Supporting Information

Identification of Phthalate and Alternative Plasticizers, Flame Retardants, and Unreacted Isocyanates in Infant Crib Mattress Covers and Foam

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Health Effects of Target Compounds Identified in this Study

Phthalates have endocrine disrupting properties (Bergman et al. 2013) and have been shown to retard male development (Adibi et al. 2003, Swan et al. 2005), alter semen quality (Hauser et al. 2006), cause irreversible changes to the male reproductive tract (Matsumoto et al. 2008), and increase the risk of allergic disease and asthma (Bornehag et al. 2004, Kolarik et al. 2008, Larsson et al. 2010). Presently, toxicological data on phthalate replacements, including DEHA, DINCH, and iso-DEHP, are limited. DEHA may induce mild developmental toxicity (Dalgaard et al. 2003) and has been shown to decrease anogenital distance and retention of nipples in rats (Jarfelt et al. 2005). Studies suggest that DINCH may not have endocrine disrupting properties or reproductive toxicity, although it has been associated with thyroid hyperplasia and renal toxicity (EFSA 2006). Polybrominated diphenyl ethers (PBDEs), including PentaBDE congeners, can interfere with thyroid hormone homeostatis, and consequently, delay neurological development in humans and rodents (Rudel and Perovich 2009). PBDE exposure has been found to impair a child's motor, cognitive, and behavioral performance and decrease fecundability (Roze et al. 2009, Herbstman et al. 2010). Adverse health effects associated with TPP include neurotoxicity (Andresen et al. 2004), cardiotoxicity (McGee et al. 2013), immunotoxicity

(Saboori et al. 1991), and contact dermatitis (Camarasa and Serra-Baldrich 1992). TDCPP has been found to be associated with increases in kidney, liver, and testicular tumors in rats (Faust and August 2011). Isocyanates may play an important role in the development of childhood asthma (Krone and Klinger 2005 and references therein) and exposure has been associated with allergic sensitization, asthma, rhinitis, and contact dermatitis (Bello et al. 2007, Verschoor and Verschoor 2014).

PAS-FT-IR Analysis

All twenty crib mattresses were screened for phthalates in the cover layer (prior to extractions and GC/MS analysis) and unreacted isocyanates in the foam layer via Photoacoustic (PAS) Fourier transform-infrared (FT-IR) spectroscopy (FTS 6000, Bio-Rad Laboratories, Inc. equipped with a MTEC 300 photoacoustic detector, as described in Wahlström et al. 2012). PAS-FT-IR is a non-destructive method that requires no pre-treatment of the samples, and thus, is suitable for screening-level analysis (McClelland et al. 1992). Cover and foam samples 10 mm in diameter were taken from near the middle of a horizontal surface of the crib mattress. Additionally, a liquid standard solution of DEHP (CAS 117-81-7) and hard polyvinyl chloride (PVC) were analyzed to produce instrument-specific spectra for qualitative comparisons. Samples were analyzed at a modulation frequency of 2.5 kHz with helium as the detector gas atmosphere.

Sample spectra were generated for all cover and foam samples and example spectra are shown in Figure S3. For the detection of phthalates in crib mattress covers, all sample spectra were compared with the reference DEHP spectrum. The sample spectra were manually inspected for peaks representing the structure of DEHP, including C-H stretching (2959, 2933, 2876 cm^{-1}), C=O stretching of O=C-O (1726 cm^{-1}), C-O stretching of O=C-O (1285 cm^{-1}), C-O stretching of O-CH_2 (1124, 1077 cm^{-1}), and out of plane bending for aromatics (745 cm^{-1}). Based on this analysis, phthalates, or plasticizers with a similar structure to that of DEHP, were determined to be likely present in nine of the eleven used cover samples (samples 10-18) and four of the nine new cover samples (samples 3, 5, 7, 20). Based on the GC/MS analysis, fifteen of the twenty predictions were correct, in that a phthalate or alternative plasticizer was detected at a concentration > 10 mg/g. The utility of PAS-FT-IR for screening of plasticizers requires more research, including generation of instrument-specific reference spectra for the numerous plasticizers in use in baby products.

Unreacted isocyanates (NCO) were identified in all crib mattress polyurethane foam samples via a peak at wavenumber of 2274 cm^{-1} (Figure S3 b and Table S1). Numerous FT-IR studies of polyurethane foam have shown that NCO groups (functional group –N=C=O) are characterized by strong asymmetric stretching vibration around 2270-2280 cm^{-1}, a region where there is minimal interference from other functional groups (e.g., Bhattacharjee and Engineer 1996, Luda et al. 2004, Hatchett et al. 2005, Delucchi 2008).

Chemicals, Solvent Extraction, and GC-MS Analysis

Standard solutions were used for chemical calibration and identification. Bis(2-ethylhexyl) phthalate (DEHP) was purchased from Absolute Standards, Inc. (Hamden, CT); bis(2-ethylhexyl) isophthalate (iso-DEHP) was purchased from SPEX CertiPrep (Metuchen, NJ); and diisononyl phthalate (DINP, specifically DINP-2, CAS 28553-12-0) and bis(2-ethylhexyl) adipate (DEHA) were purchased from Accustandard, Inc. (New Haven, CT). Pure (anhydrous, >99%) diisononyl 1,2-cyclohexanedicarboxylic acid (DINCH) was purchased from BOC Sciences (Shirley, NY), from which calibration standards were made. Bis(2-ethylhexyl) phthalate-3,4,5,6-d4 (D_4-DEHP) was used as an internal standard and purchased from Accustandard, Inc. (New Haven, CT). Hexane was used as the solvent in the extractions and purchased from Sigma-Aldrich Co. LLC (anhydrous, >99%) (St. Louis, MO).

Crib mattress cover samples, typically less than 1 mm in thickness, were taken from near the middle of a horizontal surface of the crib mattress, cut into ~ 1 cm by 1 cm pieces, and accurately weighed (~ 1 g). The “upper” horizontal surface, upon which an infant sleeps, was selected if known from the manufacturer label or packaging. Please note that the crib mattress cover described here is a structural part of the mattress, and not a secondary mattress protector, e.g., used a barrier for house dust mite allergens. Crib mattress foam samples were taken from the foam layer located immediately below the cover sample and accurately weighed (~ 1 g). The samples were ultrasonically extracted (3800 Ultrasonic Cleaner, Branson Ultrasonic Corp., Danbury, CT) for 30 min with hexane, repeated four times. The sonicator was filled with clean water and several ice bags were used to maintain a relatively low temperature and avoid chemical volatilization. The extracts were reduced to a volume of 5 to 10 mL via rotatory evaporation (RV 10, IKA®-Werke GmbH & Co. KG, Staufen, Germany) and filtered with preassembled filtration devices (Autovial™ syringeless filters, PTFE filter, Whatman®, GE Healthcare Bio-Sciences, Pittsburgh, PA). The extract was further reduced to approximately 1 mL via high purity N_2 evaporation (Reacti-Vap™ Evaporators, Thermo Scientific Inc., Waltham, MA), transferred to a 2 mL amber vial, and stored in a refrigerator at 4°C prior to GC-MS analysis.

1 µL of each sample extract was injected into a sorbent tube packed with Tenax TA, desorbed with a thermal desorber (TD, TurboMatrix ATD, PerkinElmer, Inc., Waltham, MA), and analyzed with a gas chromatograph (GC, 7890A, Agilent Technologies, Santa Clara, CA) mass spectrometer (MS, 5975, Agilent Technologies, Santa Clara, CA) (henceforth referred to as the primary GC-MS). 5 µL of D_4-DEHP (2 µg/mL) in methanol was injected in each sorbent tube as an internal standard. Additional details can be found in Liang and Xu (2014). All sorbent tubes were analyzed in two successive desorptions to ensure complete desorption of both the sorbent tube and the TD-GC-MS system. The second desorption showed concentrations below the detection limit in all cases. A calibration standard was regularly run prior to each GC injection, and the variance was always below 5% for all injections.

All analyses were performed in full scan mode and the extracted ions used for identification and quantification of the five target plasticizers can be found in Liang and Xu (2014). DINP and DINCH are mixtures of numerous isomers (e.g., Schossler et al. 2011, Nagorka et al. 2011) and elute across many peaks for a period of approximately 1 min (Figure S2), with the response derived from the total area between the first and last detected isomer. All samples were also screened for three additional phthalate plasticizers: dimethyl phthalate (DMP), di-n-butyl phthalate (DnBP), and butyl benzyl phthalate (BBP), however, none were detected at levels > 0.1 mg/g in any of the cover or foam samples. Dibutyl phthalate (DBP) was detected in two foam samples and identified through comparison with a mass spectral database (NIST08).

For the plasticizer concentrations listed in Table 1, a threshold value of 1 mg/g was selected for covers because plasticizers are typically added to soft PVC products at percent levels. Only two crib mattress cover samples contained identifiable plasticizers below the 1 mg/g threshold value. For foam samples, a threshold value of 0.1 mg/g was used because the occurrence of plasticizers is most likely associated with surface adsorption of gas-phase plasticizers originating in the overlying cover or in a residence, although plasticizers may be used in the foam itself.

Three samples containing PentaBDE congeners, as identified with the primary GC-MS through comparison with a mass spectral database (NIST08), were also analyzed with GC-µECD (micro-electron capture detector) (7890A, Agilent Technologies, Inc., Santa Clara, CA) with a 30 m column (0.25 mm ID, film thickness: 0.1 µm) (DB-5ht, Agilent Technologies, Santa Clara, CA) following our previously published methods (Xu et al. 2014). Additional flame retardants, such 2,2-bis(chloromethyl)propane-1,3-diyl-tetrakis(2-chloroethyl)bis(phosphate) (V6), were not screened for, as they require additional analytical techniques to identify (Stapleton et al. 2011, 2012).

Discussion on Unreacted Isocyanates

An excess of toluene diisocyanate (TDI, the predominate diisocyanate used in polyurethane foam production, Vangronsveld et al. 2013a) is typically added during the manufacture of polyurethane foam, above which is necessary for it to react with hydroxyl groups of polyols and water (Hugo et al. 2000). As such, unreacted isocyanate may be present in the final polyurethane foam product (Hugo et al. 2000, Krone et al. 2003, CA OEHHA 2010). Krone et al. (2003) identified NCO in polyurethane foam-containing consumer products, including a mattress and sofa padding. The foam in crib mattresses is somewhat protected from excess moisture released from the infant body, which can react with the isocyanates (Bello et al. 2006). The detection of NCO in crib mattresses by PAS-FT-IR analysis necessitates that future research measure concentrations of NCO in crib mattress foam, determine to the extent to which NCO can migrate to air, and if NCO is present in mattress dust.

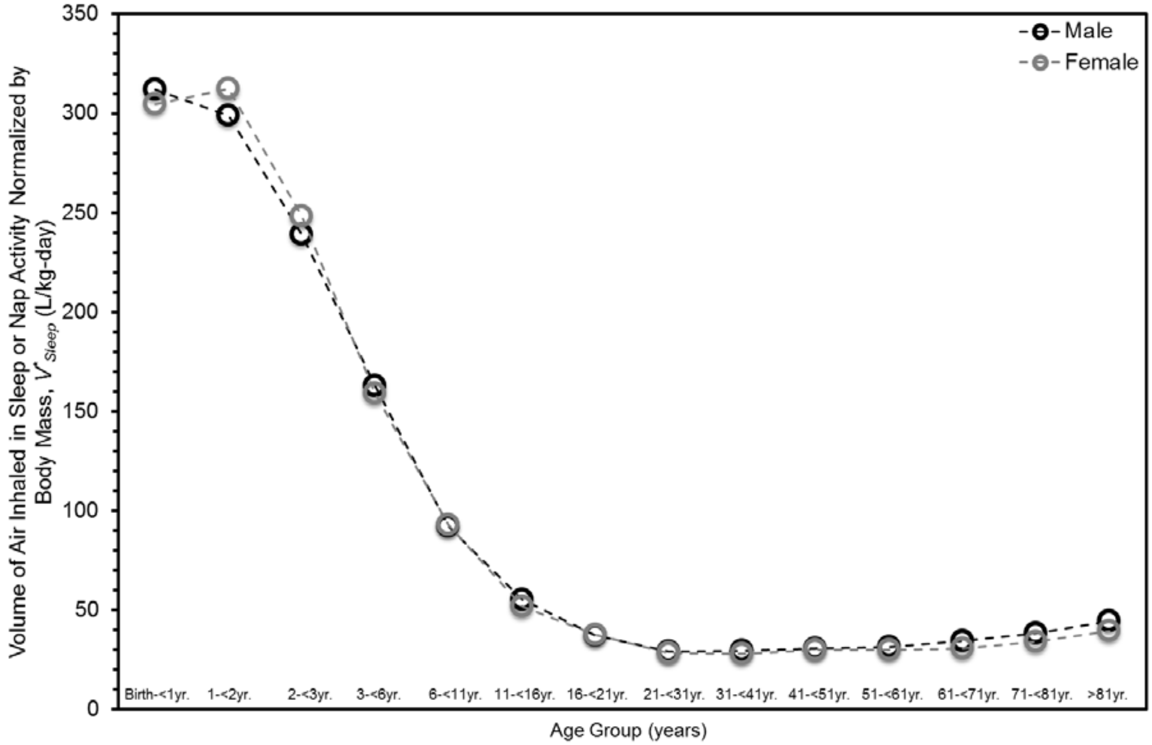

Figure S1 (a.)

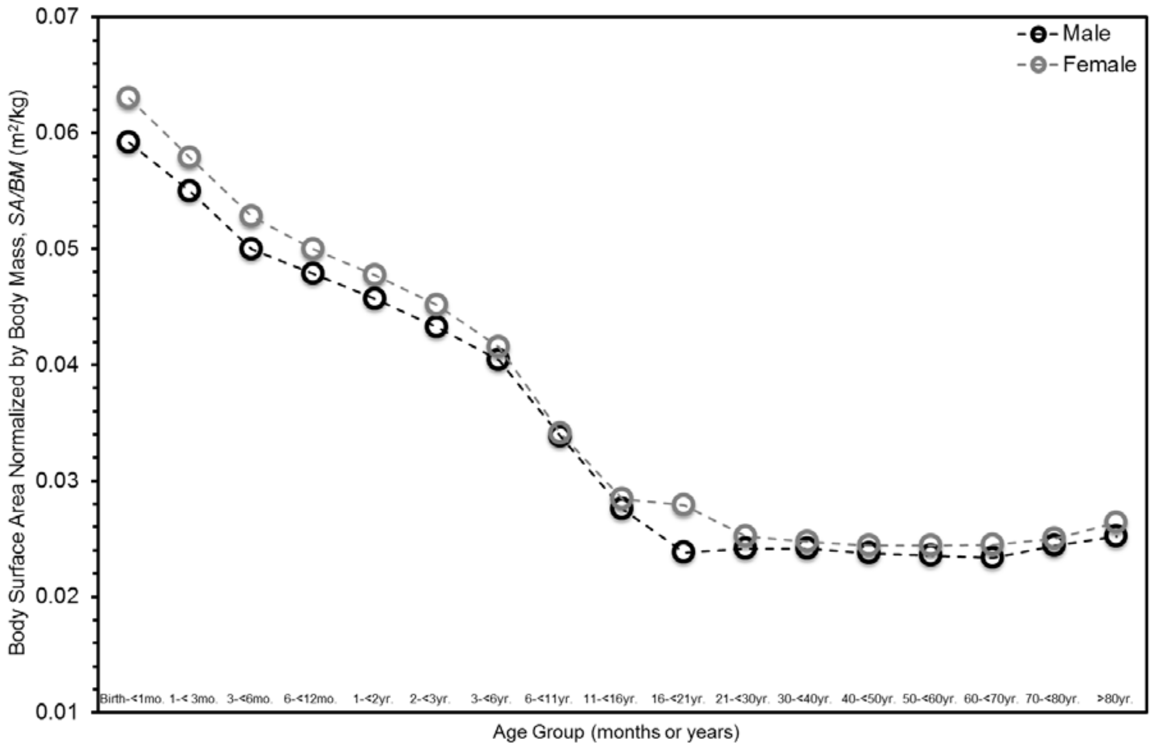

Figure S1 (b.)

Figure S1. Infant inhalation and dermal exposure dose considerations in the sleep microenvironment: (a.) volume of air inhaled during sleep or nap activity (EPA ID = 14500) per day, normalized by body mass (V^{*}_{Sleep}, L/kg-day) for each age group and gender (calculated using U.S. EPA EFH data set, U.S. EPA 2011), and (b.) body surface area normalized by body mass (*SA/BM*, m^2/kg) for each age group and gender (calculated using U.S. EPA EFH data set, U.S. EPA 2011).

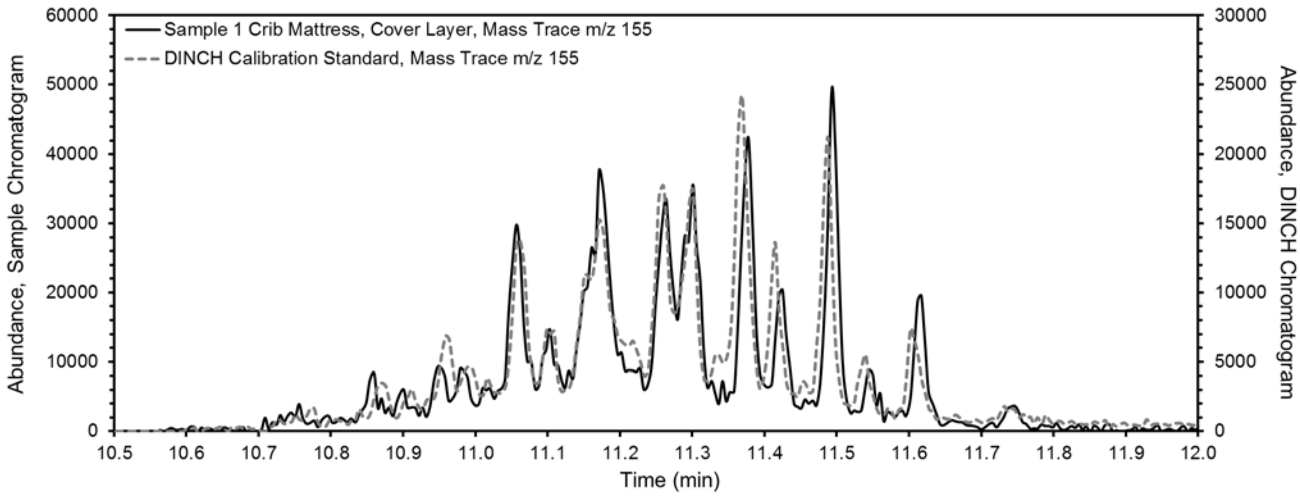

Figure S2 (a.)

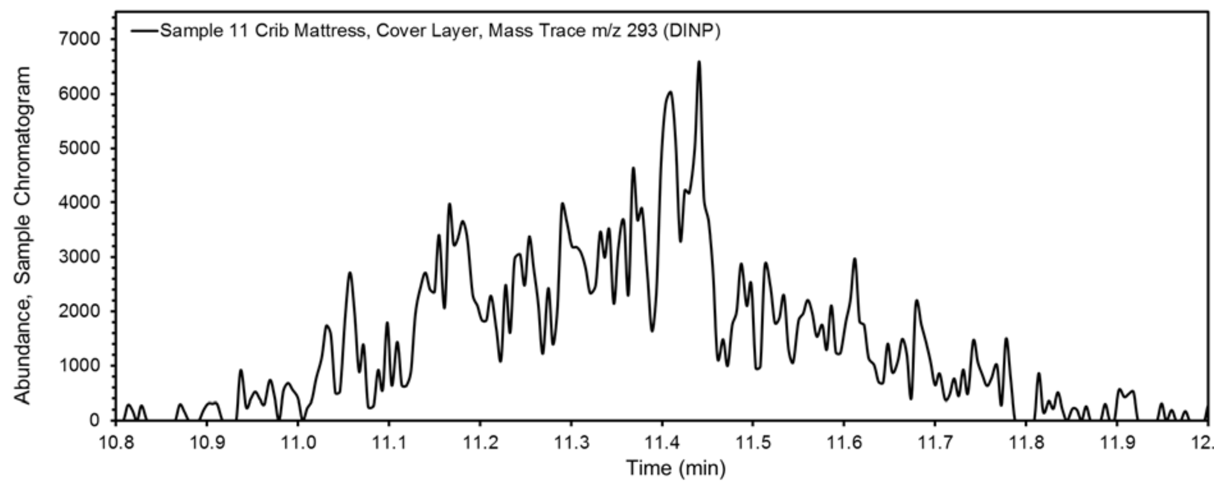

Figure S2 (b.)

Figure S2. Example GC-MS chromatograms for: (a.) sample 1 crib mattress, cover layer containing DINCH (*m/z* 155) and DINCH calibration standard (*m/z* 155), and (b.) sample 11 crib mattress, cover layer containing DINP (*m/z* 293).

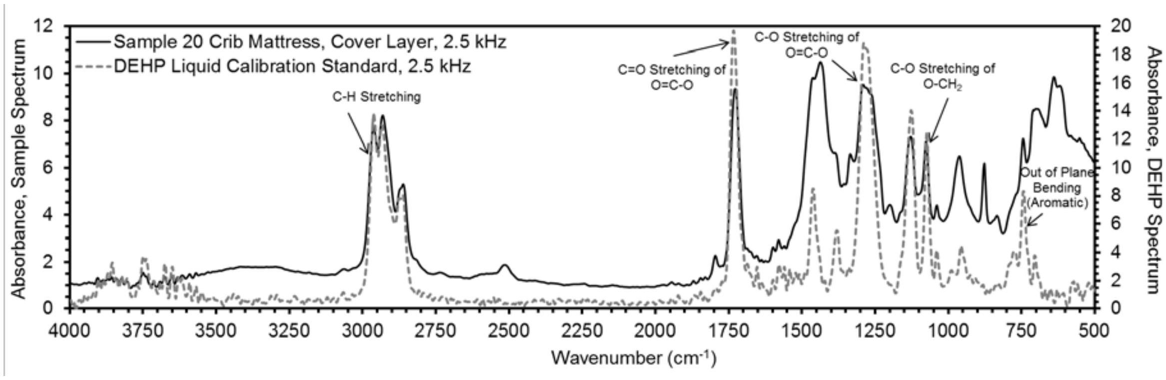

Figure S3 (a.)

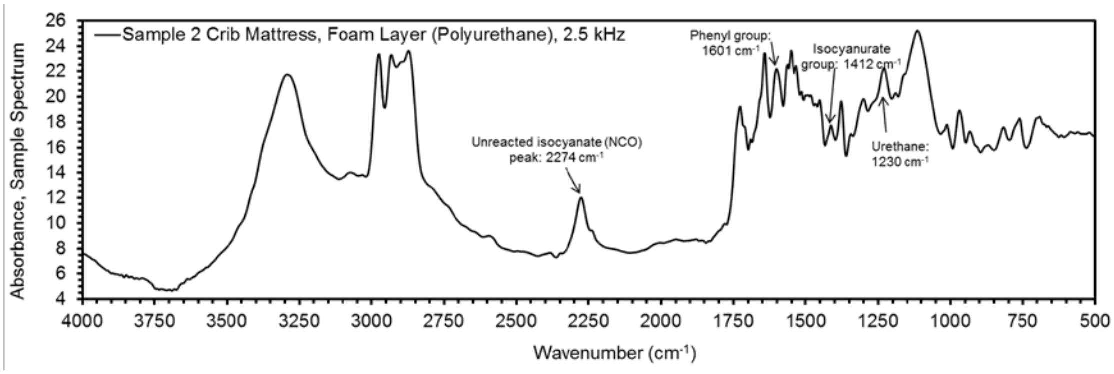

Figure S3 (b.)

Figure S3. Example PAS-FT-IR spectra (all at a 2.5 kHz modulation frequency): (a.) sample 20 crib mattress, cover layer containing DEHP and DEHP calibration standard and (b.) sample 2 crib mattress, foam layer with unreacted isocyanate group.

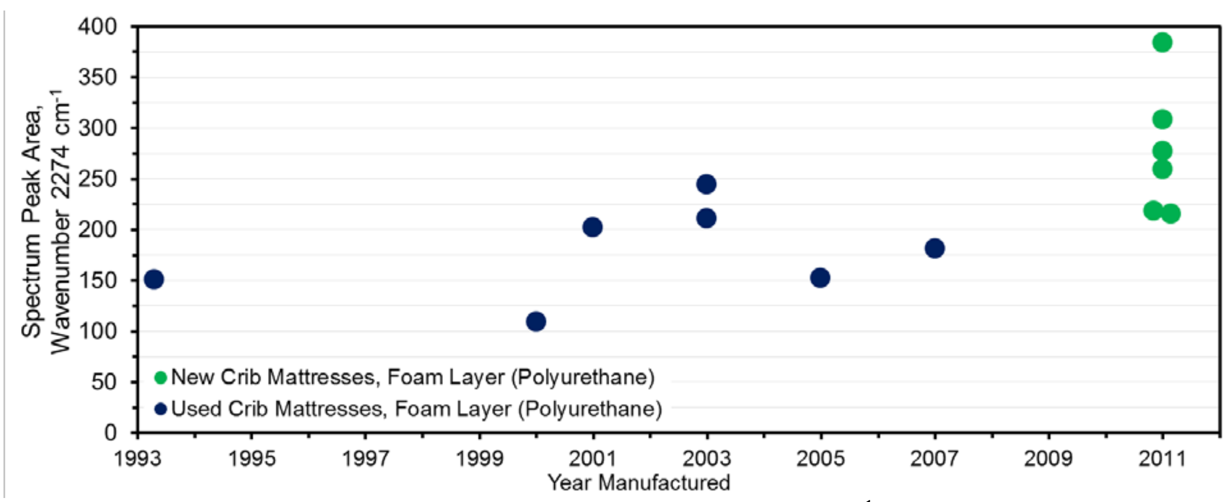

Figure S4. Unreacted isocyanate peak area (wavenumber 2274 cm^{-1}) versus the year crib mattress sample was manufactured (for polyurethane foam samples only).

Table S1. Additional Chemical Additives Detected in the Crib Mattress Cover and Foam Layers

Crib Mattress Samples[1]			Additional Chemical Additives[4]																	
New Samples (*n* = 9)			DBP		TPP[5]		TDCPP		PentaBDE (mg/g)		Phenol[5]		1-Decene[5]		1-Nonanol[5]		Palmitic Acid[5]		NCO[6]	
ID[2]	Year Manuf.	Retail Cost	Cover	Foam	Cover	Foam	Cover	Foam	Cover	Foam	Cover	Foam	Cover	Foam	Cover	Foam	Cover	Foam	Cover	Foam
1	2011	53USD																		
2	2011	43USD				X								X						X
3	2011	39USD				X								X						X
4	2011	35USD													X					
5	2011	89USD									X									
6	2011	70USD														X				X
7	2011	120USD						X			X						X			X
8	2011	148USD																		X
20	2011	22USD		X		X												X		X
Detection Frequency			**n.d.**	**11.1%**	**n.d.**	**33.3%**	**n.d.**	**11.1%**	**n.d.**	**n.d.**	**22.2%**	**n.d.**	**n.d.**	**22.2%**	**11.1%**	**11.1%**	**11.1%**	**11.1%**	**n.d.**	**66.7%**
Used Samples (*n* = 11)																				
ID	Year Manuf.	Usage																		
9	2009	1 yr.											X							
10	2005	2 yr.				X				X, 2.2		X			X					X
11	2008	2 yr.			X								X							
12	2005	2 yr.									X									
13	2001	2 yr.				X								X						X
14	2003	3.5 yr.										X			X			X		X
15	1993	10 yr.		X	X	X				X, 5.5										X
16	2007	4 yr.									X		X				X			X
17	2007	3 yr.											X							
18	2003	< 1 yr.				X				X, 14.7	X			X	X					X
19	2000	Unk.											X							X
Detection Frequency			**n.d.**	**9.1%**	**18.2%**	**36.4%**	**n.d.**	**n.d.**	**n.d.**	**27.3%**	**27.3%**	**18.2%**	**45.5%**	**18.2%**	**27.3%**	**n.d.**	**9.1%**	**9.1%**	**n.d.**	**63.6%**

[1]: All samples, excluding 19, manufactured in the U.S. Sample 19 manufactured and used in Finland. Samples 2, 3, 6-8, 20, 10, 13-16, 18, and 19 were manufactured with polyurethane foam; samples 7 and 8 were manufactured with a fraction of soy-derived foam; and samples 1, 4, 5, 9, 11, 12, and 17 were manufactured with polyester foam (as listed by manufacturer).
[2]: Sample ID consistent with crib mattress samples analyzed in Boor et al. (2014).
[3]: Blank cell: chemical additive not detected (n.d.).
[4]: All compounds (aside from NCO) identified with at least 85% match with NIST mass spectral library; quantification not performed (aside from PentaBDE).
[5]: Detected via analysis with a secondary GC-MS, as described in the SI section.
[6]: Detected via PAS-FT-IR, as described in the SI section.
Nomenclature: DBP: Dibutyl phthalate; TPP: Triphenyl phosphate; TDCPP: Tris(1,3-dichloro-2-propyl)phosphate; PentaBDE: Pentabromodiphenyl ether congener mixture (congeners detected include: BDE-47, BDE-85, BDE-99, BDE-100, BDE-153, and BDE-154; quantified via GC-μECD analysis with calibration standards, a detailed discussion on the methods can be found Xu et al. 2014); NCO: unreacted isocyanate

not detected (n.d.) X: detected

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