
Bleach-containing automatic toilet-bowl cleaners as sources of VOCs, associated indoor air concentrations and carcinogenic risk

Ilknur Ayri[a], Mesut Genisoglu[a], Handan Gaygisiz[b], Aysun Sofuoglu[c], Sait C. Sofuoglu[a]*

[a]Izmir Institute of Technology, Dept. of Environmental Engineering, Gulbahce, Urla, Turkey
[b]Izmir Institute of Technology, Environmental Research Center, Gulbahce, Urla, Turkey
[c]Izmir Institute of Technology, Dept. of Chemical Engineering, Gulbahce, Urla, Turkey

*Corresponding author. cemilsofuoglu@iyte.edu.tr and saitcemil@iit.edu

HIGHLIGHTS

- Automatic toilet-bowl cleaners were found to be sources of VOCs
- Reservoir-type products had higher VOC content than those of bowl-type
- Emission potentials are not high to cause considerable indoor air levels over their lifetimes
- Exposure in bathrooms can be well reduced with an appropriate ventilation rate
- Carcinogenic risks associated with inhalation exposure are below acceptable level

CRediT author statement

Ilknur Ayri: Writing- Original draft preparation, Investigation, Formal analysis, Visualization.
Mesut Genisoglu: Investigation, Formal analysis.
Handan Gaygisiz: Investigation, Methodology.
Aysun Sofuoglu: Resources, Methodology, Writing- Reviewing and Editing.
Sait Sofuoglu: Conceptualization, Methodology, Resources, Project administration, Writing- Reviewing and Editing.

Abstract

Household cleaning products are sources of volatile organic compounds (VOCs). Bleach containing products are a special case because reactions occur between chloride and their organic content such as surfactants, perfumes, etc., generating VOCs. This study aimed to determine concentration of 13 VOCs in bleach-containing automatic toilet cleaners, to estimate their indoor air concentrations and associated exposure and health risk levels. Experiments with products purchased from supermarkets were conducted in 20-mL head-space vials by placing 1 g of sample with and without water. Solid-phase micro extraction with a DVB/CAR/PDMS fiber assembly was used for adsorption of VOCs from the headspace, and analyzed using a GC-MS. The median carbon tetrachloride and chloroform concentrations of the studied products ranged from 5.03×10^{-3} to 2.37×10^{-2} µg/g and 2.53×10^{-2} to 2.37 µg/g, respectively. The modeled 95th percentile indoor air concentrations in a 1.6 m^3 bathroom with no ventilation were estimated to be 1 and 20 µg/m^3 for carbon tetrachloride and chloroform, respectively. The 95th percentile carcinogenic risk associated even with the use of the highest content product, 3.72×10^{-7} and 8.62×10^{-7} for carbon tetrachloride and chloroform respectively, were below the acceptable risk. In conclusion, automatic toilet-bowl cleaners were found to be sources of VOCs, but their emission potentials are not high to cause considerable indoor air concentrations over their suggested product lifetime. In turn, carcinogenic risks associated with inhalation exposure are below the *de Minimis* risk level of 10^{-6}.

Keywords. Automatic toilet-bowl cleaners, Bleach, VOCs, Ventilation, Indoor air, Exposure-risk.

1. Introduction

Volatile organic compounds (VOCs) are a major group of indoor air pollutants. There are a wide variety of VOC emission sources, including consumer and commercial products, paints and associated supplies, adhesives, furnishing and clothing, building materials, combustion materials, and appliances (Wang et al., 2005; Bello et al., 2009). Cleaning is a common human activity in order to promote hygiene, aesthetics, and material preservation (Nazaroff and Weschler, 2004). Housewives spend 26 hours per week on average, and husbands spend 12.8 hours per week for household cleaning (Lee and Waite, 2005). The use of cleaning products results in exposure to various chemicals including VOCs, and causes more than 10% of all cases of adult-onset asthma (Quirce and Barranco, 2010). Exposure to VOCs can lead to acute and chronic health effects. The major potential health effects include acute and chronic respiratory effects, neurological toxicity, lung cancer, and eye and throat irritation, fatigue, headache, dizziness, nausea, lethargy, dermatitis and depression (Wang et al., 2005; Bello et al., 2009).

Solutions of sodium hypochlorite (NaOCl), commonly known as bleach, are widely used in households as a cleaning/disinfecting agent or included in cleaning products because of its low cost, ease of use, protection provided by residual chlorine, deodorizing and strong germicide activity against a wide spectrum of microorganisms, ability to clean hard surfaces, and to bleach the laundry (Racioppi et al., 1994; Nickmilder et al., 2007). Many household cleaning products such as mildew stain removers, toilet cleaners, cleaning sprays, gels, and scouring powders contain sodium hypochlorite (NaOCl, ~5%). NaOCl may be the only active ingredient or be accompanied by many other chemicals such as surfactants, fragrances, sodium silicate, sodium hydroxide, antioxidants, and antifoaming agents (Odabasi et al., 2014). Organic chemicals in household cleaning products may react with bleach, generating halogenated VOCs that may constitute more health concern than the reactants (Odabasi, 2008; Odabasi et al., 2014). Chloroform and carbon tetrachloride are the two main carcinogenic products of reactions between bleach and organic ingredients of household products during shelf life, and natural organic matter in water during use (Odabasi, 2008; Bondi, 2011; Odabasi et al., 2014). In addition to these two compounds with chronic-toxic and carcinogenic health effects, many other VOCs are associated with chronic-toxic and/or carcinogenic human health effects and environmental damage.

Automatic toilet-bowl cleaning / anti-odor products may pose a significant source of exposure because of their continuous emission potential compared to intermittent use of other bleach-containing household cleaning products. There are two types of automatic toilet cleaning products; in-tank and on-bowl. The two may differ in terms of the amount of emitted VOCs and their composition because of the difference in contact time with water. Nonetheless, both types have long durability in use, from 44 to 357 days depending on flushing frequency. Since bathrooms generally have small volumes with limited ventilation, the products probably contribute to the bathroom/toilet indoor air VOC levels and associated exposures that occur during use.

Odabasi (2008) and Odabasi et al. (2014) have shown that the use of bleach-containing household surface cleaning products results in significant indoor VOC concentrations. This study investigates concentrations of 13 VOCs in bleach-containing automatic toilet-bowl cleaners, models bathroom indoor air concentrations for various room sizes and ventilation rates, and estimates lifetime carcinogenic risk associated with use of various reservoir and bowl-type products. Chloroform and carbon tetrachloride were chosen as the main compounds for scenario-based exposure – risk assessment. Two exposure scenarios were constructed: the mean and the 95th percentile scenarios as estimates of central tendency and upper bound risks.

2. MATERIAL and METHODS

2.1. Samples

Various automatic bleach-containing toilet-bowl cleaning products were purchased from supermarkets. Available products were classified as reservoir (in-tank) and bowl (on-bowl). Six products purchased from stores in Chicago, IL, USA were reservoir type, two products bought in Germany and four products bought in Turkey were bowl type. To estimate VOC concentrations in sole product (SP) and with water (WW), a gram of each product was placed in a 20-mL headspace vial with and without 2 mL of tap water. Tap water was preferred for a supply of natural organic matter. Our previous studies have shown that tap water is supplied from groundwater in District of Urla and its Gulbahce village where our campus is located, and that the chloroform concentrations are low, <0.5 µg/L with a median value of 0.12 µg/L in Urla (Baytak et al., 2008) and 0.06 µg/L in Gulbahce. (Kavcar et al., 2006) Samples for QA/QC purposes, however, were prepared with MilliQ ultrapure water.

2.2. Extraction

Solid-phase micro extraction (SPME) was used for collection (Arthur and Pawliszyn, 1990) of VOCs emitted from product to the headspace. A Divinylbenzene / Carboxen / Polydimethylsiloxane (DVB/CAR/PDMS) fiber assembly (Supelco 54378-U) was used as the solid phase. Vials were closed with aluminum caps, with silicone / PTFE (35° shore A, 1.3 mm) septum. Preliminary experiments were conducted to determine the time periods for experimental emission period into the headspace and sorption onto the SPME fiber: 10 min, 30 min, 60 min, and 24 h for emission, and 10 min, 20 min, 30 min, and 60 min for adsorption onto SPME with 0.5 ppb solutions prepared from a 54-compound standard, 2000 ppm each in methanol (AccuStandard, M-502A-R-10X). VOC concentrations were decreased after 30 min in both of the experiments, therefore, 30-min waiting period was selected for the emission and sorption processes for determination of product VOC concentrations.

2.3. Analysis

A GC (Agilent 6890N) equipped with a mass selective detector (Agilent 5973N MSD) was used for analysis of 13 VOCs (1,2-Dibromoethane,1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, Benzene, Bromochloromethane, Bromodichloromethane, Bromoform, Carbon tetrachloride, Chloroform, Dibromochloromethane, Naphthalene, Tetrachlroethylene) selected based on Odabasi (2008) and Odabasi et al. (2014), and availability in the calibration standard (AccuStandard, M-502A-R-10X). Ionization mode of the MS was electron impact (EI). 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. Injection mode was splitless. The inlet temperature was 250 °C. Oven temperature program was: hold for 5 min at 40 °C, ramp to 200 at 5 °C min^{-1}, then to 280 °C at 10 °C min^{-1}, hold for 10 min.

2.4. QA/QC

A 5-point calibration, with R^2>0.995 for all compounds, was used to determine analyte concentrations in ppb in MilliQ Ultrapure water. The limit of detection (LOD) of the method was defined as the 3 times the standard deviation of slope of the calibration curve (Shrivastava and Gupta, 2011; Sengul, 2016). LODs ranged between 7.35 ppt (bromochloromethane) and 3.76 ppb for carbon tetrachloride. LOD for chloroform was 0.34 ppb. Precision of the method was assessed by conducting all experiments in duplicate. Relative difference between the duplicates were <30% except for 5 of the 336 analyses (1.5 %). Duplicate averages are reported and used in modeling and exposure – risk estimation.

2.5. Exposure and Risk Assessment

Inhalation exposure to carbon tetrachloride and chloroform volatilized into bathroom/toilet indoor air during product use, and associated carcinogenic risks were studied. Carcinogenic risk assessment for inhalation exposure during bathroom/toilet use was conducted with modeled indoor air concentrations for three room volumes with four ventilation rates. Inhalation exposure and carcinogenic risk were estimated using Equations 1 and 2, respectively.

$$\mathrm{CDI}=\frac{\mathrm{C}\times\mathrm{IR}\times\mathrm{ET}\times\mathrm{EF}\times\mathrm{ED}}{\mathrm{BW}\times\mathrm{AT}} \tag{1}$$

$$\mathrm{Risk} = \mathrm{CDI} \times \mathrm{SF} \tag{2}$$

where *C* is indoor air concentration (mg/m^3); *IR* is inhalation rate (m^3/h), *ET* is exposure time (h/day), *EF* exposure frequency (days/year), *ED* is exposure duration (years), *BW* is body weight (kg), and *AT* average lifetime (Asante-Duah, 2002). *SF* is a toxicological risk factor (0.13 (mg/kg/day)$^{-1}$ for carbon tetrachloride and 0.031 (mg/kg/day)$^{-1}$ for chloroform) published in Integrated Risk Information System of the US Environmental Protection Agency. Activity level for toilet use was considered as sedentary-passive and corresponding mean and 95th percentile *IR*, *ET*, *EF*, and *BW* values were taken from Exposure Factors Handbook (Moya et al., 2011). *ED* and *AT* were considered equal to lifetime, canceling each other out. ET was assumed as equal to daily time spent in bathroom (h/day) available in Exposure Factors Handbook. Time spent for each toilet use was calculated by dividing the value obtained from Exposure Factors Handbook by the mean number of toilet use 5.6 per day (Rossi et al., 2009). A time period of 20 s for hand washing (Green et al., 2006) is added.

The product lifetimes are given as number of flushes on the package by producers. So, the emission potential of a product over its lifetime is obtained by multiplying weight of the product and the measured product VOC concentration [μg/g] divided by number of flushes. Emitted VOCs were assumed to instantly and completely mixed in the bathroom/toilet volumes of 1.6 m^3, 8.9 m^3 (Mui et al., 2017) and 18 m^3 (Lévesque et al., 2002) with no ventilation as an initial estimation for sole bowl-type products. For reservoir-type products and bowl-type products when in contact with water, indoor air concentration was estimated based on Henry's law (Equation 3) assuming VOCs dissolve into water in the reservoir from the products. The ideal gas law was used to calculate their concentration in the air (Equation 4). Then, these initial concentrations were modeled (Equation 5-6) with an air exchange rate of 0.5 h^{-1} and ventilation rates of 25.2 m^3/h, 54 m^3/h, and 72 m^3/h (Liang and Yang, 2013; Ye et al., 2017) over the lifetimes specific to each product that ranged from 44 to 357 days.

$$P_a = H \times C_w \tag{3}$$

$$C_{ia} = MW \times P_a / RT \tag{4}$$

H is the Henry's constant (mol/m^3.Pa) (Sander, 1999), and C_w is water concentration (mol/m^3), C_{ia} is indoor air concentration (g/m^3), P_a is the partial pressure (Pa), V (m^3) is room volume , R (m^3.Pa/K.mol) is the gas constant T is room temperature which is assumed to be 298 °K and MW is the molecular weight (g/mol).

In order to calculate ventilated indoor air chloroform and carbon tetrachloride concentrations, assumptions of complete mixing, constant ventilation and emission rates, and zero outdoor concentration were made.

$$V\frac{dC_{in}(t)}{dt} = Q\ (C_{out} - C_{in}(t)) + E \qquad (5)$$

$$C_{in}(t) = C_{in}(0)\ \exp(-\frac{Q}{V}t) + (C_{out} + \frac{E}{Q})(1 - \exp\ (\frac{Q}{V}t)) \qquad (6)$$

where, V is room volume (m^3), t is time (h), $C_{in}(t)$ is indoor air concentration at time t (mg/m^3), Q is ventilation rate (m^3/h), C_{out} is outdoor concentration (mg/m^3), and E is the emission rate of toilet-bowl cleaners (mg/h) calculated from the estimated emission potentials over the considered product lifetimes.

The estimated concentrations were used for exposure – risk assessment. Exposure was calculated for several age groups by using their mean and 95th inhalation rate values, body weight, exposure time and durations, listed in Table 1. The earliest age group was 2-3 years because it is when toilet training mostly starts (Horn et al., 2006). Then, summation of exposure for each age group was used to calculate the lifetime carcinogenic risk estimates. The estimates for reservoir-type products were based on WW sample concentrations due to constant contact with water during use of product. The ratio of hand washing time to toilet use time was multiplied by the WW concentration, while the remaining fraction of time was multiplied by SP concentration to obtain the concentration to be used for bowl-type products, because of intermittent water contact specific to this type of products.

3. Results and Discussion

In this study, automatic toilet-bowl cleaner samples were analyzed for 13 VOCs that were selected based on potency and frequency/concentration among those reported by Odabasi (2008) and Odabasi et al. (2014), and availability. Detection frequency of the studied 13 compounds are listed in Table 2. Tetrachloroethylene and 1,2-dibromoethane were not detected in any sample, whereas carbon tetrachloride and chloroform were detected in all samples with or without water.

3.1. Product VOC concentrations

The mean and median measured VOC concentrations in 11 products with and without water, classified as reservoir and bowl type, are presented in Table 2. Majority of the VOCs (nine based on the median values) were at higher levels when in contact with water for reservoir-type products while about one-half of the VOCs were at higher levels when with water for bowl-type products. The difference ranged from 1.5-folds (dibromochloromethane) to 46-folds (benzene) for reservoir-type. Chloroform was the highest concentration compound with higher levels in reservoir-type products, and when in contact with water (2.37 µg/g), followed by bromoform, bromochloromethane, benzene, and carbon tetrachloride (24 – 37 ng/g). For bowl-type, bromochloromethane and 1,3-dichlorobenzene were joined to not-detected-at-all compounds. The difference between sole-product and with-water concentrations for the remaining nine compounds was ranged from 1.2-folds (chloroform) to 44-folds (bromodichloromethane). Chloroform concentration (30 ng/g) was relatively high but carbon tetrachloride concentration (5 ng/g) was relatively low in bowl-type products, while the highest concentration VOC was 1,4-dichlorobenzene (61 ng/g) because some of the bowl-type products contained this compound as an anti-odorant. In fact, its SP concentration was higher (76 ng/g) along with 1,2-dichlorobenzene (40 ng/g). The difference in concentrations between sole product and with water samples could originate from either contribution of the tap water and/or reactions with natural organic matter in the water, in addition to diffusion of dissolved compounds in liquids being approximately three orders higher than those in solids.

3.2. Bathroom/toilet indoor air VOC concentrations

The initial bathroom/toilet indoor air VOC concentrations were calculated based on the estimated emission potentials with no ventilation in room sizes of 1.6 m^3, 8.9 m^3, and 18 m^3. The mean and median values of the estimated concentrations for the smallest volume room, that represents the worst case, are listed in Table 3 while Figures 1 and 2 show their variation. Reservoir-type products result in much higher bathroom air concentrations compared to bowl-type. However, even levels of those of reservoir type are lower than those reported in the literature (Odabasi, 2008; Zhou et al., 2011; Odabasi et al., 2014) probably because the literature reported concentrations are generally a result of cumulative effect of various emission sources indoors and the amount of product per use are higher. In this study, the 95th percentile chloroform and carbon tetrachloride concentrations were about 20 and 1.0 μg/m^3 for reservoir-type products, while both were <0.1 μg/m^3 for bowl-type products. The lower concentrations determined in this study are probably due to the relatively small weights of the considered products that last for long periods of time in use, such as 45 to 357 days (per person), in contrast to the larger sizes of household cleaning products used in all areas of the house that would result in higher formation during shelf life and during use (Quirce and Barranco, 2010; Odabasi et al., 2014). Moreover, presence of various other emission sources of VOCs would result in higher concentration (Wang et al., 2005; Bello et al., 2009).

Product and indoor air VOC concentrations reported in the literature are summarized in Table 4. Odabasi (2008) has examined VOC concentrations resulting from the use of bleach-containing cleaning products in bathroom, toilet, and hallways in an apartment. He reported that the concentration of VOCs increased due to the use of these products. During application of these products, chloroform concentrations were reported to vary from 2.9 µg/m^3 to 24.6 µg/m^3, whereas the range was 0.25 µg/m^3 to 459 µg/m^3 for carbon tetrachloride. Concentration ranges were reported for 1,4-dichlorobenzene, 1.3-dichlorobenzene, 1,2-dichlorobenzene bromodichloromethane, and bromoform as 0.002-0.01 µg/m^3, 0.004-0.01µg/m^3, 0.62-3 µg/m^3, 0.00-0.47 µg/m^3, 0.02-0.04 µg/m^3, respectively. Later, Odabasi et al. (2014) have investigated formation of halogenated VOCs resulting from the use of various bleach-containing cleaning products: plain, fragranced, and surfactant added. They reported that product chloroform and carbon tetrachloride concentrations were higher for higher organic-content products, i.e. fragrance and surfactant added ones. The highest chloroform concentration was reported to be 154 mg/L, while the lowest concentration was reported to be 0.08 mg/L. Carbon tetrachloride concentrations were reported to range from 0.01 to 169 mg/L. Bromodichloromethane concentration reported between 0.01 and 0.05 mg/L. The ranges for 1,2-dichlorobenzene and 1,3-dichlorobenzene concentrations were 0.003-30.0 mg/L and 0.004-0.02 mg/L. Son et al. (2003) investigated indoor and outdoor VOC concentrations in two cities of Korea. In Asan and Seoul, the mean indoor air benzene concentrations were reported as 20 µg/m^3 and 44 µg/m^3, respectively. Guo et al. (2004) studied 8-hour average methylene chloride, benzene, and chloroform concentrations in different indoor environments (home, office, school, restaurants, shopping mall, and transportation mode). The ranges for indoor chloroform and benzene were 0.30-0.83 µg/m^3 and 0.50-1.18 µg/m^3, respectively. Edwards et al. (2001) reported average residential indoor air naphthalene concentration as 0.64 µg/m^3 in Helsinki. Shin and Lim (2017) conducted a study on 15 household cleaning products. Chloroform was reported in all disinfectant samples in 0.2 - 30 µg/g range, whereas carbon tetrachloride concentrations were reported to range from 0.05 to 352 µg/g in 13 of the 15 analyzed samples. Product concentrations were reported to be between 0.084 and 0.735 µg/g for 1,2-dichlorobenzene and between 0.007 and 0.077 µg/g for 1,4-dichlorobenzene.

Shin and Lim (2017) reported indoor air VOC concentrations in a 9.3 m^3 room with 7.2 m^3/h ventilation rate for chlorine bleach and mildew remover use. Indoor air chloroform concentrations due to the use of chlorine bleach and mildew removers were reported as 316 µg/m^3 and 130 µg/m^3, respectively. Carbon tetrachloride concentrations for these two products were given as 3690 µg/m^3 and 962 µg/m^3. Indoor air 1,2-dichlorobenzene and 1,4 dichlorobenzene concentrations were much lower (2.54 µg/m^3 and 1.92 µg/m^3, and 0.11 µg/m^3 and 0.39 µg/m^3) for chlorine bleach and mildew remover products, respectively. Hence, in general, the literature reported indoor air VOC concentrations, associated with use of bleach-containing cleaning products, are in the order of µg/m^3 to mg/m^3 and vary several orders of magnitude among the studied compounds. The estimated bathroom air chloroform and carbon tetrachloride concentrations associated with the automatic toilet-bowl cleaning products investigated in this study are lower than those reported in the literature, probably because these products have low weights (between 40 g and 100 g) that last for long lifetimes (44 to 357 days). Meanwhile, the levels of the remaining VOCs measured in this study are comparable to the ranges reported in the literature.

Use of cleaning products may result with exposure to air pollutants by various mechanisms. The volatile components present in the cleaning products may volatilize into the gas phase during and after use, and may be inhaled. However, non-volatile components can also be inhaled because the cleaning process itself gives liquid or solid particulate matter to the air, or because the residual cleaning agents are then suspended, for example by abrasion (Nazaroff and Weschler, 2004). It was reported that after mopping indoor air OH and Cl radical levels could rise by photolysis of HOCl and Cl_2, which gives rise to oxidative capacity of indoor air toward VOCs (Wong et al., 2017). Recently, Mattila et al. (2020) also reported that indoor/outdoor ratio for measured HOCl, Cl_2, and $ClNO_2$ during bleaching increased to the order of 10^4, whereas the ratio was not increased considerably when no bleach was used for cleaning, and their indoor air levels were BDL when there was no occupant activity. Increase in particulate matter chloride ion mass from cooking was also a factor in addition to the bleach cleaning. The experimental approach adopted in this study, however, have not taken these factors into consideration.

3.3. Influence of ventilation rate on indoor air VOC concentrations

Indoor air concentrations of chloroform and carbon tetrachloride associated with the use of reservoir/bowl cleaners in three different sizes of bathrooms with various ventilation rates were estimated by modeling (Equation 4). The indoor air concentrations (Section 3.2) were modeled in room volumes of 1.6 m^3, 8.9 m^3, and 18 m^3 (Mui et al., 2017) for ventilation rates of 0.5 h^{-1}, 25.2 m^3/h, 54 m^3/h, and 72 m^3/h over lifetimes specific to each product (Liang and Yang, 2013; Ye et al., 2017).

Concentration box-plots at 0.5 h^{-1}, 25.2, 54, and 72 m^3/h are shown in Figure 3 for the considered room volumes. Effect of the increase in ventilation rate is readily observable in 1.6 m^3 room. The 95th percentile chloroform concentration (~20 µg/m^3, in 1.6 m^3 room without ventilation) does not considerably reduce with an air exchange rate of 0.5 h^{-1} but reduces down to 0.21 μg/m^3 with a ventilation rate 72 m^3/h. Carbon tetrachloride concentrations at no ventilation, 0.5 h^{-1}, and 72 m^3/h were 0.97 μg/m^3, 0.94 μg/m^3, and 0.01 μg/m^3, respectively. It is only possible to remove 5% of the substances in the room air at a ventilation rate of 0.5 h^{-1}, while 98% of the substances can be removed at a ventilation rate of 72 m^3/h. Exposure to these substances can therefore be reduced with appropriate ventilation rate to low levels relative to those reported in the literature (Odabasi, 2008; Odabasi et al., 2014; Shin and Lim, 2017). The contribution of automatic toilet-bowl cleaning products to indoor air levels are not considerable compared to household cleaning products even in small bathrooms with limited ventilation.

3.4. Carcinogenic risk assessment

Risk levels in this study were estimated for two exposure scenarios: the mean and 95th percentile. As for the concentrations, the lowest risk occurs in the largest room volume with the highest ventilation rate, while the highest value occurs in the lowest volume and the lowest ventilation rate. Because the concentrations, and in turn the risks, are low, all below the acceptable risk level of one-in-a-million, the 95th percentile risk values for the lowest-volume (1.6 m^3) bathroom with lowest ventilation (0.5 h^{-1}) are given for all studied products in Table 5. All carcinogenic risk values in the other studied bathroom volumes and ventilation rates are lower, therefore, Table 5 represents the worst case for 11 of the 12 products with a measurable chloroform and carbon tetrachloride content. The highest risk estimated for a reservoir-type product (8.62×10^{-7}) is close the acceptable risk of 1.00×10^{-6}, and lower than those reported by Odabasi et al. (2014) who considered surface-cleaning-product use by housewives.

4. Conclusion

This study investigated VOC concentrations in bleach-containing automatic toilet-bowl cleaning products purchased from Germany, Turkey, and USA. Two of the studied 13 compounds were not found in any product while all products contained carbon tetrachloride and chloroform. Between the two types of products, reservoir-type had higher VOC concentrations compared to that of bowl-type. The modeled bathroom indoor air chloroform and carbon tetrachloride concentrations for use of the products are much lower than those reported in the literature even in the smallest room with the lowest ventilation among three room sizes (1.6 m^3, 8.9 m^3 and 18 m^3) and four ventilation rates (0.5 h^{-1}, 25.2 m^3/h, 54 m^3/h, and 72 m^3/h). Overall, automatic toilet-bowl cleaners were found to be sources of VOCs but their emission potentials are not high to cause considerable indoor air concentrations over their suggested product lifetime. In turn, carcinogenic risks associated with inhalation exposure are below the *de Minimis* risk level of 10^{-6}.

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References

Arthur, C.L., Pawliszyn, J., 1990. Solid phase microextraction with thermal desorption using fused silica optical fibers. Anal. Chem., 62, 2145-2148.

Asante-Duah, D.K., 2002. Public health risk assessment for human exposure to chemicals. Springer.

Baytak, D., Sofuoglu, A., Inal, F., Sofuoglu, S.C., 2008. Seasonal variation in drinking water concentrations of disinfection by-products in IZMIR and associated human health risks. Sci. Total Environ., 407, 286-296.

Bello, A., Quinn, M.M., Perry, M.J., Milton, D.K., 2009. Characterization of occupational exposures to cleaning products used for common cleaning tasks-a pilot study of hospital cleaners. Environ. Health 8, 11.

Bondi, C.A., 2011. Applying the precautionary principle to consumer household cleaning product development. J. Clean. Prod., 19, 429-437.

Edwards, R.D., Jurvelin, J., Saarela, K., Jantunen, M., 2001. VOC concentrations measured in personal samples and residential indoor, outdoor and workplace microenvironments in EXPOLIS-Helsinki, Finland. Atmos. Environ. 35, 4531–4543.

Green, L.R., Selman, C.A., Radke, V., Ripley, D., Mack, J.C., Reimann, D.W., Stigger, T., Motsinger, M., Bushnell, L., 2006. Food worker hand washing practices: an observation study. J. Food Prot., 69, 2417-2423.

Guo, H., Lee, S., Chan, L., Li, W., 2004. Risk assessment of exposure to volatile organic compounds in different indoor environments. Environ. Res. 94, 57–66.

Horn, I.B., Brenner, R., Rao, M., Cheng, T.L., 2006. Beliefs about the appropriate age for initiating toilet training: Are there racial and socioeconomic differences? J. Pediatr., 149, 165-168.

Kavcar, P., Odabasi, M., Kitis, M., Inal, F., Sofuoglu, S.C., 2006. Occurrence, oral exposure and risk assessment of volatile organic compounds in drinking water for Izmir. Wat. Res., 40, 3219-3230.

Lee, Y.S., Waite, L.J., 2005. Husbands' and wives' time spent on housework: A comparison of measures. J. Marriage Fam., 67, 328-336.

Lévesque, B., Ayotte, P., Tardif, R., Ferron, L., Gingras, S., Schlouch, E., Gingras, G., Levallois, P., Dewailly, É., 2002. Cancer risk associated with household exposure to chloroform. J. Toxicol. Environ. Health Part A, 65, 489-502.

Liang, W., Yang, X., 2013. Indoor formaldehyde in real buildings: Emission source identification, overall emission rate estimation, concentration increase and decay patterns. Buil. Environ., 69, 114-120.

Mattila, J.M., Lakey, P.S., Shiraiwa, M., Wang, C., Abbatt, J.P., Arata, C., Goldstein, A.H., Ampollini, L., Katz, E.F., DeCarlo, P.F., 2020. Multiphase chemistry controls inorganic chlorinated and nitrogenated compounds in indoor air during bleach cleaning. Environ. Sci. Tech., 54, 1730-1739.

Moya, J., Phillips, L., Schuda, L., Clickner, R., Birch, R., Adjei, N., Blood, P., Chapman, K., Castro, R., Mahaffey, K., 2011. Exposure Factors Handbook, 2011 Edition. US Environmental Protection Agency, Washington. EPA/600/R-090.

Mui, K., Wong, L., Yu, H., Cheung, C., Li, N., 2017. Exhaust ventilation performance in residential washrooms for bioaerosol particle removal after water closet flushing. Build. Serv. Eng. Res. Tech., 38, 32-46.

Nazaroff, W.W., Weschler, C.J., 2004. Cleaning products and air fresheners: exposure to primary and secondary air pollutants. Atmos. Environ., 38, 2841-2865.

Nickmilder, M., Carbonnelle, S., Bernard, A., 2007. House cleaning with chlorine bleach and the risks of allergic and respiratory diseases in children. Pediatr. Allerg. Immunol., 18, 27-35.

Odabasi, M., 2008. Halogenated volatile organic compounds from the use of chlorine-bleach-containing household products. Environ. Sci. Tech., 42, 1445-1451.

Odabasi, M., Elbir, T., Dumanoglu, Y., Sofuoglu, S.C., 2014. Halogenated volatile organic compounds in chlorine-bleach-containing household products and implications for their use. Atmos. Environ., 92, 376-383.

Quirce, S., Barranco, P., 2010. Cleaning agents and asthma. J Investig Allerg Clin Immunol 20, 542-550.

Racioppi, F., Daskaleros, P., Besbelli, N., Borges, A., Deraemaeker, C., Magalini, S., Arrifta, R.M., Pulce, C., Ruggerone, M., Vlachos, P., 1994. Household bleaches based on sodium hypochlorite: review of acute toxicology and poison control center experience. Food Chem. Toxicol., 32, 845-861.

Rossi, L., Lienert, J., Larsen, T., 2009. Real-life efficiency of urine source separation. Journal of Environ. Manag., 90, 1909-1917.

Sander, R., 1999. Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry. Max-Planck Institute of Chemistry, Air Chemistry Department Mainz, Germany.

Sengul, U., 2016. Comparing determination methods of detection and quantification limits for aflatoxin analysis in hazelnut. J. Food Drug Anal., 24, 56-62.

Shin, H.-S., Lim, H.-H., 2017. Identification and determination of disinfection byproducts in chlorine-containing household cleansing products. Chemosphere 174, 157-164.

Shrivastava, A., Gupta, V.B., 2011. Methods for the determination of limit of detection and limit of quantitation of the analytical methods. Chron. Young Sci. 2, 21.

Son, B., Breysse, P., Yang, W., 2003. Volatile organic compounds concentrations in residential indoor and outdoor and its personal exposure in Korea. Environ. Int. 29, 79–85.

Wang, L.K., Pereira, N.C., Hung, Y.-T., 2005. Advanced Air and Noise Pollution Control. Springer.

Wong, J., Carslaw, N., Zhao, R., Zhou, S., Abbatt, J., 2017. Observations and impacts of bleach washing on indoor chlorine chemistry. Indoor Air 27, 1082-1090.

Ye, W., Zhang, X., Gao, J., Cao, G., Zhou, X., Su, X., 2017. Indoor air pollutants, ventilation rate determinants and potential control strategies in Chinese dwellings: a literature review. Sci. Total Environ., 586, 696-729.

Zhou, J., You, Y., Bai, Z., Hu, Y., Zhang, J., Zhang, N., 2011. Health risk assessment of personal inhalation exposure to volatile organic compounds in Tianjin, China. Sci. Total Environ., 409, 452-459.

FIGURES

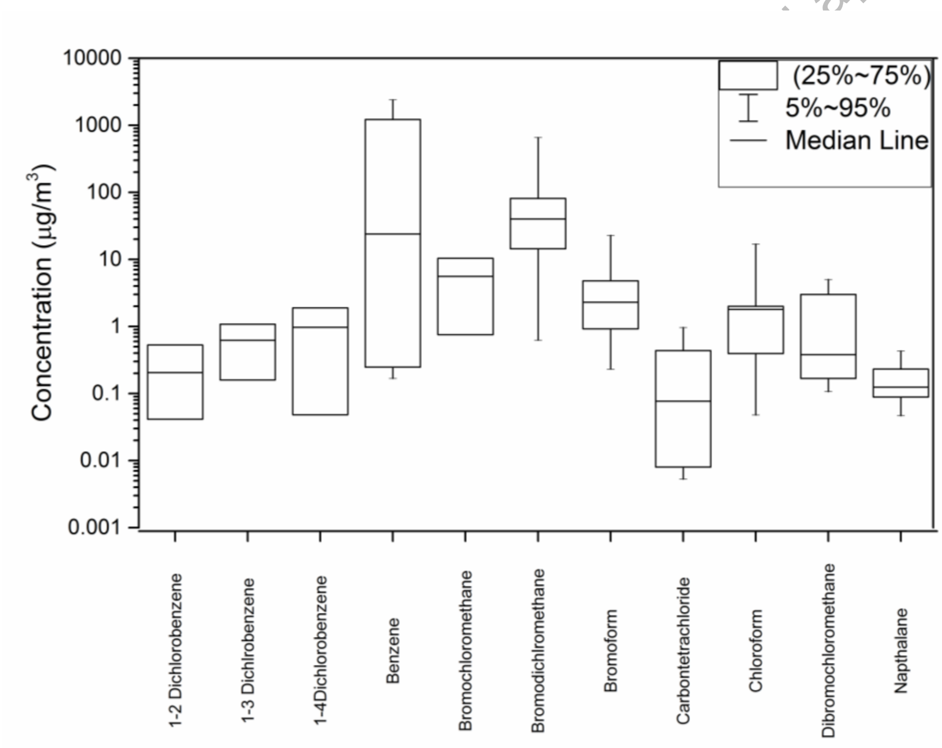
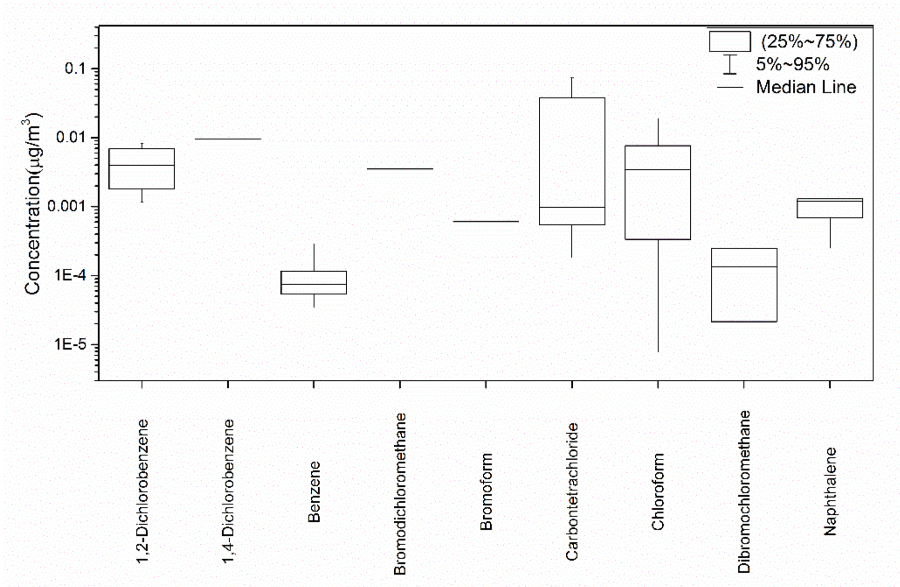


Figure 1. Concentration variation in a 1.6 m^3 bathroom due to use of various reservoir-type products

1 

2 Figure 2. Concentration variation in a 1.6 m^3 bathroom due to use of various bowl-type products

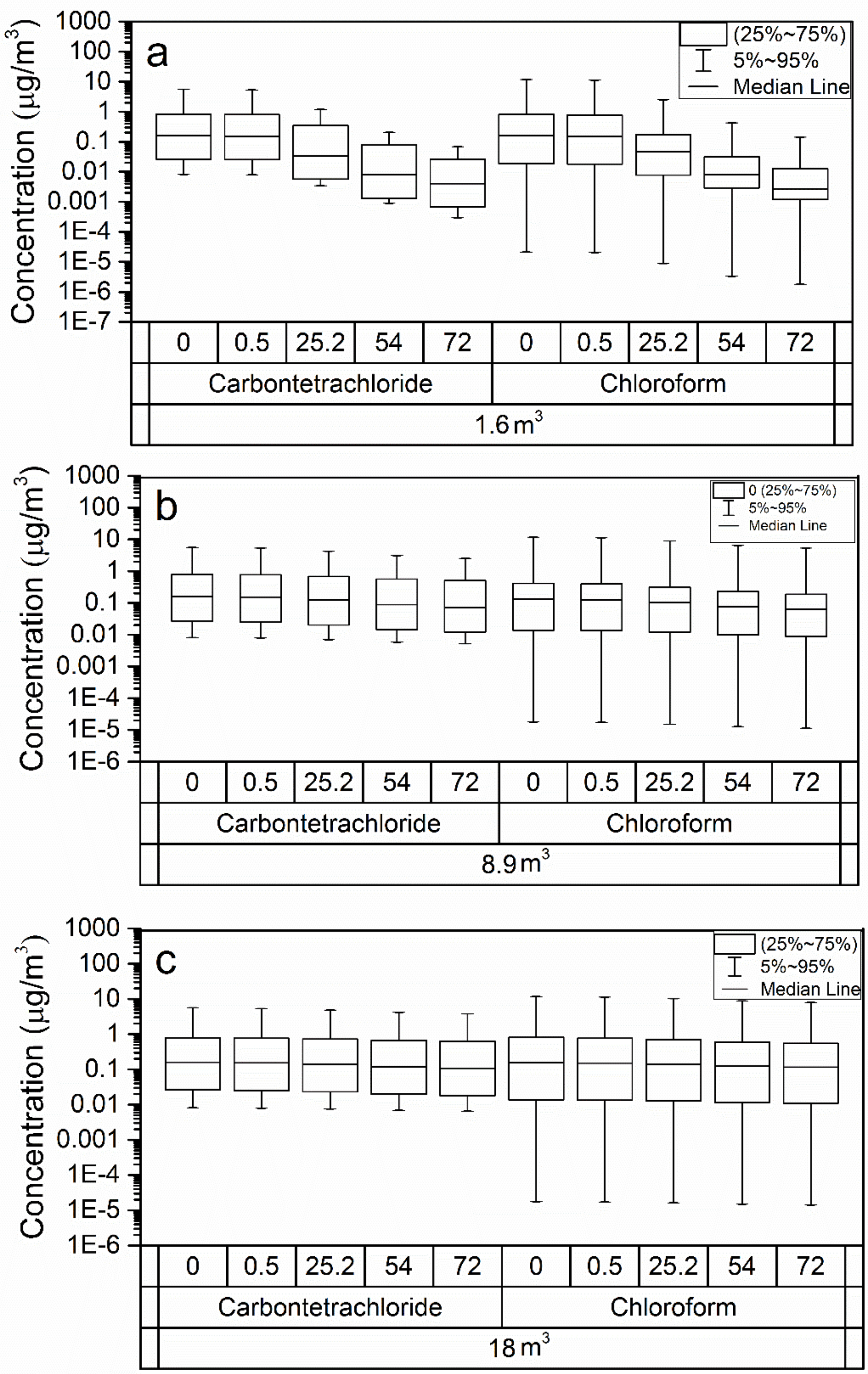


Figure 3. Indoor carbon tetrachloride and chloroform concentrations for varying ventilation rates in (a) 1.6 m^3, (b) 8.9 m^3, and (c) 18 m^3 bathrooms

TABLES

Table 1. Variable values used in inhalation exposure estimation[a]

Age Group	Mean IR[b] (m^3/h)	95[th]p.[c] IR (m^3/h)	BW[d] (kg)	ET[e] (h/day)	ED[f] (yr)
2-3	0.288	0.390	13.8	0.38	1
3-6	0.270	0.348	18.6	0.40	3
6-11	0.288	0.384	31.8	0.40	5
11-16	0.324	0.450	56.8	0.41	5
16-21	0.318	0.432	71.0	0.55	5
21-31	0.252	0.390	71.0	0.55	10
31-41	0.258	0.396	71.0	0.55	10
41-51	0.288	0.420	71.0	0.55	10
51-61	0.300	0.438	71.0	0.55	10
61-71	0.294	0.438	71.0	0.55	10

[a] EF=365 day/yr,
[b] Inhalation rate, [c] 95[th] percentile, [d] body weight, [e] exposure time, [f] exposure duration

Table 2. Measured VOC concentrations in the studied products (µg/g)

	Product Type											
	Reservoir						Bowl					
	Sole Product			With Water			Sole Product			With Water		
Compound	**n[a]**	**Mean**	**Median**	**n**	**Mean**	**Median**	**n**	**Mean**	**Median**	**n**	**Mean**	**Median**
1,2-Dibromoethane	1	BDL[b]	BDL	2	BDL	BDL	1	BDL	BDL	1	BDL	BDL
1,2-Dichlorobenzene	5	6.80×10^{-3}	7.12×10^{-4}	3	1.79×10^{-3}	1.44×10^{-3}	4	3.86×10^{-2}	4.0×10^{-2}	3	1.17×10^{-2}	2.90×10^{-3}
1,3-Dichlorobenzene	1	2.03×10^{-2}	2.03×10^{-2}	2	2.10×10^{-3}	2.10×10^{-3}	0	BDL	BDL	0	BDL	BDL
1,4-Dichlorobenzene	1	3.95×10^{-3}	3.95×10^{-3}	2	1.78×10^{-2}	1.78×10^{-2}	1	7.60×10^{-2}	7.60×10^{-2}	1	6.10×10^{-2}	6.10×10^{-2}
Benzene	4	2.13×10^{-3}	6.52×10^{-4}	5	1.07	3.02×10^{-2}	5	9.22×10^{-4}	5.44×10^{-4}	5	8.34×10^{-4}	7.68×10^{-4}
Bromochloromethane	2	1.15×10^{-2}	1.15×10^{-2}	2	3.57×10^{-2}	3.57×10^{-2}	2	BDL	BDL	3	BDL	BDL
Bromodichloromethane	6	9.82×10^{-3}	5.59×10^{-3}	6	7.87×10^{-2}	1.56×10^{-2}	1	4.08×10^{-4}	4.08×10^{-4}	3	1.73×10^{-2}	1.80×10^{-2}
Bromoform	6	3.19×10^{-2}	6.48×10^{-3}	7	7.76×10^{-2}	3.74×10^{-2}	1	4.41×10^{-3}	4.41×10^{-3}	5	2.80×10^{-2}	2.92×10^{-2}
Carbon tetrachloride	7	1.86×10^{-2}	8.59×10^{-3}	7	8.75×10^{-2}	2.37×10^{-2}	4	1.39×10^{-1}	7.44×10^{-3}	4	2.72×10^{-2}	5.03×10^{-3}
Chloroform	7	1.33	3.06×10^{-1}	7	9.37	2.37	5	4.80×10^{-2}	2.53×10^{-2}	5	2.70×10^{-1}	2.97×10^{-2}
Dibromochloromethane	6	1.27×10^{-2}	2.47×10^{-3}	7	1.14×10^{-2}	3.74×10^{-3}	2	1.02×10^{-3}	1.02×10^{-3}	5	1.52×10^{-2}	1.47×10^{-2}
Naphthalene	5	4.93×10^{-3}	2.91×10^{-3}	6	4.36×10^{-3}	2.61×10^{-3}	4	8.40×10^{-3}	9.92×10^{-3}	2	8.18×10^{-3}	8.18×10^{-3}
Tetrachloroethylene	1	BDL	BDL	1	BDL	BDL	1	BDL	BDL	2	BDL	BDL

[a] Number of samples detected, [b] BDL: Below detection limit

Table 3. Estimated indoor air VOC concentrations (μg/m^3) in a 1.6 m^3 bathroom with no ventilation

	Product Type			
	Reservoir		Bowl	
Compound	**Mean**	**Median**	**Mean**	**Median**
1,2-Dibromoethane	BDL[a]	BDL	BDL	BDL
1,2-Dichlorobenzene	0.259	0.205	4.35×10^{-3}	4.0×10^{-3}
1,3-Dichlorobenzene	0.621	0.621	BDL	BDL
1,4-Dichlorobenzene	0.973	0.973	9.50×10^{-3}	9.50×10^{-3}
Benzene	6120	24	1.14×10^{-4}	7.48×10^{-5}
Bromochloromethane	5.59	5.59	BDL	BDL
Bromodichloromethane	1390	40.2	3.50×10^{-3}	3.50×10^{-3}
Bromoform	5.33	2.31	6.06×10^{-4}	6.06×10^{-4}
Carbon tetrachloride	0.228	0.077	1.90×10^{-2}	9.78×10^{-4}
Chloroform	3.36	1.80	6.01×10^{-3}	3.48×10^{-3}
Dibromochloromethane	1.41	0.38	1.36×10^{-4}	1.36×10^{-4}
Naphthalene	68.7	0.179	9.94×10^{-4}	1.21×10^{-3}
Tetrachloroethylene	BDL	BDL	BDL	BDL

[a] BDL: Below detection limit

Table 4. Summary of product and indoor air VOC concentrations reported in the literature

Compound	**Microenvironment or Product(s)**	**Concentration**	**Reference**
1,2-Dichlorobenzene	Bathroom toilet and hallway	0.62-3[b] $\mu g/m^3$ 1.4±0.85[a] $\mu g/m^3$	Odabasi, 2008
	Product concentration	0.084-0.735[b] mg/kg	Shin and Lim, 2017
	Product concentration	0.003-0.03[b] mg/L 0.014± 0.006[a] mg/L	Odabasi et al., 2014
	Modeled indoor concentration	1.57-2.54[b] $\mu g/m^3$	Shin and Lim, 2017
1,3-Dichlorobenzene	Bathroom toilet and hallway	0.004-0.01[b] $\mu g/m^3$	Odabasi, 2008
	Product concentration	0.004-0.02[c]	Shin and Lim, 2017
	Predicted concentration	4-20[b] $\mu g/m^3$	Odabasi et al., 2014
1,4-Dichlorobenzene	Bathroom toilet and hallway	0.002-0.01[c] $\mu g/m^3$ 0.005±0.004[b] $\mu g/m^3$	Odabasi, 2008
	Product concentration	0.007-0.077[c] mg/kg	Shin and Lim, 2017
	Modeled indoor concentration	0.11-0.39[c] $\mu g/m^3$	Shin and Lim, 2017
Bromodichloromethane	Bathroom toilet and hallway	0.22-0.47[c] $\mu g/m^3$ 0.34±0.09[b] $\mu g/m^3$	Odabasi, 2008
	Product concentration	0.01-0.05[c] mg/L 0.02±0.012[a] mg/L	Odabasi et al., 2014
Bromoform	Bathroom toilet and hallway	0.02-0.04[c] $\mu g/m^3$ 0.03±0.01[b] $\mu g/m^3$	Odabasi, 2008
Benzene	Living room	20[a] $\mu g/m^3$ 40[a] $\mu g/m^3$	Son et al., 2003
Carbon tetrachloride	Home, office school, restaurant	0.50-1.18[c] $\mu g/m^3$	Guo et al., 2004
	Bathroom toilet and hallway	0.25-459[c] $\mu g/m^3$ 55.2±144[b] $\mu g/m^3$	Odabasi, 2008
	Product concentration	0.01-169[c] mg/L	Odabasi et al., 2014
	Modeled indoor concentration	82±194[b] $\mu g/m^3$	Odabasi et al., 2014
	Product concentration	0.05-352[c] $\mu g/g$	Shin and Lim, 2017
	Modeled indoor conc.	1100-3690[c] $\mu g/m^3$	Shin and Lim, 2017
Chloroform	Home, office school, restaurant	0.30-0.80c $\mu g/m^3$	Guo et al., 2004
	Bathroom toilet and hallway	2.9-24.6[c] $\mu g/m^3$ 9.5±6.7[b] $\mu g/m^3$	Odabasi, 2008
	Modeled indoor concentration	0.5-1030[c] $\mu g/m^3$ 34±123[b] $\mu g/m^3$	Odabasi et al., 2014
	Product concentration	0.08-154[c] mg/L 9.5±29[b] mg/L	Odabasi et al., 2014
	Product concentration	0.2-30[c] mg/kg	Shin and Lim, 2017
	Modeled indoor concentration	130- 316[c] $\mu g/m^3$	Shin and Lim, 2017
Dibromochloromethane	Bathroom toilet and hallway	0.11-0.24[c] $\mu g/m^3$ 0.18±0.05[b] $\mu g/m^3$	Odabasi, 2008
Naphthalene	Residential indoor	0.64[a] $\mu g/m^3$	Edwards et al., 2001

[a] Average
[b] Average ±SD (SD=Standard Deviation)
[c] Range

Table 5. The 95th percentile carcinogenic risk levels associated with use of automatic toilet cleaning products

		95th percentile carcinogenic risk	
Product	Product Type	Chloroform	Carbon tetrachloride
Product 1	Reservoir	9.12×10^{-8}	2.05×10^{-9}
Product 2	Reservoir	2.43×10^{-9}	3.10×10^{-9}
Product 3	Reservoir	2.37×10^{-8}	1.68×10^{-7}
Product 4	Reservoir	1.01×10^{-7}	2.97×10^{-8}
Product 5	Reservoir	2.00×10^{-8}	3.64×10^{-8}
Product 6	Reservoir	8.62×10^{-7}	3.72×10^{-7}
Product 7	Reservoir	9.32×10^{-8}	3.81×10^{-9}
Product 8	Bowl	8.74×10^{-10}	8.09×10^{-10}
Product 9	Bowl	6.27×10^{-11}	1.05×10^{-9}
Product 10	Bowl	9.73×10^{-10}	3.81×10^{-8}
Product 11	Bowl	2.17×10^{-9}	1.55×10^{-10}
Product 12	Bowl	NA*	NA*

*Due to BDL