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Halogenated Volatile Organic Compounds from the Use of Chlorine-Bleach-Containing Household Products

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Sodium hypochlorite (NaOCl) and many organic chemicals contained in household cleaning products may react to generate halogenated volatile organic compounds (VOCs). Halogenated VOC emissions from eight different chlorine bleach containing household products (pure and diluted) were investigated by headspace experiments. Chloroform and carbon tetrachloride were the leading compounds along with several halogenated compounds in the headspace of chlorine bleach products. One of the most surprising results was the presence of carbon tetrachloride (a probable human carcinogen and a powerful greenhouse gas that was banned for household use by the U.S. Food and Drug Administration) in very high concentrations (up to 101 mg m⁻³). By mixing surfactants or soap with NaOCl, it was shown that the formation of carbon tetrachloride and several other halogenated VOCs is possible. In addition to quantitatively determined halogenated VOCs ($n = 15$), several nitrogen-containing ($n = 4$), chlorinated ($n = 10$), oxygenated compounds ($n = 22$), and hydrocarbons ($n = 14$) were identified in the headspace of bleach products. Among these, 1,1-dichlorobutane and 2-chloro-2-nitropropane were the most abundant chlorinated VOCs, whereas trichloronitromethane and hexachloroethane were the most frequently detected ones. Indoor air halogenated VOC concentrations resulting from the use of four selected household products were also measured before, during, and 30 min after bathroom, kitchen, and floor cleaning applications. Chloroform (2.9–24.6 $\mu\text{g m}^{-3}$) and carbon tetrachloride (0.25–459 $\mu\text{g m}^{-3}$) concentrations significantly increased during the use of bleach containing products. During/ before concentration ratios ranged between 8 and 52 (25 \pm 14, average \pm SD) for chloroform and 1–1170 (146 \pm 367, average \pm SD) for carbon tetrachloride, respectively. These results indicated that the bleach use can be important in terms of inhalation exposure to carbon tetrachloride, chloroform and several other halogenated VOCs.

Introduction

The use of household cleaning agents and air fresheners in buildings has raised significant concern since building occupants and cleaning personnel are exposed to various air pollutants that many of them are recognized as carcinogens, reproductive toxicants, or irritants (1, 2). Furthermore, the

chemicals emitted from the use of cleaning agents and air fresheners may react with other air pollutants to yield potentially harmful secondary pollutants (2). For example, terpenes can react rapidly with ozone in indoor air generating many secondary gaseous pollutants (i.e., formaldehyde, acetone) and fine particles (2–4).

Another group of indoor air pollutants that has attracted significant attention are the disinfection byproducts (DBPs) (i.e., trihalomethanes, halogenated acetic acids, halo ketones) (5, 6). Ingestion, dermal, and inhalation exposure to DBPs may occur via tap water or association with swimming pool water. DBPs are formed in drinking water treatment plants or in swimming pools as a result of the reactions between the natural organic matter in water and the chemicals added as disinfectants (i.e., chlorine) (7). Recently, it was suggested that the chemicals used in cosmetics and sun screens may also be precursors of DBPs because they can react with the free chlorine in pool water (5). Triclosan, a widely used antibacterial agent, found in many personal hygiene products, reacts readily with free chlorine in tap water producing chlorophenols and chloroform (8). It was suggested that the exposure to resulting chloroform could be significant (8).

A number of household cleaning products (bleaches, mildew stain removers, toilet cleaners, cleaning sprays, gels, and scouring powders) contain sodium hypochlorite (NaOCl, ~5%). NaOCl may be the only active ingredient or it may be accompanied by many other chemicals (surfactants, fragrances, NaCl, sodium silicate, sodium hydroxide, antioxidants, and antifoaming agents) (9). As stated in the NaOCl-containing cleaning-product labels, the main concern associated with their use seems to be mixing them with other cleaning products that can generate hazardous fumes. The mixing of bleach with ammonia-based cleaners results in formation of chloramines (NH₂Cl and NHCl₂), whereas mixing with an acid-based cleaner will cause chlorine gas (Cl₂) release (2).

Previous work has raised a very important question, “Do chlorinated byproducts form when bleach-containing cleaning products react with organic matter present on dirty surfaces?” Nazaroff and Weschler (2) have pointed out that the bleach used in laundry applications and use of some other chlorine bleach containing products (i.e., scouring powder) may release chloroform. A recent study has also indicated that chloroform is formed as a result of the use of hypochlorite containing detergents in dishwashers (10). Similar to the reactions of free chlorine with the natural organic matter in drinking water or with the chemicals in cosmetics that can generate DBPs, chlorinated byproducts may also form as a result of the reactions between chlorine and organic matter on surfaces being cleaned with bleach products. However, this probability has been overlooked and the main concern associated with the bleach use has been the release of Cl₂ and chloramines as a result of inappropriate mixing of bleach with other cleaning agents.

NaOCl is generally accompanied by many other chemicals in commercial products. Another important question is “Do the hypochlorite and, the organic product ingredients (i.e., surfactants, fragrances, and other compounds) react to generate chlorinated byproducts?” There has been no previous study investigating this possibility. NaOH is generally added into bleach containing products as pH adjuster and stabilizer. Also, some proprietary stabilizers are added into these products to minimize the reaction of hypochlorite with the organic constituents. However, it is not known if the stabilizers and pH adjustment can be 100% effective to prevent hypochlorite-surfactant reactions. Considering the

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TABLE 1. Characteristics of the Commercial Products and the Mixtures Prepared in the Laboratory

	type	content	TOC ^c	TN ^d
commercial products				
bleach 1	thick liquid	NaOCl, NaOH, nonionic surfactant, soap, fragrance	2.1	699
bleach 2	thick liquid	NaOCl, NaOH, nonionic surfactant, cationic surfactant, soap, fragrance	2.7	485
bleach 3	gel	NaOCl, NaOH, anionic surfactant, fragrance	2.0	nd
bleach 4	liquid	NaOCl, fragrance	0.5	nd
bleach 5	liquid	NaOCl	0.3	nd
bleach 6	thick liquid	NaOCl, NaOH, anionic surfactant, fragrance	1.5	582
bleach 7	thick liquid	NaOCl, anionic surfactant, nonionic surfactant, fragrance	1.8	591
bleach 8	liquid-spray	NaOCl, NaOH, anionic surfactant, fragrance	2.0	nd
laboratory-prepared mixtures ^b				
mixture 1		NaOCl, deionized water, anionic surfactant (in dishwashing detergent)	3.8	378
mixture 2		NaOCl, deionized water, anionic surfactant (in hand washing liquid)	2.9	54
mixture 3		NaOCl, deionized water, soap	4.5	nd
mixture 1A		NaOCl, NaOH, anionic surfactant (in dishwashing detergent)	3.8	378
mixture 2A		NaOCl, NaOH, anionic surfactant (in hand washing liquid)	2.9	54
mixture 3A		NaOCl, NaOH, soap	4.5	nd

^a All components <5% by wt, produced by Unilever (bleach 1, 2, 3, and 8), Procter & Gamble (bleach 4 and 5), generic brands produced by a local company, Gursu Water Chemicals and Devices Inc., Antalya, Turkey (bleach 6 and 7). ^b Equal volumes of all components, the concentration of NaOCl and NaOH solutions was 0.67 M. ^c Total organic carbon (% by wt). ^d Total nitrogen (mg L⁻¹); nd, not detected.

relatively long contact time from production to use (several days to months), hypochlorite-surfactant reactions are possible and chlorine bleach containing cleaning products may contain significant amounts of chlorinated organics. The objectives of the present study was to investigate (1) the presence of halogenated VOCs in different chlorine bleach containing household products (in pure and diluted forms) and their emission characteristics (2) to determine the indoor air halogenated VOC concentrations resulting from the use of selected household products.

Materials and Methods

Headspace experiments and indoor air concentration measurements were conducted to characterize the VOCs from bleach containing products. All the experiments were run in duplicate.

Headspace Experiments. Headspace experiments were conducted to characterize the VOC contents and emissions of the commercial bleach products and laboratory prepared mixtures.

Commercial Products. The definitions and compositions (declared by the manufacturers) of the included products are given in Table 1. These products were selected from a large number of similar products that are sold around the world and in Turkey to account for the product type and manufacturer variability. The commercial bleach products contain NaOCl, surfactant, soap, and patented stabilizers to prevent the reaction of NaOCl with the organic components. NaOH is also commonly added as a stabilizer. The total organic carbon (TOC) and total nitrogen (TN) content of the bleach products were analyzed in the present study using a Total Organic Carbon Analyzer (Shimadzu, TOC-V_{C_{PN}}) (Table 1).

Prior to experiments, glass jars were cleaned by washing with detergent, rinsing with tap water, deionized water, and methanol. Then, they were dried in an oven for several hours at 105 °C. A set volume of 2.5 mL of pure products were placed into 650 mL glass jars. Then, the jars were capped with aluminum foil. After 15 min, the headspace of the jar was sampled from the hole punched in the foil ($n = 8 \times 2$). Headspace experiments ($n = 8 \times 2$) were also conducted using diluted products (1/100 with tap water). The dilution ratio was based on the manufacturer's recommendation on

the product use. The headspace of the jars containing the tap water used for dilution were also sampled and analyzed to account for the VOC background from the tap water itself ($n = 6$).

Laboratory-Prepared Mixtures. To investigate the feasibility of halogenated VOC formation in the commercial products, mixtures containing NaOCl, soap, surfactant, and NaOH were also prepared and tested using headspace experiments (Table 1). The headspace experiments for the laboratory prepared mixtures ($n = 6 \times 2$) were identical to those conducted using commercial products. The headspace of the jars containing the pure products used in these mixtures (dishwashing detergent, hand washing liquid, soap, and plain NaOCl bleach solution) were also sampled and analyzed ($n = 4 \times 2$) to determine if they contained any of the investigated VOCs.

Indoor Air Sampling during the Use of Bleach Products. Details of the experiments that were conducted in an apartment located in Izmir, Turkey are summarized in Table 2. VOC concentrations before, during, and 30 min after the applications (bathroom, kitchen, and floor cleaning) were measured ($n = 10 \times 3 \times 2$). Doors were open during all experiments except during the use of bleach 2 for bathroom cleaning. To simulate the normal use of the products, bathroom, kitchen and floors were not precleaned prior to bleach applications. The period between the duplicate applications was 1 week.

Indoor Air Sampling during Tap Water Use. Indoor air halogenated VOC concentrations resulting from tap water use were also measured. Samples were collected before, during, and 30 min after the applications (showering and hand dishwashing) ($n = 2 \times 3 \times 2$). Sampler inlet was located next to kitchen sink during dishwashing and next to bathtub during showering, at $h = 1.7$ m. The door was closed during showering and it was open during hand dishwashing.

Sampling Method. Air samples were collected using a sampling train consisting of an adsorbent tube, a flow meter, and a vacuum pump (Rocker, South Korea). Sampling flow rate and sample volume were 250 mL min⁻¹ and 2.5 L, respectively, for indoor air samples. However, because the VOC concentrations were significantly higher, a lower sampling rate (100 mL min⁻¹) and a volume (0.017 L, corresponding to 2.6% and 4.2% of the headspace volume

TABLE 2. Summary of Indoor Sampling Information

	bathroom	kitchen	corridor
characteristics of room	area = 7.1 m ² , height = 2.05 m, V = 14.6 m ³ , dimensions of door = 1.9 × 0.7 m	area = 14.3 m ² , height = 2.4 m, V = 34.3 m ³ , dimensions of door = 1.9 × 0.8 m	area = 8.4 m ² , height = 2.4 m, V = 20.1 m ³ , dimensions of door = 1.9 × 0.8 m
application	bathroom cleaning: apply pure product as a thin layer to the sink, toilet, and bathtub using a brush, wait 3 min, add some water and brush, wait 5 min, rinse thoroughly with tap water	kitchen cleaning: pour pure product to a wet piece of cloth, wipe the sink and counter, wait 5 min, rinse the cloth with tap water, wipe the counter with rinsed cloth a few times, rinse the sink with tap water	floor cleaning: prepare 5 L of diluted (1/100) product, mop the floor of kitchen and the adjacent corridor
tested products	bleach 1 bleach 2 bleach 3 bleach 5	bleach 3 bleach 5	bleach 1 bleach 3 bleach 5
sampler inlet location	between the toilet and bathtub, h = 1.7 m	next to sink, h = 1.7 m	middle of kitchen, h = 1.7 m

for pure and diluted product experiments, respectively) had to be used for headspace samples. Additional headspace samples ($n = 6 \times 2$) (sampling rate = 250 mL min⁻¹, sample volume = 1.25 L) were collected (bleach 1, 2, 3, 4, 5 and mixture 1) to identify the uncalibrated VOCs. Sampling flow rate was measured using a rotameter (Gilmont, Barnant Inc., USA). The rotameter calibration was checked occasionally (at three flow rates in duplicate, $n = 6$) using a primary standard (soap-bubble meter). The average percent difference between two flow meters was < 2.5%. The sample tubes were refrigerated and analyzed within 1–3 days as recommended (11).

Glass adsorbent tubes (6 mm OD, 17.8 mm length) were prepared according to the ambient air sampling methods recommended by the U.S. EPA (12). Each tube was packed at the upstream (sampling) end with 3 mm silanized glass-wool followed by a series of sections of 150 mg Tenax TA (60/80 mesh) (Supelco, Bellefonte, PA, USA), 3 mm silanized glass-wool, 100 mg Carboxen 1000 (Supelco, Bellefonte, PA), and finally, 3 mm silanized glass-wool at the downstream end. Prior to use, filled tubes were preconditioned for 1 h at 260 °C with a 50 mL min⁻¹ reverse flow (opposite to the sampling direction) of high-purity nitrogen. Then they were conditioned at 225 °C for 5 min with a 40 mL min⁻¹ of high-purity helium. Ends of the conditioned tubes were closed with PTFE caps and each tube was kept in tightly capped containers prior to use and after sampling. Silica gel and activated charcoal were placed at the bottom of the tube containers to control humidity and contamination, respectively.

Chemical Analysis. Samples were analyzed with a gas chromatograph (GC) (Agilent 6890N) equipped with a mass selective detector (Agilent 5973 inert MSD, Agilent, Wilmington, DE, USA) and a thermal desorber (Tekmar, Aerotrap 6000, USA). Samples were desorbed for 5 min at 225 °C using 40 mL min⁻¹ of helium flow. The internal trap temperature during sample desorption was 35 °C. The trap was desorbed for 1 min at 240 °C. Then, it was baked for 10 min at 250 °C. The valve oven and transfer line temperature of the thermal desorber was 200 °C (13).

The chromatographic column was HP5-MS (30 m, 0.25 mm, 0.25 µm) and the carrier gas was helium at 1 mL min⁻¹ flow rate and 36 cm s⁻¹ linear velocity. The split ratio was 1:40. The inlet temperature was 240 °C. Oven temperature program was: hold for 3 min at 40 °C, ramp to 120 at 5 °C min⁻¹, hold 1 min. Ionization mode of the MS was electron impact (EI). The ion source, quadrupole, and GC/MSD interface temperatures were 230, 150, and 280 °C, respectively. The MSD was run in simultaneous scan and selected ion monitoring modes. Compounds were identified based on

their retention times (within ±0.05 min of the retention time of calibration standard), target, and qualifier ions. Identified compounds were quantified using the external standard calibration procedure.

Six levels (0.1, 1, 3, 5, 20, and 100 µg mL⁻¹) of VOC solutions containing 68 compounds in methanol were used as the calibration standards. Blank thermal desorption tubes were loaded by spiking with 1 µL of the calibration standards. They were then run at specified conditions to calibrate the analytical system (Thermal desorber-GC-MS). For all compounds, the r^2 of the calibration curves were ≥ 0.999.

Other than the compounds quantified using calibration standards, several VOCs were identified in the headspace of bleach products using mass spectral library searches. Concentrations of compounds having a match quality > 80% were determined semiquantitatively using the average response factors calculated from the responses of the calibrated compounds. Calibrated compounds were grouped (i.e., halogenated compounds, hydrocarbons) while calculating the average response factors and quantifying the uncalibrated compounds. The behavior of the uncalibrated compounds in the analytical system (Thermal desorber-GC-MS) and as a result their actual response factors may deviate from those of the calibrated compounds. Therefore, the concentrations determined by this approach are only semiquantitative (14).

Quality Control and Quality Assurance. Instrumental detection limits (IDL) for VOCs (~5 pg for a split ratio of 1:40) were determined from linear extrapolation, based on the lowest standard in calibration curve and using the area of a peak having a signal/noise ratio of 3. Six blank thermal desorption tubes were analyzed as process blanks in order to determine the level of contamination during sample handling and preparation. The limit of detection (LOD, pg) of the method was defined as the mean blank mass plus three standard deviations (LOD = mean blank + 3 SD) (7, 12). LODs ranged between 5 (1,1-dichloroethane)-3660 (propanal) pg (0.002–1.5 µg m⁻³). Instrumental detection limits were used for the compounds that were not detected in blanks. In general, VOCs in the samples were substantially higher than the blanks. Sample quantities exceeding the LODs were quantified and corrected by subtracting the mean blank amount from the sample amount.

For three samples, back-up tubes were used during sampling to check if there was any breakthrough. Back-up tubes contained similar quantities of the compounds as the blanks, indicating that the breakthrough from the sample tubes was not a problem.

TABLE 3. Headspace Halogenated VOC Concentrations ($\mu\text{g m}^{-3}$) for Different Bleach types (pure)^a

VOCs	bleach 1	bleach 2	bleach 3	bleach 4	bleach 5	bleach 6	bleach 7	bleach 8
chloroform	3660	3170	1270	528	343	1450	1100	6000
carbon tetrachloride	38600	101000	3260	811	18	25900	28300	667
1,1-dichloroethane	34	176	nd	0.7	nd	13	15	nd
1,2-dichloroethane	2.2	0.6	0.7	0.6	1.0	0.6	0.6	nd
1,1-dichloroethene	1500	1400	1.4	1.9	1.1	586	1130	2.3
1,2-dichloropropane	44	183	nd	nd	nd	18	20	nd
trichloroethene	nd	1.4	0.8	1.7	5.4	1.0	1.0	1.4
tetrachloroethene	4.8	0.7	0.4	0.6	0.4	0.4	1.4	12
chlorobenzene	2.0	nd	3.8	0.2	Nd	0.4	0.7	2.3
1,4-dichlorobenzene	0.4	nd	nd	nd	nd	nd	1.7	nd
1,2-dichlorobenzene	9.3	7.6	5.0	5.2	5.4	7.1	13.9	6.0
bromodichloromethane	1.9	4.3	3.1	4.3	1.9	7.7	2.9	6.1
dibromochloromethane	1.0	1.0	1.1	1.1	0.9	2.2	1.4	0.7

^a nd, not detected. Note: 2,2-Dichloropropane, 1,1,1-trichloroethane, 1,3-dichlorobenzene, bromochloromethane, dibromomethane, and bromoform were not detected in any of the samples.

The system performance was confirmed daily by analyzing a midrange calibration standard. The relative standard deviation from the initial calibration was <5%. Analytical precision determined from three pairs of duplicate samples ranged between 2 and 5%.

The recoveries of target compounds during headspace sampling were tested by spiking experiments ($n = 3$). Ten microliters of a methanol solution containing the target compounds at $20 \mu\text{g mL}^{-1}$ was spiked into capped empty jars used in headspace experiments. After 15 min, the headspace of the jar was sampled and analyzed. Average recovery efficiencies ranged between 70% (naphthalene) and 106% (1,1-Dichloroethene) (overall average \pm SD, $81 \pm 9\%$).

Headspace samples ($n = 8$) were also analyzed by direct gas injection to the GC-MS system to check if the halogenated compounds measured with the sorbent sampling and thermal desorber-GC-MS technique were originated from a potential sampling artifact (i.e., chlorine reactions with adsorbents used, Tenax TA and Carboxen 1000) (see the Supporting Information for analytical details). The agreement between the concentrations measured with two different methods was good, indicating that the presence and levels of bleach associated VOCs determined with the sorbent sampling method were not affected by sampling artifacts (see the Supporting Information, Figure S1).

The time to reach equilibrium between the liquid and gas-phases during the headspace experiments was determined by analyzing six successive samples taken at 5–10 min intervals from a jar containing 2.5 mL of bleach 1. Results indicated that waiting 15 min before headspace sampling was sufficient to reach equilibrium between the liquid and gas-phases (see the Supporting Information, Figure S2).

Results and Discussion

Because the measured concentrations were generally very similar for duplicate experiments (relative differences were <30%), all concentrations were reported as the averages of the duplicates.

Headspace Concentrations. Headspace experiments were conducted to characterize the VOC content and emissions from the commercial bleach products. Product usages suggested by the manufacturers (pure or diluted product applications) were simulated during these experiments. Experiments with pure products characterized the VOC contents of the products, whereas experiments with diluted products provided information on the VOC emissions upon dilution. However, both experiments do not necessarily simulate the use of products during cleaning, because it is possible that additional reactions may occur between the hypochlorite and organic matter on dirty surfaces.

Commercial Products. Halogenated VOC concentrations measured in the headspaces of pure bleach containing products are presented in Table 3. Only halogenated VOCs were reported since most of the other compounds (aromatics, aldehydes, and other oxygenated compounds) were below the method detection limits. Carbon tetrachloride and chloroform were the leading compounds with very high concentrations up to 101 mg m^{-3} and they were followed by 1,1-dichloroethene and 1,1-dichloroethane. Other halogenated VOCs were also detected but their concentrations were much lower. Several halogenated compounds listed in Table 3, especially the trihalomethanes (THMs) (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) are known as disinfection byproducts forming as a result of drinking water chlorination. Since there was no contact to any other organic matter (i.e., on dirty surfaces or in tap water), the detected halogenated VOCs were those resulted from the reactions of hypochlorite and organic matter (surfactants, fragrances and other organic compounds) in the products.

Because of its excellent solvent properties and nonflammability, carbon tetrachloride has been used for many decades in commercial products such as dry cleaning solvents, grease solvents, and fire extinguishing agents. In 1970, the U.S. Food and Drug Administration (FDA) banned carbon tetrachloride and any mixture containing it for household use. The FDA classified carbon tetrachloride as a substance so hazardous that no warning label could adequately protect the householder (15, 16). In the 1990s, carbon tetrachloride was phased out under the Montreal Protocol because of its role in stratospheric ozone depletion (17). It is also a probable human carcinogen and a powerful greenhouse gas (15, 18, 19). The most surprising result of the present study is the presence of carbon tetrachloride in very high concentrations in headspaces of bleach products since it is not an added component. Several halogenated organics are produced in drinking water and wastewater treatment plants as a result of chlorination. However, there is not information in the literature on carbon tetrachloride relating its formation to chlorination of drinking or wastewater. The highest carbon tetrachloride concentrations were measured in headspace of surfactant added bleaches ($0.67\text{--}101 \text{ mg m}^{-3}$). The concentration in headspace of the fragranced bleach was relatively lower (0.81 mg m^{-3}) while a significantly lower concentration (0.02 mg m^{-3}) was measured for the plain bleach. This indicates that the formation of carbon tetrachloride is mostly associated with the organic bleach additives.

Halogenated VOC concentrations measured in the headspaces of diluted (1/100) bleach products are presented in

TABLE 4. Headspace Semiquantitative Halogenated VOC Concentrations ($\mu\text{g m}^{-3}$) for Different Bleach types (pure and diluted)^a

	CAS no.	molecular formula	MW (g mol^{-1})	pure bleach		diluted bleach	
				min.	max.	min.	max.
2-chloro-2-methylpropane	507–20–0	$\text{C}_4\text{H}_9\text{Cl}$	92.0	1.9	27	1.4	1.4
1,1-dichlorobutane	541–33–3	$\text{C}_4\text{H}_8\text{Cl}_2$	126.0	23	129	11	39
trichloronitromethane (chloropicrin)	76–06–2	CCl_3NO_2	162.9	0.3	36	6.3	6.9
2-chloro-2-nitropropane	594–71–8	$\text{C}_3\text{H}_6\text{ClNO}_2$	123.0	4.1	89	nd	6.9
dimethyl-carbamic chloride	79–44–7	$\text{C}_3\text{H}_6\text{ClNO}$	107.0	4.9	30	nd	nd
hexachloroethane	67–72–1	C_2Cl_6	233.8	0.2	29	4.3	4.4
1,1-dichloroheptane	821–25–0	$\text{C}_7\text{H}_{14}\text{Cl}_2$	168.1	4.6	18	4.9	8.0
(3-chloro-2-propenyl)-benzene	6268–37–7	$\text{C}_9\text{H}_9\text{Cl}$	152.0	14	35	nd	20
4-chloro-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane (1RS,4RS,5RS)-5-chloro-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane	88444–51–3	$\text{C}_{10}\text{H}_{17}\text{ClO}$	188.1	1.5	33	0.4	11
	88444–49–9	$\text{C}_{10}\text{H}_{17}\text{ClO}$	188.1	2.6	32	0.6	8.5

^a nd, not detected.

Table S1 of the Supporting Information along with headspace concentrations of tap water used for dilution. Similar to the pure products, carbon tetrachloride and chloroform were the most abundant compounds with concentrations ranging between 0.003 and 23 mg m^{-3} . 1,1-Dichloroethene and 1,1-dichloroethane were also detected. However, there were additional compounds in appreciable concentrations (THMs other than chloroform, bromochloromethane, and dibromomethane). The contributions of these compounds were mainly due to their presence in the dilution water as disinfection byproducts (see the Supporting Information, Table S1). Generally, the headspace VOC concentrations for diluted products were several times lower compared to those for pure products. Pure/diluted concentration ratios ranged between 1.8 (chloroform) and 4.2 (carbon tetrachloride) and averaged as 3.6 for the most frequently detected six compounds. Lower headspace VOC concentrations for diluted products were probably due to the dilution, the different phase ratios (headspace volume/liquid phase volume, 1.6 and 260 for diluted and pure product experiments, respectively), and the different partitioning characteristics of the pure and diluted products.

Laboratory Prepared Bleach Mixtures. Halogenated VOC concentrations measured in the headspaces of laboratory prepared mixtures with NaOCl, NaOH, surfactants, and soap are presented in the Supporting Information, Table S2. Similar to the commercial bleach products, chloroform and carbon tetrachloride had the highest concentrations, ranging between 0.27 and 89.4 mg m^{-3} . The presence of carbon tetrachloride and chloroform in high concentrations further confirmed that they are formed as a result of reactions between hypochlorite and surfactants/soap because the contributions from pure mixture components were insignificant (see the Supporting Information, Tables S1 and S2).

Headspace chloroform concentrations were significantly higher, whereas carbon tetrachloride concentrations were lower in the laboratory mixtures compared to commercial products. This may be due to differences in the product contents. Chloroform concentrations generally increased with TOC content of the products. Therefore, higher chloroform content of the laboratory mixtures may be due to their relatively higher TOC content (Table 1). Carbon tetrachloride concentrations also generally increased with TOC however laboratory mixtures and some commercial products did not follow this trend. Furthermore, carbon tetrachloride content may be related to product components that were not included in the laboratory mixtures.

Relatively higher carbon tetrachloride concentrations were measured in the headspace of NaOCl+surfactant mixtures

compared to those NaOCl+soap mixtures (see the Supporting Information, Table S2) while chloroform concentrations were generally high for all mixtures. Similar to the pure commercial products, 1,1-dichloroethene and 1,1-dichloroethane were also detected. However, the concentrations of THMs other than chloroform, bromochloromethane, and dibromomethane were significantly higher compared to pure and diluted bleach products. Apparently, the contribution of these compounds was mainly due to their formation as a result of reactions between hypochlorite and surfactants or soap (see the Supporting Information, Table S2). The addition of NaOH does not seem to have a clear inhibitory effect on the formation of chloroform, carbon tetrachloride, and most other VOCs. However, significantly lower bromodichloromethane and dibromochloromethane concentrations were measured for NaOH added mixtures.

Headspace Concentrations of Uncalibrated Compounds. In addition to quantitatively determined halogenated VOCs ($n = 15$), several nitrogen-containing ($n = 4$), chlorinated ($n = 10$), and oxygenated compounds ($n = 22$) and hydrocarbons ($n = 14$) were identified in the headspace of bleach products (bleach 1, 2, 3, 4, 5 and mixture 1) using mass spectral library searches. Concentrations of compounds having a match quality $>80\%$ ($n = 50$) were determined semiquantitatively using the average response factors of the calibrated compounds (Table 4 and the Supporting Information, Table S3). Tetrahydro linalool, 2-methyl-2-octanol, and eucalyptol were the most abundant compounds, with concentrations up to 62.6 mg m^{-3} . Most of the oxygenated compounds and hydrocarbons are the commonly used product components (2, 3). However, the nitrogen-containing and halogenated compounds are the byproducts of the reactions of hypochlorite with surfactants that some contain nitrogen (i.e., cocamine oxide), fragrances, and other additives because they were not detected in the headspace of pure bleach. 1,1-dichlorobutane (0.01–0.13 mg m^{-3}) and 2-chloro-2-nitropropane (0.04–0.09 mg m^{-3}) were the most abundant chlorinated compounds while trichloronitromethane and hexachloroethane were the most frequently detected ones (Table 4). Similar to the calibrated compounds, the headspace VOC concentrations for diluted products were several times lower compared to those for pure products (Table 4 and the Supporting Information, Table S3).

Indoor Halogenated VOC Concentrations. Indoor air halogenated VOC concentrations resulting from the household use of four selected bleach products were also measured. Included usages were bathroom, kitchen, and floor cleaning. VOCs were measured before, during, and 30 min after the product applications. Results of indoor VOC concentration

TABLE 5. Summary of Indoor Halogenated VOC Concentration Measurements Before, During, and 30 min After Chlorine Bleach Use ($\mu\text{g m}^{-3}$)^a

	before		during		after 30 min	
	range	average \pm SD	range	average \pm SD	range	average \pm SD
chloroform	0.13–0.97	0.41 \pm 0.25	2.9–24.6	9.5 \pm 6.7	1.1–32.1	5.3 \pm 9.5
carbon tetrachloride	0.16–0.47	0.27 \pm 0.11	0.25–459	55.2 \pm 144	0.30–212	22.7 \pm 66.4
1,1-dichloroethane	0.004–0.01	0.01 \pm 0.001	0.01–0.62	0.18 \pm 0.29	0.01–0.29	0.10 \pm 0.16
1,2-dichloroethane	0.02–0.45	0.09 \pm 0.13	0.02–0.43	0.09 \pm 0.13	0.02–0.40	0.09 \pm 0.12
1,1-dichloroethene	0.005–0.05	0.03 \pm 0.01	0.01–5.3	0.86 \pm 1.8	0.01–2.9	0.36 \pm 0.89
1,2-dichloropropane	nd	nd	0.18–0.66	0.42 \pm 0.33	0.30–0.30	0.30
1,1,1-trichloroethane	0.02–0.02	0.02 \pm 0.003	0.02–0.03	0.02 \pm 0.003	0.02–0.03	0.02 \pm 0.004
trichloroethene	0.02–0.08	0.04 \pm 0.02	0.02–0.07	0.04 \pm 0.02	0.02–0.06	0.04 \pm 0.02
tetrachloroethene	0.04–0.20	0.11 \pm 0.05	0.04–0.20	0.11 \pm 0.05	0.05–0.19	0.13 \pm 0.05
chlorobenzene	0.002–0.003	0.002 \pm 0.001	0.003–0.01	0.01 \pm 0.004	0.003–0.01	0.005 \pm 0.001
1,4-dichlorobenzene	0.003–0.01	0.004 \pm 0.003	0.002–0.01	0.005 \pm 0.004	0.003–0.01	0.01 \pm 0.01
1,2-dichlorobenzene	0.71–2.3	1.1 \pm 0.62	0.62–3.0	1.4 \pm 0.85	0.81–2.5	1.4 \pm 0.63
1,3-dichlorobenzene	0.003–0.01	0.005 \pm 0.001	0.004–0.01	0.01 \pm 0.002	0.003–0.01	0.01 \pm 0.002
bromodichloromethane	0.06–0.25	0.13 \pm 0.06	0.22–0.47	0.34 \pm 0.09	0.16–2.5	0.53 \pm 0.68
dibromochloromethane	0.04–0.14	0.08 \pm 0.03	0.11–0.24	0.18 \pm 0.05	0.08–1.2	0.28 \pm 0.34
bromoform	0.007–0.02	0.02 \pm 0.01	0.02–0.04	0.03 \pm 0.01	0.02–0.13	0.04 \pm 0.03

^a nd, not detected. Note: 2,2-Dichloropropane, bromochloromethane, and dibromomethane were not detected in any of the samples.

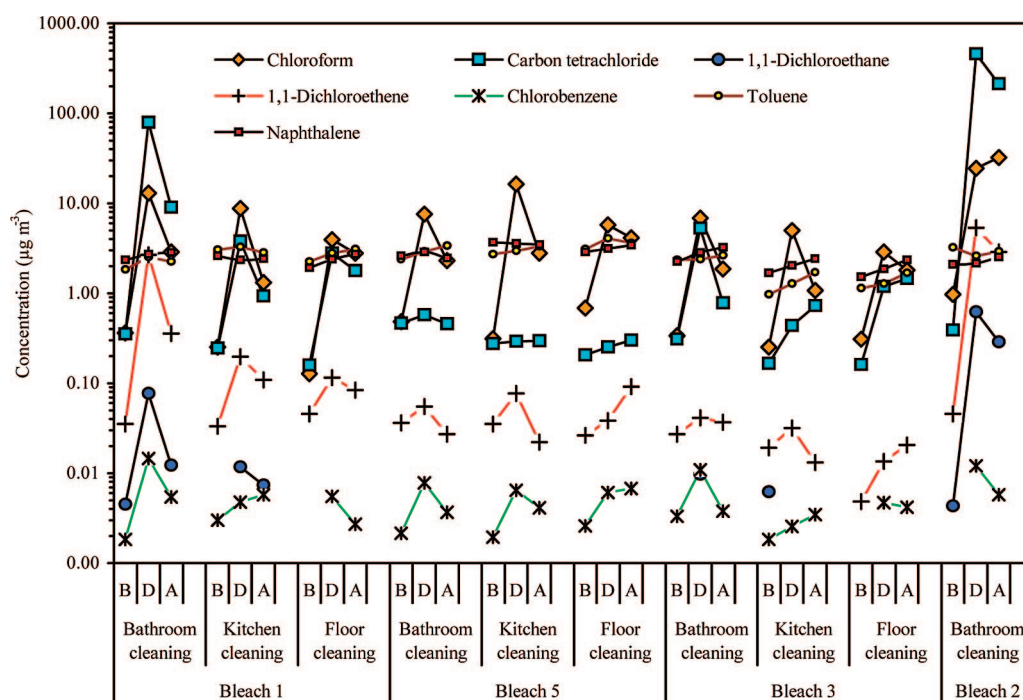


FIGURE 1. Variation in concentrations of selected bleach associated and other compounds (naphthalene and toluene) before (B), during (D), and after (A) the applications.

measurements are summarized in Table 5. In addition to halogenated VOCs, several other compounds (aromatics, aldehydes, and some oxygenated compounds) were also detected (see the Supporting Information, Table S4). Chloroform ($2.9\text{--}24.6\ \mu\text{g m}^{-3}$) and carbon tetrachloride ($0.25\text{--}459\ \mu\text{g m}^{-3}$) concentrations significantly increased during the use of bleach products. Compounds detected frequently in the headspaces of pure and diluted products (carbon tetrachloride, chloroform, 1,1-dichloroethane and 1,1-dichloroethene, and chlorobenzene) were also detected in indoor air with during/before concentration ratios significantly > 1 , confirming their association with bleach products. During/before concentration ratios ranged between 8 and 52 (25 ± 14 , average \pm SD) for chloroform and $1\text{--}1170$ (146 ± 367 , average \pm SD) for carbon tetrachloride, respectively (see the Supporting Information, Table S5). Figure 1 shows the concentration variations of selected bleach associated

compounds before, during and after the applications. They generally showed significant increases during the applications and the concentrations measured 30 min after were also higher than those measured before the applications (Figure 1, Table 5, and the Supporting Information, Table S5). THMs other than chloroform were also detected in all samples with increased concentrations measured during and 30 min after the applications. Tap water was used to dilute bleach products and to rinse the surfaces after/during the applications. As was also shown by the headspace experiments, the increase in the concentrations of these THMs was mainly due to their presence in tap water. On the other hand, their during/before concentration ratios ($2\text{--}4$) were significantly lower than that of chloroform (25). Considering that chloroform and other THMs have comparable air–water partition coefficients (K_{AW}) (20) and tap water concentrations, these ratios indicated that the indoor chloroform was mainly contributed from bleach

products or from the reactions of bleach and organic matter on the surfaces being cleaned. Several other VOCs were measured before, during and after bleach applications. However, their concentration remained relatively stable. During/before concentration ratios for aldehydes, aromatics and oxygenated VOCs were generally close to 1, indicating that their indoor air concentrations were not associated with the use of bleach products (the Supporting Information, Table S5, and Figure 1). Their relatively constant concentrations further emphasize the association of some halogenated VOCs with bleach products.

During all the bleach applications, there was not any ventilation and bathroom or kitchen doors were open. The worst possible case tested was the use of highest-VOC-containing bleach product (bleach 2) for bathroom cleaning when the door was closed. The highest bleach-associated VOC concentrations were measured during this application (Figure 1). The concentrations remained relatively high after 30 min, because the door was closed.

The tap water use has been considered as a significant route for inhalation exposure to disinfection byproducts. Because there were no previous literature values to compare the VOC concentrations measured in the present study and the use of bleach products and tap water emits some common compounds, indoor VOC concentrations before, during, and after tap water use (i.e., showering and hand dishwashing) were also measured. Significantly increased chloroform ($9.3\text{--}16.1\text{ }\mu\text{g m}^{-3}$) and bromodichloromethane ($6.5\text{--}13.3\text{ }\mu\text{g m}^{-3}$) concentrations were measured during tap water use (see the Supporting Information, Table S6). Nuckols et al. (6) have reported comparable concentration ranges during hand dishwashing ($3\text{--}17\text{ }\mu\text{g m}^{-3}$ for chloroform and $1\text{--}5\text{ }\mu\text{g m}^{-3}$ for bromodichloromethane) and higher ranges for showering ($50\text{--}351\text{ }\mu\text{g m}^{-3}$ for chloroform and $20\text{--}68\text{ }\mu\text{g m}^{-3}$ for bromodichloromethane). Concentrations of other THMs were also higher compared to those measured during the use of bleach containing products. However, the concentrations of remaining compounds including carbon tetrachloride indicated no association with tap water use (see the Supporting Information, Table S6). Chloroform concentrations measured during the uses of tap water and bleach products were comparable. However, bleach use is generally less frequent than tap water use. Consequently, chloroform exposure due to bleach use could be relatively less important for the general population compared to exposure from tap water, however it could be significant for cleaning personnel. On the other hand, the significant increases observed in indoor air concentrations of several other halogenated VOCs (especially carbon tetrachloride) indicate that the bleach use is a newly identified source that could be important in terms of inhalation exposure to these compounds.

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Supporting Information Available

Headspace air analysis by direct gas injection, comparison of headspace concentrations of bleach associated compounds measured with sorbent sampling—Thermal desorber—GC—MS analysis and direct gas injection (Figure S1), variation of headspace concentrations of bleach associated compounds with time during the experiment conducted with bleach 1 (Figure S2), headspace halogenated VOC concentrations for different bleach types (diluted, 1/100) (Table S1), headspace halogenated VOC concentrations for different laboratory-prepared mixtures (pure) (Table S2), headspace semiquantitative VOC concentrations for different bleach types (pure

and diluted) (Table S3), summary of indoor aromatic and oxygenated VOC concentration measurements before, during, and 30 min after chlorine bleach use (Table S4), during/before VOC indoor concentration ratios for different bleaches and applications (Table S5), and indoor VOC concentrations and during/before ratios for tap water use (Table S6) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Edwards, R. D.; Schweizer, C.; Llacqua, V.; Lai, H. K.; Jantunen, M.; Bayer-Oglesby, L.; Kunzli, N. Time-activity relationships to VOC personal exposure factors. *Atmos. Environ.* **2006**, *40*, 5685–5700.
- Nazaroff, W. W.; Weschler, C. J. Cleaning products and air fresheners: exposure to primary and secondary air pollutants. *Atmos. Environ.* **2004**, *38*, 2841–2865.
- Singer, B. C.; Coleman, B. K.; Destailats, H.; Hodgson, A. T.; Lunden, M. M.; Weschler, C. J.; Nazaroff, W. W. Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone. *Atmos. Environ.* **2006**, *40*, 6696–6710.
- Vartiainen, E.; Kulmala, M.; Ruuskanen, T. M.; Taipale, R.; Rinne, J.; Vehkamäki, H. Formation and growth of indoor air aerosol particles as a result of D-limonene oxidation. *Atmos. Environ.* **2006**, *40*, 7882–7892.
- Zwiener, C.; Richardson, S. D.; De Marini, D. M.; Grummt, T.; Glauner, T.; Frimmel, F. H. Drowning in disinfection byproducts? Assessing swimming pool water. *Environ. Sci. Technol.* **2007**, *41*, 363–372.
- Nuckols, J. R.; Ashley, D. L.; Lyu, C.; Gordon, S. M.; Hinckley, A. F.; Singer, P. Influence of tap water quality and household water use activities on indoor air and internal dose levels of trihalomethanes. *Environ. Health Perspect.* **2005**, *113*, 863–870.
- Kavcar, P.; Odabasi, M.; Kitis, M.; Inal, F.; Sofuoğlu, S. C. Occurrence, oral exposure and risk assessment of volatile organic compounds in drinking water for Izmir. *Water Res.* **2006**, *40*, 3219–3230.
- Fiss, E. M.; Rule, K. L.; Vikesland, P. J. Formation of chloroform and other chlorinated byproducts by chlorination of triclosan-containing antibacterial products. *Environ. Sci. Technol.* **2007**, *41*, 2387–2394.
- <http://www.unilever.com>. (2007)
- Olson, D. A.; Corsi, R. L. In-home formation and emissions of trihalomethanes: The role of residential dishwashers. *J. Exposure Anal. Environ. Epidemiol.* **2004**, *14*, 109–119.
- Peng, C.; Batterman, S. Performance evaluation of a sorbent tube sampling using short path thermal desorption for volatile organic compounds. *J. Environ. Monitor.* **2000**, *2*, 313–324.
- Compendium Method TO-17, Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes*; Center for Environmental Research Information, Office of Research and Development, U.S. Environmental Protection Agency: Cincinnati, OH, 1999.
- Dincer, F.; Odabasi, M.; Muezzinoglu, A. Chemical characterization of odorous gases at a landfill site by gas chromatography-mass spectrometry. *J. Chromatogr., A* **2006**, *1122*, 222–229.
- SemiQuant: New GC/MS Software Approaches to Estimating Compound Quantities*; Technical Overview 5989–4997EN; Agilent Technologies Inc.: Santa Clara, CA, 2006; <http://www.agilent.com/chem>.
- http://en.wikipedia.org/wiki/Carbon_tetrachloride (2007).
- <http://www.purdue.edu/dp/envirosoft/housewaste/house/carbont.htm> (2007)
- Doherty, R. E. A history of the production and use of carbon tetrachloride, tetrachloroethylene, trichloroethylene and 1,1,1-trichloroethane in the United States: Part 1—Historical background; carbon Tetrachloride and tetrachloroethylene. *Environ. Forensics* **2000**, *1*, 69–81.
- U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry (ATSDR); <http://www.atsdr.cdc.gov/tfacts30.html> (2007)
- National Toxicology Program, Department of Health and Human Services; <http://ntp.niehs.nih.gov/ntp/roc/eleventh/profiles/s029carb.pdf>
- EPI Suite Estimation Software*, V3.20; U.S. Environmental Protection Agency: Washington, D.C., 2007; <http://www.epa.gov/opptintr/exposure/pubs/episuitd.htm>.

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