Received: 27 May 2022 | Revised: 20 October 2022 | Accepted: 21 October 2022

DOI: 10.1111/ina.13162

ORIGINAL ARTICLE

WILEY

Air concentrations of volatile organic compounds associated with conventional and "green" cleaning products in real-world and laboratory settings

Lucia Calderon[1] | Randy Maddalena[2] | Marion Russell[2] | Sharon Chen[2] | James E. S. Nolan[1] | Asa Bradman[3] | Kim G. Harley[1]

[1]Center for Environmental Research and Community Health (CERCH), School of Public Health, University of California, Berkeley, Berkeley, California, USA

[2]Lawrence Berkeley National Laboratory, Berkeley, California, USA

[3]Department of Public Health, University of California, Merced, Merced, California, USA

Correspondence
Lucia Calderon, Department of Epidemiology and Biostatistics, University of California, San Francisco, San Francisco, California, USA.
Email: lucia.calderon@ucsf.edu

Present address
Lucia Calderon, Department of Epidemiology and Biostatistics, University of California, San Francisco, California, USA

Funding information
California Breast Cancer Research Program through a Community Research Collaboration Full Research Award, Grant/Award Number: 24BB-2300

Abstract

The use of household cleaning products can result in exposure to potentially hazardous volatile and semi-volatile organic compounds (VOCs and SVOCs). "Green" cleaning products have become increasingly available, but there is no official "green" standard, and it is difficult for consumers to know what chemicals they may be exposed to while cleaning. We measured air concentrations of 46 VOCs and SVOCs of concern released from conventional and "green" cleaning products during both real-world household cleaning and a controlled chamber environment, with a focus on chemicals that might increase women's risk of breast cancer, including possible carcinogens, reproductive/developmental toxicants, or endocrine disruptors. Air samples were analyzed using gas chromatography–mass spectrometry and high-performance liquid chromatography. First, in a study of 50 women cleaning their own homes using either conventional or "green" cleaning products, we recorded the products used and collected air samples from the breathing zone to determine whether specific products or types of products were associated with increased concentrations of specific VOCs and SVOCs. The results showed that women who used conventional bleach products, disinfecting wipes, and dish soap had higher breathing zone air concentrations of several VOCs, including chloroform, carbon tetrachloride, hexaldahyde, and 1,4-dioxane, than women who did not use these products. While fewer "green" products were associated with increases in VOC air concentrations, use of "green" all-purpose cleaners was associated with increases in air concentrations of some fragrance chemicals of concern. In the laboratory, we then selected 9 of the most common conventional products and 7 "green" products used in the in-home study for measurement of the same VOCs using a continuous stirred cylindrical flow-through chamber. We found that 75% of the highest VOC emissions were emitted by conventional cleaning products, but we also identified VOC emissions of concern from green products. VOC emissions in the chamber largely agreed with the modeled associations from real-world cleaning.

KEYWORDS
emissions testing, household cleaning products, personal air monitoring, volatile organic compounds

1 | INTRODUCTION

The use of household cleaning products can result in exposure to potentially hazardous volatile and semi-volatile organic compounds (VOCs and SVOCs, respectively).[1,2] In laboratory chamber experiments, application of household cleaners increased air concentrations of terpenes, glycol ethers, aldehydes, and other chemicals.[3,4] An experiment in a controlled bathroom setting showed that 10-min cleaning sessions using all-purpose cleaner, glass cleaner, and bathroom cleaner increased total VOC concentrations for up to 20 min following the cessation of cleaning tasks.[5] Other studies suggest that elevated VOC concentrations may persist for several hours, extending exposure beyond the time of active household cleaning and potentially exposing other residents, including children.[1] Several studies have linked VOC exposure from cleaning products to acute health effects, including asthma and respiratory irritation.[6,7] However, few studies have examined exposures to carcinogens, reproductive toxicants, and endocrine disruptors that are present in cleaning products and may have chronic effects on women's health. Because women are often the principal cleaners in the home environment, we focused on exposures in housecleaning products that might increase the risk of breast cancer and other reproductive harm.

It is difficult for consumers to know whether they are exposed to carcinogens, reproductive/developmental toxicants, or endocrine disruptors from their cleaning products. The U.S. Environmental Protection Agency (EPA) requires disclosure of active ingredients or ingredients that kill bacteria, viruses, or mold and the U.S. Consumer Product Safety Commission (CPSC) requires labelling for acute poisoning prevention,[8] but there is no U.S. federal law requiring that all ingredients be listed on the cleaning product label. This absence of ingredient transparency makes it challenging for consumers to avoid ingredients of public health concern. Cleaning products marketed as "green," implying that they are lower in hazardous ingredients or safer for human health and/or the environment, have become increasingly available. However, there is no official designation of "green" and no standard certification to ensure that products marketed as "green" are lower in chemicals of concern.

In the LUCIR study, an intervention study of 50 women cleaning their own homes, we recently demonstrated that personal air concentrations of 17 chemicals of concern for breast cancer (i.e., suspected carcinogens, reproductive toxicants, or endocrine disruptors) decreased when women switched from their usual conventional cleaning products to cleaning products marketed as "green."[9] However, concentrations of several fragrance compounds, including one carcinogen (β-myrcene) and two suspected endocrine disruptors (celestolide and galaxolide), increased when women cleaned with the "green" products. The previous publication only showed overall changes in concentrations when using conventional versus "green" products; we were not able to determine which individual products or types of products most contributed to personal exposure.

In the present analysis, we expand on our previous study by examining the VOC and SVOC emissions associated with use of specific conventional and "green" products. We first examined personal air monitoring data from the LUCIR intervention study to determine whether the use of specific products was associated with increased exposure to VOCs and SVOCs of concern in a real-world, in-home setting. We then conducted chamber analyses of 9 of the most common conventional products and the 7 "green" products used in the LUCIR intervention. The purpose of this research was to identify chemical exposures associated with common conventional cleaning products and with their "green" counterparts to inform interventions to reduce exposure.

2 | METHODS

We examined air concentrations of 36 VOCs and 10 SVOCs in cleaning products under real-world household cleaning conditions and 36 VOCs in a controlled chamber environment. (Due to resource constraints, the 10 SVOCs were not included in the chamber analysis.) VOCs and SVOCs of interest were chosen a priori because they are suspected carcinogens or reproductive toxicants according to California's Proposition 65 list[10] or were potential endocrine disruptors according to The Endocrine Disruption Exchange (TEDX) list.[11] A complete list of the target VOCs and SVOCs selected a priori is shown in Table S1 in Appendix S1.

2.1 | Personal air sampling during household cleaning

First, we used data from the LUCIR Study in Salinas, California[9] to examine VOC and SVOC air concentrations in the breathing zone of 50 women as they cleaned their own homes under real-world conditions. At the first study visit, participants were asked to use their regular cleaning products and conduct their usual cleaning routines in the kitchen and bathroom for 30 min total. Staff recorded the brand, name, and bar code of all cleaning products that were used during the visit. For the second study visit, scheduled 1 week later, participants were again asked to conduct their usual cleaning routine in the kitchen and bathroom, but were given 7 "green" cleaning products to use instead of their regular products. All participants received the same "green" products—two all-purpose cleaners, disposable wipes, powder cleanser, toilet bowl cleaner, dish soap, and a homemade glass cleaner made from

water, white vinegar, and the dish soap. The "green" products were from national brands that marketed themselves as being "natural," "plant-based," "safe," "non-toxic," or "free of harsh chemicals." The selected "green" products were locally available and were of similar prices to locally available conventional products. Participants selected which of the "green" products to use and again, staff recorded which cleaning products were used. At both visits, staff also recorded the ventilation conditions in the home (researcher's observation of open windows or doors or use of fans, air conditioning, or exhaust hood at time of visit) and use of air fresheners (participant's reported use of any of eight different types of air fresheners that day or researcher's observation of air freshener use at time of visit).

Air sample collection and analysis methods have been described previously.[9] Briefly, three parallel air samples were collected from the breathing zone during each 30-min cleaning session using a backpack sampler worn by the participant. Two air samples were collected at 100 ml/min according to U.S. EPA Method TO-17,[12] using a Carbopack multibed thermal desorption tube (Supelco, Bellefonte PA, 28286-U) for measurement of VOCs and a Tenax TA thermal desorption tube (Supelco, Bellefonte PA, 28281-U) for measurement of SVOCs. The third air sample was collected at 1 L/min according to U.S. EPA Method TO-11A,[12] using a silica gel cartridge coated with 2,4-dinitrophenylhydrazine (DNPH) (Waters corporation, Milford MA, XPoSure Aldehyde Sampler P/N WAT047205) with ozone scrubbers installed upstream (P/N WAT054420) for measurement of aldehydes. Before and after each sampling event, actual sampling flow rates were recorded using DryCal flow meters (Mesa Labs, Lakewood, CO, Defender Model 510). Field blanks were collected for each sample media at 12% of the locations by shipping/handling/installing sampling tubes/cartridges onto the backpack sampler in the field then collecting the tubes without drawing air through the pumps. After use, sampling media were stored at −30 C and shipped weekly to Lawrence Berkeley National Laboratory (LBNL) for analysis.

Volatile and semi-volatile organic compound tubes were analyzed after spiking with internal standard using an autosampler (Gerstel, Linthicum, MD, Model TDSA2), thermal desorption oven (Model TDS3), and cryogenically cooled injection system (Model CIS4) coupled with gas chromatography/mass spectrometry (Agilent 6890/5973 and Agilent 7890A/5977B for the VOC and SVOC analysis, respectively). Multipoint calibrations were prepared from pure standards for all target VOCs and SVOCs and the response for each analyte was normalized to the internal standard response. The DNPH-coated cartridges were extracted with 2 ml of high purity acetonitrile (P/N 018-4, Burdick & Jackson) and analyzed by high-performance liquid chromatography (HPLC; 1200 Series; Agilent Technologies). Multipoint calibration curves were prepared from certified standard hydrazone derivatives of all target analytes (CRM47651: Sigma-Aldrich). The average field blank air concentration of each analyte was subtracted from calculated air concentrations to yield blank-subtracted air concentrations ($\mu g/m^3$) for each sample.

We obtained complete air concentration data for all participants in the first home visit when they used their regular products ($n = 50$). However, 5 participants accidentally used a conventional product at the second visit and one Carbopack sorbent tube was damaged in the field, resulting in 44 air samples from the "green" product use at the second visit.

For our analysis of personal air concentrations associated with in-home product use, we limited statistical analyses to the 30 VOCs and 10 SVOCs that were detected in at least 60 percent of samples. Concentrations below the method detection limit (MDL) were assigned the machine-read concentration if available or imputed with a random value <MDL based on the log-normal distribution.[13] Air concentrations were log10 transformed for analysis.

Linear regression models were used to obtain percent change in air concentration associated with in-home use of different cleaning products (used vs. did not use). At the first visit, participants could use any conventional cleaning products they wanted resulting in a very large number of different products used. Thus, for the conventional products analyses, we classified products by type (e.g., any bleach product, any dish soap). At the second visit, participants were given only 7 "green" products to choose from, so the "green" product models examined use of individual "green" products rather than product types. All models adjusted for use of ventilation (yes/no) and air fresheners (yes/no). Analyses were conducted using Stata version 15 (StataCorp). Statistical significance was considered at $\alpha = 0.05$.

2.2 | Emission testing in continuous stirred chamber

Because environmental conditions in homes and product application amounts and methods varied, including the use of multiple products during a given cleaning event, we also analyzed VOC emissions in a controlled chamber analysis. To evaluate individual cleaning products, we selected 9 of the most popular conventional products used by participants plus the 7 "green" products given to the participants for inclusion. The 9 conventional products chosen for analysis were the 4 most popular all-purpose cleaners used by participants, plus the most popular cleaning wipes, dish soap, glass/window cleaner, powder cleaner, and toilet bowl cleaner. These products were used by 8%–42% of participants (Table 1). The 9 conventional products were selected to be parallel to the 7 "green" products given to participants, which consisted of 2 brands of all-purpose cleaners, and one each of cleaning wipes, dish soap, glass/window cleaner, powder cleaner, and toilet bowl cleaner.

Emission testing was conducted in a 0.395 m^3 continuous stirred cylindrical frame flow-through chamber ("chamber") at Lawrence Berkeley National Laboratory in October 2020. The chamber was constructed with a Teflon-coated aluminum frame wrapped in a transparent Teflon film to minimize the interaction of pollutants with the chamber walls.[14] The chamber was uniformly mixed using a rotating impeller to insure that measurements collected from the sampling ports were representative of the concentration at any point

TABLE 1 Frequency of use of conventional and "green" cleaning products during in-home cleaning, LUCIR Study, Salinas, California, 2019.

Product	*n* (%)
Visit 1: Conventional product use (*N* = 50 homes)	
Most commonly used types of products:	
Any products containing bleach	36 (72)
Any disinfecting wipes	13 (26)
Any dish soap	41 (82)
Any glass/window cleaner	27 (54)
Any toilet bowl cleaner	12 (24)
Most commonly used individual products:	
All-Purpose Cleaner 1 (APC1)	9 (18)
All-Purpose Cleaner 2 (APC2)	12 (24)
All-Purpose Cleaner 3 (APC3)	9 (18)
All-Purpose Cleaner 4 (APC4)	7 (14)
Cleaning Wipes 1 (CW1)	8 (16)
Dish Soap 1 (DS1)	21 (42)
Glass/Window Cleaner 1 (GWC1)	15 (30)
Powder Cleanser 1 (PC1)	4 (8)
Toilet Bowl Cleaner 1 (TBC1)	6 (12)
Visit 2: "Green" Product Use (*N* = 44 homes)[a]	
Most commonly used individual products:	
All-Purpose Cleaner 5 (APC5)	37 (84)
All-Purpose Cleaner 6 (APC6)	38 (86)
Cleaning Wipes 2 (CW2)	21 (48)
Dish Soap 2 (DS2)	34 (77)
Glass/Window Cleaner 2 (GWC2)	33 (75)
Powder Cleanser 2 (PC2)	28 (64)
Toilet Bowl Cleaner 2 (TBC2)	40 (91)

[a]Five homes were excluded from the analysis because the participant accidently used a conventional cleaning product during the "green" product only cleaning session, one home was excluded because laboratory analysis could not be completed.

within the chamber.[14] Tests were conducted in ambient laboratory conditions at an average temperature of 29.1°C (range 25.7–32.4°C) and an average relative humidity of 33.9% (range 14.5%–52.1%). The chamber was not equipped with heating or cooling elements. The ventilation rate was set to 5 changes per hour in order to approximate the near field exposure concentration, or the exposure concentration for the space around the emission source and the breathing zone.[15,16]

For each test, the chamber was flushed with clean air for 3 to 6 air changes, then, a clean glass sampling dish (Pyrex, 33.5 × 5.1 × 22.6 cm inch) was placed in the test chamber for 15 min (1.25 air changes). Next, one cleaning product was applied to the sampling dish in accordance with the cleaning product type. For example, with products in a spray bottle, 2–3 sprays were applied to the dish; with liquid or powder products, 10 ml were applied with or without water, as appropriate; with cleaning wipes, 2 wipes were used (see Table S2 for product-specific application methods). Mass of product applied was noted in grams by weighing the product container before and after application. Single-ply cellulose wipes (Kimtech Science Kimwipes, Kimberly-Clark Professional) were used to spread products evenly across the surface of the sampling plate and the used wipe was left in the chamber for the remainder of the test. One hour following the product application, the sampling tray was removed, and sampling continued for 45 more minutes. This sampling procedure was repeated for each of the 16 cleaning products. A new, clean sampling dish was used for each test. However, the surfaces inside the chamber were not cleaned between tests.

VOCs sample collection and analysis were the same as described earlier for personal sampling in the home except that samples were collected using peristaltic pumps (Cole-Parmer Model No. 7553-70) calibrated to pull air through the sorbent tubes at approximately 20 ml/min and through the DNPH-coated cartridges at approximately 1.25 L/min. Samples were collected for the 1 h and 45 min encompassing the application and clearance period of each test. Due to laboratory availability, we were unable to use Tenax TA thermal desorption tubes (Supelco, Bellefonte PA) for the measurement of SVOCs during chamber testing. Therefore, only 36 analytes were investigated. Three blanks were collected during emissions testing by installing the sampling tube and cartridge and following the sample collection protocol without any product application. The average chamber blank air concentration of each analyte was subtracted from calculated air concentrations to yield blank-subtracted air concentrations ($\mu g/m^3$) for each sample. Blank-subtracted air concentrations were converted to a time-averaged emission rate over the sampling period in units of micrograms of chemical emitted per gram of product used (μg/g), using the air flow rate through the chamber, product application mass and sample duration.[17]

3 | RESULTS

3.1 | In-home cleaning

A list of the most commonly used products and their frequency of use during in-home cleaning is shown in Table 1. Almost 200 different cleaning products, many of which were different fragrances or formulations of the same brand, were used during the regular cleaning session when participants used their own cleaning products. Dish soap was the most commonly used product (used by 82% of participants), followed by bleach products (72% of participants) and glass/window cleaners (54% of participants). Disinfecting wipes and toilet bowl cleaners were used by 26% and 24% of participants, respectively.

During the intervention visit when participants chose from the 7 provided "green" cleaning products, the most commonly used products were the "green" toilet bowl cleaner (91%) and the two "green" all-purpose cleaners (84% and 86%). Almost all participants (94%) used air fresheners during their regular cleaning or earlier that day and most participants (74%) used some form of ventilation (open

windows/doors or use of fans/air conditioning/hood exhaust) during their regular cleaning (not shown). Air freshener use decreased slightly to 89% and ventilation use increased slightly to 80% during the intervention visit when participants cleaned with "green" cleaning products.

Associations of personal air concentrations of target VOCs and SVOCs with use of specific conventional cleaning products are shown in Table 2. Air concentrations of chloroform and carbon tetrachloride were 1131% and 179% higher, respectively, in the breathing zones of participants who used products containing bleach while cleaning their homes compared to those who did not, after controlling for air freshener use and household ventilation. Benzaldehyde and hexaldehyde concentrations were 99% and 169% higher among participants who used conventional disinfecting wipes compared to those who did not. Using conventional dish, soap was associated with increased personal air concentrations of 1,4-dioxane (241% increase), benzene (113% increase), m/p-xylene (310% increase), o-xylene (327% increase), styrene (142% increase), hexane (407% increase), heptane (220% increase), octamethylcyclotetrasiloxane (D4) (414% increase), and β-myrcene (528% increase).

The use of some conventional cleaning products was associated with lower concentrations of target VOCs and SVOCs, possibly because these products were used instead of other products containing those chemicals. The use of products containing bleach was associated with 61% lower concentrations of galaxolide. The use of conventional disinfecting wipes was associated with 65% lower 1,4-dioxane concentrations. Carbon tetrachloride concentrations were 71% lower among participants who used conventional dish soap. Conventional glass/window cleaner use was associated with decreased chloroform (68% decrease) and benzaldehyde (44% decrease) air concentrations.

In the intervention visit, the use of certain "green" products was also associated with changes in air concentrations of target VOCs and SVOCs (Table S3). Specifically, we saw higher breathing zone air concentrations of 1,4-dioxane (176% increase), celestolide (162% increase), and galaxolide (146% increase) among participants who used one of the "green" all-purpose cleaners (APC5) compared with those who did not. We also saw higher concentrations of tonalide (100% increase) among participants who used the "green" cleaning wipes (CW2) compared to those who did not. Conversely, use of the other "green" all-purpose cleaner (APC6) was associated with lower concentrations of ethylbenzene (71% decrease), o-xylene (72% decrease), and D4 (89% decrease). Use of the "green" dish soap (DS2) was associated with lower concentrations of diethyl phthalate (47% decrease), cashmeran (81% decrease), galaxolide (51% decrease), and tonalide (59% decrease). Use of the "green" powder cleaner (PC2) was associated with lower concentrations of celestolide (50% decrease). The use of the "green" toilet bowl cleaner (TBC2) was associated with lower concentrations of naphthalene (73% decrease), 2-ethylhexanol (91% decrease), o-xylene (76% decrease), benzaldehyde (72% decrease), diisobutyl phthalate (61% decrease), and cashmeran (85% decrease).

3.2 | Chamber analysis

The results of the chamber analyses to quantify VOC emissions from 9 of the most commonly used conventional cleaning products and all 7 of the "green" products provided by the study in a controlled laboratory setting are shown in Figure 1. Among the 36 VOCs analyzed, 28 were emitted from at least one product; 26 were emitted from at least one conventional product and 18 were emitted from at least one "green" product. Twenty-one (75%) of the VOC emissions were highest among a conventional product, and 7 (25%) were highest among "green" products.

One of the conventional all-purpose cleaners (APC1) emitted the highest amounts of chloroform (65.8 μg/g) and carbon tetrachloride (11.2 μg/g). APC1 also emitted the most tetrachloroethylene (0.26 μg/g), benzene (0.32 μg/g), toluene (1.59 μg/g), and heptane (0.45 μg/g). APC2 emitted the most trichloroethene (0.35 μg/g), 1,4-dioxane (9.9 μg/g), ethylene glycol monobutyl ether (EGBE) (95.41 μg/g), and diethylene glycol monobutyl ether (DGBE) (>425.16 μg/g, above instrument limit of quantification). APC3 emitted the highest level of benzaldehyde (2.44 μg/g) and β-myrcene (15.77 μg/g). APC4 emitted the highest level of formaldehyde (6.76 μg/g). The conventional cleaning wipes (CW1) emitted the highest amount of hexaldehyde (65.5 μg/g), ethylbenzene (0.36 μg/g), styrene (0.26 μg/g), and 2-ethylhexanol (2.75 μg/g). The conventional dish soap (DS1) emitted the second highest amounts of 1,4-dioxane (1.5 μg/g). The conventional glass/window cleaner emitted the highest levels of TXIB/Kodaflex (6.01 μg/g) and D4 (0.07 μg/g). The conventional toilet bowl cleaner (TBC1) emitted the highest level of acetaldehyde (1.93 μg/g) and the conventional powder cleanser (PC1) emitted the highest amount of phenol (>72.62 μg/g, above instrument upper limit of quantification). PC1 also emitted the second highest amount of chloroform (10.2 μg/g). Chloroform appeared to be emitted from every product tested, albeit in much smaller amounts relative to APC1 and PC1—the next highest amount emitted was 0.6 μg/g from APC2.

Among the "green" products, APC5 emitted the highest levels of m/p-xylene (0.87 μg/g) and crotonaldehyde (5.78 μg/g), and APC6 emitted the highest levels of o-xylene (0.17 μg/g) and decamethylcyclopentasiloxane (D5) (0.26 μg/g). The "green" homemade glass/window cleaner (GWC2) appeared to emit the highest levels of methylene chloride (0.36 μg/g) and hexane (1.77 μg/g). The "green" toilet bowl cleaner (TBC2) emitted the highest level of butylbenzene (0.12 μg/g).

4 | DISCUSSION

In a real-world, household cleaning setting, we found that women who used certain types of conventional cleaning products experienced increased exposure to some VOCs and SVOCs of concern, including increased air concentrations of chloroform and carbon tetrachloride in the breathing zone of women using bleach-containing products, increased benzaldehyde and hexaldehyde exposure among

TABLE 2 Adjusted differences in personal air concentrations of target VOCs and SVOCs among participants using specified conventional products while cleaning home compared to those not using these products ($N = 50$), LUCIR Study, Salinas, California, 2019.

		Bleach use		Disinfecting wipes use		Dish soap use		Glass/Window cleaner use		Toilet cleaner use	
Chemical	CAS number	Percent difference[a]	(95% CI)	Percent difference[a]	(95% CI)	Percent difference[a]	(95% CI)	Percent difference[a]	(95% CI)	Percent difference[a]	(95% CI)
Volatile organic compounds											
Halogenated hydrocarbons											
Chloroform[b,c]	67-66-3	1131.36	(333.53, 3397.41)***	−61.20	(−88.06, 26.04)	−66.28	(−90.34, 17.67)	−67.97	(−87.44, −18.31)*	−50.24	(−83.55, 50.51)
Carbon tetrachloride[b,c]	56-23-5	179.43	(51.23, 416.31)**	28.20	(−35.89, 156.37)	−70.72	(−85.96, −38.94)**	−26.37	(−57.55, 27.70)	39.19	(−27.41, 166.89)
Methylene chloride[b,c]	75-09-2	30.91	(−3.88, 78.28)	−0.01	(−29.44, 41.69)	−17.45	(−42.97, 19.48)	0.58	(−23.75, 32.69)	−25.98	(−46.65, 2.70)
Tetrachloroethylene[b,c]	127-18-4	−21.14	(−63.21, 69.04)	9.63	(−53.64, 159.23)	32.02	(−47.01, 228.93)	11.52	(−43.72, 120.98)	−12.93	(−61.20, 95.44)
1,2-Dichloroethane[b]	107-06-02	−44.82	(−74.00, 17.08)	56.82	(−32.92, 266.59)	9.03	(−55.71, 168.36)	14.88	(−41.49, 125.59)	−45.65	(−75.52, 20.68)
Other											
1,4-Dioxane[b]	123-91-1	−20.10	(−63.12, 73.12)	−64.67	(−85.24, −15.44)*	240.79	(35.04, 760.06)*	21.00	(−39.52, 142.09)	−21.14	(−65.26, 79.04)
Naphthalene[b,c]	91-20-3	−15.38	(−55.61, 61.29)	−19.62	(−61.19, 66.47)	102.65	(−6.38, 338.69)	5.37	(−40.92, 87.92)	6.75	(−46.13, 111.55)
2-Ethylhexanol[c]	104-76-7	−36.79	(−72.51, 45.37)	14.82	(−55.15, 193.93)	85.90	(−31.41, 403.85)	26.89	(−39.88, 167.81)	−23.76	(−68.47, 84.35)
TXIB/Kodaflex[c]	6846-50-0	−40.12	(−75.57, 46.73)	174.10	(−0.34, 653.84)	−21.27	(−73.08, 130.25)	17.84	(−47.26, 163.28)	80.87	(−30.08, 367.88)
Benzene derivatives											
Benzene[b,c,d]	71-43-2	−34.60	(−57.62, 0.93)	−11.20	(−45.58, 44.91)	113.40	(26.94, 258.75)**	9.42	(−25.85, 61.48)	21.87	(−23.07, 93.06)
Toluene[c,d]	108-88-3	−34.40	(−68.71, 37.53)	1.62	(−55.93, 134.35)	141.24	(−0.56, 485.27)	−26.95	(−62.39, 41.91)	29.34	(−41.00, 183.55)
Ethylbenzene[b,c]	100-41-4	−30.83	(−69.35, 56.07)	4.96	(−58.11, 162.98)	76.89	(−33.23, 368.62)	12.84	(−45.61, 134.14)	79.30	(−24.34, 324.94)
m/p-Xylene[c]	106-42-3	−24.43	(−66.75, 71.77)	−19.68	(−68.21, 102.93)	310.00	(53.40, 995.82)**	0.06	(−52.09, 108.98)	62.07	(−32.14, 287.12)
o-Xylene[c]	95-47-6	−27.73	(−68.59, 66.27)	−13.18	(−66.10, 122.35)	327.20	(57.55, 1058.40)**	0.11	(−52.59, 111.36)	50.56	(−37.77, 264.23)
Styrene[b,c]	100-42-5	−16.68	(−50.25, 39.53)	−1.68	(−45.06, 75.95)	142.19	(30.64, 349.02)**	−14.60	(−46.22, 35.62)	26.53	(−26.76, 118.59)
Phenol[c]	108-95-2	−38.79	(−74.81, 48.76)	100.60	(−26.38, 446.56)	13.58	(−60.77, 228.90)	−32.26	(−69.46, 50.23)	−16.75	(−67.53, 113.45)
Butylbenzene[c]	104-51-8	−21.72	(−59.74, 52.20)	2.37	(−51.67, 116.81)	121.12	(−0.25, 390.15)	12.98	(−37.77, 105.12)	9.56	(−45.86, 121.74)
Nitrobenzene[b,c,d]	98-95-3	36.03	(−65.26, 432.63)	291.74	(−16.07, 1728.53)	247.21	(−32.26, 1679.61)	−7.15	(−72.71, 215.85)	−10.32	(−78.91, 281.30)
1,4-Dichlorobenzene[b]	106-46-7	67.80	(−56.79, 551.65)	8.58	(−76.52, 402.13)	−30.08	(−86.22, 254.89)	−70.45	(−91.25, −0.20)	−67.05	(−92.18, 38.89)
Aldehydes											
Formaldehyde[b,c]	50-00-0	−6.46	(−37.90, 40.91)	22.47	(−22.88, 94.47)	23.71	(−24.25, 102.04)	11.94	(−22.48, 61.66)	−5.12	(−38.56, 46.50)
Acetaldehyde[b,c]	75-07-0	16.30	(−34.72, 107.19)	−14.49	(−55.44, 64.10)	39.15	(−30.30, 177.82)	−5.45	(−43.67, 58.72)	−20.02	(−56.64, 47.54)
Benzaldehyde[c]	100-52-7	13.56	(−36.09, 101.78)	99.31	(4.16, 281.35)*	−18.35	(−58.97, 62.51)	−44.20	(−66.68, −6.55)*	−13.28	(−52.86, 59.53)
Hexaldehyde[c]	66-25-1	−38.28	(−63.59, 4.62)	169.03	(48.28, 388.09)**	53.40	(−18.45, 188.56)	20.05	(−25.22, 92.72)	15.44	(−34.03, 102.01)
Alkanes											

TABLE 2 (Continued)

Chemical	CAS number	Bleach use		Disinfecting wipes use		Dish soap use		Glass/Window cleaner use		Toilet cleaner use	
		Percent difference[a]	(95% CI)	Percent difference[a]	(95% CI)	Percent difference[a]	(95% CI)	Percent difference[a]	(95% CI)	Percent difference[a]	(95% CI)
Hexane[c,d]	110-54-3	18.21	(−54.30, 205.75)	36.18	(−53.41, 298.05)	406.87	(62.47, 1481.35)**	0.92	(−56.97, 136.68)	87.33	(−31.61, 413.14)
Heptane[c]	142-82-5	−50.46	(−75.35, −0.42)	−9.29	(−58.75, 99.48)	220.46	(38.92, 639.23)**	−26.57	(−60.74, 37.34)	31.28	(−37.38, 175.22)
Glycol ethers											
EGBE[c]	111-76-2	465.85	(−49.68, 6262.86)	201.41	(−80.37, 4527.81)	−48.84	(−97.18, 827.23)	265.68	(−58.27, 3104.26)	−58.36	(−96.80, 441.80)
DGBE[c]	112-34-5	−36.35	(−92.62, 448.92)	−45.73	(−95.23, 517.57)	56.82	(−88.11, 1968.47)	34.61	(−80.51, 829.66)	−4.39	(−90.26, 838.92)
Siloxanes											
D4[c]	556-67-2	12.58	(−64.15, 253.61)	21.25	(−66.68, 341.28)	413.51	(30.46, 1921.31)*	59.49	(−42.86, 345.18)	26.84	(−62.31, 326.85)
D5[c]	0541-02-06	−27.85	(−79.16, 149.8)	78.12	(−56.15, 623.53)	243.36	(−22.37, 1418.65)	68.56	(−44.66, 413.44)	6.88	(−71.36, 298.80)
Terpenes											
b-Myrcene[b]	123-35-3	−8.31	(−64.70, 138.16)	10.06	(−62.53, 223.26)	528.04	(100.29, 1869.31)**	−33.52	(−71.76, 56.51)	141.25	(−12.32, 563.77)
Semi-volatile organic compounds											
Phthalates											
Diethyl phthalate[c]	84-66-2	1.09	(−44.09, 82.79)	−29.24	(−63.74, 38.08)	6.54	(−47.57, 116.52)	52.61	(−10.29, 159.60)	−13.91	(−54.06, 61.33)
Dibutyl phthalate[c,d]	84-74-2	13.07	(−15.33, 50.98)	−10.84	(−35.67, 23.57)	−3.78	(−31.94, 36.03)	−4.44	(−26.27, 23.86)	−11.24	(−34.68, 20.61)
Diisobutyl phthalate[c]	84-69-5	−21.48	(−55.06, 37.20)	−15.56	(−55.03, 58.52)	−7.93	(−52.8, 79.60)	−17.95	(−50.26, 35.35)	−21.32	(−56.46, 42.19)
Nitro musks											
Musk xylene[c]	81-15-2	−9.56	(−60.20, 105.52)	−13.93	(−65.92, 117.41)	60.15	(−40.06, 327.91)	−30.22	(−66.58, 45.71)	−40.65	(−75.15, 41.72)
Musk ketone[c]	81-14-1	−40.74	(−74.12, 35.67)	−8.86	(−64.22, 132.12)	−6.71	(−65.39, 151.50)	6.09	(−49.53, 123.01)	−28.16	(−70.15, 72.89)
Polycyclic musk											
Cashmeran (DPMI)[c]	33704-61-9	−49.97	(−88.80, 123.50)	68.57	(−68.88, 813.13)	106.83	(−65.54, 1141.39)	−16.83	(−78.28, 218.44)	46.09	(−70.12, 614.32)
Celestolide (ADBI)[c]	13171-00-1	−46.51	(−72.75, 5.01)	−40.48	(−72.20, 27.43)	62.02	(−27.75, 263.31)	23.89	(−32.34, 126.88)	5.61	(−48.35, 115.92)
Phantolide (AHMI)[c]	15323-35-0	29.81	(−41.51, 188.12)	−17.37	(−66.40, 103.22)	37.06	(−47.23, 256.00)	12.40	(−45.02, 129.79)	44.56	(−37.93, 236.66)
Galaxolide (HHCB)[c]	1222-05-5	−61.12	(−84.22, −4.18)*	−22.60	(−72.03, 114.24)	65.51	(−43.78, 387.32)	27.03	(−43.43, 185.26)	56.28	(−39.94, 306.68)
Tonalide (AHTN)[c]	21145-77-7	30.25	(−38.66, 176.57)	−27.86	(−69.16, 68.78)	−7.94	(−62.63, 126.78)	7.85	(−45.11, 111.90)	9.41	(−50.76, 143.12)

*$p < 0.05$, **$p < 0.01$, ***$p < 0.001$.

[a]Separate models including all of the conventional cleaning product categories and adjusting for air freshener and ventilation use were run for each chemical.

[b]CA Proposition 65 Carcinogen.

[c]Suspected endocrine disrupting chemical (EDC).

[d]CA Proposition 65 Reproductive/Developmental Toxicant.

women using conventional cleaning wipes, and increased exposure to 1,4-dioxane, D4, β-myrcene, and several benzene derivatives among women using conventional dish soap. These chemical exposures may arise from intentional ingredients in products, unintentional impurities, or reactions created during the cleaning process. For example, chloroform and carbon tetrachloride are caused when the sodium hypochlorite in bleach reacts with soap or surfactants[18] while benzaldehyde and hexaldehyde can be formed when fragrance compounds react with ozone, hydroxyl radicals or nitrate radicals.[1] Of the chemicals associated with conventional dish soap use, D4 (a cyclic siloxane used as a solvent and carrier in cleaners[19]) and β-myrcene (a plant-derived fragrance compound) are likely intentional ingredients in product formulation, while the benzene derivatives are more likely to be trace impurities[20] and 1,4-dioxane is an impurity created as a by-product of surfactant synthesis.[21] "Green" products were associated with fewer increases in air concentrations but still resulted in exposure to some chemicals of concern, particularly intentional fragrance compounds including polycyclic musks such as celestolide, galaxolide, and tonalide.

In chamber analyses, we were able to analyze emissions from all of the "green" products used in the in-home study but only from 9 of many conventional products used. We found that 75% of the highest VOC emissions came from conventional cleaning products, but also identified VOC emissions from "green" products. Despite the fact that we were only able to analyze a small fraction of the conventional products used, the results of our analyses—from both real-world household cleaning and a controlled chamber environment—generally complement each other. Specifically, products containing bleach, namely APC1 and PC1, emitted the highest levels of chloroform and carbon tetrachloride in the chamber, which is consistent with our personal air sampling findings among women using bleach products in the home. The high emission of 1,4-dioxane from DS1, which was used by 42% of participants in the home, is consistent with our observation of higher 1,4-dioxane concentrations in the homes of women using conventional dish soap. Conventional CW1 emitted the highest amount of hexaldehyde, which supports our finding that use of disinfecting wipes increased personal air concentrations of hexaldehyde in real-world household cleaning.

These results also support previous findings from the LUCIR study,[9] in which we compared overall VOC and SVOC levels during the conventional versus "green" cleaning sessions. That study found significant decreases in air concentrations of several chemicals including chloroform, carbon tetrachloride, 1,4-dioxane, and hexaldahyde, in the session when the "green" products were used compared to the conventional products. The LUCIR study also found an unexpected increase in air concentrations of the fragrance chemicals

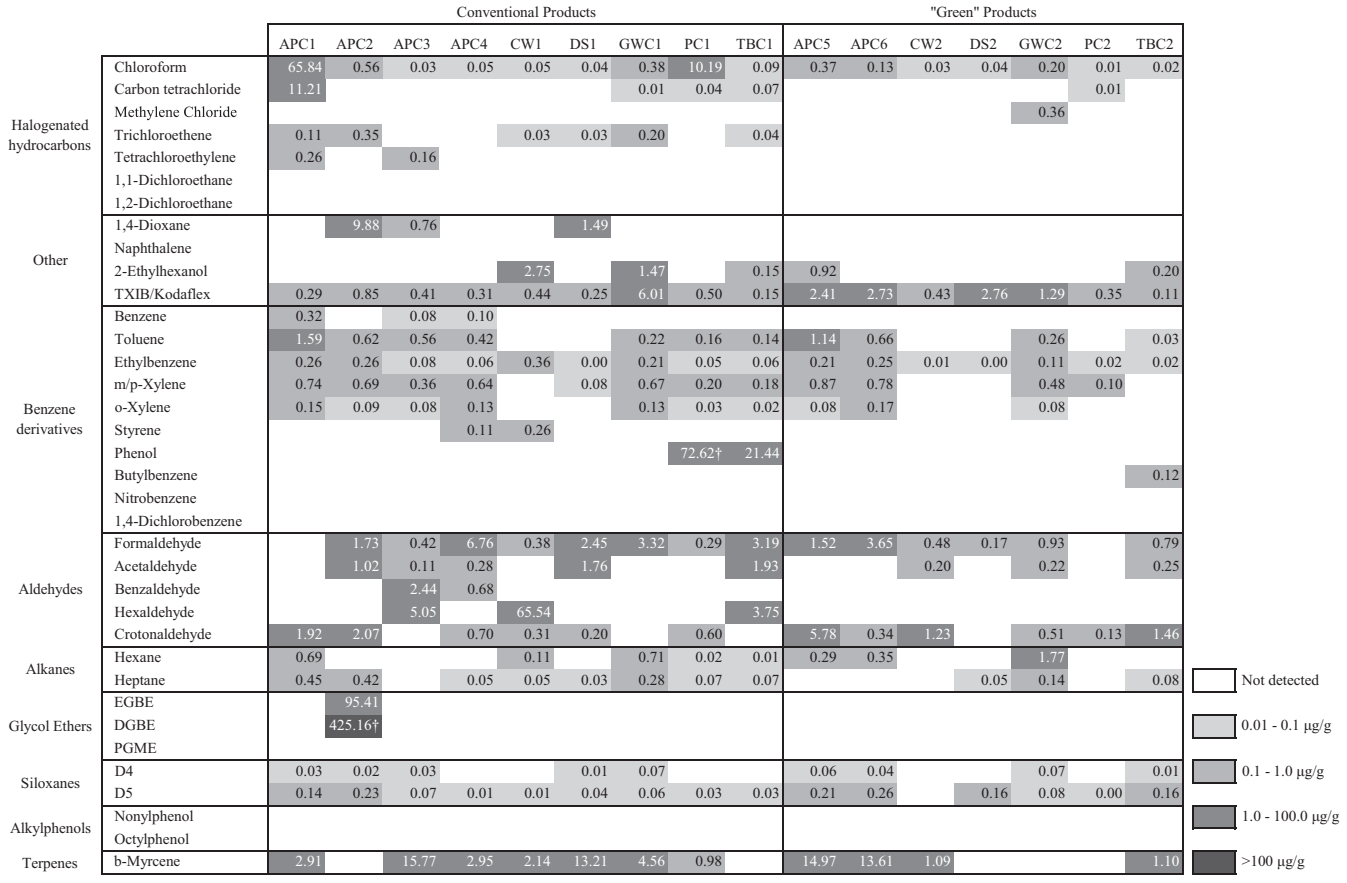

FIGURE 1 Emission of target VOCs from conventional and "green" cleaning products in stir chamber, LUCIR Study, 2020. *Notes*: APC, all-purpose cleaner; CW, cleaning wipes; DS, dish soap; GWC, glass/window cleaner; PC, powder cleaner; TBC, toilet bowl cleaner. †Above instrument upper limit of quantification.

β-myrcene, celestolide, and galaxolide. The chamber analyses of the present study show that "green" products APC5 and APC6 emitted the second and third highest amounts of the terpene β-myrcene in the chamber experiments. The high use rates of these two "green" products—84% and 86%, respectively—likely contributed to the observed increase in β-myrcene in the study. Although we were unable to measure SVOCs in our chamber experiments, in the in-home analysis we found that use of APC5 was associated with higher personal air concentrations of celestolide and galaxolide, which may account for the increase in these two synthetic musks in the intervention study. The use of fragrance chemicals, some of which may have both chronic and acute health effects, in "green" products warrants additional scrutiny.

The main strength of the current study is that data come from both real-world and laboratory settings and there is much agreement between our findings from both. Our findings allow us to understand what VOCs are emitted from cleaning products into the breathing zone, thereby going beyond information that would be found on product labels and making our findings more relevant for reducing exposures. We analyzed a large number of VOCs and SVOCs ($n = 46$), making this one of the largest targeted analyses of cleaning product chemicals.

Still, our study has a few limitations. In our analysis of personal air concentrations during household cleaning, our models were based on the overall use of products (yes/no) rather than amount of product used. Because we did not account for the mass of product used, our results could have been influenced by participants using more of one product and less of another. This limitation motivated our chamber-based emissions testing, where we were able to account for mass of product applied. Our analysis of personal air concentrations during household cleaning had a small sample size ($N = 50$) further limited by compliance and damage to sampling media, which could underpower our results. Additionally, because participants were allowed to use any of their conventional cleaning products during the first air sampling visit, a large number of different products and formulations were used. Cell sizes were small for individual conventional cleaning product use, and we were forced to analyze associations with conventional products by category of products rather than by individual cleaning products. We were unable to test all of these conventional products in the chamber analysis and were limited to the 9 most commonly used products which limits the comparability of our personal air sampling and the chamber results. Comparability was further limited because we could not measure SVOCs in our chamber experiments. Lastly, the average temperature and relative humidity of our chamber testing may not have been representative of conditions at the time of real-world air monitoring in all cases. However, much agreement exists where results are comparable.

Some unexpected findings from our chamber experiment may point to sample contamination or carryover between tests. First, GWC2 appeared to emit relatively high amounts of methylene chloride and hexane, but GWC2 was a simple homemade product made from tap water, white vinegar, and the "green" dish soap DS2, which did not emit either chemical. Since methylene chloride and hexane are common laboratory chemicals, it is possible that other activity in the laboratory contaminated the sample. Second, trace amounts of chloroform appeared to be emitted from all products in our chamber analysis. APC1, the bleach-containing product with the highest chloroform emission, was the first product applied, followed by APC2, which did not contain bleach according to the label, but appeared to emit the third highest level of chloroform (order of product tests can be seen in Table S1). Although the chamber was flushed with air between runs and a clean sampling plate was used for each test, the chamber interior surfaces were not cleaned between tests. We only collected three blanks throughout the duration of chamber testing and cannot report on blank concentrations between each test. Therefore, carryover between product applications cannot be ruled out. Finally, our chamber experiment findings are limited because they are based on only one round of sampling.

The present analysis focused on chemicals that were suspected carcinogens, endocrine disruptors, or reproductive/developmental toxicants, but it should be noted that these are not the only chemicals of concern found in cleaning products. Many cleaning products also include acute respiratory or skin irritants that were not the focus of our analysis. For example, vinegar was a component of the homemade "green" glass cleaner given to study participants, despite the fact that acetic acid is a known asthmagen. Although this analysis focused on non-irritant compounds, both non-irritant and irritant ingredients are important considerations for choosing cleaning products. Overall, we provided evidence of which conventional and "green" cleaning products or types of products contributed most to a variety of exposures of public health concern. While switching to "green" products can decrease exposure to many carcinogens, reproductive/developmental toxicants, and suspected endocrine disruptors,[9] we did see elevated levels of some chemicals, specifically fragrance chemicals, associated with use of some "green" cleaning products. Thus, choosing "green" products without fragrance might also decrease exposure to both natural and synthetic fragrance compounds and the volatile organic compounds that form from reactions with them. Improving knowledge of and access to fragrance-free "green" cleaning products can reduce household exposures to chemicals of public health concern. Moreover, cleaning product manufacturers should consider actions to minimize consumer exposure to known or suspected carcinogens, reproductive/developmental toxicants, or endocrine disruptors, such as product reformulations and transparent labeling.

AUTHOR CONTRIBUTIONS

Lucia Calderon performed formal analysis, investigation, writing—original draft preparation, and visualization. **Randy Maddalena** performed methodology, resources, writing—review and editing, and supervision. **Marion Russell** involved in resources and writing—review and editing. **Sharon Chen** investigated the study. **James E. S. Nolan** and **Asa Bradman** involved in writing—review and editing. **Kim G. Harley** performed conceptualization, methodology, writing—review qnd editing, supervision, project administration, and funding acquisition.

ACKNOWLEDGMENTS

This work was supported by the California Breast Cancer Research Program through a Community Research Collaboration Full Research Award (CRC, 24BB-2300).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

Research data are not shared.

ORCID

Lucia Calderon https://orcid.org/0000-0002-5295-3132

REFERENCES

1. Nazaroff WW, Weschler CJ. Cleaning products and air fresheners: exposure to primary and secondary air pollutants. *Atmos Environ*. 2004;38(18):2841-2865.
2. Dodson RE, Nishioka M, Standley LJ, Perovich LJ, Brody JG, Rudel RA. Endocrine disruptors and asthma-associated chemicals in consumer products. *Environ Health Perspect*. 2012;120(7):935-943.
3. Nørgaard A, Kudal J, Kofoed-Sørensen V, Koponen I, Wolkoff P. Ozone-initiated VOC and particle emissions from a cleaning agent and an air freshener: risk assessment of acute airway effects. *Environ Int*. 2014;68:209-218.
4. Singer BC, Destaillats H, Hodgson AT, Nazaroff WW. Cleaning products and air fresheners: emissions and resulting concentrations of glycol ethers and terpenoids. *Indoor Air*. 2006;16(3):179-191.
5. Bello A, Quinn MM, Perry MJ, Milton DK. Quantitative assessment of airborne exposures generated during common cleaning tasks: a pilot study. *Environ Health*. 2010;9(1):76.
6. Folletti I, Siracusa A, Paolocci G. Update on asthma and cleaning agents. *Curr Opin Allergy Clin Immunol*. 2017;17(2):90-95.
7. Zock J-P, Plana E, Jarvis D, et al. The use of household cleaning sprays and adult asthma: an International Longitudinal Study. *Am J Respir Crit Care Med*. 2007;176(8):735-741.
8. Wagner DS. *General Guide to Chemical Cleaning Product Regulation*. International Sanitary Supply Association, Inc; 2000.
9. Harley KG, Calderon L, Nolan JES, et al. Changes in Latina Women's exposure to cleaning chemicals associated with switching from conventional to "green" household cleaning products: the LUCIR intervention study. *Environ Health Perspect*. 2021;129(9):9.
10. Office of Environmental Health Hazard Assessment. The proposition 65 list. 2020. Accessed March 15, 2021. https://oehha.ca.gov/proposition-65/proposition-65-list
11. The endocrine disruption exchange. Search the TEDX List 2018. Accessed August 6, 2021. https://endocrinedisruption.org/interactive-tools/tedx-list-of-potential-endocrine-disruptors/search-the-tedx-list
12. United States Environmental Protection Agency. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - Second Edition*. Center for Environmental Research Information, Office of Research and Development; 1999.
13. Lubin JH, Colt JS, Camann D, et al. Epidemiologic evaluation of measurement data in the presence of detection limits. *Environ Health Perspect*. 2004;112(17):1691-1696.
14. Maddalena R, Parra A, Russell M, Lee W-Y. *Measurement of Passive Uptake Rates for Volatile Organic Compounds on Commercial Thermal Desorption Tubes and the Effect of Ozone on Sampling*. Lawrence Berkeley National Laboratory; 2013.
15. Nicas M. Using mathematical models to estimate exposure to workplace air contaminants. *Chemical Health & Safety*. 2003;10(1):14-21.
16. Jayjock MA, Armstrong T, Taylor M. The Daubert standard as applied to exposure assessment modeling using the two-zone (NF/FF) model estimation of indoor air breathing zone concentration as an example. *J Occup Environ Hyg*. 2011;8(11):D114-D122.
17. California Department of Public Health. Standard Method for the Testing and Evaluation of Volatile Organic Chemical Emissions from Indoor Sources Using Environmental Chambers Version 1.1. 2010.
18. Odabasi M. Halogenated volatile organic compounds from the use of chlorine-bleach-containing household products. *Environ Sci Technol*. 2008;42(5):1445-1451.
19. McKim JM Jr, Wilga PC, Breslin WJ, Plotzke KP, Gallavan RH, Meeks RG. Potential estrogenic and antiestrogenic activity of the cyclic siloxane octamethylcyclotetrasiloxane (D4) and the linear siloxane hexamethyldisiloxane (HMDS) in immature rats using the uterotrophic assay. *Toxicol Sci*. 2001;63(1):37-46.
20. Agency for Toxic Substances and Disease Registry. *Toxicological profile for Benzene*. U.S. Department of Health and Human Services, Public Health Service; 2007.
21. Tahara M, Obama T, Ikarashi Y. Development of analytical method for determination of 1,4-dioxane in cleansing products. *Int J Cosmet Sci*. 2013;35(6):575-580.

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: Calderon L, Maddalena R, Russell M, et al. Air concentrations of volatile organic compounds associated with conventional and "green" cleaning products in real-world and laboratory settings. *Indoor Air*. 2022;32:e13162. doi: 10.1111/ina.13162