernández, F., Aguayo, E., & Escalona, V. (2007). Improved strategies for keeping overall quality of fresh-cut produce. In 746 ed., (pp. 245-258): International Society for Horticultural Science (ISHS), Leuven, Belgium.
- Beltrán, F. J., Encinar, J., & González, J. F. (1997b). Industrial wastewater advanced oxidation. Part 2. Ozone combined with hydrogen peroxide or uv radiation. *Water research*, 31(10), 2415-2428.
- Beltrán, F. J., González, M., & Gonzalez, J. F. (1997a). Industrial wastewater advanced oxidation. Part 1. Uv radiation in the presence and absence of hydrogen peroxide. *Water research*, 31(10), 2405-2414.
- Betts, G., Everis, L., & Jongen, W. (2005). Alternatives to hypochlorite washing systems for the decontamination of fresh fruit and vegetables. *Improving the safety of fresh fruit and vegetables*, 351-372.
- Beuchat, L. R., Adler, B. B., & Lang, M. M. (2004). Efficacy of chlorine and a peroxyacetic acid sanitizer in killing listeria monocytogenes on iceberg and romaine lettuce using simulated commercial processing conditions. *Journal of Food Protection*®, 67(6), 1238-1242.
- Blöcher, C., Noronha, M., Fünfroeken, L., Dorda, J., Mavrov, V., Janke, H., & Chmiel, H. (2002). Recycling of spent process water in the food industry by an integrated process of biological treatment and membrane separation. *Desalination*, 144(1), 143-150.

- Bond, T., Huang, J., Templeton, M. R., & Graham, N. (2011). Occurrence and control of nitrogenous disinfection by-products in drinking water—a review. *Water research*, 45(15), 4341-4354.
- Buzby, J. C., Roberts, T., Lin, C. T. J., & MacDonald, J. M. (1996). Bacterial foodborne disease: Medical costs and productivity losses. In *U.S. Department of Agriculture. Agricultural Economic Report No. 741.* (<http://www.ers.usda.gov/publications/aer-agricultural-economic-report/aer741.aspx> (Last accessed on 04/09/2016).
- Campillo, N., Viñas, P., López-García, I., Aguinaga, N., & Hernández-Córdoba, M. (2004). Purge-and-trap capillary gas chromatography with atomic emission detection for volatile halogenated organic compounds determination in waters and beverages. *Journal of Chromatography A*, 1035(1), 1-8.
- Cardador, M. J., & Gallego, M. (2012). Effect of the chlorinated washing of minimally processed vegetables on the generation of haloacetic acids. *J Agric Food Chem*, 60(29), 7326-7332.
- Cardador, M. J., & Gallego, M. (2015). Haloacetic acids content of fruit juices and soft drinks. *Food Chem*, 173, 685-693.
- Cardador, M. J., Serrano, A., & Gallego, M. (2008). Simultaneous liquid–liquid microextraction/methylation for the determination of haloacetic acids in drinking waters by headspace gas chromatography. *Journal of Chromatography A*, 1209(1), 61-69.
- Casani, S., Rouhany, M., & Knochel, S. (2005). A discussion paper on challenges and limitations to water reuse and hygiene in the food industry. *Water Res*, 39(6), 1134-1146.
- Caudo, S., Genovese, C., Perathoner, S., & Centi, G. (2008). Copper-pillared clays (cupilc) for agro-food wastewater purification with H_2O_2 . *Microporous and mesoporous materials*, 107(1), 46-57.
- Chang, T. L., Streicher, R. P., Zimmer, H., & Munch, J. W. (1988). The interaction of aqueous solutions of chlorine with malic acid, tartaric acid, and various fruit juices. *Analytical Letters*, 21(11), 19.

- Cheeseborough, M. (2000). Waste reduction and minimisation. In *Conference: Waste Reduction for the Third Millennium. EMBRU, Environmental Management and Business Research Unit, EcoTech Centre, Swaffham (UK)*.
- CIAA. (2007). Managing environmental sustainability in the european food and drink industries: Water-conserving the source of life. In). http://www.fooddrinkeurope.eu/documents/brochures/brochure_CIAA_envi.pdf (Accessed on 03/28/2016).
- COT, Committee on Toxicity of Chemicals in Food, Consumer Products, & Environment. (2006). Cot statement on a commercial survey investigating the occurrence of disinfectants and disinfection by-products in prepared salads.
- Daft, J. L. (1988). Rapid determination of fumigant and industrial chemical residues in food. *Journal Association of Official Analytical Chemists*, 71(4), 748-760.
- EPA. (2010). Comprehensive disinfectants and disinfection byproducts rules (stage 1 and stage 2): Quick reference guide.
- Fähnrich, A., Mavrov, V., & Chmiel, H. (1998). Membrane processes for water reuse in the food industry. *Desalination*, 119(1), 213-216.
- Fan, X., & Sokorai, K. J. (2015). Formation of trichloromethane in chlorinated water and fresh-cut produce and as a result of reaction with citric acid. *Postharvest Biology and Technology*, 109, 65-72.
- FAO. (2015). Aquastat main database. Food and agriculture organization of the united nations. In). <http://www.fao.org/nr/water/aquastat/sets/index.stm#main> (Accessed on 12/18/2015).
- FDM-BREF. (2006). Integrated pollution prevention and control, reference document on best available techniques in the food, drink and milk industries In): The European Commission Joint Research Center, Institute for Prospective Technological Studies. http://eippcb.jrc.ec.europa.eu/reference/BREF/fdm_bref_0806.pdf (Accessed on 03/28/2016).
- Fleming-Jones, M. E., & Smith, R. E. (2003). Volatile organic compounds in foods: A five year study. *J Agric Food Chem*, 51(27), 8120-8127.

- Fonseca, J. M. (2006). Postharvest handling and processing: Sources of microorganisms and impact of sanitizing procedures. In *Microbiology of fresh produce*, (pp. 85-120). Washington, DC: ASM Press.
- Gómez-López, V. M., Lannoo, A.-S., Gil, M. I., & Allende, A. (2014). Minimum free chlorine residual level required for the inactivation of escherichia coli o157:H7 and trihalomethane generation during dynamic washing of fresh-cut spinach. *Food Control*, 42, 132-138.
- Gómez-López, V. M., Marín, A., Medina-Martínez, M. S., Gil, M. I., & Allende, A. (2013). Generation of trihalomethanes with chlorine-based sanitizers and impact on microbial, nutritional and sensory quality of baby spinach. *Postharvest Biology and Technology*, 85, 210-217.
- Gil, M. I., Selma, M. V., Lopez-Galvez, F., & Allende, A. (2009). Fresh-cut product sanitation and wash water disinfection: Problems and solutions. *Int J Food Microbiol*, 134(1-2), 37-45.
- Gomez-Lopez, V. M., Gil, M. I., Pupunat, L., & Allende, A. (2015). Cross-contamination of escherichia coli o157:H7 is inhibited by electrolyzed water combined with salt under dynamic conditions of increasing organic matter. *Food Microbiol*, 46, 471-478.
- Grellier, J., Rushton, L., Briggs, D. J., & Nieuwenhuijsen, M. J. (2015). Assessing the human health impacts of exposure to disinfection by-products--a critical review of concepts and methods. *Environ Int*, 78, 61-81.
- Hu, J., Song, H., Addison, J. W., & Karanfil, T. (2010). Halonitromethane formation potentials in drinking waters. *Water research*, 44(1), 105-114.
- Huang, A.-T. (2005). *Formation, fate, and risks of disinfection by-products in foods and beverages*. University of Michigan.
- Huang, A.-T., & Batterman, S. (2009). Formation of trihalomethanes in foods and beverages. *Food Additives and Contaminants*, 26(7), 11.
- Huang, Y.-R., Hung, Y.-C., Hsu, S.-Y., Huang, Y.-W., & Hwang, D.-F. (2008). Application of electrolyzed water in the food industry. *Food Control*, 19(4), 329-345.

- IARC. (1991). Chlorinated drinking-water; chlorination by-products; some other halogenated compounds; cobalt and cobalt compounds. . *IARC Monogr Eval Carcinog Risks Hum*, 52, 1-544.
- IARC. (1999). Some chemicals that cause tumours of the kidney or urinary bladder in rodents and some other substances. *IARC Monogr Eval Carcinog Risks Hum*, 73, 1-674.
- IARC. (2004). Some drinking-water disinfectants and contaminants, including arsenic. *IARC Monogr Eval Carcinog Risks Hum*, 84, 1-512.
- Klaiber, R. G., Baur, S., Magel, L., Hammes, W. P., & Carle, R. (2004). Quality of shredded, packaged carrots as affected by different washing treatments. *Journal of Food Science*, 69(4), SNQ161-SNQ166.
- Klaiber, R. G., Baur, S., Wolf, G., Hammes, W. P., & Carle, R. (2005). Quality of minimally processed carrots as affected by warm water washing and chlorination. *Innovative Food Science & Emerging Technologies*, 6(3), 351-362.
- Krasner, S. W., Weinberg, H. S., Richardson, S. D., Pastor, S. J., Chinn, R., Scrimanti, M. J., Onstad, G. D., & Thruston, A. D. (2006). Occurrence of a new generation of disinfection byproducts. *Environmental science & technology*, 40(23), 7175-7185.
- Kroyer, G. T. (1995). Impact of food processing on the environment an overview. *LWT - Food Science and Technology*, 28(6), 547-552.
- López-Gálvez, F., Allende, A., Truchado, P., Martínez-Sánchez, A., Tudela, J. A., Selma, M. V., & Gil, M. I. (2010). Suitability of aqueous chlorine dioxide versus sodium hypochlorite as an effective sanitizer for preserving quality of fresh-cut lettuce while avoiding by-product formation. *Postharvest Biology and Technology*, 55(1), 53-60.
- Maxime, D., Marcotte, M., & Arcand, Y. (2006). Development of eco-efficiency indicators for the canadian food and beverage industry. *Journal of Cleaner Production*, 14(6-7), 636-648.
- McCulloch, A. (2002). Trichloroacetic acid in the environment. *Chemosphere*, 47(7), 667-686.

- McNeal, T. P., Hollifield, H. C., & Diachenko, G. W. (1995). Survey of trihalomethanes and other volatile chemical contaminants in processed foods by purge-and-trap capillary gas chromatography with mass selective detection. *Journal of AOAC International*, 78(2), 391-397.
- Miyahara, M., Toyoda, M., K., U., Nose, N., & Saito, Y. (1995). Volatile halogenated hydrocarbons in foods. *J Agric Food Chem*, 43(2), 320-326.
- NCDENR. (2009). Water efficiency manual for commercial, industrial, and institutional facilities. In). <http://infohouse.p2ric.org/ref/01/00692.pdf> (Accessed on 03/29/2016): North Carolina Department of Environment and Natural Resources.
- Nou, X., & Luo, Y. (2010). Whole-leaf wash improves chlorine efficacy for microbial reduction and prevents pathogen cross-contamination during fresh-cut lettuce processing. *Journal of Food Science*, 75(5), M283-M290.
- Oms-Oliu, G., & Soliva-Fortuny, R. (2010). 15 future trends in fresh-cut fruit and vegetable processing. *Advances in Fresh-Cut Fruits and Vegetables Processing*, 379.
- Plewa, M. J., Muellner, M. G., Richardson, S. D., Fasano, F., Buettner, K. M., Woo, Y.-T., McKague, A. B., & Wagner, E. D. (2007). Occurrence, synthesis, and mammalian cell cytotoxicity and genotoxicity of haloacetamides: An emerging class of nitrogenous drinking water disinfection byproducts. *Environmental science & technology*, 42(3), 955-961.
- Plewa, M. J., & Wagner, E. D. (2009). Quantitative comparative mammalian cell cytotoxicity and genotoxicity of selected classes of drinking water disinfection by-products [project #3089]. In). http://www.waterrf.org/ExecutiveSummaryLibrary/91249_3089_profile.pdf (Accessed on 04/06/2016).
- Plewa, M. J., Wagner, E. D., Jazwierska, P., Richardson, S. D., Chen, P. H., & McKague, A. B. (2004). Halonitromethane drinking water disinfection byproducts: Chemical characterization and mammalian cell cytotoxicity and genotoxicity. *Environmental science & technology*, 38(1), 62-68.
- Raymer, J. H., Pellizzari, E., Childs, B., Briggs, K., & A., S. J. (2000). Analytical methods for water disinfection byproducts in foods and beverages. *Journal of Exposure Analysis and Environmental Epidemiology*, 10(6), 808-815.

- Rico, D., Mart ín-Diana, A. B., Barat, J. M., & Barry-Ryan, C. (2007). Extending and measuring the quality of fresh-cut fruit and vegetables: A review. *Trends in Food Science & Technology*, 18(7), 373-386.
- Risk, & Commission. (1997). Presidential/congressional commission on risk assessment and risk management. A framework for environmental health risk management, vol. 1 (1997); risk assessment and risk management in regulatory decision-making, vol. 2 (1997). Us government printing office, washington, dc. In).
- Rodgers, S. L., Cash, J. N., Siddiq, M., & Ryser, E. T. (2004). A comparison of different chemical sanitizers for inactivating escherichia coli o157: H7 and listeria monocytogenes in solution and on apples, lettuce, strawberries, and cantaloupe. *Journal of Food Protection*®, 67(4), 721-731.
- Sapers, G. M. (2001). Efficacy of washing and sanitizing methods for disinfection of fresh fruit and vegetable products. *Food Technology and Biotechnology*, 39(4).
- Sarri ón, M., Santos, F., & Galceran, M. (2000). In situ derivatization/solid-phase microextraction for the determination of haloacetic acids in water. *Analytical chemistry*, 72(20), 4865-4873.
- Sen, N. P., Baddoo, P. A., Weber, D., & Boyle, M. (2006). A sensitive and specific method for the determination ofn-nitrosodimethylamine in drinking water and fruit drinks. *International Journal of Environmental Analytical Chemistry*, 56(2), 149-163.
- Seymour, I. J., Campden, & Association, C. F. R. (1999). *Review of current industry practice on fruit and vegetable decontamination*: Campden and Chorleywood Food Research Association.
- Shen, C., Norris, P., Williams, O., Hagan, S., & Li, K. (2016). Generation of chlorine by-products in simulated wash water. *Food Chem*, 190, 97-102.
- Shimizu, Y., & Hurusawa, T. (1992). Antiviral, antibacterial, and antifungal actions of electrolyzed oxidizing water through electrolysis. *Dental J*, 37, 1055-1062.
- Stave, S. E. (2006). Water consumption in food processing and the service industries in norway. In): Statistics Norway/Division for Environmental Statistics.

- Tricker, A. R., Pfundstein, B., Theobald, E., Preussmann, R., & Spiegelhalder, B. (1991). Mean daily intake of volatile n-nitrosamines from foods and beverages in west germany in 1989-1990. *Food and chemical toxicology*, 29(11), 729-732.
- USFDA. (2006). Total diet study - market baskets 1991-3 through 2003-4. In). <http://www.fda.gov/Food/FoodScienceResearch/TotalDietStudy/> (Accessed on 03/06/2016).
- USFDA. (2014). Chapter v. Methods to reduce/eliminate pathogens from produce and fresh-cut produce. Analysis and evaluation of preventive control measures for the control and reduction/elimination of microbial hazards on fresh and fresh-cut produce. . In). <http://www.fda.gov/Food/FoodScienceResearch/SafePracticesforFoodProcesses/ucm090977.htm> (Accessed on 04/06/2016).
- Van Haute, S., Samper, I., Holvoet, K., & Uyttendaele, M. (2013). Physicochemical quality and chemical safety of chlorine as a reconditioning agent and wash water disinfectant for fresh-cut lettuce washing. *Appl Environ Microbiol*, 79(9), 2850-2861.
- Varanusupakul, P., Vora-Adisak, N., & Pulpoka, B. (2007). In situ derivatization and hollow fiber membrane microextraction for gas chromatographic determination of haloacetic acids in water. *Analytica chimica acta*, 598(1), 82-86.
- Venkitanarayanan, K. S., Ezeike, G. O., Hung, Y.-C., & Doyle, M. P. (1999). Efficacy of electrolyzed oxidizing water for inactivating escherichia coli o157: H7, salmonella enteritidis, and listeria monocytogenes. *Appl Environ Microbiol*, 65(9), 4276-4279.
- Wallis, D., Brook, P., & Thompson, C. (2007). Water sustainability in the australian food processing industry. *Australian Food Statistics*.
- Wang, Y., & Wong, P. (2005). Determination of dichloroacetic acid and trichloroacetic acid in drinking water by acidic methanol esterification and headspace gas chromatography. *Water research*, 39(9), 1844-1848.
- Weng, S., Luo, Y., Li, J., Zhou, B., Jacangelo, J. G., & Schwab, K. J. (2016). Assessment and speciation of chlorine demand in fresh-cut produce wash water. *Food Control*, 60, 543-551.

- WHO. (2006). Guidelines for drinking-water quality, first addendum to third edition, volume 1 recommendations. In).
http://www.who.int/water_sanitation_health/dwq/gdwq0506.pdf (Accessed on 04/02/2016).
- Wilcock, A., Pun, M., Khanona, J., & Aung, M. (2004). Consumer attitudes, knowledge and behaviour: A review of food safety issues. *Trends in Food Science & Technology*, 15(2), 56-66.
- Xie, Y. (2003). *Disinfection byproducts in drinking water: Formation, analysis, and control*: CRC press.