Bull. Environ. Contam. Toxicol. (1987) 39:601-607

Bulletin of Environmental Contamination and Toxicology

Volatile Halocarbon Compounds in Process Water and Processed Foods

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Volatile halocarbon compounds (VHCs) of low molecular weight are among the most abundant man-made industrial chemicals in the United States (Chemical and Engineering News 1985). Because of the physical properties of these compounds, in particular their high volatility, they are ubiquitous environmental contaminants. The Environmental Protection Agency (EPA) has detected numerous VHCs in groundwater and finished drinking water. The most frequently detected VHCs include chloroform, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, bromodichloromethane, and carbon tetrachloride. Many of the contamination incidents cited by EPA result from industrial disposal of waste solvents into waterways, lagoons, and landfills. Additionally, several VHCs have been found to be carcinogenic and/or mutagenic (Simmon and Tardiff 1978).

In response to these findings, EPA has proposed maximum contamination levels (MCLs) for VHCs in finished drinking water. These proposed MCLs are standards based on potential carcinogenicity and/or chronic toxicity data as well as available analytical methods for the identification and quantitation of the VHCs in water. Current proposed MCLs for these compounds are as follows: trichloroethylene, 5 µg/L; perchloroethylene, 5 µg/L; 1,1,1-trichloroethylene, 200 µg/L. Total trihalomethanes (chloroform + bromodichloromethane + chlorodibromomethane + bromoform) have an established MCL of 100 µg/L.

The Food and Drug Administration's (FDA's) Division of Contaminants Chemistry, as well as other laboratories, have detected VHCs in foods (Entz et al. 1982; Page and Charbonneau 1977; Page and Charbonneau 1978). These findings of VHCs in foods, coupled with their frequent detection in groundwaters, suggested that food contamination by VHCs could be occurring via polluted process waters. The objectives of this investigation were to determine if VHC contamination of food through contact with contaminated process water was widespread, and to ascertain the levels of contamination. The problem was addressed by collecting and analyzing process water and foods from processing plants situated in areas where contamination of the process water was most probable.

Recent data from EPA were used to select food processing plants most likely to use VHC-contaminated process water. The plants fell into two categories: (A) those with the potential to use contaminated municipal water supplies, as identified by the EPA Groundwater Supply Survey (1982); and (B) those located near hazardous waste dump sites (listed on EPA's National Priorities List (1984)) where VHCs have reportedly been leaching into groundwater. Additionally, processing plants were chosen for study only if they produced a high-fat content food that came in contact with water during processing, or produced a product that contained a high percentage of added water. These two criteria assured the highest probability of detectable levels of VHCs in the finished food product.

Findings are reported here in process water and food product analysis from 15 food processing plants located in 9 different states (CA, FL, IL, MA, MI, NY, OH, PA, WI), representing a total of 39 food products.

MATERIALS AND METHODS

Table 1 lists the food processing plants sampled, the types of food product examined, whether the plant is located near a toxic waste dump site or in a municipality suspected of using contaminated water, and the type of treatment to which the process water had been subjected. At each site visited, one sample was collected, consisting of three 40-mL vials of process water collected from the water line before direct contact with the processed foods, and three retail packages of each product type produced at the plant. Additionally, background data on the process water were collected. This information included the type of water used (well or municipal), the type of water treatment both outside the plant and within, and the results of any previous trace organic analysis of the water.

Waters for VHC analysis were collected in 40-mL glass vials with Teflon-lined butyl rubber septa. Water was obtained from a faucet or feed line after thorough flushing by running for 2-3 min before collection. The vials were overfilled to prevent air bubble (headspace) formation in the vial. Each portion of water was sealed in a contaminant-free bag and stored on ice for immediate overnight shipping. Processed foods were collected off the packaging line, placed in individual contaminant-free bags and, if possible, stored on dry ice for shipping. If the food was not amenable to freezing (e.g., soda), it was stored and shipped on ice.

VHCs in water and foods were determined by headspace capillary gas chromatography, as reported by Entz and Hollifield (1982). All materials collected were tested for chloroform, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, bromodichloromethane, and perchloroethylene. Headspace gas chromatography experiments were carried out on a Perkin-Elmer Sigma 2000 gas chromatograph coupled with a Perkin-Elmer HS-100 automatic headspace sampler. The gas chromatograph was fitted with a 30 m x 0.32 mm (i.d.) DB-5 capillary column, 1.0 µm film thickness (J&W Scientific, Inc.). Headspace conditions were as follows: 30-min sample vial thermostating time at 60°C for foods, and 20-min thermostating time for waters (optimum thermostating times were determined experimentally); 5-s injection time; transfer line temperature of 90°C; injection split ratio of 5:1. The GC conditions were follows: He carrier gas linear velocity of 32 cm/s; ^{63}Ni electron capture detector at 300°C using 28 mL/min 95-5% argon/methane makeup gas. Upon injection, the GC oven program was initiated. The gas chromatograph was programmed to hold at 40°C for 11 min, then increased to 130°C at 20°C/min.

Quantitative results were obtained by using one of two different methods, depending on the nature of the test material. All materials were analyzed in triplicate. Waters were quantitated by using an external standard curve. Aqueous standards were prepared by adding 1-5 µL of a methanolic VHC mixed standard to 2 mL of Milli-Q (Millipore, Inc.) filtered distilled water previously sparged with He gas. Calibration curves covered the range 1-50 ng/g for each component. Actual waters (2 mL) were removed from the 40-mL sample vial by using a 5-mL gas-tight syringe, and were transferred into the headspace vial. Foods (six 2-g portions) were tested by the method of standard additions, as reported by Entz and Hollifield (1982).

TABLE 1. Food processing plant information[1]

Plant code/location		Commodities produced	Category	Process water	Water treatment[2]
1	MI	Cheese	B	Municipal	1,2,3
2	CA	Soda	B	Municipal	1,8,4,9
3	CA	Soda	B	Municipal	1,4
4	PA	Bakery goods	B	Municipal	1
5	PA	Drinks	B	Well	No treatment
6	PA	Ice cream	A	Municipal	1
7	PA	Soda	A	Municipal	1,4,5,6
8	NY	Cheese	A	Municipal	1
9	NY	Bakery goods	B	Municipal	1
10	IL	Cheese	A	Municipal & well	1
11	MA	Cheese	B	Municipal	1
12	WI	Soda	A	Municipal	1
13	OH	Soda	A	Well	1,4,5,7
14	FL	Ice cream	B	Municipal	1
15	FL	Ice cream	B	Municipal	1

[1] Category A: Potentially contaminated municipal water.
Category B: Potentially contaminated water due to proximity of hazardous waste dump site (NPL).

[2] Water treatment:
1 = Chlorination by municipality.
2 = Aeration - in plant.
3 = Filtration - in plant.
4 = Charcoal filtration - in plant.
5 = Flocculation - in plant.
6 = Sand filtration - in plant.
7 = $FeSO_4/CaCl_2$/lime.
8 = Superchlorination - in plant.
9 = Millipore filtration - in plant.

RESULTS AND DISCUSSION

Table 2 lists the findings from the determination of VHCs in process waters and food commodities collected at the 15 food processing plants. Following is a summary of findings on a compound-by-compound basis:

(1) Chloroform. Detected in some process waters (6 of 15) at levels ranging from <1 to 57 ppb. Detected in some food products (14 of 39) at levels ranging from <1 to 31 ppb.

(2) 1,1,1-Trichloroethane. Found in only three process waters at very low levels (<1, 2, and 4.3 ppb), but not found in the associated food products. Found in nine food commodities at levels ranging from 1 to 37 ppb.

(3) Carbon tetrachloride. Not found in process water or foods.

(4) Trichloroethylene. Found in three process waters at levels ranging from 3 to 7.8 ppb. Not found in any food products.

(5) Bromodichloromethane. Found in seven process waters at levels ranging from <1 to 14 ppb. Found in six food commodities as levels ranging from <1 to 2.3 ppb.

(6) Perchloroethylene. Found in two waters at very low levels, <1 and 1.3 ppb. Not found in any foods.

Several general comments about the data include the following:

(1) Only low levels of VHCs (<<50 ppb) were seen in any process waters except two from Florida, which contained about 60 ppb of chloroform and about 14 ppb of bromodichloromethane. Both chloroform and bromodichloromethane are recognized by-products from the chlorination of natural waters (Rook 1974), the relative levels of which are a function of chlorine dose and salinity of the water supply (Helz et al. 1985). Note that these levels do not exceed the 100-ppb MCL established by EPA for total trihalomethanes. (2) In almost all cases, VHCs detected in process water did not appear in the finished food product at the 1-ppb level or above. Examples of this are seen in foods from Plant 6, where 7.8 ppb of trichloroethylene and 1.3 ppb of perchloroethylene were found in the process water, yet neither was found in the food commodity (sherbet).

In three instances, low levels of trichloroethylene were found in process water (3.1, 3.3, and 7.8 ppb in Plants 5, 6, and 1, respectively), yet none was detected in the food products. There are several possible reasons for this observation, including lack of significant partitioning into the food (in the case where a food is being washed), and volatilization loss of the VHCs when the water is mixed with the food product. (3) In only one case (Plant 6) was a VHC detected in the process water at a level exceeding the EPA-proposed MCL. In this case, 7.8 ppb trichloroethylene was found in the process water and none was

TABLE 2. VHCs in processed foods and process waters[1]

Plant No.	Commodity	Concentration, ng/g					
		$CHCl_3$	MC	CCl_4	TCE	$CHBrCl_2$	PCE
1	Process water	ND	ND	ND	3.3	2.2	ND
	Whey cream	ND	ND	ND	ND	ND	ND
	Longhorn cheese	ND	ND	ND	ND	ND	ND
2	Process water	TR	ND	ND	ND	ND	ND
	Cola soda	ND	ND	ND	ND	ND	ND
	Tonic water	ND	ND	ND	ND	ND	ND
	Lemon soda	ND	ND	ND	ND	ND	ND
3	Process water	ND	ND	ND	ND	ND	ND
	Cola soda	ND	ND	ND	ND	ND	ND
	Orange soda	ND	ND	ND	ND	ND	ND
	Lemonade	ND	ND	ND	ND	ND	ND
4	Process water	ND	ND	ND	ND	ND	ND
	Cream cupcakes	ND	ND	ND	ND	ND	ND
	Chocolate cupcakes	ND	ND	ND	ND	ND	ND
5	Process water	ND	2.0	ND	3.0	ND	TR
	Fruit drink	ND	ND	ND	ND	ND	ND
6	Process water	ND	4.3	ND	7.8	ND	1.3
	Orange sherbert	ND	ND	ND	ND	ND	ND
7	Process water	4.6	ND	ND	ND	ND	ND
	Ginger-ale soda	2.3	ND	ND	ND	2.3	ND
	Sparkling soda	15.6	ND	ND	ND	1.2	ND
	Cola soda	12.3	ND	ND	ND	1.2	ND
8	Process water	7.0	ND	ND	ND	8.3	ND
	Ricotta cheese	ND	ND	ND	ND	ND	ND
	Mozarella cheese	ND	ND	ND	ND	ND	ND
9	Process water	ND	ND	ND	ND	ND	ND
	Whey	TR	ND	ND	ND	ND	ND
	Bakers cheese	2.4	1.3	ND	ND	ND	ND
	Cottage cheese	ND	6.4	ND	ND	ND	ND
10	Process water	5.1	ND	ND	ND	3.0	ND
	Ricotta cheese	10.9	3.0	ND	ND	ND	ND
	Mozzarella (whole milk)	7.0	ND	ND	ND	ND	ND
	Mozzarella (skim milk)	6.5	1.2	ND	ND	ND	ND
11	Process water	ND	ND	ND	ND	TR	ND
	Lemon-lime soda	ND	ND	ND	ND	ND	ND
	Lemon soda	ND	ND	ND	ND	ND	ND
	Cola soda	ND	ND	ND	ND	ND	ND
12	Process water	ND	ND	ND	ND	ND	ND
	Cola soda	ND	ND	ND	ND	ND	ND
	Cherry soda	ND	ND	ND	ND	ND	ND
	Root beer	ND	ND	ND	ND	ND	ND
13	Process water	ND	ND	ND	ND	TR	ND
	Coffee lightener	ND	ND	ND	ND	ND	ND
	Whipped topping	ND	ND	ND	ND	ND	ND
14	Process water	57	TR	ND	ND	14.1	ND
	Vanilla ice cream	14.2	10.6	ND	ND	ND	ND
	Chocolate ice cream	19.2	30.6	ND	ND	ND	ND
	Butter pecan ice cream	31.2	37.3	ND	ND	ND	ND
15	Process water	15.7	ND	ND	ND	8.3	ND
	Vanilla ice cream	15.5	2.7	ND	ND	2.3	ND
	Chocolate ice cream	4.6	ND	ND	ND	0.6	ND
	Butter pecan ice cream	5.7	9.5	ND	ND	1.1	ND

[1] ND = <1 ng/g; TR = trace.
$CHCl_3$ = chloroform; MC = 1,1,1-trichloroethane; CCl_4 = carbon tetrachloride; TCE = trichloroethylene; $CHBrCl_2$ = bromodichloromethane; PCE = perchloroethylene.

found in the food product at Plant 6. In all other cases, when VHCs were found in a plant's process water, the concentrations were well below the proposed MCL. In the few positive findings of VHCs in foods, the levels were quite low, between 1 and 30 ppb of total VHCs. (4) 1,1,1-Trichloroethane was detected in several food commodities at the 1-37 ppb level, yet none was found in the process water (Plants 10, 11, and 15). This suggests an alternative mechanism of contamination. 1,1,1-Trichloroethane has numerous industrial uses, such as a cleaning solvent and a glue solvent. Possible contamination routes include air contact from fugitive emissions of cleaning solvent and/or contamination of the food product from the packaging process, especially if the packaging includes sealing retail packages with a 1,1,1-trichloroethane-based glue.

The information collected by FDA inspectors revealed that many food processors or municipal water suppliers in the areas sampled are aware of the potential for process water contamination and in some cases perform routine analysis of waters for volatile organic compounds. Several processing plants also treat process water within the plant to remove or minimize total organics and indirectly remove volatile compounds that may be dissolved in the water.

This study is far from comprehensive and does not offer a statistically valid representation of all food processing facilities in the U.S. Indeed, the sites chosen for study were selected on a "worst-case" basis: plants located in areas with known or suspected groundwater contamination and/or in areas where the municipal water was of dubious quality. These sites were selected in this fashion because of the realities of groundwater contamination in this country; incidents of groundwater contamination are not geographically distributed in a uniform fashion. Rather, they are localized problems, in areas where industrialization is heavy and where waste chemical dump sites are situated.

It is reassuring that only occasional, low levels of VHCs were found in process water and foods collected from plants located in areas where VHC contamination is probable. This reassurance must be viewed in light of the fact that groundwater contamination in most of the geographic areas studied had been known for several years, allowing time for municipalities and industries to rectify or minimize the problem.

Perhaps the greatest potential for gross food contamination by industrial chemicals (including VHCs) via polluted process waters is in areas where groundwater contamination is newly discovered or unknown.

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Received January 11, 1987; accepted July 8, 1987.