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Sorption of trihalomethanes in foods

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ABSTRACT

Trihalomethanes (THMs, namely, $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$) are disinfection by-products that are present in drinking water. These toxic chemicals are also present in meat, dairy products, vegetables, baked goods, beverages and other foods, although information regarding their concentrations and origin is very limited. This study investigates sorption of THMs occurring during rinsing and cooking of foods and the significance of food as an exposure source.

Initial estimates of THM uptake were measured in experiments representing rinsing with tap water at 25 C using nine types of food, and for cooking in tap water at 90 C for fourteen other foods. A subset of foods was then selected for further study over a range of THM concentrations (23.7–118.7 μg/l), temperatures (25 C and 90 C), food concentrations (0.2–1.4, food weight: water weight), and contact times (5–240 min). Data were analyzed using regression and exponential models, and diffusion models were used to help explain the trends of THM uptake.

Among vegetables, sorbed THM concentrations at 25 C were 213 to 774 ng/g for $CHCl_3$, 53 to 609 ng/g for $CHCl_2Br$, and 150–845 ng/g for $CHClBr_2$. Meats at 90 C tended to have higher concentrations, e.g., 870–2634 ng/g for $CHCl_3$. Sorbed concentrations increased with contact time and THM concentration, and decreased with food concentration in rinsing tests (using spinach, iceberg-head lettuce and cauliflower) and cooking tests (using tomato, potato, beef and miso–tofu soup). For most foods, THM uptake was diffusion limited and several hours were needed to approach steady-state levels. Swelling, hydrolysis and other physical and chemical changes in the food can significantly affect sorption. Screening level estimates for $CHCl_3$ exposures, based on experimental results and typical food consumption patterns, show that uptake via foods can dominate that due to direct tap water consumption, suggesting the importance of sorption and the need for further evaluation of THM intake due to foods.

1. Introduction

People routinely use and depend on tap water for rinsing and cooking foods. Most tap water contains low levels of trihalomethanes (THMs), namely, $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$, four toxic compounds that are formed as disinfection byproducts during and following water treatment with chlorine. Based on their molecular weight (MW) and solubility (CambridgeSoft Corporation, 2007; CRC, 1997; US EPA, 2004), $CHCl_3$ and $CHCl_2Br$ are considered weakly hydrophilic, and $CHBr_3$ is hydrophobic. Because foods such as vegetables and meats have both hydrophobic and hydrophilic properties, THMs will demonstrate a variety of sorption behaviors on foods. Thus, THMs can sorb onto foods and enter the dietary exposure pathway. However, we have not identified previous work that has investigated sorption of THMs on foods. This study aims to characterize sorption of THMs on foods. We develop laboratory methods, identify factors that affect sorption, measure sorption of THMs across a variety of foods, and evaluate models that predict uptake on select foods.

2. Background

In general, adsorption depends on adsorbate and adsorbent properties, as well as the local environment, including temperature, pH of the solution, and the concentration of the adsorbate and other components in the solution. In this study, the adsorbates are THMs, and the adsorbents are foods. We briefly review several of the characteristics of vegetables and meats that affect sorption.

Vegetables are composed of complex carbohydrates, fiber, some protein and very little fat (Vieira, 1999a). When heated or cooked, vegetables undergo a number of physical and chemical changes. Heating/cooking may change the membrane structure and cell components, e.g., glycosidic linkages, and denature the cytoplasm and cell membrane which contains the plant protein. As a result, cells cannot retain water and become limp, and cell walls and membranes lose integrity (Fennenma and Tannenbaum, 1996; Vieira, 1999a). Heating generally causes large molecules to absorb water and swell, and

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components of membrane structures (e.g., chlorophyll, lipids, and proteins) become more mobile and more available to participate in chemical reactions (Haard and Chism, 1996). Thermal processing does not just influence membrane structure and disrupt cells, but it may also denature proteins (see below) and alter the interaction of proteins with lipids, water, etc. (Haard and Chism, 1996).

Meats contain fat, protein, soluble non-protein substances, water and enzymes (Lawrie, 1998; Vieira, 1999a). Some fats are polar, e.g., cholesterol in membranes and blood (Coultate, 1989), so the possibility of sorption between fat and THMs is high. Proteins are composed of polyamides that contain both polar and nonpolar moieties. Many studies have indicated that proteins absorb to a greater amount on hydrophobic surfaces than on hydrophilic ones (Elwing et al., 1987; Golander and Kiss, 1988; Van Dulm and Norde, 1983; Wannerberger, 1996). Raje and Pinto (1998) measured the heat of adsorption of protein and showed that protein adsorption is endothermic (Raje and Pinto, 1998). However, Arnebrant et al. (1987) reported that β-lactoglobulin, a whey protein, will depart from its native form and protein sorption increases, if the temperature is higher than its denaturation temperature.

In short, vegetables and meats have both hydrophobic and hydrophilic properties. Because THMs also have hydrophobic and hydrophilic properties, THM will sorb onto foods due to both physical and chemical forces.

3. Study design and methods

In the laboratory, we investigated sorption for two simulated food preparation tasks: rinsing at room temperature (25 °C), and cooking at elevated temperature (90 °C). In initial screening experiments, we investigated sorption of THMs using a large number of solid foods and 'worst case' conditions. Then using foods that showed significant amount of sorption, effects of exposure time, THM concentration, and food concentration were examined. The study design is detailed in the following.

3.1. Sorption experiments

Screening experiments were conducted to select foods that demonstrated a significant degree of sorption at temperatures of 25 and 90 °C. Twenty-three foods were tested using the experimental conditions listed in Table 1. The 'worst case' scenario used high THM concentrations (140, 138, and 163 μg/l for $CHCl_3$, $CHCl_2Br$ and $CHClBr_2$, respectively, at 25 °C; and 147, 124, 111 and 93 μg/l for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$, respectively, at 90 °C), which exceed current drinking water standards (80 μg/l for the sum of the four THMs), and a long exposure (30 min), in order to ensure detection and improve measurement precision. Larger foods were chopped into approximately 1 cm^3 cubes. A 0.5 g quantity of food was placed into a 22 ml vial along, to which was added 5 ml of the THM solution. The vial was then sealed with a Teflon-faced septum, placed on the carousel of an autosampler, equilibrated at 25 or 90 °C for 30 min, and then headspace GC-ECD measurements were performed (described below). Each food type was prepared and tested in duplicate. Blanks used the same experimental protocols as food samples except that foods were not added to the vial.

Four sets of experiments evaluated effects of equilibrium and exposure time, THM concentration, and food concentration using selected foods: iceberg lettuce, cauliflower and spinach at 25 °C; and tomato, potato, beef and miso–tofu soup at 90 °C. Experimental conditions are listed in Table 2. The first set of experiments examined whether equilibrium was achieved, and used exposure times up to 4 h, a much longer period than would normally be used to rinse or cook foods. These tests used 5 ml of a high concentration solution (113–270 μg/l of THMs) and 0.5–1.4 g of food. The second set of experiments simulated rinsing and cooking processes and used short exposure periods, 5–15 and 5–30 min, respectively, similar to many food preparation practices. The third set used spiked THM concentrations ranging from 23.7 to 118.7 μg/l. In the fourth set of experiments, food concentrations were varied. The food concentrations used for lettuce and cauliflower could not be reached for spinach given the low density of spinach leaves (1.4 g leaves could not be covered by 5 ml of water in the 22 ml vial). Also, concentrations of miso–tofu soup differed from those used for tomato, potato and beef, reflecting the recommended soup recipe. All of these experiments followed the same protocols for sample preparation, blanks and THM concentration measurements described earlier.

3.2. Air/water partitioning experiments

Air/water partition coefficients for the different THMs, $K_{A/W}$, representing the ratio of equilibrium concentrations in air and water phases ((ng/ml)/(ng/ml)), were measured in order to calculate sorbed THM concentrations. $K_{A/W}$ was determined at 25 and 90 °C by measuring vapor (head space) concentrations in 22 ml vials containing 5 ml of distilled water (Batterman et al., 2002):

$$K_{A/W} = \frac{C_A}{C_W} = \frac{C_A}{[M_T - C_A \times (22\,\text{ml} - 5\ \ \text{ml})]/\,5\,\text{ml}} \quad (1)$$

where C_A and C_W = equilibrium concentrations in headspace and water phases, respectively (ng/ml), and M_T = total spiked THM mass (593.3 and 237.3 ng of each THM at 25 C; 237.3 ng of each THM at 90 °C). After equilibration, vial headspace concentrations were measured by GC-ECD (described below). These experiments were performed in triplicate, and $K_{A/W}$ was calculated as the average. While $K_{A/W}$ is usually measured at constant temperature and pressure (Connell, 1997), and high solute concentrations (>10 to 20% of the organic phase) can cause $K_{A/W}$ to become concentration-dependent (Chiou, 2002), the low THM concentrations should avoid these issues.

3.3. Sample analysis

THM concentrations in the vial headspace were measured using a headspace autosampler (Tekmar 7000, Cincinnati, Ohio), a gas chromatograph equipped with a linearized electron capture detector (GC/ECD, Varian 3700, Mountain View, CA), a 12-bit data acquisition

Table 1
Experimental conditions for screening experiments at 25 and 90 °C.

Experimental conditions	25 °C (rinsing test)	90 °C (cooking test)
Food type	Spinach, iceberg-head lettuce, leaf lettuce, celery, broccoli, cauliflower, tomato, mushroom, green pepper	Frozen and fresh green beans, frozen and fresh carrots, frozen and fresh corns, lima bean, cabbage, tomato, squash, potato, rice, chicken, beef
Food concentration (food weight (g)/solution (ml)	0.5/5	0.5/5
Sorption temperature (°C)	25	90
Spiked THM concentration (μg/l)	140, 138, 163 for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, respectively	147, 124, 111, 93 for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$, respectively
Exposure time (min)	30	30
Calibration range (μg/l)	1.2–142.4	1.2–142.4