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Infant Exposure to Emissions of Volatile Organic Compounds from Crib Mattresses

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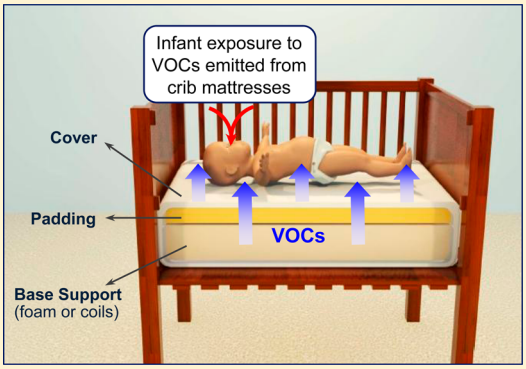
Supporting Information

ABSTRACT: Infants spend most of their time sleeping and are likely to be exposed to elevated concentrations of chemicals released from their crib mattresses. Small-scale chamber experiments were conducted to determine the area-specific emission rates (SERs) of volatile organic compounds (VOCs) in a collection of twenty new and used crib mattresses. All mattress samples were found to emit VOCs and the mean values of total VOC (TVOC) SERs were 56 $\mu g/m^2h$ at 23 °C and 139 $\mu g/m^2h$ at 36 °C. TVOC SERs were greater for new mattresses compared to used ones and were influenced by the type of foam material and the presence of mattress cover layer. A variety of VOCs were identified, with polyurethane foam releasing a greater diversity of VOCs compared to polyester foam. Large-scale chamber experiments were conducted with an infant thermal manikin. TVOC concentrations sampled in the breathing zone and interior pore air of the crib mattress foam were found to be greater than the bulk room air by factors in the range of 1.8 to 2.4 and 7.5 to 21, respectively. The results suggest that crib mattresses are an important source of VOCs and infant exposure to VOCs are possibly elevated in their sleep microenvironments.



INTRODUCTION

Infants spend a considerable amount of time sleeping, typically ranging from 12 to 13 h/day in their first three years of life, significantly more than adults (average of 8.2 h/day) (Figure S1, Table and Figure numbers preceded by an "S" are in the Supporting Information (SI)). Sleep durations greater than 14 h/day during the first year of life are also commonly reported.[1,2] The length of the sleep period makes infant sleep microenvironments particularly important in contributing to both their acute and chronic exposures to various gaseous indoor air pollutants, particularly those originating in the crib mattresses on which they sleep.

The composition of a typical crib mattress includes a thick layer of polyurethane or polyester foam padding (inner-springs are also used) encased within a thin, waterproof plastic cover to protect the mattress foam and to provide an easy-to-clean surface. The use of petroleum-derived polyurethane and plastic materials, along with various adhesives and additives used in the manufacturing and assembly processes, suggests that crib mattresses are a likely source of volatile organic compounds (VOCs).[3,4] Anderson and Anderson[5,6] identified a variety of VOCs released from one crib mattress sample and one waterproof crib mattress cover sample, many of which were solvents or chemicals likely used in the manufacture of the crib mattress. The emissions were found to cause sensory irritation, pulmonary irritation, and decreases in midexpiratory airflow velocity in mice. Furthermore, VOC emissions from consumer and building products have been shown to increase with temperature,[7−10] suggesting that VOC emissions from crib mattresses may increase due to localized elevations in mattress surface temperature caused by heat transfer from a sleeping infant.[11−13]

Infants' inhaled dose of VOCs originating in their crib mattresses may be augmented due to the significant amount of air they inhale per body mass and the impact of the source-proximity effect. The volume of air inhaled/kg-day can be estimated by taking the product of the mean normalized volumetric breathing rate during a sleep or nap activity[14] and the mean duration of time spent in a sleep or nap activity (SI Figure S2). Infants inhale about 250−300 L/kg-day, nearly an order of magnitude more air per body mass than adults. Additionally, the source-proximity effect, in which pollutant concentrations near a source are greater than those in the bulk room air, may also lead to elevated infant inhalation exposure to VOCs. There are several key factors that likely influence the source-proximity effect, including the spatial proximity of an infant's breathing zone (BZ) to the crib mattress, incomplete mixing of bedroom air, concentrations gradients near an actively emitting crib mattress, and the buoyant thermal plume

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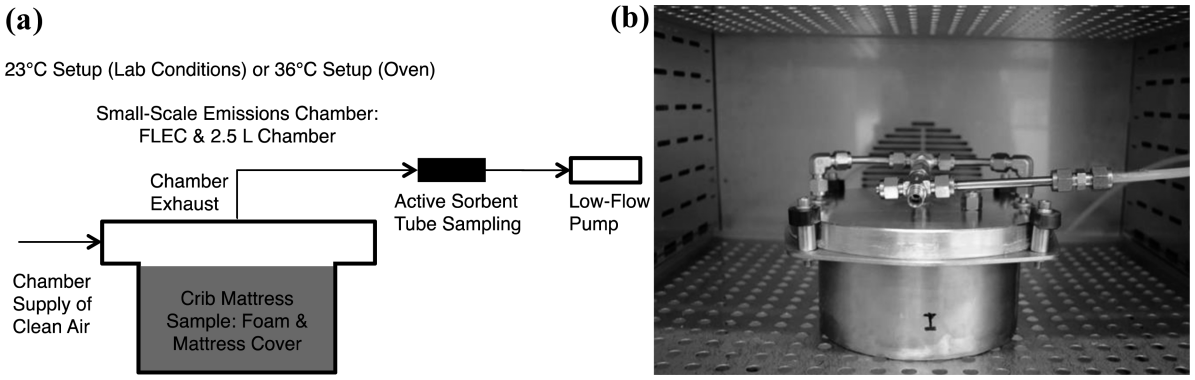

Figure 1. (a) Schematic and (b) photo of the experimental setup for small-scale chamber VOC SER experiments.

around an infant.[15−21] Laverge et al.[17] simulated the release of gaseous pollutants from an adult mattress with an inert tracer gas and found the BZ concentrations for an adult thermal manikin to be significantly greater than those measured in the bulk air, typically by a factor of 1.1 to >2, depending on sleep position and bedding arrangement.

Associations between VOC exposure and poor respiratory health have been observed among infants. Early life exposures to VOCs may impact the developing immune system and increase the risk of allergic disease in young children, even at low concentrations.[22] Diez et al.[1] found that the presence of VOCs (i.e., styrene, benzene) in a bedroom increased the risk of pulmonary infections in six-week old infants. Among a cohort of children 6 months to 3 years of age, Rumchev et al.[23] found numerous VOCs (i.e., benzene, toluene, ethylbenzene, *m*-xylene) to be a significant risk factor for asthma, with every 10 $\mu g/m^3$ increase in toluene and benzene increasing the risk of having asthma by a factor of 2 and 3, respectively. Additionally, studies have shown that the primary exposure route of VOCs in infants is through inhalation of indoor air, 25−135 fold higher than through ingestion of a mother's breast milk.[24] Strachan and Carey[25] surmised that VOCs released from pillows in close proximity to the BZ might increase mucosal permeability to inhaled allergens, which the authors believe may explain the association between the use of foam pillows and childhood asthma. Furthermore, Abraham et al.[26] applied a pharmacokinetic model to compare internal exposures to a common VOC, styrene, between infants and adults. The arterial blood concentration in newborns and 1 year old infants was found to be approximately 1.2 to >3 times higher than that of an adult exposed to the same airborne concentration. The authors attributed these findings to the relatively high alveolar ventilation rate and immature metabolism in infants.

Therefore, there is a need to understand the role of crib mattresses as a source of VOCs in infant sleep microenvironments, given the potential for elevated infant exposure to VOCs that may volatize from this source and the health implications of early life exposure to VOCs. The objectives of this paper are to: measure the area-specific emission rate (SER) of VOCs from crib mattresses in small-scale chambers; determine the parameters that may have an influence on SERs; identify common VOCs emitted from crib mattresses; and measure the VOC BZ concentration in a large-scale chamber with an infant thermal manikin to explore the source-proximity effect.

MATERIALS AND METHODS

Material Selection. Twenty crib mattresses, of varying usage, quality, and material composition, were selected for this study (SI Table S1). Nine new crib mattresses made by different manufacturers were purchased from an online retail store. Eleven used crib mattresses were obtained through donations in Austin, Texas, and Helsinki, Finland. The used crib mattresses were manufactured in various years between 1993 and 2009, were actively used for different durations, and were stored in different indoor spaces, including bedrooms, closets, and attics. The foam layers of the mattresses were manufactured out of polyurethane foam (PUF), polyester foam (Poly.), or polyurethane foam with a fraction of soy-derived foam.

SER Experiments in Small-Scale Chambers. The crib mattress samples were cut to the appropriate size (14.25 Ø × 7.5 cm) to fit within the small-scale chamber (Figure 1). The edges of the samples were sealed with aluminum foil and low-VOC aluminum tape to minimize edge effects. Following sample preparation, the samples were conditioned in the laboratory at 23 °C and 50% relative humidity (RH) for at least one month prior to the VOC SER experiments. All new samples were tested approximately six months after they were manufactured, thereby avoiding the peak emission period and better representing long-term emissions.

Small-scale emission chambers (Figure 1) were used to measure the SER of VOCs from the crib mattress samples. The small-scale chamber included a field and laboratory emission cell (FLEC) (0.035 L) mounted to a 2.5 L cylindrical stainless steel emission chamber. The small-scale chamber was supplied with clean, purified air at 23 ± 1 °C and 50 ± 2% RH. SI Table S2 provides an overview of the operational parameters. The area specific airflow rate (q, m/h) for the VOC SER experiments was 1.52 m/h, and was selected to be equivalent to the large-scale chamber experiments. Translating to a standard-size 14.4 m^3 bedroom, this area specific airflow rate equates to a bedroom air exchange rate of 0.16 h^{-1}, representative of ventilation levels in actual children's bedrooms.[27] Prior to the emissions test, all components of the small-scale emissions chamber were thoroughly cleaned with methanol and placed in an oven at 70 °C overnight for approximately 12 h.

Active air sampling was performed at the exhaust of the small-scale emission chambers using sorbent tubes packed with Tenax TA and a low-flow pump (Gillian Low Flow Sampler, model LFS-113DC, Sensidyne LP). Backup tubes were connected to each primary sampling tube to check for

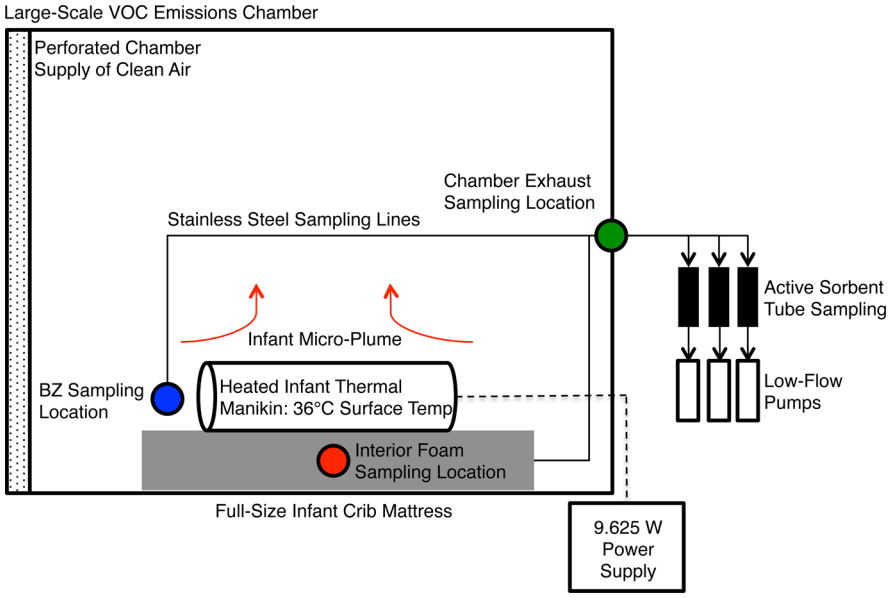

Figure 2. Schematic of the experimental setup for large-scale VOC infant manikin experiments.

breakthrough. Prior to a test, an air sample was taken from the empty chamber to ensure the background total VOC (TVOC) concentration was below 5 $\mu g/m^3$. The crib mattress was then placed in the chamber for approximately 20 h before sampling, to allow it to reach thermal equilibrium with the chamber (at 36 °C) and to avoid short-term peak emissions. The experiments were carried out at a temperature of 23 and 36 °C and, in all cases, steady-state VOC concentrations were achieved during air sampling (SI Figure S3). Additionally, three crib mattresses (samples 2, 8, and 20) were tested without the mattress cover layer. These experiments provided insight into the role of the mattress cover in acting as a barrier to the transport of VOCs originating from the foam layer and the contribution of the cover to the total VOC SER from the entire crib mattress. In total, 46 VOC SER experiments were performed.

Large-Scale Chamber Experiments. Full-scale chamber experiments were conducted in a 4.5 m^3 emission chamber with a new full-size crib mattress (sample 6, polyurethane foam) and an infant thermal manikin (Figure 2, SI Table S2). The aim of these experiments was to simulate a semirealistic exposure scenario and experimentally determine the BZ concentration for VOCs emitting from a crib mattress to explore the impact of the source-proximity effect.

A simplified infant thermal manikin was constructed using a hollow galvanized steel cylinder (oval cross section, 50 × 15 × 12 cm), with heating elements placed uniformly inside. The cylinder was wrapped with aluminum foil and aluminum tape and the edges were sealed. The manikin was heated for approximately four weeks to bake out any VOCs originating within the cylinder materials. Background TVOC concentrations in the empty full-scale chamber with the heated thermal manikin were found to be below 1 $\mu g/m^3$. To simulate the convective airflow around a sleeping infant, the surface temperature of the manikin was set to 35.6 ± 0.7 °C, the approximate skin surface temperature of a sleeping infant,[11−13] via a power input of 9.625 W for an approximate heat dissipation per unit manikin surface area of 40 W/m^2 (Varivolt Metric Power Supply). The uniformity of the heat flux was verified by taking four surface temperature measurements with thermistors (44000 Series, Omega Engineering).

The large-scale emissions chamber was supplied with clean, purified air at 23 ± 1 °C and 50 ± 2% RH. Experiments were first conducted to evaluate the "sleeping infant micro-plume" generated by the thermal manikin (measured with omnidirectional anemometers, model HT-400, Sensor Electronics). Three cases were considered: manikin heating on with mattress cover, manikin heating on without mattress cover, and manikin heating off without mattress cover. The crib mattress (sample 6) was conditioned at laboratory conditions (23 °C and 50% RH) for one-month prior the full-scale emissions test. Upon placing the crib mattress and infant thermal manikin in the chamber, conditions were allowed to equilibrate for at least 24 h prior to sampling. VOC concentrations were sampled simultaneously at three locations with stainless steel tubing and fittings: interior of the crib mattress foam, at the center of the foam block; BZ, 2.5 cm above the mattress surface, 5 cm from the top edge of the manikin, and 3 cm from the side edge of the manikin; and the chamber exhaust, representing the bulk room air. For each of the three cases, four to six samples were taken at each of the three locations, over a period of two to three days. Steady-state VOC concentrations were achieved for all cases.

Analytical Methods. The sorbent tubes were thermally desorbed at 260 °C for 6 min (cold trap temperature of −30 °C) using a thermal desorber (TurboMatrix ATD, PerkinElmer, Inc.) and analyzed with a gas chromatograph (GC) connected to a mass spectrometer detector (MSD) and flame ionization detector (FID) (Clarus 500, PerkinElmer, Inc.). The gas chromatograph was equipped with a double-capillary column (column: 50 m, 0.2 mm ID, film thickness: 0.5 μm) (HP-PONA, Agilent Technologies, Inc.) and the sample was split 1:1 between the two columns, which were connected to the MSD and FID detectors. The temperature program of the GC oven was as follows: 40 °C (5 min hold), ramp 1 (6 °C/min) to 280 °C (5 min hold), ramp 2 (45 °C/min) to 40 °C (1 min hold), with a total run time of 51 min. MSD in SCAN mode was used to identify single VOCs and individual peaks were compared with a mass spectral library (NIST08). Identification is based on a minimum of a 75% match, and therefore, should be regarded as a qualitative best estimate since

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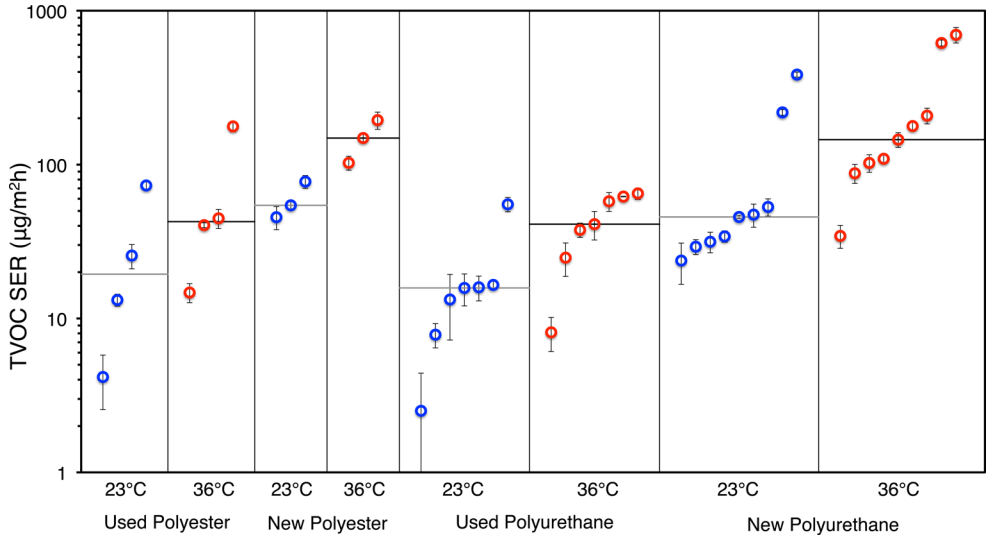

Figure 3. TVOC SER categorized by temperature, usage, and foam material (plotted on logarithmic axis).

reference standards were not used. The FID response was used for quantification. VOC concentrations (C_{VOC}, $\mu g/m^3$) were calculated as toluene equivalents (ISO 16000-6) with a bias error of ±10%. TVOC concentrations were calculated as the total integrated FID signal between hexane and hexadecane. An external toluene standard (100 ng of toluene) was used for calibration (one standard tube per ten sample sorbent tubes analyzed). The VOC SER was calculated as shown:

$$SER_{VOC}(\mu g/m^2h) = [\overline{C_{VOC}}(\mu g/m^3) - C_{VOC,Bkg.}(\mu g/m^3)] \times q(m/h) \quad (1)$$

where $\overline{C_{VOC}}$ ($\mu g/m^3$) is taken as the average concentration over the 10 h sampling period (based on 3−5 samples) and $C_{VOC,Bkg.}$ ($\mu g/m^3$) is the background concentration for an empty chamber. To determine the uncertainty in the VOC SER, the error in measuring both C_{VOC} and q was propagated. For C_{VOC}, the precision error (standard deviation) based on the 3−5 repeated concentration measurements taken at steady-state chamber conditions was combined with an instrument-calibration bias error of ±10% in C_{VOC}. The instrument error for the bubble flow meter was ±1%.

RESULTS

Small-Scale Chamber Experiments and TVOC SER. The results of the small-scale chamber experiments are presented in Figure 3, with the TVOC SERs categorized by temperature, usage, and foam material. The TVOC SERs are plotted on a logarithmic axis to improve visualization of the data and the error bars represent the calculated error in the SER. The detailed results with measurement uncertainties are also listed in SI Table S3. All new and used crib mattresses were found to emit VOCs. Across all twenty samples, TVOC SERs ranged from 3 to 385 $\mu g/m^2h$ (mean of 56 $\mu g/m^2h$) at 23 °C and from 8 to 697 $\mu g/m^2h$ (mean of 139 $\mu g/m^2h$) at 36 °C. TVOC *SERs* in this range are similar to emissions from other consumer products and building materials[9,28−32] that may be found in an infant bedroom or nursery, such as soft polyurethane foam (<10 $\mu g/m^2h$ at 23 °C and 45%RH), PVC flooring (108 $\mu g/m^2h$), laminate flooring (154 to 249 $\mu g/m^2h$, depending on floor temperature), parquet floor covering (80 $\mu g/m^2h$), wall coverings (51 $\mu g/m^2h$), and plastic toy materials (4.1 to 1080 $\mu g/m^2h$ at 23 °C and 50%RH).

VOC emissions increased with temperature, as shown in Figure 3 and SI Figure S4. The TVOC SER at 36 °C is about double that at 23 °C (SI Figure S4). The temperature dependence of the VOC emissions follows a similar trend as previous emission studies.[7−10,30] A VOC's vapor pressure tends to increase with temperature. At 36 °C, a VOC molecule has a greater affinity for the gas phase, thereby enhancing its partitioning from the solid phase (mattress cover or foam) to the chamber air. The temperature dependence is particularly relevant to the infant sleep microenvironment, because heat released from a sleeping infant will warm surrounding objects, including their mattress. Thus, VOC emissions may increase due to elevations of localized mattress surface temperature.

TVOC SERs were greater for the nine new crib mattress samples (mean of 87.1 $\mu g/m^2h$ at 23 °C, mean of 218.8 $\mu g/m^2h$ at 36 °C) compared to the eleven used samples (mean of 22.1 $\mu g/m^2h$ at 23 °C, mean of 52.1 $\mu g/m^2h$ at 36 °C) by factors of 3.9 and 4.2 at 23 and 36 °C, respectively. VOC emissions tend to decay as the material-phase concentration in the source depletes over time. Lundgren et al.[29] showed that TVOC SERs of PVC flooring can decrease about 60% from 4 to 26 weeks after manufacture. As previously discussed, the new samples were tested approximately six months after they were manufactured, thereby avoiding the peak emission period and better representing long-term emissions. Lower TVOC SERs among the used samples suggests the reuse of an older crib mattress or an extended "air out" period of a new mattress may be desirable as a preventive approach to reduce infant VOC exposures. However, crib mattress reuse must be considered carefully, because older crib mattresses may contain toxic substances (i.e., flame retardants) that have been banned for a period of time.

Mattress samples 2, 8, and 20 were also tested without the mattress cover layer. For samples 2 and 20, the TVOC SER increased as the mattress cover was removed (SI Table S3). This suggests that the crib mattress cover may act as a barrier to VOCs originating in the foam layer. Its effectiveness depends on the diffusion coefficients of the mattress cover for VOCs, which are influenced by both porosity and tortuosity of the material, as well temperature.[33] In general, the lower the

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diffusion coefficient, the more effective the layer will be in preventing transport of VOCs from the underlying foam layer.[34] Despite the findings for samples 2 and 20, the TVOC SER decreased for sample 8 when the cover layer was removed (SI Table S3). Thus, for some crib mattresses, the mattress cover layer may be a more significant source of VOCs than the foam layer. Lastly, the interior surface of the mattress cover may also act as a sink to VOCs that volatilize from the underlying foam layer. Both the adsorption of VOCs to the cover, and desorption from the cover, is a temperature-dependent process.[35−40] Thus, the dynamic VOC sorption process will be influenced by the repeated heating and cooling of the mattress cover during occupied and unoccupied periods on the crib mattress, respectively.

The foam material, polyester or polyurethane, was also found to influence TVOC SERs. TVOC SERs from new samples with polyurethane foam (mean of 70.0 $\mu g/m^2h$ at 23 °C, mean of 197.7 $\mu g/m^2h$ at 36 °C) were slightly greater than those with polyester foam (mean of at 59.1 $\mu g/m^2h$ 23 °C, mean of 148.6 $\mu g/m^2h$ at 36 °C). The three highest TVOC SERs were found for sample 2 (polyurethane with and without cover layer) and sample 20 (polyurethane without cover layer). No association was observed between TVOC SER and the quality (i.e., retail cost in USD) of the new crib mattresses.

Additional factors, such as relative humidity, chamber design, and sink effects may also influence VOC emissions from materials to varying extents; however, their impact on crib mattress emissions were not investigated here. Relative humidity is particularly relevant to the infant sleep microenvironment due to elevated moisture levels that may occur as the infant breathes and perspires. Emission studies have shown that VOC SERs tend to increase with increasing relative humidity.[7,8] Afshari et al.[41] demonstrated that chamber size and design does not have a strong impact on VOC SERs, with similar SERs determined for a FLEC, CLIMPAQ (Chamber for Laboratory Investigation of Materials Pollution and Air Quality), and a 1 m^3 emission chamber. However, interlaboratory studies have shown significant variation in VOC emission rates, suggesting lab-specific chamber setup, sampling techniques, and analytical methods may influence emission results.[42] Therefore, the SERs reported in this investigation might be specific to the experimental methods in which they are determined. Lastly, sink effects may influence SERs for crib mattresses, especially if bedding is used to wrap the crib mattress. VOCs released from the underlying crib mattress may adsorb to the bedding over time, thereby impacting airborne VOC concentrations.

VOC Speciation. The most abundant VOCs were identified and their individual VOC SERs are reported in Table 1. SI Table S5 provides a complete list of VOCs identified (some compounds having boiling points >240 °C, can be classified as semi-VOCs (SVOCs)). SERs varied widely among different compounds and crib mattress samples; they ranged from <1 to 62 $\mu g/m^2h$ at 23 °C and from 2 to 257 $\mu g/m^2h$ at 36 °C. Nearly all VOC SERs increased with temperature from 23 to 36 °C. Some VOCs exhibited a greater temperature dependence, including phenol, 2-ethyl-hexanoic acid, palmitic acid, and 2,6-bis(1,1-dimethylethyl)-4-(1-oxopropyl)phenol, whereas other VOCs were less sensitive to the temperature increase, including 3-methyl-1-heptanol and isooctanol. The temperature dependence of SER for a particular VOC likely depends on a combination of factors, including the VOC's boiling point, material-air partition coefficient, material-phase diffusion coefficient, and the way the VOC is incorporated into the solid matrix of the material.

Table 1. VOC SER of the Most Abundant and Commonly Identified VOCs among New and Used Infant Crib Mattresses in Small-Scale Chamber Experiments

		number of samples			
compound[a]	new/ used	PUF	Poly.	VOC SERs at 23 °C ($\mu g/m^2$ h)	VOC SERs at 36 °C ($\mu g/m^2$ h)
phenol	new	5	1	<1−62	3−257
	used	1	1		
isooctanol	new	1	1	<1−6	4−7
	used	1			
neodecanoic acid	new		3	3−22	9−40
	used		1		
hexanoic acid, 2-ethyl-	new	5		<1−55	5−213
	used	1	1		
1-heptanol, 3-methyl	new	2	2	7−21	7−22
	used				
D-limonene	new	2		4−11	9−18
	used				
2,6-bis(1,1-dimethylethyl)-4-(1-oxopropyl)phenol	new	2		4−14	12−61
	used				
(S)-3-ethyl-4-methylpentanol	new	1	1	2−6	3−9
	used	1			
linalool	new	2		3−41	10−44
	used				
nonanal	new	1		<1−5	2−10
	used	2	4		
decanal	new	1		<1−5	2−10
	used	1	1		
isopropyl myristate	new			<1−3	3−11
	used	3	2		
palmitic acid	new			2−10	12−43
	used	1	1		
2-ethylhexanol	new	1		3−6	7−8
	used	1	1		

[a]All compounds identified with at least 75% match with NIST mass spectral library.

The impact of foam material is evident in regard to the specific VOCs released from the crib mattress samples. Polyurethane foam showed a greater diversity of VOCs, many of which were not identified in polyester foam (or identified much less frequently), including phenol, 2-ethyl-hexanoic acid, D-limonene, and linalool. Phenol is used as an intermediate in the production of phenolic resins[43] that may be used in the production of polyurethane foam; 2-ethyl-hexanoic acid is used

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as a catalyst in the production of polyurethane foam;[44] D-limonene is commonly used as a fragrance, as well as a solvent and wetting agent in the manufacture of resins;[45] and linalool is used as a fragrance.[46] Neodecanoic acid, a carboxylic acid that is used as a polymerization initiator, was only associated with polyester foam crib mattress samples. Other compounds detected include isooctanol and 2-ethylhexanol, which are used in the production of plasticizers, as an intermediate for resin solvents, emulsifiers, and antifoaming agents.[45,47] Similar compounds and TVOC SERs were detected for the polyurethane foam samples manufactured with a fraction of soy-derived foam (samples 7 and 8) as with the normal polyurethane foam samples; however, dimethylformamide, a solvent used in production of polyurethane products,[48] was only detected in the soy-based sample 8 (SI Table S5).

Numerous VOCs were more commonly detected among new crib mattress samples, including phenol (6 new, 2 used), 2-ethyl-hexanoic acid (5 new, 2 used), 3-methyl-1-heptanol (4 new, 1 used), D-limonene (2 new, 0 used), neodecanoic acid (3 new, 1 used), and linalool (2 new, 0 used). D-limonene, a terpene, and linalool, a terpene alcohol, were only detected among new mattress samples, suggesting that the used samples were nearly depleted of these compounds, which are highly reactive with ozone.[49] In addition, several VOCs were detected more frequently among used samples, including nonanal (6 used, 1 new), isopropyl myristate (5 used, 0 new), and palmitic acid (2 used, 0 new). Nonanal, which was detected in 6 of the 11 used samples, is an alkyl aldehyde that is released by human skin[50] and also found in building materials,[51] while isopropyl myristate and palmitic acid are fatty acid esters that can be found in personal care products, such as lotions and ointments.[52,53] Because polyurethane foam has a high sorption capacity and can adsorb airborne VOCs over time,[4] the compounds detected among the used samples may represent adsorbed VOCs that originated elsewhere in a residence rather than VOCs used in the production of the mattress.

Large-Scale Chamber Experiments. As shown in Figure 4 and SI Table S4, TVOC concentrations sampled at the BZ were significantly greater than those of bulk air sampled at the chamber exhaust. BZ concentrations ranged from 14.2 to 33.2 $\mu g/m^3$ (mean of 26.2 $\mu g/m^3$), the exhaust concentrations ranged from 8.0 to 18.4 $\mu g/m^3$ (mean of 13.5 $\mu g/m^3$), and the ratio of the BZ concentration to the exhaust concentration ranged from 1.7 to 2.4 (mean of 2), depending on the particular case. These results suggest that there is a source-proximity effect associated with exposure to VOCs released from crib mattresses. It can be explained by the development of VOC concentration gradients around the emission source (crib mattress), the close proximity of the BZ sampling location (2.5 cm above the mattress surface), and the incomplete mixing of chamber air. Indeed, these ratios (i.e., concentration ratios of BZ to bulk air) follow the same trend as those reported by Laverge et al.[17] for a tracer gas and Boor et al.[54] for particles resuspended from mattresses (range of 1.07 to 1.94). However, caution should also be taken when extrapolating the experimental results to actual infant bedroom environments, because different air exchange rates and airflow distributions may significantly influence the results.

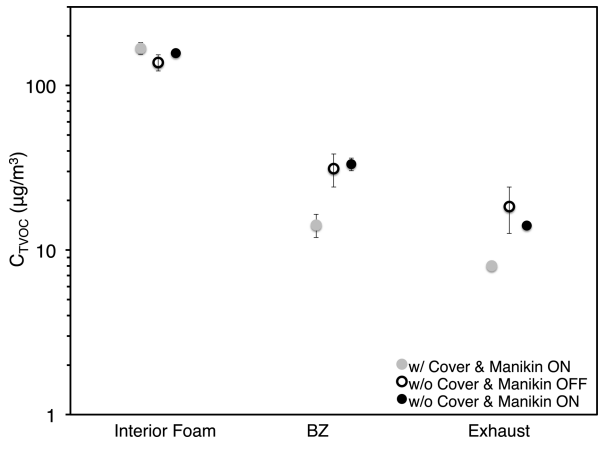

Figure 4. Spatial distribution of TVOC concentrations in large-scale emissions experiments with infant thermal manikin. Error bars represent the calculated error in C_{TVOC}.

Switching on the heat output of the infant manikin resulted in a small increase in TVOC BZ concentrations (difference within instrument error), although the ratio of the BZ concentration to the exhaust increased from 1.7 to 2.4. Because the manikin may only raise the surface temperature for a small fraction of crib mattress, the increase in emissions is not as pronounced as when the entire mattress sample in the small-scale chamber is thermally conditioned at 36 °C. In addition, TVOC BZ concentrations may also be influenced by the microplume generated by the heated infant manikin. Sharp velocity increases above the upper surface of the manikin were observed as the buoyant plume develops (SI Figure S5). Thermal plumes may serve two competing roles: effectively transporting pollutants, released from various locations in close vicinity to the human body, vertically upward, toward to BZ;[20,21] and entraining "fresh" air exterior to the BZ region, thereby diluting concentrations of gaseous pollutants and improving mixing conditions.[17] Therefore, as an infant sleeps, heat dissipation from their bodies may elevate the crib mattress surface temperature, thereby increasing VOC emissions, and generate a thermal plume that aids both in delivering VOCs upward to the BZ and diluting BZ concentrations by entraining bulk room air.

TVOC concentrations sampled in the interior foam at the center of the crib mattress (range of 137.9−168.4 $\mu g/m^3$, mean of 154.4 $\mu g/m^3$) were found to be nearly an order of magnitude greater than those in the BZ region or bulk room air. The very high pore concentration may have important implications for infant exposure. As the porous and sponge-like mattress foam is compressed and decompressed in a cyclic manner due to infant body movements, the pore air may be released in short-term bursts, thereby elevating short-term BZ concentrations. The impact of the "mattress pumping effect" requires further investigation and emphasizes the dynamic interaction between source and receptor in the sleep microenvironment. Furthermore, removing the crib mattress cover increased the BZ and bulk air TVOC concentrations, while slightly reducing the interior foam concentration (SI Table S4). Thus, depletion of VOCs in the pore air led to an elevation in airborne TVOC concentrations. Given these findings, as well as those for the VOC SER experiments, for particular products where the foam is a stronger VOC source relative to the cover, the mattress cover may play an important role in acting as a barrier to the transport of VOCs originating within the foam layer and more saturated pore air. Although not investigated here, adult mattresses typically do not include a plastic mattress cover layer, rather a porous fabric mattress encasing. Thus, VOCs

originating in polyurethane foam may be more easily released into the adult sleep microenvironment.

Estimation of Infant Inhalation Exposure. The BZ TVOC concentrations can be applied in a simple inhalation exposure analysis to estimate sleeping inhalation doses for infants. The daily inhalation intake dose[55] can be estimated as the product the BZ TVOC concentration and the volume of air inhaled/kg-day during a sleep period (SI Figure S2). Assuming BZ TVOC concentrations of 26.2 $\mu g/m^3$ from the large-scale emission chamber experiments (mean of three cases considered), the daily sleeping inhalation dose for VOCs originating in a crib mattress for infants would be approximately 8 μg/kg-day from birth to 1 year of age and 6.4 μg/kg-day for 2 years of age. Thus, infants may receive doses on the order of 1 μg/kg-day of the sum of all VOCs that may be released from their crib mattresses. For comparison, inhalation doses on this order of magnitude are greater than those reported by Masuck et al[9] for infant exposure to VOC emissions from toy fragrances (range of 2.2−220 ng/kg-day) and on the same order of magnitude as those reported by Kim et al.[24] for toluene (4.5 μg/kg-day) and benzene (1 μg/kg-day) in living room air. Furthermore, if an infant and adult are exposed to the same BZ concentration of a VOC released from a mattress, the infant normalized dose will be an order of magnitude greater than that of the adult (SI Figure S2), emphasizing the seriousness of early life exposures to gaseous indoor air pollutants. Finally, the infant thermal plume, along with the airflow patterns within an infant's crib and bedroom, will impact BZ concentrations, and thus, the inhalation intake dose. More research is needed to fully characterize airflow regimes in infant sleep microenvironments and how they impact infant exposure to gaseous and particulate pollutants originating in an infant's crib mattress and bedding.

DISCUSSION: BEYOND VOCS

In this study, small-scale chamber experiments were conducted to measure the emissions of VOCs from crib mattresses and to identify the most abundant compounds. Large-scale chamber experiments were then performed with a heated infant thermal manikin to explore the impact of the source-proximity effect on infant exposure to VOCs originating in their crib mattresses. The results suggest that crib mattresses are an important source of VOCs and infant exposure to VOCs are possibly elevated in sleep microenvironments. Therefore, efforts should be made to mitigate infant exposure to VOCs originating in their crib mattress through careful selection of low-emitting materials used in the manufacture of the mattress, including various foams, plastics, solvents, and adhesives.

In addition to VOCs, crib mattresses may contain semi-volatile organic compounds (SVOCs), including plasticizers, flame retardants, and unreacted isocyanates. Most crib mattresses have a vinyl cover for waterproofing and antibacterial purposes, and phthalates are extensively used as plasticizers to enhance the softness and flexibility of the cover. Because they are not chemically bound to the polymer matrix, they slowly volatilize from the material and migrate into surrounding environments.[56−58] In 2009, the Consumer Product Safety Improvement Act was enacted in the U.S., placing restrictions on phthalates (i.e., bis(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), and benzyl butyl phthalate (BBP)) in toys and child care articles.[59] However, there is some debate as to whether or not crib mattresses are included in the definition of "child care articles".[60,61] Furthermore, the ban on diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP) only applies to children's toys that can be placed in a child's mouth. Alternative plasticizers, such as diisononyl cyclohexane-1,2-dicarboxylate (DINCH), have emerged very recently, but toxicological information is limited. As a result, various phthalate plasticizers and their alternatives were found in crib mattress covers.[62]

Crib mattresses manufactured with polyurethane foam are highly flammable and require flame retardant additives (commonly 1−15% by weight) to meet various flammability standards.[63,64] For several decades, polybrominated diphenyl ether (PBDE) flame retardants, specifically pentaBDEs, were commonly added to crib mattress foam until industry ended production in the U.S. in 2004. Flame retardants currently used in crib mattresses include various organophosphates and industry mixtures.[63,64] There is limited published data available regarding the emissions of these compounds.[65] Additionally, unreacted isocyanates may be present in crib mattresses if excess levels of toluene diisocyanate are used in the production of the polyurethane foam.[66,67]

Therefore, a clear understanding of infant exposure to these emerging SVOC contaminants emitted from crib mattresses, which may disproportionately affect infants and children and lead to lifelong illnesses and disabilities, is urgently needed. The experimental data and the methodology developed in this study will help to achieve this goal.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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